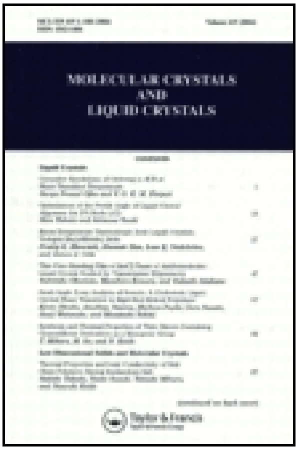

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Calculation of Birefringence Changes in Anthracene and Phenanthrene Crystals

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Birefringence changes due to thermal expansion have been calculated for anthracene and phenanthrene. The method assumes that the effective molecular polarizability calculated at room temperature is constant in the molecular axis system for small changes of molecular orientation and separation. For anthracene, the calculations reproduce the observed birefringence change quantitatively. For phenanthrene, two thirds of the observed change is due to thermal expansion, the rest to structural alterations at the 70°C phase transition; transition to a Pa structure is ruled out. Birefringence calculations could be used to test other high-temperature structures for phenanthrene which might be suggested by lattice-energy calculations.

1 INTRODUCTION

Optical birefringence studies can provide information on symmetry changes at phase transitions, and can be used to test proposed structures for the new phase if a method is available for calculating birefringences. This possibility is particularly attractive for molecular crystals, in which phase transitions change the arrangement of molecules but probably not the properties of individual molecules (at least to a first approximation). For example, in the isotopic methane crystals the calculated tetragonal lattice parameters which reproduced the observed birefringence in phase III were found[1] to be consistent with the structure of CD_4 suggested by diffraction methods. In this favourable case, the molecules are essentially isotropically polarizable, but in general both molecular and structural anisotropy must be treated. Such a treatment has become feasible after recent developments of the theory of polarization in molecular crystals.[2–5] We have therefore developed a method for calculating birefringence changes and have applied it to anthracene and phenanthrene to compare its predictions with the experimental results.[6]

The birefringence changes measured for anthracene[6] are due to ordinary thermal expansion. Our method accounts for these changes quantitatively and its assumptions are thereby shown to be reasonable. In phenanthrene the birefringence measurements[6] span the phase transition near 70°C, the origin of which is still not understood despite studies by various methods (see Ref. 6 for a list). The birefringence changes are essentially continuous and three or four times larger than for anthracene over the same temperature range, but the thermal expansion is larger too. We have therefore investigated how far thermal expansion alone can account for the changes. There are other recent birefringence measurements on phenanthrene,[7] but these refer to a possible different phase transition around 230 K. In this work it was suggested that molecules on one sublattice might be reversed at the transition, and we have therefore also investigated what birefringence changes would ensue at such a transition.

2 METHOD

2.1 Birefringence in monoclinic crystals

All the structures treated here are monoclinic. The birefringence is the difference between the extremal refractive indices for the chosen direction of incidence. All the measurements refer to normal incidence on the *ab* plane, in which case the birefringence is $n_a - n_b$. In any plane containing the *b* axis n_b is extremal since it is a principal refractive index; the opposite extremum lies perpendicular to *b* in the plane concerned (cf. Ref. 8).

These refractive indices are related to the components $\varepsilon_{\alpha\beta}$ of the relative permittivity tensor referred to the crystal *abc′* axes by

$$n_a^2 = (\varepsilon_{aa}\varepsilon_{c'c'} - \varepsilon_{ac'}^2)/\varepsilon_{c'c'} \tag{1}$$

$$n_b^2 = \varepsilon_{bb}. \tag{2}$$

These forms arise because $1/n^2$ transforms like $\boldsymbol{\varepsilon}^{-1}$. It can be verified that Eq. (1) is equivalent to Eq. (B8) of Ref. 1 when expressed in terms of the principal components of $\boldsymbol{\varepsilon}$ in the *ac* plane and the angle they make with the *a* and *c′* axes. (The required equations are given in Ref. 9.)

2.2 Electric susceptibility

We calculate $\boldsymbol{\varepsilon}$ for the structures in question from the electric susceptibility $\boldsymbol{\chi} = \boldsymbol{\varepsilon} - \mathbf{1}$. To do so, we assume that the effective molecular polarizability $\boldsymbol{\alpha}$ referred to the molecular axes always remains the same as in the room-temperature structure.

The basic equation for crystals with two molecules in the unit cell is[2,5]

$$\boldsymbol{\beta}_1^{-1} = \mathbf{M}_{11} + \mathbf{M}_{12} \cdot \boldsymbol{\rho}, \tag{3}$$

where $\boldsymbol{\beta}_1$ is the reduced polarizability $\boldsymbol{\alpha}/\varepsilon_0 v$ (with v the unit cell volume) for molecule on sublattice 1, referred to crystal axes. The quantities $\mathbf{M}_{kk'}$ are given by

$$\mathbf{M}_{kk'} = \boldsymbol{\chi}^{-1} + \mathbf{L}_{kk'}, \tag{4}$$

where $\mathbf{L}_{kk'}$ is a lattice dipole sum or Lorentz-factor tensor and the subscripts denote different sublattices; $\boldsymbol{\rho}$ is a matrix partly fixed by symmetry. A consistent description of several aromatic hydrocarbons including anthracene and phenanthrene is found to be obtained by the algebraically convenient choice $\boldsymbol{\rho} = \mathbf{1}$ with the $\mathbf{L}_{kk'}$ calculated as averages for interactions between point dipoles at the center of each aromatic ring.[5]

Now $\boldsymbol{\beta}_1$ can be related to $\boldsymbol{\alpha}$ in molecular axes through the direction cosine matrix $\mathbf{a}$ which has the direction cosines of the molecular axes relative to the crystal axes as its columns. Then setting $\boldsymbol{\rho} = \mathbf{1}$ and using Eq. (4) we can write Eq. (3) in the form

$$[\mathbf{a} \cdot (\boldsymbol{\alpha}/\varepsilon_0 v) \cdot \tilde{\mathbf{a}}]^{-1} = 2(\boldsymbol{\chi}^{-1} + \mathbf{L}) \tag{5}$$

where the superposed tilde denotes the transpose and $\mathbf{L} = \frac{1}{2}(\mathbf{L}_{11} + \mathbf{L}_{12})$. On rearranging Eq. (5) we obtain the equation

$$\varepsilon_0 \boldsymbol{\alpha}^{-1} = 2\tilde{\mathbf{a}} \cdot (\boldsymbol{\chi}^{-1} + \mathbf{L}) \cdot \mathbf{a}/v, \tag{6}$$

in which the left-hand side should be constant, according to our assumption. We equate the right-hand side of Eq. (6) to the same expression for some other structure with properties denoted by primes. The new susceptibility can then be expressed as

$$\boldsymbol{\chi}' = [r\mathbf{R} \cdot (\boldsymbol{\chi}^{-1} + \mathbf{L}) \cdot \tilde{\mathbf{R}} - \mathbf{L}']^{-1}, \tag{7}$$

where $r = v'/v$ and $\mathbf{R} = \mathbf{a}' \cdot \tilde{\mathbf{a}}$ is the rotation matrix. Since $\boldsymbol{\chi}$ is known and the other quantities can be obtained from the two structures, $\boldsymbol{\chi}'$ can be calculated and hence the new birefringence.

2.3 Molecular orientations

A knowledge of the molecular orientations in both structures is necessary to calculate $\mathbf{R}$, $\mathbf{L}$ and $\mathbf{L}'$, but has not been measured above room temperature for anthracene or phenanthrene. The changes in lattice parameters have been measured, and we use them to estimate the changes in orientation. The principal idea is that changes in the monoclinic angle β should reflect changes in molecular orientation.

We start from the detailed structures determined for 20–25°C and use separate X-ray measurements of thermal expansion to calculate the lattice parameters at 75°C. The change in lattice parameters corresponds to a homogeneous deformation described by a matrix **D** which carries a vector **x** into a vector $\mathbf{x}' = \mathbf{D} \cdot \mathbf{x}$. The components of **D** in the crystal axes are

$$\mathbf{D} = \begin{pmatrix} a'/a & 0 & (ac' \cos \beta' - a'c \cos \beta)/ac \sin \beta \\ 0 & b'/b & 0 \\ 0 & 0 & c' \sin \beta'/c \sin \beta \end{pmatrix}. \tag{8}$$

The matrix $\mathbf{D} \cdot \mathbf{a}$ then gives the direction cosines of the molecular axes after the homogeneous deformation, except that they are no longer normalized or orthogonal. To obtain a proper new direction cosine matrix we assume that the new long molecular axis direction coincides with that of the homogeneously deformed long axis and that the new molecular plane is defined by that of the homogeneously deformed long and medium axes.

Finally we assume that the fractional coordinates of the molecular centre of mass are the same in each structure and use **R** to calculate the new positions of the centres of the rings. The centres of mass are fixed by symmetry in anthracene, but not in phenanthrene.

3 ANTHRACENE

The detailed structure of anthracene is given by Cruickshank.[10] We take this to apply to 25°C and calculate the new lattice parameters at 75°C from other X-ray measurements.[11] The volume change is $1\frac{1}{2}\%$, arising mainly from changes in a and $\sin \beta$.

The calculated susceptibility at 75°C has non-zero ab and bc' elements which are forbidden by symmetry. These arise from an inconsistency between the assumed structure and the assumed constancy of $\boldsymbol{\alpha}$ and $\boldsymbol{\rho}$, but being only about 0.002 can safely be neglected. The refractive indices at room temperature are[12]

$$n_a = 1.619711,\ n_b = 1.786$$
$$\Delta n = -0.166289.$$

We calculate the new refractive indices to be

$$n'_a = 1.605286,\ n'_b = 1.770026$$
$$\Delta n' = -0.164740.$$

The decrease in Δn is therefore calculated to be 0.93 % between 25 and 75°C.

The experimental birefringences[6] are expressed as optical path differences $d\Delta n$, where d is the crystal thickness. For anthracene the path difference at 25°C is read as 6925 nm and at 75°C as 6860 nm. The change relative to that at 25°C is equal to $(\Delta n'/\Delta n) - 1$, which is calculated to be -0.94%. The uncertainty in the path difference could be some 5 nm, leading to an uncertainty in this birefringence change of 10–15%. However, it is clear that our method succeeds in calculating this small birefringence change correctly within the experimental uncertainty.

4 PHENANTHRENE

We take the detailed structure of phenanthrene at 25°C from the X-ray and neutron measurements of Kay *et al.*[13] We calculate the new lattice parameters at 75°C from X-ray thermal expansion data,[14] which are broadly compatible with capacitance dilatometric data.[15] The volume change is 2%, arising mainly from changes in a and b. In contrast to anthracene, the monoclinic angle β increases as the temperature increases, and this offsets part of the increase in c.

We calculate the electric susceptibility expected at 75°C on the basis of a constant polarizability and structural changes due to thermal expansion alone. The method is essentially as for anthracene except that the position of the molecular centre of mass is not fixed by symmetry. The refractive indices at room temperature are[16]

$$n_a = 1.557957 \qquad n_b = 1.724$$
$$\Delta n = -0.166043.$$

The birefringence is almost equal to that of anthracene. We calculate the new refractive indices to be

$$n'_a = 1.539255 \qquad n'_b = 1.701996$$
$$\Delta n' = -0.162741.$$

The calculated decrease in Δn between 25 and 75°C is 1.99%.

Experimental birefringences[6] have been published for two phenanthrene crystals. The path differences at 25°C are read as 6020 and 4815 nm, corresponding to crystal thicknesses of 36 and 29 μm, consistent with the stated thickness of about 50 μm. The changes in optical path difference between 25 and 75°C are read as -190 and -160 nm, giving fractional changes of -3.16% and -3.32%, average -3.24%. According to our calculations, nearly two thirds of this change is accounted for by ordinary thermal expansion without changes in molecular polarizability or crystal structure.

One high-temperature structure proposed[7] for phenanthrene has the direction of the molecular twofold symmetry axis reversed for molecules on one sublattice. If this reversal is effected by inversion in an appropriate point, the new structure belongs to the space group Pa, compared with the normal $P2_1$ with two molecules in the unit cell. It seems plausible that the existence of alternative ways of lowering the anthracene $P2_1/a$ symmetry to accommodate two non-centrosymmetric phenanthrene molecules in the unit cell might lead to a phase transition. The proposed structure would also allow a net electric polarization parallel to the *a* axis, as required to explain certain dielectric measurements,[17] but does appear to be incompatible with the X-ray measurements.[14]

To examine whether a Pa structure is acceptable for the high-temperature phase of phenanthrene, we have calculated the birefringence change from the $P2_1$ structure at 25°C to a Pa structure at 75°C with the same thermal expansion used previously. The Lorentz-factor tensor $\mathbf{L}''_{11}$ is unchanged, but $\mathbf{L}''_{12}$ is changed substantially. The result is to reverse the ordering of the refractive indices:

$$n''_a = 1.702 \qquad n''_b = 1.532$$
$$\Delta n'' = +0.170.$$

The birefringence is changed in sign by transition to the Pa structure and so this structure is not compatible with the observed birefringence. Note however that the magnitude of the birefringence is hardly changed, because to a good approximation the values of n_a and n_b are exchanged by the transition.

It should be emphasized that the phenanthrene structure with one set of molecules reversed in direction, here taken to be a Pa structure, was proposed[7] to account for a possible phase transition below room temperature, and not the 70°C phase transition. In examining the suitability of a Pa structure for the latter transition, we are therefore going beyond anything suggested by the original authors. Their birefringence method also gives no detectable change at the higher temperature transition.[18]

5 DISCUSSION

The birefringence changes observed in both anthracene and phenanthrene are small, implying small changes in the molecular arrangement (unless in phenanthrene there are larger changes with fortuitously opposed effects). The change in anthracene is quantitatively accounted for by the present method, indicating the basic soundness of the assumptions. Nearly two thirds of the change in phenanthrene is accounted for by thermal expansion with no change of structure; transition to a Pa structure is ruled out.

The calculations are not rigorous, owing to the choice $\boldsymbol{\rho} = \mathbf{1}$ and the representation of the molecular charge distributions by three points. However, the severity of these approximations (which in any case yield plausible results in other applications) is mitigated by their application to each structure in the same way, so that some cancellation of errors should occur. A more realistic representation of charge distributions by a larger number of points produces relatively minor changes,[19] and so should not alter the conclusions reached here.

Granted that the method used here is reliable, it could be applied to other hypothetical structures for phenanthrene. For example, instead of the Pa structure one could investigate structures produced by inversion in different points, such as the molecular centre of mass. However, in this structure the molecules are no longer crystallographically equivalent. Once such structures are admitted, one could also investigate much smaller molecular reorientations yielding structures akin to that of tetracene, in which the molecules pack much as in anthracene or normal phenanthrene. There are so many structures like this that it would not seem worthwhile to study them without independent evidence that the true structure is of this type.

It may well be profitable to use atom–atom potentials to examine what structures might be acceptable energetically. The method has proved useful in elucidating the phase transition in *p*-terphenyl.[20] It has also shown that there are at least three crystal structures of anthracene close in energy to the observed one,[21] and electron microscopy has now provided experimental evidence for the existence of metastable phases of anthracene.[22] If calculations indicate that there are similarly low-energy structures for phenanthrene, birefringence calculations would provide a means of checking which structures could account for the phase transition.

It would also be possible to examine the birefringence change due to the suggested change in molecular conformation,[17] but this would require a more detailed treatment of the molecular polarizability. In any case, recent Raman measurements[23] seem to rule out this change of conformation, since the appropriate molecular mode shows no significant change at the transition.

The calculations reported here show that birefringence changes due to thermal expansion in anthracene, and by implication other crystals, can be understood quantitatively. In phenanthrene probably only about one third of the birefringence change in a 50 K range spanning the phase transition is attributable to specific changes of crystal structure or molecular polarizability. Birefringence calculations could be a valuable adjunct to lattice energy calculations in elucidating the nature of this phase transition. The calculation of birefringence changes is straightforward given adequate data, and represents another useful application of the theory of polarization in molecular crystals.

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