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On the Planarity of Benzyl Cyanide

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KEYWORDS

Microwave spectroscopy; Quantum chemistry; Nuclear quadrupole coupling; Inertial defect

ABSTRACT

The microwave spectra of benzyl cyanide, C₆H₅CH₂CN, were recorded using a molecular jet Fourier transform microwave spectrometer operating in the frequency range 2 – 26.5 GHz. Analyses of the ¹⁴N quadrupole hyperfine structures were performed simultaneously with the rotational frequencies. Rotational constants, centrifugal distortion constants, and nuclear quadrupole coupling constants χ_{aa} and $\chi_{bb} - \chi_{cc}$ were all accurately determined with very high accuracy in a fit containing 465 lines with standard deviation within the measurement accuracy. Results from quantum chemical calculations at many levels of theory employing the MP2 method indicate a non-planar heavy atom skeleton structure, where the CH₂CN group is tilted up to 50° with respect to the phenyl ring. This conflicts with results from many calculations employing density functional theory methods and also with the conclusion of a previous microwave spectroscopic work (X.-Z. Liu, R.K. Bohn, S.A. Sorenson, N.S. True, *J. Mol. Struct.* **243** (1991) 325-339), stating that the CH₂CN group and the phenyl ring are in-plane. By comparing the planar defect with those of several planar molecules reported in the literature, and with extensive support from quantum chemistry, [we present for the first time elements indicating that the heavy atom structure of benzyl cyanide is probably not planar.](#)

1. Introduction

“Planar, or not planar, that is the question” [1], not only in the recent study on 2-propionylthiophene, but also in a number of microwave spectroscopic investigations aiming at the determination of molecular structures. In 2-propionylthiophene, quantum chemistry results obtained at several MP2 levels of theory showed that the ethyl group of the propionyl moiety is slightly tilted out of the thiophene ring plane. This conflicts with results from many other methods, stating that the ethyl group is in-plane with the thiophene ring. The experimental heavy atom skeleton determined by isotopic substitutions using Fourier transform microwave (FTMW) spectroscopy revealed a very small, but non-zero tilt angle of the ethyl group out of the thiophene plane. This convincingly confirms that 2-propionylthiophene is not planar [1]. Similarly, controversial results between theoretical studies and experimental methods using NMR, IR, UV, Raman spectroscopy had made the planarity of *gauche* 1,3-butadiene an ambiguity for decades until 2018, when its gas phase structure was revealed by FTMW spectroscopy with evidence that also *gauche* 1,3-butadiene is not planar [2]. Therefore, a planar conformation must be first adopted for Diels-Alder reactions.

The structure-reactivity relationship is not only demonstrated with the Diels-Alder reaction in the investigation on *gauche* 1,3-butadiene mentioned above. In many other reactions, it is important to know if the molecular structure is planar or not, as far as a planar structure would favor a long-range stabilizing interaction due to p-p interactions between sp^2 or sp atoms, counterbalancing possible steric hindrance between two unsaturated groups. [The fundamental question concerns](#) for example penta-1,4-diene [3], 3-phenylpropyne [4,5], allylcyanide [6], and benzyl cyanide [7]. Furthermore, knowing the configuration of the most stable molecular conformation is crucial in theoretical chemistry. Agreements between predictions by computational chemistry with the experimental data validate the levels of theory in use, [presupposing](#) that the experimental data are reliable. Regarding the structure determination and conformational analysis, microwave spectroscopy is probably the most powerful technique. It delivers accurate molecular gas phase structures which can be directly compared to quantum chemical results.

We faced the planarity problem while studying benzyl isocyanide by quantum chemistry. During a calculation to optimize the geometry of benzyl isocyanide, we obtained an unexpected planar structure as stable conformation. Various potential energy curves were subsequently performed at different computational levels by rotating the CH_2NC group. All of them agree on a planar heavy atom structure as the most stable conformation, except MP2/6-311++G(d,p) [8,9]. Density functional theory (DFT) methods like PBE0 (Perdew-Burke-Ernzerhof) [10] or Truhlar's M06-2X [11] paired with Pople's 6-311++G(d,p) [9] or Dunning's AVTZ basis sets

[12] also contradicts the MP2/6-311++G(d,p) calculation. Repeating these calculations with the isomer benzyl cyanide led to the same results. The MP2/6-311++G(d,p) level revealed a non-planar geometry where the CH₂CN group is tilted out of the phenol ring plane by about 40°. Calculations at some other levels yielded a planar structure.

In a previous study, Liu et al. reported on a planar heavy atom structure of benzyl cyanide deduced from its microwave spectrum between 7.5 and 17 GHz using the planar defect P_{cc} and analysis of the ¹⁴N quadrupole coupling constants [7]. The high-resolution spectrum was supplemented by a low-resolution spectrum from 18 to 26.5 GHz. This experimental conclusion on the geometry of benzyl cyanide agrees with our quantum chemical results at many levels of theory, but the reason why a planar conformation is the most stable remained questionable. From chemical intuition, a non-planar structure should be favored by sterical hindrance for such kind of molecule when the phenyl ring and the CN groups are separated by a CH₂ group.

This contradiction motivated us to reinvestigate the title molecule using a combination of FTMW spectroscopy with quantum chemical calculations. For the experimental part, we extended the frequency range to cover the region from 2 to 26.5 GHz at high resolution and enlarged the data set. Benzyl cyanide contains a nitrogen nucleus with a nuclear spin $I = 1$, implying an electric nuclear quadrupole moment. Therefore, hyperfine structures are observed for all rotational levels of the rigid rotor [13]. Instead of treating these hyperfine splittings separately as in Liu et al. [7], we performed a global fit where structural parameters such as the rotational constants and centrifugal distortion constants can be obtained together with the nuclear quadrupole coupling constants. For the theoretical part, we performed extensive quantum chemical calculations at various levels of theory to benchmark the geometry of the lowest energetic configuration.

2. Quantum chemical calculations

Since the phenyl ring is planar, all conformational changes in benzyl cyanide are only obtained when rotating the dihedral angle $\alpha = \angle(C_6, C_1, C_7, C_8)$ (for atom numbering, see Figure 1). Structure optimizations were performed under full geometry relaxation using various combinations of methods and basis sets. We employed two *ab initio* methods MP2 [8] and CCSD [14] as well as several DFT methods like B3LYP [15,16] (with Grimme's dispersion corrections D3 [17] and with or without Becke-Johnson damping (BJ) [18] or the Coulomb-attenuating method (CAM) [19]), M06-2X [11], and ω B97X-D [20]. They were combined with Pople's basis sets 6-31G or 6-311G [9] with or without diffuse functions, but always with polarization functions, as well as with Dunning's basis sets like cc-pVDZ and cc-pVTZ [12]. A planar starting geometry was chosen

with α set at 0° and frequency calculations were subsequently performed on the optimized structures to verify the energetic minimum nature of the obtained conformation. The results containing the rotational constants and the imaginary frequency (0 for non-imaginary or 1 for one imaginary frequency) are summarized in Table S1 of the Supplementary Material. For all levels where an imaginary frequency is obtained, potential energy curves were calculated by varying α in a grid of 10° for an interval from 0° and 180° due to symmetry. All of these curves possess two double minima, as shown exemplarily for the MP2/6-311++G(d,p) and MP2/6-31G(d,p) levels in Figure 2. The non-planar geometries at $\alpha = 180^\circ \pm \Theta$ obtained from calculations at the MP2/6-311++G(d,p) level, where Θ is the tilt angle of the CH_2CN group, represent the image (I_a) and mirror image (I_a^*) of the minimum conformer. The conformations at $\alpha = 0^\circ \pm 40^\circ$ (I_b and I_b^*) are obtained while rotating the phenyl group of I_a and I_a^* by 180° , respectively. For comparison, Figure 2 also illustrates the potential energy curve calculated at the B3LYP-D3BJ/6-311++G(d,p) level which predicts a stable planar conformer. The non-planar minimum conformations were subsequently optimized under full geometry relaxation. Figure 1 shows the molecular structure optimized at the MP2/6-311++G(d,p) level of theory where the cyanide group clearly tilted out of the phenyl ring plane by an angle of 46° . The atomic Cartesian coordinates of this structure are available in Table S2 of the Supplementary Material along with those of the planar structure calculated at the same level.

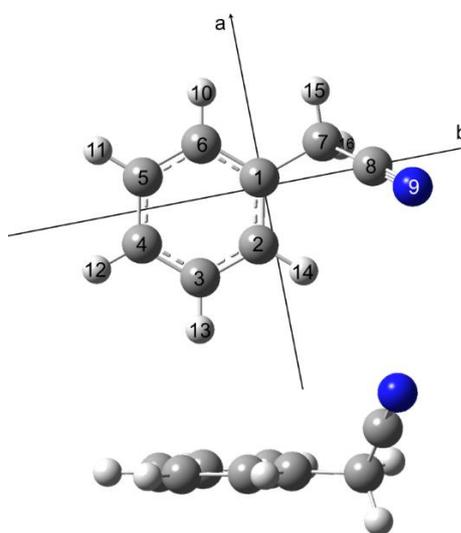


Figure 1. Molecular structure of benzyl cyanide optimized at the MP2/6-311++G(d,p) level of theory in the principal inertia axes, showing a non-planar geometry. The hydrogen atoms are white and carbon atoms grey. The nitrogen atom is blue. Upper trace: view onto the phenyl ring. Lower trace: view along the ring plane to visualize the non-planarity of the molecular geometry obtained at this level with the cyanide group clearly tilted out of the phenyl ring plane.

It is obvious from Table S1 that most of the levels predicting a non-planar stable conformer for benzyl cyanide are those with the MP2 method. Only four B3LYP levels agree on a non-planar structure. The rotational constants, dipole moment components, imaginary frequency, and the tilt angle Θ obtained from full geometry optimizations at the MP2/6-311++G(d,p) level on a planar and a non-planar starting geometry, as well as at the B3LYP-D3BJ/6-311++G(d,p) level are given in Table 1.

Table 1. Equilibrium rotational constants, dipole moment components, and the tilt angle Θ of benzyl cyanide optimized at the MP2/6-311++G(d,p) level on a planar and a non-planar starting geometry as well as at the B3LYP-D3BJ/6-311++G(d,p) level. Imag stands for imaginary frequency.

Par.	Unit.	MP2 planar	MP2 non-planar	B3LYP-D3BJ
A_e	MHz	4312.5	4077.4	4387.9
B_e	MHz	1055.0	1046.9	1052.8
C_e	MHz	852.1	885.8	853.5
$ \mu_a $	D	3.04	3.37	3.23
$ \mu_b $	D	2.29	2.08	2.37
$ \mu_c $	D	0.00	1.76	0.00
Θ	$^\circ$	0.08	46.15	0.04
Imag		1	0	0

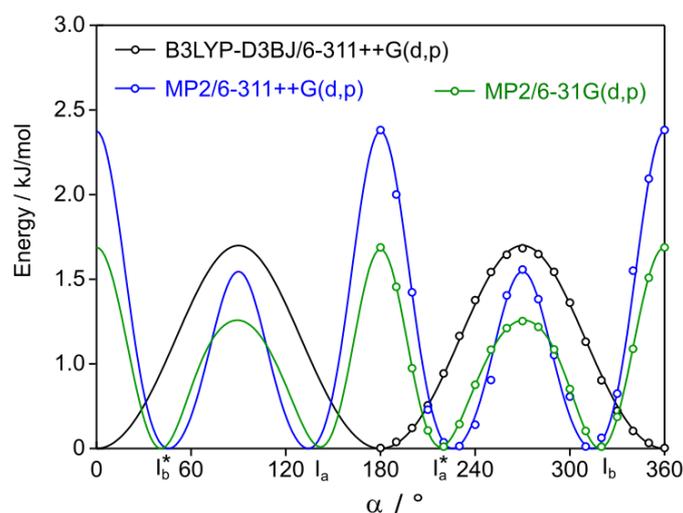


Figure 2. The potential energy curves obtained at the MP2/6-311++G(d,p), MP2/6-31G(d,p), and B3LYP-D3BJ/6-311++G(d,p) levels of theory by varying the dihedral angle $\alpha = \angle(C_6, C_1, C_7, C_8)$ in 10° steps, corresponding to the rotation of the CH_2CN group. All other geometry parameters were optimized. The energies are given relative to the lowest values of -362.8181593 Hartree, -362.6909763 Hartree, and -363.9282494 Hartree, respectively.

3. Experimental section

3.1. Synthesis of benzyl cyanide

Benzyl cyanide was synthesized using the procedure proposed by Shang et al. [21]. A mixture of BnBr (11.9 mL, 0.1 mol, 1 eq) and K_2CO_3 (16.75 g, 0.12 mol, 1.2 eq) in MeCN (185 mL) was added to TMSCN (18.75 mL, 0.15 mol, 1.5 eq). The reaction mixture was refluxed for 24 h, then cooled to room temperature and diluted with aqueous 2 N NaOH (200 mL). The layers were separated, and the aqueous layer was extracted with ether (4×150 mL). The combined organic phases were washed with aqueous 1 N NaOH (10 mL) and brine (150 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by distillation (116-117°C under 20 mmHg) to yield benzyl cyanide as a yellow oil (8.78 g, 0.075 mol, 75% yield). 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.30-7.41$ (m, 5 H, Ar-*H*), 3.74 (s, 2 H, *CH*₂). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 129.9$ (*C*^{IV}-Ar), 129.1 (*C*^{ortho}-Ar), 128.0 (*C*^{para}-Ar), 127.9 (*C*^{meta}-Ar), 117.8 (CN), 23.5 (*CH*₂).

3.2. Microwave spectroscopy measurements

At the beginning, we remeasured some rotational transitions listed in Table 1 of Ref. [7] using the sample synthesized as described section 3.1. The spectrometer in use is a molecular jet FTMW machine with the coaxially oriented beam-resonator arrangement (COBRA) [22] and an experimental accuracy of 2 kHz [23]. Benzyl cyanide was put on a piece of a pipe cleaner and placed in a steel-tube [upstream of the nozzle](#) which was heated to 70°C. Helium flowed over the sample at a backing pressure of 1 – 2 bar, and the helium-benzyl cyanide mixture was expanded through the pulsed nozzle into the cavity. The hyperfine splittings arising from the ^{14}N nucleus could be completely resolved and assigned. Figure 3 depicts a typical spectrum of the $4_{14} \leftarrow 3_{03}$ transition. We then used the rotational constants and nuclear quadrupole coupling constants fitted with the program *XIAM* [24] to predict and measure further transitions in the frequency range 2 – 26.5 GHz measurable with the spectrometer. Note that the frequency given for the $2_{21} \leftarrow 1_{10}$ transition was misprinted in Ref. [7].

After the measurements of the main isotopologues, we searched for the spectra of ^{13}C isotopologues, aiming at a microwave structure determination. However, the isotopologue spectra were too weak. The number of observed lines were very limited and no fits were possible.

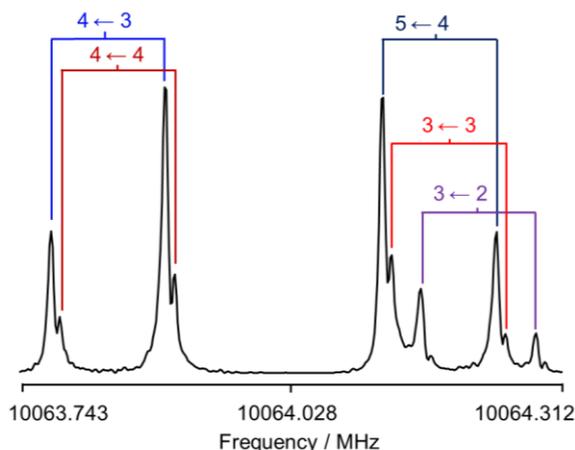


Figure 3. A typical high-resolution spectrum of the b -type R -branch rotational transition $4_{14} \leftarrow 3_{03}$. The ^{14}N quadrupole hyperfine components are given with the quantum numbers $F' \leftarrow F$. The Doppler components are connected by brackets.

4. Results and discussion

4.1. Fit results

Our final fit contains 465 rotational transitions including their hyperfine components compared to 69 lines reported in Ref. [7]. The global *XIAM* fit achieved a standard deviation of 1.9 kHz which is essentially the measurement accuracy of the spectrometer in use. The molecular parameters including the three rotational constants, five quartic centrifugal distortion constants, and the ^{14}N nuclear quadrupole coupling constants as obtained with the program *XIAM* are given in Table 2 and compared with results from quantum chemical calculations. All fitted frequencies are collected Table S3 of the Supplementary Materials along with their observed-minus-calculated values.

Table 2. Molecular parameters of benzyl cyanide obtained with the program *XIAM* in comparison with theoretical values.

Par. ^a	Unit	<i>XIAM</i>	Calc.
A	MHz	4346.815613(74)	4312.5 ^b
B	MHz	1057.372670(28)	1055.0 ^b
C	MHz	856.641252(25)	852.1 ^b
D_J	kHz	0.07309(16)	
D_{JK}	kHz	-0.37191(77)	
D_K	kHz	2.3641(43)	
d_1	kHz	-0.021002(99)	
d_2	kHz	-0.001299(57)	
χ_{aa}	MHz	-1.31174(71)	-1.1115 ^c
χ_{bb}^d	MHz	-0.6556(11)	-0.6443 ^c
χ_{cc}^d	MHz	1.9674(24)	1.7558 ^c
N^e		465	
σ^f	kHz	1.9	

^a All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. Standard errors in parentheses are in the units of the last digits.

^b Calculated at the MP2/6-311++G(d,p) level of theory.

^c Obtained with Bailey's calibration [25,26] from electric field gradient calculations at the B3PW91/6-311+G(d,p) level of theory on the MP2/6-311++G(d,p) optimized structure with a correction factor $eQ/h = -4.599$ MHz/a.u. recommended for a molecule containing a conjugated double bond system [27].

^d Derived from the fitted parameters χ_{aa} and $\chi_{bb}-\chi_{cc} = -0.0026230(14)$ MHz.

^e Number of lines.

^f Standard deviation of the fit.

4.2. Planar, or not planar?

To measure the planarity while [lacking information on minor isotopologues](#), the inertial defect, $\Delta_0 = I_{cc} - I_{aa} - I_{bb} = -2\sum_i m_i c_i^2$, is most often utilized. If the molecule is planar, all *c*-coordinates are required to be zero, leading to a value of zero for this parameter. The inertial defect is negative for a non-planar molecule. Approximately, each out-of-plane hydrogen atom contributes $-1.6 \text{ u}\text{\AA}^2$ to the value. If benzyl cyanide is planar and rigid, only the two hydrogen atoms in the CH₂ group are out-of-plane and the estimated inertial defect would be $-3.2 \text{ u}\text{\AA}^2$.

The value deduced from the rotational constants given in Table 2 for the inertial defect of benzyl cyanide is $-4.267 \text{ u}\text{\AA}^2$, significantly larger than $-3.2 \text{ u}\text{\AA}^2$. This value is essentially the same as that deduced by Liu et al. [7]. By comparing Δ_0 of benzyl cyanide with those of 17 compounds of the type X-CH₂-Y possessing planar heavy atom structures [28], Liu et al. found that their inertial defects range from $-2.82 \text{ u}\text{\AA}^2$ for NC-CH₂-CN [29] to $-3.56 \text{ u}\text{\AA}^2$ for Br-CH₂-CN [30]. Despite the significant difference, the authors still concluded a structure with all heavy atoms co-planar using the argument that benzyl cyanide, with its 16 atoms, is larger than all other compounds in comparison with less than 10 atoms. Therefore, the difference could be [traced back to larger](#) zero-point vibration contributions in benzyl cyanide.

In general, contributions to the inertial defect of out-of-plane hydrogen atoms [remain relatively constant](#). Therefore, we could consider also a comparison with any molecules possessing two out-of-plane hydrogen atoms. Exemplarily, as summarized by Buschmann et al. [31], the Δ_0 value found for vanillin, a molecule of similar size as benzyl cyanide and also featuring a phenyl ring, is $-3.56 \text{ u}\text{\AA}^2$ for the *a-cis-trans* conformer and $-3.74 \text{ u}\text{\AA}^2$ for the *a-trans-trans* conformer [32]. The values of methyl vinyl sulfide [33] and methyl vinyl ether [34] are $-3.14 \text{ u}\text{\AA}^2$ and $-3.18 \text{ u}\text{\AA}^2$, respectively. Other planar molecules containing a phenyl ring like 2-fluoro-4-chlorotoluene ($-3.12 \text{ u}\text{\AA}^2$) [35] and 2-chloro-4-fluorotoluene ($-3.10 \text{ u}\text{\AA}^2$) [36] or a five-

membered aromatic ring such as 2-acetylthiophene [37] and 2-acetylfuran (-3.3 u\AA^2 in both molecules) [38] all have values close to -3.2 u\AA^2 .

On the zero-point vibration contributions, it is now well known that low frequency out of plane vibrations can result in a small negative value of the inertial defect for a planar molecule. For example, we found a value of -0.294 u\AA^2 for coumarin, whose molecular structure was determined experimentally by isotopic substitutions to be planar [39]. As summarized by Oka [40], styrene and its halogenated derivatives feature inertial defects with the largest magnitude ranging from -0.6 u\AA^2 to -0.8 u\AA^2 . They all possess many more low-frequency out-of-plane normal modes than benzyl cyanide. Taking the largest value given by Oka [40] and assuming the zero-point vibrations of benzyl cyanide contributes -0.8 u\AA^2 to the value of -3.2 u\AA^2 estimated for a planar rigid molecule with two out-of-plane hydrogen atoms, the sum of -4.0 u\AA^2 still has an absolute value smaller than that of -4.267 u\AA^2 deduced from the experimental rotational constants. This result suggests a non-planar heavy atom structure of benzyl cyanide, in agreements with results of most MP2 calculations shown in Table S1 in the Supplementary Materials. Therefore, [though obtaining almost the same planar defect as Liu et al. \[7\]](#), the current state-of-the-art [puts the planarity of benzyl cyanide under question](#). Because the spectra of minor isotopologues are not observable with our experimental setup, it is [not possible to precisely determine the magnitude](#) of the non-planarity, [i.e. by how much is the \$\text{CH}_2\text{CN}\$ group tilted out of the phenyl ring plane](#). However, from the value of the inertial defect, we estimate that the out-of-plane angle should be relatively small, [and that the angles of up to \$50^\circ\$ predicted at many MP2 levels are overestimated](#). This is in very good agreement with the counterbalance between a long-range stabilizing p-p interaction between sp^2 or sp atoms favoring a planar structure and steric hindrance between two unsaturated groups favoring a non-planar structure. This also agrees well with the non-observation of *c*-type transitions in the spectrum. [However, it is not completely excluded that the absence of *c*-type transitions is due to an effectively planar structure of the zero-point averaged heavy atom geometry, with the zero-point level lying above the barrier to planarity](#). The situation found for benzyl cyanide is very similar to that of the difluorocyanomethyl radical $\dot{\text{C}}\text{F}_2\text{CN}$ for which we suggested “a nearly flat pyramidal structure” [41].

From many levels of theory used to calculate the structure of benzyl cyanide, the MP2/6-31G(d,p) level predicts equilibrium rotational constants which are in good agreement with the experimental values (see Table S1 in the Supplementary Materials) and we recommend this level for the assignment of microwave spectra of related molecules, for example benzyl isocyanide. Though it is physically not meaningful to compare rotational constants deduced from experimental spectra obtained for the vibrational ground state with the predicted

constants referring to equilibrium structures, this has become an accepted standard nowadays to guide the spectral assignment. Though some other levels perform slightly better than MP2/6-31G(d,p), we still recommend this level because it is known from many previous studies to constantly give reliable results for molecules containing a phenyl ring, such as coumarin [39], phenetole [42], *o*-methylanisole [43], quinolone [44], and isoquinoline [44].

Finding a definitive answer to the question “planar, or not planar” [1] of benzyl cyanide by searching for the spectra of minor isotopologues with a spectrometer of higher sensitivity will be an interesting future investigation to confirm the present results. Using the same experimental setup, it was possible to detect minor isotopologues, even the ^{18}O species with a natural abundance of only 0.2 %, of many other molecules such as 2-methyltetrahydrofuran [45], 2-ethylfuran [46], and coffee furanone [47]. Therefore, we were quite surprised that the search was not successful for benzyl cyanide where only a very small number of lines could be observed for the ^{13}C isotopologues, while transitions of the parent species are intense. This might be due to the fact that benzyl cyanide features more vibrational modes which decrease the line intensities upon isotopic substitutions.

5. Conclusion

The microwave spectra of benzyl cyanide were recorded in the frequency range between 2 and 26.5 GHz, aiming at understanding the ambiguous planarity of this molecule from both experimental and theoretical approaches. With large data set and precisely determined rotational constants, the inertial defect of $-4.267 \text{ u}\text{\AA}^2$ was deduced, being significantly larger than the value of $-3.2 \text{ u}\text{\AA}^2$ estimated for a planar rigid molecule with two out-of-plane hydrogen atoms. By comparing this value with that of other molecules with a methylene or a methyl group, we came to a cautious conclusion that the CH_2CN group of benzyl cyanide is slightly tilted out of the phenyl plane and the molecule is close to, but not planar. The hyperfine structures arising from the ^{14}N nuclear quadrupole coupling effects were observed for all rotational lines of the rigid rotor and fitted in a global fit where structural parameters such as the rotational constants and centrifugal distortion constants can be obtained together with the nuclear quadrupole coupling constants.

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