and is of particular interest from the polymer point of view, as fluctuations in this particular angle may have an important effect on directional persistence of the chains. The large angle for compound **5** (124.2°) presumably serves to relieve steric repulsions caused by a T dihedral angle of unusually small magnitude (33°). Also of note is the observation that the C1–C3–C4 and C2–C3–C4 angles deviate from 120° by ca. −2.5° and +2.5° respectively, presumably a result of steric repulsion between O6 and H2 (Figure 1).

Dihedral angles, however, vary more widely. It is generally found that ambient temperature crystal structure geometries are close in energy though not necessarily in geometry to that of the minimum enthalpy gas-phase geometry, so this is not unexpected. It is merely indicative that there are a number of possible dihedral geometries of low energy, so, in principle, one should be able to chart low areas of the rotational energy profiles for each bond by looking at a large enough sample of structures. For example, a very narrow dihedral angle distribution for a particular bond indicates that the bond lies in a deep rotational energy well, and conversely a broad distribution over a particular range indicates a shallow well.

On this basis, for the R bond, there is a region of low energy ±10° around 0°. That the absolute energy minima for the R bond are ca. 6° either side of 0° is suggested by the fact that (a) the majority of the angles are distributed in the range 3–9° and (b) there is a high inverse correlation between the rotational sense of the angles for bonds R and T.

The S bond dihedral angles deviate from 0° within a similar range (up to 17°) as do those of the R bond. However, the average magnitude of deviation is significantly less for the S bond (4.3° versus 7.4°), indicating steeper walls to the energy well. There is no obvious correlation between the rotational sense of S and R or between S and T, so in the absence of significant statistical evidence for a bimodal angle distribution around 0°, a value of 0° has been assigned to the "idealized" S bond dihedral (last column of Table I).

The dihedral angles for T deviate from 0° by between 33° and 90°, that is to say, nearly two-thirds of the available range (bearing in mind the 4-fold symmetry of the rotation). This strongly suggests a much broader energy well for the T bond rotation and an energy maximum below 30° deviation, consistent with the expected H8–O5 steric repulsion at the lower angle. However, 10 out of 15 of the angles were clustered in an 8° range around 67° deviation from 0°, suggesting that the absolute minimum is around there. It is interesting to note that three of the four compounds (**4**, **5**, **8a**) with angles below this range have a π-electron withdrawing substituent at the C10 position (Figure 1). This implies that electron-withdrawing groups at the C10 position of the phenyl benzoate moiety induce significant additional $O6_p$ to Ph_{π^*} donation, thereby permitting a decrease of the T bond rotation angle in order to improve the overlap of these orbitals.

Thus, the crystal structure analyses indicate a unique idealized low-energy conformation for the ester group in a phenyl benzoate type environment, which is a useful starting point for aromatic polyester modeling purposes (last column of Table I). Additionally, there are qualitative indications concerning the rotational energy profile of the three rotatable ester bonds, and this subject will be now be examined more closely.

Details of Computational Methods

There is a proliferation of acronyms commonly used in the field of computational chemistry, and these terms are summarized in Table II. All structure computation was performed by using a microVax II computer (VMS operating system).

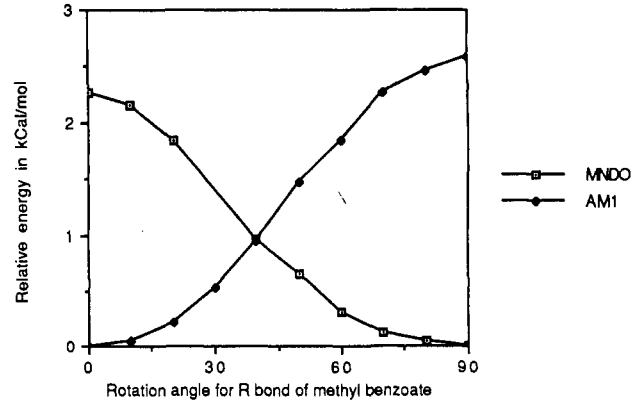

Figure 2. Comparison of MNDO and AM1 results for R bond rotational profile in methyl benzoate.

Table II
Computational Chemistry Acronyms Used in This Paper

MM2	Molecular Mechanics 2 (a popular molecular mechanics program)
PCILO	Perturbative Configurational Interaction using Localized Orbitals (a method in semiempirical quantum mechanics)
MNDO	Modified Neglect of Differential Overlap (a method in semiempirical quantum mechanics)
AM1	Austin Model 1 (an improved MNDO)
AMPAC	Austin Method 1 Package (program containing MNDO and AM1 Hamiltonians)
PRDDO	Partial Retention of Diatomic Differential Overlap (an "approximate ab initio" method)
STO-3G	Slater Type Orbitals approximated by three Gaussian functions (minimal orbital basis set for ab initio quantum mechanics calculations)
GAUSSIAN 80	program package for ab initio quantum mechanics
SCF	Self Consistent Field
QCPE	Quantum Chemistry Program Exchange

AM1 and MNDO calculations used AMPAC.[18] Calculations on phenyl benzoate used the AMPAC keyword "PRECISE" to ensure full convergence to the minimum energy. Otherwise defaults were applied.

Ab initio calculations with the STO-3G basis set were performed using the GAUSSIAN 80[19] program.

MM2[20] calculations used program defaults, except a "nonplanar π-system" calculation was applied in all cases and additional parameters were supplied as described below.

Rotational Energy Barriers for Aromatic Ester Groups and Parameterization of the MM2 Program

Table III shows rotational barrier information for the three rotatable bonds of the ester group from model compounds, as calculated from experiment or theory. The theoretical method makes the approximation that the true rotational transition state is the same as the highest energy "rotational state".

R Bond. The key stereoelectronic features concerning the nature of the R bond rotation profile are (i) ester oxygen–phenyl steric repulsions and (ii) ester–phenyl π-type resonance stabilization. These opposing features are expected to be at a maximum with the R bond at 0°, so it is their relative strengths that determine the overall minimum energy rotation angle.

The danger of putting too great a trust in a single theoretical method for barrier determination is illustrated by the MNDO result for the R bond rotation (Figure 2). MNDO suggests that the minimum is at 90°, which is contrary to all other calculations listed and to crystallographic observations. It is, however, well established that MNDO

Table III
Information on Rotational Profiles of Rotatable Aromatic Ester Bonds

bond	model compd	method	information (energies in kcal mol^{-1})	ref
R	methyl benzoate	STO-3G SCF with optimization	5.05 barrier, min 0°, max 90°	21
R	methyl benzoate	indirect infrared method	5.30 barrier, min 0°, max 90°	22
R	methyl benzoate	molecular mechanics "inference method"	~5.2 barrier, min 0°, max 90°	4
R	methyl benzoate	MNDO SCF	2.3 barrier, min 90°, max 0°	this work
R	methyl benzoate	AM1 SCF	2.6 barrier, min 0°, max 90°	this work
R	benzoic acid	STO-3G, rigid rotor approximation[a] on "standard geometrical model"	5.76 barrier, min 0°, max 90°	23
R	dimethyl terephthalate	PCILO, rigid rotor approximation	2.9 barrier, min 0°, max 90°	1
R	phenyl benzoate	AM1 SCF	2.35 barrier, min 0°, max 90°	this work
R	phenyl benzoate	PRDDO[b]	6.7 barrier,[b] min 0°, max 90°	24
S	benzoic acid	STO-3G SCF rigid rotor approximation[a] on "standard geometrical model"	$\Delta E_{cis-trans}$ 6.92	23
S	phenyl benzoate	AM1 SCF	$\Delta E_{cis-trans}$ 5.1, 5.8 barrier at 90°	this work
S	aliphatic esters and carboxylic acids	experimental and ab initio	estimates of $\Delta E_{cis-trans}$ range from 2.3 upward, where actual gap depends on steric effect of ester substituents; estimates of barrier at ~90° in range 11 ± 3	25, 26
S	methyl formate	AM1 SCF	$\Delta E_{cis-trans}$ 5.6, 10.5 barrier at 90°	this work
S	methyl acetate	AM1 SCF	$\Delta E_{cis-trans}$ 5.4, 9.1 barrier at 90°	this work
S	vinyl acrylate	STO-3G SCF rigid rotor approximation	barrier <9.3[c] (linear conformation)	this work
T	phenyl acetate	molecular mechanics "inference method"	min ~60°, 1.2 barrier at 0°, 0.25 barrier at 90°	4
T	phenyl benzoate	AM1 SCF	min 50.3°, 1.32 barrier at 0°, 0.42° barrier at 90°	this work
T	phenyl formate	STO-3G SCF	min 63°	this work

[a] The "rigid rotor approximation" greatly saves computational time by assuming a constant geometry on rotation but will, therefore, be expected to overestimate the barrier. [b] This calculation did not use a full optimization at either the minimum or the transition state, so the usefulness of the result is hard to interpret. [c] The STO-3G barrier was approximated by a single-point calculation on the optimized trans conformation with the S bond twisted to 90°. Therefore, the value of 9.3 kcal mol^{-1} represents an upper limit to the STO-3G barrier.

overestimates internuclear repulsions at van der Waals distances and will, therefore, overestimate feature (i) described above. This failing was specifically corrected for in the design of the more recent AM1 method,[27] and indeed, AM1 predicts a minimum at 0° (Figure 2).

Discounting the MNDO result, all R barrier estimates are found in the range 2–6 kcal mol^{-1}, minimum at 0°, maximum at 90°, suggesting that feature (ii) greatly outweighs feature (i). The one experimental measurement, the two most thorough quantum mechanical treatments, and the inferred value of Hummel and Flory fall into the top end of this range. Therefore, 5 ± 1 kcal represents a sound estimate based on the available data. How such a value can be modified by the presence of aromatic ester substituents will be discussed later in the paper.

S Bond. There are two aspects to consider concerning the rotational profile for this bond. The first is the trans–cis barrier usually just above 90°, whose origin is the partial double bond character of the S bond, brought about by O_p–C_{π^*} overlap. The second is the energy difference between the trans (0°) and cis (180°) conformers. The cis is intrinsically higher than the trans in esters and carboxylic acids, owing to better O_n–C_{σ^*} "hyperconjugation" in the trans form. Additionally, the cis is made even higher by steric effects roughly proportional to the size of the two ester substituents. Thus, when the ester has particularly bulky groups attached, such as phenyls, the cis conformation becomes a second rotational barrier, possibly greater than the once at 90°.

The 5.8-kcal S bond trans–cis barrier (at 90°) calculated by the AM1 method (Figure 4) is about half that of estimates for aliphatic esters. There are two reasons why this may not be unreasonable. Firstly, extension of the ester π system at the ether-type oxygen enables some electron density from the partial O_p–C_{π^*} portion of the S bond, which is responsible for the barrier, to be transferred to the π system attached to the ether-type oxygen, thereby lowering the S bond energy barrier and bond order. This lower bond order is borne out by experimental observation from crystallography: the S bond length in alkyl benzoate moieties is typically 1.33 Å[28] and in alkyl alkoate moieties 1.33–1.34 Å,[29] whereas in phenyl benzoate moieities it is 1.36 Å (Table III), closer to the typical ether C–O length of 1.42–1.43 Å[30] by around 30%. Secondly, in the case of phenyl benzoate, though not aliphatic esters, it is apparent from molecular models and evidenced in the AM1 calculations that the energy of the transition state can be relieved to an extent by the rotation of the T bond toward a lower angle. This is because, in transition-state geometry where the S angle is ca. 90°, the T bond can be rotated toward 0° and thus gain favorable O_p–Ph_{π^*} overlap without as large a steric penalty.

In order to examine whether the actual extent of barrier lowering on transferring from an aliphatic to aromatic environment is reasonable, the AM1 method was "calibrated" by calculating the barriers for methyl formate and methyl acetate and making the comparison with experimental and ab initio quantum mechanical estimations. It can be seen from Table III that AM1 barriers for the two compounds (10.5 and 9.1 kcal mol^{-1}) fall within the range of the well-established values, possibly a little on the low side. If one takes the view, based on this calibration, that AM1 generally underestimates barrier for the ester C–O bond by about 15%, then the AM1 value of 5.8 kcal mol^{-1} for the trans–cis barrier should be modified to 6.7 kcal mol^{-1}.

A second estimate for the cis–trans barrier can be made on the basis of relative bond lengths. It was seen above that the S bond length of aryl arylates is approximately 30% closer to the average C–O single bond length than are those of alkyl arylates and alkyl alkoates. If one assumes a bond order of 30% less for the S bond of phenyl benzoate compared to that of typical alkyl esters, for which the barrier is assumed to be 11 kcal mol^{-1}, then a value around 7.7 kcal mol^{-1} is deduced. This value neglects the additional barrier lowering that could arise from cooperative T bond rotation mentioned above.

The energy difference between the cis and trans conformers of esters in general has been found to be highly dependent on the steric properties of their two substituents. This is because, in the cis conformation, the substituents are necessarily close, so large groups will lead to

Table IV
Supplementary MM2 Parameters Derived for Aromatic Ester Moieties

	new parameters (old parameters[32] given in parentheses)	
	K	*L*(0)
bond stretching		
1–6	5.36 (5.36)	1.44 (1.402)
2–6	6.0 (6.0)	1.40 (1.355)
3–7	10.8 (10.8)	1.19 (1.208)
in-plane bending		
2–3–6	0.7 (0.7)	109.0 (124.3)
2–3–7	0.46 (0.46)	126.0 (123.0)
6–3–7	0.4 (0.8)	122.0 (122.0)
2–6–3	0.45 (none)	112.0 (none)

torsionals	V1	V2	V3
2–2–3–6	0.0	11.0	0.0
5–2–3–6	0.0	11.0	0.0
2–2–6–3	−0.75	6.0	0.0
5–2–6–3	0.0	6.0	0.0
1–3–6–1	−0.75 (−2.5)	6.0 (1.39)	0.0 (0.0)
2–3–6–1	−0.75 (3.53)	6.0 (2.3)	0.0 (3.53)
2–3–6–2	−0.75	6.0	0.0
2–3–6–20	0.0	0.0	0.0
2–3–6–24	−0.75	6.0	0.0
5–3–6–2	−0.75	6.0	0.0
5–3–6–24	−0.75 (−0.77)	6.0 (0.85)	0.0 (0.0)
7–3–6–1	−2.5 (−1.66)	14.0 (8.98)	0.0 (0.0)
7–3–6–2	−2.5	9.5	0.0
7–3–6–24	−2.5 (−3.285)	14.0 (5.6)	0.0 (0.0)

[a] Key to atom types: 1 = C sp3, 2 = C sp2, 3 = C sp2–carbonyl, 5 = hydrogen, 6 = O sp3 (single bonded), 7 = O sp2 (double bonded), 20 = lone pair, 24 = hydrogen in carboxylic acid.

high cis-conformer energies. In the case of phenyl benzoate, it is apparent from molecular models that the mutual obstructivity of the two phenyl substituents is highly dependent on the rotational states of the R and T bonds, least obstruction being when R and T are between 60° and 120°. Thus, the AM1 energy for the *cis*-phenyl benzoate conformer is likely to be too low, because AM1 is believed to substantially underestimate the R bond rotation barrier. Therefore, we elected to estimate the cis-conformer energy using the molecular mechanics inference method described in the Introduction. This method has the particular advantage when treating strained structures that one can parameterize the force field to reproduce known rotational barriers accurately. This work is dealt with in the section on MM2 parameterization below.

T Bond. The T bond is characterized by two stereoelectronic features analogous to those for the R bond, only in this case the steric repulsion at 0° outweighs the Ph_{π^*}–O_p resonance stabilization, resulting in a nonplanar minimum energy conformation.

The T bond rotational profile predicted by the AM1 method shows the minimum around 15° lower than the crystal (phenyl benzoate moiety), Hummel (derived from crystals), and STO-3G (phenyl formate) values (Tables I and II). This is accounted for by the shallowness of the energy well for this rotation, whereby a small error in estimation of either the steric repulsion or the resonance stabilization by AM1 will necessarily cause a relatively large error in the optimum bond angle. The discrepancy does not, therefore, imply that the AM1 method has made a huge error. Indeed the crystallographic minimum angle (67°) corresponds to an AM1 energy only 0.25 kcal above that of the AM1 optimized structure (Figure 5). From inspection of space filling models it is clear that there occurs substantial steric repulsion between the carbonyl oxygen and phenyl ortho-hydrogen atoms when the T bond rotation angle is 0°.

Table V
Comparison between MM2 Optimized Geometry and Crystallographic Geometries for Phenyl Benzoate and AM1 Optimized Geometry

	crystal	idealized	AM1	MM2
bond lengths				
C3–C4	1.49	1.48	1.47	1.49
C4–O5	1.19	1.20	1.23	1.20
C4–O6	1.37	1.36	1.38	1.36
O6–C7	1.41	1.41	1.39	1.41
bond angles				
C2–C3–C4	123.2	122.5	120.8	122.0
C1–C3–C4	117.9	118.1	118.9	118.8
C3–C4–O5	126.0	126.2	127.9	125.2
C3–C4–O6	110.8	111.7	113.1	112.4
C4–O5–C7	118.3	118.8	119.0	118.3
O6–C7–C8	121.0	120.6	122.7	121.8
O6–C7–C9	116.7	116.7	115.9	120.9
dihedral angles				
R	−9.6	−6.2	−1.1	0.4
S	−0.1	0.3	0.2	2.3
T	67.2	68.4	50.3	66.2

It is interesting, therefore, that both the work of Hummel et al. and the AM1 calculations suggest a low barrier of roughly 1.25 kcal at 0° (Table III). This is accommodated, according to AM1, by an opening of the C–O–C bond angle from 118.6° when the T angle is 60° to 123.8° when T is 0°. If we assume that the AM1 calculations are essentially good models for reality, except that either the steric repulsion contribution to total energy has been underestimated or the resonance contribution has been overestimated, and that these contributions display a sinusoidal form; then a "corrected" AM1 profile with the minimum shifted to around 67° should show an increased barrier at 0° and decreased one at 90°. Hummel et al. using their molecular mechanics inference technique find a lower barrier at 90°, but an even lower one at 0° also (Table III). The application to this problem of a similar, but in our opinion better, inference method is described in the next section.

Parameterization of MM2[31] for Aromatic Esters. The purpose of parameterization of MM2 for aromatic esters is 2-fold. Firstly, it can be used to estimate rotational energy profiles using the molecular mechanics inference technique alluded to above. Secondly, the program, with the derived parameters, can be used to estimate conformational energies for any aromatic ester moiety that might be incorporated into a polymer.

Parameterization was performed by an "iterative intuitive" fitting process, that is to say, by running the MM2 program with a set of chemically sensible trial parameters, assessing the difference between the optimized geometry and idealized crystal structure geometries for aromatic esters, refining the set, and so on. Further refinements were then introduced in light of knowledge concerning the R, S, and T bond barriers. Two particular aspects of the parameterization are worthy of comment.

Firstly, in the initial stages of parameterization, particular emphasis was placed upon obtaining the correct bond angles around the ester carbonyl carbon, as the parameters supplied with MM2[32] and those used by Hummel and Flory[4] give a poor result. This necessitated a partly arbitrary assignment of force constants and minimum energy bond angles around this atom, in order to get a reasonable fit (results in Table V). We have concluded that the root problem in assigning the ester in-plane bond angle parameters lies with the steric properties assigned to oxygen atoms by MM2. By default, MM2 adds lone pair to ether-type oxygens, but not to carbonyl-type oxygens, and our parameterization has maintained this convention.

Table VI
MM2 Rotational Profiles of Esters and Acids Using New Parameters

	energy of barrier or conformer rel to min energy[a]				
	R	S		T	
molecule	barrier 90°	cis	barrier 90°	barrier 0°	barrier 90°
formic acid		3.8	11.7		
methyl acetate		6.2	9.9		
vinyl acrylate		7.5	7.3		
benzoic acid	5.0	5.3	12.6		
phenyl benzoate	4.7	7.9	7.1	1.96	0.15

[a] For experimental and theoretical values, refer to Table III.

However, in the case of aromatic esters, such as benzoates, there is significant steric interaction between the phenyl ring and both of the ester oxygen atoms, and therefore, although beyond the scope of our studies, it would be desirable to examine their close-contact steric properties more closely.

Secondly, it was found that supplied torsional parameters for the ester C–O bond, if present, lacked the consistency one would expect for the same bond (see Table IV), presumably because they were derived in order to fit specific molecules to experiment, rather than to account for orbital overlap effects in a more general sense. Also, the supplied V2 terms for the bond are inappropriate if the ether-type oxygen is to be considered a "π atom", as is the default in the most recent version of MM2.[31] Therefore, the parameters for the bond were completely reworked according to the following rationale. As alluded to in the section on the S bond, above, there are two key features to the torsional behavior for the central C–O of esters and carboxylic acids, which can be classified as (i) C_{σ^*}–O_n bonding and (ii) C_{π^*}–O_p bonding. (i) is a 1-fold effect, and V1[33] terms for H–C–O–H and O–C–O–H of formic acid were derived by fitting to what is believed to be the best experimental value for the trans–cis gap of formic acid (3.64 kcal mol^{-1}).[26] It was assumed that both H–C–O–H and O–C–O–H prefer a cis conformation, as it is this configuration that permits C_{σ^*}–O_n bonding, so a small negative V1 term (–0.75) was assigned to H–C–O–H and a larger negative one (–2.5) to O–C–O–H. These V1 terms representing an "intrinsic" 1.75-kcal gap between trans and cis ester or carboxylic acid conformers were then applied to all types of C–O studied. (ii) is a 2-fold effect, and V2[33] terms were derived firstly for X–C–O–aliphatic and then for X–C–O–aromatic. For the aliphatic case, terms were picked to fit the cis–trans barrier at ~90° to be ~11 kcal mol^{-1} (see the results in Table VI). In the aromatic case, it was found that the SCF calculation by MM2 does not pick out a significant difference in bond order of C–O from the aliphatic case, contrary to the conclusions in the discussion on the S bond, above. Therefore, the total V2 term from X–C–O–aromatic was reduced to the level necessary to obtain approximately 7 kcal mol^{-1} for the trans–cis barrier of phenyl benzoate.

The final parameters are shown in Table IV, and Figures 3–5 show a comparison between AM2 and MM2 profiles for the R, S, and T bonds of phenyl benzoate. Table V shows a comparison of the MM2-optimized geometry, using this parameter set, for phenyl benzoate with crystal structure and AM1 data. Table VI shows some energy barriers calculated for esters and carboxylic acids. It should be emphasized that the new parameters are not proven to be, nor are likely to be, generally applicable in use with the MM2 program, but are useful for the specific case of aromatic esters.

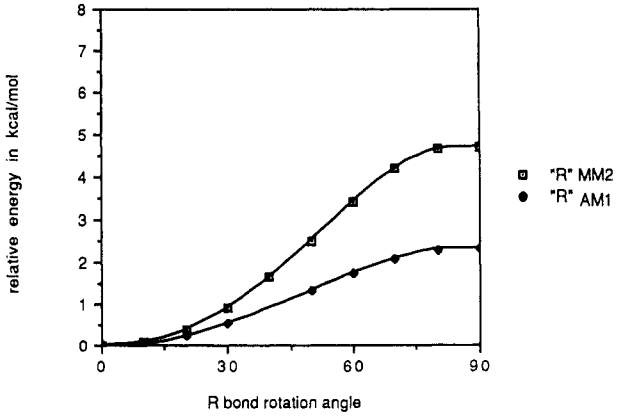

Figure 3. Rotation potentials for the R bond.

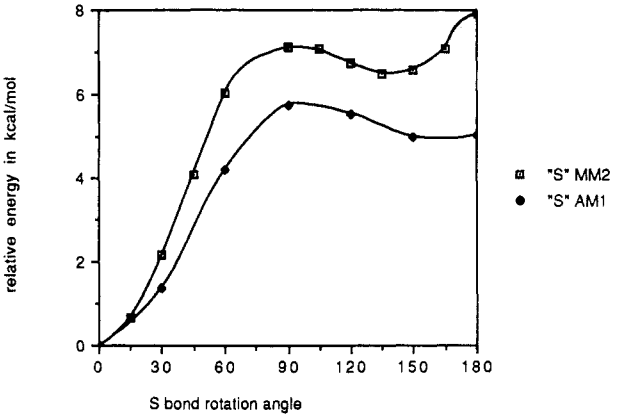

Figure 4. Rotation potentials for the S bond.

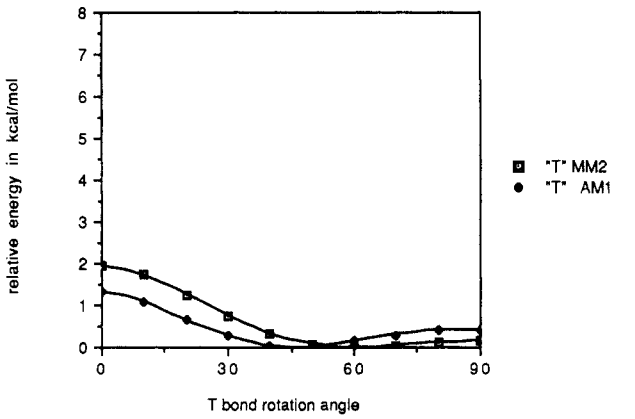

Figure 5. Rotation potentials for the T bond.

The MM2 results in Figures 3–5 represent our best efforts to model the rotational energy profiles of phenyl benzoate within the limitations of the available data. They incorporate the conclusions of the discussion of R, S, and T bonds above and infer some features of the rotational energy profiles which were poorly resolved in that discussion.

With respect to the S bond rotational profile (Figure 4), the MM2 program thus parameterized infers a value of 7.9 kcal mol^{-1} for the cis conformation relative to the trans. This is at a maximum on the rotation profile and represents the overall barrier to rotation around the S bond. It should be noted, however, that no charges or dipoles for the phenyls have been included in the MM2 calculation and so, as the face-to-face contact of benzene rings is believed to be a strongly repulsive interaction,[34] an "improved" MM2 cis-conformer energy may be somewhat higher.

For rotation of the T bond of phenyl benzoate (Figure 5), barriers of 1.96 kcal mol^{-1} at 0° and 0.15 kcal mol^{-1} at

Table VII
Effect of Substituents on the R Bond Rotational Barrier of Methyl Benzoate

methyl benzoate substituent of molecule name	change in AM1 barrier height rel to methyl benzoate (2.57 kcal mol^{-1})	σ[36]
p-CO_2CH_3	−0.23	+0.48 (σ_p^+)
m-CO_2CH_3	−0.20	+0.37 (σ_m)
none	0.0	0.0
methyl 2-naphthoate	+0.24	−0.14 to −0.56 (σ_a^+)
p-O_2CH	+0.44	not available
p-OMe	+0.58	−0.78 (σ_p^+)
phenyl benzoate	−0.22	not applicable

90° were calculated, using MM2. We believe these to be better estimates than those of Hummel et al. (Table IV) because firstly they rely on a force field the basis of which is more thoroughly tested than that adopted by Hummel and secondly they are consistent with "corrected" AM1 values as defined in the section on the T bond above.

The Influence of Aromatic Group Substituents on Aromatic Ester Rotation Barriers

In typical polymers, the ester group is connected to a variety of substituted benzene moieties. Therefore, given a good indication of the rotational barriers of ester group bonds in model compounds, it is still necessary to be able to estimate how these barriers will be modified by different aromatic environments. The nature of the attached aromatic ring can have a significant effect on aromatic ester rotational barriers, as the π orbitals of the aromatic ring are conjugated with the π orbitals of the ester, where they are attached to the carbon or the oxygen link of the group. Simple organic chemists "arrow-pushing" theory would predict, for example, that (a) relative to phenyl benzoate the R bond rotation barrier would be increased given a π-electron-donating substituent, X (Figure 1), on the phenyl ring and decreased given a π-electron-withdrawing substituent; and (b) a π-electron-withdrawing group, Y (Figure 1), on the other phenyl ring, should decrease the bond order and hence rigidity of bond rotation S and increase the bond order and hence lower the angle and modify the rotational energy profile for the T bond.

This knowledge is a useful tool for the "fine-tuning" of polymer composition and design. However, at this level of theory there is little indication of the scale of such substituent effects. Table VII shows the relative change in the R bond barrier of a series of substituted methyl benzoates, according to AM1. We had hoped to apply MM2 to the same problem, but difficulties with the program have prevented this.[35]

As a test of the ability of AM1 to predict substituent effects, the last column of Table VII lists appropriate Hammett σ constants[36] for the various substituents. These have been derived from experimental data to explain the different reactivity of variously substituted benzene rings and are, in effect, a measure of the electron donor–acceptor power of the substituent. Relative to an unsubstituted ring, a negative σ value indicates an electron-donating substituent, whereas a positive value indicates an electron-withdrawing one. The σ values chosen take account of both the π- and σ-orbital aspects of electron distribution in phenyl rings. There is a good qualitative agreement between σ values and the change of AM1 barriers, indicating that AM1 is a reliable method for showing the direction, though not necessarily the scale, of the substituent effect in these cases.

If the scale of the effects can be trusted, one can imply the different behavior of the R bond in various polymers. For instance, the R bond in poly(p-hydroxybenzoic acid) is expected to be more rigid than that in its isomer, poly(phenylene terephthalate), by about 0.7 kcal mol^{-1}.

AM1 was also used to assess the scale of effect of substituent Y (Figure 1) on the S bond barrier at 90°. For this purpose, the barrier was calculated for a series of phenyl formates having the same substituents as the methyl benzoate series in Table VII, only leaving out m-CO_2Me. The T bond was fixed at 60°, as optimization of this geometric variable would result in lower angles than are expected for the real molecules. All four barriers were within 5% of each other, indicating that the "tuning" of the S bond flexibility that can be achieved by changing the substituent Y is small. As expected, the lowest barrier was found for the most electron-withdrawing group, p-CO_2Me, having a barrier 4% below that of phenyl formate itself. This experiment is not entirely satisfactory, as the T bond rotation angle is fixed. If is were to optimize correctly under AM1, a slightly more marked substituent effect would be expected.

We had hoped to study the effect of substituent on the barriers and minimum energy position for the T bond using MM2 together with the parameters in Table III. This was felt, in principle, to be a more useful method than AM1, as it is considerably faster and because we believe it more accurately predicts the rotational energy profile of the T bond, at least for phenyl benzoate. However, we have been unable to use MM2 with the necessary molecules, owing to the program deficiencies[35] mentioned above. Preliminary X-ray results, to be reported elsewhere, suggest that in crystalline poly(phenylene terephthalate) (electron-donating para substituent O_2CR) the mean T bond rotation angle is approximately 10° greater than in crystals of its isomer, poly(p-hydroxybenzoic acid) (electron-withdrawing para substituent CO_2R). Consistent with this chain conformational difference there is a marked difference in unit cell dimensions. A method for predicting substituent effects on the T bond rotation angle would thus feed into the understanding and prediction of the three-dimensional structure of aromatic polyesters.

Conclusion

A report has been made of information, old and new, concerning the conformational energetics of aromatic ester moieties which we believe will be of use to those who undertake structural, molecular dynamical, and modeling studies of substances containing aromatic ester moieties. In the near future we intend to present studies on the structure of aromatic polyesters and on the relationship between polymer composition and liquid crystallinity, based on the conformational energy parameters derived here.

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Registry No. Methyl benzoate, 93-58-3; phenyl benzoate, 93-99-2; methyl formate, 107-31-3; methyl acetate, 79-20-9; vinyl acrylate, 2177-18-6; formic acid, 64-18-6; benzoic acid, 65-85-0.

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(32) Parameters as supplied by N. L. Allinger in early 1987.
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