Conformational Analysis and Dipole Moments of Dialkyl Esters of Some Simple Dicarboxylic Acids

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Abstract: Conformational energies of the dimethyl esters of a series of dicarboxylic acids $CH_3OOC(CH_2)_nCOOCH_3$ (n = 1-4 and 8) were calculated by using semiempirical potential energy functions. Dipole moments of these compounds were evaluated and compared with the experimental results. Various models, which have been proposed for the conformation around the $C{-}C \nrightarrow C(O){-}O$ bond in the literature, were taken into consideration. The observed values of the dipole moment were found to be reasonably reproduced by two models: one expressed in the six-state scheme and the other in the three-state scheme. The latter model has provided a better explanation for the dielectric behavior of diethyl succinate, which is known to be abnormal. This model is also compatible with that suggested by Moravie and Corset. Both models, however, failed to give an agreement with experiment in the trans-gauche energy difference for diethyl succinate.

Dielectric properties of diethyl esters of the type $[CH_2]_n(COOEt)_2$ having n = 0, 1, 2, 3, 4, and 8 were studied by Smyth and Walls[1] as early as 1931. They noted a sharp decrease in the dipole moment at n = 2 (succinate) in this homologous series. While experimental values of the other esters are scattered in a rather confined range from 2.54 (n = 1) to 2.40 D (n = 4), the dipole moment of succinate was found to be 2.14 D. Smyth et al.[2] investigated the variation of the dipole moment of succinate over a wide range of temperature by using kerosene as the solvent. They found that the moment increases regularly from 2.01 D at 0 °C to 2.47 D at 180 °C. The latter value is equivalent to the observed moments for the higher members of the series. Similar studies were reported later by Ketelaar and van Meurs[3] and by Aroney, Izsak, and LeFevre[4] for a series of diethyl esters with n = 0, 1, 2, 4, and 8. The former group carried out dielectric measurements in benzene as well as in dioxane over a temperature range 20-70 °C. The latter group used carbon tetrachloride as the solvent at 25 °C. In accord with the results reported by Smyth et al.,[1] substantially lower values were found for succinate in all the solvents used. Dipole moments of dimethyl esters (n = 1, 2, 3, and 4) were reported by Granzhan and Vlasov.[5] The aforementioned results for diethyl esters were well reproduced within some marginal differences, suggesting that the replacement of the terminal groups from ethyl to methyl does not result in any change of the overall dipole moment of these esters. The authors[5] recognized a small decrease in the dipole moment at n = 4. Combined with the large fall at n = 2, they termed the phenomenon an odd-even oscillation.

LeFevre et al.[4,6] measured molar Kerr constants as well for the same series of esters. They calculated the dipole moment and the molar Kerr constant for some representative conformations. In each case, experimental values were found to fall somewhere in between the highest and lowest calculated values. Since the relative stabilities among these conformers are not considered, comparison is inevitably qualitative.

In the present investigation, we have performed conformational analyses on a series of dimethyl esters. Conformational energies have been elucidated by using semiempirical potential energy functions of Yoon et al.[7] The geometry of the ester group including the direction of its dipole moment has been established in the dipole moment studies on various esters by Saiz et al.[8] As for the rotation around the $CH_2 \nrightarrow COOCH_3$ bond, however, the location of the most preferred conformation has been a subject of controversy. From the infrared and Raman studies on methyl propionate, $CH_3CH_2COOCH_3$, Dirlikov, Stokr, and Schneider[9] inferred that the lowest energy conformation arises when the $C{=}O$ group eclipses the CH bond, while Moravie and Corset[10] concluded that the $C{=}O/CC$ eclipsed form is more stable than the $C{=}O/CH$ eclipsed form (the enthalpy difference $\Delta H = 1.1 \pm 0.3$ kcal mol^{-1}). An intermediate value $\Delta H = 0.08$ kcal mol^{-1} also has been reported for the same molecule.[11] The height of the potential barrier to the rotation seems to be relatively low: the microwave studies on methyl acetate[12,13] and acetic acid[14] suggest a threefold rotational potential with barriers of 0.3-0.5 kcal mol^{-1}. Williams, Owen, and Sheridan[12] speculated that one reason for the low value for these compounds may be due to the sixfold character of the potential intrinsic to the $CH_3 \nrightarrow C(O)O$ group. In an effort to elucidate the most probable conformations for the dialkyl esters, we have examined various models relevant to the aforementioned arguments. Root-mean-square (rms) values of the dipole moment evaluated on these bases have been compared with those observed. The information thus acquired regarding the conformation of dialkyl esters will be used in the configura-

Table I. Geometrical Parameters and Partial Electronic Charges Used in Energy Calculations

bond	length, Å	bond angle	angle, deg	charged atom or group	partial electronic charge
C–C	1.53	∠CCC	112.0	C*	0.54
C–C*	1.53	∠CCC*	112.0	O*	−0.43
C–H	1.10	∠CCH	110.0	O	−0.22
C*–O	1.35	∠CC*O	111.4	(CH_3)	0.11
C*=O*	1.20	∠CC*O*	126.3		
$O{-}(CH_3)$	1.43	$\angle C^*O(CH_3)$	116.7		

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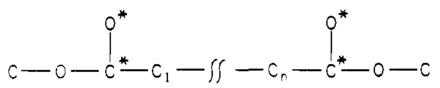

$$C-O-\overset{O^*}{\overset{|}{C^*}}-C_1-\int\!\!\int-C_n-\overset{O^*}{\overset{|}{C^*}}-O-C$$

Figure 1.

tional studies on semiflexible polymers of the general formula $[-OC(O)(CH_2)_nC(O)OR-]_x$ where R carries rod-like properties. This is the subject of the forthcoming paper.[15]

Conformational Analysis

Geometrical Parameters. Bond lengths and bond angles used in this study are given in Table I, where the carbon and oxygen atoms associated with the carbonyl group are marked with an asterisk (Figure 1). Geometrical parameters of the ester group are those used in the dipole moment analysis of dimethyl *trans*-1,4-cyclohexanedicarboxylate by Saiz et al.[8] The value for $\angle C^*O(CH_3)$ was taken from the paper by Mattice and Saiz.[16] The C–C bond length and $\angle CCC$ bond angle were assumed to be identical for all the esters treated.

Potential Energy Function. Nonbonded interatomic van der Waals interactions were evaluated by using 6–12 potential expressions prescribed by Yoon et al.[7] The terminal methyl groups were approximated by a spherical domain having a given van der Waals diameter.[7] A threefold torsional potential with a barrier of 2.8 kcal mol^{-1} was adopted for all the internal $CH_2 \overset{\circlearrowright}{-} CH_2$ bonds of the esters. Partial electronic charges were assigned to the carbon and oxygen atoms of the ester group: values given in Table I yield a group dipole moment $\mu_{ester} = 1.76$ D when the angle between the dipole and the C–C* bond is taken[8] to be 123°. Coulombic interactions were assessed according to the conventional procedure by assigning a value of 3.5 for the effective dielectric constant.

Rotational States. The ester group was assumed to be in the planar, trans configuration, thus O–C eclipsing C*═O*.[8] For the rotation around the C*–C bond, we have examined two models, which emerged from various observations on simpler esters as mentioned in the introductory section.

Model I: In this model, we adopt a six-state scheme, in which the ester groups are allowed to take the *reversed* orientation to a certain extent, besides the regular C*═O*/CC and C*═O*/CH eclipsings. In the trans C*–C conformation ($\psi_{C^*C} = 0$), the carbonyl group C*═O* is opposed by the C_1–C_2 bond (cf. Figure 1). By the rotation $\psi_{C^*C} \simeq 2\pi/3$ and $-2\pi/3$, C*═O* eclipses one of the C_1–H bonds. The reverse conformations, in which the ester C*–O bond eclipses one of the vicinal bonds (thus C*═O* being trans to these bonds), may be defined at three rotational angles: i.e., $\psi_{C^*C} \simeq \pm\pi/3$ and $\psi_{C^*C} = \pi$. To account for the possible existence of the intrinsic energy difference (E_α) associated with these reversal of conformations, we assign a statistical weight of $\alpha = \exp(-E_\alpha/RT)$ to all of the *reversed* states. When the two alternative conformations (i.e., ψ_{C^*C} and $\psi_{C^*C} + \pi$) are equally probable for an ester group, the weight α is unity. For the limiting case with $\alpha = 0$ or $1/\alpha = 0$, the eclipse occurs either with C*═O* or with C*–O exclusively.

Severe steric repulsions may be expected for the conformation $\psi_{C^*C} = \pi$ (i.e., C*–O is cis to C_1–C_2), the ester oxygen and C_2-methylene group being situated at the separation of 2.6 Å. Since the bond angle $\angle O^*C^*C$ (126.3°) is larger than $\angle OC^*C$ (111.4°), a similar interaction taking place between O* and C_2 in the $\psi_{C^*C} = 0$ conformation should be alleviated to a considerable degree. Energy calculations were performed for the six rotational states defined as above around the C*–C_1 bond. Essentially the same argument should apply to the conformation for the C_n–C* bond (cf. Figure 1).

Model II: In the regular three-state scheme, C*═O* eclipses C_1–C_2 and two C_1–H bonds. According to the analysis of Moravie et al.,[10] the conformation in which C*═O* is cis to C_1–C_2 is energetically more favorable than the other two states. Following their suggestion, we assign a statistical weight parameter $\beta = \exp(E_\beta/RT)$ to the $C^*{=}O^*/C_1C_2$ eclipsed form. Here E_β (≥ 0) represents the *stabilization* energy inherent to this conformation. The model we adopted is therefore expressed in a three-state scheme: with $\beta = 1$ (i.e., $E_\beta = 0$), model II reduces to the limiting form (three-state scheme) of model I at $\alpha = 0$. Interactions between nonbonded groups were estimated in the same manner as in model I. We assume an identical model for the C_n–C* bond.

For the C–C bonds joining two methylene carbons in succinate ($n = 2$) and glutarate ($n = 3$), rotational energy minima were determined by calculating the conformational energies as a function of the rotation angles. For the higher homologues ($n \geq 4$), short-range interactions between the two terminal ester groups become less important. Rotational angles and statistical weights were therefore deduced from calculations on a model compound of a simpler form.

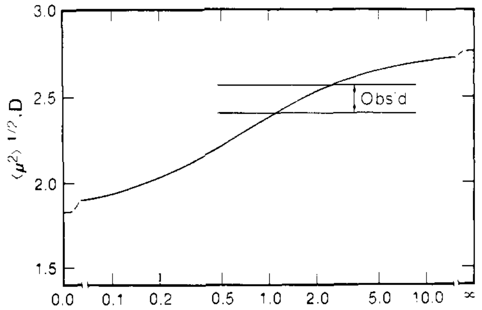

Figure 2. Variation of the dipole moment $\langle\mu^2\rangle^{1/2}$ with α, calculated for dimethyl malonate (model I, 25 °C). Experimental values[1,3–5] were reported in the range specified by the two horizontal lines.

Results of Calculation

Dimethyl Malonate. The conformational energies of the molecule were obtained as a function of bond rotations around C*–C and C–C*. The matrix of a priori statistical weights $\mathbf{U}_{M-I}$ derived for model I with $\alpha = 1$ is given in eq 1 in a symmetric 6 × 6 form[17]

$$\mathbf{U}_{M-I} = \begin{array}{c} \\ (2\pi/3) \\ -(2\pi/3) \\ (0) \\ (\pi/3) \\ -(\pi/3) \\ (\pi) \end{array} \begin{array}{c} \begin{array}{cccccc} (2\pi/3) & -(2\pi/3) & (0) & (\pi/3) & -(\pi/3) & (\pi) \end{array} \\ \begin{bmatrix} 1.00 & 0.22 & 0.50 & 0.54 & 0.79 & 0.01 \\ 0.22 & 1.00 & 0.50 & 0.79 & 0.54 & 0.01 \\ 0.50 & 0.50 & 0.04 & 0.34 & 0.34 & 0.00 \\ 0.54 & 0.79 & 0.34 & 0.69 & 0.36 & 0.03 \\ 0.79 & 0.54 & 0.34 & 0.36 & 0.69 & 0.03 \\ 0.01 & 0.01 & 0.00 & 0.03 & 0.03 & 0.00 \end{bmatrix} \end{array} \qquad (1)$$

where calculations were carried out for the temperature of 25 °C. In practice, a small displacement ($\Delta\psi = 2.7°$) from the regular $\pm 2\pi/3$ and $\pm\pi/3$ states is required when bond angles $\angle C^*CC^* = 112°$ and $\angle CCH = 110°$ are adopted (see Table I); i.e., the exact locations are at ±122.7° and ±57.3°, respectively. For simplicity, however, we shall retain the notations used in eq 1. The a priori statistical weights computed for $\alpha = 1$ include only nonbonded contributions such as the van der Waals and Coulombic interactions. The conformations associated with $\psi_{C^*C} = \pi$ (the last row) and by symmetry $\psi_{CC^*} = \pi$ (the last column) involve severe steric repulsions and, therefore, their weights are low (see eq 1). In the following treatment, we adopt an expression (ψ_{C^*C}, ψ_{CC^*}) to specify the orientation of the ester groups in a given conformation of the molecule. As indicated in eq 1, the lowest energy pairs occur at ($2\pi/3$, $2\pi/3$) and ($-2\pi/3$, $-2\pi/3$) for which the statistical weight of unity is assigned. The (0, 0) conformation is considerably disfavored. When α takes its limiting values, i.e., $\alpha = 0$ or $1/\alpha = 0$, the statistical weight matrix reduces to a 3 × 3 form: with $\alpha = 0$, it may be effectively identified with the upper-left quarter of eq 1, whereas that for $1/\alpha = 0$ is given by the lower-right quarter of the same equation.

The rms dipole moment was calculated by using the parameters given in Table I. The results obtained for model I are shown in Figure 2 as a function of α in the logarithmic scale. The corresponding experimental values[1,3–5] may be found in the range specified by the two horizontal lines. The agreement is satisfactory in the range $\alpha = 1$ to 2 or $E_\alpha = 0$ to -0.4 kcal mol^{-1}; e.g., $\langle\mu^2\rangle^{1/2} = 2.44$ D at $\alpha = 1.0$. To alleviate steric conflicts, rotational minima may be displaced somewhat. A small deviation ($\Delta\psi = 10°$) from the exact eclipsing, $\psi_{C^*C} = \psi_{CC^*} = \pm 2\pi/3$ and $\pm\pi/3$, did not show any significant effect on the calculated values of the dipole moment. The temperature coefficient $d \ln \langle\mu^2\rangle^{1/2}/dT$ was calculated to be 0.2×10^{-3} K^{-1} for $\alpha = 1.0$.

The three-state model for $\alpha = 0$ gives a value $\langle\mu^2\rangle^{1/2} = 1.83$ D, which is too low. Introduction of the β parameter into this scheme leads to model II (see above). In Figure 3, the calculated values of $\langle\mu^2\rangle^{1/2}$ are plotted as a function of E_β ($= RT \ln \beta$) (curve 1 for malonate). As the magnitude of E_β increases, the conformations in which the carbonyl group C*═O* eclipses the vicinal

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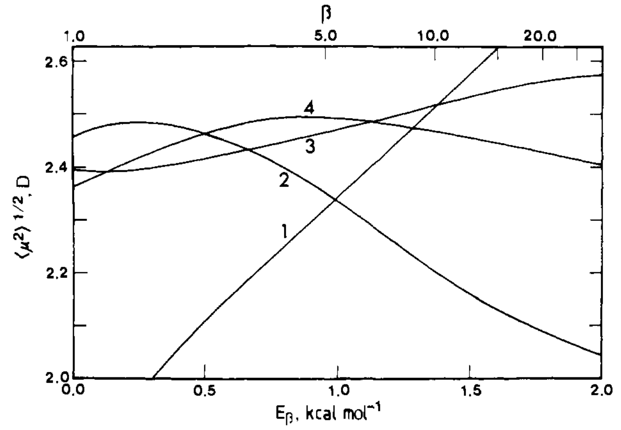

Figure 3. The values of $\langle\mu^2\rangle^{1/2}$ calculated according to model II as a function of E_β (25 °C). Scales on the upper abscissa indicate $\beta = \exp(E_\beta/RT)$. Results are shown for dimethyl esters of (1) malonic acid, (2) succinic acid, (3) glutaric acid, and (4) adipic acid.

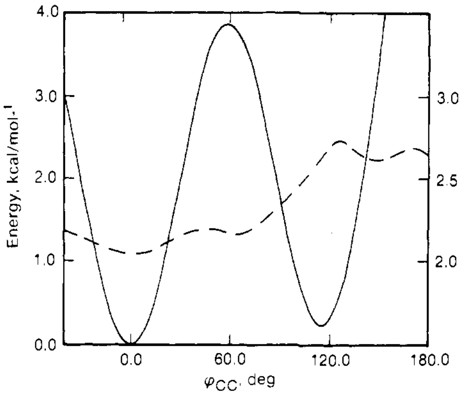

Figure 4. Conformational energies of dimethyl succinate expressed as a function of the rotational angle ϕ_{CC} for the central C–C bond (model I, 25 °C). Also shown by the dotted curve is the variation of the dipole moment $\langle\mu^2\rangle^{1/2}$ calculated for given values of ϕ_{CC} (note that the averages were taken for the neighboring bond rotations, i.e., $\psi_{C^*C_1}$ and $\psi_{C_2C^*}$).

C–C bond tend to be more stabilized. In consequence, the value of $\langle\mu^2\rangle^{1/2}$ rises steadily. The observed values are reasonably reproduced in the range E_β = 1.1 to 1.5 kcal mol^{-1}. At E_β = 1.2 kcal mol^{-1}, $\langle\mu^2\rangle^{1/2}$ is calculated to be 2.44 D for the temperature of 25 °C. The corresponding a priori statistical weights are assembled in eq 2. In this model, the major contribution arises

$$\mathrm{U}_{\mathrm{M-II}} = \begin{array}{c} \\ (2\pi/3) \\ -(2\pi/3) \\ (0) \end{array} \begin{array}{c} \begin{array}{ccc} (2\pi/3) & -(2\pi/3) & (0) \end{array} \\ \begin{bmatrix} 0.26 & 0.06 & 1.00 \\ 0.06 & 0.26 & 1.00 \\ 1.00 & 1.00 & 0.53 \end{bmatrix} \end{array} \tag{2}$$

from the conformations which involve either $\psi_{C^*C} = 0$ or $\psi_{CC^*} = 0$. The weight of unity is assigned to the corresponding elements in eq 2. The relative importance of the ($\pm 2\pi/3$, $\pm 2\pi/3$) states is lowered significantly as compared to that in eq 1. With a displacement of $\Delta\psi = 10°$ from the regularly eclipsed $\pm 2\pi/3$ states, the calculated dipole moment $\langle\mu^2\rangle^{1/2}$ was found to vary somewhat: ca. 5% at E_β = 1.2 kcal mol^{-1}. For the same value of E_β, the temperature coefficient d ln $\langle\mu^2\rangle^{1/2}$/d$T$ was calculated to be slightly negative (−0.1 × 10^{-3} K^{-1}).

Dimethyl Succinate. Energy calculations were carried out as a function of the rotation angles $\psi_{C^*C_1}$, $\phi_{C_1C_2}$, and $\psi_{C_2C^*}$ defined for the bond sequence C*–C$_1$–C$_2$–C*. We examined two models for the bond rotation about C*–C$_1$ and C$_2$–C* in a similar manner as described in the preceding example. In Figure 4, the results obtained by adopting model I are plotted against the rotation angle $\phi_{C_1C_2}$ about the central C$_1$–C$_2$ bond (solid curve), the parameter α required in this model being kept unity. Thus, each point on the curve represents contributions from 36 conformers (6 for each terminal C*–C bond) in equilibrium at 25 °C. Since the two gauche states defined for the C$_1$–C$_2$ bond are symmetric, the one for the negative rotation is omitted from the diagram. As is easily shown by inspection of a proper molecular model, two terminal carbonyl groups may repel each other at a close distance depending on their mutual orientations. In Figure 4, the two energy minima, located at 0 and 115.0°, are well defined, suggesting that the perturbation due to the steric interactions mentioned above is minor. The energy difference ΔE (= $E_g - E_t$) between the gauche and trans minima is estimated to be 0.23 kcal mol^{-1} for α = 1.0. As shown in Figure 5, the magnitude of ΔE thus defined varies little with α (solid curve). Locations of the energy minima remain nearly unaffected by the choice of α within the range shown in the figure. Zetta and Gatti[18] reported NMR studies of dimethyl succinate in the neat liquid. They concluded that the trans form is slightly more stable than the gauche form (ΔE = 0.2 kcal mol^{-1}). However, this conclusion has been derived on the basis of an incorrect formula for ΔE. Use of the corrected expression[19] leads to a value of ΔE in a similar magnitude, but opposite in sign, indicating that the gauche form is more stable. These observations are obviously at variance with the results derived from calculations (Figure 5).

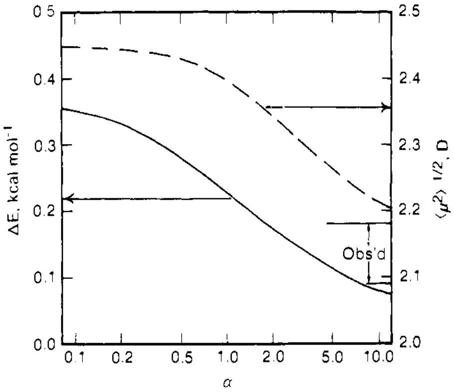

Figure 5. Dependence of ΔE (= $E_g - E_t$) (solid curve) and $\langle\mu^2\rangle^{1/2}$ (dotted curve) on α, calculated for dimethyl succinate (model I, 25 °C). The value of ΔE re-evaluated from the experimental data of Zetta and Gatti[18] is negative (see text) and therefore not included in the figure. Experimental values[1,3–5] of the dipole moment are found in the range specified on the right-hand ordinate.

Values of the dipole moment may be more sensitive to the relative orientation of the ester groups (see above). To examine this effect, we have calculated the rms dipole moment for the fixed conformations of the central C$_1$–C$_2$ bond, rotations around the neighboring C–C* bonds being permitted. The results obtained for α = 1.0 are included in Figure 4 (dotted curve). Here again, 36 conformers differing in the ester group orientation contribute to each point on the curve. The value of $\langle\mu^2\rangle^{1/2}$ defined in this manner exhibits the minimum (2.05 D) for the trans form ($\phi_{C_1C_2}$ = 0) and reaches the maximum (2.73 D) in the neighborhood of the gauche state ($\phi_{C_1C_2}$ = 126°). Although the shape of the entire curve is somewhat complicated in the intermediate region, adoption of the three-state scheme (t, g$^+$, and g$^-$) for this bond may still be justified. The rms dipole moment $\langle\mu^2\rangle^{1/2}$ for the molecule was calculated by choosing the rotational isomeric states at the minima of the potential energy curve (cf. Figure 4) for the temperature of 25 °C: at α = 1.0, $\langle\mu^2\rangle^{1/2}$ = 2.39 D and d ln $\langle\mu^2\rangle^{1/2}$/d$T$ = 0.02 × 10^{-3} K^{-1}. Variation of $\langle\mu^2\rangle^{1/2}$ with α is shown in Figure 5 (dotted curve), where the range for observed values is indicated on the right ordinate. The agreement between the calculated and observed results is poor except for a large value of α. As suggested in Figure 4, suppression of the gauche conformation for the C$_1$C$_2$ bond may improve the agreement by lowering the $\langle\mu^2\rangle^{1/2}$ value. A large increase in ΔE ($\simeq$ 1.0 kcal mol^{-1}) should be required to

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(19) In the expression for ΔE derived by Zetta and Gatti,[18] the vicinal coupling constant J_{24} is incorrectly used in place of J_{14}. Adoption of the corrected equation with J_{14} = 6.04 Hz (cf. ref 18) gives a negative value of ΔE (−0.26 kcal mol^{-1}).

Table II. Locations of the Minima and the Associated Energies Estimated for Dimethyl Glutarate (Model I)[a]

conformation	$\phi_{C_1C_2}$, deg	$\phi_{C_2C_3}$, deg	E_{min},[b] kcal mol^{-1}
tt	0.0	0.0	0.0
tg^+	114.0	114.0	0.31
g^+g^+	120.2	120.2	0.45
g^+g^-	108.8	108.8	0.79

[a] Rotational states for the C^*C_1 and C_2C^* bonds were defined according to model I with $\alpha = 1.0$. Calculations were carried out for the temperature of 25 °C. [b] Expressed relative to the tt state.

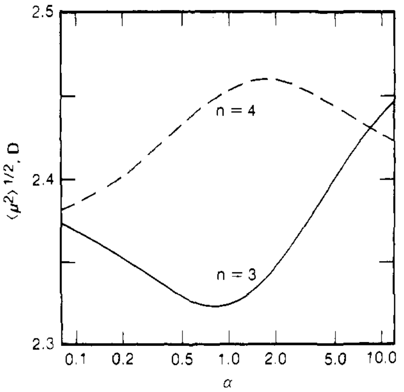

Figure 6. Dependence of $\langle\mu^2\rangle^{1/2}$ on α, calculated for dimethyl glutarate ($n = 3$) and adipate ($n = 4$) (model I, 25 °C).

get a good fit for the region $\alpha \leq 1.0$. This is very unlikely the case, however. Finally, an alternative attempt to estimate the dipole moment of the molecule by minimizing the energy for each of the 36 ($\psi_{C^*C_1}$, $\psi_{C_2C^*}$) conformers through adjustment of $\phi_{C_1C_2}$ yielded little improvement in the agreement.

At the limit $\alpha = 0$, the $\langle\mu^2\rangle^{1/2}$ vs. α curve reaches its asymptotic value 2.45 D (cf. Figure 5). Adoption of model II with $\beta > 1$, thus, E_β (= $RT \ln \beta$) > 0, lowers the value of $\langle\mu^2\rangle^{1/2}$ according to curve 2 in Figure 3. Locations of the gauche minima were displaced slightly from $\phi_{C_1C_2} = 114.5°$ at $E_\beta = 0$ to $\phi_{C_1C_2} = 112.0°$ at $E_\beta = 2.0$ kcal mol^{-1}. Experimental values of the dipole moment were reproduced in the range $E_\beta = 1.4$ to 1.8 kcal mol^{-1}; e.g., with $E_\beta = 1.5$ kcal mol^{-1}, we obtain $\langle\mu^2\rangle^{1/2} = 2.16$ D and d ln $\langle\mu^2\rangle^{1/2}$/d$T$ = 0.7×10^{-3} K^{-1} (at 25 °C). With an increase in the magnitude of E_β over the range from 0 to 2.0 kcal mol^{-1}, the energy difference ΔE between the gauche and trans state (defined around the C_1–C_2 bond) was found to decrease monotonically from 0.38 to 0.10 kcal mol^{-1}. The value of ΔE is small, but still positive (0.17–0.12 kcal mol^{-1}) in the range $E_\beta = 1.4$ to 1.8 kcal mol^{-1}, in opposition to that suggested by the experimental observations.[18,19]

Dimethyl Glutarate. The molecule comprises two CH_2–CH_2 bonds. Following the previous treatment, energy calculations were performed for given pairs of the internal rotation ($\phi_{C_1C_2}$, $\phi_{C_2C_3}$). According to model I, each of these pairs consists of 36 conformers (equilibrated at 25 °C) differing in the orientation of the ester group. Locations of the minima and the associated energies (E_{min}) calculated for model I with $\alpha = 1.0$ are listed in Table II. The results for the conformations other than those given in the table can be deduced by symmetry. Short-range interactions between the two terminal ester groups involved in the g^+g^- state are only moderately repulsive as manifested in its relatively low E_{min} value. The dipole moment $\langle\mu^2\rangle^{1/2}$ calculated by adopting $\phi_{g\pm} = \pm 114.0°$ (cf. Table II) for the gauche states is 2.32 D. The dipole moment decreases slightly to 2.31 D if the energies of the $g^\pm g^\pm$ and $g^\pm g^\mp$ states are replaced by their minimum values, i.e., $E_{g\pm g\pm} = 0.45$ and $E_{g\pm g\mp} = 0.79$ kcal mol^{-1} (cf. Table II), in keeping $\phi_{g\pm}$ at ±114.0°. Variation of $\langle\mu^2\rangle^{1/2}$ with α is shown by the solid curve in Figure 6. In these calculations, the gauche states were taken to occur at ±114.0° for all the values of α. The curve exhibits a shallow minimum at about $\alpha = 0.8$. The agreement with observations (2.31–2.41 D)[1,3-5] is reasonable for the entire range of α examined. The temperature coefficient d ln $\langle\mu^2\rangle^{1/2}$/d$T$ was calculated to be 0.1×10^{-3} K^{-1} for $\alpha = 1.0$ (at 25 °C).

Table III. Locations of Energy Minima and the Associated Energies Estimated for the Bond Pair C^*–C_1–C_2 in Dialkyl Esters with $n \geqslant 4$[a]

	C_1–C_2				
	trans[b]		gauche$^+$		
$\psi_{C^*C_1}$	statistical wt factors	E_{min}, kcal mol^{-1}	statistical wt factors	ϕ_{g^+}, deg	E_{min}, kcal mol^{-1}
$2\pi/3$	η_1	0.0	$\eta_1\xi_1$	117.0	−0.14
$-2\pi/3$	η_1	0.0	$\eta_1\xi_2$		
0	η_2	0.18	$\eta_2\xi_3$	109.5	0.57
$\pi/3$	η_3	0.09	$\eta_3\xi_4$	105.0	0.80
$-\pi/3$	η_3	0.09	$\eta_3\xi_5$	116.0	−0.05

[a] Calculations were carried out for methyl pentanoate, $CH_3(CH_2)_3COOCH_3$. [b] $\phi_t = 0$ for all values of $\psi_{C^*C_1}$.

Calculations were also carried out for the three-state scheme designated as model II. Locations of the energy minima for the gauche states (about the C_1–C_2 and C_2–C_3 bonds) were estimated for given values of E_β in a similar manner as above (cf. Table II). Values of $\phi_{g\pm}$ thus deduced vary from ±113.5° for $E_\beta = 0$ to ±108.5° for $E_\beta = 2.0$ kcal mol^{-1}. The gauche energies expressed relative to the trans state (cf. definition of E_{min} for tg^+ given in Table II) vary slightly from 0.36 to 0.23 kcal mol^{-1} over the same range of E_β. The rms dipole moment $\langle\mu^2\rangle^{1/2}$ calculated for the temperature of 25 °C is plotted against E_β in Figure 3 (curve 3). The curve passes through the minimum (2.39 D) at $E_\beta \simeq 0.2$ kcal mol^{-1} and then tends to increase gradually as the magnitude of E_β becomes large. At $E_\beta = 1.2$ kcal mol^{-1}, $\langle\mu^2\rangle^{1/2} = 2.49$ D. The calculated value exceeds slightly those observed. The corresponding value of the temperature coefficient d ln $\langle\mu^2\rangle^{1/2}$/d$T$ was calculated to be -0.2×10^{-3} K^{-1}.

Dimethyl Adipate and Higher Homologues. In these molecules, the two terminal ester groups are separated by more than five C–C bonds. Short-range interactions between these two groups inevitably precipitate severe second-order steric conflicts[17] along the chain, except when n is very large. For the dialkyl esters with $n \geq 4$, therefore, the spatial arrangements of the ester groups located on both terminals may be treated independently from each other. Conformational energies depending on rotations about the first two bonds, i.e., C^*–C_1 and C_1–C_2, were estimated from calculations for methyl pentanoate, a monoester model compound. Geometrical parameters of this compound were taken from Table I, the terminal methyl group being assumed to have a tetrahedral arrangement. Coulombic interactions are insignificant in this system. The results obtained for the six-state scheme (C^*–C_1) with $\alpha = 1.0$ are summarized in Table III, where energies are expressed relative to the ($\pm 2\pi/3$, t) states. Statistical weight factors are assigned to each rotational state to facilitate formulation of the statistical weight matrices. The location of the trans minimum ($\phi_t = 0$) for C_1–C_2 should not be much affected by the choice of the rotational states for the preceding bond (C^*–C_1). Thus, ϕ_t is not listed in the table. The conformational energies associated with $\psi_{C^*C_1} = \pi$ are always high due to the steric repulsion between the ester oxygen and C_2-methylene group. Accordingly, the π states are entirely omitted from the table. The arrangement ($-2\pi/3$, g^+) is also of rare occurrence. The minimum energies for the (0, g^+) and ($\pi/3$, g^+) states exceed the rotational potential barrier (0.3–0.5 kcal mol^{-1}) estimated for simpler analogues.[12,13] If the latter value is literally taken, these states must be dismissed. Since the importance of these states varies with the choice of α and β (cf. sq.), however, we shall retain these in our treatment.

Following the conventional procedure,[17] the statistical weight matrix for the first bond, C^*–C_1, can be formulated in a 1 × 5 row form:

$$\mathbf{U}_1 = [1 \quad 1 \quad \beta\eta_2 \quad \alpha\eta_3 \quad \alpha\eta_3] \tag{3}$$

where statistical weight parameters η_i (i = 2, 3) may be easily deduced as Boltzmann factors for the corresponding energies listed in the thrid column of Table III. In the above expression, α is the parameter characteristic to model I, for which β = 1.0. The matrix can be reduced to a 1 × 3 form by setting $\alpha = 0$ for model II, β being treated as a variable. The statistical weight matrix for the second bond, C_1–C_2, takes in general a 5 × 3 form:

$$\mathbf{U}_2 = \begin{bmatrix} 1 & \xi_1 & 0 \\ 1 & 0 & \xi_1 \\ 1 & \xi_3 & \xi_3 \\ 1 & \xi_4 & \xi_5 \\ 1 & \xi_5 & \xi_4 \end{bmatrix} \tag{4}$$

where $\xi_i = \exp(-E_{\xi_i}/RT)$, E_{ξ_i} (i = 1–5) being obtained by taking the difference between the energies given in the sixth and third columns of Table III. In eq 4, the columns are indexed in the order t, g$^+$, g$^-$. When model II is adopted for the preceding bond, the last two rows should be eliminated from this equation. For dimethyl adipate (n = 4), interactions involved in the conformations dependent on rotations about C_3–C_4 and C_4–C* are identical with those discussed above. Statistical weight matrix $\mathbf{U}_5$ for this bond pair may thus be given as the transpose of $\mathbf{U}_2$, i.e.

$$\mathbf{U}_5 = \mathbf{U}_2^{\mathrm{T}} \tag{5}$$

and then a column vector

$$\mathbf{J} = \mathbf{U}_1^{\mathrm{T}} \tag{6}$$

is responsible for the rest.[17] As is easily shown by inspection of a model, statistical weight matrices $\mathbf{U}_3$ and $\mathbf{U}_4$ associated with the intervening C–C bonds can be given by

$$\mathbf{U}_3 = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \tag{7}$$

and

$$\mathbf{U}_4 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \tag{8}$$

where $\sigma = \exp(-E_\sigma/RT)$ represents the interaction between two methylene groups in a gauche arrangement, for which a value of E_σ = 0.5 kcal mol^{-1} has been assessed.[20] The null elements in these matrices correspond to the g$^\pm$g$^\mp$ conformation, which involve severe second-order repulsion between the C*═O* and one of the methylene groups.[21] Finally, the partition function Z for dimethyl adipate can be given by

$$Z = \mathbf{U}_1\mathbf{U}_2\mathbf{U}_3\mathbf{U}_4\mathbf{U}_5\mathbf{J} \tag{9}$$

Similarly, for the higher homologues ($n > 4$),

$$Z = \mathbf{U}_1\mathbf{U}_2\mathbf{U}_3\mathbf{U}^{n-4}\mathbf{U}_n\mathbf{U}_{n+1}\mathbf{J} \tag{10}$$

where

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{11}$$

is applicable to all the internal C–C bonds. In analogy to normal alkane chains,[20] we adopt $\omega = \exp(-E_\omega/RT)$ with E_ω = 2.0 kcal mol^{-1}. Accordingly, the replacements $\mathbf{U}_{n-1} = \mathbf{U}_4$ and $\mathbf{U}_n = \mathbf{U}_5$ are required.

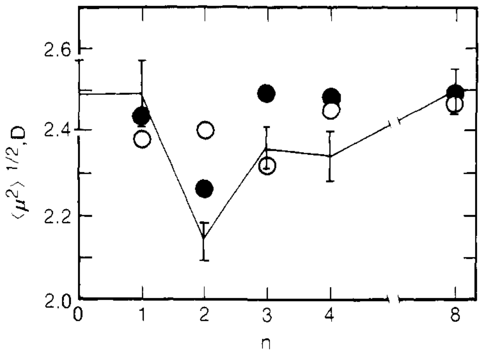

Figure 7. Variation of dipole moments $\langle\mu^2\rangle^{1/2}$ with methylene chain length n. Calculated values are indicated by open circles for model I (at α = 1.0) and by filled circles for model II (at E_β = 1.2 kcal mol^{-1}), temperatures being taken to be 25 °C. The corresponding experimental values[1,3–6] are found in the range specified by the bar notation.

Dipole moments were calculated for dimethyl esters of adipic and sebacic acids by the conventional procedure.[17] The results obtained for adipate (n = 4) with model I are shown in Figure 6 (dotted curve). Rotation angles were taken to be $\phi_{C_1C_2} = \phi_{C_{n-1}C_n}$ = 0 and ±117.0°, and ϕ_{CC} = 0 and ±112.5° for all the internal C–C bonds. In contrast to the behavior derived for glutarate (shown by the solid curve in the same figure), adipate exhibits the maximum at about α = 1.6. Variation of $\langle\mu^2\rangle^{1/2}$ is small (less than 0.1 D) throughout the entire range of α. At α = 1.0, $\langle\mu^2\rangle^{1/2}$ = 2.45 D and d ln $\langle\mu^2\rangle^{1/2}/\mathrm{d}T = 0.03 \times 10^{-3}$ K^{-1}. The dipole moment thus obtained exceeds slightly those (2.28–2.40 D) found in experiments.[1,3–5] For sebacate (n = 8), values calculated at α = 1.0 are $\langle\mu^2\rangle^{1/2}$ = 2.47 D and d ln $\langle\mu^2\rangle^{1/2}/\mathrm{d}T = 0.01 \times 10^{-3}$ K^{-1}. Experimental values of the dipole moment[1,3,4] are ranging from 2.44 to 2.55 D.

Dipole moments were also calculated by using the expressions prescribed for model II. With this model, locations of the gauche minima around the C_1–C_2 and C_{n-1}–C_n bonds were found to be displaced from $\phi_{g\pm}$ = ±115.4° for E_β = 0 to $\phi_{g\pm}$ = ±110.7° for E_β = 2.0 kcal mol^{-1}. The results obtained for adipate are plotted against E_β in Figure 3 (curve 4), together with the curves for the lower members. In Figure 3, curve 4 resembles most closely curve 2: both curves exhibit the maximum within the range of E_β examined, although the locations of these maxima are quite different. Curve 4 decreases more slowly after it reaches the maximum at $E_\beta \simeq$ 0.8 kcal mol^{-1}. Experimental values (2.28–2.40 D)[1,3–5] are a little smaller than those calculated (cf. curve 4). For example, with E_β = 1.2 kcal mol^{-1} and $\phi_{g\pm}$ = ±112.1° (C_1–C_2 and C_{n-1}–C_n), $\langle\mu^2\rangle^{1/2}$ = 2.48 D and d ln $\langle\mu^2\rangle^{1/2}/\mathrm{d}T = 0.2 \times 10^{-3}$ K^{-1}. The dipole moment $\langle\mu^2\rangle^{1/2}$ of sebacate calculated by using the identical values of E_β and $\phi_{g\pm}$ is 2.49 D, being in fair agreement with experiments.[1,3,4] The corresponding temperature coefficient d ln $\langle\mu^2\rangle^{1/2}/\mathrm{d}T$ computed for the same set of parameters is 0.02 × 10^{-3} K^{-1}.

Discussion

The results of calculations for model I are shown in Figures 2, 5, and 6. Variation of $\langle\mu^2\rangle^{1/2}$ with α is significant only for the first two members (n = 1, 2) of the series. An unambiguous selection of a single α value applicable commonly to all the systems is difficult. Experimental observations indicate that the dipole moment falls sharply at n = 2 and increases again at n = 3. This requires $\alpha > 2$. The observed tendency may be almost satisfactorily reproduced with $\alpha \simeq 10$, including a small decrease in the dipole moment on going from n = 3 to n = 4; e.g., at α = 10, the calculated values of $\langle\mu^2\rangle^{1/2}$ are 2.70, 2.21, 2.44, and 2.43 D for a series of n from 1 to 4, respectively. However, a large value of α implies that the ester C*–O bond eclipses predominantly the vicinal C–H and/or C–C bonds in the most stable conformation. Such a scheme is apparently inconsistent with the experimental evidence established by various spectroscopic studies.[9–14] As α decreases toward zero, on the other hand, the agreement with the observed results becomes less satisfactory. A value of α = 1.0

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[20] A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

[21] The interactions considered here depend not only on rotations about C_1–C_2 and C_2–C_3 but also on the orientation (around C*–C_1) of the ester group. The exact treatment of such interactions requires some elaboration. In reality, however, the conformational energy estimated for the least repulsive orientation is of the order of 2 kcal mol^{-1}. Inclusion of an energy of this magnitude was found to cause only a minor effect in the dipole moment. The contribution from the g$^\pm$g$^\mp$ conformation was therefore entirely ignored.

Table IV. Comparison between the Calculated and Observed Values of the Temperature Coefficient d ln $\langle\mu^2\rangle^{1/2}/dT$ for $[CH_2]_n(COOR)_2$ ($R = CH_3$ or C_2H_5)

	$[d \ln \langle\mu^2\rangle^{1/2}/dT] \times 10^3$, K^{-1}		
	calculated		
n	model I[a]	model II[b]	experimental
1	0.2	−0.1	0.5,[c] 0.2,[d] 0.4[e]
2	0.02	0.7	1.3,[c] 0.8,[d] 1.2,[e] 0.8,[f] 1.1,[g] 0.2[h]
3	0.1	−0.2	0.2,[c] 0.1[f]
4	0.03	0.2	0.3,[c] 0.5,[d] 0.6[e]
8	0.01	0.02	0.2,[c] 0.2,[d] 0.4[e]

[a] Calculated for $\alpha = 1.0$ [b] Calculated by using $E_\beta = 1.2$ kcal mol^{-1}. [c] In benzene, 25–50 °C, ref 1. [d] In benzene, 20–70 °C, ref 3. [e] In dioxane, 20–70 °C, ref 3. [f] In benzene, 20–50 °C, ref 5. [g] In kerosene, 0–180 °C, ref 2. [h] Estimated from the experimental data measured in the gas phase over the range 156.3–246.2 °C, ref 23.

seems to be an optimum choice.[22]

In Figure 7, the values of $\langle\mu^2\rangle^{1/2}$ calculated for $\alpha = 1.0$ (indicated by open circles) are compared with the observed dipole moments. The bar notation is used to indicate the range within which observed values are scattered. The experimental data cited[1,3–6] include values determined on dimethyl as well as diethyl esters in benzene, dioxane, or carbon tetrachloride at ordinary temperatures (20–25 °C). Experimental values for diethyl oxalate ($n = 0$)[1,3,6] are also included for comparison. As indicated in the figure, the disparity between the computed and experimental values is significant in the case of succinate ($n = 2$). Except for $n = 2$, the calculated results may be favorably compared with those observed. The present calculations failed, however, to reproduce the observed "oscillation" phenomenon with *n*.

The results of calculations obtained by assuming the three-state scheme for the $C^*–C_1$ and $C_n–C^*$ bonds (termed model II) have been assembled in Figure 3. Curve 1 for malonate increases rapidly with an increase in the magnitude of E_β while curve 2 for succinate tends to decrease for $E_\beta > 0.3$ kcal mol^{-1}. The value of $\langle\mu^2\rangle^{1/2}$ calculated for $n = 1$ exceeds that for $n = 2$ in the range $E_\beta > 1.0$ kcal mol^{-1}. Curve 3 for glutarate catches up with curve 4 for adipate at $E_\beta \simeq 1.1$ kcal mol^{-1}. As a consequence, the calculated values of $\langle\mu^2\rangle^{1/2}$ exhibit an odd–even oscillation with *n* when a value of $E_\beta \geq 1.2$ kcal mol^{-1} is adopted. Shown in Figure 7 (by filled circles) are the dipole moments $\langle\mu^2\rangle^{1/2}$ computed by using $E_\beta = 1.2$ kcal mol^{-1}. The value chosen for E_β is in accord with the suggestion made by Moravie and Corset.[10] In Figure 7, the observed trend is favorably reproduced except that the values are somewhat overestimated at $n = 2$, 3, and 4. The agreement with experimental observations is slightly improved when model II is adopted. The preference of model II over model I cannot be decisive, however.

Temperature coefficients of the dipole moment d ln $\langle\mu^2\rangle^{1/2}/dT$ calculated for the individual compounds are summarized in Table IV, where the corresponding experimental values are included for comparison in the last column. Except in the case of $n = 2$, experimental values of the temperature coefficient are fairly small. As first noted by Smyth et al.,[1,2] the dipole moment of diethyl succinate increases rapidly with temperature. The temperature coefficient determined by using kerosene as the solvent is large (1.4×10^{-3} K^{-1}) at an ordinary temperature, but it decreases somewhat (0.8×10^{-3} K^{-1}) at higher temperatures (160–180 °C). An averaged value (1.1×10^{-3} K^{-1}) is cited in the table. The dipole moment of diethyl succinate in the vapor phase was measured over the range 156.3–246.2 °C by Zahn.[23] The temperature coefficient estimated therefrom amounts to ca. 0.2×10^{-3} K^{-1}. As pointed out by Smyth et al.,[2] the anomaly associated with succinate becomes less marked at higher temperatures. These observations on diethyl succinate can be reasonably reproduced by the calculation based on model II (cf. Table IV): the value of d ln $\langle\mu^2\rangle^{1/2}/dT$ was estimated to be 0.7×10^{-3} K^{-1} at 25 °C, which reduced to 0.3×10^{-3} K^{-1} at 200 °C. The corresponding values obtained for model I ($\alpha = 1.0$) are much lower. As indicated in Table IV, the experimental values of the temperature coefficient exhibit a small odd–even oscillation, but in the order opposite to that observed in the dipole moment. Calculations by using model II yielded the results which reproduce such an oscillation with *n*. In these calculations, however, the values of d ln $\langle\mu^2\rangle^{1/2}/dT$ become negative at $n = 1$ and 3, being at variance with those observed. The results for model I do not show any similar oscillation, but the calculated values of d ln $\langle\mu^2\rangle^{1/2}/dT$ are positive for all *n*. As for the temperature coefficient, adoption of model II seems to give a better agreement with experimental observations. However, if we consider the fact[2] that the temperature coefficient of the dipole moment of ethyl acetate has been reported to be of the order of 0.6×10^{-3} K^{-1} in *n*-heptane, any argument below this level may be of limited significance.

It should also be recalled that both models I and II yielded a small but definitely positive value of ΔE ($= E_g - E_t$) for succinate. These results are inconsistent with NMR measurements,[19,24] which suggest that the gauche form is energetically more favored. Experimental studies are in progress[24] for a more accurate determination of ΔE.

Finally, we examined the scheme proposed for succinate by Smyth et al.[2] some years ago. They stated that the low value of the dipole moment and the abnormal temperature coefficient of the diethyl ester indicate a bending of the molecule in such a way that the dipoles of the ester groups were brought close together so as to cancel one another partially. The candidates were searched for among gauche conformers previously deduced in connection with model I. Two enantiomorphic forms, $(\pi/3, g^+, \pi/3)$ and $(-\pi/3, g^-, -\pi/3)$, were found to be one of the most stable arrangements with very low polarity (0.67 D). No other forms are qualified for the requirement set forth by Smyth et al.[2] In the calculation based on model I, the energy of these equivalent forms was tentatively depressed. An extra stabilization of 1.0 to 1.25 kcal mol^{-1} was required to bring the value of $\langle\mu^2\rangle^{1/2}$ to the range of experimental observations (2.08–2.19 D).[1–5] Adopting a stabilization energy of 1.25 kcal mol^{-1}, the temperature coefficient d ln $\langle\mu^2\rangle^{1/2}/dT$ was calculated to be 1.0×10^{-3} K^{-1}, being in agreement with that (1.1×10^{-3} K^{-1}) observed. With this modification, the conformational energy of the gauche state defined for the C–C bond decreased desirably to the order slightly lower than that of the trans form ($\Delta E = -0.05$ kcal mol^{-1}). However, the present treatment rests on the assumption that the ester C*–O eclipses the vicinal C–H's (i.e., $\psi_{C^*C} = \pm\pi/3$) predominantly in the most stable conformations. As stated earlier, this scheme is incompatible with spectroscopic evidence.[9–14] In conclusion, the gauche effect such as that suggested by Smyth et al.[2] should not be the major cause of the anomaly associated with the succinate system.

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Registry No. $CH_3OOCCH_2COOCH_3$, 108-59-8; $CH_3OOC(CH_2)_2COOCH_3$, 106-65-0; $CH_3OOC(CH_2)_3COOCH_3$, 1119-40-0; $CH_3OOC(CH_2)_4COOCH_3$, 627-93-0; $CH_3OOC(CH_2)_8COOCH_3$, 106-79-6; diethyl succinate, 123-25-1.

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(22) In the dipole moment analysis on dimethyl *trans*-1,4-cyclohexanedicarboxylate, Saiz et al.[8] introduced a statistical weight ω to express relative importance of the conformation in which the ester C*–O eclipses CH. According to their analysis, two of the ordinary energy minima (corresponding to the C*=O*/C*C eclipsed forms) should be eliminated due to the severe steric repulsions. Alternatively, the aforementioned conformation (the C*O/CH eclipsed form) becomes relatively stable. Saiz et al.[8] obtained $\omega = 0.7$ to 1.0 for the distribution of the conformers between the two preferred states, i.e., the C*=O*/CH and C*O/CH eclipsed forms. The ω parameter thus defined differs somewhat from the α used in this paper.

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