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Kerr Effect Studies of the Conformations of Mono- and Di-carboxylic Aliphatic Esters

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The dipole moments and molar Kerr constants of dimethyl and diethyl malonate in carbon tetrachloride at 25 °C are recorded. Details of the equipment and procedures are given. A re-examination of polarity and polarizability of $-CO_2Me$ group and the $C(sp_2)-O$ bond indicates that the CO_2Me group is planar. The CNDO/2 method has been used to deduce the preferred gas-phase conformations of dimethyl malonate. The preferred solution-state conformations of dimethyl and diethyl malonate, indicated by the analysis of experimental and calculated dipole moments and by molar Kerr constants, are shown to be consistent with the theoretical predictions. The experimental data for the investigated dicarboxylic esters may be well interpreted in terms of two rotamer populations centred on two energy minima separated by a barrier of 2—3 kcal mol^{-1} ($\tau_1 = 90°$; $\tau_2 = 90°$, and $\tau_1 = 90°$; $\tau_2 = 270°$).

The conformation of monocarboxylic acid esters has been studied by a variety of methods.[1,2] The literature contains little information, however, on the conformation of dicarboxylic acid esters of $R_2C(CO_2R^1)_2$ type,[3–6] and none, as far as we know, on the tricarboxylic acid esters of $H[CH_2]_n$-$C(CO_2R^1)_3$ type. We have undertaken a study of conformation of ethyl esters (R^1 = Et) of these compounds [7] and in this paper we report experimental and theoretical results on the conformation of dimethyl and diethyl malonate (Figure 1), selected as the first necessary step towards the determination of the conformation of tricarboxylic acid esters.

As our conformational studies on bicyclo[*n*.1.0] derivatives [8] have also shown, the use of a single technique, such as dipole moment, is of restricted significance when dealing with non-conjugated compounds and other physical methods must be used in a complementary manner. Among these, the electro-optical Kerr effect seems to be the property of choice for these problems.

The complete approach to this property is briefly as follows. (i) Experimental determination of the Kerr constant of the substance under examination as a solute; this cannot be achieved using a commercially available apparatus. (ii) Experimental determination of the semi-axes b_1, b_2, and b_3 of the molecular polarizability ellipsoid which, in general, also requires the measurement of the degree of depolarization, Δ_u, and the molar electronic polarization, $_EP$.[9] (iii) Calculation of the theoretical Kerr constant for possible conformations. Details of the laboratory-built apparatus for Kerr constant measurements as well as of the computing technique used are also reported in the present paper.

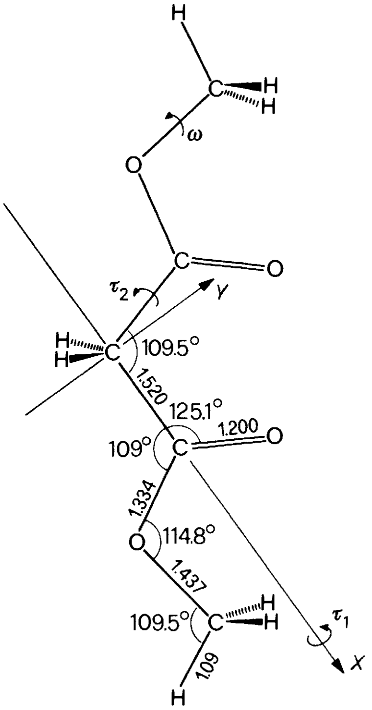

Figure 1. Structural model and internal rotation angles ($\tau_1 = \tau_2 = 0°$)

Experimental

The samples were commercial products (Fluka AG, Buchs) with purity >99% and were purified by distillation. Carbon tetrachloride (Analytical Reagent, Carlo Erba, Milano) was treated with alcoholic NaOH and distilled.

Physical Measurements and Results.—Electric dipole moments and molar Kerr constants of solutes at infinite dilution were determined by measuring the dielectric constants, the refractive indices, the densities, and the Kerr constants of anhydrous carbon tetrachloride solutions at 25.00 ± 0.05 °C (the Kerr apparatus is in a thermostatted room). Usually, at least five solutions with weight fractions w_2 in the range 10^{-2} to 10^{-3} were employed.

For dielectric-constant measurements a Dipolmeter W.T.W., model DM01, equipped with a gold-plated DFL2 measuring cell was used ($\Delta\varepsilon/\varepsilon \simeq 10^{-5}$ at 2 MHz).

The refractive indices were measured using a Jenoptik Jena PR2 Pulfrich refractometer (accuracy of about $\pm 5 \times 10^{-6}$). The light sources are Na and Hg lamps as well as He and H_2 Geissler tubes. The appropriate number of filters gives the following wavelengths: C = H_α = 6 563, D = Na = 5 893, d = He = 5 876, e = Hg = 5 461, F = H_β = 4 861, g = Hg = 4 358, and h = Hg = 4 047 Å.

The densities were measured using a *ca.* 6 ml Sprengel-Ostwald pycnometer (accuracy of about $\pm 5 \times 10^{-6}$) calibrated using the solvent.

The Kerr constants were determined by an apparatus that uses the photometric technique [10] and is similar in principle to the arrangement described by Le Fèvre and co-workers.[11,12] A Beckman DU spectrophotometer furnished the light

Table 1. Incremental values of dielectric constant, density, refractive index, square of refractive index, and Kerr constant for solutions in CCl_4 at 25 °C

Compound	10^5w_2	$10^5\Delta\varepsilon$	$-10^5\Delta d$	$-10^5\Delta n$	$-10^5\Delta n^2$	$10^{10}\Delta B$
Dimethyl malonate (1)						
	792	6 658	794	60	176	4
	1 737	14 410	1 392	128	372	23
	2 915	24 120	2 152	210	612	42
	3 688	29 820	2 674	266	775	54
	4 405	36 000	3 155	315	916	61
Diethyl malonate (2)						
	393	3 062	145	28	83	4
	1 105	8 434	744	92	267	19
	1 539	12 110	1 040	126	367	27
	2 056	15 780	1 541	150	436	39
	2 596	19 910	2 184	187	545	46

source and the monochromator. The polarizing prisms, the Kerr cell, and the compensator were enclosed within a black polymethylmethacrylate cupboard. The detection system (photomultiplier, amplifier, and digital voltmeter) with a high sensitivity was a Circus 10 apparatus (Circus Instruments, Milan). A lens with suitable focal length was inserted near the monochromator slit to obtain a parallel beam. The polarizing prism was a square-ended Nicol of area 1 cm^2. The body of the Kerr cell was a PTFE tube of i.d. 2.0 cm and length 10.3 cm. Each window of strain-free optical glass was fixed against one end of the tube by means of a compressible silicone rubber ring and a turned PTFE cup; the absence of strain birifringence and the hydraulic seal was thus ensured. Care was taken to ensure that the optical glasses were perfectly parallel between themselves and perpendicular to the axis of the cylinder. The filling or emptying of the cell was carried out by means of two small tapered holes. Within the cell, each of the two plane-parallel brass electrodes (length 10.3 cm) was fixed by means of two screws crossing the body of the cell; this arrangement gave rigidity, a uniform inter-electrode gap (0.20 cm), and provided the electrical contact. The opposing faces of the electrodes were milled flat and coated with platinum black to diminish surface reflection. The compensator was a thin whole-plate of mica sandwiched between two polished optical windows and mounted in a precision rotator (Oriel 1641); the entire apparatus enables angular settings to be read to better than 0.01°. Several compensators have been prepared and the compensator factor of the various sheets of mica have been obtained from measurements on pure benzene using for the Kerr constant of benzene the standard value of 0.410×10^{-7} (at 25 °C and with Na light). The phase difference of the compensator used for the measurements reported here was 4.682 ± 0.326 as determined from *ca.* 40 measurements with a voltage range between 4 and 10 kV. A power supply (model 90/1300, E. Pesatori, Milano) was used to produce precise high voltages of 0.5—30 kV; this high tension d.c. output was read on a meter calibrated in kV. Loss of dielectric properties of the medium caused by too high a tension or conductibility of the tested solutions was checked by means of a 0—30 µA current meter inserted on the earth connection of one of the two electrodes.

Table 1 shows, for solutions each containing weight fractions w_2 of solute in CCl_4, the differences $\Delta\varepsilon$, Δd, Δn, Δn^2, and ΔB between the dielectric constants, the densities, the refractive indices, the squares of the refractive indices, and the Kerr constants, respectively, of the solutions and the solvent. For the pure solvent (CCl_4), the physical properties named have the values, at $T = 25$ °C and $\lambda = 589.3$ nm, as follows: ε_1, 2.2270; d_1, 1.584 54; n_1, 1.45732; $10^{10}B_1$, 83; ${}_{\mathrm{s}}K_1$, 8.9×10^{-15}; h, 0.484 99; and J, 0.473 15.

Calculations

Experimental Dipole Moments and Molar Kerr Constants.—The method of Hedestrand [13] as modified by Le Fèvre and Vine [14] was used to calculate solute specific polarizations (${}_{\infty}p_2$) and refractions at the Na D line (${}_{\infty}r_2$) at infinite dilution, assuming the reported solvent properties. The dependence of dielectric constants, ε_{12}, densities, d_{12}, and squared refractive indices at the Na D line, n_{12}^2, on weight fraction, w_2, is usually expressed as equations (1)—(3).

$$\varepsilon_{12} = \varepsilon_1(1 + \alpha\, w_2) \qquad (1)$$

$$d_{12} = d_1(1 + \beta\, w_2) \qquad (2)$$

$$n_{12}^2 = n_1^2(1 + \Gamma\, w_2) \qquad (3)$$

Sometimes, ε_{12}, d_{12}, or n_{12}^2 deviate from these linear relationships as w_2 increases: in such instances a quadratic equation was employed and the parameters were estimated by a non-linear regression.

The appropriate values of α, β, and Γ were selected and ${}_{\infty}p_2$ and ${}_{\infty}r_2$ were calculated from equations (4) and (5),

$${}_{\infty}p_2 = p_1(1 - \beta) + C\,\varepsilon_1\alpha \qquad (4)$$

$${}_{\infty}r_2 = r_1(1 - \beta) + D\,n_1^2\Gamma \qquad (5)$$

where $p_1 = (\varepsilon_1 - 1)/d_1(\varepsilon_1 + 2)$, $C = 3/d_1(\varepsilon_1 + 2)^2$, $r_1 = (n_1^2 - 1)/d_1(n_1^2 + 2)$, and $D = 3/d_1(n_1^2 + 2)^2$.

The solute molar electronic polarization (${}_{\mathrm{E}}P$) was determined from solution measurement of refractive indices at the seven previously indicated wavelengths. At each wavelength, the $({}_{\infty}r_2)\lambda$ value was calculated from equation (5); in all cases a plot of $({}_{\infty}R_2)\lambda$ *versus* $1/\lambda^2$ fitted equation (6)

$$({}_{\infty}R_2)\lambda = {}_{\mathrm{E}}P + (\text{constant})\,\lambda^{-2} \qquad (6)$$

and the ${}_{\mathrm{E}}P$ value was estimated by a least-squares fit, where R = molar refraction. When possible, the solute ${}_{\mathrm{E}}P$ was also determined from measurements on the pure substance.

To estimate the contribution of atomic polarization, ${}_{\mathrm{A}}P$, it was assumed that a correction for atomic polarization of 5—15% of ${}_{\mathrm{E}}P$ is reasonable, *i.e.*, the ratio ${}_{\mathrm{D}}P/{}_{\mathrm{E}}P$ lies between 1.05 and 1.15. Where the ratio $R_{\mathrm{D}}/{}_{\mathrm{E}}P$ lies in the same range,

Table 2. Molar refraction of pure compounds and molar refraction at infinite dilution for solutions of compounds (1) and (2) in CCl_4 as a function of wavelength (T = 25 °C)

Compound	Molar refraction	λ/nm 656.3	589.3	587.6	546.1	486.1	435.8	404.7
Dimethyl malonate (1)	R_M	28.42	28.54	28.55	28.65	28.85	29.09	29.30
	${}_\infty R_2$	29.48	29.62	29.63	29.74	29.96	30.20	30.42
Diethyl malonate (2)	R_M	37.64	37.80	37.81	37.95	38.22	38.53	38.80
	${}_\infty R_2$	38.20	38.35	38.39	38.45	38.78	39.09	39.36

Table 3. Polarizations, refractions, dipole moments, and molar Kerr constants of compounds (1) and (2) in CCl_4 at 25 °C

	Dimethyl malonate (1)			Diethyl malonate (2)	
Parameter	This work	Ref. 6[a]	Ref. 4[b]	This work	Ref. 3[c]
α	3.65 ± 0.03	4.79		3.45 ± 0.003	3.46[d]
β	−0.438 ± 0.015	−0.22		−0.529 ± 0.035	−0.516
γ	−0.049 ± 0.0003			−0.050 ± 0.002	−0.047
Γ	−0.098 ± 0.0007			−0.100 ± 0.005	
δ	18.0 ± 1.0			22.6 ± 1.0	28.4
${}_\infty P_2$	148.6 ± 0.9	156.97	153.0	175.2 ± 1.5	175.2
R_D	29.6 ± 0.4		28.131	38.4 ± 1.0	38.3
${}_EP$	27.9 ± 0.004[e] 28.9 ± 0.001[f]			36.9 ± 0.01[e] 37.5 ± 0.001[f]	
μ	7.95 ± 0.03	7.64[g]	8.04[h]	8.63 ± 0.06	8.57[i]
${}_\infty({}_mK_2)$	20.6 ± 1.3			32.8 ± 1.6	35.2

[a] In benzene at 30 °C. [b] In benzene at 20 °C. [c] In CCl_4 at 25 °C. [d] Non-linear regression. [e] From measurements on the pure substance. [f] From measurements on solutions. [g] ${}_EP + {}_AP$ computed from bond refractions. [h] ${}_DP = R_D$. [i] ${}_DP = 1.05\ R_D$.

the condition ${}_DP = R_D$ was imposed; otherwise, the adopted correction will be specified.

A slightly modified version of the method of Le Fèvre and Le Fèvre[15] was used to calculate the specific Kerr constant at infinite dilution. The specific Kerr constant is defined in equation (7), where B is the Kerr constant, λ is the wavelength

$$ {}_sK_i = 6\ \lambda\ n_iB_i/d_i\ (\varepsilon_i + 2)^2(n_i^2 + 2)^2 \qquad (7)$$

of the light, and i refers to the pure solvent, 1, the pure solute, 2, or the solution, 12.

The following assumptions were used: (a) the specific Kerr constants of the component materials are additive, *i.e.* ${}_sK_{12} = {}_sK_1\ (1 - w_2) + {}_sK_2w_2$; (b) the dependence of ε_{12}, d_{12}, n_{12}^2, n_{12}, and B_{12} on w_2 are expressed by equations (1)—(3) together with equations (8) and (9). Where necessary, the

$$n_{12} = n_1(1 + \gamma\ w_2) \qquad (8)$$

$$B_{12} = B_1(1 + \delta\ w_2) \qquad (9)$$

dependence of n_{12} or B_{12} on w_2 was expressed by a quadratic equation. Therefore, the specific Kerr constant at infinite dilution is given by equation (10) where $J = 2/(\varepsilon_1 + 2)$ and

$${}_\infty({}_sK_2) = {}_sK_1(1 + \delta + \gamma - \beta - J\,\varepsilon_1\alpha - hn_1^2\Gamma) \qquad (10)$$

$h = 2/(n_1^2 + 2)$. The values used in the calculations are reported earlier.

Equation (10) is different from the corresponding equation (11) in ref. 15 in the term $hn_1^2\Gamma$, which substitutes the term $H\gamma$ where $H = 4n_1^2/(n_1^2 + 2)$. The difference is due to an approximation introduced in equation (11) of ref. 15; such an approximation is generally satisfactory, but does not seem necessary.

Table 2 reports the molecular refractions obtained from measurements of the refractive indices of the pure compounds (R_M) and of the solutions in CCl_4 (${}_\infty R_2$) as a function of wavelength. Table 3 shows polarizations, refractions, dipole moments, and molar Kerr constants calculated from the values in Table 1. All these quantities are given throughout in SI 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 with standard deviations.

Theoretical Dipole Moments and Molar Kerr Constants.—Dipole moments were calculated as reported in the Discussion section. The method of calculating the Kerr constant, ${}_mK$, starts with the concept of apparent bond polarizability. This is a tensor, which is characteristic of each bond, with a longitudinal polarizability b_L in the bond direction and with two transverse polarizabilities b_T and b_V, the latter usually being equal in the case of single bonds. The effect of lone pairs is generally included in the bond polarizabilities.

To obtain the molecular polarizability ellipsoid, specified with respect to a convenient set of orthogonal axes X, Y, and Z, the tensors of individual bonds were added according to the rules of tensor algebra, using the actual or calculated geometry. The symmetric tensor of molecular polarizability was diagonalized by means of a sub-routine, which calculates the three principal polarizability components b_1, b_2, and b_3 together with the unit vectors specifying the corresponding principal axes of the molecules. With this information, the components μ_X, μ_Y, and μ_Z of the permanent electric moment may be resolved along the principal axes to obtain μ_1, μ_2, and μ_3. Substitution of the calculated quantities b_i and μ_i (i =

Table 4. Bond moments and bond polarizabilities

Bond	M^a	b_L	b_T	b_V	Ref.
H–C	0.00	0.712	0.712	0.712	16
$C(sp_3)$–$C(sp_2)$	1.00	1.08	0.29	0.29	16
C=O		2.56	1.56	0.51	16
$C(sp_3)$–O		0.99	0.51	0.51	18
$C(sp_2)$–O		0.800	0.590	0.590	9
$C(sp_2)$–Cl	5.30	4.70	2.20	1.70	16

[a] Ref. 17.

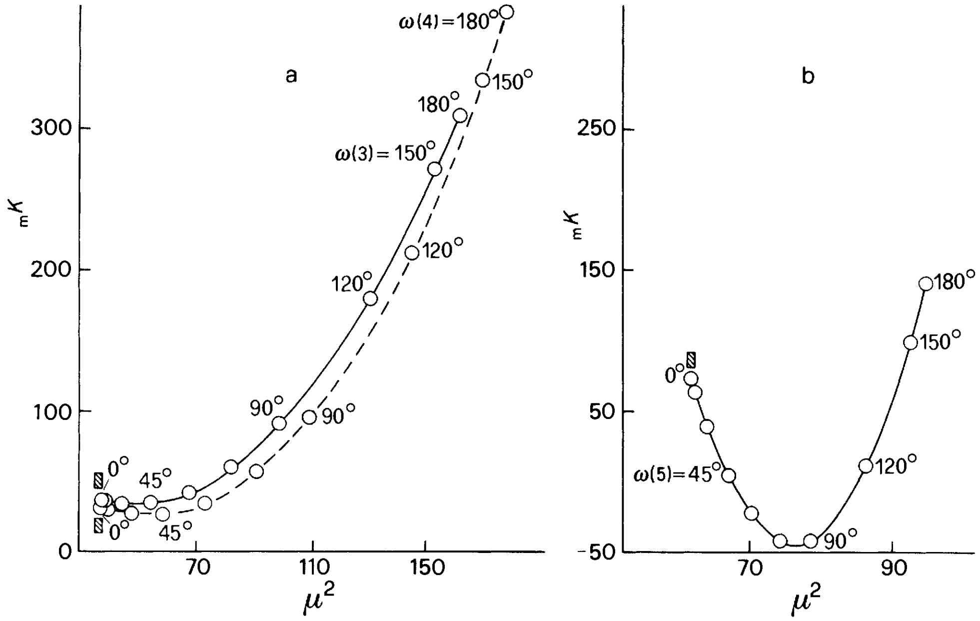

Figure 2. Plot of $_mK$ *versus* μ^2 for: a, methyl formate (3) and methyl acetate (4); and b, methyl chloroformate (5). ○ Theoretical; ■ experimental

1—3) in the appropriate equation [10,16] yields the theoretical molar Kerr constant for the geometric form of the molecule under study.

The bond moments and polarizabilities used in the calculations are reported in Table 4.

Conformational Energy and Molecular Geometry.—Calculations of conformational energy of dicarboxylic acid esters as a function of the torsional angles τ_1 and τ_2 (Figure 1) were carried out by the CNDO/2 semi-empirical method; [19] a modified version of QCPE program no. 141 was used. Since structural determinations for our derivatives are lacking, the ground-state molecular geometry of methyl acetate [20] was used.

Discussion

The conformation of the ester group in monocarboxylic acid esters has been determined by many experimental methods to be in the planar *Z*-form.[21] However, the results of conformational analysis based on dipole moments and molar Kerr constants indicate a nearly planar *Z*-conformation with the C–O–R triangle rotated about the CO–O bond by an angle $\omega \simeq 30°$.[22]

In order to settle this discrepancy, we have thoroughly re-investigated this problem focusing our attention particularly on two factors, which are especially important in the evaluation of the theoretical value of $_mK$ of these compounds: (i) the modulus and direction of the dipole moments; and (ii) the values of bond polarizabilities. In fact, the scheme of bond values can be used to predict dipole moments and anisotropic polarizabilities providing the data are applied to molecular situations analogous to those from which they were derived, because the bond data are not constant throughout all molecular environments. For the compounds under examination, it seems that the most critical values are those relative to $C(sp_2)$–O and $C(sp_3)$–O bonds, which are commonly assumed to be equal.

As far as the first factor is concerned, the best way to overcome this difficulty seemed to be to obtain the group dipole moment, $\mu(CO_2Me)$, from the experimental dipole-moment values of methyl formate [compound (3)], methyl acetate [compound (4)], and methyl chloroformate [compound (5)].[22] As it has recently been shown [23] that there is a very strong preference for the planarity of the carboxyalkyl group and the rotation about the $C(sp_2)$–O bond is hindered by a barrier of some kcal mol^{-1}, the calculation was performed on compounds (4) and (5), while compound (3) was used as a check. This calculation was carried out by using the experimental geometry of (4) and the bond moments of Table 4; the following values were obtained (axes as in Figure 1): $\mu_X = 0.18$; $\mu_Y = 5.99$; $\mu_Z = 0$, and $\mu = 6.00$. This value practically coincides with the experimental value for μ (3), because a bond-moment scale based on M(H–C) = 0.00 is used.

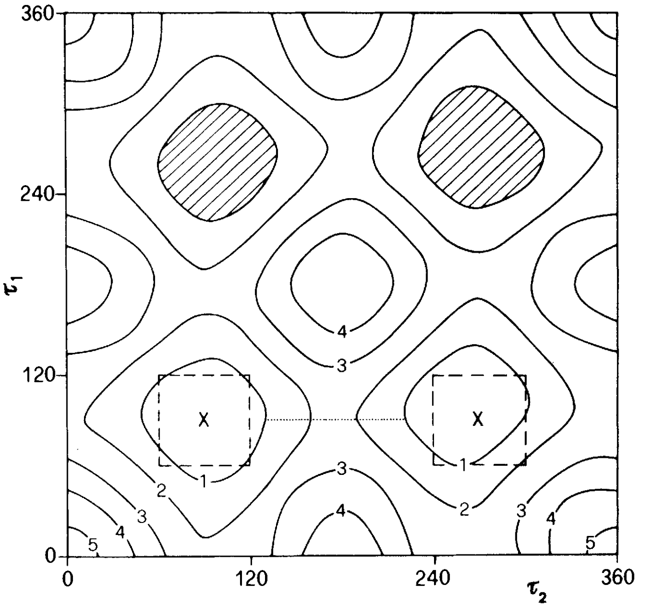

Figure 3. Conformational energy map for dimethyl malonate (1); isoergic curves in kcal mol^{-1}. The energy is relative to a zero at the most stable conformation; the approximate minima are designated by ×. The shaded areas represent the stable conformational space that lies inside the 1 kcal mol^{-1} region. The dotted line indicates the one-ring flip mechanism

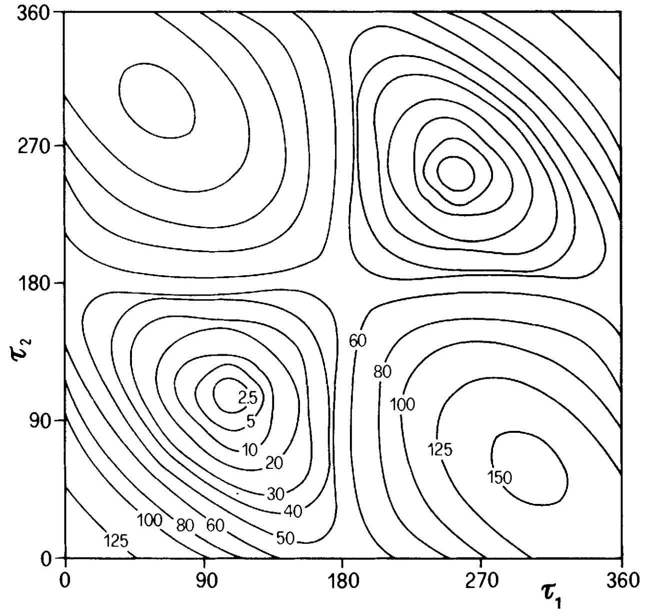

Figure 4. Square-dipole moment (10^{-60} C^2 m^2) contour map for dimethyl malonate (1)

Therefore, the postulated planarity of the CO_2Me group seems justified *a posteriori*.

With regard to bond polarizabilities, the values for the $C(sp_2)$–O bond appear to be the least accurately defined in the literature. Because the length of this bond in the ester group and in the oxirane are practically equal, we have adopted polarizability values previously obtained for that group.[9] For the other bonds the values of Table 4 were used.

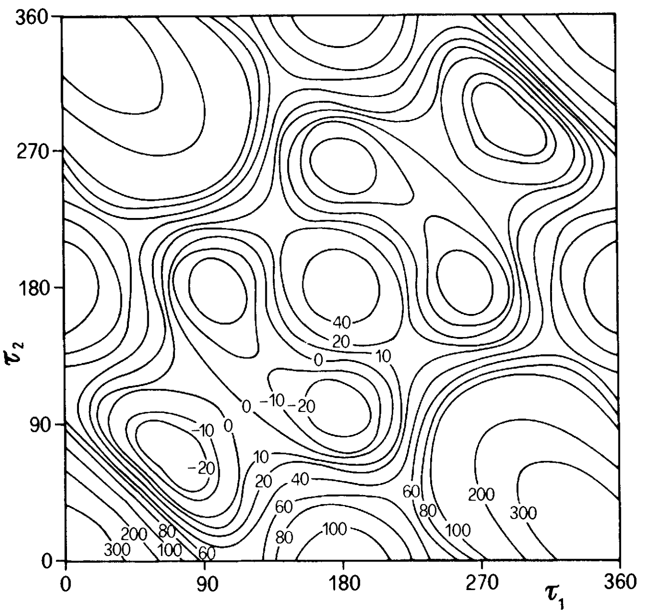

Figure 5. Molar Kerr constant (10^{-27} m^5 V^{-2} mol^{-1}) contour map for dimethyl malonate (1)

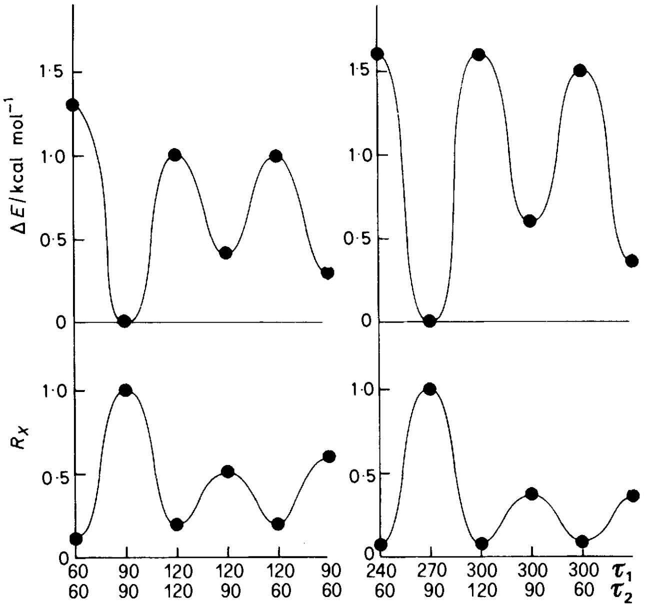

Figure 6. Conformational energy function and population of rotamers (T = 298 K) for compound (1); the lines joining the calculated points are qualitatively drawn

The results of calculations of $_mK$ and μ as functions of the dihedral angle ω are shown in Figure 2 as plots of $_mK$ against μ^2 for compounds (3), (4), and (5). Comparison with the experimental data suggests that a planar conformation of the CO_2Me group is highly probable. This conformation was therefore assumed in all subsequent calculations.

Relying on this information and employing the values reported in Figure 1 for the other parameters, the conformational energy, dipole moment, and molar Kerr constant of dimethyl malonate [compound (1)] were calculated as functions of the torsional angles τ_1 and τ_2. The results are reported as contour maps of E, μ^2, and $_mK$ in Figures 3, 4, and 5, respectively.

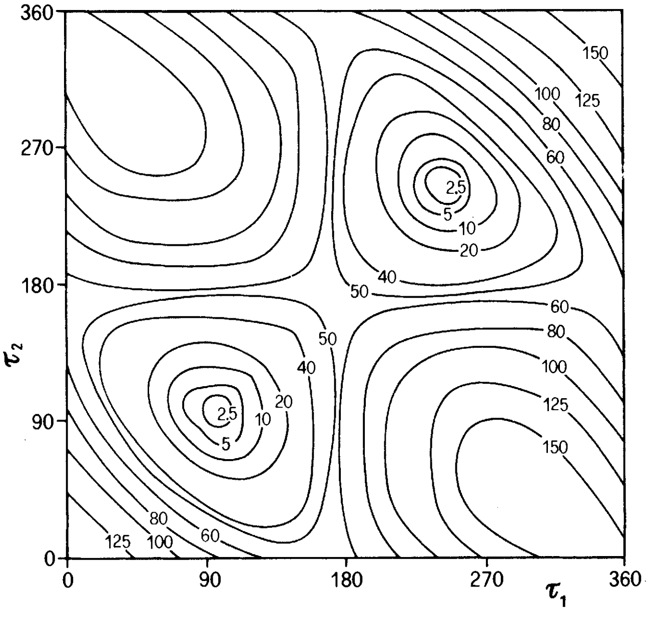

Figure 7. Square-dipole moment (10^{-60} C^2 m^2) contour map for diethyl malonate (2)

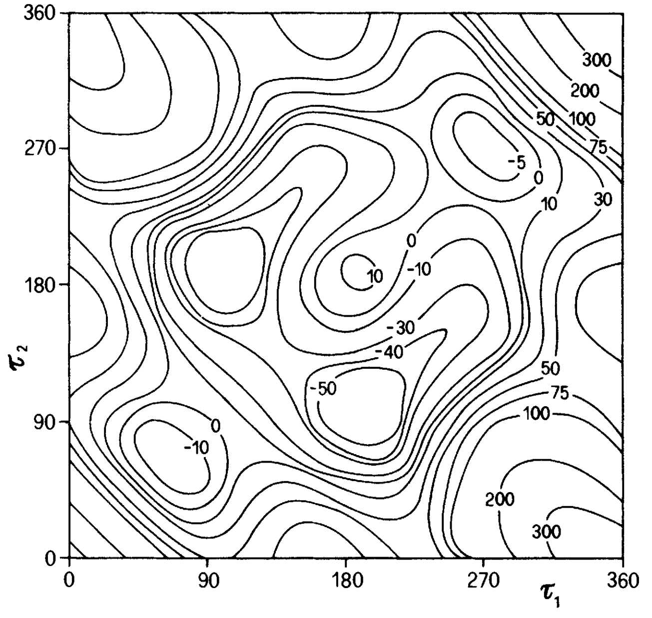

Figure 8. Molar Kerr constant (10^{-27} m^5 V^{-2} mol^{-1}) contour map for diethyl malonate (2)

On the intramolecular energy map of dimethyl malonate the shaded areas represent the portions of the conformational space that are ' energetically allowed,' *i.e.* lie inside the 1 kcal mol^{-1} region. The lowest energy path (dotted line in Figure 3) for the interconversion between the two flat minima * requires a one-ring flip mechanism[24] having a perpendicular ($\tau_1 = 90°$; $\tau_2 = 180°$) conformation as approximate geometry of the transition state with an energy barrier of 2—3 kcal mol^{-1}. The (*Z*,*Z*) form (Figure 1) as well as the (*E*,*E*) form and the (*E*,*Z*) forms are those of highest energy. As a result, the molecular population is distributed over a wide range of torsional angles and hence the conformation of compound (1) may approximately be described as the time average of two ' mean ' molecular populations each of which is distributed over a square region of torsional angles (compared with the dashed contour in Figure 3). The variation of the conformational energy together with the population of rotamers (expressed as fractions R_X) are shown in Figure 6. Using these populations and taking into account the statistical weights, the ' mean ' values of μ^2 and $_mK$ result in $\mu^2 = 13.6$ and $_mK = -7.29$, and $\mu^2 = 158$ and $_mK = 110$, respectively. The means weighted on the two energy minima give, finally, $\mu = 7.89$ and $_mK = 32.3$. These values are in satisfactory agreement with the experimental ones ($\mu = 7.95 \pm 0.03$; $_mK = 20.6 \pm 1.3$) especially if we consider that the energy differences are small while these molecular parameters show large differences in the two square boxes.

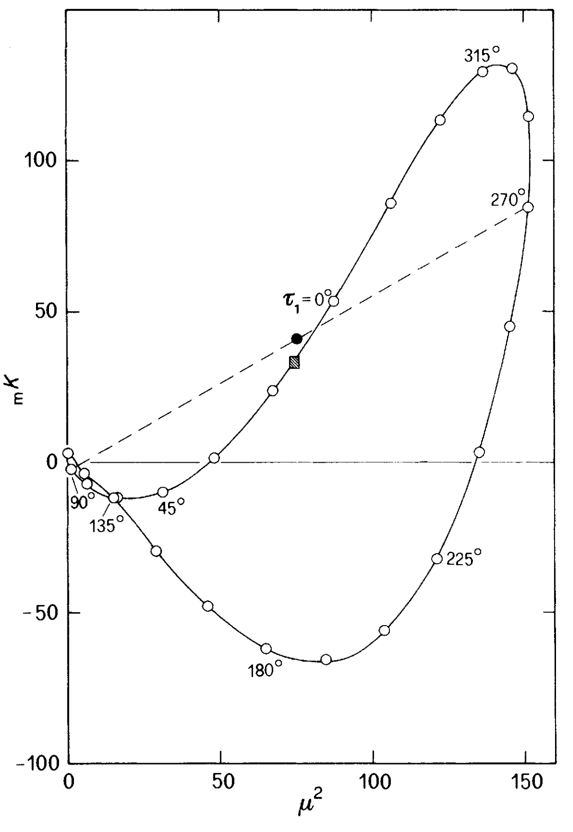

Figure 9. Correlation between calculated $_mK$ and μ^2 as functions of the dihedral angle τ_1 (τ_2 = cost. = 90°) and comparison with experimental (■) values

The contour maps of μ^2 and $_mK$ for diethyl malonate (2) are shown in Figures 7 and 8. The values of the dipole moment and molar Kerr constant as functions of the dihedral angle τ_1 (τ_2 = constant = 90°) are reported in Figure 9 as a plot of $_mK$ *versus* μ^2. The results may be interpreted either as a single helical conformation with $\tau_1 \simeq 10°$ or as mixtures of different pairs of conformations. Based on the conformational energy map for compound (1), the first possibility can be ruled out; as far as the second possibility is concerned, it seems reasonable, as a first approximation, to describe the conformation of compound (2) as a mixture of two butterfly conformations ($\tau_2 = 90°$, $\tau_1 = 90°$ or $\tau_1 = 270°$) in a ratio of *ca.* 1 : 1 (dashed line in Figure 9). The corresponding calculation gives the values $\mu = 8.73$ and $_mK = 42.1$ (full circle

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* The minima correspond approximately to the butterfly[24] conformations, $\tau_1 = \tau_2 = 90°$, and $\tau_1 = 90°$, $\tau_2 = 270°$.

in Figure 9), in good agreement with the experimental results ($\mu = 8.63 \pm 0.06$ and ${}_{m}K = 32.8 \pm 1.6$).

In conclusion, the re-examination of polarity and polarizability of the CO_2Me group and $C(sp_2)$–O bond indicates that the CO_2Me group in carboxylic esters is planar. Moreover, the superposition of the conformational energy contour map and the theoretical dipole moment and Kerr constant contour maps shows that the experimental data for dicarboxylic esters (1) and (2) may well be interpreted in terms of two rotamer populations centred on two energy minima separated by a barrier of 2—3 kcal mol^{-1}.

References

1 G. I. L. Jones and N. L. Owen, *J. Mol. Struct.*, 1973, **18**, 1.
2 O. Exner, in ' Chemistry of the Functional Groups: Supplement A: The Chemistry of Double-bonded Functional Groups,' ed. S. Patai, Wiley, New York, 1977, ch. 1.
3 M. J. Aroney, D. Izsak, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1962, 3997.
4 V. A. Granzhan and O. N. Vlasov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 1963, **37**, 1091.
5 B. Krishna, S. K. Bhargava, and B. Prakash, *J. Mol. Struct.*, 1971, **8**, 195.
6 A. R. Saksena, C. K. Moghe, and B. Krishna, *J. Chem. Phys.*, 1974, **60**, 3345.
7 M. T. Cataldi, B. Marcandalli, and D. Pitea, unpublished data.
8 G. Favini, D. Pitea, M. Sottocornola, and R. Todeschini, *J. Mol. Struct.*, 1982, **87**, 53.
9 D. Pitea, R. Todeschini, and F. Gatti, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1611.
10 C. G. Le Fèvre and R. J. W. Le Fèvre, in ' Physical Methods of Chemistry,' ed. A. Weissberger, Wiley, New York, 1972, vol. I, part III C, p. 399.
11 R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933; 1965, 3520.
12 R. J. W. Le Fèvre and S. C. Solomons, *Aust. J. Chem.*, 1968, **21**, 1703.
13 G. Hedestrand, *Z. Phys. Chem.* (*Frankfurt am Main*), 1928, **B2**, 428.
14 R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1937, 1805; R. J. W. Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1.
15 C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041.
16 M. J. Aroney, *Angew. Chem. Int. Ed. Engl.*, 1977, **16**, 663.
17 C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.
18 R. J. W. Le Fèvre, K. Pierens, and A. Sundaram, *J. Chem. Soc.*, 1963, 479.
19 J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 5129.
20 G. Williams, N. L. Owen, and J. Sheridan, *Trans. Faraday Soc.*, 1971, **67**, 922.
21 O. Exner, in ' Dipole Moments in Organic Chemistry,' G. Thieme, Stuttgart, 1975.
22 R. J. W. Le Fèvre and A. Sundaram, *J. Chem. Soc.*, 1962, 3904.
23 N. K. Allinger and S. H. M. Chang, *Tetrahedron*, 1977, **33**, 1561.
24 D. Pitea and A. Ferrazza, *J. Mol. Struct., Theochem.*, 1983, **92**, 41.

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