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# Liquid Crystals

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# The anisotropic forces acting on the bonds of benzene in liquid crystals

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# The anisotropic forces acting on the bonds of benzene in liquid crystals

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The HH and CH dipolar couplings of benzene measured in five different liquid crystal solvents are subjected to an analysis which allows for the correlation between the molecular reorientational and vibrational motions. The number of adjustable parameters is reduced by treating the CH bonds or both the CH and CC bonds as effectively cylindrically symmetric entities. In this way detailed information on the anisotropic forces acting on the bonds of benzene dissolved in liquid crystals is obtained. The behaviour of the CC bonds, but not that of the CH bonds, may be explained by anisotropic dispersion forces. There is an approximately linear relation between the torques acting on the CH bonds of benzene and methane in the same liquid crystal environment. This suggests that these forces stem from a common interaction mechanism, possibly the van der Waals interaction between the atoms of the solute molecule and the liquid crystal surroundings or the interaction between the molecular quadrupole moment and the electric field gradient due to the surrounding medium. A bond additivity model for the molecular quadrupole moment tensor is developed and discussed.

## 1. Introduction

It has been shown recently that the N.M.R. spectral parameters of molecules dissolved in liquid crystals may include quite detailed information on anisotropic intermolecular forces [1–3]. This information may be extracted from the N.M.R. data by a new method of analysis which allows for the orientation-dependent perturbations of the molecular geometry. The perturbations depend on the distribution of the anisotropic forces within the molecule and may be described in terms of the torques acting on its bonds. In the present work the HH and CH dipolar couplings of benzene measured in five different liquid crystal solvents are analysed by the new method. The torques acting on its CC and CH bonds are determined as unambiguously as possible by using the minimum number of adjustable parameters. The resulting information on the anisotropic forces in liquid crystals gives ideas of the physical nature of the underlying interaction mechanism.

## 2. Theory

Consider the single particle potential energy $U_{\text{ext}}$ which is assumed to specify the external anisotropic forces acting on a molecule in a uniaxial liquid crystal environment. Its truncated series expansion in terms of the direction cosines made by the director in the molecular frame, $\cos\theta_\alpha$, defines the symmetric and traceless *interaction tensor* $A_{\alpha\beta}$ [1–3],

$$U_{\text{ext}} = -\frac{3}{2}\sum_{\alpha,\beta} A_{\alpha\beta}\cos\theta_\alpha\cos\theta_\beta. \tag{1}$$

There is a one-to-one correspondence between $A_{\alpha\beta}$ and the orientational tensor $S_{\alpha\beta}$ of the molecule; if one of these tensors is known, the other can be calculated.

The forces experienced by the molecule are made up of the forces acting on its segments (e.g. the bonds). The external potential energy of the segment $n$, $U^n_{\text{ext}}$, has the same functional form as $U_{\mathrm{ext}}$ given in equation (1), and may be specified by the *segmental* interaction tensor $A^n_{\alpha\beta}$ [1–3]. The forces acting on the segments tend to rotate them (as a whole, if they are rigid), resulting in two effects. First, the reorientational motion of the molecule may become anisotropic, giving rise to a non-zero orientational tensor $S_{\alpha\beta}$. Secondly, the segments may bend with respect to the molecule fixed frame, i.e. the forces induce orientation-dependent deformations on the molecular geometry [1–3]. Both of these effects, orientation and deformation, are determined by the segmental interaction tensors. These (traceless) tensors can be specified by their *anisotropies*

$$\begin{aligned} \Delta A_n &= A^n_3 - \tfrac{1}{2}(A^n_1 + A^n_2), \\ &= \tfrac{3}{2}A^n_3, \end{aligned} \tag{2}$$

and *asymmetries*

$$\eta_n = \frac{A^n_1 - A^n_2}{A^n_3}, \tag{3}$$

where $A^n_1$, $A^n_2$ and $A^n_3$ are their principal values. If the segments are considered as rigid isolated entities, the interaction parameters $\Delta A_n$ and $\eta_n$ can be treated as deformation-independent constants. The molecular interaction tensor $A_{\alpha\beta}$ is the sum of the segmental tensors $A^n_{\alpha\beta}$ (referred to a common molecular frame) and can be expressed as a function of the molecular geometry and the set of parameters $\Delta A_n$ and $\eta_n$.

Experimental information on the values of the parameters $\Delta A_n$ and $\eta_n$ is available from the N.M.R. observables of the molecule, such as dipolar and quadrupolar couplings. These observables are composed of *orientational* and *deformational* contributions (as well as small higher order terms, which can be ignored) [3]. The former is determined by the orientational tensor $S_{\alpha\beta}$ (which is specified by the molecular interaction tensor $A_{\alpha\beta}$) while the latter depends on the individual parameters $\Delta A_n$ and $\eta_n$. When the expressions for the deformational contributions are introduced into the equations of the observables, the parameters $\Delta A_n$ and $\eta_n$ can be determined by fitting these equations to the experimental values of the observables [2].

## 3. Results and discussion

For the benzene molecule the interaction tensor $A_{\alpha\beta}$ is built up from the bond tensors $A^{\mathrm{CC}}_{\alpha\beta}$ and $A^{\mathrm{CH}}_{\alpha\beta}$ (for the CC and CH bonds). Hence, assuming that the principal value $A^n_3$ is in the bond direction and the principal value $A^n_1$ is perpendicular to the bond in the molecular plane, the anisotropic forces acting on the molecule are characterized by four parameters: $\Delta A_{\mathrm{CC}}$, $\eta_{\mathrm{CC}}$, $\Delta A_{\mathrm{CH}}$ and $\eta_{\mathrm{CH}}$. These quantities, together with the geometry and harmonic force field of the molecule, can be taken to provide a complete specification for all the dipolar couplings of benzene.

In [2] the experimental HH and CH dipolar couplings of benzene were used to resolve the values of its four interaction parameters and the bond length ratio $r_{\mathrm{CH}}/r_{\mathrm{CC}}$ in two different liquid crystal solvents. There were five unknowns to be fitted for seven dipolar couplings in each case and consequently it was not possible to obtain accurate information on the interactions (whereas the bond length ratio was determined with standard deviations of 0·4 per cent). In seeking to reduce the number of unknowns, it is tempting to assume that the bond interaction tensors are nearly axially symmetric. A straightforward procedure is to fix the asymmetry parameter of the CH bond to zero and adjust $\Delta A_{\mathrm{CC}}$, $\eta_{\mathrm{CC}}$, $\Delta A_{\mathrm{CH}}$ and $r_{\mathrm{CH}}/r_{\mathrm{CC}}$. It turns out that there are very strong correlations between the resulting values of the adjustable parameters. These are shown in figures 1 and 2, where the interaction parameters $\Delta A_{CC}$, $\eta_{CC}$ and $\Delta A_{CH}$ are plotted as a function of $r_{CH}/r_{CC}$ in the region of good fit. These results have been obtained from sets of constrained fits where the ratio $r_{CH}/r_{CC}$ has been fixed to different values in its physically reasonable range (and $\eta_{CH}$ has been kept fixed to zero); these solutions are well determined because there are only three unknowns for seven dipolar couplings. The analyses have been carried out by using the most complete sets of experimental data available for the benzene molecule, measured in five different liquid crystal solvents, two sets by Diehl *et al.* [4] and three by Hiltunen *et al.* [5].

There are four checks on the credibility of the present results. First, the results must be capable of explaining the experimental data, in the sense that good fits are obtained for all sets of dipolar couplings. This is the case; the weighted R.M.S. error of the joint analysis of all the 35 couplings is 0·039 Hz. Secondly, the resulting solvent-independent bond length ratio $r_{CH}/r_{CC}$ should be in agreement with the result 0·777 ± 0·004 obtained by combining electron diffraction and infrared data [6]. Indeed, the value of $r_{CH}/r_{CC}$ does fall on this range, the best fit being obtained around $r_{CH}/r_{CC} = 0{\cdot}775$. Thirdly, because the CC bond interaction tensors are expected to be approximately axially symmetric (in view of the constraint $\eta_{CH} = 0$), there should exist a solution for which all the absolute values of $\eta_{CC}$ (in all the liquid crystal solvents) are simultaneously small. Finally, this solution should fall on the reasonable range of the bond length ratio. As can be seen from figure 1, both of these conditions are met; there is a region about $r_{CH}/r_{CC} = 0{\cdot}776$ where none of the absolute values of $\eta_{CC}$ is larger than 0·3.

In fact, it is possible to obtain quite good fits even by fixing both $\eta_{CH}$ and $\eta_{CC}$ to zero. Then there are three unknowns ($\Delta A_{CC}$, $\Delta A_{CH}$ and $r_{CH}/r_{CC}$) for seven dipolar couplings in each case, except that $r_{CH}/r_{CC}$ is constrained to be the same in all the liquid crystal solvents. At $r_{CH}/r_{CC} = 0{\cdot}77544$ the weighted R.M.S. error of the joint analysis of the 35 couplings is 0·059 Hz and the interaction parameters $\Delta A_{CC}$ and $\Delta A_{CH}$ shown in the table are obtained. If $\eta_{CC}$ is used as an additional adjustable parameter, the corresponding R.M.S. error is 0·039 Hz (around $r_{CH}/r_{CC} = 0{\cdot}775$), as discussed previously. Hence, the four parameter fit is not really decidedly better than the three parameter fit, in view of the fact that the conventional two parameter fit (in terms of $r_{CH}/r_{CC}$ and the orientational order parameter $S$, entirely neglecting the deformational contributions) is drastically worse, having an R.M.S. error of 2·210 Hz.

It is possible that the asymmetry parameters $\eta_{CH}$ and $\eta_{CC}$ are in fact negligible. The non-zero values obtained for $\eta_{CC}$ by the four parameter fit are small enough to allow of the interpretation that they might just be artifacts; especially as the analysis involves many approximations (rigidity of the bonds, etc.) which increase the uncertainty margins of the resulting parameters. At any rate, it may be concluded that the true values of the interaction parameters are within the ranges shown in figures 1 and 2.

Despite the considerable margin of the results, detailed information on the forces acting on the bonds of the benzene molecule is obtained. First, the values of $\Delta A_{CC}$ in all the liquid crystals are of the order of $10 \times 10^{-22}$ J; thus the CC bonds experience torques of this magnitude tending to orient them parallel with the director. This is reminiscent of the effects of anisotropic dispersion forces in the Maier–Saupe theory [7]. Secondly, $\Delta A_{CH}$ is *negative* (of the order of $-2 \times 10^{-22}$ J) in the liquid crystal phase IV and positive (of the order of $2 \times 10^{-22}$ J) in the other liquid crystals; thus

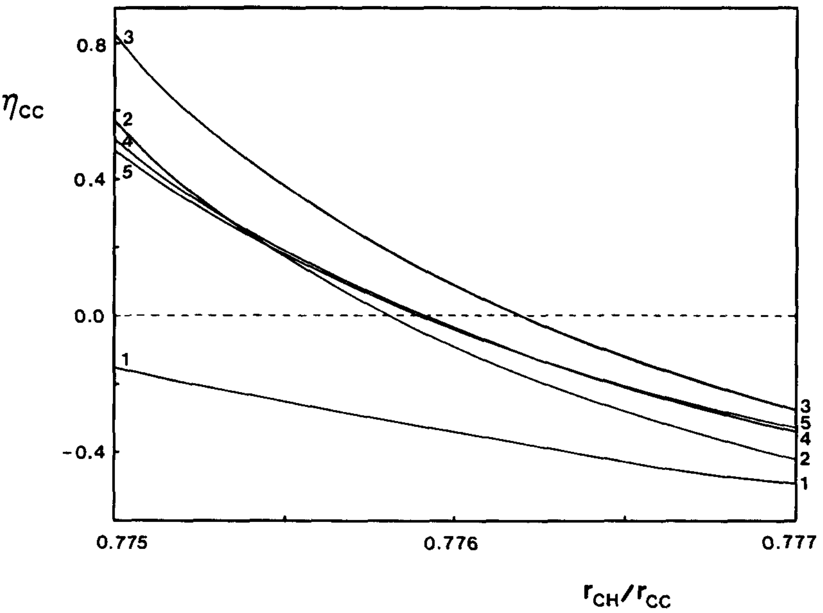

Figure 1. Relationships between the asymmetry parameters $\eta_{CC}$ of the CC bond interaction tensors and the bond length ratio $r_{CH}/r_{CC}$ of benzene in five different liquid crystal solvents (at 300 K), calculated by fixing the asymmetry parameters $\eta_{CH}$ of the CH bond interaction tensors to zero. The liquid crystals used in the experiments were: (1) phase IV (eutectic mixture of *p*-methoxy-*p*′-*n*-butyl-azoxybenzenes by Merck) [4]; (2) ZLI 1167 (a mixture of three cyclohexyl-cyclohexanes by Merck) [4]; (3) 65·0 wt % ZLI 1167 + 35·0 wt % EBBA (*N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline) [5]; (4) 60·8 wt % ZLI 1132 (a mixture of three phenylcyclohexanes and one biphenylcyclohexane by Merck) + 39·2 wt % phase IV [5]; (5) 67·3 wt % phase 1221 (mixture of phenylcyclohexanes, biphenylcyclohexane and phenylcyclohexane esters by Merck) + 32·7 wt % phase 997 (mixture of azoxy compounds and a biphenyl ester by Merck) [5].

Parameters obtained from the constrained least-squares fit to the 35 dipolar couplings of benzene in the five liquid crystal solvents (fixing the asymmetry parameters $\eta_{CC}$ and $\eta_{CH}$ to zero and treating the bond length ratio $r_{CH}/r_{CC}$ as a single solvent-independent parameter), and the interaction parameters $\Delta A_{CH}$ of methane in the same liquid crystal solvents (calculated from the dipolar couplings $D_{CH}$ of methane [3, 5, 8]).

| Liquid crystal† | $\Delta A_{CC}/10^{-22}$ J | $\Delta A_{CH}/10^{-22}$ J | $\Delta A_{CH}(CH_4)/10^{-22}$ J |
|---|---|---|---|
| 1 | 10·51(2)‡ | −2·68(2) | −4.4(4) |
| 2 | 11·78(3) | 3·57(4) | 2·3(2) |
| 3 | 10·77(5) | 1·91(5) | 0·0(2) |
| 4 | 13·06(4) | 2·10(4) | −0·8(2) |
| 5 | 13·19(4) | 1·47(4) | −0·9(2) |

Bond length ratio $r_{CH}/r_{CC}$ = 0·77544(5).

Weighted R.M.S. error of the fit 0·059 Hz.

† The numbering of the liquid crystals is given in the caption of figure 1.

‡ Uncertainties in parentheses are one standard deviation in the last figure quoted (neglecting the uncertainties in the theoretical expressions for the dipolar couplings).

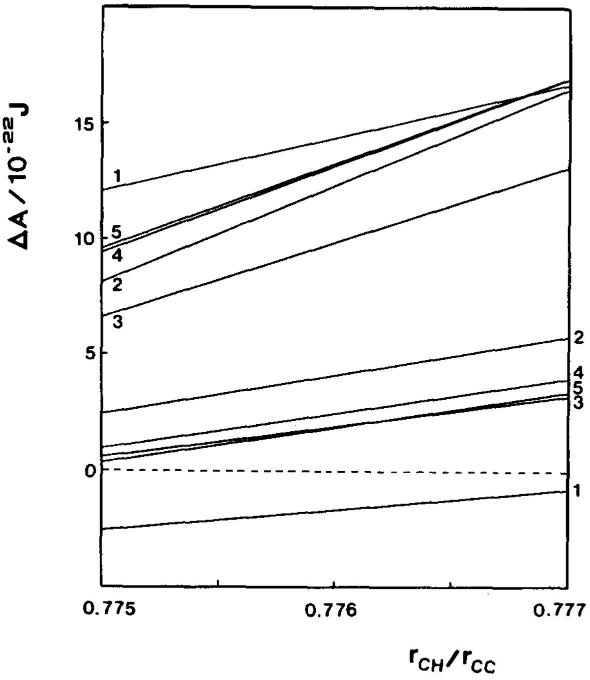

Figure 2. Relationships between the anisotropies of the CC bond interaction tensors, $\Delta A_{CC}$ (upper lines), the anisotropies of the CH bond interaction tensors, $\Delta A_{CH}$ (lower lines), and the bond length ratio $r_{CH}/r_{CC}$, calculated by fixing the asymmetry parameters $\eta_{CH}$ of the CH bond interaction tensors to zero. The numbering of the liquid crystals is given in the caption of figure 1.

the torques acting on the CH bonds in phase IV tend to orient them *perpendicular* to the director. This behaviour cannot be accounted for by the anisotropic dispersion forces. Finally, there is an approximately linear relation between the values of $\Delta A_{CH}$ of benzene and *methane* in the same sample tube: for both of these molecules $\Delta A_{CH}$ is lowest (actually negative) in phase IV and highest (positive) in ZLI 1167, and the intermediate values are all approximately equal (see the table and figure 2). This parallel behaviour implies that the torques acting on the CH bonds of benzene and methane (and some other molecules as well [8–11]) stem from a common interaction mechanism. This mechanism could be the van der Waals interaction between the atoms of the solute molecule and the liquid crystal surroundings, which has recently been shown to be capable of explaining the behaviour of methane in different liquid crystals [3].

The behaviour of the CH bonds could also be rationalized in terms of the interaction between the molecular quadrupole moment and the average electric field gradient due to the liquid crystal environment. Patey *et al.* [12] have suggested that this interaction makes a considerable contribution to the alignment of several molecules in liquid crystals. The corresponding molecular interaction tensor is $A_{\alpha\beta} = \frac{1}{3}F_{\parallel}Q_{\alpha\beta}$ where $F_{\parallel}$ is the field gradient in the direction of the director at the centre of the molecule and $Q_{\alpha\beta}$ is the molecular quadrupole moment tensor referred to the centre of the molecule. Owing to its definition, the quadrupole moment tensor can be written as a sum of contributions associated with each segment of the molecule. For example, an uncharged bond at the point **r** from the centre of the molecule makes the contribution

$$Q_{\alpha\beta} = Q^0_{\alpha\beta} + \tfrac{3}{2}\left(\mu_\alpha r_\beta + \mu_\beta r_\alpha - \tfrac{2}{3}\delta_{\alpha\beta}\sum_\gamma \mu_\gamma r_\gamma\right), \qquad (4)$$

where $\mathbf{Q}^0$ is the 'intrinsic' quadrupole moment tensor of the bond, referred to the centre of the bond, and $\boldsymbol{\mu}$ is its dipole moment [13]. (Equation (4) is exact and shows that the molecular quadrupole moment tensor is strictly bond additive, contrary to a recent claim [14]. However, if the so-called zero-order formulation of the bond additivity is used in calculating the *derivatives* of the tensor with respect to the nuclear displacements [3], then approximations are involved, as discussed in the Appendix.)

Because the dipole moment of a $C^-H^+$ bond of benzene is parallel with its position vector **r**, the $\boldsymbol{\mu}$-dependent part of the bond quadrupole moment tensor (4), $\mathbf{Q}^\mu_{CH} \equiv \mathbf{Q}_{CH} - \mathbf{Q}^0_{CH}$ ($\mathbf{Q}^0_{CH}$ is probably small in comparison with $\mathbf{Q}^\mu_{CH}$), is axially symmetric and has the anisotropy $\Delta Q^\mu_{CH} = 3\mu r$. Thus the anisotropy of the corresponding bond interaction tensor is $\Delta A^\mu_{CH} = F_\parallel \mu r$. It is possible to obtain an approximate idea of its value in the liquid crystals phase IV and ZLI 1167 by resorting to the field gradients derived by Patey *et al.* [12]. Their estimates of the $F_\parallel$s in phase V (which is closely related to phase IV) and in ZLI 1167 are $-1{\cdot}7 \times 10^{18}\,\mathrm{V\,m^{-2}}$ and $1{\cdot}8 \times 10^{18}\,\mathrm{V\,m^{-2}}$, respectively (actually the field gradients given in [12] are the elements in the direction of the magnetic field; thus in the case of ZLI 1167 whose director is perpendicular to the field they are equal to $-\tfrac{1}{2}F_\parallel$). Hence, using the estimate $\mu = 1 \times 10^{-30}$ Asm for the CH bond moment [15] and the value $r = r_{CC} + \tfrac{1}{2}r_{CH} = 1{\cdot}939$ Å for the distance of the centre of the CH bond from the centre of the molecule [6], the anisotropies $\Delta A^\mu_{CH}$ of $-3{\cdot}3 \times 10^{-22}$ J and $3{\cdot}5 \times 10^{-22}$ J are obtained in phase IV and ZLI 1167, respectively. These numbers are similar in sign and magnitude to the corresponding values of $\Delta A_{CH}$ resulting from the present analyses (e.g. if $\eta_{CC}$ and $\eta_{CH}$ are zero, then $\Delta A_{CH}$ is $-2{\cdot}68 \times 10^{-22}$ J and $3{\cdot}57 \times 10^{-22}$ J in phase IV and ZLI 1167, as shown in the table).

Thus the suggestion of Patey *et al.* [12] is not in conflict with the present results. However, the quadrupole moment–electric field gradient mechanism cannot explain the positive sign of $\Delta A_{CC}$ in all the liquid crystals. As noted previously, this finding could be accounted for by the anisotropic dispersion forces of the Maier–Saupe theory [7]. These forces are proportional to the polarizability anisotropy, which is very small for the CH bond [15]. Thus the present results do not rule out the possibility that both the electric field gradient and dispersion interactions make important contributions to the orienting forces; the CH bonds experience primarily the former interaction while the forces acting on the CC bonds are dominated by the latter interaction.

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## Appendix

The contribution to the quadrupole moment tensor of an uncharged bond due to its dipole moment is

$$Q^\mu_{\alpha\beta} = \tfrac{3}{2}\mu r\left(l_\alpha l'_\beta + l_\beta l'_\alpha - \tfrac{2}{3}\delta_{\alpha\beta}\sum_\gamma l_\gamma l'_\gamma\right), \qquad (\mathrm{A\,1})$$

where **l** and **l**′ are unit vectors in the direction of $\boldsymbol{\mu}$ and **r**, respectively (see equation (4)). The directions of the principal axes of this tensor are specified by the unit vectors

$$\mathbf{l}_1 = (\mathbf{l} - \mathbf{l}')\bigg/\left(2\sin\frac{\alpha}{2}\right), \quad \mathbf{l}_2 = (\mathbf{l}' \times \mathbf{l})/\sin\alpha, \quad \mathbf{l}_3 = (\mathbf{l} + \mathbf{l}')\bigg/\left(2\cos\frac{\alpha}{2}\right),$$

and the corresponding principal values are

$$Q_1^\mu = \tfrac{1}{2}\mu r(\cos\alpha - 3), \quad Q_2^\mu = -\mu r\cos\alpha, \quad Q_3^\mu = \tfrac{1}{2}\mu r(\cos\alpha + 3),$$

where $\alpha$ is the angle between $\mathbf{l}$ and $\mathbf{l}'$. Thus the tensor (A 1) does not, in general, fully fit in with the zero-order formulation of the bond additivity theory [3]: the tensor is not strictly an isolated entity, in the sense that the 3 axis does not coincide with the bond direction and the principal values depend not only on the bond length but on other variables as well.

The zero-order bond additivity approximation provides an efficient method to treat the molecular interaction tensor $A_{\alpha\beta}$ (whose functional dependence on the properties of the molecule and its environment is generally not known) [3]. In this connection its most important application is in the calculation of the derivatives of $A_{\alpha\beta}$ with respect to the vibrational normal coordinates, as they appear in the expressions of the deformational contributions to the N.M.R. observables [1–3].

Because the functional form of the tensor $Q^\mu_{\alpha\beta}$ (A 1) is known, it is not necessary to use the zero-order approximation in the calculation of its derivatives. Hence, assuming that $\boldsymbol{\mu}$ is in the direction of the bond (from nucleus $i$ to nucleus $j$) and its magnitude $\mu = |\boldsymbol{\mu}|$ depends only on the length of the bond, $r_{ij}$, then the derivatives of $Q^\mu_{\alpha\beta}$ with respect to the cartesian displacement coordinates $\Delta_{n\nu}$ (= the displacement of the coordinate $\nu$ of the nucleus $n$ from its equilibrium position) are

$$\begin{aligned}\frac{\partial Q^\mu_{\alpha\beta}}{\partial \Delta_{n\nu}} = (\delta_{jn} - \delta_{in})\Bigg[&\frac{3\mu r}{2r_{ij}}(l'_\alpha\delta_{\beta\nu} + l'_\beta\delta_{\alpha\nu} - \tfrac{2}{3}l'_\nu\delta_{\alpha\beta})\\ &- \frac{3rl_\nu}{2}\left(\frac{\mu}{r_{ij}} - \mu'\right)\left(l_\alpha l'_\beta + l_\beta l'_\alpha - \tfrac{2}{3}\delta_{\alpha\beta}\sum_\gamma l_\gamma l'_\gamma\right)\Bigg]\\ &+ (\delta_{jn} + \delta_{in})\frac{3\mu}{4}(l_\alpha\delta_{\beta\nu} + l_\beta\delta_{\alpha\nu} - \tfrac{2}{3}l_\nu\delta_{\alpha\beta}).\end{aligned} \tag{A 2}$$

Here $\mu'$ is the derivative of $\mu$ with respect to the bond length $r_{ij}$. Equation (A 2) is based on rather safe assumptions about the behaviour of bond dipole moments [15] and should provide a quite reliable prescription for the calculation of the derivatives of $Q^\mu_{\alpha\beta}$.

In the special case of a CH bond of benzene (and methane, etc.) the vectors $\boldsymbol{\mu}$ and $\mathbf{r}$ are parallel; $\mathbf{l} = \mathbf{l}'$. Then the derivatives of $Q^\mu_{\alpha\beta}$ with respect to the displacement coordinates of the hydrogen nucleus, $\Delta_{j\nu}$, can be written as

$$\begin{aligned}\frac{\partial Q^\mu_{\alpha\beta}}{\partial \Delta_{j\nu}} = &\frac{\Delta Q_\mu}{r_{ij}}\left(\frac{1}{2} + \frac{r_{ij}}{4r}\right)(l_\alpha\delta_{\beta\nu} + l_\beta\delta_{\alpha\nu} - 2l_\alpha l_\beta l_\nu)\\ &+ \Delta Q'_\mu l_\nu(l_\alpha l_\beta - \tfrac{1}{3}\delta_{\alpha\beta}).\end{aligned} \tag{A 3}$$

Here $\Delta Q_\mu = 3\mu r$ is the anisotropy of $\mathbf{Q}_\mu$ and $\Delta Q'_\mu = 3\mu' r + \frac{3}{2}\mu$ is its derivative with respect to $r_{ij}$. If the corresponding equation is derived by the zero-order bond additivity theory (using equation (41) of [3]), a very similar result is obtained. The zero-order equation has exactly the same form as equation (A 3) but the factor $1/2 + r_{ij}/4r$ (= 0·64 for benzene, 1 for methane, etc.) is reduced to 1.

The derivatives of $Q^\mu_{\alpha\beta}$ with respect to the normal coordinates, $Q_k$, are

$$\begin{aligned}\frac{\partial Q^\mu_{\alpha\beta}}{\partial Q_k} &= \sum_n\sum_\nu b^k_{n\nu}\frac{\partial Q^\mu_{\alpha\beta}}{\partial \Delta_{n\nu}},\\ &= \sum_\nu\left(b^k_{i\nu}\frac{\partial Q^\mu_{\alpha\beta}}{\partial \Delta_{i\nu}} + b^k_{j\nu}\frac{\partial Q^\mu_{\alpha\beta}}{\partial \Delta_{j\nu}}\right),\end{aligned} \tag{A 4}$$

where $b^k_{n\nu}$ are the derivatives of $\Delta_{n\nu}$ with respect to $Q_k$ [2]. Owing to the conditions that no motion of the centre of mass and no rotation of the molecule as a whole takes place during the normal vibrations, the displacements $\Delta_{n\nu}$ in $Q_k$ and the coefficients $b^k_{n\nu}$ of light nuclei are usually much larger than those of heavier nuclei. Thus, for the CH bond, equation (A 4) can be approximated by setting $b^k_{i\nu}$ to zero. The resulting equation contains the derivatives of $Q^\mu_{\alpha\beta}$ with respect to the displacements of the hydrogen nucleus only, for which equation (A 3) is valid. Because there is a close resemblance between equation (A 3) and its zero-order counterpart, it may be concluded that in the present case the zero-order bond additivity formulation provides a viable treatment for the molecular quadrupole moment tensor.

In the general case the more exact bond additivity equation (A 2) should be preferred in treating $Q^\mu_{\alpha\beta}$. None the less, the zero-order formulation continues to provide a reasonable method for treating the molecular interaction tensor $A_{\alpha\beta}$, because $A^\mu_{\alpha\beta} = \frac{1}{3}F_{\|}Q^\mu_{\alpha\beta}$ can never make the sole contribution to $A_{\alpha\beta}$.

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