



HAL
open science

Calculations of the molecular interactions in 1,3-dibromo-2,4,6-trimethyl-benzene: which methyl groups are quasi-free rotors in the crystal?

Jean Meinnel, Soria Zeroual, Mohammed Sadok Mahboub, Abdou Boucekkine, Fanni Juranyi, Colin Carlile, Mourad Mimouni, Imad Hamadneh,
Ali Boudjada

► To cite this version:

Jean Meinnel, Soria Zeroual, Mohammed Sadok Mahboub, Abdou Boucekkine, Fanni Juranyi, et al.. Calculations of the molecular interactions in 1,3-dibromo-2,4,6-trimethyl-benzene: which methyl groups are quasi-free rotors in the crystal?. *Physical Chemistry Chemical Physics*, 2021, 23 (37), pp.21272-21285. 10.1039/d1cp02581c . hal-03367793

HAL Id: hal-03367793

<https://hal.science/hal-03367793>

Submitted on 28 Jun 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Calculations of the molecular interactions in 1,3-dibromo-2,4,6-trimethyl-benzene: which methyl groups are quasi-free rotors in the crystal?

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Jean Meinel,^{†a} Soria Zeroual,^{*b} Mohammed Sadok Mahboub,^b Abdou Boueckine,^a Fanni Juranyi,^c Colin Carlile,^d Mourad Mimouni,^b Imad Hamadneh^e and Ali Boudjada^f

Dibromomesitylene (DBM) is one of the few molecules in which a methyl group is a quasi-free rotor in the crystal state. Density functional theory calculations –using Born-Oppenheimer approximation (BOa)- indicate that in isolated DBM, the Me4 and Me6 are highly hindered in a 3-fold potential $V_3 > 55$ meV while the Me2 symmetrically located between two Br atoms has a small 6-fold rotation hindering potential: $V_6 \sim 8$ meV. Inelastic neutron scattering studies had shown that this is also true in the crystal, the Me2 tunneling gap being 390 μ eV at 4.2 K and $V_6 \sim 18$ meV. In the monoclinic DBM crystal, molecules are packed in an anti-ferroelectric manner along the oblique a axis, favoring strong van der Waals interactions, while in the corrugated bc planes each molecule has a quasi hexagonal environment and weaker interactions. It results that the nearby environment of Me2 is only composed of hydrogen atoms. This explains why the Me2 rotation barrier remains small in the crystal and mainly 6-fold. Using the same potentials in the Schrödinger equation for a $-CD_3$ rotor has allowed predicting a tunneling gap of 69 μ eV for deuterated Me2 in a very good agreement with inelastic neutron scattering measurements. Therefore, because of a rare and unexpected local symmetry in the crystal, the Me2 rotation barrier remains small and 6-fold and hydrogen nuclei are highly delocalized and not relevant to Born-Oppenheimer approximation. This and the neglect of spin states explain the failure of Density functional theory calculations for finding the rotation energy levels of Me₂.

Introduction

Many spectroscopic experiments have been interpreted treating the hydrogenated methyl (Me) group as a one-dimensional quantum rotor. The splitting of the ground state in two levels of respective spins 3/2 and 1/2, also known as the tunneling gap, varies on a range of more than 8 decades, indicating that the rotational hindering potential varies in a very broad range from less than one meV to more than 400 meV. For pure materials in the crystal state, the number of which one Me behaves as a quasi-free rotor is limited to four. The 1,3-dibromo-2,4,6-trimethyl-benzene also known as dibromomesitylene (DBM) is one of those. This paper examines the intramolecular and intermolecular interactions to explain the huge discrepancies between the behavior of Me2 squeezed between two “big” Br atoms but nevertheless quasi-free rotor, and that of Me4 and Me6 less hindered from a “geometrical point of view” but very well localized.

For isolated molecules in the vapor state, the first results have been obtained by microwave absorption [1, 2]. In such spectra, it has been possible to classify the numerous absorption lines as due to the rotation of the large molecule around its three principal axes of symmetry to which are superposed lines coming from transitions between the hindered rotational levels of the Me treated as a quantum uniaxial top. Such model has been confirmed by results of stimulated fluorescence on supersonic molecular jets [3, 4], these experiments have the advantage to work with molecules at very low temperature, say below 20 K while microwaves study vapors above room temperature, but their disadvantage comes from the fact that transitions are happening between levels of two different electronic states rendering more difficult their assignment. From the numerous experiments done with gases, and also with crystals [5,6], it appears that in all the methylated molecules, the energies of transition between the rotational levels of the quantum top $-CH_3$ are well described as solutions of the Schrödinger equation {1} of a uniaxial rotor of inertia momentum I evolving as a “single-particle” in a hindering potential $V_h(\theta)$ [7]:

$$H_{ik}\Psi_{ik}(-B_H \delta^2/\delta\theta^2 + V_h(\theta))\Psi_{ik} = E_{ik}\Psi_{ik} \quad \{1\}$$

$$V_h(\theta) = (V_{3n}/2)(1 - \cos(3n\theta - \Phi_n)) \quad \{2\}$$

In equation {1}, the Me group is characterized by its rotational constant $B_H = \hbar^2 / 2I = 0.655$ meV. The subscript i indicates the “rotational” level (0, 1, 2...), it corresponds to the spatial part of the Hamiltonian, the subscript k correspond to the spin dependant part,

^a Univ Rennes 1, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.

^b LEVRES Laboratory, University of El Oued, 39000 El Oued, Algeria.

^c Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland.

^d Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden

^e Department of Chemistry, Faculty of Science, University of Jordan, Amman 11942, Jordan.

^f Laboratoire de Cristallographie, Département de Physique, Faculté des Sciences Exactes, Université des Frères Mentouri Constantine-1, 25000, Algeria.

[†]Tribute to Emeritus Professor Jean Meinel who directed the study until his death on August 5th, 2018, at 92 years old.

* Corresponding author: soria-zeroual@univ-eloued.dz

the levels of spin 3/2 had energies labeled $0_A, 1_A, 2_A, \dots$, levels of spin 1/2 had energies $0_E, 1_E, 2_E, \dots$. For the great majority of molecules in the Fourier expansion of $V_h(\theta)$ the first term V_3 is much larger than the other terms, it amounts to tenths or even hundredths meV. Thanks to *ab initio* quantum chemistry programs it is also possible to calculate the Me rotation hindering potential. The methyl group is described by three punctual protons on an almost equilateral triangle, one dihedral angle defining the orientation of a $-C_mH$ bond relative to the rest of the molecule is fixed and then, an optimization of the molecular conformation is calculated while relaxing all other coordinates. In this treatment, it is admitted the validity of the Born-Oppenheimer approximation for all the atomic nuclei in particular for hydrogen. Such calculations give generally barriers $V_h(\theta)$ in good agreement with those deduced from NMR experiments, for example, they find with a high accuracy that a large 3-fold barrier to Me rotation is produced by a single ortho-substituent like in o-halogenotoluenes, o-toluidine, o-xylene, as it could be suggested by the appearance of steric repulsion due to geometric reasons. But very early, it has been established that some microwaves results [1, 2] obtained with molecules having a C_{2v} symmetry may only be interpreted doing the hypothesis that the methyl top had a 6-fold symmetry. It is the case of methylboron difluoride [8], γ -picoline [9,10], toluene [11], para-halogenotoluenes [12,13]... Then, for all these molecules in the gaseous state, the hindering potential {2} may be written simply as

$$V_h(\theta) = (V_6/2) (1 - \cos(6\theta)) \quad \{3\}$$

For the molecules quoted above, V_6 is smaller than 6 meV and the proton probability density (PPD) is almost uniformly spread on a circle of radius 1.02 Å.

Rather unexpected have been the results of laser-induced fluorescence and resonant two-photon ionization experiments [2, 14,15] done on symmetric 2,6-difluoro- or 2,6-dichloro-toluenes: the Me surrounded by two "big" halogens is not highly hindered, but it seems a potential V_6 always smaller than 7 meV. At first sight, this seems abnormal, from a pure concept of steric hindrance, with atoms looking like balls, one thinks to double the intensities of two separate ortho influences this gives a precious indication about the importance of keeping in mind the molecular symmetry with quantum objects: the two V_3 potentials seen by the two ortho substituents must be taken as opposite in phase so that the next component of the Fourier decomposition of the potential $V_h(\theta)$ in equation {2} is the term V_6 . For these methyl groups, in a local environment of C_{2v} symmetry, the quantum chemistry calculations of energy of formation give also small hindering potentials with a 6-fold symmetry [14, 16], but as we will show in &4, they fail to give the methyl conformation and the HMe "libration frequencies" in agreement with the results obtained solving the Schrödinger equation of HMe "single-particle". All microwave studies have now been beautifully extended by optical studies of fluorescence on supersonic jets [2, 14, 17] that also give news on electronic excited states.

The problem is more complicated when methylated molecules are strongly packed in the solid state, because of the variability of the intermolecular interactions with the methyl group rotor. In a compilation published in 1997, Prager and Heidemann [5] had already given more than 200 references to tunneling studies for hydrogenated methyl groups (Me) done on molecules in the solid state. Almost all the experimental results presented are well interpreted with the model of methyl groups located in deep 3-fold

hindering potentials and in consequence showing small tunneling gaps, in general, smaller than 1 μ eV. One can say that these studies have been one of the great successes of the NMR applied to molecular solids. For about two dozen materials, the gap must be studied by INS, being in the range 1- 200 μ eV, in these cases, the barrier has always the main component of 6-fold symmetry. Then, if we admit that the Me is a "quasi-free rotor" when the tunneling excitation energy is larger than 330 μ eV, (i.e. half the value of the rotating constant there are less than ten cases of molecules with a Me group quasi-free in the solid state. Three cases correspond to aromatic molecules where the HMe is surrounded by two hydrogens in di-ortho position on the ring, they correspond to "single" molecules trapped in calixarenes cages (CAC): toluene (Tol) [18], paraxylene (pX) [19, 20] and γ -picoline (γ P) [21], one can say it is an intermediate case between gas and crystal state. A particular material corresponds to small quantities of methyl fluoride (<1%) trapped in argon [5], in this case, the intermolecular interactions seem to have been efficiently reduced. Only in four cases, molecules in crystals of pure materials have a Me quasi-free rotor: γ P [21], 4-methyl pyridine oxide [22], the last two cases are rather unexpected the Me is located between two "big" halogen atoms in 1,3-dichloro- and 1,3-dibromo-2,4,6-trimethyl-benzenes also named 2,4-dichloro-mesitylene (DCM) and 2,4-dibromo-mesitylene (DBM) [23]. The tunneling energies in these four pure materials are respectively 520, 337, 451, and 390 μ eV. So, except in these four cases, the hindering potential of the Me group is largely enhanced when molecules are going from the gas state or isolated in a cage, to a strong packing in a crystal. For example, in the case of Tol crystal, two tunneling gaps were measured amounting to 26.0 and 28.5 μ eV, they correspond to threefold hindering potentials V_3 around 24 meV [24] instead of V_6 equal to 0.4 meV for the gas, and 1.2 meV if Tol is encaged in CAC. It can be said as a rule that the crystal environment largely enhances the HMe rotation hindering potential, the only exceptions occurring for four molecules of C_{2v} symmetry. Then two questions arise: Does the crystal packing respect the 3-fold symmetry of the Me group? What is the shape of the proton probability density adopted by the Me group in the crystal, has it a 3, 4, or 6-fold symmetry? To answer unambiguously these questions, it is necessary: **1-** to know by calculation (and if possible experimentally) the barrier seen by Me in the isolated molecule, **2-** to know in details the molecular environment of the Me tunneling group and evaluate its contribution to the rotation hindering potential. **3-** to know the tunneling gap and at least two other librational transitions characteristic of the quantum behavior of the Me group. Such kind of studies is presented in this paper for the methyl groups of DBM. A highly wanted way to extend this study would be to determine if after deuteration of the methyl group (DMe) the potential hindering the "rotation" remains the same, the levels energy of the rotor is only affected by the change of the inertia momentum.

Many works have been done on the methyl rotation barriers and molecular conformation in substituted benzenes by correlated quantum chemistry methods [14-17]. Barriers were computed using different methods: Hartree-Fock (HF), post-HF Møller-Plesset (MP2, MP4), Density Functional Theory, and different basis sets. It was verified that the Me is always highly hindered in o-halogenotoluenes (o-XTol) and that it was a quasi-free rotor in Tol and o-dXTol. Our group has studied also: toluene (Tol), ortho-substituted (o-XTol) and 2,6-dihalogeno-toluenes (o-dXTol) [17]. Then, in studies of the molecular conformation and spectroscopic properties of the tribromo- (TBM) and triodo-mesitylene (TIM), it

has been demonstrated [25,26,27,28,29] that DFT calculations using B3LYP or MPW1PW91 functionals and LanL2DZ(d,p) or 6-311+G(d,p) basis sets, not only allow a precise prediction of the molecular conformation in good agreement with that observed by neutron diffraction, in the crystal at low temperature (15 K) but that they also give with a precision better than a few %, all the internal modes frequencies. It is why we have done DFT computations for this study of the DBM conformation and of the rotation barriers of its Me groups.

Methodology

MPW computations were done using the MPW1PW91 functional and; The basis set used being the LANL2DZ(d,p) and 6-311+G(d,p), improving previous calculations done with the smaller 3-21G* basis set [30].

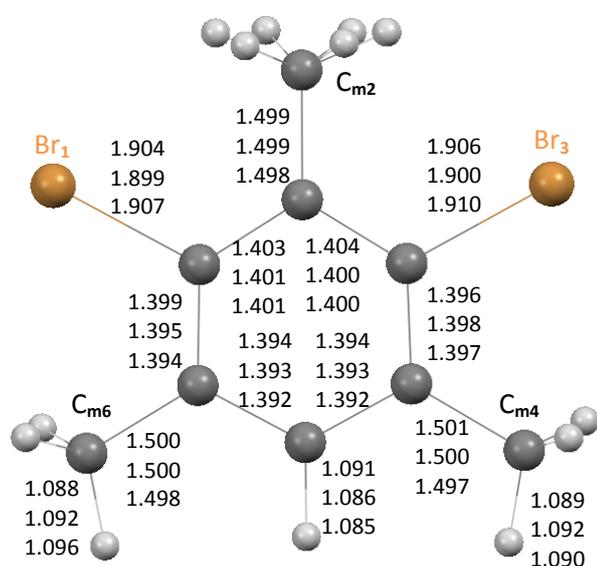


Figure 1 Bond lengths in DBMH molecule. In bold: experimental values from neutron diffraction experiment with a single crystal at 14 K. In script: DFT calculations with MPW1PW91 functional, up LANL2DZ basis set, down 6-311+G(d,p).

The difference between the angles calculated by these two functionals was always smaller than 0.1° , so it is only presented in **FIG.1** the bond lengths of the conformation optimized using MPW with the two different bases in comparison with the experimental conformation given by Hernandez using neutron diffraction (ND) with a single crystal at 14 K [30].

The agreement is very good and always better than 0.005 \AA , *i.e.* 0.3 %. For the angles, the comparison between calculation and experiment is illustrated by **FIG.2a** and **2b**. To facilitate the comparison, the angles are given in degrees with only one decimal. It appears that the two figures are quasi identical except for the Me2 lying between the two bromines. The molecule is rigorously planar (except naturally staggered protons of methyl groups). For the computed structure, each of the three methyl groups has one C-H bond lying in the plane of the aromatic ring, while the Me2 protons are found highly delocalized by ND.

For DFT and ND, each of the two coplanar C-H bonds in Me4 and Me6 is pointing towards the bond C_5H_5 , and the angles $C_{m4}C_4C_5$ and

$C_5C_6C_{m6}$ are equal to $120.2 \pm 0.1^\circ$, the staggered protons of the HMe groups are slightly repulsed by the bromine atoms, the angles $C_1C_6C_{m6}$ and $C_3C_4C_{m4}$ being equal to $122.7 \pm 0.05^\circ$. The calculated and

For the Inelastic neutron scattering, the experiments have been done with the backscattering time of flight spectrometer IRIS at ISIS, Chilton. Using pyrolytic graphite monochromators, the resolution was 16 \mu eV , the energy range explored has been extended from -500 to $+500 \text{ \mu eV}$.

Results and discussions

1-DBM molecular conformation: Comparison of that found by DFT calculations with that found by neutron diffraction at 14 K.

Fig. 1 and Fig. 2 gives the bond lengths and angles calculated by DFT method in comparison with the experimental values from neutron diffraction.

The experimental angles of the hexagonal ring facing Me4 and Me6 are equal to $117.1 \pm 0.1^\circ$. At this stage for two-third of the DBM molecule, DFT and ND results are almost in perfect agreement, they have found that C_{2v} molecular symmetry is respected in a limit of 2×10^{-3} for the angles and the bond lengths [30].

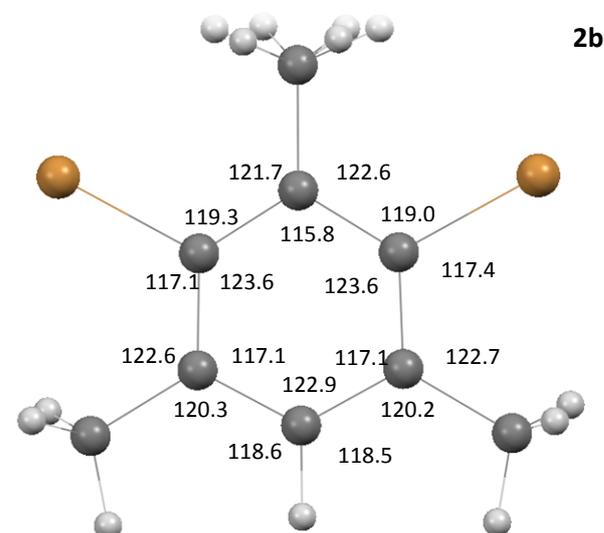
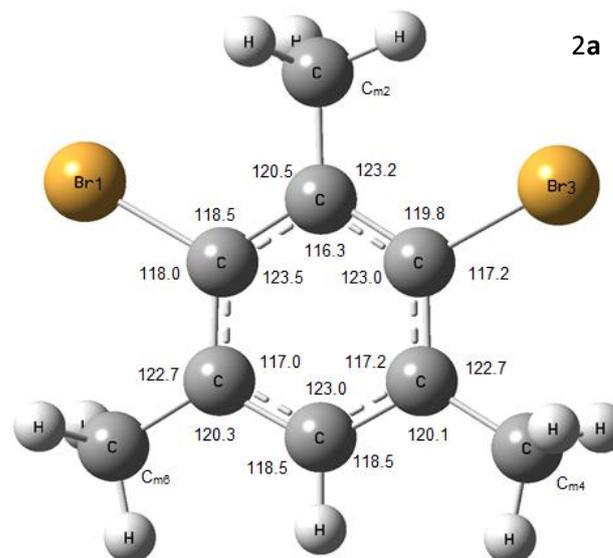


Figure 2 Bond angles in DBMH molecule, **2a**: DFT calculations with MPW1PW91 functional and 6-311+G(d,p) basis set. **2b**: Experimental values from neutron diffraction experiment with a single crystal at 14 K.

A discrepancy occurs for the environment of Me2: for QMC the extra ring CCC angles are 120.5° and 123.2°, the eclipsed CH bond of Me2 having equal chance to be on the right or the left of **FIG.2a**, depending on the orientation chosen for the HMe at the beginning of the optimization process. **In fact, DFT calculations optimize the position of three protons on a quasi-equilateral triangle, because they admit that the Born-Oppenheimer approximation (BOa) is valid for all nuclei, even the protons of Me2, and at last, they do not take in account the spin states.** The result is that the perfect local C_{2v} symmetry due to the presence of the two bromines Br₁ and Br₃ is lost. The repulsion being significantly smaller between Br₁ and H₂₁ than between Br₃ and the pair H₂₂ + H₂₃. The quantitative result is that the angles Br₁C₁C₂ = 118.5° and C₁C₂C_{m2} = 120.5° are smaller than the angles Br₃C₃C₂ = 119.8° and C₃C₂C_{m2} = 123.2°.

In **FIG. 2b**, it can be seen that the conformation found by ND at 14 K is quasi-symmetrical, contrary to that calculated: the experimental angles are Br₁C₁C₂ = 119.3° and C₃C₂C_{m2} = 121.7° on one side, and Br₃C₃C₂ = 119.0° and C₃C₂C_{m2} = 122.6° on the other side. Moreover, experimentally, the localization of all the carbon atoms is effectively very well defined, in particular C₁, C₂, C₃, and also C_{m2} while for the Me2 group, the proton probability density (PPD) is largely spread on more than three sites. It had been necessary to introduce six sites and a large thermal motion parameter to obtain a satisfactory refinement of the ND data concerning this Me2. **FIG.3** gives another representation of the PPD for the Me2 at 14 K: it corresponds to a cut done in the plane of the PPD maxima, confirming that protons of Me2 are present all around the C₂C_{m2} bond with six broad maxima, three being slightly larger than the three others. On the contrary, Me4 and Me6 are localized around only three maxima [30].

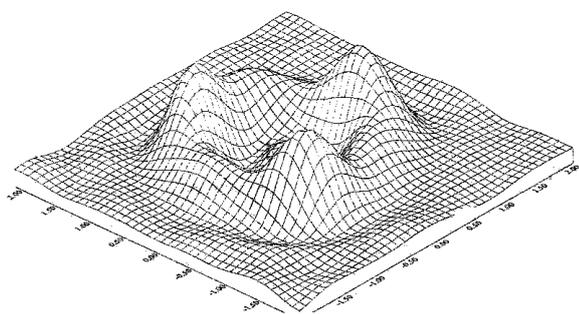


Figure 3 Fourier difference showing the Proton Probability Density in the "protons plane" for Me2 found by neutron diffraction in DBMH molecule

How to explain this large difference between the Me2 geometry and tunneling gap and the behavior of Me4 and Me6? To answer this question, we present first DFT calculations of the Me groups hindering potentials in an isolated DBM molecule and after a classical calculation of the intermolecular van der Waals and Coulomb interactions due to the molecular packing in the crystal.

4 - Particularities of the Me groups "rotation" modes among the DBM internal modes of vibration

4-1- Proposals for an assignment of the Me rotation modes frequencies using DFT calculations and spectroscopy data

Having established the ability of DFT calculations to reproduce accurately the DBM conformation, we have used complementary programs to predict several other physical properties and particularly the frequencies of the internal modes of vibration. The agreement between our calculations and our spectroscopic measurements (Raman and infra-red at 293 K, INS at 30 K) is very good, it has been presented in detail in a special publication [31]. Here we are focusing our discussion on the properties of the Me groups, so we must begin to explain how the "Me excitations" have been discriminated. DBM has 57 internal modes of vibration. Twenty-six of the thirty modes implying more specifically the skeleton have been assigned in the range of frequencies 200-1700 cm^{-1} with an agreement better than 3%. For Me groups, vibrations corresponding to Me rocking, bending and stretching modes have been found above 1000 cm^{-1} , the agreement calculus-experiment is better than 6 %, it remains to assign the three "rotation-libration" modes, which are always located in the low-frequency range say below 200 cm^{-1} , as out of plane modes. In this low-frequency range, it has been calculated 7 vibration frequencies, only one is an *in-plane* vibration mode: the C-Br symmetrical bending ν_5 has been calculated at 158,4 cm^{-1} it has been measured as intense in Raman: at 159 cm^{-1} . It remains to assign 6 *out-of-plane* modes. The C-Me symmetrical bending calculated at 188.4 cm^{-1} is seen as intense at 191 cm^{-1} in infra-red and at 193 cm^{-1} by INS. The five other modes have rather small intensities in all spectra, all are always accompanied by a "rotation" of Me groups. We propose to assign the C-Br symmetrical bending calculated as ν_1 at 71 cm^{-1} seen at 78 cm^{-1} by IR and INS, the C-Br asymmetrical bending calculated as ν_2 at 81 cm^{-1} , probably seen at $94 \pm 3 \text{ cm}^{-1}$ by Raman and IR, at 91 cm^{-1} by INS. For these two modes, there is also a "rotation" of Me2 when inspecting the calculated data, but it is for ν_3 computed at 119 cm^{-1} that the amplitude of Me2 rotation is the largest **FIG. 4**, ν_3 could be the excitation seen at $124 \pm 3 \text{ cm}^{-1}$ by Raman and $117 \pm 3 \text{ cm}^{-1}$ by INS. The remaining frequencies are: ν_4 computed at 157 cm^{-1} , experimentally it is probably hidden by the intense ν_5 , it corresponds to Me4 rotation accompanied by bending motion of the three bonds C-Me_i; the last frequency ν_6 computed at 167 cm^{-1} could correspond to Me6 rotation also coupled to C-Me_i bending motions. The results of these calculations (results of the diagonalization of the dynamic matrix) are in remarkable agreement for almost all the vibration modes, they are ambiguous for the Me groups rotation modes. In consequence, we have done complementary DFT computations to evaluate separately the rotation barrier height for each Me group.

4-2- DFT calculations of the rotation barriers heights and energy levels for the three DBM Me groups

The only difference with calculations of &3 was that rather than searching an extremum for the molecule formation energy by optimization of all the molecular angles and bond lengths, now the

dihedral angle defining **the orientation of a specific Me group is fixed and varied step by step** while all other coordinates are optimized, for example, $\gamma_2 = C_1C_2C_{m2}H_{21}$ has been varied from 0° until 120° by 15° steps to obtain the Me2 barrier. Only MPW data are discussed here. Two types of basis sets have been used for the calculations: either the LanL2DZ(d,p) basis, case said MPWL, either the 6-311+G(d,p) basis, case MPW6. In each case two options have been studied, either (free) all coordinates except γ_i for the Me_i studied are optimized, either (plane) the molecular ring is constrained to be planar for each value of γ while the other coordinates are optimized. The calculated barrier height is rather few affected by the constraint.

For Me₄ (and Me₆) the barrier has only a 3-fold component amounting to 56 meV for MPWL calculations and to 61 meV for MPW6. This confirms the results of **FIG 2a**: already in the isolated molecule, these two Me groups are located in deep wells and their protons are well confined. Using equation {1} with $V_h = 60$ meV it is found a transition $0_A \rightarrow 1_A \sim 0_E \rightarrow 1_E$ equal to 17 meV, this value is close to those proposed for the assignment of rotation modes of Me₄ and Me₆ found by spectroscopy: at 19.6 meV (158 cm^{-1}) for Me₄ and at 20.7 meV (167 cm^{-1}) for Me₆. Then, the calculated intramolecular hindering potential is the main part of the total hindering potentials V_T^4 or V_T^6 in the crystal, this is also in agreement with previous INS results [23]. For the interpretation of a "neutron energy fixed window" experiment studying the relaxation of the Me₄ or Me₆ groups excitations, it has been proposed: a hindering potential $V_T^4 = V_T^6 \sim 90$ meV with $V_3 = 75$ meV, $V_6 = 15$ meV and $\Phi_6 = 150^\circ$ [32]. To such V_T^4 will correspond a tunneling gap $\hbar\omega \sim 0.8\ \mu\text{eV}$ and a transition energy $0_A \rightarrow 1_A \sim 13$ meV, while "a small variation in phase $\Phi_6 = 105^\circ$ gives $0_A \rightarrow 1_A \sim 20$ meV value compatible with the excitations ν_4 and ν_6 detected by spectroscopy and assigned to Me₄ or Me₆ in &4-1.

On the contrary, in accordance with the symmetry of the substitution, the hindering potential calculated for Me₂ has only a small 6-fold contribution and its value depends partly on the constraints introduced during the calculations. The calculated V_6^2 is equal to 5.1 meV for MPW6-free and 5.8 meV for MPW6-plane, it amounts to 6.9 meV for MPWL-free and 7.5 meV for MPWL-plane, these values are very close to the 6 and 7 meV found with MPW6 for the orthodichloro- and orthodibromo-toluene [16]. Then, using the approximate potential {4} to solve equation {1} it is found that the PPD for Me₂ in the isolated molecule of DBM may be described by the equation {5}.

$$V_T = (6.6 / 2) (1 - \cos 6\alpha) \quad \{4\}$$

$$\rho = 3 (0.92 + 0.04 \cos 6\alpha) \quad \{5\}$$

At this stage of our argument, we must already add a few remarks for the interpretation of our last DFT calculations: the optimized molecule has not exactly the C_{2v} symmetry; the Me₂ keeps always a 3-fold symmetry as in **FIG.2a**. *To maintain the symmetry, one must imagine that the C_2C_{m2} bond is oscillating or rotating around the direction C_2C_5 , on a cone of directing angle nearly equal to 2° . Moreover, this Me₂ motion must be fully concerted with out-of-plane motions of the ring atoms and C_{m2} amounting to $0.05\ \text{\AA}$, motions that are not in agreement with the localization of carbon atoms found by ND: **FIG.1** and **2b**. Then we must remind that **all the MPW calculations have been done using the BOa** for all the atoms, in particular for the methyl protons, **then the methyl is treated as a classical macroscopic hindered rotor oscillating in a harmonic potential**. Furthermore, such calculations give only "one rotational*

or torsional mode" for each Me group ignoring the spin states of the Me rotor. Despite these restrictions, the DFT calculations have indicated unambiguously that the potential well seen by Me₂ in the vapor is shallow and may involve a 6-fold symmetry hindering potential, contrary to Me₄ and Me₆ that are highly hindered in 3-fold potentials. If a mean value $V_6 = 6$ meV for the hindering potential is used when solving the Schrödinger equation {1} for the Me₂ uniaxial rotor, the PPD found is highly spread in the isolated molecule, in disagreement with the BO approximation admitted in DFT calculations. We may also remark that when solving equation {1} it has been admitted that Me₂ is a "single-particle" submitted to the fixed constraints of an external bath. In fact, as the methyl group is linked to the benzene ring, its specific motions are more or less coupled with those of the neighboring atoms. Nevertheless, there is an ambiguity when speaking about the rotation of a Me group, as it corresponds to define the proton probability density in a local environment, that may be perturbed when going to the crystal state. This is the reason why now, are examined the local particularities of the DBM crystal structure and is proposed a calculation of the intermolecular contribution to the Me rotation hindering potential.

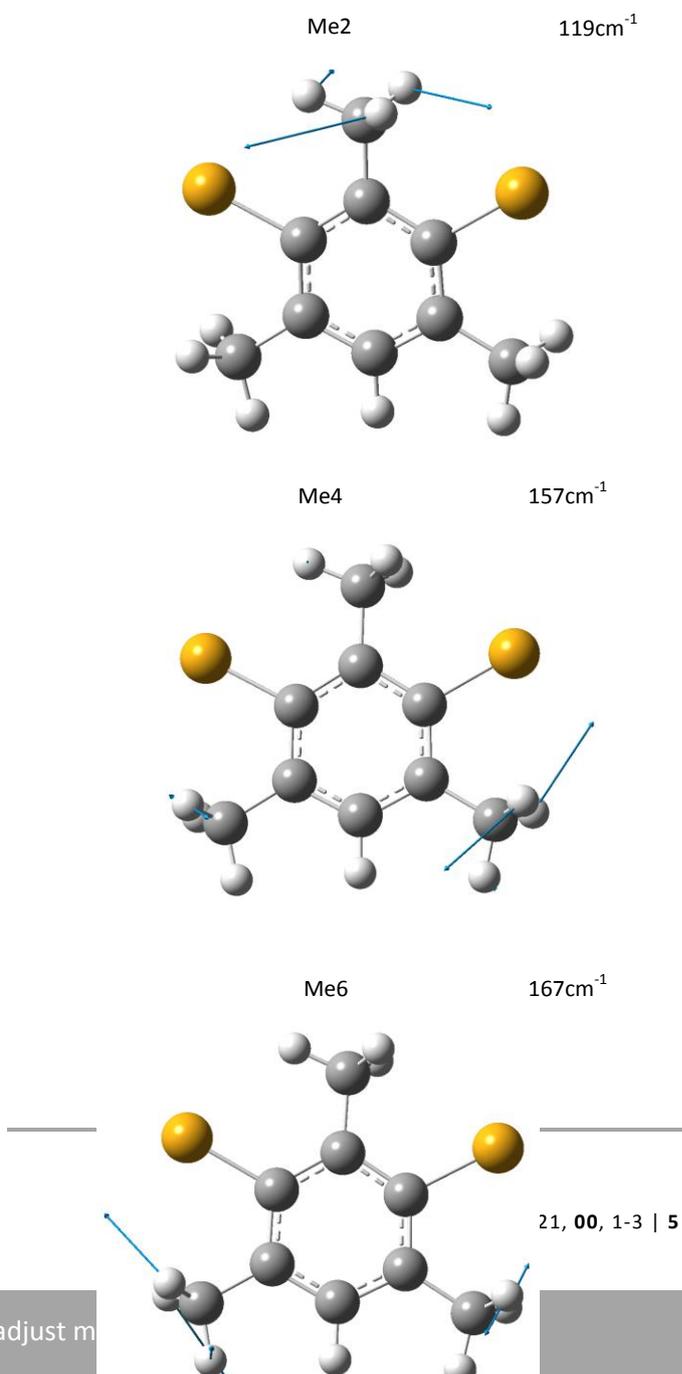


Figure 4 Illustration of the motions with frequencies ν_3, ν_4, ν_6 calculated by MPW1PW91 (LANL2DZ) at 119, 157, and 167 cm^{-1} and allocated respectively to rotation hindered motion of Me2, Me4, and Me6.

5 – Calculation of the intermolecular interactions in the monoclinic phase of DBM: Lattice phonons modes.

To understand why the environment of Me2 adds only a small contribution to its rotation hindering barrier, it is necessary to examine in detail the crystal structure, and then to evaluate quantitatively the various contributions to the cohesion forces. Now, is often evoked the possibility of "halogen bonding" when halogen atoms are neighbors in a crystal cell. Therefore, we would have to examine the strength of Br-Br interactions relatively to all other interactions in DBM crystal. However, already, as the DBM crystallizes with a monoclinic $P 2_1/n$ cell, like C_6Cl_6 and C_6Br_6 , it is possible to remind some conclusions done by Reddy et al [33], in a study of hexa-halogenated benzenes crystals. Examining the C_6Cl_6 packing he said: "The planar molecules form " π stacks." and added "no Cl-Cl interactions appear to be particularly important and " π stacking dominates this packing as it also does in the isostructural C_6Br_6 ". In consequence, to calculate the crystal building energy, we have evaluated separately: i- the van der Waals interactions (vdW) which take into account the dispersion attractions of London type and the repulsion due to the possibility of overlap of the electron clouds, and ii- the electrostatic interactions (Ei) due to interactions between dipolar molecules disposed in an antiferroelectric manner. To make sure the validity of the semi-empirical parameters used in these calculations; we have studied the influence of small variations in the position of a "probe" molecule in the crystal. Therefore, we will give proofs that the calculated potential energy has its extremum value for crystal positions and that also it allows us to calculate phonons in the crystal cell. Such precautions are necessary to have confidence when, not only the local interactions with Me2 are extracted from all the others in the crystal, but also small variations are studied while rotating its protons.

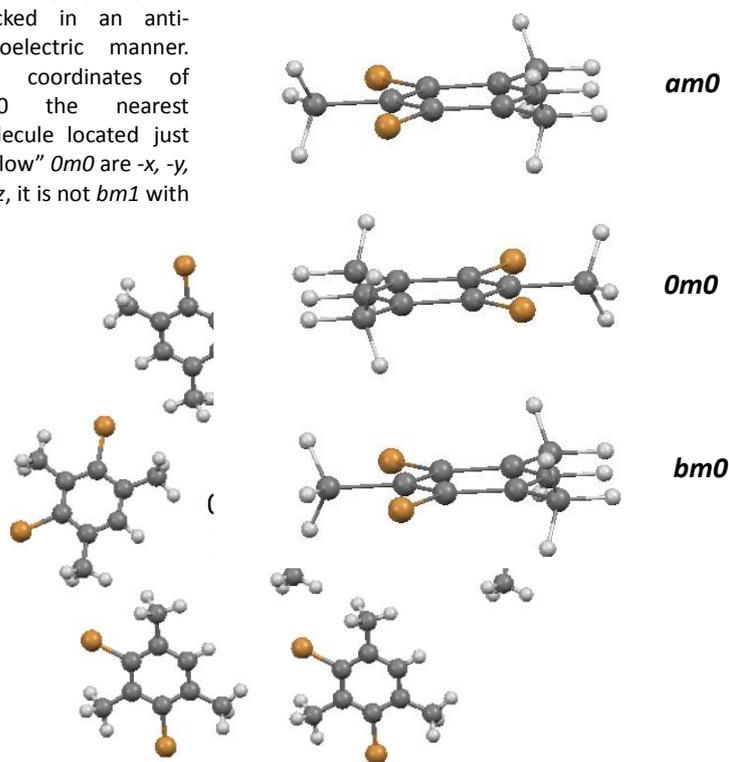
5-1- Description of the relative positions of close neighbors around a probe molecule

DBM crystallizes at 335 K, it gives a disordered phase I and undergoes a phase change at 291 K, leading to a phase II stable until 2 K. We have studied this last phase; It is monoclinic, space group $P2_1/n$ with four molecules in the unit cell, the molecules are perfectly ordered in the crystal. We have used the atomic coordinates determined at 14 K by Hernandez et al. [30];

The use of neutron diffraction gives confidence about hydrogen nuclei positioning. Orthonormal coordinates X, Y, and Z must be employed for distances calculation, the unitary reference axes have been chosen as: B^0 along the monoclinic axis b , C^0 along c , and A^0 along $a^* = b \wedge c$. The origin O is a center of symmetry. The "probe"

molecule, that for which is calculated the interaction with its neighbors is named $Om0$, it has coordinates x, y, z in the monoclinic cell: the probe molecule seems to have a quasi hexagonal environment (Fig.5) and one can describe the crystal as having a corrugated bi-dimensional texture. Already, it must be remarked that each of the six nearest neighbors of $Om0$ has less than forty atom-atom vdW interactions at distances smaller than 5.0 Å among a total of 441, and then able to give a significant contribution to the crystal vdW packing energy.

What is happening in a perpendicular direction? FIG.6 shows the orthogonal projection on the a^*c plane, it illustrates the fact that along a axis molecules $bm0, Om0$, and $am0$, located respectively at levels $-x, x, 1-x$, are stacked in an anti-ferroelectric manner. The coordinates of $bm0$ the nearest molecule located just "below" $Om0$ are $-x, -y, 1-z$, it is not $bm1$ with



coordinates $-x, -y, -z$. The pair $bm0 - Om0$ has 185 interactions at distances shorter than 5.0 Å, about five times more than each bimolecular interaction in the same plane.

Figure 5 Orthogonal projection along a^* of the probe molecule $Om0$ and its nearest neighbors.

"Almost" symmetrically to $bm0$ one can find a molecule $am0$ located just "above" $Om0$, its coordinates are: $1-x, -y, 1-z$.

Nevertheless, as there are 187 "short" interactions at distances smaller than 5.0 Å for the pair $Om0 - am0$, the contribution to the potential would be quite the same as that of $bm0 - Om0$.

Figure 6 Projection along c^* , of the three neighbor molecules $bm0, Om0, am0$.

5-2- Choice of the (exp -6) interatomic interaction coefficients to calculate the vdW energy potential in DBM

The van der Waals interaction is one of the important fundamental noncovalent interactions in molecular systems. Accurate treatment of vdW interaction is crucial in molecular modeling [34].

We have used a Buckingham type potential {6} for vdW interactions between two atoms labeled i and j , their distance d_{ij} (in Å) being that given by neutron diffraction at 14 K [31].

$$V_w = \sum_{ij} (-A_{ij} d_{ij}^{-6} + B_{ij} \exp(-C_{ij} * d_{ij})) \quad \{6\}$$

The attractive term is proportional to d_{ij}^{-6} and the repulsion term is an exponential of the distance. Such treatment is justified by the successes obtained for example by Williams [35], Kitaigorodsky [36], Pertsin and Kitaigorodsky [37], Gavezzotti [38,39], Bondi [40] ..., since the sixties. We have tried several values of coefficients A_{ij} , B_{ij} , C_{ij} for the calculus of the vdW interaction, we have chosen a modified Williams set, (Table 1).

Table 1- Coefficients A_{ij} , B_{ij} , and C_{ij} used in Buckingham potentials, while $A_{ij} = (A_i * A_j)^{1/2}$, $B_{ij} = (B_i * B_j)^{1/2}$ and $C_{ij} = (C_i + C_j) / 2$

	Br-Br	C-C	H-H	
A_{ij}	21000	2150	102.2	kJ/mole Å ⁻⁶
B_{ij}	88000	300500	9090	kJ/mole
C_{ij}	2.60	3.60	3.74	Å ⁻¹

The modifications of the coefficients A_{ij} , B_{ij} , C_{ij} have allowed us to find the minimum formation energy when a probe molecule is rotated or translated in the crystal from its crystallographic position, while, for simplicity, the environment does not move.

There is a maximum attraction at distances in the range: 4.0 to 4.5 Å for Br-Br, 3.55 to 4.6 Å for C-C, and 2.9 to 3.8 Å for H-H. The H-H maximal interaction is about 20 times smaller than the maximal Br-Br interaction.

This region of largest attraction is located at distances larger than the value admitted for the sum of two vdW radii. Reminding that in principle the vdW radius is defined in terms of that distance d_{ij} at which the electronic repulsion just balances the attraction forces between the two atoms i and j . Bondi [40] proposed: 2.1 Å for H, 3.06 Å for C, and 3.74 Å for Br, while for our set of A, B, C coefficients the interaction is canceling out for 2.9, 3.35, and 3.45 Å.

The molecules having the shape of oblate ellipsoids, have naturally the opportunity to be packed in piles like C_6Cl_6 [41], and in consequence, the easiest motion in the crystal cell is the libration of molecules in their molecular plane. To simplify the calculations at this stage, the protons are considered as point entities located at the positions where the ND has found the maximum for the PPD.

FIG.7 shows how varies the hindering potential V_w for such libration; The position for the minimum found by calculation is 1° apart from the position determined by crystallography, the agreement is even better when dipolar interactions are added. Such differences about 1° have been obtained for rotation of molecules around two other axes located in the molecular plane and differences of 0.2 Å for translations of the molecules in the crystal, along their principal axes of inertia.

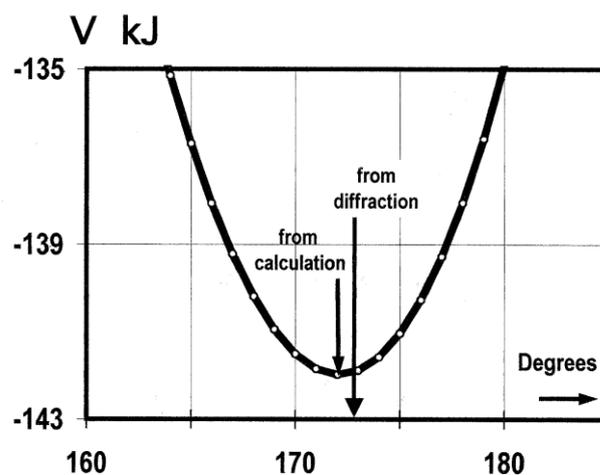


Figure 7 Variation of the Van der Waals interaction energy for a rotation of the probe $Om0$ around an axis normal to the molecular plane.

5-3- Comparison of lattice phonons modes calculated and observed

To obtain still better confidence about the importance of vdW potential to represent the main intermolecular interactions in DBM crystal, we have used them for computation of the lattice phonons modes and done a comparison with infrared and Raman excitations observed at 4 K (See Table 2).

Table 2- Excitations calculated and observed in meV. For each symmetry species, calculated frequencies in the first column, observed in the second.

Infrared				Raman			
A_u	B_u	A_g	B_g	A_g	B_g	A_g	B_g
0.0	-	0.0	-	4.4	3.2	3.3	2.5
3.7	2.6	0.0	-	5.9	5.1	5.4	5.6
6.0	6.0	7.4	7.2	6.7	6.8	7.6	-
7.6	7.2	9.3	9.5	8.2	8.1	8.4	8.1
15.0	15.4	14.8	15.4	9.7	11.6	9.5	9.7
18.2	-	18.4	-	18.1	16.7	18.1	16.7

The agreement between calculations using Table 1 coefficients and the experimental observations is sufficiently satisfactory for undertaking a detailed analysis of the interaction potential of each neighbor molecule with the probe molecule $Om0$, and in particular, with each Me group in $Om0$.

5-4- vdW packing energy due to interaction of $Om0$ with each of its neighbors

Examine now the importance of the intermolecular interactions contributing to the crystal formation and after that, what are the characteristics of the fractional energy potential to be attributed to the different methyl groups. V_w the total vdW energy of packing calculated is approximately equal to that of the interaction energy of a probe molecule with its 38 nearest neighbors given in Tables 3, 4, and 5, it amounts to -194kJ (2173 meV).

In & 5-1 it was established that the two molecules *am0* and *bm0* have about five times more interactions at distances smaller than 5 Å than every other neighbor, and their contribution amounts to nearly half the total V_w : they are -46.9 kJ for *bm0* and -46.8 for *am0*. **Table 3** gives the individual contributions to the crystal energy formation, for interactions between *Om0* with *Om1* and *Om2* and with *Om11* ...*Om14*. Each of them is comprised between -8.9 and -6.1 kJ/mole; For each other molecule in *Om3* ...*Om8* the vdW contribution is always smaller than -0.15 kJ/mole. So the nearer neighbors shown at levels P_o (at the height $X_o = 1.663$ Å: molecules *Om1* to *Om8*) and P'_o (at the height $X'_o = 1.873$ Å: four molecules *Om11* to *Om14*) are contributing to V_w for a total amounting to -45.2 kJ/mole, i.e. less than *bm0* or *am0*. This gives proof that DMB crystal packing consists of associations of needles of molecules packed along the crystallographic axis **a**, and not of a two-dimensional arrangement in parallel **bc** planes.

Table 3 - Interaction potential energy of the probe molecule *Om0* with each of its neighbors in plane P_o and P'_o . Units: kJ/mole.

coordinates	-1 + z	0.5 - z	z	1.5 - z	1 + z
1 + y	<i>Om6</i> -0.04	-	<i>Om7</i> -0.15	-	<i>Om8</i> -0.06
0.5 + y	-	<i>Om13</i> -7.9	-	<i>Om14</i> -9.0	-
y	<i>Om1</i> -6.1	-	<i>Om0</i> PROBE	-	<i>Om2</i> -6.2
-0.5 + y	-	<i>Om11</i> -7.7	-	<i>Om12</i> -8.2	-
-1 + y	<i>Om3</i> -0.05	-	<i>Om4</i> -0.15	-	<i>Om5</i> -0.04

Examine now the interactions of the molecules located "below" the probe *Om0* in the planes P_b (at the height $X_o = -1.663$ Å, it contains molecules *bm1* until *bm8*) and P'_b (at the height -1.873 Å, containing molecules *bm11*, *bm12*, *bm13*, *bm14*) their individual contributions are given in **Table 4**. It can be seen that the three molecules *bm1*, *bm11*, and *bm13* have larger than all others: they amount to -8.5, -11.1, and -4.0 kJ/mole, other contributions are smaller than 2.0 kJ/mole and decrease quickly with the distance to the probe *Om0*.

Table 4 - Interaction potential energy of the probe molecule *Om0* with each of its neighbors in-plane P_b , and P'_b , below *Om0*. Units: kJ/mole.

coordinates	-z	-0.5 + z	1 - z	0.5 + z	2 - z
1 - y	<i>bm6</i> -0.04	-	<i>bm7</i> -0.12	-	<i>bm8</i> -0.03
0.5 - y	-	<i>bm13</i> -4.0	-	<i>bm14</i> -1.6	-
-y	<i>bm1</i> -11.1	-	<i>bm0</i> -46.9	-	<i>bm2</i> -0.9
-0.5 - y	-	<i>bm11</i> -8.5	-	<i>bm12</i> -2.0	-
-1 - y	<i>bm3</i> -0.06	-	<i>bm4</i> -0.12	-	<i>bm5</i> -0.02

Above the plane P_o , in planes P_a (at the height $X = 5.410$ Å) and P'_a (at the height $X' = 5.200$ Å), there are also only three other molecules which have significant overlap with the probe *Om0*, they are *am2*, *am12*, and *am14*, their individual contributions amount to -6.8, -8.6 and -7.6 kJ/mole. In **Table 5** it can be seen that all other contributions are smaller than 2.0 kJ/mole and decrease quickly with the distance to *Om0*.

Table 5 - Interaction potential energy of the probe molecule *Om0* with each of its neighbors in-plane P_a and P'_a above *Om0*. Units: kJ/mole.

coordinates	-z	-0.5 + z	1 - z	0.5 + z	2 - z
1 - y	<i>am6</i> -	-	<i>am7</i> -0.08	-	<i>am8</i> -
0.5 - y	-	<i>am13</i> -1.5	-	<i>am14</i> -6.8	-
-y	<i>am1</i> -0.8	-	<i>am0</i> -46.7	-	<i>am2</i> -8.6
-0.5 - y	-	<i>am11</i> -2.0	-	<i>am12</i> -7.6	-
-1 - y	<i>am3</i> -	-	<i>am4</i> -0.11	-	<i>am5</i> -

5-5- Dipolar packing energy of the pair (*Om0* + *bm0*) or (*Om0* + *am0*), interaction energy between neighboring pairs

The neutral DBM molecule has a dipolar momentum, it has been calculated as 1.61 D by MPWL. We have seen **Fig. 7** that the planar molecules are superposed like pancakes in an anti-ferroelectric arrangement; in consequence, we have to take into consideration the cohesion energy resulting from Coulomb forces. The main part is due to pairs like *bm0*-*Om0*, and *am0* - *Om0*. We have tried to do an evaluation using the mean punctual charges located on atomic nuclei calculated by MPWL. In an electronic unit, for a symmetrical molecule, the mean respective charges calculated are: -0.18 for C_1 , C_3 , -0.56 for C_5 ; +0.42 for C_4 , C_6 , +0.36 for C_2 , -0.64 for C_m ; +0.19 for H_m , +0.18 for H_5 and -0.13 for Br. The attractive potential Coulomb energies are maximum for the pairs *bm0*-*Om0* and *am0* - *Om0*, but the absolute values found summing atom-atom interactions are much too large, about 30 times the vdW, and depend largely on the functional and basis set used in the calculation, even NBO charges do not give very different values. Smaller values for atomic charges have been found for the semi-empirical program PM3. In fact, the calculations of the Coulomb interactions between *Om0* and farther molecules gives always attractive contributions, but for finding an accurate value for the total potential, such calculation is open to other criticisms, because it does not take into account the screen effect. In fact, to understand the electrostatic interactions, we think that it is simpler to reason saying that the packing results from strong dipolar interactions between pairs like *Om0*-*bm0*, which represent the nearest anti-parallel arrangement compatible with vdW interactions and then to add the much smaller interactions between similar pairs of dipoles.

In conclusion, the packing of molecules in DBMH is a complicated result of several small interactions, but it appears clearly, that the anti-ferroelectric packing along the axis **a**, is the source of the strongest vdW and Coulomb inter-molecular interactions in the crystal. In a first approximation, the crystal is built by rods of molecules strongly packed along the axis **a**, each rod is interacting with other parallel rods with molecules arranged in a herringbone manner, while molecules in the **bc** planes have a corrugated bi-dimensional texture with neighboring molecules more smoothly linked between them.

6 – Calculation of the Me₂ rotation hindering potential part created by its molecular environment

In § 5, it was established that the probe molecule *Om0* is almost symmetrically located between *am0* and *bm0*, so it is possible now to say that the main contributions to the van der Waals and Coulomb interactions on the Me₂ protons in the crystal are due to these two molecules. Fig.8 presents a stylized view of an orthogonal projection along *a** onto a *bc* plane, atoms being represented as small balls. This picture shows the effect of the translation along *a** when going from *bm0* unto *Om0* and after that unto *am0*: these molecules are strongly overlapping. Obviously, only hydrogen atoms surround Me₂ in the probe *Om0* in an “almost” symmetrical arrangement and each of these H atoms gives only a relatively small vdW contribution to the potential V_h , seen by Me₂ in *Om0*.

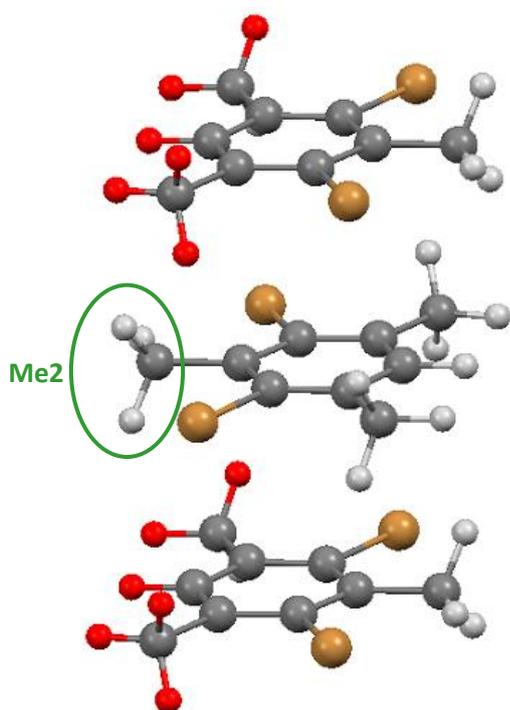


Figure 8 Surrounding of Me₂ of the probe molecule *Om0* between *am0* and *bm0* molecules.

To obtain an approximate value of V_h , we have done calculations for a “simplified” Me₂ with three punctual protons located at 1.07 Å of the carbon C_{m2} within (*Om0*), they are rotating around the bond C₂ C_{m2}. This C_{m2} (*Om0*) is distant of 3.9047 Å from H₅ (*bm0*) and 3.8073 Å from H₅ (*am0*). During the C_{m2} rotation, the distance of each C_{m2} proton in the probe unto H₅ (*am0*) varies from 2.56 Å until 4.61 Å. Their individual contributions to vW vary respectively between +0.26 when one C-H in the probe is pointing towards H₅ (*am0*) and -0.25 kJ/mole when two protons of C_{m2} in *Om0* are symmetrically located around H₅. The total interaction energy for the three “punctual” protons with the carbon, bromine, and hydrogen atoms in *am0* is varying from -0.87 and -1.53 kJ/mole. The interaction of H₅ (*bm0*) with Me₂ protons in the probe, is slightly less than for

H₅ (*am0*): between +0.08 and -0.07 kJ/mole, while the total interaction with all the atoms of *bm0* varies between -0.26 and -1.38 kJ/mole. The total variation in potential energy due to the 38 nearest neighbors of *Om0* is smaller than 3.5 kJ/mole if we rotate three “punctual” protons, but it will decrease by more than a factor two if we take protons delocalized in six sites (model closer the experiment (Fig.3a and 4) and will retain a six-fold symmetry for its main component. Therefore, despite all kinds of uncertainties due to the huge number of interactions and to the difficult choice of vdW parameters, it has been found that the crystal lattice does not give rise to an important contribution to the Me₂ rotation hindering potential.

For Me₄ and Me₆, which are located between two big bromine atoms within the neighbor molecules *bm0* and *am0*, along the oblique direction *a*, the intensity of the interactions vary much more during the Me “rotation” process than for Me₂. The total variation in potential energy for Me₄ is around 12 kJ/mole, it has to be added to the 7 kJ calculated § 4-2 for the intra-molecular interactions. Therefore, the intermolecular interactions enhance definitely the barrier for Me₄ and similarly for Me₆, in agreement with experiments [23], even if it is difficult to do a precise comparison from a quantitative viewpoint.

7 – About periodic DFT calculations of molecular structure and methyl group rotational potential

In §3 it has been presented a study of the DBM single-molecule conformation using B3LYP or MPW1PW91 functional in DFT calculations. The agreement with the experimental results was remarkably good except for Me₂ and its environment, we have explained that this “local” failure of DFT calculations is inherent of the use of the BO approximation to Me₂ protons located in a symmetrical environment and then submitted to a six-fold potential. As shown in §4-2, the results of DFT calculations done with relaxation of the molecular conformation for each Me group orientation would lead to a precession motion of the C₂C_{m2} bond on a cone of directing angle 2° coupled with in phase out of plane deformations of the rest of the molecule. This is in contradiction with the localization of the C and Br atoms observed by ND, even if the molecular conformation is slightly disturbed by the environment. In a previous publication [31] it has been presented the results for DBM crystal employing the periodic DFT code CASTEP which uses plane waves to simulate the electron density throughout the simulated cell of the periodic crystal. In that work was used the GGA approximation for the exchange-correlation energy, this leads to an unphysical expansion of the unit cell if its dimensional parameters are relaxed, this result has been attributed to the absence of dispersive interactions in the GGA approximation. So the stability of the crystal structure cannot be obtained without taking into account a kind of additional anisotropic pressure, which compensates for the absence of dispersive interactions. Then the Me group rotational hindering potential was obtained by calculating the crystal energy when rotating the Me step by step (as us in § 4-2). The calculations were made in particular (i) for experimental atomic positions and cell parameters (ii) for optimized atomic positions and the experimental cell parameters. The respective tunneling gaps found were 71 μeV for (i) and 3.9 μeV for (ii) instead of 390 μeV measured by INS, furthermore, the hindering potentials calculated have a 3-fold component much larger than the 6-fold and cannot allow finding the delocalized PPD found by ND. The authors had concluded: “the agreement between the calculation and experiment is mediocre”. So such periodic calculations, not only do not overcome the inadequacy of admitting the BO approximation,

but they also have problems for the calculation of the experimental unit cell and the Me2 PPD. These DFT periodic calculations as those for isolated molecules find that Me4 and Me6 “rotations” are highly hindered in 3-fold potentials larger than 100 meV.

8 – HMe protons tunneling and libration energy transitions observed in DBMH by INS, hindering potential proposed.

In our previous work using powders [23], it has been proposed that the tunneling barrier for Me2 protons is:

$$V_h = 11((1 - 0.24 \cos 3\theta) + (1 - 0.76 \cos 6\theta)) \text{ meV} \quad \{7\}$$

The intensity of this potential is significantly larger than the 6 or 7 meV calculated in § 4-2 for the gas, but the main part of V_h still keeps the 6-fold symmetry. In those experiments, the tunneling transitions were detected only on the neutron energy loss side of the INS spectrum. The spectrometer used was the triple-axis 4F2 at LLB, Saclay. A new series of experiments have been done with IRIS spectrometer.

The tunneling peak corresponding to transitions $\pm h\nu_i$ between 0_A and 0_E occurs at $389 \pm 2 \mu\text{eV}$ (FIG.9).

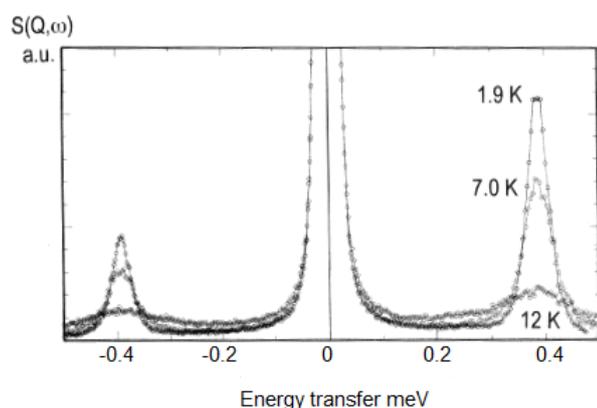


Figure 9 Variation of the shape and intensity of the tunneling excitations of Me2 in DBMH powder in the function of temperature at 1.9, 7.0, and 12 K (IRIS spectrometer at ISIS).

There is presumably a small shift upwards when the temperature rises.

The shape of the tunneling excitation is the same in energy gain or loss.

The INS spectrum has been also studied in the range 1 to 10 meV with the triple-axis 4F2, operating at constant $k_f = 1.50 \text{ \AA}^{-1}$ and constant $Q = 2.50 \text{ \AA}^{-1}$, resolution $160 \mu\text{eV}$ (FIG. 10).

It is also shown on these figures a decomposition of the experimental spectra in four Lorentzian curves in the range 1 to 5 meV. Furthermore, in Table 6, it is given a comparison between these experimental frequencies and those calculated using the rotation hindering potential given in equation {7}. The agreement between calculus and experiment is very satisfactory.

One may remark that the intensities of the transitions allocated to $0_A \rightarrow 1_E$ and $0_A \rightarrow 1_A$ are diminishing relatively to those allocated to $0_E \rightarrow 1_E$ and $0_E \rightarrow 1_A$ when the temperature rises from 1.7 to 25 K. This is due because the population of the level 0_A decreases approximately by more than a factor two in this temperature range.

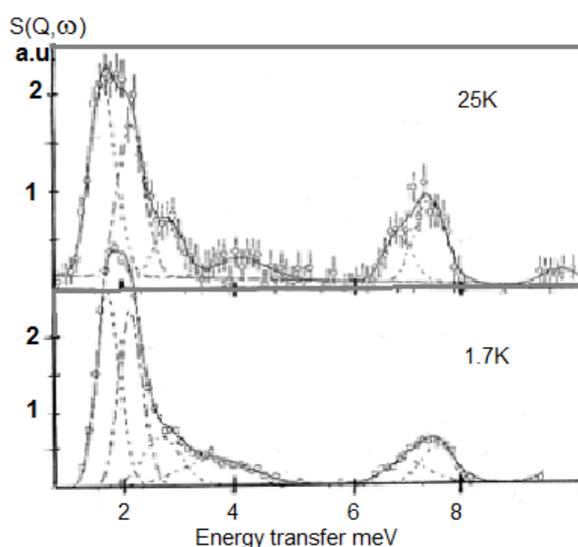


Figure 10 INS spectra showing transitions between different quantum rotation levels of Me2 in DBM (4F2 spectrometer at LLB) obtained respectively at $T = 1.7$ and 25 K.

So, an essential result is highly confirmed: to explain the INS results, it is necessary to use for the Me2 a hindering potential in which the main component has 6-fold symmetry. This justifies why it has been necessary to have a precise description of the crystal structure at 12 K (or below) and explains the “unusual” shape of the proton probability density found for Me2. It gives confidence in the calculus of the intermolecular interactions that indicate that Me2 remains a quasi-free rotor in the crystal.

Table 6- Comparison of the experimental transitions measured by INS and those calculated using the potential of equation {4}. The spectrometer used: 4F2 at LLB for DBMH, MARS at PSI for DBMD

		DBMH		DBMD	
origin	final	Experiment	Calculus	Experiment	Calculus
0_A	0_E	0.39	0.39	0.067	0.069
	1_E	2.3	2.23	Broad	0.89
	1_A	3.1	3.07	1 unto 2	1.00
	2_A	10?	11.3		8.8
	2_E	-	13.4		
0_E	1_E	1.9	1.84	Broad	0.83
	1_A	2.6	2.68	1 unto 2	0.93
	2_A	10	10.9		8.7
	2_E	-	13.0		9.3
1_E	1_A	?	0.84		0.11
	2_A	7.7?	9.02		7.9
	2_E	-	11.2		9.0
$A1$	2_A	7.2	8.2		7.8
	2_E	-	10.4		8.4

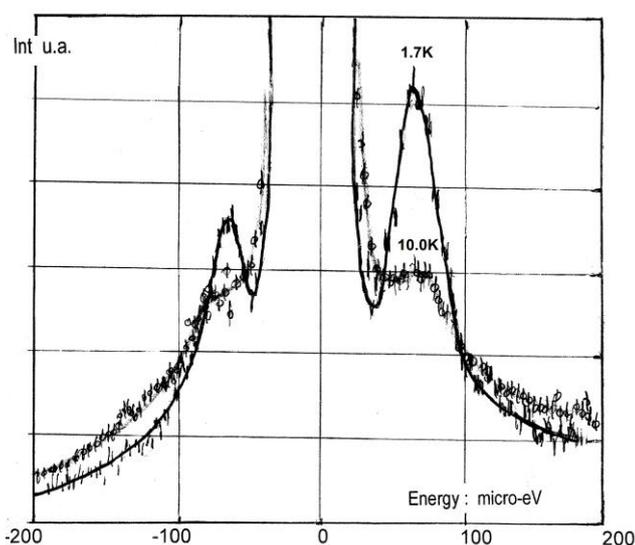


Figure 11 INS spectra at 1.7 and 10.0 K showing the tunneling of Me₂ deuterons in fully deuterated DBM.

9 – DMe deuterons tunneling and libration energy transitions observed by INS in DBMD crystal.

The perdeuterated DBMD has been synthesized by bromination of a commercial fully deuterated mesitylene, using Br₂ at 80 °C in a solution in pure acetic acid. The mass spectrum indicates that the final sample is deuterated at 99 %. A DSC experiment done with heating from -100 °C, at a speed of 5 K / minute, has found melting temperature at 59 °C and a phase change, phase II to phase I at 19 °C. These temperatures are the same as in DBMH at less than 1 °C. This result suggests that the crystal packing is the same for the pure isotopic DBMH and DBMD.

INS experiments were undertaken on DBMD to determine the behavior of -CD₃ in position Me₂ in view to compare it relative to that of -CH₃. The experiments were performed on the inverted time-of-flight backscattering spectrometer MARS, at SINQ PSI Villigen. The spectra were recorded using the 006 Bragg reflection of mica analyzers, with an energy resolution of 13 μeV. The energy range was either between -0.20 to +0.20 meV, or between 0.35 unto +0.35meV. Below 10 K, the spectra show a pair of excitations at ± 67(± 3) μeV. This value is very close to the calculated one (Tab.6), assuming the same potential as for HMe and taking the masse difference into account. These first results give also a strong argument in favor of the main component with 6-fold symmetry in the hindering potential of Me₂ in DBM crystals.

In table 6 are given the values of the transition energies between the quantum levels of a -CD₃ rotor using equation {5} and a constant $B_D = 0.327$ meV. It appears that several transitions between rotational levels 0, 1, and 2 are predicted in the range 0.9 – 1.0 meV.

We have explored the range 0.6 unto 1.3 meV with a resolution of 13 μeV, no narrow line has been detected but a continuous rise in intensity with the energy.

Using the potential of equation {7} it has been calculated the shape of the proton (PPD) or deuteron (DPD) probability density on a circle of 1.02 Å radius in HMe₂ and DMe₂. They are represented on **FIG.12**, It appears that there are six probability density peaks; they are of different heights because of the 3-fold component in V_h and in satisfactory agreement with the experimental observation of PPD in **Fig. 3**.

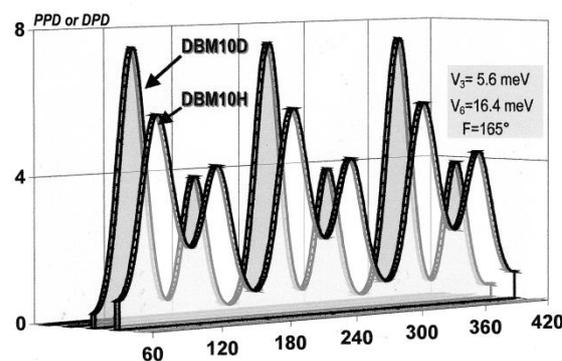


Figure 12 Proton or deuteron probability density calculated for Me₂ on a circle of 1.02 Å radius around the C-Cm bond: result for the ground level solving Schrödinger equation {1} and potential {7}.

Conclusions

Quantum mechanical DFT calculations using different functionals and basis sets have been done to establish the rotation hindering potentials of the methyl groups in dibromomesitylene. They have all found that in DBMH isolated molecules, the Me₂ symmetrically located between two Br is weakly hindered by a small 6-fold potential V_h while the two others which are located between two different substituents (Br and H) are highly hindered. Therefore, the respect of symmetry is more important than the influence of "bulky" atoms. The molecular packing in the crystal consists of piles of molecules, there are strong vdW and dipolar interactions between molecules arranged in antiferroelectric orientations in such piles. As each molecule has a quasi-hexagonal environment in a corrugated plane, it has smaller interactions with its neighbors in these planes. The study of the crystal environment of Me₂ explains that its influence on the Me rotation hindering potential is small: only hydrogen atoms are at distances smaller than 4.5 Å around Me₂, in consequence, their contribution to the vdW hindering potential is small. Earlier INS measurements have been re-examined, they all may be interpreted with the hypothesis of a Me₂ hindering potential of approximately 22 meV, of which 74% has a 6-fold symmetry, the remaining 26% having a 3-fold symmetry and being nearly in opposition of phase. The tunneling energy at 390 μeV does not vary significantly between 2 and 20 K; the activation energy for the broadening of the line width is about 2.6 meV and is explained by the deactivation of the excited rotation state with simultaneous spin changes.

It has been established that the deuterated DBMD has the same crystal structure as the DBMH, in consequence for the same

reasons; the intermolecular interactions on the deuterated Me2 group are also small. The tunneling of the CD₃ has been detected by INS and studied in the temperature range of 1.7 – 20 K. Tunneling energy has been measured at $67 \pm 2 \mu\text{eV}$. Such value corresponds to the same hindering potential that was established for Me2 in DBMH, taking into account the fact that the rotation constant B_D must be doubled going from –CH₃ to –CD₃. Now, to go further, it would be useful: i- to obtain a precise structure of DBMD by neutron diffraction and so to obtain the shape of the Me2 deuteron density probability and probably a confirmation of its spreading onto six maxima. ii- to obtain INS spectra in the range 1 unto 10 meV to detect the excited rotation states of the deuterated Me2 group.

Author Contributions

J. M.: Conceptualization, Supervision, Writing – original draft, Methodology; S. Z.: Conceptualization, Writing – original draft, Methodology, Software; M. S. M.: Writing – review & editing, Data curation; A. B.: Software, Validation; F. J.: Investigation, Validation; C. C.: Investigation; M.M.: Data curation; I.H.: Visualization; A. B.: Supervision. All authors contributed to the article and approved the submitted version.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The Authors acknowledge co-authors in previous works: A. Cousson, O. Hernandez, M. R. Johnson, M. Plazanet, H. P. Trommsdorff, F. Fernandez-Alonso, M. Prager and W. Prandl for discussions.

Notes and references

- W. Gordy and R. L. Cook, *Microwave Molecular Spectra* ed. John Wiley & Sons N.Y. 1984 3rd Edition.
- Von D. G. Lister, J. N. Macdonald, and N. L. Owen. *Internal Rotation and Inversion. An Introduction to Large Amplitude Motions in Molecules.* ed. Academic Press, London 1978.
- J. Murakami, M. Ito, and K. Kaya, The multiphoton ionization spectrum of toluene in a supersonic free jet: internal rotation of the methyl group, *Chem. Phys. Lett.*, 1981, **80**, 203.
- L.H. Spangler and D.W. Pratt, In: J.M. Hollas and D. Phillips (Eds.) *Jet Spectroscopy and Molecular Dynamics*, Chapman and Hall, London, 1994.
- M. Prager, and A. Heidemann, Rotational Tunneling and Neutron Spectroscopy: A Compilation, *Chem. Rev.* 1997, **97**, 8, 2933.
- O. Kirstein, M. Prager, and G. J. Schneider, Rotational dynamics and coupling of methyl group rotations in methyl fluoride studied by high resolution inelastic neutron scattering, *The Journal of Chemical Physics*, 2009, **130**, 214508.
- W. Press, *Single Particle Rotations in Molecular Crystals*, Springer-Verlag, Berlin, 1981.
- E. B. Wilson, C. C. Lin, and D. R. Lide, Calculation of Energy Levels for Internal Torsion and Over-All Rotation. I. CH₃BF₂ Type Molecules, *J. Chem. Phys.*, 1955, **23**, 136.
- H. D. Rudolph, H. Dreizler, and H. Seiler, Hinderungspotential der internen Rotation, Dipolmoment und Quadrupolkopplungs-konstanten aus dem Mikrowellenspektrum des 4-Methyl-Pyridins, *Z. Naturforsch.*, 1967, **22A**, 1738.
- S. Khazaei, and D. Sebastiani, Methyl rotor quantum states and the effect of chemical environment in organic crystals: γ -picoline and toluene, *J. Chem. Phys.*, 2016, **145** (23), 234506.
- H. D. Rudolph, H. Dreizler, A. Jaeschke, and P. Wendling, Mikrowellenspektrum, Hinderungspotential der internen Rotation und Dipolmoment des Toluols, *Z. Naturforsch.*, 1967, **22A**, 940.
- H. D. Rudolph, and A. Trinkaus, Mikrowellenspektrum, Hinderungspotential der internen Rotation und Dipolmoment des meta-Fluortoluols, *Z. Naturforsch.*, 1968, **23A**, 68.
- A. E. Dorigo, D. W. Pratt, and K. N. Houk, Origin of methyl conformational preferences and rotational barriers in the ground states, excited triplet states, radical cations, and radical anions of molecules having CH₃-C:X functionalities, *J. Am. Chem. Soc.* 1987, **109**, 6591.
- S. Yan, and L. H. Spangler, Ring mediated coupling of the internal motions of the amine and methyl groups in *p*-methylaniline, *J. Chem. Phys.*, 1992, **96**, 4106.
- K. P. R. Nair, M. K. Jahn, A. Lesarri, V. V. Ilyushinc and J.-U. Grabow, Six-fold-symmetry internal rotation in toluenes: the low barrier challenge of 2,6- and 3,5-difluorotoluene, *Phys. Chem. Chem. Phys.*, 2015, **17**, 26463.
- A. Del Rio, A. Boucekine, and J. Meinnel, Reassessment of methyl rotation barriers and conformations by correlated quantum chemistry methods, *J. Comput. Chem.*, 2003, **24**, 2093.
- D. B. Moss, C. S. Parmenter, and G. E. Ewing, On the contributions of van der Waals interactions to vibrational level mixing. Torsion–vibration coupling in *p*-fluorotoluene, *J. Chem. Phys.*, 1987, **86**, 51.
- R. Caciuffo, O. Francescangeli, S. Melone, M. Prager, F. Ugozzoli, G. Andretti, G. Amoretti, G. Coddens, and H. Blank, An almost free methyl quantum rotor in *p*-tert-butylcalix [4] arene(1:1)toluene, *Physica B*, 1992, **180 & 181**, 691.
- M. Prager, R. Caciuffo, G. Amoretti, C.J. Carlile, G. Coddens, F. Fillaux, O. Francescangeli, and F. Ugozzoli, Molecular tunnelling in *p*-tert-butylcalix [4] arene (2:1) *p*-xylene, *Molecular Physics*, 1994, **81**, 609.
- R. Caciuffo, G. Amoretti, C. J. Carlile, F. Fillaux, O. Francescangeli, M. Prager, and F. Ugozzoli, Methyl group tunnelling studies in calixarenes, *Physica B*, 1994, **202**, 279.
- B. Alefeld, A. Kollmar, and B. A. Dasannacharya, The one-dimensional CH₃-quantumrotator in solid 4-methyl-pyridine studied by inelastic neutron scattering, *J. Chem. Phys.*, 1975, **63**, 4415.
- N. Le Calvé, D. Cavagnat, and F. Fillaux, Neutron inelastic scattering of the methyl torsional mode in hydrogenated and deuterated 4-methylpyridine crystals at 5 K, *Chem. Phys. Letters*, 1988, **146**, 549.
- J. Meinnel, B. Hennion, M. Mani, B. Wyncke, and C. J. Carlile, Methyl tunnelling in dibromomesitylene, *Physica B*, 1995, **213 & 214**, 649.
- D. Cavagnat, A. Magerl, C. Vettier, and S. Clough, Methyl tunnelling in α -crystallised toluene by inelastic neutron scattering: temperature and pressure effects, *J. Phys. C*, 1986, **19**, 6665.

- 25 F. Boudjada, J. Meinnel, A. Cousson, W. Paulus, M. Mani, and M. Sanquer, Tribromomesitylenestructure at 14 K. Methyl conformation and tunneling, *Neutrons and Num. Methods A.I.P. Conf. Proc.*, 1999, **479**, 217.
- 26 J. Meinnel, M. Mani, A. Cousson, F. Boudjada, W. Paulus, and M. Johnson, Structure of trihalogenomesitylenes and tunneling of the methyl groups protons: II. Protonated tribromomesitylene, *Chem. Phys.*, 2000, **261**, 165.
- 27 J. Meinnel, A. Cousson, F. Boudjada, M. Plazanet, and M. Mani, Delocalization of Methyl Groups Protons or Deuterons in Molecular Compounds, *J. Low Temp. Phys.*, 2001, **122**, 257.
- 28 A. Boudjada, J. Meinnel, A. Boucekkine, O. Hernandez and M-T. Fernandez-Diaz, Molecular conformation and methyl proton delocalization in triiodomesitylene: A combined density functional theory and single-crystal neutron diffraction study, *J. Chem. Phys.*, 2002, **117**, 10173.
- 29 J. Meinnel, A. Boudjada, A. Boucekkine, F. Boudjada, A. Moréac, and S. Parker, Vibrational Spectra of Triiodomesitylene: Combination of DFT Calculations and Experimental Studies. Effects of the Environment, *J. Phys. Chem. A*, 2008, **112**, 11124.
- 30 O. Hernandez, A. Cousson, M. Plazanet, M. Nierlich, and J. Meinnel, The low-temperature phase of 1,3-di-bromo-2,4,6-tri-methyl-benzene: a single-crystal neutron diffraction study at 120 and 14 K, *Acta Cryst. C*, 2003, **59**, o445.
- 31 S. Zeroual, J. Meinnel, C. Lapinski, S. Parker, A. Boudjada, and A. Boucekkine, Vibrational spectroscopy and DFT calculations of 1,3-dibromo-2,4,6-trimethylbenzene: Anharmonicity, coupling and methyl group tunneling, *Vibrational Spectroscopy*, 2013, **67**, 27.
- 32 M. Plazanet, M.R. Johnson, A. Cousson, J. Meinnel, and H.P. Trommsdorff, Molecular deformations of halogenomesitylenes in the crystal: structure, methyl group rotational tunneling, and numerical modeling, *Chem. Phys.*, 2002, **285**, 299.
- 33 C. M. Reddy, M. T. Kirchner, R. C. Gundakaram, K. A. Padmanabhan, and G. R. Desiraju, Isostructurality, Polymorphism and Mechanical Properties of Some Hexahalogenated Benzenes: The Nature of Halogen...Halogen Interactions, *Chem. Eur. J.*, 2006, **12**, 2222.
- 34 R. Qi, Q. Wang, and P. Ren, General van der Waals potential for common organic molecules, *Bioorganic & Medicinal Chemistry*, 2016, **24**, 4911.
- 35 D. E. Williams, Nonbonded Potential Parameters Derived from Crystalline Hydrocarbons, *J. Chem. Phys.*, 1967, **47**, 4680.
- 36 A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press N.Y., 1973.
- 37 A. J. Pertsin, and A. I. Kitaigorodsky, *The Atom-Atom Potential Method*, Springer-Verlag, Berlin, 1987.
- 38 A. Gavezzotti, and G. R. Desiraju, A systematic analysis of packing energies and other packing parameters for fused-ring aromatic hydrocarbons, *Acta Cryst. B*, 1988, **44**, 427.
- 39 A. Gavezzotti, The calculation of molecular volumes and the use of volume analysis in the investigation of structured media and of solid-state organic reactivity, *J. Am. Chem. Soc.*, 1983, **105**, 5220.
- 40 A. Bondi, *J. Physical Chem.* 68 (1964) 441-451. A. Bondi, *Physical Properties of Molecular Crystals, Liquids, and Glasses*. John Wiley and Sons, N. Y., 1968.
- 41 A. Gavezzotti, *Molecular Aggregation*, Oxford University Press, 2006.