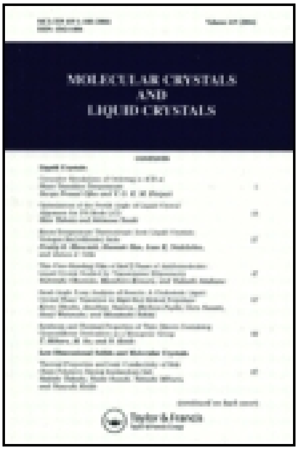

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Theoretical Conformational Analysis of Substituted Phenylbenzoates

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Theoretical Conformational Analysis of Substituted Phenylbenzoates

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Conformational analysis of phenylbenzoate, a characteristic moiety of several liquid crystal compounds, was done using the NDDO semiempirical molecular orbital method. Calculated and experimental torsional angles (the latter found in various model molecules) agree nicely. The most probable conformation of DB-PBB (4-butylphenyl-4′-butylbenzoyloxy benzoate), existing in the solid phase and probably also in the mesophase, is an extended one. The C3-C4-C7-O8-torsional angle is synclinal while C4-C7-O9-C10X is periplanar. Calculations indicate that substituted phenyl-4-benzoyloxybenzoates are rather flexible molecules. Rotation by an angle less than 20° around any of the C4C7, C7O9 and O9C10 bonds needs at most 10 kJ/mol energy.

INTRODUCTION

Study of the conformational behavior of molecules which form liquid crystals may help considerably in understanding the structure and microdynamics of the mesophase. In this work we continue previous molecular orbital calculation[1,2] and combine them with available X-ray diffraction data to gain information on substituted 4-benzoyloxy phenylbenzoate, **1**, and 4-nitrophenyl

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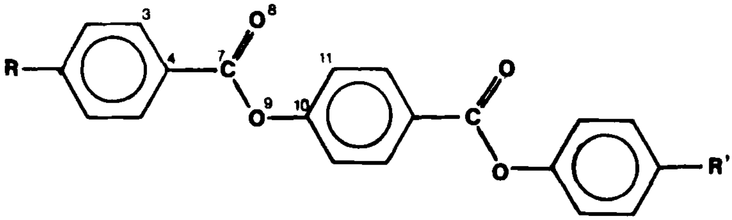
benzoate, **2**, derivatives (See Digrams 1 and 2 below). Both types of compounds have a common phenylbenzoate moiety for which calculations were done.



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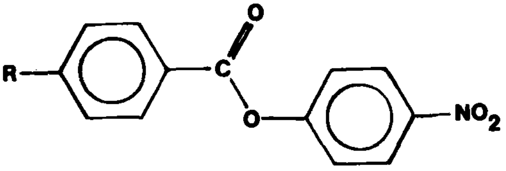

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METHOD

We used a version of the semiempirical NDDO (Neglect of Diatomic Differential Overlap) method[3] which describes rotations around single bonds connecting delocalized systems correctly.[4–6] The calculations for phenylbenzoate were done using experimental bond lengths and bond angles.[7] No geometrical optimization for the various conformers was performed. We used the Cambridge Crystallographic Data Bank[8] to collect torsional angles for model molecules. The molecular diagrams of the proposed equilibrium conformations were plotted by the PLUTO program.[9]

RESULTS

An isoenergy contour map for the conformations, obtained by rotating the phenoxy group around the C7O9 bond (t_2 = C4-C7-O9-C10∡) and the phenyl group around the O9C10 bond (t_3 = C7-O9-C10-C11∡) simultaneously, is depicted in Figure 1. The torsional angle, t_1 = C3-C4-C7-O8∡ was held at a constant value of 0°. Contours connect points, defined by t_2 and t_3, which refer to equal relative conformational energies. For the minimum energy, i.e. stable, conformation $t_2 = 180°$ and $t_3 = 60°$ was found. Its relative energy content with respect to an arbitrary zero level is −71 kJ/mol. X-ray crystallographic measurements yield $t_2 = 180°$ and $t_3 = 67°$ for phenylbenzoate.[7]

Values of t_2 and t_3, obtained experimentally for various molecules containing the phenylbenzoate moiety, are given in Table I. The corresponding points are also depicted in Figure 1.

Chemical evidence and the data in Table I indicate that the equilibrium value of t_1 varies around 0° in molecules containing the phenylbenzoate moiety. This was also confirmed by our NDDO calculations. Changing t_1 by $\pm 15°$ relative to the equilibrium value ($t_1 = 0°$) in the conformation characterized by $t_2 = 180°$ and $t_3 = 60°$, raised the energy content of the molecule. The increase in energy is, however, very small 0.2 kJ/mol.

DISCUSSION

Theoretically derived minimum energy conformation of phenylbenzoate corresponds to chemical evidence predicting those conformers to be more stable in which conjugation is possible. The π-bond of the C7O8 carbonyl lies in the

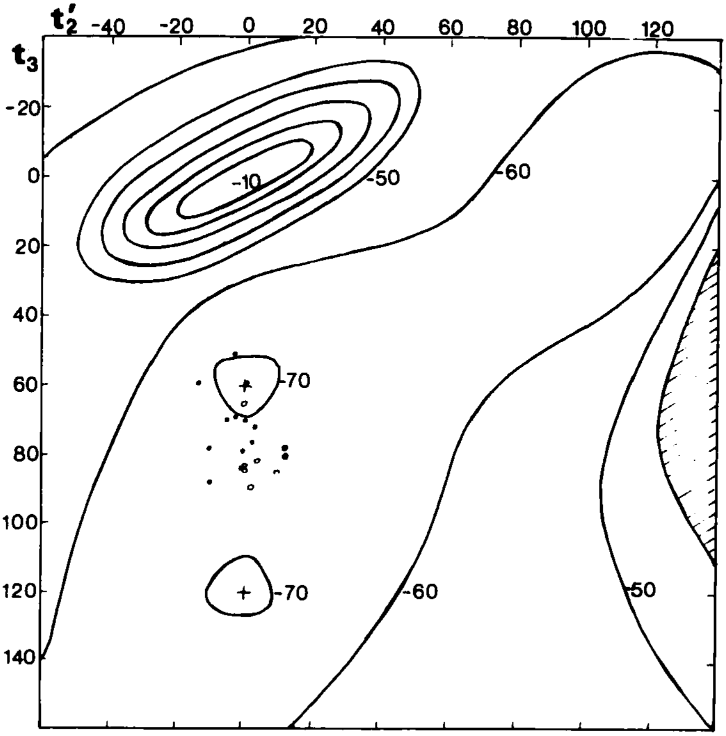

FIGURE 1 Isoenergy contour map (in kJ/mol) for internal rotations in phenylbenzoate as obtained by the NDDO method. t_1 = C3-C4-C7-O8∡ = 0°, t_2' = 180° − C4-C7-O9-C10∡, t_3 = C7-O9-C10-C11∡. Crosses denote local minima, circles indicate experimental equilibrium conformations for the molecules of Table I.

TABLE I

Torsion angles of compounds containing the phenylbenzoate moiety (taken from the Cambridge Crystallographic Data Files[8]). For the definition of t_1, t_2 and t_3 see text, $t_2' = 180° - t_2$. Due to symmetry we restricted the search for t_3 values lying between the range of ±90°. Entries in the table refer to the enantiomer for which $t_3 \geqq 0°$.

compound	t_1	t_2'	t_3	ref.
phenylbenzoate	−10	0	67	7
4'-nitrophenyl-4-octyloxy-benzoate	−1	1	60	10
9,10-antrahydroquinone dibenzoate	−10	3	90	12
7-hydroxycalamenene *p*-bromobenzoate	−2	10	85	13
p-bromobenzoyl-leukopleurotin	9	−1	84	14
2,4-dibromo-*o*-cresyl-3',5'-dinitrosalicylate	−2	4	82	15
kinamycin C *p*-bromobenzoate	10	−15	78	16
	8	12	75	
sterigmatocystin *p*-bromobenzoate	−7	−2	82	17
1,2,3,4-tetrahydro-9-phenantrol *p*-bromobenzoate	−5	0	85	18
estradiol 3-*p*-bromobenzoate	−7	−15	89	19
ferroverdin sodium salt acetone solvate	4	−3	51	20
	−17	−5	73	
	−6	6	76	
ferroverdin sodium salt carbon tetrachloride-methanol solvate	−5	−6	70	21
pristimerol bis(*p*-bromobenzoate)	−14	−1	80	22
	−12	15	87	
tolypomycinone tri-*m*-bromobenzoate	1	−15	58	23
ilamycin B-1-*p*-bromobenzoate ethanol solvate monohydrate	0	3	74	24
2,9-dimethyl-3'hydroxy-5-phenyl-6,7-benzomorphan	−11	0	68	25

plane of the benzene ring formed by C1C2C3C4C5C6 atoms. The torsional angle, t_3, is 60° to ensure maximum conjugation of the lone pair at O9 with the C10C11C12C13C14C15 benzene ring.

Comparison of the data in Table I and Figure 1 indicates that theory and experiment agree nicely. The energy content of the conformers, corresponding to the molecules of Table I, lies at most 2 kJ/mol higher than the minimum value. This is comparable to kT at room temperature indicating that slight differences in the measured values of t_2 and t_3 in various molecules are due to statistical fluctuations (difference in packing forces). According to Figure 1 there exists a large number of significantly different conformations with about the same energy. This means that, in the gaseous phase or in solution, molecules with the phenylbenzoate moiety are rather flexible. The flipping process of the phenyl ring in **2** ($R = n$-octyl), indicated by proton relaxation-time measurements and mentioned by Kaiser *et al.*[10] in their crystallographic work on 4'-nitrophenyl-4-octyloxybenzoate (NPOB), may be attributed to this flexibility.

A PLUTO plot of the skeleton of molecules with the general formula **1** in the minimum energy conformation is given in Figure 2. The conformation, depicted in Figure 3, differs in energy from the former by only 4.3 kJ/mol. We suppose that the most probable conformation of DB-PBB (**1** with $R = R' = n\text{-}Bu$) is that indicated in Figure 2. Alkyl chains are supposed to be in an extended conformation like in NPOB[10] they are omitted from the drawing. Dielectric measurements of Bata and Buka[11] indicate that the dipole moment component which is perpendicular to the para axis of DB-PBB is 3.36 D. This relatively large value suggests that carbonyl groups are positioned parallel to each other as depicted in Figure 2.

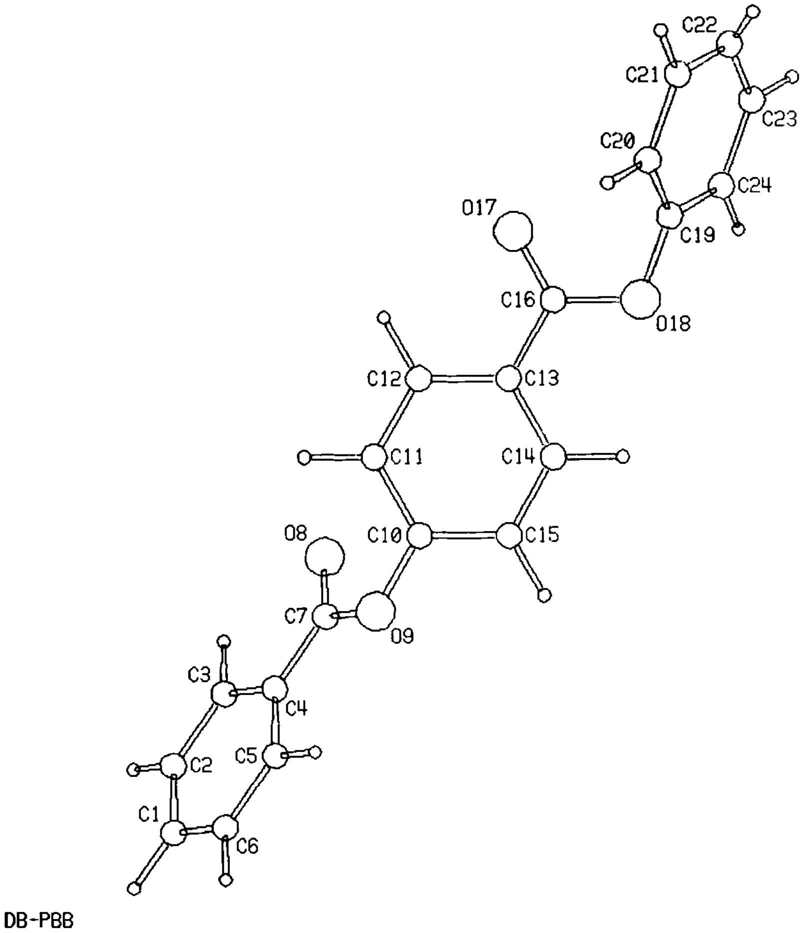

FIGURE 2 PLUTO plot of the theoretically predicted minimum energy conformation of **1** ($R = R' = H$). C3-C4-C7-O8∢ = C12-C13-C16-O17∢ = 0°, C4-C7-O9-C10∢ = C13-C16-O18-C19∢ = 180°, C7-O9-C10-C11∢ = C16-O18-C19-C20∢ = 60°.

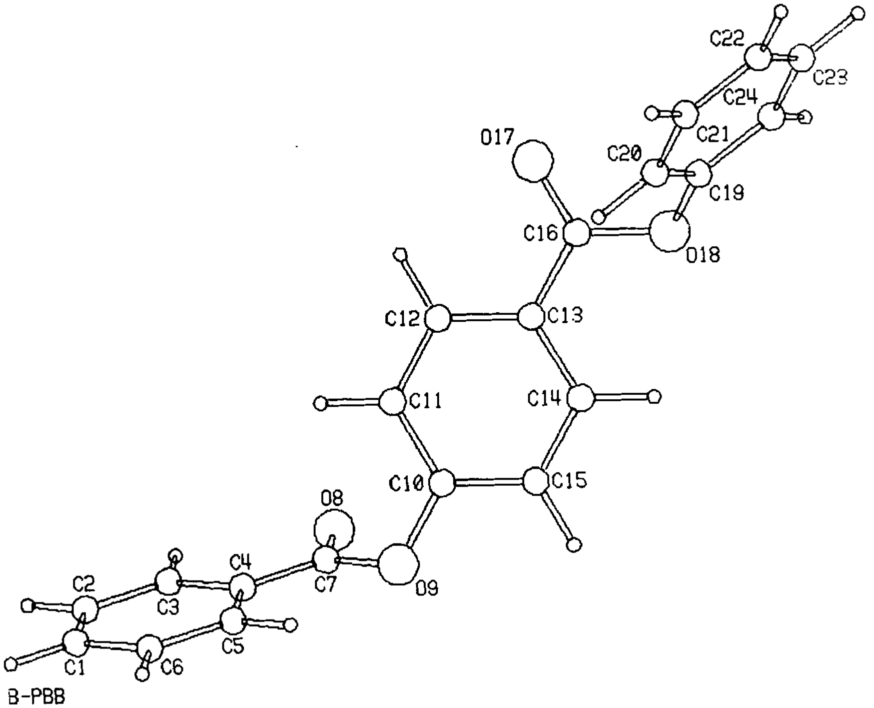

FIGURE 3 PLUTO plot of a low energy conformation of 1. ($R = R' = H$). C3-C4-C7-O8∡ = C12-C13-C16-O17∡ = 0°, C4-C7-O9-C10∡ = C13-C16-O18-C19∡ = 120°, C7-O9-C10-C11∡ = C16-O18-C19-C20∡ = 40°.

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