Optical Anisotropies of Methyl Benzoate and Diesters of Benzenedicarboxylic Acids as Determined from the Analysis of Kerr Constants and Depolarized Light Scattering Measurements

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Mean-square optical anisotropies of methyl esters of benzoic, terephthalic, isophthalic and phthalic acids have been measured at $T = 25$ °C by analysis of the depolarized Rayleigh spectra of their dilute solutions in CCl_4 and $CHCl_3$. A planar Fabry–Perot interferometer was used to record the spectra and the VH spectrum of benzene was used as standard. The experimental values thus obtained were $\langle\gamma^2\rangle = 46$, 136, 97 and 58 $Å^6$ respectively, for methyl benzoate, dimethyl terephthalate, dimethyl isophthalate and dimethyl phthalate. The analysis of these experimental results, together with values of Kerr constants of the same molecules taken from the literature, allows the formulation of the anisotropic part of the optical polarizability tensors of phenyl and ester groups, including the inductive effects produced when these groups are linked together. The results seem to indicate that the inductive effects do not depend on the number of ester groups or the positions by which they are attached to the benzene ring; however they are very sensitive to whether both groups are coplanar.

Optical properties such as mean-square optical anisotropy or either electric or magnetic birefringence are frequently used as probes in conformational analysis of polymers.[1] The applicability of these properties to test the conformational properties of a given system arises from their great sensitivity to many microscopic features of polymers, including aspects like molecular geometry, rotational states, conformational energies, *etc.* The standard procedure used in this kind of analysis consists of a critical comparison between theoretical and experimental values of the property used as probe.

Since most properties of polymeric chains are usually computed by adding contributions from their constitutive elements,[2] either bonds or groups of bonds, the whole analysis relies on the strict additivity of those contributions. Bond lengths used in the calculation of end to end distances are perfectly additive, however, neither dipole moments nor optical anisotropies can be assigned to different chemical bonds in such a way that the overall dipole moment or optical anisotropy of a given molecule can be computed by adding those bond contributions. The reason is that when two polar groups are close in a molecule, each of them modifies the polarity of the other; conversely, two groups having large electron mobility and therefore high optical polarizability, *e.g.* two conjugated C=C bonds, produce a delocalization which is much larger than the sum of their contributions. This so called *inductive effect* prevents strict additivity of properties such as dipole moments or optical anisotropies.

It is well documented in the literature that inductive effects on dipole moments do not propagate across more than a few non-polar bonds[1] so that additive contributions μ_i can be obtained by assigning values to polar groups rather than to polar bonds. These contributions can be added to compute the total dipole moment of any given molecule provided that each μ_i represents the dipole moment of a group which is separated by at least two or three non-polar bonds from any other polar group. A typical example of this procedure will be given below when the dipole moments of several molecules are computed by adding contributions assigned to their polar groups.

Unfortunately, inductive effects on optical polarizabilities are not yet well understood and a result, a standard procedure for assigning contributions to the optical polarizability tensor $\boldsymbol{\alpha}$ or to its anisotropic part $\hat{\boldsymbol{\alpha}}$ is not available at present. This is probably the worst limitation that the calculation of optical properties of polymers faces nowadays since in most cases the parameters defining the $\hat{\boldsymbol{\alpha}}_i$ tensors of each unit have to be adjusted for the polymer of interest prior to being used to compute the optical properties of the whole chain.

The best procedure for obviating this problem would be to perform an *ab initio* calculation of the $\hat{\boldsymbol{\alpha}}$ tensor for several molecules having chemical structures similar to the repeating units of the studied polymer. Unfortunately, this calculation is too complicated for most of the molecules that could be used for this purpose and, although some attempts are being made to use approximate quantum mechanics procedures to compute those tensors,[3–5] the results are not yet accurate enough to allow an unambiguous evaluation of inductive effects.

An alternative procedure often used[6–13] for obtaining the $\hat{\boldsymbol{\alpha}}$ tensors consists of the analysis of optical properties of model molecules whose conformational statistics are well established so that a comparison between experimental and theoretical values of those properties can be used to determine the parameters defining the $\hat{\boldsymbol{\alpha}}$ tensors.

In this paper we present the determination of the $\hat{\boldsymbol{\alpha}}$ tensors of phenyl and ester groups, including the inductive effects produced when these two kinds of groups are linked together, by the analysis of the experimental values of mean-square optical anisotropies $\langle\gamma^2\rangle$ and Kerr contatns ${}_mK$ of methyl benzoate (MB), dimethyl terephthalate (DMT), dimethyl isophthalate (DMI) and dimethyl phthalate (DMP). The phenyl and ester groups are of particular interest because they are constitutive units for polyesters derived from benzenedicarboxylic acids, and several attempts have been made to obtain these tensors.[10–13] In fact, one of us participated in a recent determination of these tensors[13] through the analysis of the ${}_mK$ values of the same molecules studied in the present work. However, this analysis relied on a value for $\langle\gamma^2\rangle$ of MB obtained several years ago,[10] a value which, according to more recent determinations,[14] was probably overestimated owing to the inclusion of collision-induced anisotropic scattering. Thus, the difference between the present work and the previous

Table 1 Experimental values of dipole moments $\langle\mu^2\rangle^{\frac{1}{2}}$, mean-square optical anisotropies $\langle\gamma^2\rangle$, and Kerr constants $_mK$ for the molecules of methyl benzoate (MB), dimethyl terephthalate (DMT), dimethyl isophthalate (DMI) and dimtehyl phthalate (DMP)

Molecule	$\langle\mu^2\rangle^{\frac{1}{2}a}$/D	$\langle\gamma^2\rangle^b$/Å^6	$_mK^c/10^{-25}$ m^5 V^{-2} mol^{-1}
MB	1.89	46	9.0
DMT	2.30	136	8.0
DMI	2.23	97	30.6
DMP	2.6–2.8	58	0.7

[a] Taken from reference 15. Solvent: benzene, T = 25 °C. [b] Present work. Solvent: CCl_4 for MB, DMI and DMP; $CHCl_3$ for DMT, T = 25 °C. Experimental error not higher than ±4%. [c] Taken from reference 13. Averages over three solvents (cyclohexane, *p*-dioxane and carbon tetrachloride), T = 20 °C.

analysis comes from the availability of experimental values of $\langle\gamma^2\rangle$ for the four molecules. These values allow for a more secure determination of the $\hat{\alpha}$ tensors, and permit us to test the conclusions suggested in the previous analysis which indicated that the inductive effects between ester and phenyl modify the optical parameters of both groups. These modifications seemed to be rather independent of the number of ester groups and the positions at which they are attached to the phenyl ring, but it was impossible to elucidate whether they change from planar to non-planar molecules.

Experimental

Materials.—Methyl benzoate (MB), dimethyl terephthalate (DMT), dimethyl phthalate (DMP), dimethyl isophthalate (DMI) and the solvents carbon tetrachloride and chloroform were purchased from Aldrich; all were of analytical grade and were used without further purification. Dust-free solutions were obtained by filtering through a 0.2 μm Teflon millipore filter directly into the rectangular Hellma cuvette. Solute concentrations were in the range from 2–7 wt.%.

Depolarized Rayleigh Scattering.—The depolarized Rayleigh spectra $I_{VH}(\omega)$ for the solutions of MB, DMI and DMP in CCl_4 and DMT in $CHCl_3$ were taken at 25 °C and at a scattering angle of 90° with the apparatus described elsewhere.[14] The absolute Rayleigh ratio R_{VH} was obtained from the integrated intensities of the solution, solvent and standard benzene. The optical anisotropies $\langle\gamma^2\rangle$ computed from eqn. (1), were found to be experimentally insensitive to

$$\langle\gamma^2\rangle = 15\left(\frac{\lambda}{2\pi}\right)^4\left(\frac{3}{n^2+2}\right)^2\left(\frac{R_{VH}}{\rho}\right) \quad (1)$$

concentration variations over the range 2–7 wt.%. The physical quantities in eqn. (1) are λ = 498 nm, the wavelength of the laser *in vacuo*, n the refractive index of the solution and ρ the solute number density. We have used the second power Lorentz local field correction in eqn. (1); the exact form of this correction is still a point of controversy.[14] The main advantage of using Fabry–Perot interferometry to determine $\langle\gamma^2\rangle$ is the elimination of the unwanted high frequency component of the collision-induced scattering which appears in the non-zero background of the $I_{VH}(\omega)$.

Table 1 summarizes the results obtained for the four molecules, together with their respective values of dipole moments[15] and Kerr constants[13] taken from the literature. All of these results will be used in the next section.

We have also determined the orientational relaxation time τ_o of the solute molecules by recording the $I_{VH}(\omega)$ using a Burleigh plane Fabry–Perot at a free spectral range of 240 GHz. The experimental spectra were represented by a single Lorentzian function plus a baseline and the relaxation times calculated as the inverse of the half-width at half-height of the peak. At 25 °C and the range of concentrations mentioned above, τ_o amounts to 4.3, 15, 26 and 33 ps for DMT, MB, DMP and DMI, respectively. It is noteworthy that, among the isomeric compounds, the approximately symmetric top DMT undergoes very fast reorientation owing to its very low hydrodynamic volume.

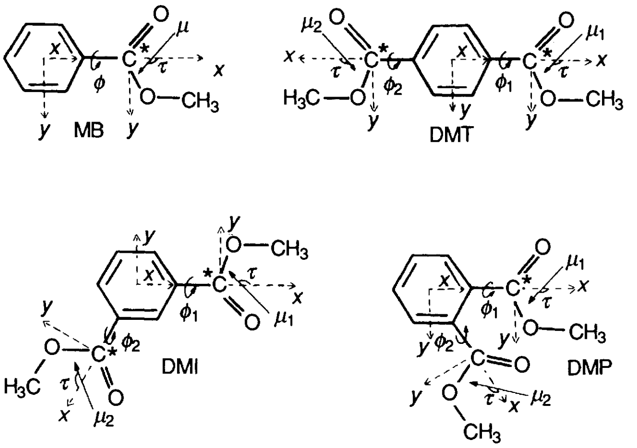

Fig. 1 Planar conformations of the MB, DMT, DMI and DMP molecules taken as origin for the rotations over the C^{ar}–C^* bonds. Dipole moments of the ester group are represented by an arrow pointing from the negative to the positive centre of charge. Co-ordinate systems used to write the $\hat{\alpha}$ tensors of ester and phenyl residues are also indicated.

Results and Discussion

Theoretical Analysis.—The geometries and conformational energies of these molecules were taken from the literature.[13] Fig. 1 shows a sketch of the four molecules in the planar conformation that is taken as the origin for rotations over the C^{ar}–C^* bonds. The direction of the dipole moments of the ester groups and co-ordinate systems used in the analysis are also indicated in Fig. 1. Each ester group was considered to have a dipole moment of μ = 1.89 D in a direction that makes an angle τ = 123° with the C^{ar}–C^* bond.

Only planar conformations were considered in the cases of MB, DMT and DMI molecules. Two conformations defined as $\varphi_1 = \varphi_2$ (as shown in Fig. 1) and $\varphi_1 = \varphi_2 + 180$ were allowed for DMT. The energy difference between these two conformations is too small to be significant, and therefore both conformations were equally weighted in the computation of averages. The DMI molecule has four allowed conformations obtained by taking each of φ_1 and φ_2 equal to either 0 or 180°. The only significant interaction between the two ester groups of this molecule is the dipole–dipole interaction that is *ca.* $E_\gamma \approx$ 0.2 kcal mol^{-1} higher in $\varphi_1 = \varphi_2 = 0$ (as shown in Fig. 1) than in the other three conformations.* We have used the value E_γ = 0.2 kcal mol^{-1} through all the calculations described in this work. The dipole moments calculated for the two molecules with this very simple conformational model are $\langle\mu^2\rangle^{\frac{1}{2}}$ = 2.24 and 2.33 D for DMT and DMI, respectively, are in good agreement with the experimental results indicated in Table 1. This agreement between theory and experience validates the conformational model used in the calculation.

In the case of DMP, planar conformations are forbidden because of steric repulsions between the two ester groups. However, the exact departure from planarity has not yet been well determined.[13,16] We have performed semiempirical

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* 1 cal = 4.184 J.

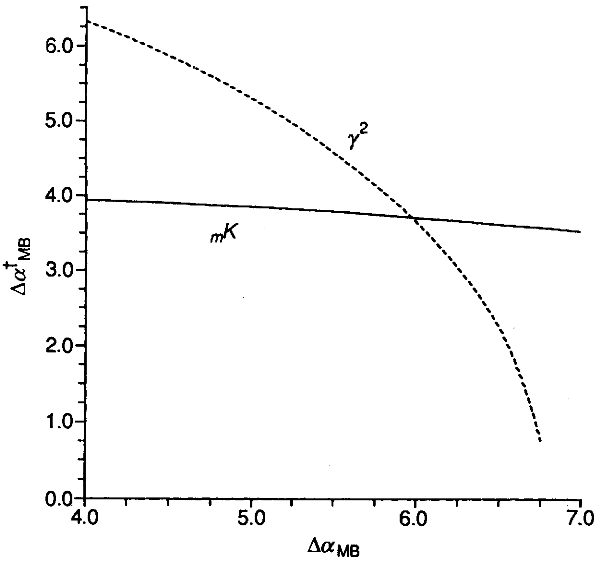

Fig 2 Values of the parameters $\Delta\alpha_{MB}$ and $\Delta\alpha^{\dagger}_{MB}$ that reproduce the experimental results of $\langle\gamma^2\rangle$ and $_mK$ of the methyl benzoate molecule. Calculations were preformed at T = 20°C taking $\alpha_{xy} = 0$.

Table 2 Values of the optical parameters, in units of Å^3, that reproduce the experimental results of $\langle\gamma^2\rangle$ and $_mK$ of the MB and DMT molecules.

	Value of the non-diagonal elements		
	$\alpha_{xy} = -0.2$	$\alpha_{xy} = 0.0$	$\alpha_{xy} = 0.2$
(*a*) Anisotropies of actual molecules			
$\Delta\alpha_{MB}$	6.2	5.9	5.7
$\Delta\alpha^{\dagger}_{MB}$	3.2	3.7	4.2
$\Delta\alpha_{DMT}$	10.0	10.0	10.0
$\Delta\alpha^{\dagger}_{DMT}$	6.9	6.9	6.9
(*b*) Anisotropies of constitutive groups [eqn. (8)]			
$\Delta\alpha_E$	3.8	4.1	4.3
$\Delta\alpha^{\dagger}_E$	3.7	3.2	2.7
$\Delta\alpha_{Ph}$	2.4	1.8	1.4
$\Delta\alpha^{\dagger}_{Ph}$	−0.5	0.5	1.5
(*c*) Anisotropies produced by inductive effects [eqns. (9) and (10)]			
δ_E	2.3	2.6	2.8
$\delta^{\dagger}_E$	2.5	2.0	1.5
δ_B	0.6	0.0	−0.4
$\delta^{\dagger}_B$	−4.1	−3.1	−2.1

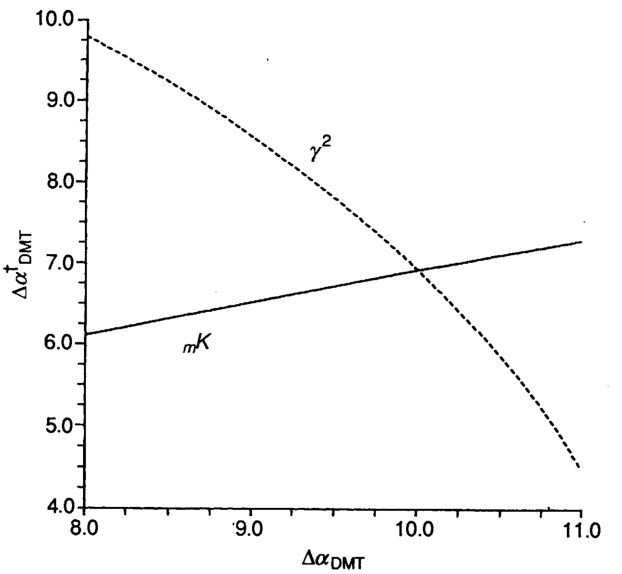

Fig. 3 Values of the parameters $\Delta\alpha_{DMT}$ and $\Delta\alpha^{\dagger}_{DMT}$ that reproduce the experimental results of $\langle\gamma^2\rangle$ and $_mK$ of the dimethyl terephthalate molecule. Calculations were performed at T = 20 °C taking $\alpha_{xy} = 0$.

calculations of the conformational energy as a function of φ_1 and φ_2 rotations using the same functions employed by Hummel and Flory[17] in their analysis of MB, plus a term representing dipole–dipole interactions. The results of these calculations show four minima located at $(\varphi_1, \varphi_2) = (45, 45), (45, 225), (225, 45)$ and $(225, 225)$ with relative energies of 0, 0.3, 0.3 and 0.6 kcal mol^{-1}, respectively. The dipole moment of the DMP molecule calculated with this conformational model gives $\langle\mu^2\rangle^{\frac{1}{2}} = 2.63$ D in good concordance with the experimental value. We have used this four-states model in all the calculations carried out for DMP in the present work.

Values of mean-square optical anisotropy $\langle\gamma^2\rangle$ and Kerr constants $_mK$ were computed according to the standard equations,[1,2,18] eqns. (2) and (3), where $\hat{\alpha}$ is the anisotropic part

$$\langle\gamma^2\rangle = (3/2)\,\mathrm{trace}\,\langle(\hat{\alpha}\hat{\alpha})\rangle \qquad (2)$$

$$_mK = C_1[C_2\langle\boldsymbol{\mu}^{\mathrm{T}}\hat{\alpha}\boldsymbol{\mu}\rangle + (2.2/3)\langle\gamma^2\rangle] \qquad (3)$$

of the polarizability tensor of the molecule; $\boldsymbol{\mu}^{\mathrm{T}}$ and $\boldsymbol{\mu}$ represent the dipole moment written as 1 × 3 row and 3 × 1 column matrices, respectively. Numerical values of the constants C_1 and C_2 are $C_1 = (2\pi N)/(kT) = (20.33/T)\ 10^{-25}$ and $C_2 = 1/(kT) = 7244/T$ when $\boldsymbol{\mu}$, $\hat{\alpha}$, T and $_mK$ are given, respectively in D, Å^3, K and m^5 V^{-2} mol^{-1}.

The $\hat{\alpha}$ tensors of phenyl and ester groups can be written as eqn. (4), where $\Delta\alpha = \alpha_{xx} - (\alpha_{yy} + \alpha_{zz})/2$ and

$$\hat{\alpha}_{Ph} = \Delta\alpha_{Ph}\,\boldsymbol{J} + \Delta\alpha^{\dagger}_{Ph}\,\boldsymbol{K} \quad \text{and}$$
$$\hat{\alpha}_E = \Delta\alpha_E\,\boldsymbol{J} + \Delta\alpha^{\dagger}_E\,\boldsymbol{K} + \alpha_{xy}\,\boldsymbol{L} \qquad (4)$$

$\Delta\alpha^{\dagger} = \alpha_{yy} - \alpha_{zz}$ represent the longitudinal and transverse anisotropies respectively, while α_{xy} appearing in the contribution of the ester group takes into account the fact that the $\hat{\alpha}_E$ tensor is not exactly diagonal. The matrices $\boldsymbol{J}$, $\boldsymbol{K}$ and $\boldsymbol{L}$ are defined as eqn. (5).

$$\boldsymbol{J} = \mathrm{diag}\,(\tfrac{2}{3}, -\tfrac{1}{3}, -\tfrac{1}{3})\ \boldsymbol{K} = \mathrm{diag}\,(0, \tfrac{1}{2}, -\tfrac{1}{2})\quad \mathrm{L} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad (5)$$

In the case of MB, since the axes used to write the contributions of both phenyl and ester groups are parallel, the $\hat{\alpha}$ tensors for the whole molecule can be written as

$$\hat{\alpha}_{MB} = \Delta\alpha_{MB}\,\boldsymbol{J} + \Delta\alpha^{\dagger}_{MB}\,\boldsymbol{K} + \alpha_{xy}\boldsymbol{L} \qquad (6)$$

Disregarding for the moment the contribution from the off-diagonal term α_{xy}, eqn. (6) contains only two unknowns, $\Delta\alpha_{MB}$ and $\Delta\alpha^{\dagger}_{MB}$ and can be solved for pairs of values of these parameters that reproduce the experimental values of $\langle\gamma^2\rangle$ and $_mK$. This solution is shown grapically in Fig. 2, where the intersection between the two lines indicates the set of parameters that simultaneously reproduce the experimental values of both $\langle\gamma^2\rangle$ and $_mK$. Repetition of the same calculations with non-zero values for α_{xy} gives different solutions, some of which are summarized in part (*a*) of Table 2 as sets of values of the three optical parameters that reproduce both $\langle\gamma^2\rangle$ and $_mK$ for this molecule.

The DMT molecule can be analysed with the same procedure used for MB. Thus, the $\hat{\alpha}_{DMT}$ tensor can be written as eqn. (7).

$$\hat{\alpha}_{DMT} = \Delta\alpha_{DMT}\boldsymbol{J} + \Delta\alpha^{\dagger}_{DMT}\boldsymbol{K} + \alpha_{xy}\boldsymbol{L} \qquad (7)$$

Fig. 3 shows the pair of values of $\Delta\alpha_{DMT}$ and $\Delta\alpha^{\dagger}_{DMT}$ that reproduce each of the experimental results for this molecule when $\alpha_{xy} = 0$ while lines three and four in Table 2 summarize some sets of values of the three parameters that simultaneously reproduce both experimental results.

The $\hat{\boldsymbol{\alpha}}_{MB}$ and $\hat{\boldsymbol{\alpha}}_{DMT}$ tensors can be formulated as the sum of contributions from their constitutive phenyl and ester groups, shown in eqn. (8), where $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$ represent the transformation matrices required to bring the co-ordinate system of each ester group into coincidence with those of the phenyl ring. These transformations depend on the values of the angles φ_1 and φ_2, but in the case of DMT the transformation only reverses the signs of the axes. As a result the diagonal terms of the $\hat{\boldsymbol{\alpha}}_{DMT}$ tensor, which are much more important than the off-diagonal terms, are left unchanged.

$$\hat{\boldsymbol{\alpha}}_{MB} = \hat{\boldsymbol{\alpha}}_{Ph} + \hat{\boldsymbol{\alpha}}_{E} \quad \text{and} \quad \hat{\boldsymbol{\alpha}}_{DMT} = \hat{\boldsymbol{\alpha}}_{Ph} + \boldsymbol{T}_1\hat{\boldsymbol{\alpha}}_{E}\boldsymbol{T}_1^{T} + \boldsymbol{T}_2\hat{\boldsymbol{\alpha}}_{E}\boldsymbol{T}_2^{T} \qquad (8)$$

Writing the $\hat{\boldsymbol{\alpha}}$ tensors of eqn. (8) as function of the $\Delta\alpha$ and $\Delta\alpha^{\dagger}$ anisotropies defined by eqn. (4) and introducing the numerical values of $\Delta\alpha_{MB}$, $\Delta\alpha^{\dagger}_{MB}$, $\Delta\alpha_{DMT}$ and $\Delta\alpha^{\dagger}_{DMT}$ indicated in part (*a*) of Table 2, one obtains a set of four equations with four unknowns for each value of α_{xy}. The solutions of these equations are summarized in part (*b*) of Table 2, which list the parameters for phenyl and ester groups that are required in order to simultaneously reproduce the experimental values of $\langle\gamma^2\rangle$ and ${}_mK$ of both molecules.

The values of longitudinal $\Delta\alpha$ and transverse $\Delta\alpha^{\dagger}$ anisotropies indicated in Table 2 for ester and phenyl groups are quite different from their corresponding values in molecules having only one of such groups. For instance, a molecule of methyl acetate (MA) has[9] $\Delta\alpha_{MA} = 1.5$ and $\Delta\alpha^{\dagger}_{MA} = 1.2$, which are both noticeably smaller than the values shown in Table 2 for ester groups attached to a phenyl ring. In the latter case, the anisotropies can be written as eqn. (9), where δ_E and $\delta^{\dagger}_E$ indicate the inductive effects produced in the anisotropy of the ester group by the phenyl ring. The values of these parameters are summarized in part (*c*) of Table 2 which indicates that the inductive effects are in the sense of increasing both longitudinal and transverse anisotropies.

$$\Delta\alpha_E = \Delta\alpha_{MA} + \delta_E \quad \text{and} \quad \Delta\alpha^{\dagger}_E = \Delta\alpha^{\dagger}_{MA} + \delta^{\dagger}_E \qquad (9)$$

In the case of a benzene ring,[8] we can take as reference either the parameters for an isolated molecule of benzene (B), $\Delta\alpha_B = 1.8$ and $\Delta\alpha^{\dagger}_B = 3.6$, or the values assigned to phenyl rings attached to aliphatic residues (PhAl), as in toluene, isopropyl benzene or *tert*-butyl benzene, which are: $\Delta\alpha_{PhAl} = 3.85$ and $\Delta\alpha^{\dagger}_{PhAl} = 3.0$. Taking the isolated molecule of benzene as reference one can write eqn. (10), with δ_B and $\delta^{\dagger}_B$ representing the inductive effects produced by the ester group into the ring. The last two lines of part (*c*) of Table 2 show that δ_B is small and $\delta^{\dagger}_B$ is negative, *i.e.* the ester group produces small effects on the longitudinal anisotropy of benzene, but it significantly decreases the transverse component.

$$\Delta\alpha_{Ph} = \Delta\alpha_B + \delta_B \quad \text{and} \quad \Delta\alpha^{\dagger}_{Ph} = \Delta\alpha^{\dagger}_B + \delta^{\dagger}_B \qquad (10)$$

It is quite intuitive to think that if the ester group appearing in the MB molecule produces inductive effects δ_B and $\delta^{\dagger}_B$ in one benzene molecule, the two ester groups contained in the DMT molecule would produce inductive effects of $2\delta_B$ and $2\delta^{\dagger}_B$. Consequently the parameters for the DMT molecule would be formulated as eqn. (11), instead of eqn. (12) as follows from eqns. (8)–(10). However, it is impossible to assign the values of the four δ parameters in such a way that they simultaneously reproduce the experimental magnitudes of MB and DMT molecules, using benzene as reference, as indicated in eqn. (11), or using the analogous equation with $\hat{\boldsymbol{\alpha}}_{PhAl}$ as reference. Consequently, the inductive effects produced into the ring by attachment of either one or two ester groups are identical.

$$\Delta\alpha_{DMT} = \Delta\alpha_B + 2\Delta\alpha_E + 2(\delta_B + \delta_E) \quad \text{and} \quad \Delta\alpha^{\dagger}_{DMT} = \Delta\alpha^{\dagger}_B + 2\Delta\alpha^{\dagger}_E + 2(\delta^{\dagger}_B + \delta^{\dagger}_E) \qquad (11)$$

$$\Delta\alpha_{DMT} = \Delta\alpha_B + 2\Delta\alpha_E + \delta_B + 2\delta_E \quad \text{and} \quad \Delta\alpha^{\dagger}_{DMT} = \Delta\alpha^{\dagger}_B + 2\Delta\alpha^{\dagger}_E + \delta^{\dagger}_B + 2\delta^{\dagger}_E \qquad (12)$$

The $\hat{\boldsymbol{\alpha}}_{DMI}$ tensor for the DMI molecule can be formulated in the same way as for the DMT molecule with an equation which is formally identical to the second part of eqn. (8), the only noteworthy difference being that in DMI one of the $\boldsymbol{T}$ matrices requires a rotation of 120° over the z axis and therefore modifies the diagonal terms of the $\hat{\boldsymbol{\alpha}}_E$ tensor. The three sets of optical parameters summarized in Table 2 give a good account of the experimental value of ${}_mK$ for DMI but all of them overestimate the result of $\langle\gamma^2\rangle$ by *ca.* 15–20%. As an example, the first line of Table 3 shows the values calculated for both magnitudes of all four molecules with the set having $\alpha_{xy} = 0$, which of course reproduces the exact experimental values of both $\langle\gamma^2\rangle$ and ${}_mK$ for MB and DMT molecules. Small adjustments of the optical parameters produce a better overall fit for the six experimental results, leaving for the moment the results for DMP. For instance, the second line in Table 3 shows that the largest deviation between theoretical and experimental results for MB, DMT and DMI molecules, again for $\langle\gamma^2\rangle$ of DMI, amounts to *ca.* 10%. Therefore, it seems that the set of parameters indicated as b in Table 3, with uncertainties of *ca.* ±0.1 Å^3, is able to simultaneously reproduce the experimental values of both $\langle\gamma^2\rangle$ and ${}_mK$ of the MB, DMT and DMI molecules. Table 3 lists values of inductive effects, *i.e.* parameters δ and $\delta^{\dagger}$, that can be easily converted into anisotropies of constitutive groups, *i.e.* parameters $\Delta\alpha$ and $\Delta\alpha^{\dagger}$, using eqns. (9) and (10). For instance, set b of Table 3 amounts to the following group contributions: $\alpha_{xy} = 0.1$, $\Delta\alpha_{Ph} = 1.9$, $\Delta\alpha^{\dagger}_{Ph} = 1.4$, $\Delta\alpha_E = 3.9$ and $\Delta\alpha^{\dagger}_E = 2.7$.

In the case of the DMP molecule, the $\hat{\boldsymbol{\alpha}}_{DMP}$ tensor is formally identical to those of DMT and DMI, although in DMP the $\boldsymbol{T}$ matrices include out-of-plane rotations performed over the x axis. There is no single set of values for the optical parameters that could simultaneously reproduce the experimental values for the four molecules. Thus the second line of Table 3 shows that using set b, which gives a good account of the experimental magnitudes of the other three molecules, the value of $\langle\gamma^2\rangle$ for DMP is overestimated by only 15%, but the value of ${}_mK$ is more than 30 times larger than the experimental result. Moreover, no small adjustment of this set of parameters will bring agreement between theoretical and experimental values of $\langle\gamma^2\rangle$ and ${}_mK$ for the DMP molecule. Consequently, the optical parameters of phenyl and ester groups should be different in DMP than in the other three molecules.

We therefore confirm the conclusion indicated in the previous analysis[13] in the sense that the inductive effects between the benzene ring and ester groups are independent of the number of ester groups and the positions at which they are attached to the ring. However, they are sensitive to the dihedral angle formed by the planes containing the phenyl and the ester.

Since there are five optical parameters, they cannot be unambiguously determined using only the two experimental magnitudes for DMP. However, it is interesting to notice that set c shown in the third line of Table 3, which is obtained from set b by interchanging the inductive effects of phenyl and ester

Table 3 Calculated values of mean-square optical anisotropies and Kerr constants for the MB, DMT, DMI and DMP molecules. Computations performed at T = 20 °C using different sets of optical parameters:

	Optical parameters/Å^3					$\langle\gamma^2\rangle$/Å^6				$_mK$/10^{-25} m^5 V^{-2} mol^{-1})			
Set	α_{xy}	δ_E	$\delta_E^{\dagger}$	δ_B	$\delta_B^{\dagger}$	MB	DMT	DMI	DMP	MB	DMT	DMI	DMP
a	0.0	2.6	2.0	0.0	−3.1	45	136	113	71	8.9	7.9	29.7	27.1
b	0.1	2.4	1.5	0.1	−2.2	46	129	107	67	9.3	8.0	28.7	22.2
c	0.1	0.1	−2.2	2.4	1.5	46	62	44	65	9.3	−4.7	13.9	−2.3
d	−0.2	−0.2	−2.3	2.4	1.5	42	53	38	59	10.6	−4.3	13.6	0.7
Experimental[a]						46	136	97	58	9.0	8.0	30.6	0.7

[a] Experimental values from Table 1

groups, improves the agreement between theory and experience for DMP, although it does not work for the other three molecules. A small modification of this set, indicated as set d in the fourth row of Table 3, gives a good account of both experimental results for the DMP molecule.

Obviously, set c of Table 3 represents only one of the many assignations of the five optical parameters that can be used to reproduce (or at least to get close to) the experimental values of $\langle\gamma^2\rangle$ and $_mK$ of the DMP molecule. Therefore, no rigorous conclusion can be obtained from that set of values. However, it allows for a rather interesting speculation. This interchange in the numerical values of the parameters defining the inductive effects, from set b that represents the planar molecules MB, DMT and DMI to set c used for the non planar molecule DMP could be easily explained in the following way. The tensor $\hat{\boldsymbol{\delta}}_E$ represents the inductive effects produced by the phenyl ring and therefore it is reasonable to assume that it should have the same main axes as the group producing it; consequently, it can be written in the diagonal form $\delta_E = \delta_E \boldsymbol{J} + \delta_E^{\dagger}\boldsymbol{K}$ only when it is referred to the co-ordinate system of the ring. Conversely, $\hat{\boldsymbol{\delta}}_B$ represents the inductive effects produced by the ester groups and its diagonal expression $\delta_B = \delta_B\boldsymbol{J} + \delta_B^{\dagger}\boldsymbol{K}$ implies the use of the co-ordinate system of the ester. If the interpretation were correct, the inductive effects should be written in the main system of the group producing them and with this condition, the same numerical parameters could be used for the planar MB, DMT and DMI molecules as for the non-planar DMP.

Acknowledgements

This work was supported by the DGICYT of Spain through grant number PB88-0152 and facilitated by the Greek–Spanish scientific bilateral agreement. The technical assistance of Mrs. F. Kotsifaki is gratefully acknowledged.

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Paper 2/01280D
Received 9th March 1992
Accepted 26th March 1992