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RESEARCH ARTICLE

An Experimental and Computational Study of the Valence Photoelectron Spectra of Halogenated Pyrimidines

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The electronic structures of pyrimidine and a selection of its halogen substituted derivatives have been investigated using ultraviolet photoelectron spectroscopy and *ab initio* quantum chemical methods. Assignments are proposed for all of the features in the PES spectra by comparison with the vertical ionisation energies of the molecular orbitals calculated using the partial third order quasiparticle approximation as applied to electron propagator theory and a corrected density functional method based on the B3LYP functional. The shifts of the outermost five molecular orbitals of the pyrimidine ring structure in the halogen substituted derivatives with respect to the binding energies of the equivalent orbitals in the parent pyrimidine molecule are discussed as a function of the identity and ring position of the halogen atom.

Keywords: Photoelectron spectra; Halogenated pyrimidines; Substituent effects; Density functional theory; Electron propagator theory.

1. Introduction

Pyrimidines are an important class of organic molecules mainly due to the fact that the pyrimidine ring forms the base structure of three nucleic acids, i.e. uracil, cytosine and thymine. Furthermore, halogenated pyrimidine bases have found applications as radiosensitisers in radiotherapy where, for example, it has been discovered more than 40 years ago that 5-bromodeoxyuridine (an analogue of thymidine) radiosensitises cells [1, 2]. A deep understanding of valence photoelectron spectra of the halogenated pyrimidines will help a greater understanding of the electronic structure of the halogenated bases. In addition, a study of the valence shell structure of a molecule provides the basis for further studies on the fragmentation of such molecules following both valence shell and inner shell ionisation.

This work is part of an overall investigation of the valence and inner shell electronic structure and electronic spectra of this class of molecules undertaken by probing them with laboratory sources [3] and synchrotron radiation. In particular, results of the present work constitute the basis to interpret the resonant Auger structure produced after innershell excitation.

The photoelectron spectrum (PES) of pyrimidine and some of its derivatives have been studied in the past [4, 5], however to the best of our knowledge no work has

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1 been published on the effect of the halogen substitution of the pyrimidine ring on
2 the valence photoelectron spectrum of the molecule. In particular the valence PES
3 of pyrimidine has been analysed in detail in the work of Holland *et al.* [4]. This
4 group has also performed a systematic experimental and computational study of the
5 halobenzenes [6, 7], halothiophenes [8–10] and, most recently, the halouracils [11].
6 In this work we concentrate on the substituent effects of the halogen atoms on the
7 pyrimidine parent molecule as a function of ring position and halogen character.
8 The analysis of experimental valence photoelectron spectra are supported by a
9 detailed computational analysis of the orbitals energies and ionisation potentials.

13 2. Experimental Section

15 The photoelectron spectra were measured using a resonance noble gas discharge
16 lamp operated on the He I line at 21.22 eV in combination with a home-built hemi-
17 spherical analyser (mean radius = 60 mm). The He I radiation was transported
18 to the interaction region by means of a capillary tube where it intersected the gas
19 flow at an angle of 90° . The kinetic energy of the photoelectrons emitted into an
20 acceptance angle of $\pm 5^\circ$ oriented at 90° with respect to the direction of propaga-
21 tion of the radiation was measured.

23 Energy calibration of the spectra was achieved by adding a small amount of Argon
24 to the gas flow and the resulting photoelectron peaks at 15.759 eV and 15.937 eV,
25 corresponding to the $3p^{-1} \ ^2P_{3/2} \text{Ar}^+ \leftarrow \text{Ar} \ (^1S_0)$ and $3p^{-1} \ ^2P_{1/2} \text{Ar}^+ \leftarrow \text{Ar} \ (^1S_0)$ tran-
26 sitions, were then used to correct the energy scale of the molecular photoelectrons.
27 The photoelectron spectra were also corrected for the non-linear transmission of
28 the analyser by measurement of the known spectra of benzene [12, 13] and methyl
29 oxirane [14]. The transmission function of our apparatus was extracted by compar-
30 ing the intensities of the peaks of the literature spectra with the raw intensities of
31 the equivalent spectra recorded using the electron spectrometer used in this work.
32 The different collection angle: magic angle in the case of the reference spectra and
33 90° in the case of the electron spectrometer used here was also taken into account
34 by using the β parameter for each peak. All spectra were measured at a resolution
35 of 160 meV (FWHM) as determined from the width of the above Argon photoelec-
36 tron peaks. Furthermore, the low binding energy region of each molecule (typically
37 9.5 to 13.5 eV) were scanned at the higher resolution of 75 meV (FWHM). The
38 peak positions were determined using standard peak fitting procedures.
39 Finally, all compounds were purchased from Sigma Aldrich and used without fur-
40 ther purification (see Figure 1). The compounds were introduced into the inter-
41 action region *via* a leak valve where the room temperature vapour pressures of
42 the samples were sufficient to provide a high enough gas density in the interaction
43 region to allow the electron spectra to be recorded.

48 3. Computational Details

50 All *ab initio* calculations were performed using the Gaussian03 package of pro-
51 grams [15] where the geometries were optimised at the B3LYP density func-
52 tional level of theory [16–18] using the split valence plus polarisation basis set
53 6-311++G(d,p) [19]. These geometries, the resulting vibrational frequencies and
54 total energies can be found in the supporting information section of this article.
55 Subsequently a number of methods were employed to calculate the vertical ionisa-
56 tion energies of the molecules using these geometries in order to achieve a reliable
57 interpretation of their photoelectron spectra. The three computational methods
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employed to calculate the vertical ionisation energies were: 1) Hartree Fock together with Koopmans' Theory, [20] 2) Partial third order (P3) quasiparticle approximation as applied to electron propagator theory (implemented by Ortiz *et al.* [21] in the Gaussian suite of programs) and 3) SCF molecular orbital energies of the Kohn-Sham orbitals calculated at the B3LYP/6-311++G(d,p) level of theory and corrected for the vertical ionisation energy by calculating the energy of the cation in the ground state neutral geometry, i.e. essentially the equivalent of Koopmans' theorem for DFT calculations [22] (discussed in more detail below). Furthermore, the effects of the basis set on the P3 calculation were investigated by performing the calculations on all molecules using the following basis sets: 6-311G(2df,2p) and cc-pVTZ [19, 23] while in addition P3 calculation with the 6-311G(2df,2p) basis augmented by the SDD basis set on the heavy halogen atom were performed on the bromine containing molecules.

4. Results and Discussion

4.1. Pyrimidine

In order to be able to discuss the effect of the substituents on the electronic structure of the halogenated pyrimidines it is first necessary to briefly re-examine the photoelectron spectrum of the parent molecule: pyrimidine. To this end the He I PES of pyrimidine has been measured and is presented in Figure 2 and the results of the *ab initio* calculations on this molecule are summarised and compared to the experimental peaks in Table 1.

At the Hartree-Fock (HF) level of theory the ground state valence orbital configuration of pyrimidine in C_{2v} symmetry is

$$\begin{aligned} \text{inner valence: } & (1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2 \\ \text{outer valence: } & (3b_2)^2(5a_1)^2(4b_2)^2(6a_1)^2(1b_1)^2(7a_1)^2 \\ & (1a_2)^2(5b_2)^2(2b_1)^2 \end{aligned}$$

where the orbitals of a_1 and b_2 symmetry correspond to σ orbitals while those of a_2 and b_1 symmetry correspond to π type orbitals. In particular for the outermost 5 molecular orbitals (MOs) we adopt the notation of Lotermoser *et al.* [5] in which the $5b_2$ and $7a_1$ orbitals are denoted as n_{N_-} and n_{N_+} , respectively, and the $2b_1$, $1a_2$ and $1b_1$ orbitals are denoted as π_3 , π_2 and π_1 orbitals. These HF molecular orbitals are shown in Figure 3 where it can be seen that the three π orbitals are localised above and below the pyrimidine ring while the n_{N_-} and n_{N_+} orbitals are principally the nitrogen lone pairs where the + and - symbols indicate symmetric and antisymmetric combinations. The influence of electronegative halogen substituents on the composition and binding energy of these orbitals will be discussed in detail in the following subsection.

The first intriguing point to note from the *ab initio* calculations lies in the change of the energy ordering of the orbitals on passing from the Hartree-Fock/Koopmans' theorem to the higher level methods involving electron propagator theory (EPT) and the modified density functional theory (DFT) method. These changes, which have already been noted in the past [4, 5], include the inversion of the ordering of the HOMO and HOMO-1 as well as the inversion of the HOMO-2 and HOMO-3 (see Table 1). This is mainly due to the fact that the energy of the π_3 and π_2 orbitals change very little while the energy of the n_{N_-} and n_{N_+} orbitals are reduced by > 1.5 eV on passing to the higher level theories. These changes are due to a greater effect of electron correlation and final state orbital relaxation on the n_{N_-}

1 and n_{N_+} orbitals with respect to the π_3 and π_2 orbitals as these effects are not
2 taken into account at the HF level of theory.

3 The DFT method also determines the correct energy ordering of the orbitals as
4 determined by an examination of the symmetry of the Kohn Sham orbitals. Fur-
5 thermore, the absolute energies of the orbitals can be corrected by the following
6 procedure: 1) single point calculation of the energy of the cation at the neutral
7 state optimised geometry (-264.39394 Hartree) 2) comparison of this value to the
8 energy of the neutral state (-264.03967 Hartree) and thus extraction of the vertical
9 ionisation energy of the HOMO (9.64 eV) 3) Use of the difference between the cal-
10 culated binding energy of the HOMO orbital and the above value as a correction
11 for all MO energies. This method leads to very good agreement with the experi-
12 mental values of the binding energies as can be seen from Table 1 and the work of
13 Lotermoser *et al.* [5]

14 The effect of the basis set was also briefly examined. In contrast to the work
15 of Potts *et al.* [4] no large difference in the basis set effect was observed when
16 comparing the nitrogen lone pair orbitals and the π orbitals. Those authors pointed
17 out that the nitrogen lone pair orbitals might be sensitive to the approximation
18 scheme being used. This is supported by the fact that the approximation scheme
19 used in this work [21] is different with respect to Potts *et al.* [24] thus explaining
20 the difference basis set effect in the two calculations. Indeed the P3/6-311G(2df,2p)
21 and P3/cc-pVTZ give very similar results with the difference in ionisation energy
22 calculated using these two basis sets not exceeding 0.07 eV for any orbital. It should
23 be noted in the tables comparing the *ab initio* calculations with the experimental
24 results that the pole strengths are shown only for the P3/cc-pVTZ calculation as
25 they do not vary significantly with basis set.

26 The P3 and B3LYP computational methods give similar results when compared
27 to the experimental ionisation energies with both methods predicting the same
28 energy ordering of the molecular orbitals. A numerical comparison of the two com-
29 putational methods show that the P3/6-311G(2df,2p) calculation results in a rms
30 deviation of the calculated ionisation energies from the experimental ones for the 4
31 outermost orbitals of 0.08 eV while the B3LYP method gives an rms deviation for
32 these orbitals of 0.13 eV. When considering the complete energy range (excluding
33 the bands under the broad feature in the range 13-15 eV) the rms deviation of the
34 P3/6-311G(2df,2p) method increases to 0.26 eV while that of the B3LYP calcula-
35 tion increases to 0.19 eV. This is due to the larger error of the P3 method in the
36 inner valence region especially for ionisation energies > 17 eV. Although the P3
37 method is a higher level method (and therefore should be more reliable) than the
38 B3LYP based method we will present the results of both methods for all molecules
39 for comparative purposes.

47 4.2. Mono Halogenated Pyrimidines

48 When a halogen substituent is added to the aromatic ring of pyrimidine the elec-
49 tronic structure of the molecule changes quite significantly. First of all two new
50 orbitals which correspond to the p orbitals of the halogen atom are added to the
51 outer valence orbital manifold. The orientation of these orbitals can be parallel
52 n_{\parallel} or perpendicular n_{\perp} to the ring as shown in Figure 4. In addition, the added
53 electronegative substituent can perturb the π_3 , π_2 , π_1 , n_{N_-} and n_{N_+} orbitals in
54 the pyrimidine ring with respect to the parent molecule either by the inductive (I)
55 or resonant (R) effect. The changes in the electronic structure of the monohalo-
56 genated pyrimidines studied in this work is illustrated by a correlation diagram
57 (see Figure 5) where the evolution of the binding energies of the various π and σ
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1 orbitals are shown at the B3LYP/6-311++G(d,p) level of theory. However, before
2 proceeding to a detailed discussion of the interplay of the above mentioned effects
3 we will first give a brief description of the individual PES for each molecule.
4

5 4.2.1. 2-bromopyrimidine

6 The first significant change in the PES with respect to the pyrimidine parent is
7 the shift of the lowest band to higher ionisation energy by 0.2 eV (see Figure 6).
8 The comparison with the *ab initio* calculations leads to some uncertainties in the
9 assignment of the identity of the HOMO and HOMO-1. While the B3LYP based
10 method suggests that these orbitals are the n_{N_-} and π_3 orbitals, the P3 method
11 implies that they are the π_3 and $n_{||}$ orbitals. This uncertainty can be resolved by
12 examining the next band in the spectrum at 10.83 eV. This is a much sharper
13 band with respect to the other features in the spectrum and indeed on passing
14 to the higher resolution scan (see the upper part of Fig. 6) this band becomes
15 narrower while the other bands do not and so appears to be limited by the resolution
16 of the electron spectrometer. It has been noted in the literature [25] that sharp
17 narrow bands in the PES of halogenated aromatic systems correspond to ionisation
18 from strongly localised non-bonding orbitals as one would expect from the Franck
19 Condon principle. In this energy region the best candidate for such an orbital is the
20 $n_{||}$ orbital which is strongly localised on the bromine atom. In order to definitively
21 resolve the difficulty in assigning this band, photoelectron spectra in this kinetic
22 energy range have been recorded following ionisation of this molecule at different
23 excitation energies using synchrotron radiation at the GasPhase photoemission
24 beamline at Elettra. This experiment was motivated by the work of Potts *et al.* [9]
25 who observed a reduction in the relative intensities of the photoelectron lines due
26 to the ionisation of bromine lone pair orbitals in the bromothiophenes at energies
27 in the region of the Cooper minimum due to the Br 4p subshell around 70 eV.
28 The comparison of the photoelectron spectra of the 2-bromopyrimidine excited
29 following ionisation at 30 eV and 70 eV showed a drastic reduction ($>$ factor of 2)
30 in the relative intensity of the photoelectron line at an ionisation energy of 10.83
31 eV when the molecule is ionised with a photon energy of 70 eV. This confirms
32 that this peak is due to ionisation of the lone pair of the Br atom. These results
33 suggest that the B3LYP calculation gives the correct HOMO/HOMO-1 assignment
34 although the ordering from an experimental point of view remains unclear. In order
35 to test the possibility that the basis set used for the P3 calculation do not describe
36 sufficiently the Br atom, the calculation has been repeated with the 6-311G(2df,2p)
37 augmented by the SDD (Stuttgart/Dresden effective core potential) [26] basis set
38 for the heavy halogen atom. The results, which are shown in Table 2 show that
39 although the ionisation energies of the molecular orbitals with large electron density
40 on the halogen atom do shift by a larger amount than those with little density on
41 the halogen atom the energy ordering of the orbitals remain the same in the two
42 calculations.
43

44 It should be noted that the largest difference between the P3/6-311G(2df,2p) and
45 the B3LYP calculations resides in the ionisation energy, E_i , of the n_{N_-} orbital (Δ
46 = 0.91 eV) while the two methods give a similar result for the E_i of the $n_{||}$ orbital.
47 Comparing to the experiment we find that both methods underestimate the E_i of
48 the $n_{||}$ by ~ 0.5 eV while the P3 method overestimates the E_i of the n_{N_-} orbital
49 and the B3LYP underestimates the same quantity. Therefore, although the B3LYP
50 does correctly predict the $n_{||}$ to be the HOMO-2 while the P3 method does not
51 the overall quality of the two results in comparison with the experiment are similar.
52

53 The next part of the spectrum is again quite different from the corresponding
54 energy range of the 2-bromopyrimidine spectrum and a broad structured band
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centered at 11.89 eV is observed. Comparison with the results of both the B3LYP and P3 calculations leads to the conclusion that the three MOs contributing to this band are the n_{N_+}, π_2 and n_{\perp} orbitals, however, considering how close they are in energy to each other a definitive assignment of the energy ordering is difficult.

The absolute error of the *ab initio* calculations increases on going to higher binding energy orbitals. This is to be expected due to the increase of the contribution of shake-up satellite peaks and many-electron effects [4]. However, the deviations appear to be quite uniform and therefore it is still possible to at least discuss the principal contributions to these peaks. Three distinct bands are observed in the energy range from 13.5 eV to 16.5 eV with the intensity of the central band appearing to be larger than the other two. Both sets of calculations suggest that the first peak is due to ionisation of an inner σ orbital, while the second contains contributions from ionisation of both the π_1 and σ orbital and finally the last of these series is due to ionisation of a single σ orbital.

4.2.2. 5-bromopyrimidine

The lowest energy band in the PES of 5-bromopyrimidine (see Figure 7) occurs at the same energy as the corresponding band in the PES of 5-bromopyrimidine and again consists of contributions from both the HOMO and the HOMO-1. Comparison with the *ab initio* calculations suggests that this band consists of contributions due to ionization of both the HOMO and the HOMO-1 (π_3 and n_{N_-} MOs). This is in contrast to the parent pyrimidine molecule where the binding energies of these two orbitals differed by 0.8 eV. Both the P3 and the B3LYP computational methods predict a stabilisation of the n_{N_-} orbital and a destabilisation of the π_3 orbital. However, while the B3LYP based method predicts the ordering to be $BE(n_{N_-}) < BE(\pi_3)$ the P3 method predicts the opposite although the energy differences are small in both cases (0.15 and 0.21 eV, respectively). From an experimental point of view however (even at the higher resolution scan - FWHM \approx 75 meV) it is not possible to separate the two contributions but the relative intensity of the band is consistent with contributions from ionization of two MOs under this band. Again the comparison of the next highest electronic system with the *ab initio* calculations suggest that it is the result of contributions from the ionisation of no less than three different MOs (n_{\parallel} , n_{N_+} and π_2) and furthermore the two computational methods used are in agreement on the ordering of the MOs. Also in this case the experimental intensity of the band is in agreement with this conclusion. The next band (at 12.34 eV) is well separated and corresponds to the n_{\perp} MO.

As in the case of the 2-bromopyrimidine the PES of 5-bromopyrimidine were recorded with photon energies of 30 and 70 eV at the GasPhase beamline at Elettra. Comparing these spectra reveals a reduction in the relative intensity of the band at 12.34 eV when passing from the spectra produced using photons at 30 eV with respect to that recorded following ionisation with a photon energy of 70 eV. This is consistent with the assignment arising from the both computational methods indicating that this band is due to ionisation of the n_{\perp} MO which is principally located on the Br atom. The decrease in intensity of the central part of the band located at 11.42 eV when comparing the PESs recorded at 30 and 70 eV respectively suggest that the ionisation of the n_{\parallel} contributes to the central part of this band and not to the lower energy shoulder as the comparison with both computational methods would suggest.

The inner binding energy region (13 - 18 eV) of the spectrum is also quite different from the corresponding region of the 2-bromopyrimidine molecule. The broad band

1 between the ionisation energies 14 and 16 eV consists of contributions from the
2 ionisation of four MOs which are the three σ orbitals and the most highly bound π
3 orbital, π_1 . The last band in the spectrum of the 5-bromopyrimidine appears to be
4 less intense and broader than the corresponding feature in the 2-bromopyrimidine
5 spectrum. Again by comparison to the calculations one can see that this is most
6 likely due to the close matching of the ionisation energies of two σ orbitals in the
7 case of the 2-bromopyrimidine (see Table 2) while the corresponding orbitals in
8 5-bromopyrimidine are separated by 0.25 eV (see Table 3).

9 4.2.3. 2-chloropyrimidine

10 The PES of 2-chloropyrimidine is shown in Figure 8 and the experimental band
11 energies are compared to the *ab initio* calculations in Table 4. Here the P3 calcu-
12 lations are presented only for the cc-pVTZ and 6-311G(2df,2p) basis sets as the
13 ionisation energies do not change with the SDD basis set for the lighter halogen
14 atom chlorine. In this case on the lower energy side of the lowest energy band it
15 is possible to see a partially resolved shoulder due to the ionisation of the HOMO.
16 Both the P3 and B3LYP *ab initio* methods agree that the ordering of the HOMO
17 and the HOMO-1 is $BE(n_{N_-}) < BE(\pi_3)$ although the splitting in the case of the
18 B3LYP method (0.29 eV) is more consistent with the observed experimental split-
19 ting than the case of the P3 calculation (0.11 eV). The next part of the spectrum
20 would appear to be quite similar to that of 5-bromopyrimidine in that it consists
21 of a broad peak with contributions from 3 MOs (partially resolved in the higher
22 resolution scan) the identity of which are predicted by both *ab initio* methods used
23 here to be the $n_{||}$, n_{N_+} and π_2 orbitals although the ordering of the latter two is
24 unclear. Finally, a low intensity band appears at higher energy (12.40 eV) and is
25 due to ionisation of the n_{\perp} orbital. The second half of the PES on the other hand
26 is more similar to that of 2-bromopyrimidine and indeed the order of the MOs is
27 predicted to be identical to that molecule by the *ab initio* calculations.

28 4.2.4. Substituent effects in the monohalogenated pyrimidines

29 We begin this section with a discussion of the effects of the halogen atom on
30 the energies of the π orbitals. As mentioned above, the halogen atom acts on the
31 electronic structure of the pyrimidine derivatives *via* two main mechanisms: the in-
32 ductive effect (I) and the resonance effect (R). The energy changes induced by these
33 effects on the π orbitals localised on the pyrimidine ring are often antagonistic. The
34 I effect is due to the electronegativity of the halogen substituent which withdraws
35 electron density from the ring thus reducing the electron repulsion within the π
36 orbitals hence increasing their binding energies. The R effect, on the other hand,
37 is due to conjugation between the lone pair orbitals of the halogen atom and the
38 π orbitals of the ring. The effect on the energy of the π orbital depends on the
39 type of conjugation. For example, in the case of the π_3 orbital the interaction of
40 the electron density in the out of plane p orbitals of the halogen atom with the
41 π electrons on the pyrimidine ring leads to a nodal/anti-bonding plane along the
42 C-X bond. This in turn leads to a destabilisation of the π_3 orbital (decrease in
43 binding energy). In order to be able to perform a quantitative discussion on the
44 resonance effects we have performed a Mulliken population analysis on each of the
45 Hartree-Fock MOs (see Table 5). In this table the contributions of all orbitals on
46 each atom is summed in order to give the overall contribution of each atom to the
47 electron density to the individual molecular orbitals.

48 The net effect on the π_3 orbitals in all of the molecules is a destabilisation with
49 the effect being more pronounced in the case of the bromopyrimidines with respect
50 to the chloropyrimidine (see Figure 5). As described above the I effect stabilises the
51 π_3 orbital while the R effect destabilises it. Since the net effect is a destabilisation
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1 it is clear that the R effect dominates in this case. The relative magnitude of the
2 destabilisation ($\text{Br} > \text{Cl}$) can be rationalised by an inspection of the population
3 analysis (see Table 5) for these orbitals which shows that chlorine contributes 31.9%
4 to the electron density of the π_3 orbital in 2-chloropyrimidine while Br contributes
5 47.6% and 50.1% to the corresponding orbitals in 5-bromo and 2-bromopyrimidine,
6 respectively. This explains why the π_3 orbital is more destabilised in the bromine
7 substituted molecules.
8

9 The π_2 orbital shows the opposite effect in that it is stabilised by the addition of
10 the halogen atoms in all cases. This observation can again be explained by consult-
11 ing the population analysis where it can be seen that the halogen atoms contribute
12 zero to the electron density of these orbitals which means that the R effect has no
13 influence on the energy of these orbitals. This is due to nodal plane perpendicular
14 to the ring and passing through C1 and C5. Therefore, only the I effect operates
15 in this case and as expected (due to the relative electronegativities) the effect is
16 larger in the case of chlorine than for bromine.
17

18 The last π orbital, π_1 , is also stabilised but in this case both the inductive and the
19 resonance effects stabilise the orbital as the n_{\perp} conjugates in a bonding fashion
20 with the π_1 orbital on the pyrimidine ring thus further stabilising this orbital.

21 The energy of the lone pair orbitals on the nitrogen atoms (n_{N_+} and n_{N_-}) are
22 also changed by the presence of the halogen atom. Indeed, the n_{N_+} orbitals are
23 changed in a very similar way to the π_2 orbitals suggesting that the principal effect
24 operating is the inductive effect, i.e. withdrawal of electron density from the lone
25 pair thus stabilising the MO and furthermore the effect is larger for chlorine than
26 for bromine. The energy dependence of the n_{N_-} orbital is more complicated be-
27 cause in addition to the I effect there is a through space resonance effect between
28 the n_{\parallel} and the antisymmetric lone pair orbitals of the nitrogen atoms resulting
29 in further stabilisation of the n_{N_-} orbital. In the case of 5-bromopyrimidine the
30 bromine atom is on the opposite side of the molecule with respect to the nitrogen
31 lone pairs and thus the resonance effect is no longer possible.
32

33 The lone pairs on the halogen atoms (n_{\parallel} and n_{\perp}) are destabilised by the induc-
34 tive effect (increased electron density on the halogen atoms due to the electron
35 withdrawing effects decreases the binding energy of these orbitals) and hence the
36 average binding energy of these orbitals, $\langle n \rangle = n_{\parallel} + n_{\perp}$, is lower than in the
37 isolated atoms (see Figure 5). However, the resonance effects further modify the
38 energies of these orbitals. In the case of the n_{\perp} the resonance effect leads to some
39 π bonding character along the C-X bond leading to a stabilisation of this orbital.
40 In contrast, the n_{\parallel} in which the lone pair orbital lies in the plane of the pyrimidine
41 ring interacts with the σ orbitals of the pyrimidine ring. In all cases this leads
42 to destabilisation of this orbital. For the 2-bromopyrimidine this effect is particu-
43 larly marked due to the nodal planes which arise between the lobes of the bromine
44 lone pair and the electron density on the nitrogen lone pairs. Indeed this effect is
45 complementary to that described for the n_{N_-} in the previous paragraph.
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47
48
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50 51 4.3. Dihalogenated Pyrimidines: 5-bromo-2-chloropyrimidine

52 The He I PES of 5-bromo-2-chloropyrimidine is shown in Figure 9 while the band
53 energies are compared to the *ab initio* calculation results in Table 6. The first band
54 (lowest ionisation energy) again consists of contribution from ionisation of both the
55 HOMO and the HOMO-1 and the two higher level sets of *ab initio* calculations
56 agree that these are the π_3 and n_{N_-} orbitals, respectively. The second peak at
57 11.9 eV consists of contributions from five different MOs among which are the π_2
58 orbital, three lone pair orbitals on the chlorine and bromine atoms and the n_{N_+}
59
60

1 orbital although the two sets of calculations predicts quite different relative energy
2 ordering. The relative intensity of this band is in agreement with the contribution
3 of five MOs. A small band at 13.1 eV is due to ionisation of the n_{\perp} (Br/Cl) orbital.
4 The more tightly bound region from 14.0 - 17.5 eV contains two broad structured
5 band, the first of which contains contributions from the ionisation of 4 MOs while
6 the second is due to ionisation of 2 MOs. All of these MOs (apart from the π_1
7 orbital) are of σ character.
8

9 4.3.1. Substituent effects

10
11 The first noticeable substituent effect is that this molecule has the lowest IP of all
12 of the molecules examined. This is due to the change of the binding energy of the
13 π_3 orbital which is destabilised by the resonance effect with the substituted halo-
14 gen atoms. It appears that this effect is additive because in the 5-bromopyrimidine
15 molecule the experimentally observed shift of this orbital with respect to the par-
16 ent pyrimidine molecule is $\Delta = -0.60$ eV while the equivalent shift in the 2-
17 chloropyrimidine molecule is $\Delta = -0.38$ eV : the sum of these value is quite close
18 to the shift in the 5-bromo-2-chloropyrimidine molecule, i.e. $\Delta = -0.85$ eV. In-
19 deed, due to this resonance effect the π_3 becomes the HOMO in this molecule.
20 The $n_{N_{-}}$ orbital is stabilised by the inductive effect of the halogen atoms by 0.15
21 eV and becomes the HOMO-1. In this case it is difficult to conclude whether the
22 effects are additive or not because the size of the shifts are comparable to the width
23 of the peaks in the PES. However, it is consistent that the shift is very similar to the
24 case of the 2-chloropyrimidine molecule ($\Delta = 0.11$ eV) as the chlorine substituent
25 is likely to be dominant due to its proximity to the nitrogen lone pairs.
26
27

28 Both the π_2 and $n_{N_{+}}$ orbitals are stabilised by the presence of the halogen atoms
29 however as the electrons produced by the ionisation of these two MOs appear in
30 the PES of the 5-bromo-2-chloropyrimidine molecule under a broad peak centered
31 at 11.6 eV it is difficult to discuss from an experimental point of view the shifts of
32 these orbitals with respect to the parent molecule.

33 The more surprising aspect of the substituent effects in the dihalogen species
34 is the effect on the non-bonding orbitals on the halogen atoms themselves. While
35 in the case of the mono-halogenated pyrimidines the addition of the halogen atom
36 adds three MOs to the valence manifold (one of which lies in the inner valence shell,
37 the other two being the n_{\parallel} and n_{\perp} orbitals), the substitution with two halogen
38 atoms leads to the addition of six new MOs in the valence shell. By analogy to
39 the monohalogenated species the four of these which lie in the outer valence shell
40 would be expected to be two n_{\parallel} orbitals and two n_{\perp} orbitals with one of each on the
41 chlorine and bromine atom. This is exactly what happens for the n_{\parallel} orbitals where
42 two quite distinct orbitals are attributable to the n_{\parallel} (Cl) and the n_{\parallel} (Br) orbitals. A
43 Mulliken population analysis on the HF/6-311++G(d,p) orbitals revealed that the
44 chlorine atom contributes 38.3% to the n_{\parallel} (Cl) while the bromine atoms contributes
45 53.9% to the n_{\parallel} (Br) orbitals. The binding energies of these are predicted to be
46 very close by the *ab initio* calculations and on comparison with the experimental
47 PES they are suggested to lie on the low energy side of the broad peak centered
48 at 11.6 eV. These orbitals are close in energy in spite of the fact that the binding
49 energy in the isolated atom is much higher for the chlorine atoms because the n_{\parallel}
50 (Cl) orbital experiences additional destabilisation with respect to the n_{\parallel} (Br) due
51 to its proximity to the nitrogen lone pairs.
52

53 The situation of the n_{\perp} orbitals is slightly more complicated. Upon performing a
54 Mulliken population analysis on the first of these orbitals (lowest binding energy)
55 it was found that it contains almost equal contributions from the chlorine (46.2%)
56 and bromine (45.5%). In this orbital there is little or no binding along the C-X bond
57 and therefore the orbitals is not stabilised by the resonance effect and thus has a
58
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1 binding energy similar to that of the n_{\parallel} orbitals. The other n_{\perp} orbital also contains
2 comparable contributions from the chlorine (47.0%) and bromine (26.9%) atoms
3 but in this case there is significant π bonding along the C-X bonds and indeed the
4 energy of this orbital is strongly stabilised by the resonance effect (binding energy
5 = 13.03 eV).
6
7
8

9 5. Conclusions

10
11 The valence shell photoelectron spectra of gas phase 5-bromopyrimidine, 2-
12 bromopyrimidine, 2-chloropyrimidine and 5-bromo-2-chloropyrimidine have been
13 recorded following excitation with He I radiation. The computational methods
14 were tested by comparison to the known assignment of the pyrimidine PES. As-
15 signments are then proposed for all features in these PES by comparison to the
16 vertical ionisation energies calculated by three different *ab initio* methods and in
17 the cases of the 2-bromopyrimidine and 5-bromopyrimidine by comparing the rel-
18 ative intensities of the PES recorded with photon energies of 30 and 70 eV (the
19 latter of which corresponds to the Cooper minimum of the Bromine atom. This
20 experiment allowed a definitive assignment of the bands due to ionisation of molec-
21 ular orbitals dominated by bromine lone pairs. Comparison of the B3LYP based
22 method and the P3 method with these results showed similar quality results for the
23 two methods which is surprising considering the lower level of the B3LYP calcula-
24 tions. It should also be noted that the remaining uncertainties in the assignments
25 of the bands of the halogenated pyrimidines presented in this work (principally
26 due to overlapping bands) may be resolved by future measurements on the angular
27 distributions of the photoelectrons.
28
29

30 The substituent effects on the π and σ orbitals of the pyrimidine ring have been
31 discussed as a function of the identity and position of the halogen atom. The shifts
32 of the binding energies of these orbitals can be accounted for by a combination of
33 the inductive and resonance effects of the halogen atoms of the ring orbitals.
34

35 Furthermore, the results presented in this work will provide the basis in order to
36 permit an in depth interpretation of future experiments on the electron-ion coinci-
37 dence studies on these molecules following either resonant inner shell excitation or
38 valence shell ionisation. The fact that a knowledge of the valence shell electronic
39 structure of a molecule is necessary to interpret electron-ion coincidence studies on
40 that molecule is demonstrated by the recent work on pyrimidine [27, 28].
41
42

43 6. Acknowledgments

44
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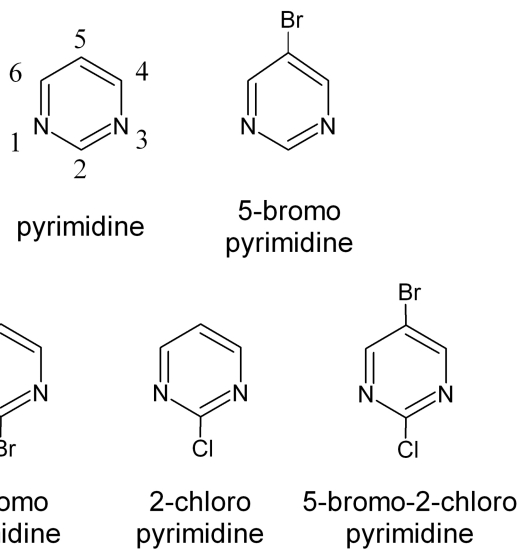


Figure 1. Schematic representation of the pyrimidine molecule and its halogen substituted derivatives investigated in this work. Structure 1 also indicates the numbering of the ring atoms employed.

FIGURES

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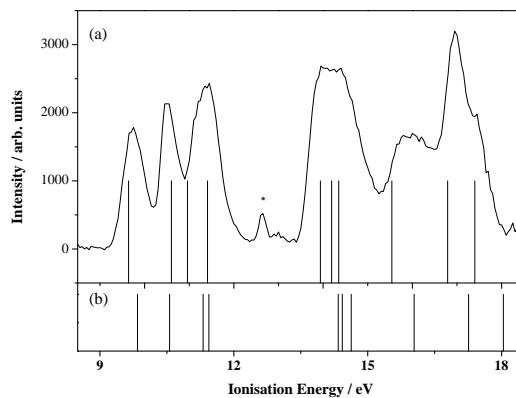


Figure 2. He I photoelectron spectrum of pyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p) method. The asterisk marks a peak due to ionisation of water molecules in the sample.

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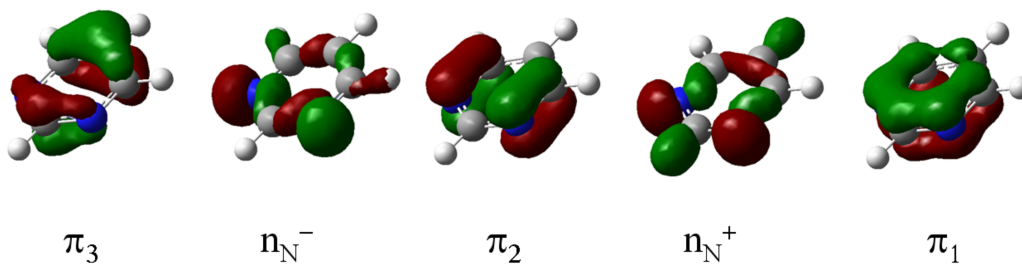


Figure 3. Hartree Fock molecular orbitals of pyrimidine together with the notation adopted in this work.

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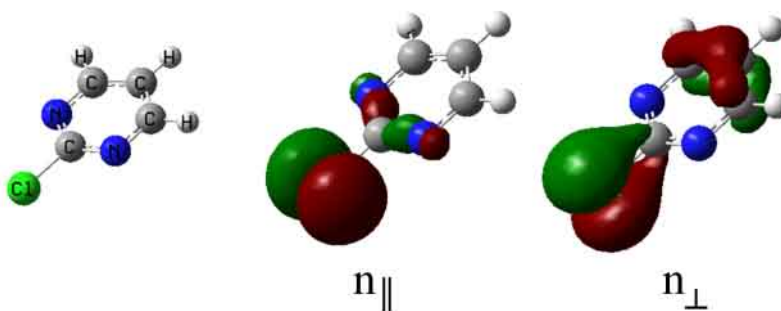


Figure 4. Hartree Fock molecular orbitals of the halogen atom lone pairs (in 2-chloropyrimidine) together with the notation adopted in this work.

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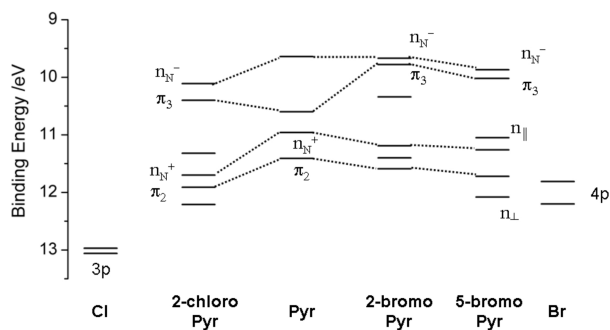


Figure 5. Correlation diagram for the halogenated pyrimidines as calculated using the B3LYP method (see text for details).

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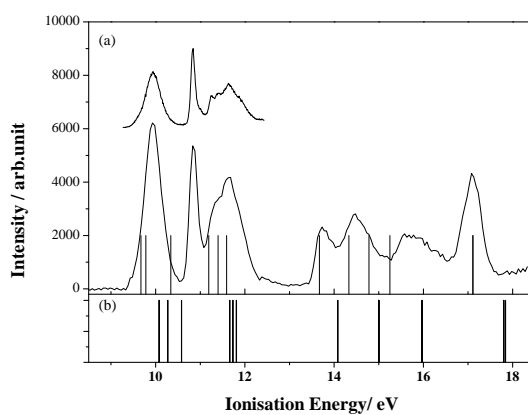


Figure 6. He I photoelectron spectrum of 2-bromopyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p)/SDD method. The inset represents a high resolution scan of the ionisation energy region 9 - 12.5 eV.

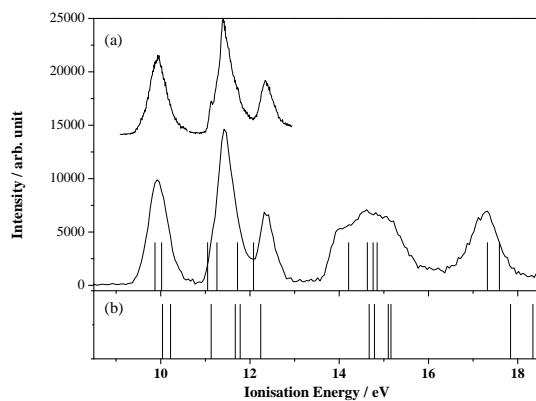


Figure 7. He I photoelectron spectrum of 5-bromopyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) is due to the P3/6-311G(2df,2p)/SDD method. The inset represents a high resolution scan of the ionisation energy region 9 - 13 eV.

FIGURES

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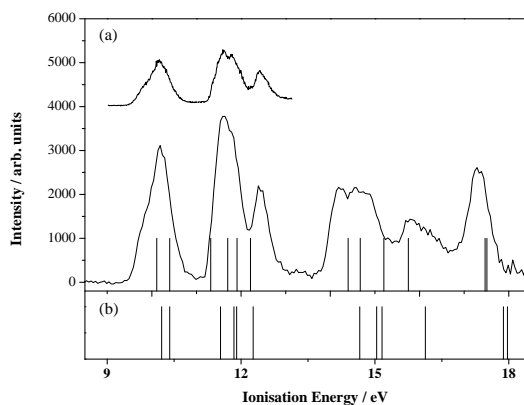


Figure 8. He I photoelectron spectrum of 2-chloropyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p) method. The inset represents a high resolution scan of the ionisation energy region 9 - 13 eV.

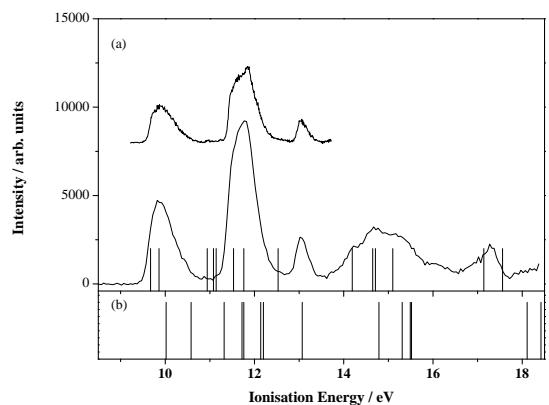


Figure 9. He I photoelectron spectrum of 5-bromo-2-chloropyrimidine. The stick spectrum in a) indicates the *ab initio* ionisation energies calculated using the B3LYP method outlined in the text, while that in b) show the ionisation energies calculated using the P3/6-311G(2df,2p)/SDD method . The inset represents a high resolution scan of the ionisation energy region 9 - 14 eV.

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| Exp. | Orb. | MO | HF cc-pVTZ | P3(PS) cc-pVTZ | P3 6-311G(2df,2p) | B3LYP |
|----------|--------|-----------|---------------|-------------------|----------------------|-------|
| 9.73 | $5b_2$ | n_{N_-} | 11.29 | 9.90 (0.89) | 9.84 | 9.64 |
| 10.53 | $2b_1$ | π_3 | 10.26 | 10.60 (0.89) | 10.56 | 10.59 |
| 11.20 sh | $7a_1$ | n_{N_+} | 12.88 | 11.37 (0.88) | 11.31 | 10.96 |
| 11.40 | $1a_2$ | π_2 | 11.48 | 11.48 (0.88) | 11.44 | 11.40 |
| 13.95 | $1b_1$ | π_1 | 15.68 | 14.38 (0.81) | 14.34 | 13.94 |
| | $6a_1$ | σ | 15.95 | 14.49 (0.87) | 14.43 | 14.18 |
| 14.40 | $5a_1$ | σ | 16.19 | 14.69 (0.88) | 14.63 | 14.35 |
| 15.95 | $3b_2$ | σ | 17.71 | 16.10 (0.86) | 16.04 | 15.52 |
| 16.95 | $4a_1$ | σ | 19.07 | 17.31 (0.85) | 17.26 | 16.78 |
| 17.45 | $3a_1$ | σ | 20.09 | 18.10 (0.84) | 18.06 | 17.38 |

Table 1. Experimental band energies taken from the He I PES of pyrimidine together with the assignments of each band. sh indicates a shoulder in experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. The results of the HF and P3 calculations are reported for two different basis sets: cc-pVTZ and 6-311G(2df,2p). The pole strengths of the P3 calculations are presented in brackets after P3 ionisation energies for the cc-pVTZ basis set. All energies are in eV.

| Orbital | MO | Exp. | HF cc-pVTZ | P3 (PS) cc-pVTZ | P3 6-311G(2df,2p) | P3 6-311G(2df,2p) SDD | B3LYP |
|---------|-------------|---------|---------------|--------------------|----------------------|-----------------------------|-------|
| $5b_2$ | n_{N_-} | 9.93 | 11.97 | 10.61 (0.88) | 10.56 | 10.58 | 9.67 |
| $3b_1$ | π_3 | | 10.12 | 10.09 (0.89) | 10.05 | 10.08 | 9.78 |
| $6b_2$ | $n_{ }$ | 10.83 | 11.19 | 10.27 (0.90) | 10.19 | 10.27 | 10.34 |
| $8a_1$ | n_{N_+} | 11.24sh | 12.97 | 11.76 (0.88) | 11.70 | 11.73 | 11.19 |
| $2b_1$ | n_{\perp} | 11.63 | 12.16 | 11.65 (0.89) | 11.59 | 11.66 | 11.40 |
| $1a_2$ | π_2 | 11.89 | 11.99 | 11.85 (0.87) | 11.81 | 11.81 | 11.59 |
| $7a_1$ | σ | 13.73 | 15.49 | 14.10 (0.87) | 14.05 | 14.08 | 13.67 |
| $4b_2$ | σ | 14.48 | 16.66 | 15.04 (0.87) | 15.00 | 15.00 | 14.34 |
| $1b_1$ | π_1 | | 16.52 | 15.03 (0.80) | 15.00 | 15.00 | 14.78 |
| $6a_1$ | σ | 15.58 | 19.74 | 16.01 (0.86) | 15.96 | 15.97 | 15.26 |
| $3b_2$ | σ | 17.08 | 17.62 | 17.84 (0.84) | 17.80 | 17.80 | 17.11 |
| $5a_1$ | σ | | 19.85 | 17.88 (0.84) | 17.83 | 17.84 | 17.12 |

Table 2. Experimental band energies derived from the He I PES of 2-bromopyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

| Orbital | MO | Exp. | HF cc-pVTZ | P3 (PS) cc-pVTZ | P3 6-311G(2df,2p) | P3 6-311G(2df,2p) SDD | B3LYP |
|---------|-------------|---------|---------------|--------------------|----------------------|-----------------------------|-------|
| $6b_2$ | n_{N-} | 9.93 | 11.45 | 10.26 (0.89) | 10.19 | 10.22 | 9.87 |
| $3b_1$ | π_3 | | 9.97 | 10.05 (0.89) | 10.00 | 10.04 | 10.02 |
| $5b_2$ | $n_{ }$ | 11.13sh | 12.19 | 11.12 (0.89) | 11.06 | 11.13 | 11.05 |
| $8a_1$ | n_{N+} | 11.42 | 13.05 | 11.71 (0.88) | 11.65 | 11.67 | 11.27 |
| $1a_2$ | π_2 | 11.42 | 11.92 | 11.81 (0.87) | 11.78 | 11.78 | 11.72 |
| $2b_1$ | n_{\perp} | 12.34 | 12.90 | 12.24 (0.88) | 12.18 | 12.24 | 12.09 |
| $7a_1$ | σ | 14.02sh | 16.10 | 14.70 (0.86) | 14.63 | 14.67 | 14.21 |
| $4b_2$ | σ | 14.60 | 16.51 | 15.14 (0.87) | 15.16 | 15.16 | 14.63 |
| $1b_1$ | π_1 | 15.22sh | 16.28 | 14.82 (0.80) | 14.79 | 14.79 | 14.77 |
| $6a_1$ | σ | | 16.79 | 15.20 (0.87) | 15.10 | 15.10 | 14.86 |
| $3b_2$ | σ | 17.1sh | 19.77 | 17.88 (0.84) | 17.84 | 17.84 | 17.32 |
| $5a_1$ | σ | 17.3 | 20.42 | 18.38 (0.84) | 18.33 | 18.34 | 17.58 |

Table 3. Experimental band energies derived from the He I PES of 5-bromopyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

| Orbital | MO | Exp. | HF cc-pVTZ | P3 (PS) cc-pVTZ | P3 6-311G(2df,2p) | B3LYP |
|---------|-------------|---------|---------------|--------------------|----------------------|-------|
| $6b_2$ | n_{N-} | 9.84 | 11.77 | 10.26 (0.88) | 10.22 | 10.11 |
| $3b_1$ | π_3 | 10.15 | 10.28 | 10.37 (0.89) | 10.40 | 10.40 |
| $5b_2$ | $n_{ }$ | 11.38 | 12.62 | 11.55 (0.89) | 11.54 | 11.32 |
| $8a_1$ | n_{N+} | 11.61 | 13.41 | 11.94 (0.88) | 11.90 | 11.69 |
| $1a_2$ | π_2 | 11.80 | 11.99 | 11.86 (0.87) | 11.84 | 11.90 |
| $2b_1$ | n_{\perp} | 12.40 | 13.15 | 12.29 (0.88) | 12.27 | 12.21 |
| $7a_1$ | σ | 14.2 sh | 16.02 | 14.68 (0.87) | 14.66 | 14.40 |
| $4b_2$ | σ | 14.5 | 16.66 | 15.07 (0.87) | 15.04 | 14.66 |
| $1b_1$ | π_1 | 14.9 sh | 16.65 | 15.17 (0.81) | 15.16 | 15.20 |
| $6a_1$ | σ | 15.8 | 17.75 | 16.16 (0.86) | 16.13 | 15.74 |
| $3b_2$ | σ | 17.3 | 19.78 | 17.91 (0.85) | 17.88 | 17.47 |
| $5a_1$ | σ | | 19.94 | 17.99 (0.84) | 17.97 | 17.51 |

Table 4. Experimental band energies derived from the He I PES of 2-chloropyrimidine together with the assignments of each band. sh indicates a shoulder in the experimental spectrum. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

| | π_3 | n_{N_-} | π_2 | n_{N_+} | $n_{ }$ | n_{\perp} |
|--------------------|---------|-----------|---------|-----------|----------|-------------|
| Pyrimidine | | | | | | |
| N1 | 7.7 | 33.4 | 32.9 | 28.8 | | |
| C2 | 22.2 | 5.2 | 0.4 | 8.2 | | |
| N3 | 7.7 | 33.4 | 32.9 | 28.8 | | |
| C4 | 9.7 | 8.1 | 16.9 | 6.9 | | |
| C5 | 42.9 | 7.1 | 0.1 | 13.4 | | |
| C6 | 9.7 | 8.4 | 16.9 | 6.9 | | |
| 5-bromopyrimidine | | | | | | |
| N1 | 3.2 | 13.4 | 32.4 | 25.7 | 11.8 | 3.9 |
| C2 | 11.4 | 1.8 | 0.4 | 7.9 | 2.1 | 6.6 |
| N3 | 3.2 | 13.4 | 32.4 | 25.7 | 11.8 | 3.9 |
| C4 | 6.4 | 17.8 | 17.3 | 5.6 | 7.3 | 0.4 |
| C5 | 21.9 | 7.9 | 0.1 | 11.2 | 5.3 | 11.0 |
| C6 | 6.4 | 17.8 | 17.3 | 5.6 | 7.3 | 0.4 |
| Br | 47.6 | 26.3 | 0.0 | 14.4 | 52.7 | 73.9 |
| 2-bromopyrimidine | | | | | | |
| N1 | 6.0 | 27.6 | 33.7 | 20.7 | 10.8 | 0.1 |
| C2 | 9.7 | 7.4 | 0.4 | 14.7 | 1.7 | 6.3 |
| N3 | 6.0 | 27.6 | 33.7 | 20.7 | 10.8 | 0.1 |
| C4 | 3.6 | 6.5 | 16.0 | 5.5 | 5.0 | 5.1 |
| C5 | 21.0 | 5.7 | 0.1 | 12.3 | 1.4 | 12.6 |
| C6 | 3.6 | 6.5 | 16.0 | 5.5 | 5.0 | 5.1 |
| Br | 50.1 | 14.1 | 0.0 | 18.7 | 64.6 | 70.7 |
| 2-chloropyrimidine | | | | | | |
| N1 | 7.1 | 29.0 | 33.8 | 24.0 | 11.4 | 0.5 |
| C2 | 14.0 | 4.1 | 0.5 | 11.6 | 10.6 | 2.0 |
| N3 | 7.1 | 29.0 | 33.8 | 24.0 | 11.4 | 0.5 |
| C4 | 5.5 | 9.7 | 15.9 | 5.7 | 2.6 | 3.7 |
| C5 | 28.9 | 5.5 | 0.1 | 15.4 | 1.8 | 6.7 |
| C6 | 5.5 | 9.7 | 15.9 | 5.7 | 2.6 | 3.7 |
| Cl | 31.9 | 9.6 | 0.0 | 11.0 | 58.7 | 82.9 |

Table 5. Mulliken population analysis on the MOs of pyrimidine, 5-bromopyrimidine, 2-bromopyrimidine and 2-chloropyrimidine (sum of contributions of all AOs belonging to the same atom to the electron density of a given MO expressed as a percentage of the total electron density on that MO).

| Orbital | MO | Exp. | HF cc-pVTZ | P3 (PS) cc-pVTZ | P3 6-311G(2df,2p) | P3 6-311G(2df,2p) SDD | B3LYP |
|-------------------------|---------------------|----------|---------------|--------------------|----------------------|-----------------------------|-------|
| 4 <i>b</i> ₁ | π_3 | 9.68 | 10.04 | 10.01 (0.89) | 9.99 | 10.02 | 9.66 |
| 7 <i>b</i> ₂ | n_{N_-} | 9.88 | 11.75 | 10.58 (0.89) | 10.54 | 10.58 | 9.85 |
| 6 <i>b</i> ₂ | $n_{ }$ (Br) | 11.47 sh | 12.49 | 11.31 (0.89) | 11.23 | 11.32 | 10.93 |
| 5 <i>b</i> ₂ | $n_{ }$ (Cl) | | 12.90 | 11.76 (0.89) | 11.76 | 11.76 | 11.06 |
| 3 <i>b</i> ₁ | n_{\perp} (Br/Cl) | 11.6 | 12.57 | 11.71 (0.89) | 11.67 | 11.72 | 11.12 |
| 9 <i>a</i> ₁ | n_{N_+} | | 13.53 | 12.22 (0.88) | 12.18 | 12.20 | 11.52 |
| 1 <i>a</i> ₂ | π_2 | 11.85 | 12.39 | 12.16 (0.86) | 12.14 | 12.14 | 11.75 |
| 2 <i>b</i> ₁ | n_{\perp} (Br/Cl) | 13.03 | 13.95 | 13.07 (0.88) | 13.05 | 13.07 | 12.52 |
| 8 <i>a</i> ₁ | σ | 14.20 | 16.49 | 14.81 (0.86) | 15.28 | 15.31 | 14.18 |
| 4 <i>b</i> ₂ | σ | 14.64 | 17.21 | 15.54 (0.87) | 15.52 | 15.52 | 14.64 |
| 7 <i>a</i> ₁ | σ | | 16.28 | 15.30 (0.87) | 14.78 | 14.79 | 14.70 |
| 1 <i>b</i> ₁ | π_1 | 15.25 | 17.12 | 15.50 (0.80) | 15.49 | 15.49 | 15.09 |
| 6 <i>a</i> ₁ | σ | 17.28 | 20.01 | 18.14 (0.84) | 18.11 | 18.11 | 17.13 |
| 3 <i>b</i> ₂ | σ | | 20.43 | 18.44 (0.84) | 18.42 | 18.42 | 17.55 |

Table 6. Experimental band energies derived from the He I PES of 5-bromo-2-chloropyrimidine together with the assignments of each band. Also shown are the calculated ionisation energies obtained using the three computational methods outlined in the text. All energies are in eV.

Supporting Information for

“An Experimental and Computational Study of the Valence Photoelectron Spectra of Halogenated Pyrimidines”

Patrick O'Keeffe, Paola Bolognesi, Anna Rita Casavola, Daniele Catone, Nicola Zema, Stefano Turchini and Lorenzo Avaldi.

1. Pyrimidine:

1.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C, 1, B1
C, 2, B2, 1, A1
C, 3, B3, 2, A2, 1, D1, 0
N, 1, B4, 4, A3, 3, D2, 0
N, 1, B5, 5, A4, 4, D3, 0
H, 1, B6, 4, A5, 3, D4, 0
H, 2, B7, 1, A6, 4, D5, 0
H, 3, B8, 2, A7, 1, D6, 0
H, 4, B9, 3, A8, 2, D7, 0
```

Variables:

```
B1=2.26549454
B2=1.39104925
B3=1.39104925
B4=1.33514491
B5=1.33514491
B6=1.08595857
B7=1.08648567
B8=1.0829271
B9=1.08648567
A1=90.23498617
A2=116.5577385
A3=32.0180741
A4=127.00843738
A5=148.51385542
A6=148.51866006
A7=121.72113075
A8=121.24635377
D1=0.
D2=180.
D3=0.
D4=180.
D5=180.
D6=180.
D7=180.
```

1.2 Total Energy

E(RB+HF-LYP) = -264.393935420 Hartrees

1.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

| | | 1 | | | 2 | | | 3 | | |
|-------------|----|-----------|-------|-------|-----------|------|------|-----------|-------|-------|
| | | B1 | | | A2 | | | B2 | | |
| Frequencies | -- | 346.9748 | | | 406.8478 | | | 636.1803 | | |
| Red. masses | -- | 2.6629 | | | 4.1300 | | | 7.9786 | | |
| Frc consts | -- | 0.1889 | | | 0.4028 | | | 1.9025 | | |
| IR Inten | -- | 3.4903 | | | 0.0000 | | | 9.9897 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.14 | 0.00 |
| 2 | 6 | -0.12 | 0.00 | 0.00 | 0.23 | 0.00 | 0.00 | 0.00 | 0.26 | 0.23 |
| 3 | 6 | 0.24 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.21 | 0.00 |
| 4 | 6 | -0.12 | 0.00 | 0.00 | -0.23 | 0.00 | 0.00 | 0.00 | 0.26 | -0.23 |
| 5 | 7 | -0.10 | 0.00 | 0.00 | 0.27 | 0.00 | 0.00 | 0.00 | -0.28 | -0.25 |
| 6 | 7 | -0.10 | 0.00 | 0.00 | -0.27 | 0.00 | 0.00 | 0.00 | -0.28 | 0.25 |
| 7 | 1 | 0.59 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.20 | 0.00 |
| 8 | 1 | -0.38 | 0.00 | 0.00 | 0.61 | 0.00 | 0.00 | 0.00 | 0.40 | -0.03 |
| 9 | 1 | 0.47 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.25 | 0.00 |
| 10 | 1 | -0.38 | 0.00 | 0.00 | -0.61 | 0.00 | 0.00 | 0.00 | 0.40 | 0.03 |
| | | 4 | | | 5 | | | 6 | | |
| | | A1 | | | B1 | | | B1 | | |
| Frequencies | -- | 696.0192 | | | 732.9806 | | | 820.9289 | | |
| Red. masses | -- | 7.3288 | | | 1.7381 | | | 1.7356 | | |
| Frc consts | -- | 2.0918 | | | 0.5502 | | | 0.6891 | | |
| IR Inten | -- | 3.0989 | | | 43.7288 | | | 6.8741 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.00 | 0.00 | -0.34 | -0.10 | 0.00 | 0.00 | 0.09 | 0.00 | 0.00 |
| 2 | 6 | 0.00 | -0.26 | 0.02 | -0.07 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 |
| 3 | 6 | 0.00 | 0.00 | 0.40 | 0.14 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| 4 | 6 | 0.00 | 0.26 | 0.02 | -0.07 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 |
| 5 | 7 | 0.00 | 0.26 | -0.02 | 0.11 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 |
| 6 | 7 | 0.00 | -0.26 | -0.02 | 0.11 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 |
| 7 | 1 | 0.00 | 0.00 | -0.35 | -0.55 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 |
| 8 | 1 | 0.00 | -0.12 | -0.26 | -0.52 | 0.00 | 0.00 | -0.31 | 0.00 | 0.00 |
| 9 | 1 | 0.00 | 0.00 | 0.40 | -0.31 | 0.00 | 0.00 | -0.87 | 0.00 | 0.00 |
| 10 | 1 | 0.00 | 0.12 | -0.26 | -0.52 | 0.00 | 0.00 | -0.31 | 0.00 | 0.00 |
| | | 7 | | | 8 | | | 9 | | |
| | | B1 | | | A2 | | | B1 | | |
| Frequencies | -- | 975.9093 | | | 993.2509 | | | 1010.7519 | | |
| Red. masses | -- | 1.3674 | | | 1.3792 | | | 1.4915 | | |
| Frc consts | -- | 0.7673 | | | 0.8017 | | | 0.8978 | | |
| IR Inten | -- | 0.0274 | | | 0.0000 | | | 0.0024 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | -0.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 |
| 2 | 6 | -0.05 | 0.00 | 0.00 | -0.13 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 |
| 3 | 6 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.08 | 0.00 | 0.00 |
| 4 | 6 | -0.05 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 |
| 5 | 7 | 0.02 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 |
| 6 | 7 | 0.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 |
| 7 | 1 | 0.67 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.64 | 0.00 | 0.00 |
| 8 | 1 | 0.28 | 0.00 | 0.00 | 0.70 | 0.00 | 0.00 | -0.47 | 0.00 | 0.00 |
| 9 | 1 | -0.60 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.33 | 0.00 | 0.00 |
| 10 | 1 | 0.28 | 0.00 | 0.00 | -0.70 | 0.00 | 0.00 | -0.47 | 0.00 | 0.00 |
| | | 10 | | | 11 | | | 12 | | |
| | | A1 | | | A1 | | | B2 | | |
| Frequencies | -- | 1011.1710 | | | 1079.5348 | | | 1093.8032 | | |
| Red. masses | -- | 9.8208 | | | 3.5422 | | | 1.5209 | | |
| Frc consts | -- | 5.9163 | | | 2.4322 | | | 1.0721 | | |

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|-------------|----|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|
| IR Inten | -- | 3.5487 | | | 1.0178 | | | 3.8101 | | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 6 | | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | -0.15 | 0.00 | 0.08 | 0.00 |
| 2 6 | | 0.00 | 0.00 | -0.05 | 0.00 | 0.30 | 0.07 | 0.00 | -0.08 | -0.04 |
| 3 6 | | 0.00 | 0.00 | -0.49 | 0.00 | 0.00 | 0.09 | 0.00 | 0.09 | 0.00 |
| 4 6 | | 0.00 | 0.00 | -0.05 | 0.00 | -0.30 | 0.07 | 0.00 | -0.08 | 0.04 |
| 5 7 | | 0.00 | 0.42 | 0.24 | 0.00 | 0.07 | -0.01 | 0.00 | -0.04 | -0.07 |
| 6 7 | | 0.00 | -0.42 | 0.24 | 0.00 | -0.07 | -0.01 | 0.00 | -0.04 | 0.07 |
| 7 1 | | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | -0.16 | 0.00 | 0.31 | 0.00 |
| 8 1 | | 0.00 | -0.01 | -0.06 | 0.00 | 0.51 | -0.32 | 0.00 | -0.10 | 0.00 |
| 9 1 | | 0.00 | 0.00 | -0.52 | 0.00 | 0.00 | 0.12 | 0.00 | 0.92 | 0.00 |
| 10 1 | | 0.00 | 0.01 | -0.06 | 0.00 | -0.51 | -0.32 | 0.00 | -0.10 | 0.00 |
| | | 13 | | | 14 | | | 15 | | |
| | | A1 | | | B2 | | | B2 | | |
| Frequencies | -- | 1160.5048 | | | 1214.6016 | | | 1252.9535 | | |
| Red. masses | -- | 2.5374 | | | 3.8605 | | | 1.7531 | | |
| Frc consts | -- | 2.0134 | | | 3.3556 | | | 1.6216 | | |
| IR Inten | -- | 0.9044 | | | 4.7018 | | | 9.7736 | | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 6 | | 0.00 | 0.00 | 0.29 | 0.00 | 0.12 | 0.00 | 0.00 | 0.21 | 0.00 |
| 2 6 | | 0.00 | -0.01 | -0.13 | 0.00 | -0.05 | 0.24 | 0.00 | -0.05 | 0.00 |
| 3 6 | | 0.00 | 0.00 | 0.12 | 0.00 | 0.16 | 0.00 | 0.00 | 0.04 | 0.00 |
| 4 6 | | 0.00 | 0.01 | -0.13 | 0.00 | -0.05 | -0.24 | 0.00 | -0.05 | 0.00 |
| 5 7 | | 0.00 | 0.05 | -0.04 | 0.00 | -0.06 | 0.19 | 0.00 | -0.07 | 0.05 |
| 6 7 | | 0.00 | -0.05 | -0.04 | 0.00 | -0.06 | -0.19 | 0.00 | -0.07 | -0.05 |
| 7 1 | | 0.00 | 0.00 | 0.30 | 0.00 | -0.46 | 0.00 | 0.00 | 0.45 | 0.00 |
| 8 1 | | 0.00 | 0.21 | -0.58 | 0.00 | -0.17 | 0.44 | 0.00 | 0.18 | -0.48 |
| 9 1 | | 0.00 | 0.00 | 0.13 | 0.00 | 0.31 | 0.00 | 0.00 | -0.45 | 0.00 |
| 10 1 | | 0.00 | -0.21 | -0.58 | 0.00 | -0.17 | -0.44 | 0.00 | 0.18 | 0.48 |
| | | 16 | | | 17 | | | 18 | | |
| | | B2 | | | A1 | | | B2 | | |
| Frequencies | -- | 1392.8901 | | | 1435.2697 | | | 1491.6820 | | |
| Red. masses | -- | 1.1539 | | | 2.1627 | | | 1.8776 | | |
| Frc consts | -- | 1.3190 | | | 2.6249 | | | 2.4616 | | |
| IR Inten | -- | 0.2725 | | | 59.1471 | | | 6.3967 | | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 6 | | 0.00 | -0.02 | 0.00 | 0.00 | 0.00 | -0.12 | 0.00 | 0.12 | 0.00 |
| 2 6 | | 0.00 | 0.02 | -0.05 | 0.00 | -0.07 | -0.01 | 0.00 | -0.04 | -0.10 |
| 3 6 | | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | -0.06 | 0.00 | 0.16 | 0.00 |
| 4 6 | | 0.00 | 0.02 | 0.05 | 0.00 | 0.07 | -0.01 | 0.00 | -0.04 | 0.10 |
| 5 7 | | 0.00 | -0.03 | 0.04 | 0.00 | -0.11 | 0.14 | 0.00 | -0.03 | -0.08 |
| 6 7 | | 0.00 | -0.03 | -0.04 | 0.00 | 0.11 | 0.14 | 0.00 | -0.03 | 0.08 |
| 7 1 | | 0.00 | 0.70 | 0.00 | 0.00 | 0.00 | -0.13 | 0.00 | -0.68 | 0.00 |
| 8 1 | | 0.00 | -0.21 | 0.41 | 0.00 | 0.23 | -0.62 | 0.00 | -0.21 | 0.22 |
| 9 1 | | 0.00 | -0.26 | 0.00 | 0.00 | 0.00 | -0.08 | 0.00 | -0.52 | 0.00 |
| 10 1 | | 0.00 | -0.21 | -0.41 | 0.00 | -0.23 | -0.62 | 0.00 | -0.21 | -0.22 |
| | | 19 | | | 20 | | | 21 | | |
| | | A1 | | | B2 | | | A1 | | |
| Frequencies | -- | 1607.7053 | | | 1607.7645 | | | 3151.5715 | | |
| Red. masses | -- | 5.0888 | | | 5.5197 | | | 1.0887 | | |
| Frc consts | -- | 7.7496 | | | 8.4064 | | | 6.3712 | | |
| IR Inten | -- | 46.3669 | | | 85.0123 | | | 13.9594 | | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 6 | | 0.00 | 0.00 | 0.09 | 0.00 | 0.32 | 0.00 | 0.00 | 0.00 | -0.01 |
| 2 6 | | 0.00 | -0.11 | 0.32 | 0.00 | 0.21 | -0.10 | 0.00 | -0.05 | -0.02 |
| 3 6 | | 0.00 | 0.00 | -0.18 | 0.00 | -0.38 | 0.00 | 0.00 | 0.00 | 0.02 |
| 4 6 | | 0.00 | 0.11 | 0.32 | 0.00 | 0.21 | 0.10 | 0.00 | 0.05 | -0.02 |
| 5 7 | | 0.00 | 0.03 | -0.20 | 0.00 | -0.16 | 0.04 | 0.00 | 0.00 | 0.00 |
| 6 7 | | 0.00 | -0.03 | -0.20 | 0.00 | -0.16 | -0.04 | 0.00 | 0.00 | 0.00 |
| 7 1 | | 0.00 | 0.00 | 0.08 | 0.00 | -0.41 | 0.00 | 0.00 | 0.00 | 0.14 |
| 8 1 | | 0.00 | 0.26 | -0.47 | 0.00 | 0.02 | 0.34 | 0.00 | 0.60 | 0.30 |
| 9 1 | | 0.00 | 0.00 | -0.22 | 0.00 | 0.44 | 0.00 | 0.00 | 0.00 | -0.25 |
| 10 1 | | 0.00 | -0.26 | -0.47 | 0.00 | 0.02 | -0.34 | 0.00 | -0.60 | 0.30 |

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| | | 22 | | | 23 | | | 24 | | |
|-------------|----|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|
| | | B2 | | | A1 | | | A1 | | |
| Frequencies | -- | 3154.7726 | | | 3167.4200 | | | 3197.5350 | | |
| Red. masses | -- | 1.0918 | | | 1.0917 | | | 1.0964 | | |
| Frc consts | -- | 6.4024 | | | 6.4533 | | | 6.6045 | | |
| IR Inten | -- | 18.1584 | | | 13.7417 | | | 9.0240 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.09 | 0.00 | 0.00 | 0.00 |
| 2 | 6 | 0.00 | 0.06 | 0.03 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.00 |
| 3 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.09 |
| 4 | 6 | 0.00 | 0.06 | -0.03 | 0.00 | -0.01 | 0.00 | 0.00 | -0.02 | 0.00 |
| 5 | 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.99 | 0.00 | 0.00 | 0.04 |
| 8 | 1 | 0.00 | -0.63 | -0.32 | 0.00 | -0.07 | -0.04 | 0.00 | -0.16 | -0.08 |
| 9 | 1 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | -0.96 |
| 10 | 1 | 0.00 | -0.63 | 0.32 | 0.00 | 0.07 | -0.04 | 0.00 | 0.16 | -0.08 |

2. 2-bromopyrimidine:

2.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C, 1, B1
C, 2, B2, 1, A1
C, 3, B3, 2, A2, 1, D1, 0
N, 1, B4, 2, A3, 3, D2, 0
N, 2, B5, 1, A4, 5, D3, 0
H, 3, B6, 2, A5, 1, D4, 0
H, 4, B7, 3, A6, 2, D5, 0
H, 2, B8, 1, A7, 5, D6, 0
Br, 1, B9, 5, A8, 4, D7, 0
```

Variables:

```
B1=2.25061328
B2=1.39063884
B3=1.39063884
B4=1.32426991
B5=1.33722206
B6=1.08214206
B7=1.08585572
B8=1.08585572
B9=1.91679851
A1=90.1662816
A2=116.33613981
A3=95.76921093
A4=32.085896
A5=121.83193009
A6=121.60067615
A7=148.23304224
A8=115.89643756
D1=0.
D2=0.
D3=180.
D4=180.
D5=180.
D6=180.
D7=180.
```

2.2 Total Energy

E(RB+HF-LYP) = -2837.93615700 Hartrees

2.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

| | | 1 | 2 | 3 | | | | | | |
|-------------|----|----------|----------|----------|------|-------|-------|------|------|------|
| | | B1 | B2 | A1 | | | | | | |
| Frequencies | -- | 141.9332 | 270.5296 | 322.6271 | | | | | | |
| Red. masses | -- | 6.3832 | 7.7210 | 15.1030 | | | | | | |
| Frc consts | -- | 0.0758 | 0.3329 | 0.9262 | | | | | | |
| IR Inten | -- | 5.1145 | 5.0751 | 5.9056 | | | | | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | -0.29 | 0.00 | 0.00 | 0.00 | 0.36 | 0.00 | 0.00 | 0.00 | 0.18 |
| 2 | 6 | 0.03 | 0.00 | 0.00 | 0.00 | -0.02 | -0.22 | 0.00 | 0.04 | 0.33 |
| 3 | 6 | 0.37 | 0.00 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.39 |

| | | | | | | | | | | | |
|----|-------------|----|-----------|-------|-------|-------|-----------|-------|-------|-----------|-------|
| 1 | | | | | | | | | | | |
| 2 | | | | | | | | | | | |
| 3 | 4 | 6 | 0.03 | 0.00 | 0.00 | 0.00 | -0.02 | 0.22 | 0.00 | -0.04 | 0.33 |
| 4 | 5 | 7 | -0.31 | 0.00 | 0.00 | 0.00 | 0.27 | 0.19 | 0.00 | -0.06 | 0.30 |
| 5 | 6 | 7 | -0.31 | 0.00 | 0.00 | 0.00 | 0.27 | -0.19 | 0.00 | 0.06 | 0.30 |
| 6 | 7 | 1 | 0.76 | 0.00 | 0.00 | 0.00 | -0.35 | 0.00 | 0.00 | 0.00 | 0.39 |
| 7 | 8 | 1 | 0.05 | 0.00 | 0.00 | 0.00 | -0.12 | 0.42 | 0.00 | -0.01 | 0.28 |
| 8 | 9 | 1 | 0.05 | 0.00 | 0.00 | 0.00 | -0.12 | -0.42 | 0.00 | 0.01 | 0.28 |
| 9 | 10 | 35 | 0.08 | 0.00 | 0.00 | 0.00 | -0.12 | 0.00 | 0.00 | 0.00 | -0.30 |
| 10 | | | | 4 | | | 5 | | | 6 | |
| 11 | | | | A2 | | | B1 | | | B2 | |
| 12 | Frequencies | -- | 409.6389 | | | | 472.2586 | | | 633.7788 | |
| 13 | Red. masses | -- | 4.2212 | | | | 3.0790 | | | 8.2498 | |
| 14 | Frc consts | -- | 0.4173 | | | | 0.4046 | | | 1.9524 | |
| 15 | IR Inten | -- | 0.0000 | | | | 1.8957 | | | 9.8586 | |
| 16 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 17 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.30 | 0.00 | 0.00 | 0.00 | -0.10 | 0.00 |
| 18 | 2 | 6 | -0.23 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.26 | -0.26 |
| 19 | 3 | 6 | 0.00 | 0.00 | 0.00 | 0.22 | 0.00 | 0.00 | 0.00 | 0.20 | 0.00 |
| 20 | 4 | 6 | 0.23 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.26 | 0.26 |
| 21 | 5 | 7 | -0.28 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | -0.26 | 0.27 |
| 22 | 6 | 7 | 0.28 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | -0.26 | -0.27 |
| 23 | 7 | 1 | 0.00 | 0.00 | 0.00 | 0.25 | 0.00 | 0.00 | 0.00 | -0.30 | 0.00 |
| 24 | 8 | 1 | 0.61 | 0.00 | 0.00 | -0.61 | 0.00 | 0.00 | 0.00 | 0.39 | 0.02 |
| 25 | 9 | 1 | -0.61 | 0.00 | 0.00 | -0.61 | 0.00 | 0.00 | 0.00 | 0.39 | -0.02 |
| 26 | 10 | 35 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 |
| 27 | | | | 7 | | | 8 | | | 9 | |
| 28 | | | | A1 | | | B1 | | | B1 | |
| 29 | Frequencies | -- | 749.3143 | | | | 784.0197 | | | 818.4156 | |
| 30 | Red. masses | -- | 7.8907 | | | | 7.6713 | | | 1.2156 | |
| 31 | Frc consts | -- | 2.6103 | | | | 2.7783 | | | 0.4797 | |
| 32 | IR Inten | -- | 37.9108 | | | | 11.1410 | | | 27.2525 | |
| 33 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 34 | 1 | 6 | 0.00 | 0.00 | 0.36 | 0.51 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 |
| 35 | 2 | 6 | 0.00 | -0.29 | 0.04 | 0.20 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 |
| 36 | 3 | 6 | 0.00 | 0.00 | -0.38 | -0.23 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 |
| 37 | 4 | 6 | 0.00 | 0.29 | 0.04 | 0.20 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 |
| 38 | 5 | 7 | 0.00 | 0.27 | 0.06 | -0.30 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 |
| 39 | 6 | 7 | 0.00 | -0.27 | 0.06 | -0.30 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 |
| 40 | 7 | 1 | 0.00 | 0.00 | -0.38 | -0.08 | 0.00 | 0.00 | -0.85 | 0.00 | 0.00 |
| 41 | 8 | 1 | 0.00 | 0.15 | 0.33 | 0.46 | 0.00 | 0.00 | -0.36 | 0.00 | 0.00 |
| 42 | 9 | 1 | 0.00 | -0.15 | 0.33 | 0.46 | 0.00 | 0.00 | -0.36 | 0.00 | 0.00 |
| 43 | 10 | 35 | 0.00 | 0.00 | -0.03 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 44 | | | | 10 | | | 11 | | | 12 | |
| 45 | | | | A2 | | | B1 | | | A1 | |
| 46 | Frequencies | -- | 997.4480 | | | | 998.1127 | | | 1002.1739 | |
| 47 | Red. masses | -- | 1.3704 | | | | 1.4104 | | | 9.9849 | |
| 48 | Frc consts | -- | 0.8033 | | | | 0.8278 | | | 5.9085 | |
| 49 | IR Inten | -- | 0.0000 | | | | 0.1154 | | | 0.3353 | |
| 50 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 51 | 1 | 6 | 0.00 | 0.00 | 0.00 | -0.04 | 0.00 | 0.00 | 0.00 | 0.00 | -0.08 |
| 52 | 2 | 6 | 0.13 | 0.00 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.05 | 0.04 |
| 53 | 3 | 6 | 0.00 | 0.00 | 0.00 | -0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.47 |
| 54 | 4 | 6 | -0.13 | 0.00 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | -0.05 | 0.04 |
| 55 | 5 | 7 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.44 | -0.23 |
| 56 | 6 | 7 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.44 | -0.23 |
| 57 | 7 | 1 | 0.00 | 0.00 | 0.00 | 0.59 | 0.00 | 0.00 | 0.00 | 0.00 | 0.50 |
| 58 | 8 | 1 | 0.70 | 0.00 | 0.00 | -0.56 | 0.00 | 0.00 | 0.00 | -0.07 | 0.09 |
| 59 | 9 | 1 | -0.70 | 0.00 | 0.00 | -0.56 | 0.00 | 0.00 | 0.00 | 0.07 | 0.09 |
| 60 | 10 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | | 13 | | | 14 | | | 15 | |
| | | | | A1 | | | B2 | | | A1 | |
| | Frequencies | -- | 1087.0553 | | | | 1109.2006 | | | 1169.1629 | |
| | Red. masses | -- | 2.9448 | | | | 1.4452 | | | 3.8904 | |
| | Frc consts | -- | 2.0503 | | | | 1.0476 | | | 3.1333 | |

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|-------------|------|-----------|-------|------|-----------|-------|------|-----------|-------|--|
| IR Inten | -- | 7.0117 | | | 0.6871 | | | 194.5912 | | |
| Atom AN | X | Y | Z | X | Y | Z | X | Y | Z | |
| 1 6 | 0.00 | 0.00 | 0.10 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.43 | |
| 2 6 | 0.00 | 0.26 | -0.03 | 0.00 | -0.07 | 0.01 | 0.00 | 0.05 | -0.14 | |
| 3 6 | 0.00 | 0.00 | -0.14 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.13 | |
| 4 6 | 0.00 | -0.26 | -0.03 | 0.00 | -0.07 | -0.01 | 0.00 | -0.05 | -0.14 | |
| 5 7 | 0.00 | 0.06 | 0.03 | 0.00 | -0.04 | 0.07 | 0.00 | -0.04 | -0.05 | |
| 6 7 | 0.00 | -0.06 | 0.03 | 0.00 | -0.04 | -0.07 | 0.00 | 0.04 | -0.05 | |
| 7 1 | 0.00 | 0.00 | -0.16 | 0.00 | 0.96 | 0.00 | 0.00 | 0.00 | 0.13 | |
| 8 1 | 0.00 | -0.49 | 0.40 | 0.00 | -0.12 | 0.08 | 0.00 | 0.16 | -0.58 | |
| 9 1 | 0.00 | 0.49 | 0.40 | 0.00 | -0.12 | -0.08 | 0.00 | -0.16 | -0.58 | |
| 10 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | |
| | | 16 | | | 17 | | | 18 | | |
| | | B2 | | | B2 | | | A1 | | |
| Frequencies | -- | 1226.3659 | | | 1289.5484 | | | 1417.8813 | | |
| Red. masses | -- | 9.5816 | | | 1.5900 | | | 2.1216 | | |
| Frc consts | -- | 8.4904 | | | 1.5579 | | | 2.5130 | | |
| IR Inten | -- | 0.2547 | | | 8.2626 | | | 242.4240 | | |
| Atom AN | X | Y | Z | X | Y | Z | X | Y | Z | |
| 1 6 | 0.00 | -0.30 | 0.00 | 0.00 | 0.19 | 0.00 | 0.00 | 0.00 | 0.11 | |
| 2 6 | 0.00 | 0.10 | 0.34 | 0.00 | -0.05 | 0.04 | 0.00 | -0.07 | 0.03 | |
| 3 6 | 0.00 | -0.24 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.06 | |
| 4 6 | 0.00 | 0.10 | -0.34 | 0.00 | -0.05 | -0.04 | 0.00 | 0.07 | 0.03 | |
| 5 7 | 0.00 | 0.14 | 0.37 | 0.00 | -0.04 | 0.03 | 0.00 | -0.10 | -0.15 | |
| 6 7 | 0.00 | 0.14 | -0.37 | 0.00 | -0.04 | -0.03 | 0.00 | 0.10 | -0.15 | |
| 7 1 | 0.00 | 0.22 | 0.00 | 0.00 | -0.26 | 0.00 | 0.00 | 0.00 | 0.07 | |
| 8 1 | 0.00 | 0.11 | -0.32 | 0.00 | 0.23 | -0.62 | 0.00 | -0.23 | 0.63 | |
| 9 1 | 0.00 | 0.11 | 0.32 | 0.00 | 0.23 | 0.62 | 0.00 | 0.23 | 0.63 | |
| 10 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| | | 19 | | | 20 | | | 21 | | |
| | | B2 | | | B2 | | | A1 | | |
| Frequencies | -- | 1452.1664 | | | 1587.6783 | | | 1596.9566 | | |
| Red. masses | -- | 1.8935 | | | 6.2180 | | | 4.7210 | | |
| Frc consts | -- | 2.3526 | | | 9.2347 | | | 7.0937 | | |
| IR Inten | -- | 0.4779 | | | 107.8272 | | | 141.3138 | | |
| Atom AN | X | Y | Z | X | Y | Z | X | Y | Z | |
| 1 6 | 0.00 | 0.12 | 0.00 | 0.00 | -0.29 | 0.00 | 0.00 | 0.00 | 0.05 | |
| 2 6 | 0.00 | -0.01 | 0.13 | 0.00 | -0.23 | -0.09 | 0.00 | 0.11 | 0.32 | |
| 3 6 | 0.00 | 0.14 | 0.00 | 0.00 | 0.44 | 0.00 | 0.00 | 0.00 | -0.18 | |
| 4 6 | 0.00 | -0.01 | -0.13 | 0.00 | -0.23 | 0.09 | 0.00 | -0.11 | 0.32 | |
| 5 7 | 0.00 | -0.06 | 0.04 | 0.00 | 0.16 | 0.07 | 0.00 | -0.02 | -0.18 | |
| 6 7 | 0.00 | -0.06 | -0.04 | 0.00 | 0.16 | -0.07 | 0.00 | 0.02 | -0.18 | |
| 7 1 | 0.00 | -0.61 | 0.00 | 0.00 | -0.56 | 0.00 | 0.00 | 0.00 | -0.22 | |
| 8 1 | 0.00 | -0.30 | 0.43 | 0.00 | -0.05 | -0.33 | 0.00 | 0.26 | -0.49 | |
| 9 1 | 0.00 | -0.30 | -0.43 | 0.00 | -0.05 | 0.33 | 0.00 | -0.26 | -0.49 | |
| 10 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| | | 22 | | | 23 | | | 24 | | |
| | | A1 | | | B2 | | | A1 | | |
| Frequencies | -- | 3162.1133 | | | 3165.0691 | | | 3207.8318 | | |
| Red. masses | -- | 1.0901 | | | 1.0922 | | | 1.0965 | | |
| Frc consts | -- | 6.4220 | | | 6.4467 | | | 6.6477 | | |
| IR Inten | -- | 11.8041 | | | 12.4157 | | | 5.1310 | | |
| Atom AN | X | Y | Z | X | Y | Z | X | Y | Z | |
| 1 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| 2 6 | 0.00 | 0.05 | -0.02 | 0.00 | -0.06 | 0.03 | 0.00 | 0.02 | 0.00 | |
| 3 6 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.09 | |
| 4 6 | 0.00 | -0.05 | -0.02 | 0.00 | -0.06 | -0.03 | 0.00 | -0.02 | 0.00 | |
| 5 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| 6 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| 7 1 | 0.00 | 0.00 | -0.24 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.97 | |
| 8 1 | 0.00 | 0.61 | 0.30 | 0.00 | 0.63 | 0.31 | 0.00 | 0.15 | 0.07 | |
| 9 1 | 0.00 | -0.61 | 0.30 | 0.00 | 0.63 | -0.31 | 0.00 | -0.15 | 0.07 | |
| 10 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |

3. 5-bromopyrimidine:

3.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C, 1, B1
C, 2, B2, 1, A1
C, 3, B3, 2, A2, 1, D1, 0
N, 1, B4, 2, A3, 3, D2, 0
N, 2, B5, 1, A4, 5, D3, 0
H, 4, B6, 3, A5, 2, D4, 0
H, 2, B7, 1, A6, 5, D5, 0
Br, 3, B8, 2, A7, 1, D6, 0
H, 1, B9, 5, A8, 4, D7, 0
```

Variables:

```
B1=2.2703905
B2=1.39179689
B3=1.39179689
B4=1.33437731
B5=1.33403597
B6=1.08527625
B7=1.08527625
B8=1.90578858
B9=1.0851449
A1=89.49191149
A2=117.72118914
A3=94.98740399
A4=31.70146814
A5=121.31626098
A6=149.19182753
A7=121.13940543
A8=116.66008996
D1=0.
D2=0.
D3=180.
D4=180.
D5=180.
D6=180.
D7=180.
```

3.2 Total Energy

E(RB+HF-LYP) = -2837.93398026 Hartrees

3.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

| | | 1 | | | 2 | | | 3 | | |
|-------------|----|----------|------|------|----------|-------|-------|----------|------|------|
| | | B1 | | | B2 | | | A1 | | |
| Frequencies | -- | 163.3838 | | | 241.8699 | | | 321.2182 | | |
| Red. masses | -- | 4.1375 | | | 6.2541 | | | 13.3842 | | |
| Frc consts | -- | 0.0651 | | | 0.2156 | | | 0.8137 | | |
| IR Inten | -- | 0.2971 | | | 1.1221 | | | 2.6204 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.27 | 0.00 | 0.00 | 0.00 | -0.12 | 0.00 | 0.00 | 0.00 | 0.37 |
| 2 | 6 | -0.24 | 0.00 | 0.00 | 0.00 | 0.24 | -0.18 | 0.00 | 0.04 | 0.28 |
| 3 | 6 | -0.25 | 0.00 | 0.00 | 0.00 | 0.34 | 0.00 | 0.00 | 0.00 | 0.12 |

| | | | | | | | | | | | |
|----|-------------|----|-----------|------|------|-------|-----------|-------|-------|-----------|-------|
| 1 | | | | | | | | | | | |
| 2 | | | | | | | | | | | |
| 3 | 4 | 6 | -0.24 | 0.00 | 0.00 | 0.00 | 0.24 | 0.18 | 0.00 | -0.04 | 0.28 |
| 4 | 5 | 7 | 0.04 | 0.00 | 0.00 | 0.00 | -0.02 | 0.20 | 0.00 | -0.04 | 0.32 |
| 5 | 6 | 7 | 0.04 | 0.00 | 0.00 | 0.00 | -0.02 | -0.20 | 0.00 | 0.04 | 0.32 |
| 6 | 7 | 1 | -0.40 | 0.00 | 0.00 | 0.00 | 0.34 | 0.37 | 0.00 | 0.00 | 0.37 |
| 7 | 8 | 1 | -0.40 | 0.00 | 0.00 | 0.00 | 0.34 | -0.37 | 0.00 | 0.00 | 0.37 |
| 8 | 9 | 35 | 0.06 | 0.00 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 | 0.00 | -0.29 |
| 9 | 10 | 1 | 0.64 | 0.00 | 0.00 | 0.00 | -0.30 | 0.00 | 0.00 | 0.00 | 0.37 |
| 10 | | | | 4 | | | 5 | | | 6 | |
| 11 | | | | A2 | | | B1 | | | B2 | |
| 12 | Frequencies | -- | 412.6071 | | | | 420.6792 | | | 629.1750 | |
| 13 | Red. masses | -- | 4.2054 | | | | 4.3323 | | | 8.9424 | |
| 14 | Frc consts | -- | 0.4218 | | | | 0.4517 | | | 2.0857 | |
| 15 | IR Inten | -- | 0.0000 | | | | 0.4197 | | | 13.8198 | |
| 16 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 17 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.17 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 |
| 18 | 2 | 6 | 0.23 | 0.00 | 0.00 | -0.07 | 0.00 | 0.00 | 0.00 | -0.24 | -0.25 |
| 19 | 3 | 6 | 0.00 | 0.00 | 0.00 | 0.46 | 0.00 | 0.00 | 0.00 | -0.21 | 0.00 |
| 20 | 4 | 6 | -0.23 | 0.00 | 0.00 | -0.07 | 0.00 | 0.00 | 0.00 | -0.24 | 0.25 |
| 21 | 5 | 7 | 0.28 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.30 | 0.30 |
| 22 | 6 | 7 | -0.28 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.30 | -0.30 |
| 23 | 7 | 1 | -0.61 | 0.00 | 0.00 | -0.49 | 0.00 | 0.00 | 0.00 | -0.37 | 0.02 |
| 24 | 8 | 1 | 0.61 | 0.00 | 0.00 | -0.49 | 0.00 | 0.00 | 0.00 | -0.37 | -0.02 |
| 25 | 9 | 35 | 0.00 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 |
| 26 | 10 | 1 | 0.00 | 0.00 | 0.00 | 0.47 | 0.00 | 0.00 | 0.00 | -0.26 | 0.00 |
| 27 | | | | 7 | | | 8 | | | 9 | |
| 28 | | | | B1 | | | A1 | | | B1 | |
| 29 | Frequencies | -- | 729.9382 | | | | 744.8655 | | | 907.7513 | |
| 30 | Red. masses | -- | 2.4451 | | | | 9.5447 | | | 1.6123 | |
| 31 | Frc consts | -- | 0.7676 | | | | 3.1201 | | | 0.7828 | |
| 32 | IR Inten | -- | 29.5164 | | | | 6.2089 | | | 6.6819 | |
| 33 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 34 | 1 | 6 | -0.15 | 0.00 | 0.00 | 0.00 | 0.00 | -0.33 | 0.09 | 0.00 | 0.00 |
| 35 | 2 | 6 | -0.12 | 0.00 | 0.00 | 0.00 | -0.32 | 0.05 | 0.13 | 0.00 | 0.00 |
| 36 | 3 | 6 | 0.12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.42 | -0.10 | 0.00 | 0.00 |
| 37 | 4 | 6 | -0.12 | 0.00 | 0.00 | 0.00 | 0.32 | 0.05 | 0.13 | 0.00 | 0.00 |
| 38 | 5 | 7 | 0.17 | 0.00 | 0.00 | 0.00 | 0.33 | 0.06 | -0.05 | 0.00 | 0.00 |
| 39 | 6 | 7 | 0.17 | 0.00 | 0.00 | 0.00 | -0.33 | 0.06 | -0.05 | 0.00 | 0.00 |
| 40 | 7 | 1 | -0.47 | 0.00 | 0.00 | 0.00 | 0.19 | -0.21 | -0.60 | 0.00 | 0.00 |
| 41 | 8 | 1 | -0.47 | 0.00 | 0.00 | 0.00 | -0.19 | -0.21 | -0.60 | 0.00 | 0.00 |
| 42 | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.04 | 0.00 | 0.00 | 0.00 |
| 43 | 10 | 1 | -0.66 | 0.00 | 0.00 | 0.00 | 0.00 | -0.34 | -0.47 | 0.00 | 0.00 |
| 44 | | | | 10 | | | 11 | | | 12 | |
| 45 | | | | A2 | | | B1 | | | A1 | |
| 46 | Frequencies | -- | 975.1222 | | | | 992.7439 | | | 1028.7472 | |
| 47 | Red. masses | -- | 1.3708 | | | | 1.4830 | | | 8.2121 | |
| 48 | Frc consts | -- | 0.7680 | | | | 0.8611 | | | 5.1206 | |
| 49 | IR Inten | -- | 0.0000 | | | | 0.0048 | | | 61.2852 | |
| 50 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 51 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 | -0.03 |
| 52 | 2 | 6 | -0.13 | 0.00 | 0.00 | -0.06 | 0.00 | 0.00 | 0.00 | 0.24 | -0.01 |
| 53 | 3 | 6 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | -0.38 |
| 54 | 4 | 6 | 0.13 | 0.00 | 0.00 | -0.06 | 0.00 | 0.00 | 0.00 | -0.24 | -0.01 |
| 55 | 5 | 7 | -0.02 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 | 0.00 | 0.37 | 0.17 |
| 56 | 6 | 7 | 0.02 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 | 0.00 | -0.37 | 0.17 |
| 57 | 7 | 1 | -0.70 | 0.00 | 0.00 | 0.34 | 0.00 | 0.00 | 0.00 | -0.37 | -0.26 |
| 58 | 8 | 1 | 0.70 | 0.00 | 0.00 | 0.34 | 0.00 | 0.00 | 0.00 | 0.37 | -0.26 |
| 59 | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 |
| 60 | 10 | 1 | 0.00 | 0.00 | 0.00 | -0.85 | 0.00 | 0.00 | 0.00 | 0.00 | -0.03 |
| | | | | 13 | | | 14 | | | 15 | |
| | | | | A1 | | | A1 | | | B2 | |
| | Frequencies | -- | 1099.9895 | | | | 1161.1637 | | | 1205.9251 | |
| | Red. masses | -- | 5.2004 | | | | 2.2578 | | | 2.3954 | |
| | Frc consts | -- | 3.7074 | | | | 1.7936 | | | 2.0524 | |

| | | | | | | | | | | |
|----|-------------|------|-----------|-------|-----------|-------|-----------|------|-------|-------|
| 1 | | | | | | | | | | |
| 2 | | | | | | | | | | |
| 3 | IR Inten | -- | 8.1337 | | 30.2899 | | 13.6869 | | | |
| 4 | Atom AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 5 | 1 6 | 0.00 | 0.00 | -0.29 | 0.00 | 0.00 | 0.23 | 0.00 | -0.04 | 0.00 |
| 6 | 2 6 | 0.00 | 0.29 | 0.13 | 0.00 | 0.02 | -0.10 | 0.00 | 0.02 | 0.20 |
| 7 | 3 6 | 0.00 | 0.00 | 0.29 | 0.00 | 0.00 | 0.17 | 0.00 | 0.04 | 0.00 |
| 8 | 4 6 | 0.00 | -0.29 | 0.13 | 0.00 | -0.02 | -0.10 | 0.00 | 0.02 | -0.20 |
| 9 | 5 7 | 0.00 | -0.06 | -0.05 | 0.00 | 0.04 | -0.04 | 0.00 | 0.01 | 0.14 |
| 10 | 6 7 | 0.00 | 0.06 | -0.05 | 0.00 | -0.04 | -0.04 | 0.00 | 0.01 | -0.14 |
| 11 | 7 1 | 0.00 | -0.48 | -0.18 | 0.00 | -0.27 | -0.58 | 0.00 | -0.11 | -0.46 |
| 12 | 8 1 | 0.00 | 0.48 | -0.18 | 0.00 | 0.27 | -0.58 | 0.00 | -0.11 | 0.46 |
| 13 | 9 35 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 14 | 10 1 | 0.00 | 0.00 | -0.31 | 0.00 | 0.00 | 0.25 | 0.00 | -0.66 | 0.00 |
| 15 | | | 16 | | | 17 | | | 18 | |
| 16 | | | B2 | | | B2 | | | A1 | |
| 17 | Frequencies | -- | 1217.6389 | | 1360.9646 | | 1436.3278 | | | |
| 18 | Red. masses | -- | 5.3970 | | 1.2322 | | 2.1819 | | | |
| 19 | Frc consts | -- | 4.7145 | | 1.3447 | | 2.6521 | | | |
| 20 | IR Inten | -- | 2.3611 | | 3.1059 | | 78.7633 | | | |
| 21 | Atom AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 22 | 1 6 | 0.00 | 0.40 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.12 |
| 23 | 2 6 | 0.00 | -0.17 | 0.09 | 0.00 | 0.00 | 0.07 | 0.00 | 0.08 | 0.00 |
| 24 | 3 6 | 0.00 | 0.25 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 | 0.00 | 0.10 |
| 25 | 4 6 | 0.00 | -0.17 | -0.09 | 0.00 | 0.00 | -0.07 | 0.00 | -0.08 | 0.00 |
| 26 | 5 7 | 0.00 | -0.16 | 0.13 | 0.00 | 0.02 | 0.00 | 0.00 | 0.11 | -0.13 |
| 27 | 6 7 | 0.00 | -0.16 | -0.13 | 0.00 | 0.02 | 0.00 | 0.00 | -0.11 | -0.13 |
| 28 | 7 1 | 0.00 | 0.04 | 0.36 | 0.00 | 0.31 | 0.54 | 0.00 | 0.23 | 0.63 |
| 29 | 8 1 | 0.00 | 0.04 | -0.36 | 0.00 | 0.31 | -0.54 | 0.00 | -0.23 | 0.63 |
| 30 | 9 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 31 | 10 1 | 0.00 | 0.59 | 0.00 | 0.00 | -0.46 | 0.00 | 0.00 | 0.00 | 0.12 |
| 32 | | | 19 | | | 20 | | | 21 | |
| 33 | | | B2 | | | A1 | | | B2 | |
| 34 | Frequencies | -- | 1450.7022 | | 1581.4764 | | 1583.1277 | | | |
| 35 | Red. masses | -- | 1.8683 | | 5.6690 | | 5.8096 | | | |
| 36 | Frc consts | -- | 2.3166 | | 8.3538 | | 8.5788 | | | |
| 37 | IR Inten | -- | 13.8141 | | 1.9578 | | 57.7146 | | | |
| 38 | Atom AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 39 | 1 6 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.10 | 0.00 | 0.37 | 0.00 |
| 40 | 2 6 | 0.00 | -0.07 | -0.07 | 0.00 | -0.11 | 0.34 | 0.00 | 0.20 | -0.12 |
| 41 | 3 6 | 0.00 | 0.16 | 0.00 | 0.00 | 0.00 | -0.19 | 0.00 | -0.33 | 0.00 |
| 42 | 4 6 | 0.00 | -0.07 | 0.07 | 0.00 | 0.11 | 0.34 | 0.00 | 0.20 | 0.12 |
| 43 | 5 7 | 0.00 | 0.00 | -0.11 | 0.00 | 0.05 | -0.22 | 0.00 | -0.17 | 0.04 |
| 44 | 6 7 | 0.00 | 0.00 | 0.11 | 0.00 | -0.05 | -0.22 | 0.00 | -0.17 | -0.04 |
| 45 | 7 1 | 0.00 | -0.15 | -0.07 | 0.00 | -0.28 | -0.46 | 0.00 | -0.03 | -0.38 |
| 46 | 8 1 | 0.00 | -0.15 | 0.07 | 0.00 | 0.28 | -0.46 | 0.00 | -0.03 | 0.38 |
| 47 | 9 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 48 | 10 1 | 0.00 | -0.93 | 0.00 | 0.00 | 0.00 | 0.10 | 0.00 | -0.53 | 0.00 |
| 49 | | | 22 | | | 23 | | | 24 | |
| 50 | | | B2 | | | A1 | | | A1 | |
| 51 | Frequencies | -- | 3171.2125 | | 3171.2227 | | 3178.9094 | | | |
| 52 | Red. masses | -- | 1.0924 | | 1.0910 | | 1.0935 | | | |
| 53 | Frc consts | -- | 6.4729 | | 6.4647 | | 6.5106 | | | |
| 54 | IR Inten | -- | 2.6874 | | 10.4263 | | 5.7922 | | | |
| 55 | Atom AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 56 | 1 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.08 |
| 57 | 2 6 | 0.00 | -0.06 | -0.03 | 0.00 | 0.05 | 0.02 | 0.00 | -0.02 | -0.01 |
| 58 | 3 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 59 | 4 6 | 0.00 | -0.06 | 0.03 | 0.00 | -0.05 | 0.02 | 0.00 | 0.02 | -0.01 |
| 60 | 5 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 6 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 7 1 | 0.00 | 0.63 | -0.32 | 0.00 | 0.59 | -0.30 | 0.00 | -0.21 | 0.11 |
| | 8 1 | 0.00 | 0.63 | 0.32 | 0.00 | -0.59 | -0.30 | 0.00 | 0.21 | 0.11 |
| | 9 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 10 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.34 | 0.00 | 0.00 | -0.94 |

4. 2-chloropyrimidine:

4.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

C

C, 1, B1
 C, 2, B2, 1, A1
 C, 3, B3, 2, A2, 1, D1, 0
 N, 1, B4, 4, A3, 3, D2, 0
 N, 1, B5, 5, A4, 4, D3, 0
 H, 2, B6, 1, A5, 6, D4, 0
 H, 3, B7, 2, A6, 1, D5, 0
 H, 4, B8, 3, A7, 2, D6, 0
 Cl, 1, B9, 6, A8, 2, D7, 0

Variables:

B1=2.25087191
 B2=1.39055831
 B3=1.39055831
 B4=1.32504869
 B5=1.32504869
 B6=1.08579192
 B7=1.08201766
 B8=1.08579192
 B9=1.75082293
 A1=90.19963159
 A2=116.29673926
 A3=32.41441955
 A4=128.13283666
 A5=148.21565593
 A6=121.85163037
 A7=121.58471247
 A8=115.93358167
 D1=0.
 D2=180.
 D3=0.
 D4=0.
 D5=180.
 D6=180.
 D7=180.

4.2 Total Energy

b3lyp/6-311++g(d,p) level of theory

E(RB+HF-LYP) = -724.017721191 Hartrees

3.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

| | 1 | 2 | 3 |
|----------------|----------|----------|----------|
| | B1 | B2 | A2 |
| Frequencies -- | 156.9259 | 329.3429 | 412.6434 |
| Red. masses -- | 6.6929 | 8.6759 | 4.2137 |
| Frc consts -- | 0.0971 | 0.5545 | 0.4227 |
| IR Inten -- | 4.0106 | 3.7167 | 0.0000 |

| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
|------|----|-------|------|------|------|-------|-------|-------|------|------|
| 1 | 6 | -0.25 | 0.00 | 0.00 | 0.00 | 0.35 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2 | 6 | 0.02 | 0.00 | 0.00 | 0.00 | -0.02 | -0.21 | -0.23 | 0.00 | 0.00 |
| 3 | 6 | 0.37 | 0.00 | 0.00 | 0.00 | -0.15 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4 | 6 | 0.02 | 0.00 | 0.00 | 0.00 | -0.02 | 0.21 | 0.23 | 0.00 | 0.00 |
| 5 | 7 | -0.31 | 0.00 | 0.00 | 0.00 | 0.28 | 0.17 | -0.28 | 0.00 | 0.00 |
| 6 | 7 | -0.31 | 0.00 | 0.00 | 0.00 | 0.28 | -0.17 | 0.28 | 0.00 | 0.00 |

| | | | | | | | | | | | |
|----|-------------|----|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|
| 1 | | | | | | | | | | | |
| 2 | | | | | | | | | | | |
| 3 | 7 | 1 | 0.01 | 0.00 | 0.00 | 0.00 | -0.12 | -0.41 | -0.61 | 0.00 | 0.00 |
| 4 | 8 | 1 | 0.76 | 0.00 | 0.00 | 0.00 | -0.34 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5 | 9 | 1 | 0.01 | 0.00 | 0.00 | 0.00 | -0.12 | 0.41 | 0.61 | 0.00 | 0.00 |
| 6 | 10 | 17 | 0.17 | 0.00 | 0.00 | 0.00 | -0.26 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | | | 4 | | | 5 | | | 6 | | |
| 8 | | | A1 | | | B1 | | | B2 | | |
| 9 | Frequencies | -- | 440.1012 | | | 490.9697 | | | 638.0703 | | |
| 10 | Red. masses | -- | 16.3001 | | | 2.9718 | | | 8.1824 | | |
| 11 | Frc consts | -- | 1.8601 | | | 0.4221 | | | 1.9628 | | |
| 12 | IR Inten | -- | 9.8159 | | | 1.7882 | | | 8.8438 | | |
| 13 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 14 | 1 | 6 | 0.00 | 0.00 | 0.01 | 0.28 | 0.00 | 0.00 | 0.00 | -0.09 | 0.00 |
| 15 | 2 | 6 | 0.00 | 0.08 | 0.28 | -0.15 | 0.00 | 0.00 | 0.00 | 0.26 | -0.27 |
| 16 | 3 | 6 | 0.00 | 0.00 | 0.41 | 0.22 | 0.00 | 0.00 | 0.00 | 0.20 | 0.00 |
| 17 | 4 | 6 | 0.00 | -0.08 | 0.28 | -0.15 | 0.00 | 0.00 | 0.00 | 0.26 | 0.27 |
| 18 | 5 | 7 | 0.00 | -0.11 | 0.23 | 0.00 | 0.00 | 0.00 | 0.00 | -0.25 | 0.27 |
| 19 | 6 | 7 | 0.00 | 0.11 | 0.23 | 0.00 | 0.00 | 0.00 | 0.00 | -0.25 | -0.27 |
| 20 | 7 | 1 | 0.00 | 0.03 | 0.19 | -0.62 | 0.00 | 0.00 | 0.00 | 0.39 | -0.03 |
| 21 | 8 | 1 | 0.00 | 0.00 | 0.41 | 0.22 | 0.00 | 0.00 | 0.00 | -0.31 | 0.00 |
| 22 | 9 | 1 | 0.00 | -0.03 | 0.19 | -0.62 | 0.00 | 0.00 | 0.00 | 0.39 | 0.03 |
| 23 | 10 | 17 | 0.00 | 0.00 | -0.54 | -0.04 | 0.00 | 0.00 | 0.00 | -0.03 | 0.00 |
| 24 | | | 7 | | | 8 | | | 9 | | |
| 25 | | | A1 | | | B1 | | | B1 | | |
| 26 | Frequencies | -- | 771.0900 | | | 794.6226 | | | 818.9335 | | |
| 27 | Red. masses | -- | 7.8502 | | | 8.8428 | | | 1.2088 | | |
| 28 | Frc consts | -- | 2.7501 | | | 3.2897 | | | 0.4777 | | |
| 29 | IR Inten | -- | 41.8704 | | | 9.7078 | | | 30.1620 | | |
| 30 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 31 | 1 | 6 | 0.00 | 0.00 | 0.32 | 0.56 | 0.00 | 0.00 | -0.05 | 0.00 | 0.00 |
| 32 | 2 | 6 | 0.00 | -0.29 | 0.07 | 0.22 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 |
| 33 | 3 | 6 | 0.00 | 0.00 | -0.35 | -0.22 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 |
| 34 | 4 | 6 | 0.00 | 0.29 | 0.07 | 0.22 | 0.00 | 0.00 | 0.07 | 0.00 | 0.00 |
| 35 | 5 | 7 | 0.00 | 0.27 | 0.07 | -0.33 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 |
| 36 | 6 | 7 | 0.00 | -0.27 | 0.07 | -0.33 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 |
| 37 | 7 | 1 | 0.00 | -0.15 | 0.36 | 0.37 | 0.00 | 0.00 | -0.36 | 0.00 | 0.00 |
| 38 | 8 | 1 | 0.00 | 0.00 | -0.35 | -0.22 | 0.00 | 0.00 | -0.85 | 0.00 | 0.00 |
| 39 | 9 | 1 | 0.00 | 0.15 | 0.36 | 0.37 | 0.00 | 0.00 | -0.36 | 0.00 | 0.00 |
| 40 | 10 | 17 | 0.00 | 0.00 | -0.11 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 41 | | | 10 | | | 11 | | | 12 | | |
| 42 | | | A2 | | | B1 | | | A1 | | |
| 43 | Frequencies | -- | 998.8553 | | | 1000.7750 | | | 1004.2248 | | |
| 44 | Red. masses | -- | 1.3712 | | | 1.4171 | | | 9.9668 | | |
| 45 | Frc consts | -- | 0.8060 | | | 0.8362 | | | 5.9220 | | |
| 46 | IR Inten | -- | 0.0000 | | | 0.1791 | | | 0.1534 | | |
| 47 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 48 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | -0.08 |
| 49 | 2 | 6 | 0.13 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 | 0.00 | 0.06 | 0.03 |
| 50 | 3 | 6 | 0.00 | 0.00 | 0.00 | 0.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.48 |
| 51 | 4 | 6 | -0.13 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 | 0.00 | -0.06 | 0.03 |
| 52 | 5 | 7 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.43 | -0.23 |
| 53 | 6 | 7 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.43 | -0.23 |
| 54 | 7 | 1 | -0.70 | 0.00 | 0.00 | 0.56 | 0.00 | 0.00 | 0.00 | 0.07 | 0.08 |
| 55 | 8 | 1 | 0.00 | 0.00 | 0.00 | -0.58 | 0.00 | 0.00 | 0.00 | 0.00 | 0.50 |
| 56 | 9 | 1 | 0.70 | 0.00 | 0.00 | 0.56 | 0.00 | 0.00 | 0.00 | -0.07 | 0.08 |
| 57 | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| 58 | | | 13 | | | 14 | | | 15 | | |
| 59 | | | A1 | | | B2 | | | A1 | | |
| 60 | Frequencies | -- | 1089.8833 | | | 1111.3335 | | | 1190.3909 | | |
| | Red. masses | -- | 2.7526 | | | 1.4327 | | | 4.2108 | | |
| | Frc consts | -- | 1.9264 | | | 1.0425 | | | 3.5156 | | |
| | IR Inten | -- | 5.1067 | | | 0.5982 | | | 186.4327 | | |
| | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| | 1 | 6 | 0.00 | 0.00 | 0.08 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.47 |

| | | | | | | | | | | | |
|----|-------------|----|-----------|-------|-------|-----------|-------|-------|-----------|-------|-------|
| 1 | | | | | | | | | | | |
| 2 | | | | | | | | | | | |
| 3 | 2 | 6 | 0.00 | 0.24 | -0.02 | 0.00 | -0.07 | 0.00 | 0.00 | 0.07 | -0.15 |
| 4 | 3 | 6 | 0.00 | 0.00 | -0.14 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.11 |
| 5 | 4 | 6 | 0.00 | -0.24 | -0.02 | 0.00 | -0.07 | 0.00 | 0.00 | -0.07 | -0.15 |
| 6 | 5 | 7 | 0.00 | 0.06 | 0.04 | 0.00 | -0.04 | 0.06 | 0.00 | -0.03 | -0.04 |
| 7 | 6 | 7 | 0.00 | -0.06 | 0.04 | 0.00 | -0.04 | -0.06 | 0.00 | 0.03 | -0.04 |
| 8 | 7 | 1 | 0.00 | 0.48 | 0.42 | 0.00 | -0.12 | -0.09 | 0.00 | -0.13 | -0.58 |
| 9 | 8 | 1 | 0.00 | 0.00 | -0.17 | 0.00 | 0.96 | 0.00 | 0.00 | 0.00 | 0.11 |
| 10 | 9 | 1 | 0.00 | -0.48 | 0.42 | 0.00 | -0.12 | 0.09 | 0.00 | 0.13 | -0.58 |
| 11 | 10 | 17 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.03 |
| 12 | | | | 16 | | | 17 | | | 18 | |
| 13 | | | | B2 | | | B2 | | | A1 | |
| 14 | Frequencies | -- | 1233.1390 | | | 1293.3151 | | | 1423.2475 | | |
| 15 | Red. masses | -- | 9.6511 | | | 1.5742 | | | 2.1258 | | |
| 16 | Frc consts | -- | 8.6467 | | | 1.5514 | | | 2.5370 | | |
| 17 | IR Inten | -- | 0.7996 | | | 8.7442 | | | 219.3075 | | |
| 18 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 19 | 1 | 6 | 0.00 | -0.31 | 0.00 | 0.00 | 0.19 | 0.00 | 0.00 | 0.00 | 0.11 |
| 20 | 2 | 6 | 0.00 | 0.10 | 0.34 | 0.00 | -0.06 | 0.04 | 0.00 | -0.07 | 0.02 |
| 21 | 3 | 6 | 0.00 | -0.24 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.06 |
| 22 | 4 | 6 | 0.00 | 0.10 | -0.34 | 0.00 | -0.06 | -0.04 | 0.00 | 0.07 | 0.02 |
| 23 | 5 | 7 | 0.00 | 0.15 | 0.37 | 0.00 | -0.04 | 0.04 | 0.00 | -0.10 | -0.14 |
| 24 | 6 | 7 | 0.00 | 0.15 | -0.37 | 0.00 | -0.04 | -0.04 | 0.00 | 0.10 | -0.14 |
| 25 | 7 | 1 | 0.00 | 0.10 | 0.30 | 0.00 | 0.23 | 0.63 | 0.00 | 0.23 | 0.63 |
| 26 | 8 | 1 | 0.00 | 0.27 | 0.00 | 0.00 | -0.23 | 0.00 | 0.00 | 0.00 | 0.08 |
| 27 | 9 | 1 | 0.00 | 0.10 | -0.30 | 0.00 | 0.23 | -0.63 | 0.00 | -0.23 | 0.63 |
| 28 | 10 | 17 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 29 | | | | 19 | | | 20 | | | 21 | |
| 30 | | | | B2 | | | B2 | | | A1 | |
| 31 | Frequencies | -- | 1455.2160 | | | 1592.1744 | | | 1602.2692 | | |
| 32 | Red. masses | -- | 1.9360 | | | 6.3151 | | | 4.8984 | | |
| 33 | Frc consts | -- | 2.4155 | | | 9.4321 | | | 7.4093 | | |
| 34 | IR Inten | -- | 0.4549 | | | 109.4327 | | | 128.9889 | | |
| 35 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 36 | 1 | 6 | 0.00 | 0.12 | 0.00 | 0.00 | -0.31 | 0.00 | 0.00 | 0.00 | 0.06 |
| 37 | 2 | 6 | 0.00 | -0.01 | 0.14 | 0.00 | -0.23 | -0.09 | 0.00 | 0.11 | 0.32 |
| 38 | 3 | 6 | 0.00 | 0.14 | 0.00 | 0.00 | 0.44 | 0.00 | 0.00 | 0.00 | -0.18 |
| 39 | 4 | 6 | 0.00 | -0.01 | -0.14 | 0.00 | -0.23 | 0.09 | 0.00 | -0.11 | 0.32 |
| 40 | 5 | 7 | 0.00 | -0.06 | 0.05 | 0.00 | 0.16 | 0.07 | 0.00 | -0.02 | -0.19 |
| 41 | 6 | 7 | 0.00 | -0.06 | -0.05 | 0.00 | 0.16 | -0.07 | 0.00 | 0.02 | -0.19 |
| 42 | 7 | 1 | 0.00 | -0.30 | -0.42 | 0.00 | -0.05 | 0.34 | 0.00 | -0.26 | -0.49 |
| 43 | 8 | 1 | 0.00 | -0.62 | 0.00 | 0.00 | -0.54 | 0.00 | 0.00 | 0.00 | -0.22 |
| 44 | 9 | 1 | 0.00 | -0.30 | 0.42 | 0.00 | -0.05 | -0.34 | 0.00 | 0.26 | -0.49 |
| 45 | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| 46 | | | | 22 | | | 23 | | | 24 | |
| 47 | | | | A1 | | | B2 | | | A1 | |
| 48 | Frequencies | -- | 3162.7949 | | | 3165.6497 | | | 3209.1206 | | |
| 49 | Red. masses | -- | 1.0901 | | | 1.0923 | | | 1.0965 | | |
| 50 | Frc consts | -- | 6.4251 | | | 6.4492 | | | 6.6529 | | |
| 51 | IR Inten | -- | 10.9331 | | | 12.2231 | | | 4.7280 | | |
| 52 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 53 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 54 | 2 | 6 | 0.00 | -0.05 | 0.02 | 0.00 | -0.06 | 0.03 | 0.00 | 0.02 | 0.00 |
| 55 | 3 | 6 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.09 |
| 56 | 4 | 6 | 0.00 | 0.05 | 0.02 | 0.00 | -0.06 | -0.03 | 0.00 | -0.02 | 0.00 |
| 57 | 5 | 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 58 | 6 | 7 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 59 | 7 | 1 | 0.00 | 0.61 | -0.30 | 0.00 | 0.63 | -0.31 | 0.00 | -0.15 | 0.07 |
| 60 | 8 | 1 | 0.00 | 0.00 | 0.24 | 0.00 | -0.01 | 0.00 | 0.00 | 0.00 | 0.97 |
| 61 | 9 | 1 | 0.00 | -0.61 | -0.30 | 0.00 | 0.63 | 0.31 | 0.00 | 0.15 | 0.07 |
| 62 | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

5. 5-bromo-2-chloropyrimidine

5.1 Geometry

optimised Z-matrix at the b3lyp/6-311++g(d,p) level of theory

```
C
C, 1, B1
C, 2, B2, 1, A1
C, 3, B3, 2, A2, 1, D1, 0
N, 1, B4, 2, A3, 3, D2, 0
N, 2, B5, 1, A4, 5, D3, 0
H, 4, B6, 3, A5, 2, D4, 0
H, 2, B7, 1, A6, 5, D5, 0
Br, 3, B8, 2, A7, 1, D6, 0
Cl, 1, B9, 5, A8, 4, D7, 0
```

Variables:

```
B1=2.25652417
B2=1.39139133
B3=1.39139133
B4=1.32538811
B5=1.33418218
B6=1.08535985
B7=1.08535985
B8=1.90159178
B9=1.74627798
A1=89.55344634
A2=117.33113531
A3=95.63639006
A4=31.83805397
A5=121.61662495
A6=148.82992871
A7=121.33443234
A8=116.14459594
D1=0.
D2=0.
D3=180.
D4=180.
D5=180.
D6=180.
D7=180.
```

5.2 Total Energy

b3lyp/6-311++g(d,p) level of theory
E(RB+HF-LYP) = -3297.55621429

5.3 Frequencies

Output from the "b3lyp/6-311++g(d,p) freq" calculation

| | | 1 | | | 2 | | | 3 | | |
|-------------|----|---------|------|------|----------|------|-------|----------|-------|-------|
| | | B1 | | | B2 | | | A1 | | |
| Frequencies | -- | 76.3961 | | | 186.4347 | | | 271.2891 | | |
| Red. masses | -- | 12.2663 | | | 11.4942 | | | 30.5523 | | |
| Frc consts | -- | 0.0422 | | | 0.2354 | | | 1.3248 | | |
| IR Inten | -- | 0.1853 | | | 0.3974 | | | 0.0335 | | |
| Atom | AN | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.17 | 0.00 | 0.00 | 0.00 | 0.17 | 0.00 | 0.00 | 0.00 | -0.36 |
| 2 | 6 | 0.34 | 0.00 | 0.00 | 0.00 | 0.34 | 0.08 | 0.00 | 0.06 | -0.18 |
| 3 | 6 | 0.24 | 0.00 | 0.00 | 0.00 | 0.38 | 0.00 | 0.00 | 0.00 | 0.01 |
| 4 | 6 | 0.34 | 0.00 | 0.00 | 0.00 | 0.34 | -0.08 | 0.00 | -0.06 | -0.18 |
| 5 | 7 | 0.31 | 0.00 | 0.00 | 0.00 | 0.22 | -0.11 | 0.00 | -0.06 | -0.24 |

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| | | | | | | | | | | |
|-------------|----|-------|----------|------|------|-----------|-------|-------|-----------|-------|
| 6 | 7 | 0.31 | 0.00 | 0.00 | 0.00 | 0.22 | 0.11 | 0.00 | 0.06 | -0.24 |
| 7 | 1 | 0.42 | 0.00 | 0.00 | 0.00 | 0.39 | -0.17 | 0.00 | 0.00 | -0.29 |
| 8 | 1 | 0.42 | 0.00 | 0.00 | 0.00 | 0.39 | 0.17 | 0.00 | 0.00 | -0.29 |
| 9 | 35 | -0.14 | 0.00 | 0.00 | 0.00 | -0.16 | 0.00 | 0.00 | 0.00 | 0.44 |
| 10 | 17 | -0.33 | 0.00 | 0.00 | 0.00 | -0.27 | 0.00 | 0.00 | 0.00 | -0.55 |
| | | | 4 | | | 5 | | | 6 | |
| | | | B1 | | | B2 | | | A2 | |
| Frequencies | -- | | 287.7225 | | | 362.9228 | | | 417.3407 | |
| Red. masses | -- | | 11.2682 | | | 7.4664 | | | 4.2935 | |
| Frc consts | -- | | 0.5496 | | | 0.5794 | | | 0.4406 | |
| IR Inten | -- | | 1.9768 | | | 4.6253 | | | 0.0000 | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | -0.36 | 0.00 | 0.00 | 0.00 | 0.31 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2 | 6 | 0.25 | 0.00 | 0.00 | 0.00 | -0.13 | -0.20 | -0.24 | 0.00 | 0.00 |
| 3 | 6 | 0.62 | 0.00 | 0.00 | 0.00 | -0.24 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4 | 6 | 0.25 | 0.00 | 0.00 | 0.00 | -0.13 | 0.20 | 0.24 | 0.00 | 0.00 |
| 5 | 7 | -0.32 | 0.00 | 0.00 | 0.00 | 0.23 | 0.18 | -0.28 | 0.00 | 0.00 |
| 6 | 7 | -0.32 | 0.00 | 0.00 | 0.00 | 0.23 | -0.18 | 0.28 | 0.00 | 0.00 |
| 7 | 1 | 0.27 | 0.00 | 0.00 | 0.00 | -0.25 | 0.45 | 0.60 | 0.00 | 0.00 |
| 8 | 1 | 0.27 | 0.00 | 0.00 | 0.00 | -0.25 | -0.45 | -0.60 | 0.00 | 0.00 |
| 9 | 35 | -0.06 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 |
| 10 | 17 | 0.11 | 0.00 | 0.00 | 0.00 | -0.19 | 0.00 | 0.00 | 0.00 | 0.00 |
| | | | 7 | | | 8 | | | 9 | |
| | | | B1 | | | A1 | | | B2 | |
| Frequencies | -- | | 485.8950 | | | 505.6901 | | | 638.5912 | |
| Red. masses | -- | | 3.1004 | | | 14.7294 | | | 9.7079 | |
| Frc consts | -- | | 0.4313 | | | 2.2192 | | | 2.3325 | |
| IR Inten | -- | | 2.6247 | | | 32.6460 | | | 10.7875 | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.26 | 0.00 | 0.00 | 0.00 | 0.00 | 0.15 | 0.00 | -0.07 | 0.00 |
| 2 | 6 | -0.13 | 0.00 | 0.00 | 0.00 | 0.03 | 0.34 | 0.00 | 0.25 | -0.31 |
| 3 | 6 | 0.29 | 0.00 | 0.00 | 0.00 | 0.00 | 0.30 | 0.00 | 0.19 | 0.00 |
| 4 | 6 | -0.13 | 0.00 | 0.00 | 0.00 | -0.03 | 0.34 | 0.00 | 0.25 | 0.31 |
| 5 | 7 | -0.02 | 0.00 | 0.00 | 0.00 | -0.08 | 0.33 | 0.00 | -0.27 | 0.33 |
| 6 | 7 | -0.02 | 0.00 | 0.00 | 0.00 | 0.08 | 0.33 | 0.00 | -0.27 | -0.33 |
| 7 | 1 | -0.64 | 0.00 | 0.00 | 0.00 | -0.03 | 0.34 | 0.00 | 0.36 | 0.11 |
| 8 | 1 | -0.64 | 0.00 | 0.00 | 0.00 | 0.03 | 0.34 | 0.00 | 0.36 | -0.11 |
| 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.11 | 0.00 | 0.01 | 0.00 |
| 10 | 17 | -0.03 | 0.00 | 0.00 | 0.00 | 0.00 | -0.42 | 0.00 | -0.04 | 0.00 |
| | | | 10 | | | 11 | | | 12 | |
| | | | B1 | | | A1 | | | B1 | |
| Frequencies | -- | | 783.5255 | | | 797.5251 | | | 943.6251 | |
| Red. masses | -- | | 9.1074 | | | 9.3889 | | | 1.4854 | |
| Frc consts | -- | | 3.2942 | | | 3.5185 | | | 0.7793 | |
| IR Inten | -- | | 10.9571 | | | 3.0298 | | | 8.9914 | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 1 | 6 | 0.58 | 0.00 | 0.00 | 0.00 | 0.00 | 0.30 | 0.06 | 0.00 | 0.00 |
| 2 | 6 | 0.21 | 0.00 | 0.00 | 0.00 | -0.35 | 0.04 | -0.13 | 0.00 | 0.00 |
| 3 | 6 | -0.24 | 0.00 | 0.00 | 0.00 | 0.00 | -0.35 | 0.09 | 0.00 | 0.00 |
| 4 | 6 | 0.21 | 0.00 | 0.00 | 0.00 | 0.35 | 0.04 | -0.13 | 0.00 | 0.00 |
| 5 | 7 | -0.33 | 0.00 | 0.00 | 0.00 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6 | 7 | -0.33 | 0.00 | 0.00 | 0.00 | -0.33 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7 | 1 | 0.39 | 0.00 | 0.00 | 0.00 | 0.22 | 0.32 | 0.69 | 0.00 | 0.00 |
| 8 | 1 | 0.39 | 0.00 | 0.00 | 0.00 | -0.22 | 0.32 | 0.69 | 0.00 | 0.00 |
| 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 |
| 10 | 17 | -0.02 | 0.00 | 0.00 | 0.00 | 0.00 | -0.10 | 0.00 | 0.00 | 0.00 |
| | | | 13 | | | 14 | | | 15 | |
| | | | A2 | | | A1 | | | A1 | |
| Frequencies | -- | | 983.0345 | | | 1023.6157 | | | 1123.7697 | |
| Red. masses | -- | | 1.3628 | | | 7.8833 | | | 3.3428 | |
| Frc consts | -- | | 0.7759 | | | 4.8667 | | | 2.4872 | |
| IR Inten | -- | | 0.0000 | | | 35.0351 | | | 1.7276 | |
| Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |

| | | | | | | | | | | | |
|----|-------------|----|-----------|-------|-------|------|-----------|-------|------|-----------|-------|
| 1 | | | | | | | | | | | |
| 2 | | | | | | | | | | | |
| 3 | 1 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | -0.13 |
| 4 | 2 | 6 | 0.13 | 0.00 | 0.00 | 0.00 | 0.24 | 0.03 | 0.00 | -0.21 | 0.04 |
| 5 | 3 | 6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.36 | 0.00 | 0.00 | 0.30 |
| 6 | 4 | 6 | -0.13 | 0.00 | 0.00 | 0.00 | -0.24 | 0.03 | 0.00 | 0.21 | 0.04 |
| 7 | 5 | 7 | 0.02 | 0.00 | 0.00 | 0.00 | 0.38 | -0.15 | 0.00 | 0.01 | -0.06 |
| 8 | 6 | 7 | -0.02 | 0.00 | 0.00 | 0.00 | -0.38 | -0.15 | 0.00 | -0.01 | -0.06 |
| 9 | 7 | 1 | 0.70 | 0.00 | 0.00 | 0.00 | -0.37 | 0.29 | 0.00 | 0.47 | -0.42 |
| 10 | 8 | 1 | -0.70 | 0.00 | 0.00 | 0.00 | 0.37 | 0.29 | 0.00 | -0.47 | -0.42 |
| 11 | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | -0.02 | 0.00 | 0.00 | -0.01 |
| 12 | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 |
| 13 | | | | 16 | | | 17 | | | 18 | |
| 14 | | | | A1 | | | B2 | | | B2 | |
| 15 | Frequencies | -- | 1189.5070 | | | | 1220.4837 | | | 1278.6112 | |
| 16 | Red. masses | -- | 3.9208 | | | | 11.9234 | | | 2.0429 | |
| 17 | Frc consts | -- | 3.2686 | | | | 10.4644 | | | 1.9678 | |
| 18 | IR Inten | -- | 301.5755 | | | | 0.6996 | | | 9.7829 | |
| 19 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 20 | 1 | 6 | 0.00 | 0.00 | 0.44 | 0.00 | 0.47 | 0.00 | 0.00 | 0.20 | 0.00 |
| 21 | 2 | 6 | 0.00 | 0.05 | -0.14 | 0.00 | -0.20 | -0.32 | 0.00 | -0.07 | 0.09 |
| 22 | 3 | 6 | 0.00 | 0.00 | 0.12 | 0.00 | 0.38 | 0.00 | 0.00 | 0.03 | 0.00 |
| 23 | 4 | 6 | 0.00 | -0.05 | -0.14 | 0.00 | -0.20 | 0.32 | 0.00 | -0.07 | -0.09 |
| 24 | 5 | 7 | 0.00 | -0.03 | -0.03 | 0.00 | -0.19 | -0.33 | 0.00 | -0.04 | 0.10 |
| 25 | 6 | 7 | 0.00 | 0.03 | -0.03 | 0.00 | -0.19 | 0.33 | 0.00 | -0.04 | -0.10 |
| 26 | 7 | 1 | 0.00 | 0.17 | -0.58 | 0.00 | -0.13 | 0.11 | 0.00 | 0.19 | -0.65 |
| 27 | 8 | 1 | 0.00 | -0.17 | -0.58 | 0.00 | -0.13 | -0.11 | 0.00 | 0.19 | 0.65 |
| 28 | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 29 | 10 | 17 | 0.00 | 0.00 | -0.03 | 0.00 | 0.01 | 0.00 | 0.00 | -0.01 | 0.00 |
| 30 | | | | 19 | | | 20 | | | 21 | |
| 31 | | | | B2 | | | A1 | | | B2 | |
| 32 | Frequencies | -- | 1386.9337 | | | | 1425.7893 | | | 1564.8893 | |
| 33 | Red. masses | -- | 2.1207 | | | | 2.1546 | | | 7.7993 | |
| 34 | Frc consts | -- | 2.4035 | | | | 2.5807 | | | 11.2531 | |
| 35 | IR Inten | -- | 6.5546 | | | | 263.8659 | | | 80.5431 | |
| 36 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 37 | 1 | 6 | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 0.40 | 0.00 |
| 38 | 2 | 6 | 0.00 | -0.04 | 0.14 | 0.00 | -0.07 | 0.01 | 0.00 | 0.25 | 0.13 |
| 39 | 3 | 6 | 0.00 | 0.19 | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | -0.43 | 0.00 |
| 40 | 4 | 6 | 0.00 | -0.04 | -0.14 | 0.00 | 0.07 | 0.01 | 0.00 | 0.25 | -0.13 |
| 41 | 5 | 7 | 0.00 | -0.04 | 0.08 | 0.00 | -0.10 | -0.14 | 0.00 | -0.20 | -0.09 |
| 42 | 6 | 7 | 0.00 | -0.04 | -0.08 | 0.00 | 0.10 | -0.14 | 0.00 | -0.20 | 0.09 |
| 43 | 7 | 1 | 0.00 | -0.39 | 0.55 | 0.00 | -0.23 | 0.63 | 0.00 | -0.01 | 0.45 |
| 44 | 8 | 1 | 0.00 | -0.39 | -0.55 | 0.00 | 0.23 | 0.63 | 0.00 | -0.01 | -0.45 |
| 45 | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 46 | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 47 | | | | 22 | | | 23 | | | 24 | |
| 48 | | | | A1 | | | B2 | | | A1 | |
| 49 | Frequencies | -- | 1582.7715 | | | | 3173.8549 | | | 3174.4721 | |
| 50 | Red. masses | -- | 5.4647 | | | | 1.0928 | | | 1.0935 | |
| 51 | Frc consts | -- | 8.0659 | | | | 6.4857 | | | 6.4925 | |
| 52 | IR Inten | -- | 43.5463 | | | | 1.2304 | | | 4.9072 | |
| 53 | Atom AN | | X | Y | Z | X | Y | Z | X | Y | Z |
| 54 | 1 | 6 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 55 | 2 | 6 | 0.00 | 0.11 | 0.34 | 0.00 | -0.06 | 0.03 | 0.00 | 0.06 | -0.03 |
| 56 | 3 | 6 | 0.00 | 0.00 | -0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 57 | 4 | 6 | 0.00 | -0.11 | 0.34 | 0.00 | -0.06 | -0.03 | 0.00 | -0.06 | -0.03 |
| 58 | 5 | 7 | 0.00 | -0.04 | -0.21 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 59 | 6 | 7 | 0.00 | 0.04 | -0.21 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 60 | 7 | 1 | 0.00 | 0.28 | -0.48 | 0.00 | 0.63 | 0.31 | 0.00 | 0.63 | 0.31 |
| | 8 | 1 | 0.00 | -0.28 | -0.48 | 0.00 | 0.63 | -0.31 | 0.00 | -0.63 | 0.31 |
| | 9 | 35 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 10 | 17 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |