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A Constrained Refinement of the Structure of Durene Including 'Wagging' Vibrations of the Methyl Groups

BY JEAN-LOUIS BAUDOUR AND MARC SANQUER
Département de Physique Cristalline et Chimie Structurale, E.R.A. au CNRS no. 015,
Université de Rennes, avenue du Général Leclerc, 35031 *Rennes Cedex, France*

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It has been possible to improve a previous constrained refinement of durene based on a procedure relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters. The improvement results from two factors. First, the use of a temperature-factor expression which is better adapted to great librational amplitudes, gave a weighted R of 0·095 instead of 0·115 in the previous analysis, without using additional parameters. Secondly, the inclusion of wagging vibrations reduced the weighted R to 0·086. For a methyl group and the corresponding ring atom, wagging is described as a libration about an axis lying in the ring plane and perpendicular to the single bond. A displacement of the wagging centre on the single bond strongly modifies the values of some external and internal libration tensors, even though the R value is almost insensitive to this displacement. A reasonable mechanistic model has been chosen on the basis of the best agreement between spectroscopic frequencies and frequencies calculated from libration tensors. The wagging centre is a distance of 0·69 Å from the carbon atom of the ring. The average wagging tensor is $55{\cdot}7(°)^2$. The unusual result that the Raman frequency of libration around the OY axis (103 cm^{-1}) is considerably higher than that around the OX axis (72 cm^{-1}), even though the moment of inertia around OY is twice that around OX, is very well confirmed in a refinement including wagging, the calculated frequencies from librational tensor being respectively 130 and 50 cm^{-1}.

Introduction

Recently, Prince & Finger (1973) have described a procedure applicable to centrosymmetric rigid molecules for refining directly the usual rigid-body parameters L_{ij} and T_{ij}, and the librational tensor θ of side groups free to librate around a single bond. This treatment, which generalizes Johnson's (1970*a*,*b*) procedure for relating the second and third cumulant coefficients in the structure-factor formula to the molecular motion parameters, has been applied to a refinement of the structure of durene from neutron diffraction data (Prince, Schroeder & Rush, 1973). The test using the R-factor ratio (Hamilton, 1965) shows that a conventional unconstrained refinement gives a significantly better fit to the data than does the constrained one. On the other hand, the usual unrestrained model gives some positional and thermal parameters which are physically unreasonable. Those obtained in the restrained model have more physical significance. However, Prince *et al.*, when they compare librational and torsional frequencies of durene derived from their rigid-body motion analysis with spectroscopic frequencies, find a particularly serious discrepancy (Table 4) for the librational frequency around the *OY* axis (Fig. 4). As suggested by Prince *et al.* the contribution of wagging vibrations of the methyl groups, neglected in their treatment, could explain in part this lack of agreement. Therefore we have tried the program *ANHAR* (Baudour, 1972, available on request) slightly modified (version *WAG*) in order to allow for the effects of wagging in durene.

The wagging vibrations

We have to specify what we mean by 'wagging' vibrations in the following. In spectroscopy the wagging motion is an out-of-plane motion defined by the respective phases of the atomic displacements. For example, in durene, the wagging modes are the particular modes given in Fig. 1(*a*) and (*b*). Fig. 1(*c*) and (*d*) shows the relative atomic displacements in the twisting modes.

From diffraction data it is possible to obtain only the r.m.s. amplitudes. It is impossible to separate the contributions of the different modes *a,b,c,d* to the vibrational tensor. Therefore what we call wagging vibrations include statistically all out-of-plane vibrations affecting a side group and the ring atom to which it is attached. These vibrations are approximately described as librations around an axis lying in the ring plane between the ring and the side group and perpendicular to the single bond.

There are no complete spectroscopic experimental data concerning the low-frequency internal modes because the intensities of librational and wagging motions of methyl groups are expected to be low, both in Raman and infrared spectra. The complete analysis of Kovner (1956) has only a theoretical basis.

Recent treatments

A number of analyses have been performed for the temperature factor of an atom, a group or a rigid molecule undergoing librations of large amplitude. Examination of the most recent treatments reveals the difficulties encountered in correctly taking into account all principal external and internal vibrations when a molecule has strongly vibrating side groups.

Considering the torsional oscillations about an axis, with no other modes of motion, the procedure of Chidambaram & Brown (1973) assuming a Gaussian distribution for the angular displacements from the mean position is extremely accurate. In this case, the contribution to the structure factor is given by a Bessel function series expansion which can include up to 15 terms (Brown & Chidambaram, 1973). However, the additional intramolecular motions are treated in a conventional way with the inclusion of an individual atomic temperature factor,

$$T_i=\exp|-2\pi^2\tilde{s}\mathbf{U}s|,$$

where s is the column matrix of components of the reflexion vector referred to a Cartesian system, $\tilde{s}$ the transpose of s and $\mathbf{U}$ a 3×3 symmetric tensor with the usual sense (Cruickshank, 1956*a*). We think that the interpretation of these individual **U** tensors in terms of segmented-body motions such as wagging vibrations, has less significance than the inclusion of a collective wagging tensor in the structure-factor formula. Besides in order to take into account rigid-body motion of the molecular core, Chidambaram & Brown introduce an additional atomic temperature factor of the usual form

$$T_R=\exp|-\tilde{h}\beta^R h|$$

(the symbols having their usual sense) for which the parameters β^R_{ij} are available from a previous rigid-body or segmented-body analysis (Cruickshank, 1956; Schomaker & Trueblood, 1968; Johnson, 1970*a*; Johnson, 1970*b*). But the case of durene (Prince, Schroeder & Rush, 1973) shows that a conventional refinement can give physically unreasonable thermal parameters: for example, a number of the hydrogen atoms have components of the longest axes of their thermal ellipsoids parallel to the C–H bond. It is probable that in such a case, the rigid-body parameters determined from a conventional refinement will be appreciably in error.

In the constrained refinement performed by Prince & Finger (1973), the entire molecule is permitted to translate and librate and, in addition, each side group can oscillate around its single bond. This procedure is very likely to give physically reasonable thermal parameters, provided that no important internal mode is neglected. But it is possible that wagging vibrations of the side groups, neglected in this analysis, are in fact not negligible. Besides, we think that their structure factor formula based on a series expansion to the third cumulant is not always a sufficient approximation for high-order reflexions in the case of large amplitudes of libration (Baudour, 1972).

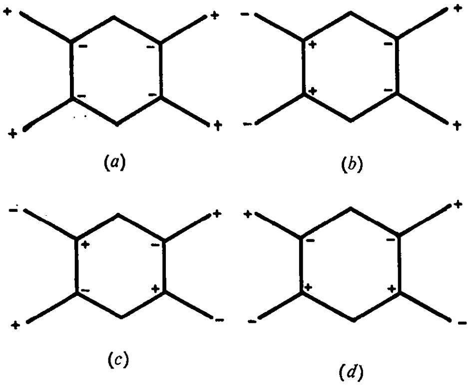

(*a*) (*b*)
(*c*) (*d*)

Fig. 1. Wagging modes (*a*), (*b*) and twisting modes (*c*), (*d*) in the durene molecule. The atomic displacements are out-of-plane.

Mathematical analysis

The temperature factor we use is given by the expression derived by Kay & Behrendt (1963). This formula has in fact been established for a two-dimensional librational motion, making the assumption that the probability distribution function of positions is Gaussian. Its generalization to the three-dimensional case is immediate. It has been shown (Baudour, 1972) that in the case of great amplitudes of libration, this expression is a good approximation, even for high-order reflexions. The contribution of an atom to the structure factor is given by:

$$F(\mathbf{h})=f(\mathbf{h})\exp|2i\pi\tilde{h}x|T \qquad (1)$$

where $f(\mathbf{h})$ is the scattering factor, $\mathbf{x}$ the vector from the unit-cell origin to the equilibrium position of the atom; x is the column matrix of components of vector $\mathbf{x}$ referred to the base vectors $\mathbf{a}_i$ of the unit cell, $\tilde{h}$ is the row matrix of components of the reflexion vector $\mathbf{h}$ referred to the reciprocal vectors $\mathbf{a}^i$, such that $\mathbf{a}_i\mathbf{a}^j=\delta_{ij}$ (δ_{ij} is the Kronecker delta), T is the temperature factor. For an atom A of a rigid core (Fig. 2) it may be written (Baudour, 1972):

$$T=T_T T_L \qquad (2)$$

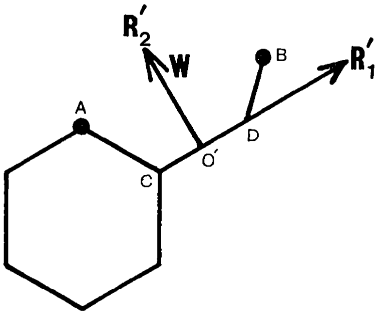


Fig. 2. The atom A is on the molecular core. The atom B is on a side group which librates about CD. Wagging about the axis $O'W$ affects B, D and C.

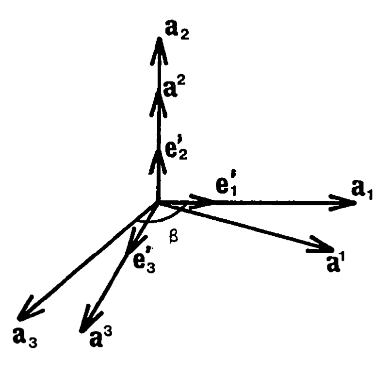


Fig. 3. In the monoclinic system the direct axes are a_1, a_2 (unique axis), a_3. The reciprocal axes are a^1,a^2,a^3; e'_1,e'_2,e'_3 define a Cartesian system.

where the first term resulting from translation is given by

$$T_T=\exp|-2\pi^2(H_1^2T_{11}+H_2^2T_{22}+H_3^2T_{33}+2H_1H_2T_{12}+2H_1H_3T_{13}+2H_2H_3T_{23})| \qquad (3)$$

and the second term resulting from libration is written:

$$\begin{aligned}T_L=&|1+4\pi^2\Omega_2^2(H_1R_1+H_3R_3)^2|^{-1/4}\times\ldots\times\ldots\\&\times\exp\left|-\frac{2\pi^2\Omega_2(H_1R_3-H_3R_1)^2}{1+4\pi^2\Omega_2^2(H_1R_1+H_3R_3)^2}\right|\times\ldots\times\ldots\\&\times\exp\left|-i\left\{\tfrac{1}{2}\tan^{-1}(2\pi\Omega_2|H_1R_1+H_3R_3|)\right.\right.\\&\left.\left.-\frac{4\pi^3\Omega_2^2(H_1R_3-H_3R_1)^2(H_1R_1+H_3R_3)}{1+4\pi^2\Omega_2^2(H_1R_1+H_3R_3)^2}\right\}\right|\\&\times\ldots\times\ldots.\end{aligned} \qquad (4)$$

The symbols × ... represent the terms derived from the first by a cyclic permutation of the subscripts. In these expressions all the components H_i for the reciprocal vector, R_i for the atomic coordinates, T_{ij} for the molecular translational tensor and Ω_i for the rigid-body librational tensor, are expressed in a cartesian coordinate system chosen in such a way that the tensor Ω is diagonal; the axes are generally the axes of inertia of the molecule. The origin O is on the centre of libration fixed by symmetry, which is also the centre of inertia of the molecule.

T_L is obtained by multiplying three terms, each corresponding to a libration around a principal axis. We are assuming that these three librations are uncorrelated.

Now for an atom B of a librating side group (Fig. 2) we can consider three types of vibrations about three perpendicular but not necessarily intersecting axes: a libration about the single bond CD, a wagging vibration about $O'W$ and an in-plane libration about an axis through C. For such an atom B, it is necessary to include in the temperature factor an additional term T'_L taking these internal librations into account. T'_L is exactly of the same form as T_L [equation (4)] but the components H'_i, R'_i, Ω'_i must be defined in an appropriate way. H'_i and R'_i are first expressed in a new Cartesian coordinate system localized on the side group. The directions of the axes are defined as mentioned above. The choice of the origin O' which is also the centre of wagging, must be based on physical arguments as we shall see. If in-plane librations about C are taken into account, the component R'_1 must be changed into R'_1+CO' (Fig. 2), but uniquely for this particular mode.

Finally for a side group atom or a core atom affected by wagging librations, the temperature factor is given by:

$$T=T_T T_L T'_L\,. \qquad (5)$$

In this procedure all librations are considered as uncorrelated.

Structure-factor calculation and least-squares refinement

For convenience, the product $\tilde{h}x$ in formula (1) is first replaced by the equal product $\tilde{h}'x'$, where the components of the row matrix $\tilde{h}'$ and the column matrix x' are referred to the same Cartesian system $\mathbf{e}_i'$. For example, in the monoclinic system (considered here for the application to durene) $\mathbf{e}_1'||\mathbf{a}_1$, $\mathbf{e}_2'||\mathbf{a}_2$ (unique axis), $\mathbf{e}_3'=\mathbf{e}_1'\wedge\mathbf{e}_2'$ (Fig. 3).

The equilibrium position of the atom in the unit cell is given by:

$$\mathbf{x}=x^1\mathbf{a}_1+x^2\mathbf{a}_2+x^3\mathbf{a}_3$$

where the x^i are the contravariant components of $\mathbf{x}$. We obtain

$$\begin{aligned}x^{1\prime}&=x^1|\mathbf{a}_1|+x^3|\mathbf{a}_3|\cos\beta\\x^{2\prime}&=x^2|\mathbf{a}_2|\\x^{3\prime}&=x^3|\mathbf{a}_3|\sin\beta\,.\end{aligned}$$

The reflexion vector is expressed as

$$\mathbf{h}=h_1\mathbf{a}^1+h_2\mathbf{a}^2+h_3\mathbf{a}^3$$

where the h_i are the covariant components of $\mathbf{h}$. Using the relation $\mathbf{a}_i\mathbf{a}^j=\delta_{ij}$, we obtain

$$\begin{aligned}h_1'&=h_1|\mathbf{a}^1|\sin\beta=h_1/|\mathbf{a}_1|\\h_2'&=h_2|\mathbf{a}^2|=h_2/|\mathbf{a}_2|\\h_3'&=-h_1|\mathbf{a}^1|\cos\beta+h_3|\mathbf{a}^3|\\&=-h_1\cos\beta/|\mathbf{a}_1|\sin\beta+h_3/|\mathbf{a}_3|\sin\beta\,.\end{aligned}$$

Then $\tilde{h}'x'$ is transformed into $\tilde{H}X$, the components H_i and X^i being referred to a new Cartesian system $\mathbf{e}_i$ attached to the molecular core and corresponding to the axes of inertia. Covariant and contravariant components being identical in a Cartesian system, the same orthogonal matrix A is used for the two transformations:

$$\begin{aligned}H&=Ah'\\X&=A(x'-O')\,,\end{aligned}$$

O' defining the librational centre in the system $\mathbf{e}_i'$. The components H_i and X_i (with $R_i=X_i$) are used in equation (4) in order to calculate T_L, the temperature factor resulting from the librations of the molecular core.

In the same way, for each librating side group k, we define a Cartesian coordinate system. The origin is the aforementioned centre of wagging and the axes the principal axes of libration for the proper internal motions of the side group and the core atom to which it is attached. A suitable orthogonal matrix A_k is used for the transformations:

$$\begin{aligned}H'&=A_kh'\\X'&=A_k(x'-O_k')\,,\end{aligned}$$

O_k' defining the centre of wagging of the side group in the system $\mathbf{e}_i'$. The components H_i' and X_i' are used in equation (4) in order to calculate T_L', the temperature factor resulting from the internal librations of the side group.

For a structure-factor least-squares refinement, the derivatives of $F(\mathbf{h})$ with respect to $R_i, T_{ij}, \Omega_i, \Omega_i'$ are needed. They are readily deduced from equations (1) to (5). The only approximation made in our calculation of derivatives is:

$$|1+4\pi^2\Omega_i^2(H_jR_j+H_kR_k)^2|^{1/4}=1\,.$$

Application to durene

Constrained refinement without including wagging vibrations

The neutron diffraction data published by Prince, Schroeder & Rush (1973) (PSR) have been used. The refinement has been performed with their non-unique data set of 832 reflexions with significant intensity. The function used for minimization was $\sum w(F_{\rm obs}-F_{\rm calc})^2$. Weights w were taken from PSR. As in their treatment, a correction was applied to account for the effects of isotropic extinction; the formula used was

$$F_c^*=kF_c(1+2r^*|F_c|^2/\sin 2\theta)^{-1/4}$$

where F_c^* is the corrected structure factor and k the scale factor. The value of r^* was included as an adjustable parameter. Its final value was $1{\cdot}3\times10^{-2}$ for all refinements. The neutron scattering lengths of C and H were taken from *International Tables for X-ray Crystallography* (1962). The librations of the rigid core were fixed around the three principal axes of inertia of the molecule and the torsional motion of the methyl groups around the C–C axes. The number of adjustable parameters was 49, of which 36 corresponded to atomic coordinates, and the remainder to the extinction parameter, the scale factor, 6 T_{ij}, and the following components of librational tensors: Ω_X^C, Ω_Y^C, Ω_Z^C for the rigid core, Ω_X^{M1}, Ω_X^{M2} for the methyl groups (Fig. 4). The initial parameters were those of PSR. All parameters were allowed to vary for four cycles. They quickly converged to stable values. The final discrepancy index R was 0·064 ($R=\sum||F_o|-|F_c||/\sum|F_o|$). The final weighted R was $R_w=0{\cdot}095$ ($R_w=|\sum w(F_o-F_c)^2/\sum wF_o^2|^{1/2}$) which improves significantly the value $R_w=0{\cdot}115$ obtained by PSR, with the same number of variable parameters. The final atomic coordinates are given in Table 1. Bond distances and angles are shown in Fig. 5. The rigid-body thermal parameters are similar to those found by PSR, but the librations of the methyl groups around the C–C bonds are significantly smaller in our analysis (Table 2).

Constrained refinement including wagging vibrations

A constrained refinement was then performed including wagging vibrations of the methyl groups. For each group an axis of wagging $OY_{\rm M}$ (Fig. 4) has been defined lying in the ring plane between the methyl group and the carbon atom of the core. Indeed wagging motion can affect not only the methyl group but also the carbon atom of the core to which it is attached, one going up while the other is going down. In addition the atom H(4) was permitted to librate around the axes $OX_{H(4)}$, $OZ_{H(4)}$ which increased the number of additional parameters to refine by four. Several refinements were performed, all 53 parameters being allowed to vary but in each refinement with the centre of wagging held fixed. It was first observed that the R index was almost insensitive to the position of the centre of wagging on the C–C bond, R_w varying from 0·086 to 0·088. On the other hand, some thermal parameters were very sensitive to this position. Table 2 gives as an example the thermal parameters obtained when the centres of wagging were fixed respectively on C(2) and C(4) for the two methyl groups. The negative value $\Omega_Y^C = -13(°)^2$ has no physical significance, although $R_w = 0{\cdot}088$. Since the R value was not an adequate test, the positions of the centres of wagging were varied on the basis of physical arguments, *i.e.* a reasonable agreement between spectroscopic frequencies and frequencies calculated from librational tensors. This was realized by a choice of O' and O'' such that $O'\text{–C(2)}/\text{C(1)–C(2)} = O''\text{–C(4)}/\text{C(4)–C(5)} = 0{\cdot}45$. The final values of R and R_w were respectively 0·061 and 0·086. Structure factors are given in Table 3. In the conventional unconstrained refinement performed

Table 1. *Positional parameters for the constrained refinements of durene*

The upper number refers to the constrained refinement without wagging, the lower one to the constrained refinement including wagging vibrations. Values have been multiplied by 10^5. Standard deviations are given in parenthesis.

	x	y	z
C(1)	19050 (12)	32187 (24)	26628 (26)
	19110 (12)	32194 (24)	26839 (26)
C(2)	9212 (8)	15635 (17)	12728 (17)
	9197 (8)	15560 (17)	12713 (17)
C(3)	3818 (8)	−1132 (17)	21050 (15)
	3816 (8)	−1131 (17)	21074 (15)
C(4)	−5322 (8)	−16786 (17)	8946 (17)
	−5274 (8)	−16705 (17)	8966 (17)
C(5)	−10689 (13)	−34403 (25)	19210 (26)
	−10695 (13)	−34468 (25)	19222 (26)
H(1)	27647 (32)	31131 (57)	23259 (70)
	27883 (33)	31080 (58)	23631 (72)
H(2)	16408 (30)	50235 (55)	24232 (69)
	16423 (31)	50356 (58)	24603 (72)
H(3)	20887 (49)	28574 (81)	43317 (55)
	21052 (50)	28378 (83)	43445 (56)
H(4)	7082 (22)	−1939 (44)	38349 (35)
	7083 (23)	−2008 (46)	38361 (36)
H(5)	−20917 (29)	−32227 (54)	14682 (65)
	−21020 (30)	−32360 (56)	14586 (67)
H(6)	−9021 (29)	−52302 (56)	15468 (74)
	−9019 (30)	−52437 (58)	15423 (76)
H(7)	−6470 (44)	−33079 (74)	35961 (56)
	−6577 (44)	−33159 (74)	35841 (56)

Table 2. *Thermal parameters determined from constrained refinements*

The system designated 'crystal axes' is an orthonormal coordinate system with x parallel to the a axis, y parallel to the b axis and z parallel to $a \times b$. The system designated 'molecular axes' corresponds to the axes of inertia. The axes for external librations (axes of inertia) and those for internal librations are shown in Fig. 4. The methyl group designated M_1 includes C(1). The methyl group designated M_2 includes C(5).

I – Refers to the analysis of Prince, Schroeder & Rush (1973). Translational tensor is referred to crystal axes.
II – Refers to our constrained refinement without including wagging.
III – Constrained refinement including wagging with the centres of wagging on C(2) and C(4).
IV – Constrained refinement including wagging with the centres of wagging at a distance of 0·69 Å from C(2) and C(4).

	I	II	III	IV
Parameter	Crystal axes	Molecular axes	Molecular axes	Molecular axes
Translations (Å)^2				
T_{11}	0·044 (1)	0·0515 (4)	0·0498 (4)	0·0497 (4)
T_{22}	0·049 (1)	0·0568 (4)	0·0574 (4)	0·0577 (4)
T_{33}	0·064 (1)	0·0308 (4)	0·0476 (8)	0·0283 (5)
T_{12}	0·010 (1)	−0·0004 (2)	−0·0016 (2)	−0·0017 (2)
T_{13}	−0·003 (1)	0·0007 (2)	0·0008 (2)	0·0009 (2)
T_{23}	−0·001 (1)	0·0007 (2)	−0·0004 (2)	−0·0005 (2)
External librations (°)^2				
Ω_X^C	37·7	37·7 (0·7)	7·6 (1·5)	38·6 (1·0)
Ω_Y^C	11·1	9·7 (0·3)	−13·1 (1·0)	2·8 (0·4)
Ω_Z^C	27·8	26·5 (0·3)	25·4 (0·3)	24·7 (0·3)
Internal librations (°)^2				
Methyl librations around the C–C axis				
$\Omega_X^{M_1}$	504	414·9 (6·6)	449·0 (7·0)	418·3 (7·0)
$\Omega_X^{M_2}$	435	368·2 (6·2)	405·9 (6·7)	387·6 (6·7)
Wagging vibrations				
$\Omega_Y^{M_1}$			64·3 (2·7)	61·9 (2·5)
$\Omega_Y^{M_2}$			62·4 (2·7)	49·5 (2·5)
Hydrogen H(4)				
$\Omega_X^{H(4)}$			114·5 (7·3)	9·4 (6·0)
$\Omega_Z^{H(4)}$			24·1 (4·8)	30·4 (5·0)
R_w	0·115	0·095	0·088	0·086

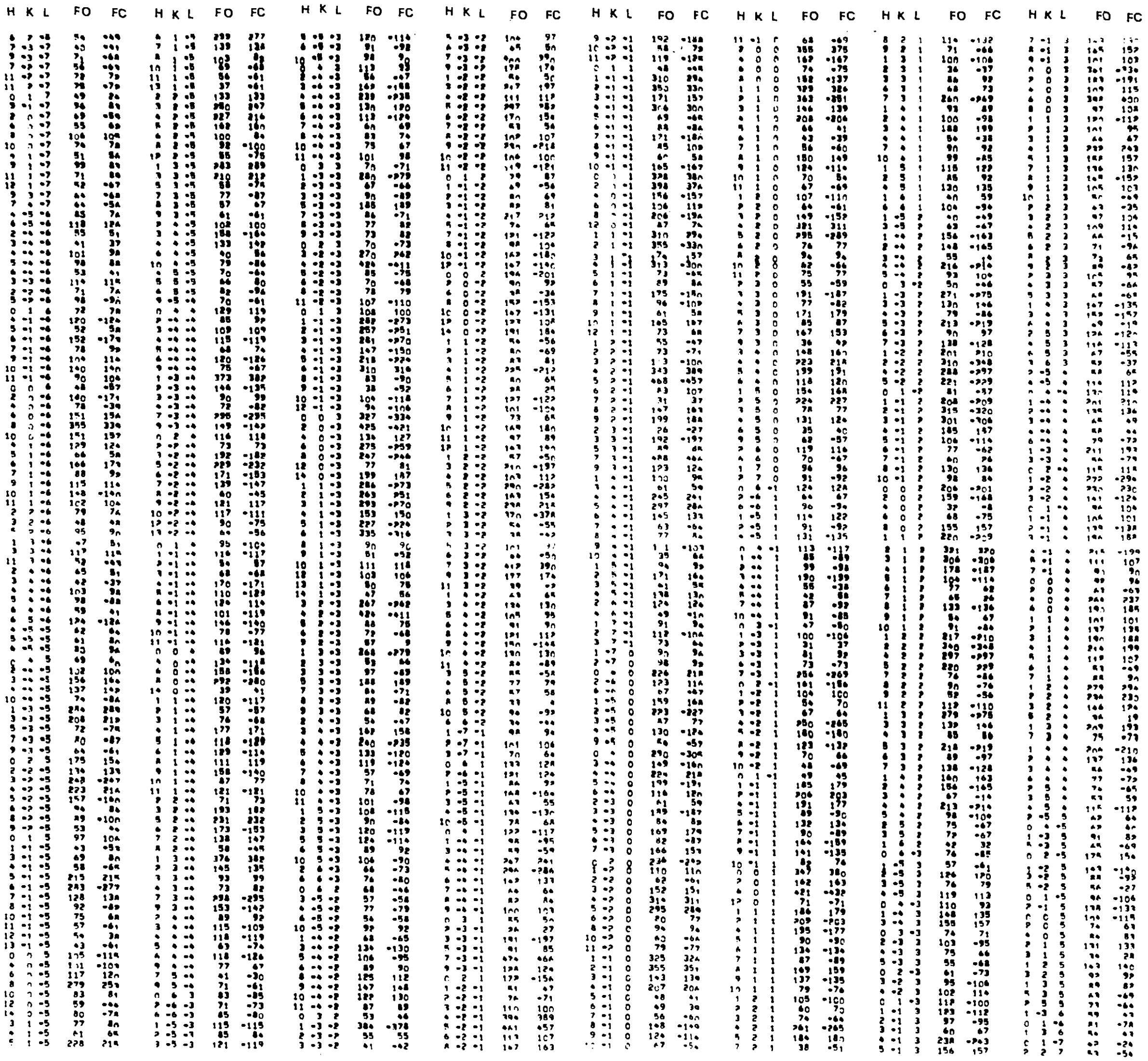
by PSR the final weighted R_w was 0·085. The observed R-index ratio (Hamilton, 1965) is 1·012. For 485 independent reflexions, 110 parameters in the unconstrained model and 53 in our constrained model, the 0·5 probability point is 1·06. Therefore Hamilton's test is very unfavourable to the usual unconstrained model.

Now we have to weigh the significance of the improved fit when wagging is included. The R-index ratio is 1·10. The dimension of the hypothesis is 4 (2 for wagging and 2 for the internal librations of H(4) which have much less influence on R_w than wagging). The ratio required for significance at the 0·005 level is 1·018. The model including wagging therefore gives a significantly better fit to the data. But we must stress that these considerations prove only that the model without wagging is insufficient. Since several models giving approximately the same R_w by displacement of the centre of wagging can be chosen, the choice must be based on physical arguments.

The in-plane librations of the methyl groups about the ring atoms to which they are attached are expected to have small amplitudes because of the high values of the moment of inertia and the frequency involved in this motion. Indeed the inclusion in the refinement of the corresponding librational tensors found equal to about $17(°)^2$ improves the R_w value very slightly by 0·0009. The R value ratio is only 1·010: it is however significant at a level of less than 0·025. But as stressed by Hamilton (1965) the test on the R value ratio is valuable when there are no systematic errors either in the data or in the use of an incorrect model for the calculated structure factors. In addition these internal

Table 3. *Observed and calculated structure factors for the constrained refinement of durene including wagging*

Columns are h, k, l, $100F_{\text{obs}}$, $100F_{\text{calc}}$.



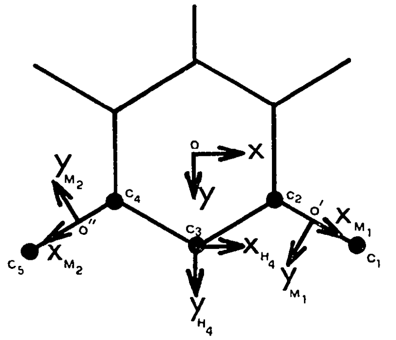


Fig. 4. Definition of the different systems. $OX, OY, OZ = OX \wedge OY$ are the molecular axes. Torsional oscillations are about $O'X_{M1}$ and $O''X_{M2}$. Wagging vibrations are about $O'Y_{M1}$ and $O''Y_{M2}$. For H(4) librations are considered about C(3)-$X_{H(4)}$ and C(3)-$Z_{H(4)}$.

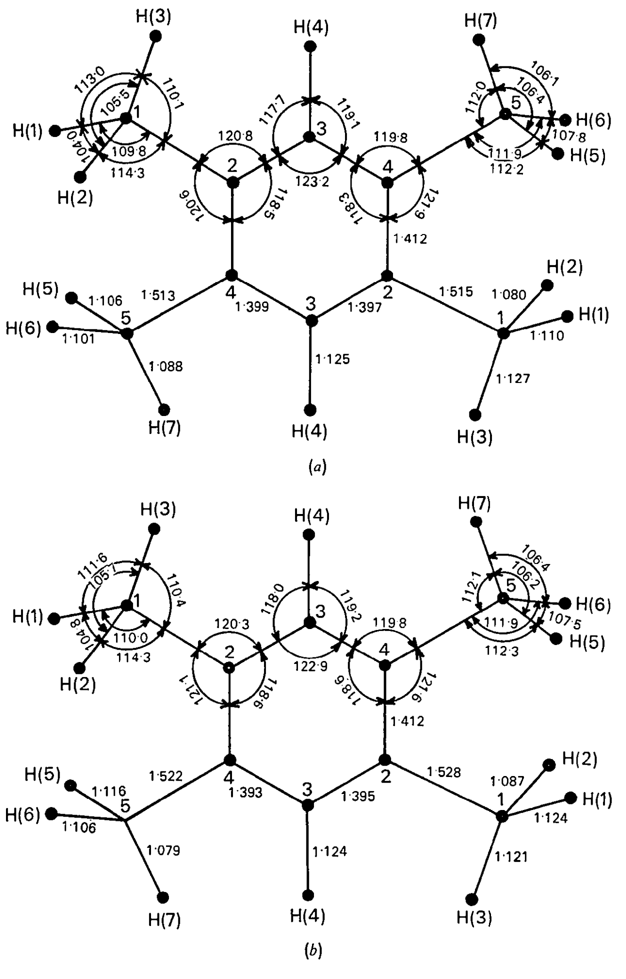


Fig. 5. Bond distances and angles in the durene molecule (*a*) refinement without wagging, (*b*) refinement including wagging. Mean standard deviations: C–C 0·002 Å, C–H 0·005 Å, C–C–C 0·1°, C–C–H 0·2°, H–C–H 0·4°.

librations interact strongly in the refinement with the core librations about the normal to the ring. In these conditions it is prudent not to attach much physical significance to this result.

Discussion

Molecular geometry

The bond lengths and angles are shown in Fig. 5. In the analysis including wagging, the average C–C distance from the ring to the methyl groups is 1·525 Å. The shorter values 1·514 Å found in our refinement without wagging and 1·51 Å found by Prince *et al.*, are due, as they supposed, to neglect of the wagging motions of the methyl groups. There is a range of 0·045 Å in the C–H bond lengths, smaller than that of 0·075 Å found by PSR. The average length 1·108 Å is very close to the mean separation 1·107 Å ($\sigma = 0{\cdot}001$ Å) reported by Bartell, Kuchitsu & De Neui (1961) from an electron-diffraction study of gaseous methane.

Molecular librations

The librational tensors when wagging motions are taken into account are given in Table 2. The frequencies calculated from the thermal motion parameters derived from our constrained refinement are compared with the frequencies measured by spectroscopy (Table 4). The frequencies are calculated using Cruickshank's (1956*b*) formula:

$$\theta^2 = (h/8\pi^2 I\nu) \coth (h\nu/2kT)$$

where I is the moment of inertia involved in the libration, ν the frequency and θ^2 the mean-square amplitude in rad^2. For the torsional motion of the methyl groups and the wagging motion, we use the averages of θ^2, respectively 402·9 and 55·7(°)^2. The position of the wagging centre chosen in order to obtain the best frequency agreement is a distance of 0·69 Å from the carbon atom of the ring. The agreement is quite reasonable except for the core libration Ω_X^C which is too large and, probably as a consequence of this, the libration of H(4) $\Omega_X^{H(4)}$ which seems too small. For wagging vibrations instead of an average frequency, an average tensor may be calculated using the four frequencies (two for wagging and two for twisting) predicted by Kovner (1956) in his theoretical study: 134, 162, 162, 339 cm^{-1}. In this case, the Cruickshank (1956*b*) formula is used in the form:

$$\langle\theta^2\rangle = \tfrac{1}{4} \sum_{i=1}^{4} (h/8\pi^2 I\nu_i) \coth (h\nu_i/2kT)$$

$\langle\theta^2\rangle = 64{\cdot}4(°)^2$ which compares well with the value 55·7(°)^2 obtained in our analysis from diffraction data.

An important feature already found by Prince *et al.* and first established by spectroscopic results (Sanquer & Meinnel, 1972) is reinforced by the inclusion of wagging vibrations. It is the fact that the frequency of libration around the OY axis is considerably higher than that around the *OX* axis, even though the moment of inertia around *OY* is twice that around *OX*. Such a result is confirmed by potential energy calculations (Sanquer & Meinnel, 1972).

Table 4. *Comparison of librational, torsional and wagging frequencies of durene derived from constrained analyses with spectroscopic frequencies*

OX, *OY* and *OZ* refer to the principal axes of inertia (Fig. 4).

Axis of libration	I (10^{-40} g cm^2)	Prince *et al.*	This work	Spectroscopic frequencies
OX	390	50 cm^{-1}	50 cm^{-1}	72* cm^{-1}
OY	803	65	130	103*
OZ	1172	34	36	32*
Methyl torsion	5·24	130	139	144 179†
Wagging vibration	21·5		183	134 162 162 339‡

* From Sanquer & Meinnel (1972).
† From Livingston, Grant, Pugmire & Strong (1973).
‡ From Kovner's (1956) theoretical study.

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Structure Cristalline de K_3AsS_4

Par M. Palazzi, S. Jaulmes et P. Laruelle

Laboratoire de Physique et Laboratoire de Chimie Minérale (*L.A. CNRS n°* 200), *Faculté des Sciences Pharmaceutiques et Biologiques de Paris-Luxembourg*, 4 *Avenue de l'Observatoire*, 75270 *Paris Cedex* 06, *France*

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The crystal structure of K_3AsS_4 has been determined by single-crystal X-ray diffraction analysis. Intensities were collected on an XRD-7 diffractometer with Mo $K\alpha$ radiation. Crystals are orthorhombic, space group $Pc2_1n$, $a=9{\cdot}28$, $b=10{\cdot}58$, $c=9{\cdot}11$ Å, and $Z=4$. The structure has been solved by direct methods and parameters refined by the least-squares method. The final R value is 0·043. In the unsymmetrical cell there are four independent tetrahedra (AsS_4). In K_3AsS_4, two potassium atoms are in the centre of a $K(AsS_4)_4$ tetrahedron; the number of first neighbours (sulphur) is seven for one and six for the other, while for the third potassium, surrounded by five (AsS_4) tetrahedra, the number of sulphur neighbours is six.

Introduction

Dans le cadre d'une étude générale des thioarséniates et thioarsénites de métaux alcalins, nous avons, dans un premier temps, préparé ces sels par différentes méthodes (en solution et dans l'état solide) puis étudié certaines de leurs propriétés. Pour chacun d'eux, nous avons déterminé le système cristallin, les paramètres, le nombre de groupements par maille, les groupes spatiaux probables et la densité (Palazzi, 1972).

En ce qui concerne K_3AsS_4, Palazzi & Remy (1970) ont montré qu'il cristallise dans le système orthorhombique avec, pour paramètres: $a=9{,}13\pm0{,}01$; $b=9{,}31\pm0{,}01$; $c=10{,}64\pm0{,}01$ Å.

Pour compléter ces données cristallographiques obtenues à l'aide de diagrammes de poudre, nous envisageons de déterminer la structure cristalline de quelques thioarséniates et de quelques thioarsénites. Dans la présente note, nous étudions l'orthotétrathioarséniate tripotassique anhydre.