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Diamagnetism and Thermal Motion in Rigid-Body Molecules. Application to Biphenyl

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Abstract

The elements of the diamagnetic molecular tensor **K** are expressed in terms of the librational tensor **L** of a rigid-body molecule. This formulation is then applied to biphenyl at 293 and 80 K with accurate X-ray data. The calculations of the intrinsic principal molecular susceptibilities from the 293 and 80 K data give similar results.

Introduction

As first pointed out by Londsdale & Krishnan (1936), molecular diamagnetic susceptibilities may be derived from crystal measurements, if the configuration and orientation of the molecules in the crystal are known. Van den Bossche & Sobry (1974) developed a least-squares method, based on the study of several molecules with a common skeleton, to obtain diamagnetic molecular tensors. Now, the physical interpretation of the nature of diamagnetic phenomena is strongly connected with the accuracy of the available data. As an intrinsic molecular tensor is assigned to each molecule, thermal motion should introduce some change in the measurements of crystal susceptibilities.

The present paper details a formulation of thermal motion, analysed in a rigid-body model, in terms of a diamagnetic molecular tensor. This formulation is then applied to biphenyl which provides a good illustration for studying the relationships between diamagnetic anisotropy and the librations of the molecules in the crystal. X-ray analysis at 293 and 110 K (Charbonneau & Delugeard, 1976, 1977) indicated a very large libration about the long axis of the molecule. On the other hand, Lumbroso-Bader (1956) observed a large difference between the crystal anisotropy in biphenyl at 80 K and at room temperature.

Magnetic susceptibility of a librating molecule

The mean thermal displacement of a rigid molecule can be described by the molecular tensors T (translation), **L** (libration) and **S** (translation–libration) (Willis & Pryor, 1975). When the molecule occupies a site of symmetry $\bar{1}$, the **S** matrix vanishes. **T** and **L** are symmetric matrices which describe the translational and librational motion of the molecule about three Cartesian axes passing through the centre of mass of the molecule. Since translational motion does not affect magnetic susceptibilities, we are only concerned with librations of a rigid molecule.

Let U_i (i = 1, 2, 3) be the Cartesian directions of three axes of the molecule. They correspond to the equilibrium position given by X-ray analysis. For an instantaneous angular displacement, the position of the molecule will be given by the U_j^* (j = 1, 2, 3) directions. The transformation from the base vector system U_i to the base vector system U_j^* is

$$U_i = a_{ij} U_j^*.$$

Expanding this relation, for typical components of a second-order molecular tensor **K**, we obtain

$$\begin{aligned} K_1 &= a_{11}^2 K_1^* + a_{12}^2 K_2^* + a_{13}^2 K_3^*, \\ K_2 &= a_{21}^2 K_1^* + a_{22}^2 K_2^* + a_{23}^2 K_3^*, \\ K_3 &= a_{31}^2 K_1^* + a_{32}^2 K_2^* + a_{33}^2 K_3^*. \end{aligned} \qquad (1)$$

The off-diagonal terms are omitted in (1). If we assume that both systems are related by small rotations θ_i about U_i, the Cartesian direction cosines are

$$\begin{aligned} a_{11} &= \cos\theta_2 \cos\theta_3, \\ a_{12} &= -\sin\theta_3 \cos\theta_2, \\ a_{13} &= -\sin\theta_2, \\ a_{21} &= \cos\theta_1 \sin\theta_3 + \sin\theta_1 \sin\theta_2 \cos\theta_3, \\ a_{22} &= -\sin\theta_1 \sin\theta_2 \sin\theta_3 + \cos\theta_1 \cos\theta_3, \\ a_{23} &= -\sin\theta_1 \cos\theta_2, \\ a_{31} &= -\cos\theta_1 \sin\theta_2 \cos\theta_3 + \sin\theta_1 \sin\theta_3, \\ a_{32} &= \cos\theta_1 \sin\theta_2 \sin\theta_3 + \sin\theta_1 \cos\theta_3, \\ a_{33} &= \cos\theta_1 \cos\theta_2. \end{aligned} \qquad (2)$$

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For a molecule librating about the U_i axes, (1) becomes

$$\begin{aligned} K_1 &= \langle a_{11}^2\rangle K_1^* + \langle a_{12}^2\rangle K_2^* + \langle a_{13}^2\rangle K_3^*, \\ K_2 &= \langle a_{21}^2\rangle K_1^* + \langle a_{22}^2\rangle K_2^* + \langle a_{22}^2\rangle K_3^*, \\ K_3 &= \langle a_{31}^2\rangle K_1^* + \langle a_{32}^2\rangle K_2^* + \langle a_{33}^2\rangle K_3^*. \end{aligned} \tag{3}$$

K_1^*, K_2^*, K_3^* represent the intrinsic principal molecular susceptibilities (*i.e.* for a molecule supposed to be at rest) while K_1, K_2, K_3 are those which are obtained from magnetic measurements. The coefficients $\langle a_{ij}^2\rangle$, related to the librations of the molecule, can be calculated from the thermal motion X-ray analysis.

Let us consider the probability density function (p.d.f.) of a molecule. The p.d.f. denoted $p(\theta)$ is defined as the probability of finding the molecule displaced by θ from its equilibrium position. The p.d.f. of an individual molecule, a Gaussian function, is, in one dimension,

$$p(\theta) = 2\pi\langle\theta^2\rangle^{-1/2}\exp(-\theta^2/2\langle\theta^2\rangle).$$

Now, harmonic angular oscillations can be written

$$\theta_i = \theta_{mi}\cos(\omega t - \varphi_i).$$

Thus, the principal mean-square amplitudes are

$$\begin{aligned} L_{11} &= \langle\theta_1^2\rangle = \theta_{m_1}^2/2, \\ L_{22} &= \langle\theta_2^2\rangle = \theta_{m_2}^2/2, \\ L_{33} &= \langle\theta_3^2\rangle = \theta_{m_3}^2/2. \end{aligned}$$

With the small-angle approximations $\langle\sin^2\theta_i\rangle = \theta_{m_i}^2/2$ and $\langle\cos^2\theta_i\rangle = 1 - \theta_{m_i}^2/2$, the coefficients $\langle a_{ij}^2\rangle$ are expressed in terms of the librational tensor **L**.

Equations (3) become

$$\begin{aligned} K_1 &= (1 - L_{22} - L_{33})K_1^* + L_{33}K_2^* + L_{22}K_3^*, \\ K_2 &= L_{33}K_1^* + (1 - L_{11} - L_{33})K_2^* + L_{11}K_3^*, \\ K_3 &= L_{22}K_1^* + L_{11}K_2^* + (1 - L_{11} - L_{22})K_3^*. \end{aligned} \tag{4}$$

It is easy to check that the off-diagonal elements omitted in (1) should vanish because of the time average over the coefficients a_{ij}. From (4) the mean susceptibility is

$$\bar{\chi}_m = \tfrac{1}{3}(K_1 + K_2 + K_3) = \tfrac{1}{3}(K_1^* + K_2^* + K_3^*).$$

Application to biphenyl and discussion

Crystal magnetic anisotropies have been measured at 293 K (Krishnan, Guha & Banerjee, 1933; Lasheen, 1964) and at 80 K (Lumbroso-Bader, 1956), Table 1. The crystal susceptibility parallel to [010] is taken as χ_2, while χ_1 and χ_3 denote those in the (010) plane. If we assume that the principal axes of **K** (Fig. 1) coincide with the molecular axes, the agreement between the measured and calculated value of ψ constitutes a check on the determined values of the molecular susceptibilities. In fact, obtaining ψ amounts to the calculation of the crystal anisotropy from the tensor **K** and the direction cosines. The structure used was refined at both temperatures by least squares to $R(293) = 0{\cdot}063$ and $R(110) = 0{\cdot}066$. However, results differ slightly according to the atoms introduced in the calculation of the direction cosines. In fact, the bond lengths and the angles in the aromatic ring are not equal. Different sets of direction cosines led to values of $\Delta\psi = \psi_{\text{obs}} - \psi_{\text{calc}}$ varying from 0·50 to 1·5°. So, ψ_{obs} was taken as a reference and we got, by small adjustments, a new set which makes an angle of about 1° with the molecular axes.

The direction cosines and the ψ angle used at 80 K are those obtained from X-ray analysis at 110 K. We assume that the orientation in the crystal is the same at 80 and 110 K. For this case, $\Delta\psi = 0{\cdot}20°$. The molecular susceptibilities calculated are given in Table 2.

The librational tensor **L** at 80 K is extrapolated from the 110 K data. For harmonic oscillations, **L** is proportional to the absolute temperature (Cruickshank, 1956). The components of **L** are shown in Table 3.

By inserting L_{11}, L_{22}, L_{33} in (4) and with the approximation $L_{ii}K_j = L_{ii}K_j^*$ ($i, j = 1, 2, 3$), calculations of K_1^*, K_2^*, K_3^* are straightforward.

293 K data: $K_1^* = -68{\cdot}40$; $K_2^* = -62{\cdot}10$; $K_3^* = -187{\cdot}50$.
80 K data: $K_1^* = -68{\cdot}70$; $K_2^* = -62{\cdot}90$; $K_3^* = -187{\cdot}40$.

These two series of values show good agreement. As we have already pointed out, the tensor **K*** corresponds to a molecule at rest in the crystal. It is clear that **K*** is the very tensor to which we must refer for studying magnetic properties, and not **K**(293) or **K**(80), though at low temperature the thermal motion is small. The diamagnetic data were collected at both

Table 1. *Crystal anisotropy of biphenyl* (*Lumbroso-Bader*, 1956)

The units throughout this paper are 10^{-6} g^{-1}.

	$\chi_3 - \chi_1$	$\chi_a - \chi_2$	$\bar{\chi}_M$	χ_1	χ_2	χ_3	ψ
293 K	−80·4	−41·7	−106	−68·70	−100·10	−149·10	22° 40*
80 K	−84·3	−48	−106	−68·10	−97·40	−152·10	21° 40

* Lasheen (1964).

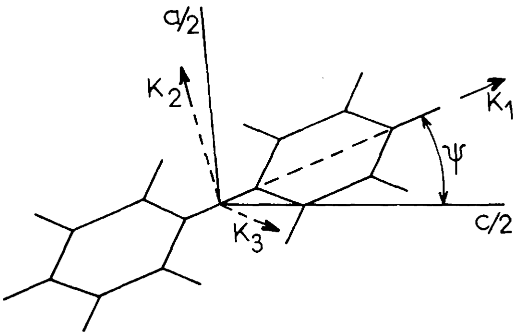

Fig. 1. Principal magnetic axes of biphenyl.

Table 2. *Cosine directions and molecular susceptibility of biphenyl*

	293 K			80 K		
	1 Length	2 Breadth	3 Normal	1 Length	2 Breadth	3 Normal
a	0·2960	0·5160	0·8038	0·2890	0·5015	0·8157
b	−0·0001	−0·8415	0·5402	−0·0140	−0·8482	0·5288
c^*	0·9552	−0·1599	−0·2491	0·9573	−0·1696	−0·2346
	$K_1 = -68{\cdot}70$ $K_2 = -66{\cdot}10$ $K_3 = -183{\cdot}20$			$K_1 = -68{\cdot}80$ $K_2 = -63{\cdot}10$ $K_3 = -186{\cdot}10$		
	$\psi_{\rm obs} - \psi_{\rm calc} = 0{\cdot}10°$			$\psi_{\rm obs} - \psi_{\rm calc} = 0{\cdot}20°$		

Table 3. *Molecular thermal motion tensors in biphenyl*

The axes are OX in the direction of the long molecular axis, OZ perpendicular to the molecular plane, $OZ = OX \times OY$. E.s.d.'s are given in parentheses.

Libration (°)^2	293 K	110 K	80 K*
L_{11}	109·17 (2·82)	45·70 (2·06)	33·23
L_{22}	8·39 (0·55)	2·46 (0·43)	1·78
L_{33}	11·47 (0·52)	3·45 (0·40)	2·50

* See comment in the text.

temperatures with the same crystals and the error on $\Delta K_i = K_i(293) - K_i(80)$ was estimated at about $\pm 0{\cdot}20$.

$$\Delta K_1 = 0{\cdot}10 \pm 0{\cdot}2; \quad \Delta K_2 = 3{\cdot}00 \pm 0{\cdot}2;$$
$$\Delta K_3 = 2{\cdot}90 \pm 0{\cdot}2.$$

In benzene (Pacault, Lemanceau & Joussot-Dubien, 1956) and naphthalene (Lumbroso & Pacault, 1957) the molecular susceptibilities do not depend on the temperature. This can be easily understood from (4); the principal mean-square amplitudes L_{ii} lie in the range 15 to 20(°)^2 (Cruickshank, 1957; Pawley, 1967) so that contribution from these terms can be ignored. It is a quite different case for biphenyl.

Now, the question arises as to whether the difference of 1° found at 293 K between the magnetic and molecular axes has a physical meaning or if it is simply caused by the inaccuracy in the determination of axes. The good agreement between **K***(293) and **K***(80) suggests that we should keep the magnetic axes as a reference. A possible error might come from X-ray analysis which was carried out with harmonic approximations. Biphenyl exhibits a large anisotropic thermal expansion (Kozhin & Mirskaya, 1969), which is another characteristic feature of anharmonic vibrations. Scheringer (1978) suggests that account be taken of anharmonic contributions to the Debye–Waller factor for molecules undergoing large librations. In that case, the refinement of the structure might lead to a slightly different orientation of the molecular axes in agreement with the magnetic axes as noticed at 80 K.

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