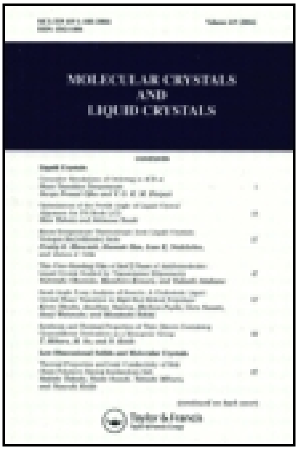

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Calculation of Birefringence Changes in the Carbazole Crystal

A. Hinchliffe [a] , R. W. Munn [a] & C. J. Spicer [a]
[a] Department of Chemistry, UMIST, Manchester, M60 1QD, U.K.

To cite this article: A. Hinchliffe , R. W. Munn & C. J. Spicer (1981): Calculation of Birefringence Changes in the Carbazole Crystal, Molecular Crystals and Liquid Crystals, 73:3-4, 181-191

To link to this article: http://dx.doi.org/10.1080/00268948108072333

Mol. Cryst. Liq. Cryst., 1981, Vol. 73, pp. 181–191
0026-8941/81/7304-0181$06.50/0

Calculation of Birefringence Changes in the Carbazole Crystal

A. HINCHLIFFE, R. W. MUNN and C. J. SPICER
Department of Chemistry, UMIST, Manchester M60 1QD, U.K.

(*Received February 12, 1981*)

The temperature derivative of birefringence in the crystallographic *ac* plane of carbazole is calculated as a function of molecular rotations and translations in the *ac* plane. The experimental thermal expansion and effective polarizabilities deduced from the crystal refractive indices are used; for comparison, the polarizability is also derived from an empirically modified INDO calculation. The effect of molecular rotation on the birefringence is particularly sensitive to the polarizability anisotropy, but the effect of translations is not. The birefringence depends linearly on rotation and on translation along the *a* direction, but quadratically on translation along *c*. The internal displacements cannot be determined uniquely from the single measured birefringence derivative, but could be determined given the other two birefringence derivatives.

1 INTRODUCTION

When a molecular crystal is subjected to a change of stress or temperature, the size and shape of the unit cell change. These changes in turn lead to changes in the positions and orientations of the molecules in the unit cell. Such internal strains play an important role in the interpretation of thermodynamic,[1] vibrational[2] and optical[3,4] properties of molecular crystals, for example, in elucidating the mechanism of some of the subtle phase transitions which molecular crystals may undergo. They are however rather difficult to determine accurately from direct experimental measurements, such as crystal structure analyses at different temperatures. It is therefore attractive to seek other experimental quantities sensitive to the internal strains.

One such property is the optical birefringence (difference in refractive indices), which can be measured very precisely:[5–7] much more so, in fact, than the individual refractive indices. The problem is then to develop suitable methods for deducing the changes in molecular position and orientation from the measured changes in birefringence and unit cell parameters. In recent years, theories have been developed which give the refractive indices in terms of dipole lattice sums and the effective molecular polarizability in the crystal environment.[8-13] With the assumptions that the molecules are mechanically rigid and that the effective polarizability in the molecular axes is independent of (small) changes in the relative molecular orientations and separations, these theories provide the required link between the internal strains and the birefringence changes.

Thus birefringence changes were calculated[3] for anthracene and phenanthrene crystals for comparison with experimental measurements.[14] However, the calculations used an empirical prescription for the molecular rotation due to strain, and also neglected the contribution of thermal expansion to measured optical path lengths.[7,15] A more general treatment of elastooptic effects with the same prescription for the rotation was successfully applied to the orthorhombic sulphur crystal.[4] Precise birefringence measurements for carbazole were analysed using an anisotropic Lorentz local-field approximation to yield the temperature derivative of the molecular orientation angle.[7] However, this method could not take account of molecular translations due to strain, which were also neglected in the earlier treatments.[3,4]

The present paper reports more rigorous calculations of birefringence changes in carbazole as a function of molecular rotation and translation. Changes in the unit cell size and shape with temperature are included through the measured thermal expansion.[7] Comparison of the calculated birefringence changes with the observed[7] temperature coefficient of birefringence then defines a domain of possible rotations and translations. The rotations depend very sensitively on the anisotropy of the molecular polarizability used. Polarizabilities are therefore treated in Section 2, the birefringence calculations are presented in Section 3, and the results are discussed in Section 4.

2 POLARIZABILITIES

2.1 Crystal effective polarizabilities

An internally consistent dielectric theory requires the use of a crystal-phase effective polarizability derived from the refractive indices at any one temperature (i.e. any one crystal structure). This polarizability, assumed independent of strain, then determines the refractive indices in any other structure.[4] The derivation of the effective polarizability depends in its details on the crystal structure.

Carbazole crystallizes[15] in the orthorhombic space group Pnma, with $Z = 4$. The molecules, sketched in Figure 1, retain the MN mirror symmetry plane in the crystal. The molecular L axes lie parallel to the crystallographic b axis. There are no symmetry constraints on the orientation of the M and N axes in the crystallographic ac plane or on the position of the center of mass in that plane. Internal strains are then defined by an angle of rotation about the L axis and two components of translation in the ac plane.

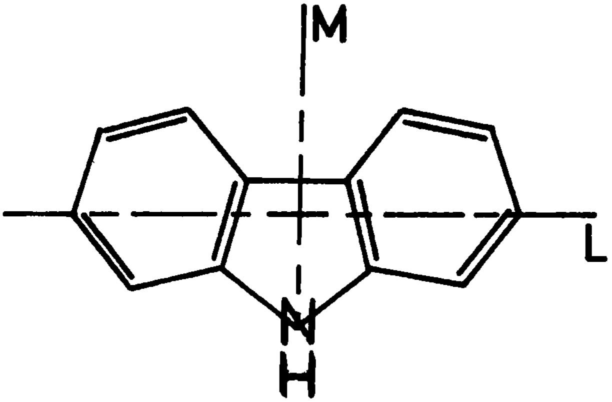

FIGURE 1 The carbazole molecule, showing the molecular L and M axes. The N axis is perpendicular to the molecular plane.

Molecules on the four sublattices are related in pairs by inversion. The algebraic theory is then the same as for orthorhombic sulphur[4] except that for carbazole the unique axis is b instead of c. The polarizability for molecules on sublattice 1 follows directly from

$$\boldsymbol{\beta}_1^{-1} = \mathbf{M}_1 + \begin{pmatrix} A(1+q^2)^{1/2} & 0 & (AC)^{1/2}q \\ 0 & B & 0 \\ (AC)^{1/2}q & 0 & C(1+q^2)^{1/2} \end{pmatrix} \tag{1}$$

The various quantities here are defined as follows: $\boldsymbol{\beta}_1 = \boldsymbol{\alpha}_1/\epsilon_0 v$, where $\boldsymbol{\alpha}_1$ is the polarizability tensor and v is the unit-cell volume; $\mathbf{M}_1 = \mathbf{M}_{11} + \mathbf{M}_{12}$; A, B and C are the diagonal elements of $\mathbf{M}_3 = \mathbf{M}_{13} + \mathbf{M}_{14}$; $\mathbf{M}_{kk'} + \boldsymbol{\chi}^{-1} = \mathbf{L}_{kk'}$, where $\boldsymbol{\chi} = \boldsymbol{\varepsilon} - \mathbf{1}$ is the optical susceptibility of the crystal and the $\mathbf{L}_{kk'}$ are Lorentz-factor tensors.[17] The parameter q is arbitrary; it effectively determines the difference in sublattice polarizations whereas the susceptibility determines their sum,[9] but can be determined from Stark spectra,[18] or the intensities of lattice Raman[19] or infrared[20] spectra.

In the absence of suitable such data for carbazole, we select two values of q: (i) the algebraically convenient choice[21] $q = 0$, and (ii) the value of q which makes the polarizability diagonal in the molecular axes. This second value of q is determined algebraically by transforming $\boldsymbol{\beta}_1^{-1}$ to molecular axes using the direction cosine matrix[7]

$$\mathbf{a}_1 = \begin{pmatrix} 0 & -h & -(1-h^2)^{1/2} \\ 1 & 0 & 0 \\ 0 & -(1-h^2)^{1/2} & h \end{pmatrix}, \tag{2}$$

TABLE I

Lorentz-factor tensor components $L_{\alpha\beta}(kk')$ averaged over carbon and nitrogen atoms for carbazole, referred to crystal axes. Components not quoted are zero by symmetry.

	$\alpha\beta$			
kk'	aa	$ac = ca$	bb	cc
11	0.290	−0.210	−0.525	1.235
12	0.068	−0.006	0.950	−0.018
13	−0.047	0	1.014	0.034
14	1.716	0	−0.970	0.255

where the rows denote crystal axes and the columns molecular axes; $h = \cos\theta$, where θ is the angle between the crystal c axis and the molecular N axis. Equating the one independent nonzero off-diagonal element of the transformed polarizability to zero yields a quadratic equation for q. The correct root corresponds to the positive square root of $1 + q^2$ in Eq. (1).

For elongated molecules like carbazole, Lorentz-factor tensors calculated treating each molecule as a point tend to yield physically unacceptable polarizabilities, with for example excessive anisotropy.[12] More acceptable polarizabilities are obtained using average Lorentz-factor tensors calculated treating each aromatic ring as a point.[11,12] For carbazole even this procedure yields rather unsatisfactory polarizabilities, and so each carbon and nitrogen atom was treated as a point in the averaging. The resulting Lorentz-factor tensors are summarized in Table I.

The two sets of effective polarizabilities, quoted for convenience as polarizability volumes $\mathbf{V} = \boldsymbol{\alpha}/4\pi\epsilon_0$ referred to the molecular axes, are given in Table II. The long-axis components are independent of q, which essentially determines the orientation of the principal axes of the polarizability tensor in the molecular MN plane (the crystal ac plane). For $q = 0$, the smallest principal component lies at an angle of 19.5° to the N axis, corresponding to a polariza-

TABLE II

Polarizability volumes $V_{AB}/10^{-30}$ m^3 for carbazole, referred to the molecular axes. Components not quoted are zero by symmetry.

	AB			
Source	LL	MM	$MN = NM$	NN
Crystal $q = 0$	39.8	18.8	−1.7	14.6
Crystal $q = -0.475$	39.8	22.4	0	11.7
Corrected INDO results	26.6	22.1	0	13.3
From bond polarizabilities[7]	26.4	21.9	0	14.8

bility volume of 14.0×10^{-30} m^3; the remaining principal component corresponds to 19.5×10^{-30} m^3.

The solutions for the different values of q are seen to vary most in their anisotropy in the *MN* plane. The trace of the polarizability tensor hardly changes, but the second anisotropy η, defined as the difference between the principal components in the *MN* plane, corresponds to polarizability volumes of 5.5×10^{-30} m^3 for $q = 0$ and 10.7×10^{-30} m^3 for $q = -0.475$. This difference affects particularly the birefringence change for molecular rotation about the *L* axis; for $\eta = 0$, there would be only small changes arising from the Lorentz-factor tensor averaging. Further information was therefore sought by theoretical calculations of polarizability.

2.2 INDO molecular polarizabilities

Theoretical molecular polarizability tensors tend to have reasonable traces, i.e. mean values, but rather poor anisotropies. For example, even *ab initio* calculations[22] on aromatic hydrocarbons, admittedly with a minimal basis set, give considerable underestimates of the out-of-plane polarizabilities α_{NN}. However, the semi-empirical INDO method gives improved anisotropies for aromatic hydrocarbons, although all the polarizability components tend to be underestimated.[23] Following an earlier scheme for the mean polarizabilities,[24] an empirical scheme of anisotropic atomic polarizability corrections for carbon atoms (isotropic for hydrogen atoms) was therefore devised to give realistic anisotropic polarizabilities from INDO calculated polarizabilities.[23] We have used a similar scheme for carbazole.

INDO calculations for pyridine yield polarizability volumes in the molecular *LMN* axis system of 5.06, 4.92 and 2.10×10^{-30} m^3. Comparison with the experimental values[25] of 11.9, 10.8 and 5.8×10^{-30} m^3 and the previous corrections[24] for carbon and hydrogen leads to corrections for nitrogen of 1.94, 1.44 and -0.76×10^{-30} m^3. INDO calculations for carbazole yield 14.1, 11.1 and 4.5×10^{-30} m^3, leading to the estimated polarizability volumes shown in Table II. Although pyrrole would presumably be a more suitable small molecule to compare with carbazole, there appear to be no experimental values of its polarizability.

As Table II shows, the corrected INDO polarizabilities in the *MN* plane lie between those for the crystal with $q = 0$ and $q = -0.475$; the second anisotropy η is 8.8×10^{-30} m^3. The long-axis polarizability is much smaller, although this does not affect the present birefringence calculations. The INDO polarizabilities agree well with the values derived[7] from bond polarizabilities, as shown in Table II, though the latter show still less anisotropy in the *MN* plane ($\eta = 7.1 \times 10^{-30}$ m^3). It appears that in the molecular *MN* plane or the crystal *ac* plane the two crystal effective polarizabilities probably bracket the true values. It is not clear why the long-axis effective polarizability should be so much bigger than the INDO and bond polarizabilities, and in any case this problem lies beyond the scope of the present paper.

3 BIREFRINGENCES

The experimental birefringence measurements[7] give B_{13} as a function of temperature where

$$B_{13} = n_1 - n_3 = n_a - n_c \tag{3}$$

and the n_i are principal refractive indices. These follow from the susceptibility tensor as $n_i^2 = \chi_{ii} + 1$, while χ is given by[13,20]

$$\boldsymbol{\chi} = \sum_{kk'} (\boldsymbol{\beta}^{-1} - \mathbf{L})^{-1}_{kk'}. \tag{4}$$

Here $\boldsymbol{\beta}$ is a $3\mathbf{Z} \times 3\mathbf{Z}$ matrix having $\boldsymbol{\beta}_k \delta_{kk'}$ as submatrices and $\mathbf{L}$ is a $3\mathbf{Z} \cdot 3\mathbf{Z}$ matrix having the $\mathbf{L}_{kk'}$ as submatrices. In practice the crystal symmetry of carbazole simplifies the calculation of $\boldsymbol{\chi}$ to the inversion of 6 × 6 matrices rather than 12 × 12 ones.

The strain dependence of $\boldsymbol{\chi}$ and hence of the birefringence can be calculated analytically, using analytical expressions for the strain derivatives of the Lorentz-factor tensors.[4,26] However, these calculations become rather involved in the submolecule treatment.[4] We have therefore used a direct numerical method, which also reveals certain nonlinearities which the analytical first derivatives would not describe.

From the measured thermal expansion tensor[7] $\boldsymbol{\delta}$ we calculate the strain $\boldsymbol{\eta}$ from the room-temperature lattice structure for a temperature increase ΔT as

$$\boldsymbol{\eta} = \boldsymbol{\delta}\Delta T. \tag{5}$$

This gives the new unit-cell parameters and volume. Molecular rotations and translations from the old orientation and fractional coordinates are then imposed to give the new crystal structure. This yields new Lorentz-factor tensors and new effective polarizability components (assuming a constant polarizability in the molecular axes), and hence a new birefringence. The birefringence change is divided by ΔT to give dB_{13}/dT, which is observed[7] to be independent of temperature from 20 to about 155°C, where a phase transition appears to take place.

Calculations have been performed using the two crystal effective polarizabilities in Table II. The calculated values of dB_{13}/dT are plotted in Figures 2–4 for the three different internal strains. For comparison, the observed value of dB_{13}/dT is[7] $8.31 \times 10^{-5}\ \mathrm{K}^{-1}$. The calculated values of dB_{13}/dT for zero internal strain represent the contribution from the pure homogeneous deformation due to thermal expansion, namely $1.67 \times 10^{-5}\ \mathrm{K}^{-1}$ for polarizability (*i*) and $1.73 \times 10^{-5}\ \mathrm{K}^{-1}$ for polarizability (*ii*). These are both only 20% of the observed birefringence derivative, in contrast to the 70% ascribed to the volume dilution of polarizability density in the previous calculations.[7] The difference arises principally through the effect of strain on the Lorentz-factor tensors, which cannot be included in the previous treatment and acts against the volume dilution effect.

Figure 2 shows dB_{13}/dT calculated as a function of the temperature derivative of the molecular rotation θ taking the molecular N axis towards the crystal c axis. The two polarizabilities give very different results, as can be seen, except that both show a linear dependence of dB_{13}/dT on $d\theta/dT$. The difference can be traced to the large difference in their second anisotropies η, already noted: the polarizability (*ii*) with the larger anisotropy gives larger changes in B_{13} on rotation. If the contribution of translation to dB_{13}/dT is ignored, the observed value of dB_{13}/dT corresponds to $d\theta/dT$ having the value 63×10^{-5} rad K^{-1} (36×10^{-3} deg K^{-1}) for polarizability (*i*), and 8×10^{-5} rad K^{-1} (4×10^{-3} deg K^{-1}) for polarizability (*ii*). The previous calculations[7] gave $d\theta/dT$ as 48×10^{-5} rad K^{-1} (27×10^{-3} deg K^{-1}) using the bond polarizability in Table II. No further comparison is possible because of the different methods of calculation. Note that negative values of θ reduce dB_{13}/dT below the thermal expansion contribution to become negative eventually.

Figure 3 shows dB_{13}/dT calculated as a function of u for the rate of change of internal displacement (u, 0, 0) relative to the lattice structure after thermal expansion. Because no rotation is involved, the two polarizabilities give sim-

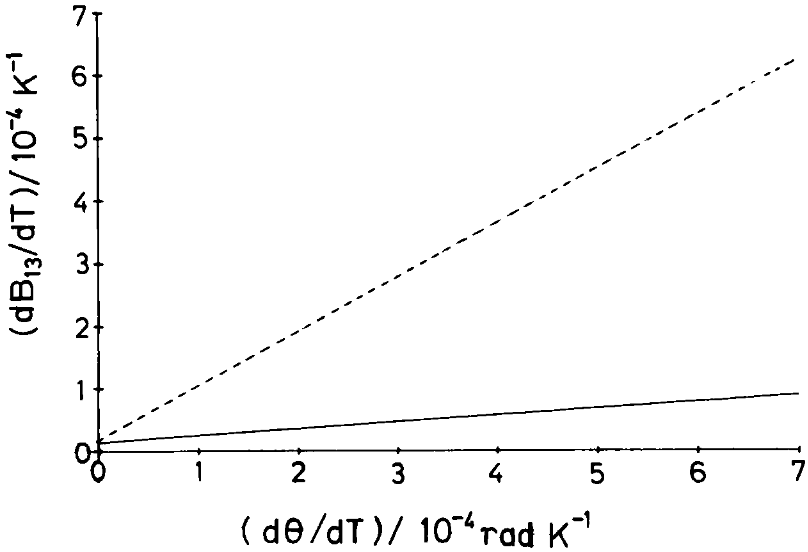

FIGURE 2 Temperature derivative of the birefringence as a function of the temperature derivative of the molecular rotation.

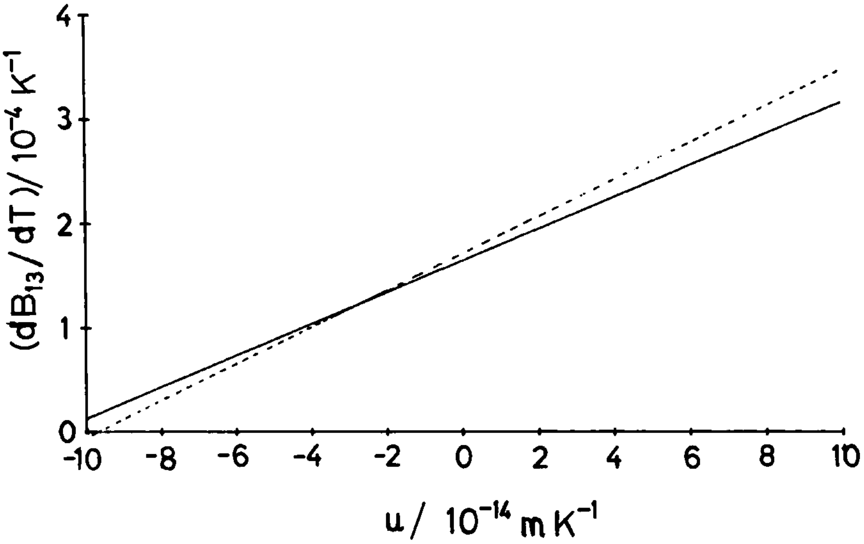

FIGURE 3 Temperature derivative of the birefringence as a function of the temperature derivative of the molecular displacement parallel to the *a* axis.

ilar results, with a linear dependence of dB_{13}/dT on u for u between −0.1 and +0.1 pm K^{-1}. In this range, the changes in dB_{13}/dT are of the same size as those caused by a 2° rotation for the molecular polarizability (*i*) with the smaller anisotropy (note the different ordinate scales in Figures 2 and 3).

Figure 4 shows dB_{13}/dT calculated as a function of w for the rate of change of internal displacement $(0, 0, w)$ relative to the lattice structure after thermal expansion. Again the two polarizabilities give similar results, but dB_{13}/dT is found to have a strong quadratic dependence on w in addition to a linear dependence comparable to that on u. (A larger range is shown for w than for u to emphasize the quadratic behavior.) Its origin is not clear, except that a given absolute displacement is a larger percentage change in the c direction than in the a direction, since c is only 74% of a.

Comparison of Figures 2, 3 and 4 shows that a wide range of possible combinations of rotations and displacements can reproduce the experimental value of dB_{13}/dT. This assumes that the effects of the different internal strains are simply additive, which is possibly not correct for combinations involving w because of the nonlinear dependence shown in Figure 4. This nonlinear behavior has two consequences. First, it allows two different displacements w to give the same dB_{13}/dT. Secondly, it prevents θ and u from both being large and positive, since there is a minimum value of dB_{13}/dT accessible by changing w. In practice, the intermolecular repulsions should ensure that none of the internal strains is large. The internal strains required to fit the experimental dB_{13}/dT are smaller when the more anisotropic polarizability (*ii*) is used.

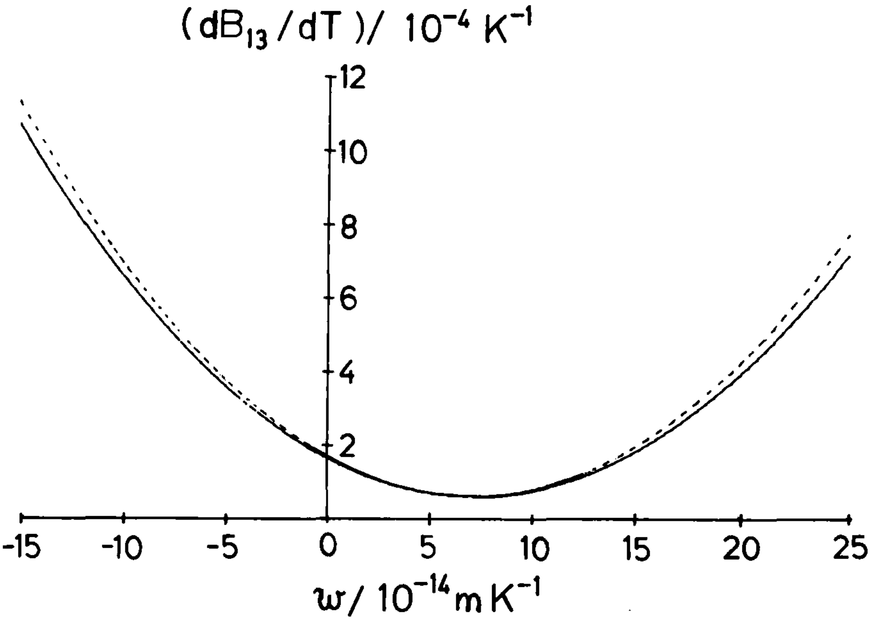

FIGURE 4 Temperature derivative of the birefringence as a function of the temperature derivative of the molecular displacement parallel to the *c* axis.

4 DISCUSSION

We have presented calculations of the temperature derivative of the birefringence B_{13} in the carbazole crystal as a function of the independent temperature derivatives of internal strain (internal thermal expansion coefficients[1]). The experimentally observed[7] value of dB_{13}/dT can be reproduced by a wide value of internal strains for a given polarizability; the required strains are smaller for a more anisotropic polarizability.

The earlier calculations of molecular rotation from the birefringence change[7] are unfortunately subject to large uncertainties because of the more empirical method used there. The anisotropic Lorentz field provides a simple and broadly correct method of treating the dielectric properties of molecular crystals, but it should not be relied upon too heavily. It cannot take account of individual molecular displacements. It is also known to be deficient in showing anisotropy which is too small or in the wrong direction.[27,28] Treatments based on the anisotropic Lorentz local field are therefore very likely to lead to erroneous results for subtle anisotropic strain derivatives of dielectric properties.

Because carbazole has three internal degrees of freedom for rigid molecules, measurements of the single birefringence B_{13} as a function of temperature do not serve to define all three displacements. Measurements of all three birefringences could define all the displacements by the solution of three simultaneous equations, although the birefringences B_{23} and B_{12} might be less sensitive to the displacements than B_{13}.

It would also be of interest to perform an analysis of the present sort on a crystal where the internal displacements have been determined by X-ray measurements, so that for example the appropriate polarizability could be ascertained. One crystal for which the structural information is available is anthraquinone.[29] The molecules lie on centers of symmetry allowing no translational displacements but arbitrary rotational displacements. The molecular rotations could therefore be determined from measurements of the three birefringences as a function of temperature. It is hoped that such measurements could be performed to establish conclusively the validity of the present method of deducing internal strains from birefringences. By lifting the restrictive assumptions in previous work[3,4,7] the present calculations do however confirm that birefringence is a sensitive function of internal strains.

Acknowledgments

We are grateful to Dr. W. J. Kusto and Professor J. W. Rohleder for helpful correspondence and discussions. We thank the Science Research Council for a Research Studentship to C. J. S.

References

1. T. H. K. Barron, T. G. Gibbons and R. W. Munn, *J. Phys. C: Solid St. Phys.*, **4**, 2805 (1971).
2. R. W. Munn and T. Luty, *Faraday Disc. Roy. Soc. Chem.*, **69**, 107 (1980).
3. P. J. Bounds and R. W. Munn, *Mol. Cryst. Liq. Cryst.*, **44**, 301 (1978).
4. P. J. Bounds and R. W. Munn, *Chem. Phys.*, **39**, 165 (1979).
5. E. A. Ballik, D. J. Gannon and J. A. Morrison, *J. Chem. Phys.*, **58**, 5639 (1973).
6. W. J. Kusto and J. W. Rohleder, *Mol. Cryst. Liq. Cryst.*, **51**, 215 (1979).
7. W. J. Kusto and J. W. Rohleder, *Mol. Cryst. Liq. Cryst.*, **55**, 151 (1979).
8. P. G. Cummins, D. A. Dunmur and R. W. Munn, *Chem. Phys. Letters*, **22**, 519 (1973); **36**, 199 (1975).
9. F. P. Chen, D. M. Hanson and D. Fox, *Chem. Phys. Letters*, **30**, 337 (1975); *J. Chem. Phys.*, **63**, 3878 (1975).
10. L. M. Hafkenschied and J. Vlieger, *Physica*, **75**, 57 (1974); **79A**, 517 (1975); **85A**, 129 (1976).
11. T. Luty, *Chem. Phys. Letters*, **44**, 335 (1976).
12. P. J. Bounds and R. W. Munn, *Chem. Phys.*, **24**, 343 (1977).
13. R. W. Munn, *Chem. Phys.*, **50**, 119 (1980).
14. L. J. Soltzberg, P. A. Piliero and M. R. O'Shea, *Mol. Cryst. Liq. Cryst.*, **29**, 151 (1974).
15. P. J. Bounds, Ph.D. Thesis, UMIST (1978).
16. M. Kurahashi, M. Fukuyo, A. Shimada, A. Furusaki and I. Nitta, *Bull. Chem. Soc. Japan*, **42**, 2174 (1969).
17. P. G. Cummins, D. A. Dunmur, R. W. Munn and R. J. Newham, *Acta Cryst.*, **A32**, 847 (1976).
18. D. A. Dunmur, W. H. Miller and R. W. Munn, *Chem. Phys. Letters*, **47**, 592 (1977).
19. T. Luty, A. Mierzejewski and R. W. Munn, *Chem. Phys.*, **29**, 353 (1978).
20. T. Luty and R. W. Munn, *Chem. Phys.*, **43**, 295 (1979).

21. A. H. Price, J. O. Williams and R. W. Munn, *Chem. Phys.*, **14,** 413 (1976).
22. A. Chablo and A. Hinchliffe, *Chem. Phys. Letters*, **72,** 149 (1980).
23. P. J. Bounds, *Chem. Phys. Letters*, **79,** 143 (1980).
24. N. S. Hush and M. L. Williams, *Chem. Phys. Letters*, **6,** 163 (1970); M. J. S. Dewar, Y. Yamaguchi and S. H. Suck, *Chem. Phys. Letters*, **59,** 541 (1978).
25. H. A. Stuart and H. Volkmann, *Z. Physik*, **80,** 107 (1933).
26. P. G. Cummins, D. A. Dunmur, R. W. Munn and R. J. Newham, *Acta Cryst.*, **A32,** 854 (1976).
27. J. H. Meyling, P. J. Bounds and R. W. Munn, *Chem. Phys. Letters.*, **51,** 234 (1977).
28. R. W. Munn and S. M. Bourne, *Chem. Phys. Letters*, **75,** 403 (1980).
29. K. Lonsdale, H. J. Milledge and K. El Sayed, *Acta Cryst.*, **20,** 1 (1966).