Conformational Analysis and Kerr Effect Studies of Tricarboxylic Aliphatic Esters

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The electronic polarizations, dipole moments, and molar Kerr constants of tricarboxylic aliphatic esters $H(CH_2)_nC(CO_2Et)_3$ with $n = 1$—8, in benzene and carbon tetrachloride at 25 °C, are recorded. The PCILO method has been used to deduce the preferred gas-phase conformations. The preferred solution-state conformation of derivatives with $n = 1$ and 2, indicated by the analysis of experimental and calculated electronic polarizations, dipole moments, and molar Kerr constants, is shown to be consistent with the predictions based on quantum chemical calculations. The experimental data for the investigated tricarboxylic esters can be interpreted in terms of a 'propeller-type' conformation with $120° < \tau_1 = \tau_2 = \tau_3 < 140°$.

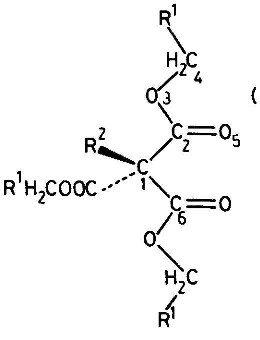
In a previous paper,[1] we reported a conformational study of mono- and di-carboxylic aliphatic esters. It was shown that the CO_2Me group is planar and that the experimental dipole moments and molar Kerr constants of the investigated dicarboxylic esters can be interpreted in terms of the populations of two rotamers centred on two energy minima ($\tau_1 = \tau_2 = 90°$ and $\tau_1 = 90°$, $\tau_2 = 270°$) separated by a barrier of 2—3 kcal mol^{-1}. That study was performed as an initial step towards the determination of the conformation of tricarboxylic esters (**3**)—(**10**). As far as we know, the literature gives no information on these compounds.

In the previous paper, the theoretical conformational analysis was performed using the CNDO/2 method. In the last few years however, it has been reported that this method fails to reproduce the conformational properties of compounds with localized and delocalized bonds[2–7] and, as we have to investigate molecules having many degrees of freedom, we decided to use the Perturbative Configuration Interaction procedure using Localized Orbitals (PCILO).[8] The PCILO method based on the CNDO approximations is able to provide qualitatively correct potential functions,[7] due to the fact that the third-order perturbative CI expansion may properly describe polarization and delocalization effects as well as the partial correction for intra-pair and inter-pair electron correlation. In addition, the PCILO procedure requires a computational time much shorter than the iterative SCF CNDO method (see ref. 9).

Experimental

The esters (**3**)—(**10**) were synthesized according to Ferreira and Miyata;[10] each compound was purified by fractionation. Its purity (>99%) was checked by g.l.c. The physical properties of the pure liquids (boiling points, refractive indices, as a function of wavelength, and specific volumes) are reported in Supplementary Publication No. SUP 56653 (9 pp.).†

Benzene was carefully dried by a standard method,[11] stored over phosphorus pentaoxide, and distilled immediately before use. Carbon tetrachloride was treated with alcoholic NaOH and distilled.



(**1**) $R^1 = R^2 = H$
(**2**) $R^1 = H$, $R^2 = Me$
(**3**)-(**10**) $R^1 = Me$, $R^2 = H-(CH_2)_n$
$n = 1-8$

The densities of pure compounds were measured by a Sprengel–Ostwald pycnometer (*ca.* 12 ml) calibrated with air-free distilled water.

Details of equipment, measurements on solutions, procedures, symbols, and calculations are given elsewhere.[1]

The incremental values of the dielectric constant, the density, the refractive index, the square of the refractive index, and the Kerr constant for the solutions in benzene and carbon tetrachloride at 25.00 ± 0.05 °C are collected in SUP 56653.

Table 1 reports the molar refractions obtained from the measurement of the refractive indices of the pure compounds (R_M) and of the solutions in CCl_4 ($_\infty R_2$) as a function of the wavelength. Tables 2 and 3 show polarizations, refractions, dipole moments, and molar Kerr constants in C_6H_6 and CCl_4. All these quantities are given throughout in S.I. units: R_M (or $_EP$) 10^{-6} m^3, b 10^{-40} C m^2 V^{-1}, μ 10^{-30} C m, and $_mK$ 10^{-27} m^5 V^{-2} mol^{-1}. All errors are quoted as standard deviations.

The experimental dipole moments were calculated using two different estimates of the distortion polarization, $_DP$: (a) $_DP = (_\infty R_2)_D$, *i.e.* the molar refraction at the Na$_D$ line; (b) $_DP = {_AP} + {_EP}$. The atomic polarizations, $_AP$, were estimated from group contributions.[12] The electronic polarizations, $_EP$, were calculated both from bond polarizations[13] and from experimental molar refractions. All these polarizations are reported in Table 4. The mean values of the ratios $R_M/_EP$ and $(_\infty R_2)_D/_EP$ are

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† For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1.

Table 1. Molar refraction of pure compounds (R_M) and molar refraction at infinite dilution ($_{\infty}R_2$) for solutions in carbon tetrachloride as a function of wavelength (T 25 °C)

		λ/nm									
Compound	Molar refraction	667.8	656.3	589.3	587.6	546.1	501.6	486.1	447.1	435.8	404.7
(3)	R_M	58.08		58.38	58.38	58.60	58.89		59.39	59.52	
(3)	$_{\infty}R_2$		59.50	59.69	59.69	59.95		60.33		60.83	61.27
(4)	R_M	62.53		62.86	62.86	63.09	63.40		63.93	64.08	
(4)	$_{\infty}R_2$		62.65	62.96	62.96	63.15		63.63		64.19	64.65
(5)	R_M	67.16		67.51	67.51	67.76	68.10		68.67	68.82	
(6)	R_M	71.63		71.99	72.00	72.27	72.63		73.24	73.40	
(7)	R_M	76.22		76.61	76.61	76.89	77.28		77.93	78.09	
(8)	R_M	81.01		81.42	81.43	81.73	82.14		82.83	83.01	
(9)	R_M	85.64		86.08	86.08	86.40	86.83		87.57	87.75	
(10)	R_M	90.55		91.01	91.02	91.35	91.81		92.58	92.79	

Table 2. Slopes of the least-squares fits of the dependence of dielectric constants, densities, refractive indices, square of refractive indices, and molar Kerr constants on weight fraction for compounds **(3)**—**(10)** at 25 °C

Compound	α	β	$-\gamma$	$-\Gamma$	δ
(3)[a]	1.93 ± 0.02	0.196 ± 0.0007	0.040 ± 0.001	0.081 ± 0.002	
(3)[b]	3.67 ± 0.15	−0.504 ± 0.020	0.035 ± 0.002	0.070 ± 0.003	25.3 ± 1.3
(4)[a]	1.71 ± 0.03	0.186 ± 0.004	0.075 ± 0.001	0.038 ± 0.0005	
(4)[b]	2.89 ± 0.03	−0.481 ± 0.017	0.028 ± 0.0002	0.055 ± 0.0004	23.1 ± 2.2
(5)[a]	1.59 ± 0.01	0.180 ± 0.0001	0.038 ± 0.0004	0.077 ± 0.0007	
(6)[a]	1.51 ± 0.02	0.164 ± 0.0005	0.037 ± 0.0003	0.075 ± 0.0006	
(7)[a]	1.44 ± 0.01	0.154 ± 0.0005	0.037 ± 0.001	0.074 ± 0.002	
(8)[a]	1.33 ± 0.02	0.143 ± 0.0005	0.036 ± 0.0009	0.071 ± 0.002	
(9)[a]	1.33 ± 0.02	0.135 ± 0.0004	0.037 ± 0.0004	0.075 ± 0.0009	
(10)[a]	1.26 ± 0.02	0.123 ± 0.0005	0.036 ± 0.002	0.071 ± 0.0004	

[a] In C_6H_6. [b] In CCl_4.

Table 3. Experimental total polarizations, refractions, dipole moments, and molar Kerr constants of compounds **(3)**—**(10)** at 25 °C

Compound	$_{\infty}P_2$	$(_{\infty}R_2)_D$	μ[a]	$_mK$
(3)[b]	270.7 ± 1.8	57.8 ± 0.2	10.8 ± 0.05	
(3)[c]	281.2 ± 9.0	59.7 ± 0.9	11.0 ± 0.22	56.3 ± 3.3
(4)[b]	262.4 ± 3.0	62.7 ± 0.1	10.4 ± 0.08	
(4)[c]	248.4 ± 2.0	63.0 ± 0.7	10.0 ± 0.06	55.9 ± 5.8
(5)[b]	262.7 ± 0.9	66.5 ± 0.1	10.3 ± 0.02	
(6)[b]	267.8 ± 2.4	71.7 ± 0.1	10.3 ± 0.06	
(7)[b]	273.7 ± 1.3	76.3 ± 0.3	10.4 ± 0.03	
(8)[b]	272.6 ± 2.3	81.3 ± 0.3	10.2 ± 0.06	
(9)[b]	285.9 ± 2.6	85.3 ± 0.1	10.5 ± 0.07	
(10)[b]	289.1 ± 2.4	90.9 ± 0.6	10.4 ± 0.06	

[a] Calculated with $_DP = (_{\infty}R_2)_D$; see text. [b] In C_6H_6. [c] In CCl_4.

Table 4. Values of atomic and electronic polarizations of compounds **(3)**—**(10)**

		$_EP$	
Compound	$_AP$ (calc.)	calc.	exp.[a]
(3)	3.25	57.7	57.0 ± 0.005[b] 58.4 ± 0.000[c]
(4)	3.35	61.2	61.4 ± 0.008[b] 61.4 ± 0.000[c]
(5)	3.45	65.8	65.9 ± 0.005[b]
(6)	3.55	70.3	70.3 ± 0.006[b]
(7)	3.65	74.8	74.8 ± 0.007[b]
(8)	3.75	79.4	79.5 ± 0.007[b]
(9)	3.85	83.9	84.1 ± 0.008[b]
(10)	3.95	88.5	88.9 ± 0.010[b]

[a] From $R(\lambda) = {}_EP + (\text{constant})\lambda^{-2}$; $R = R_M$ or $_{\infty}R_2$; $r^2 > 0.999$. [b] From measurements on the pure substance at 25 °C. [c] In CCl_4.

1.024 ± 0.0003 and 1.018 ± 0.005 respectively, in good agreement with that found for straight-chain paraffins,[14] but lower than that commonly assumed.[15] On the other hand, the mean value of the ratio $(_EP + {}_AP)/_EP$ is 1.050 ± 0.004 and is consistent with a correction of 5% $_EP$ for atomic polarization. The two sets of dipole moment values (SUP 56653) are practically coincident. The μ values reported in Table 3 are those calculated with $_DP = (_{\infty}R_2)_D$.

Calculations

Theoretical dipole moments and molar Kerr constants were calculated as previously reported.[1,16] Calculations of molecular geometries and conformational energies were carried out by means of the PCILO semiempirical method.[17]

Before undertaking calculations on the present compounds, the previously reported conformational energy map for dimethyl malonate[1] was checked by PCILO calculations. Using both the geometrical parameters quoted in ref. 1 and the PCILO-optimized geometry, the results parallel those of ref. 1. Both CNDO and PCILO methods favour the non-planar arrangements for dimethyl malonate and indicate the same two low-energy conformations. The PCILO energy contour maps are not reproduced here; these, as well as the subsequent energy maps which are referred to but are not reported, are available upon request.

In a rigid rotor model, the conformational energy of the tricarboxylic esters depends only on the torsional angles τ_1—τ_3 [τ is defined by the dihedral angle RC(1)C(2)O(5)]. The full four-dimensional hypersurface, $E = E(\tau_1, \tau_2, \tau_3)$, was depicted by means of conformational energy contours drawn in the three-dimensional space defined by the co-ordinates τ_1—τ_3 (Figure 1).

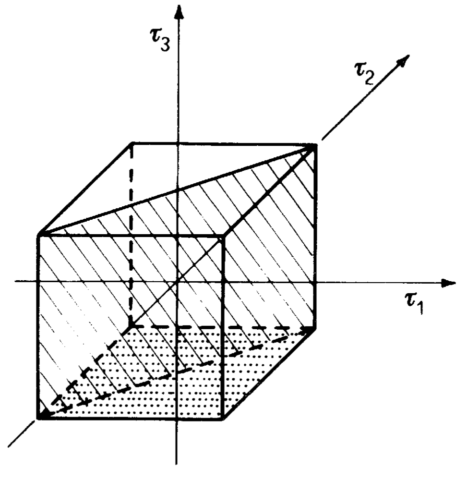

Figure 1. Representation of the $E = E(\tau_1,\tau_2,\tau_3)$ space

For a systematic representation of the four-dimensional space two types of subspace were selected. The first is the 'diagonal plane' shown as the shaded plane in Figure 1; it has co-ordinates $\tau_1 = \tau_2$ and τ_3 and gives a picture of the simultaneous variation of the three co-ordinates. The second type has co-ordinates τ_1 and τ_2, while τ_3 is fixed at different constant values, and is shown as the dotted plane in Figure 1.

The mean values of the geometrical parameters calculated for the most stable conformation of compounds (**1**)—(**4**) are given in Table 5. Here, the significance of the range given for the values of the torsional angles τ is as follows: the energy minimum of each compound lies in a rather flat conformational space where variations of τ in the range ±5° produce energy differences as small as 0.1 kcal mol^{-1} and lower than the numerical accuracy of the computational method. Furthermore, the τ values corresponding to the energy minima of the various compounds differ by not more than ±2°.

Discussion

The molecular structure of the tricarboxylic esters has a high number of degrees of freedom. The complexity of the problem can be simplified by using a rigid rotor model in which the conformational energy is assumed to be dependent only on the torsional angles τ_1—τ_3 [τ is defined by the dihedral angle RC(1)C(2)O(5)]; this model may give good results only in the

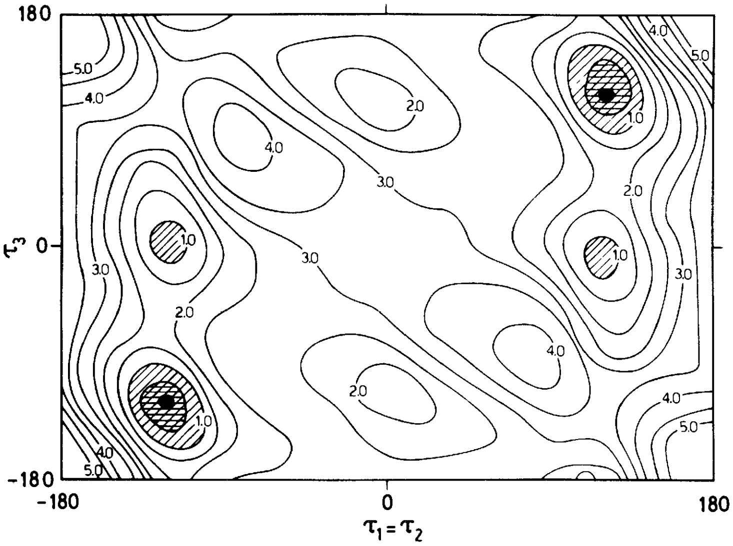

Figure 2. Conformational energy map on the 'diagonal plane' for triethyl ethane-1,1,1-tricarboxylate (**3**). Isoenergy curves are in kcal mol^{-1}; τ in degrees. The energy is relative to zero at the most stable conformation. The shaded, cross-hatched, and full areas represent the conformational space that lies inside the 1, 0.5 and 0.1 kcal mol^{-1} regions, respectively

Table 5. Mean values of the geometrical parameters for the most stable conformations of tricarboxylic acid esters (**1**)—(**4**)

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
C(1)–C(2)^{a}	1.477; 1.483	C(2)C(1)C(6)^{a}	110.3; 109.6	O(5)C(2)O(3)C(4)	0.0
C(2)–O(3)	1.369	C(2)C(1)R^{2a}	108.6; 109.3	C(2)O(3)C(4)R^{1}	179.7
O(3)–C(4)	1.383	C(1)C(2)O(3)	116.5	τ^{d}	125.0 ± 5.0
C(2)–O(5)	1.274	C(1)C(2)O(5)	124.1		
C(1)–R^{2a}	1.146; 1.503	C(2)O(3)C(4)	108.8		
C–C^{b}	1.500	O(3)C(4)R^{1c}	110.6; 109.5		
C(4)–R^{1c}	1.130; 1.480	C(1)CC^{b}	112.8		

[a] The two values refers to R^2 = H and R^2 = Me, respectively. [b] In H_2C–CH_3. [c] The two values refers to R^1 = H and R^1 = Me, respectively. [d] See Discussion section.

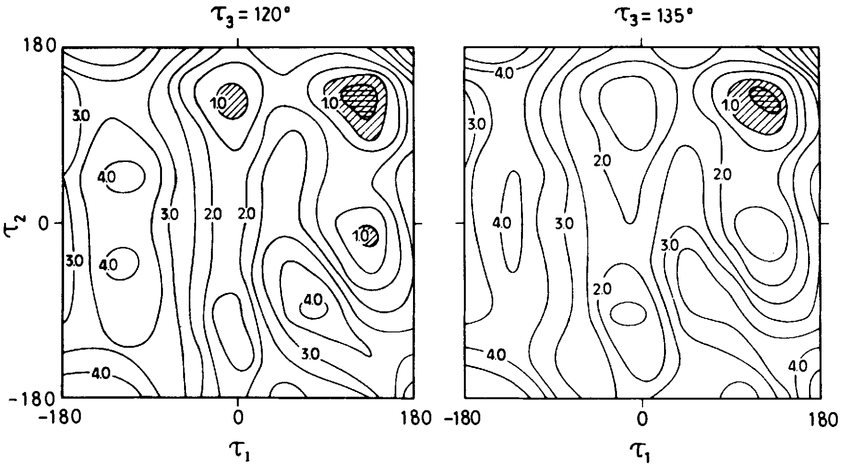

Figure 3. Conformational energy maps on the τ_3 = 120 and 135° planes for compound (**3**). Symbols as in Figure 2

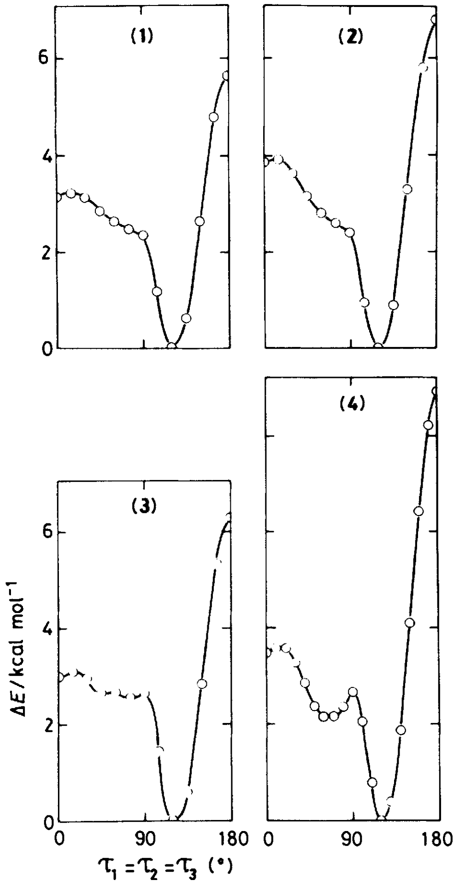

Figure 4. Conformational energy profiles along the 'diagonal' $\tau_1 = \tau_2 = \tau_3$ for compounds (**1**)—(**4**)

case that all the other geometrical parameters are nearly independent of the τ internal co-ordinates.

To test if the molecules here considered fulfil this requirement, the geometrical parameters of compound (**1**) were optimized by the following stepwise procedure starting from the PCILO-optimized geometry of dimethyl malonate. (a) The most critical parameters *i.e.*, the length of C–C bonds and the C–C–C bond angles, were optimized. The calculations were performed for rotamers with C_{3v}, C_3, C_s, and C_1 symmetries. As the calculated values of these geometrical parameters are practically coincident for the four types of structure, the averaged values were used for the optimization of the geometry of the CO_2Me group. (b) This optimization was performed on the two 'propeller-type' conformations (C_3 symmetry) with τ = 120 and 60° (or their enantiomers) approximately corresponding to a minimum and a maximum of the conformational energy, respectively. Also in this case, the two geometrical parameter sets were found to be very similar. (c) A final calculation was then carried out by fully relaxing all geometrical parameters; no significant differences were found.

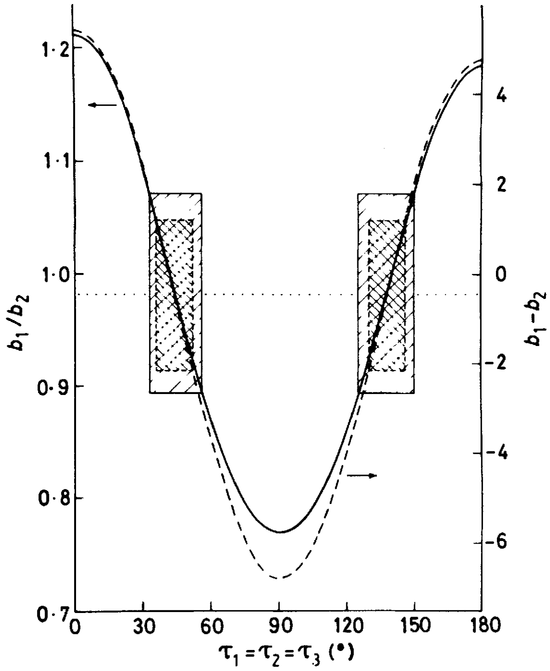

Figure 5. Plot of the calculated b_1/b_2 (solid line) and $b_1 - b_2$ (dashed line) values *versus* τ for compound (**3**). The dotted line corresponds to the experimental values; the rectangles are built taking into account the experimental errors

For compounds (**2**)—(**4**), the optimized skeleton of compound (**1**) was taken as constant and only the new bond lengths, bond angles, and torsional angles were optimized. For compound (**4**), the geometry of the ethyl group at C(1) was optimized step by step; afterwards, fully relaxed geometry calculations were performed.

The whole of these molecular geometry optimizations of compounds (**1**)—(**4**) shows that there is, in any case, a preference for a 'propeller-type' conformation with τ values in the range 120—140°.

The search of other possible minima was carried out on triethyl ethane-1,1,1-tricarboxylate (**3**) as this is the smallest compound for which theoretical and experimental results can be compared.

The intramolecular energy map on the 'diagonal plane' (see Calculations section) is shown in Figure 2: the 'propeller-type' conformation is in the centre ($\tau_1 = \tau_2 = 125°$ and $\tau_3 = 125°$) of an approximately square area with a side of *ca.* 10°.

The search was then extended to the other types of energy maps; these calculations were performed for $0° \leq \tau_3 \leq 360°$ with a 45° step. The complete set of energy maps is not reported here. Their examination shows that there are three regions of the conformational space that are 'energetically allowed', *i.e.* that lie inside the 1 kcal mol^{-1} region. One of these is a coarse three-dimensional box of which the lower and upper faces are approximately the planes at $\tau_3 = 120$ and $\tau_3 = 135°$, respectively. The conformational energy maps relative to these planes are shown in Figure 3: the lack of energy values lower than 0.3 kcal mol^{-1} in the cross-hatched areas indicates that the 'propeller-type' energy minimum is an absolute minimum. The other two regions are rather flat with the relative minima at 0.8 kcal mol^{-1}.

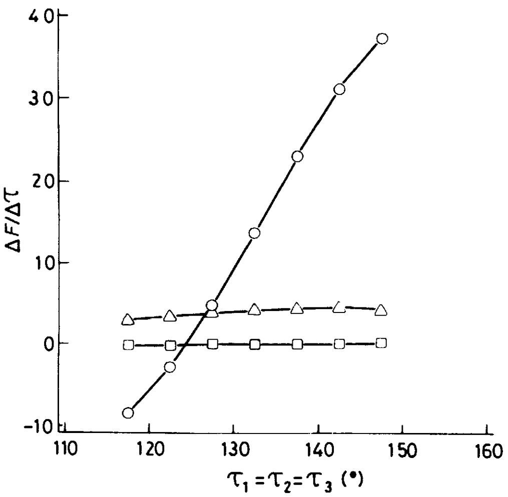

Figure 6. $\tau - \Delta F/\Delta\tau$ Profile for compound (**3**): □, $F = E$; △, $F = \mu$; ○, $F = {}_mK$

Finally, a random search for energy minima was performed starting from some points in the τ_1—τ_3 space. Energy values lower than those previously reported were not found.

It seemed reasonable to assume that the conformational characteristics of compounds (**1**)—(**4**) are very similar. However, this hypothesis was also checked by calculation of the energy profiles along the $\tau_1 = \tau_2 = \tau_3$ co-ordinate. As shown in Figure 4, the profiles for compounds (**1**), (**2**), and (**4**) are very similar to that for compound (**3**). Once more, the validity of the rigid rotor model was confirmed by fully relaxed geometry calculations.

Thus we can conclude that the minima of conformational energy for compounds (**1**)—(**4**) are approximately located at values of $\tau_1 = \tau_2 = \tau_3 = \pm 125°$ (C_3 symmetry); librations of *ca.* 5° change the energy values within the precision of the computational method. The main geometrical parameters calculated for the most stable conformations are reported in Table 5.

The conformational energy results allow an analysis of the experimental values of the electron polarizations, dipole

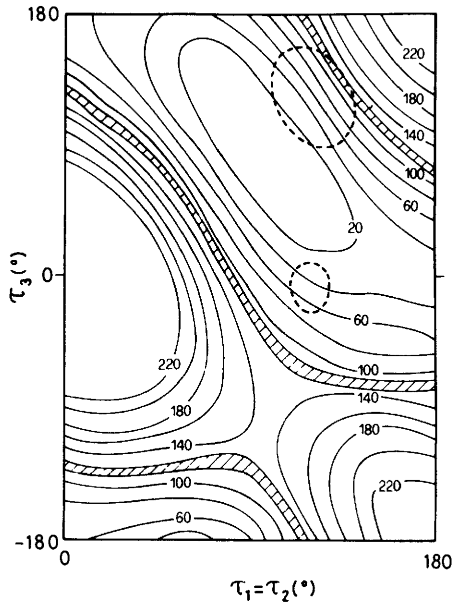

Figure 8. Square-dipole moment contour map on the 'diagonal plane' for compound (**3**). The shaded areas represent the experimental value with its error. The dashed contours represent the conformational space that lies inside the 1 kcal mol^{-1} region

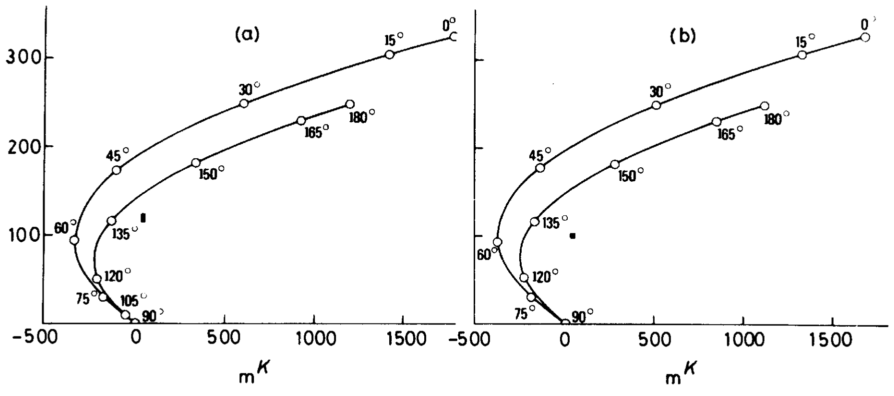

Figure 7. Plot of μ^2 *versus* ${}_mK$ for: (a), compound (**3**); and (b), compound (**4**). ○, Theoretical; ■, experimental

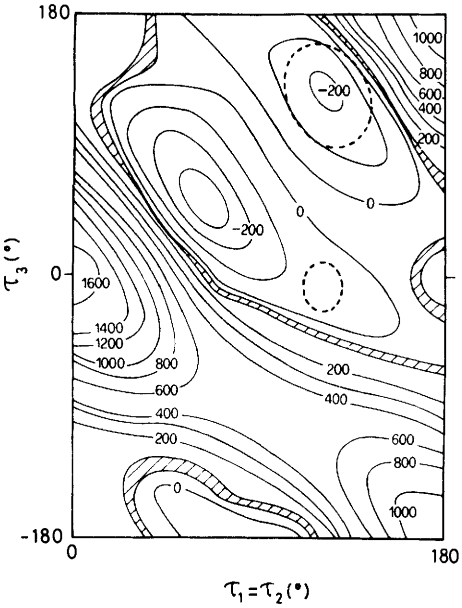

Figure 9. Molar Kerr constant contour map on the 'diagonal plane' for compound (**3**). Symbols as in Figure 8

moments, and molar Kerr constants. For molecules which belong to the point group C_3, the calculation of the principal semi-axes of the molecular polarizability ellipsoid requires only two equations. In fact, the conformations of C_3 symmetry must have* $b_2 = b_3$ and $\mu_2 = \mu_3 = 0$ (*i.e.*, the resultant dipole moment lies in a direction which is parallel to axis b_1); only two experimental data, which in our case are the electron polarization and the molar Kerr constant, are required to calculate b_1 and b_2. For triethyl ethane-1,1,1-tricarboxylate (**3**), the use of the experimental ${}_{\mathrm{E}}P$ and ${}_{\mathrm{m}}K$ (Tables 3 and 4) furnishes $b_1 = 25.42 \pm 1.66$ and $b_2 = 25.89 \pm 1.66$.

The comparison between theoretical and experimental values of b_1/b_2 and $(b_1 - b_2)$ as functions of $\tau_1 = \tau_2 = \tau_3$ is shown in Figure 5. It can be seen that there are two cross-points between theoretical and experimental values at $\tau = 42$ and 138°; taking into account standard deviations, the τ values range between 35—50° and 130—145°. In the same intervals, the calculated energy differences are 2.6—2.8 and 0.2—1.9 kcal mol^{-1} (Figure 4); therefore, the conformations in the latter range should be preferred. For this range, Figure 6 shows the slopes $\Delta F/\Delta\tau$ ($F = E$, μ, and ${}_{\mathrm{m}}K$) as function of τ: the rates of change of $\Delta E/\Delta\tau$ and $\Delta\mu/\Delta\tau$ are negligible in comparison with that of $\Delta_{\mathrm{m}}K/\Delta\tau$. As a consequence, the agreement between calculated and experimental values shown in Figure 7a can be considered satisfactory.

To draw the contour maps of μ^2 and ${}_{\mathrm{m}}K$, the proper four-dimensional hypersurfaces were partitioned into subspaces analogous to those described for the energy hypersurface. These maps were compared with the corresponding conformational energy maps.

For compound (**3**), the maps on the 'diagonal plane' are shown in Figures 8 and 9. It can be seen that the experimental values of both the dipole moment and molar Kerr constant lie on the borderline of the principal 'energetically allowed' conformational space, which is shown as the dashed contour in these figures. No other cross regions were found.

For triethyl propene-1,1,1-tricarboxylate (**4**), the lack of C_3 symmetry does not allow the experimental analysis of the polarizabilities; moreover, the presence of the ethyl group at C(1) introduces new degrees of freedom and the analysis of the total conformational space becomes computationally very heavy. According to the energy calculations and the results obtained for compound (**3**), only the variation of μ and ${}_{\mathrm{m}}K$ with $\tau_1 = \tau_2 = \tau_3$ were examined: the agreement between calculated and experimental data is satisfactory (Figure 7b).

Taking into account the rather large 'energetically allowed' conformational space, the conformation of compounds (**3**) and (**4**) should be described as a weighted mean of the population of rotamers. However, the complexity of the analysis, the method of calculation, and the large variations of the molecular properties with τ suggest that the best information is given by the general trend of the maps. In this view, a 'propeller-type' conformation with $120° < \tau < 140°$ seems to be the most reliable for compounds (**3**) and (**4**).

Acknowledgements

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* In the case of polar molecules, the commonly adopted convention is to denote the semi-axes lying nearest to the direction of the resultant dipole moment as b_1.