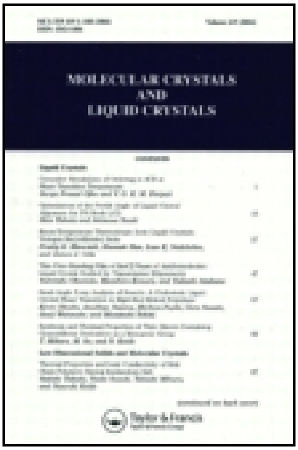

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The Molecular Structure of Mesogenic 4-Butylphenyl 4′-Butylbenzoyloxybenzoate in the Crystalline State

W. Haase [a] , H. Paulus [a] & R. Pendzialek [a]

[a] Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 20, D-6100, Darmstadt, Germany

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The Molecular Structure of Mesogenic 4-Butylphenyl 4′-Butylbenzoyloxybenzoate in the Crystalline State

W. HAASE, H. PAULUS and R. PENDZIALEK

Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt, Germany

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The crystal and molecular structure of the title compound were determined: $a = 14.375(3)$, $b = 11.534(3)$, $c = 7.972(2)$ Å, $\alpha = 71.694(5)$, $\beta = 79.125(5)$, $\gamma = 74.861(5)$°; space group $P\bar{1}$. Refinement including all of the observed reflections (3145) leads to $R = 0.086$ ($R_w = 0.074$).

The molecular form in the crystalline state is fully extended in agreement with the suggestion by Birner *et al.* (*Mol. Cryst. Liq. Cryst.*, **80**, 11 (1982)), based on a NDDO-semiempirical calculation.

Whereas for the molecular form in the nematic liquid crystalline state a slightly parallel arrangement (~ 60°) of the dipole moment components perpendicular to the long axis is proposed, in the crystalline state these components are at an angle ~ 120° to each other, and somewhat antiparallel.

Preceding the melting point by approximately 10 degrees, DSC and thermal microscopy signals were observed; these depend eventually on solid-state polymorphism.

INTRODUCTION

The mesogenic 4-butylphenyl 4′-butylbenzoyloxybenzoate (DB-PBB), first prepared by Steinsträßer,[1] is a member of the well known phenyl *p*-benzoyloxybenzoate group of compounds.[2] It has often been investigated by different methods either as the individual compound[3,4] or as part of multicomponent mixtures.[5-10] Recently Birner *et al.*[11] used the NDDO semiempirical molecular orbital method, to calculate the conformational freedom of the phenyl benzoate moiety. They suggested that for DB-PBB the extended conformation is the most probable one in the solid and nematic liquid crystalline phases. Dielectric measurements[3,10] indicated a dipole moment of 3.36 D perpendicular to the long axis of the molecule, resulting from the perpendicular component of each carboxylate group of $\mu_{\perp} = 1.68$ D.[12,13] This suggests that the carbonyl groups should be nearly parallel to each other as depicted in Figure 2 in reference 11. As a consequence of the low energy barriers between the various conformations in question, it was suggested[11] that this type of molecule is relatively flexible.

EXPERIMENTAL

For single crystal X-ray investigations, the compound was allowed to crystallize from an acetone-methanol mixture. The investigations were performed on a STOE-four-circle-diffractometer. The lattice dimensions were obtained from the setting angles based on fifty strong reflections. The crystal data for DB-PBB are given in Table I. The centrosymmetric space group $P\bar{1}$ was extracted by a statistical test. The reflection intensities were also obtained on the STOE-4-circle diffractometer. A set of 3145 independent reflections was measured and included in the subsequent calculations. The structure was solved by means of a MULTAN 80 program. The refinement ended at $R = 0.096$ through consideration of the anisotropic thermal parameters and with geometrically fixed H-positions related to their respective carbon atoms and a fixed C-H distance of 0.96 Å. The last difference Fourier map showed a slight variance in the electron density around one of the butyl residues (C(25) to C(28), Table II). To integrate the six strongest maxima, partially occupied carbon atom

TABLE I

Crystal Data

Molecular formula : $C_{28}H_{30}O_4$
Molecular weight : 430.52 g/mol
Space group : $P\bar{1}$
$a = 14.357(3)$ Å; $b = 11.534(3)$ Å; $c = 7.972(2)$ Å;
$\alpha = 71.694(5)°$; $\beta = 79.125(5)°$; $\gamma = 74.861(5)°$;
V_c : 1201.6 Å^3; $Z = 2$
D_c : 1.19 g/cm^3; $\mu(\mathrm{MoK}_\alpha) = 0.44$
Independent reflections: 3145

TABLE II

Atomic parameters

Atom	x/a	y/b	z/c	U_{eq}
Butyl group A				
C(1)	1.5176(3)	.1683(4)	.2648(7)	.121(4)
C(2)	1.4766(2)	.3051(4)	.2005(6)	.091(3)
C(3)	1.3660(2)	.3409(3)	.2282(5)	.076(3)
C(4)	1.3242(2)	.4791(4)	.1611(5)	.081(3)
Phenyl ring I				
C(5)	1.2166(2)	.5211(3)	.2041(5)	.062(3)
C(6)	1.1798(3)	.6168(3)	.2798(5)	.069(3)
C(7)	1.0827(3)	.6580(3)	.3159(5)	.069(3)
C(8)	1.0174(2)	.6051(3)	.2753(4)	.055(2)
C(9)	1.0530(2)	.5079(3)	.1985(5)	.066(3)
C(10)	1.1513(2)	.4663(3)	.1640(5)	.072(3)
Carboxylate group 1				
C(11)	.9124(3)	.6583(4)	.3117(5)	.068(3)
O(1)	.8774(2)	.7389(3)	.3831(4)	.100(2)
O(2)	.8564(2)	.6054(2)	.2467(3)	.069(2)
Phenyl ring II				
C(12)	.7549(2)	.6509(3)	.2576(4)	.061(2)
C(13)	.6990(2)	.5640(3)	.3273(5)	.069(3)
C(14)	.5999(2)	.6027(3)	.3332(5)	.067(3)
C(15)	.5567(2)	.7268(3)	.2712(4)	.056(2)
C(16)	.6149(2)	.8118(3)	.2000(5)	.070(3)
C(17)	.7132(2)	.7763(3)	.1914(5)	.074(3)
Carboxylate group 2				
C(18)	.4502(3)	.7628(3)	.2880(5)	.063(3)
O(3)	.3952(2)	.6958(2)	.3575(4)	.085(2)
O(4)	.4194(2)	.8870(2)	.2161(3)	.077(2)
Phenyl ring III				
C(19)	.3197(2)	.9417(3)	.2241(5)	.062(2)
C(20)	.2614(3)	.9178(3)	.1285(5)	.076(3)
C(21)	.1667(3)	.9834(4)	.1266(6)	.089(3)
C(22)	.1299(3)	1.0736(4)	.2161(6)	.093(3)
C(23)	.1898(3)	1.0939(4)	.3111(6)	.093(3)
C(24)	.2853(3)	1.0290(3)	.3154(5)	.079(3)
Butyl group B				
C(25)	.0223(4)	1.1522(6)	.1928(9)	.125(5)
C(26)	−.0514(9)	1.1205(14)	.2743(22)	.183(14)
C(27)	−.1430(5)	1.2379(12)	.2842(24)	.162(10)
C(28)	−.2190(6)	1.2126(10)	.2449(15)	.140(8)

TABLE II *Continued*

Atom	x/a	y/b	z/c	U_{eq}
		Butyl group B *Continued*		
C(25)′	.031(2)	1.158(2)	.334(4)	.069[a]
C(26)′	−.051(2)	1.064(2)	.247(4)	.068[a]
C(26)″	−.037(3)	1.140(3)	.358(4)	.069[a]
C(27)′	−.186(3)	1.221(3)	.361(3)	.067[a]
C(27)″	−.191(5)	1.264(4)	.294(8)	.070[a]
C(28)′	−.163(1)	1.140(1)	.224(2)	.068[a]

[a] fixed value. The occupation factor is 1 for all atoms with the following exceptions: C(25) : 0.85; C(25)′ : 0.15; C(26) : 0.65; C(26)′ : 0.20; C(26)″ : 0.15; C(27) : 0.70; C(27)′ : 0.20; C(27)″ : 0.10; C(28) : 0.75; C(28)′ : 0.25. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

positions (occupation factor 0.10 to 0.25) were used. The final R-value was $R = 0.086$ ($R_W = 0.074$). At this stage the hydrogen atoms at the carbon atoms C(26) to C(28) were not positioned as a consequence of above-mentioned partial occupancy. The atomic parameters can be found in Table II. A list of the positioned hydrogen atoms and the anisotropic thermal parameters of all atoms, with the exception of the hydrogen atoms, as well as a list of F_o/F_c can be obtained from the authors on request.

Molecular structure

The molecule is presented in Figure 1, being projected perpendicular to the phenyl ring II. The molecular form is, as can be seen, fully extended. Its longest extension is ~ 27.2 Å (the calculated distance C(1) to C(28) amounts to 24.70 Å and H(1) to C(28) is 25.63 Å); this takes the covalent radii of the hydrogen atoms into account, as well as the fact that the hydrogen atoms at C(28) are not fixed. The extension perpendicular to the longest axis is nearly equal to the extensions of the phenyl rings.

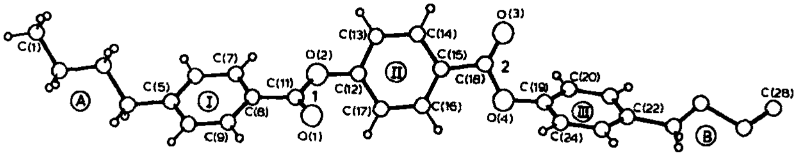

FIGURE 1 Molecule projected perpendicular to phenyl ring II (plane C(12), C(14), C(16)).

TABLE III

Selected intramolecular distances and bond angles

Atoms	[Å]	Atoms	[°]
C(8)—C(11)	1.483(5)	C(8)—C(11)—O(1)	126.5(4)
C(11)—O(1)	1.192(5)	C(8)—C(11)—O(2)	111.4(3)
C(11)—O(2)	1.379(5)	O(1)—C(11)—O(2)	122.0(3)
O(1) ··· O(2)	2.250(4)	C(11)—O(2)—C(12)	119.5(4)
O(2)—C(12)	1.409(4)	C(15)—C(18)—O(3)	126.8(4)
C(15)—C(18)	1.468(5)	C(15)—C(18)—O(4)	111.1(3)
C(18)—O(3)	1.189(5)	O(3)—C(18)—O(4)	122.2(3)
C(18)—O(4)	1.351(4)	C(18)—O(4)—C(19)	120.2(4)
O(3) ··· O(4)	2.225(3)		
O(4)—C(19)	1.404(4)		

The mean value of the carbon-carbon bond lengths in the three phenyl rings is 1.370(10) Å. The standard deviation is given in brackets. The individual distances range from 1.353 to 1.390 Å. These values, as well as the bond angles within the phenyl rings, are of normal magnitude. The bond lengths and bond angles in the butyl group A also agree very well with known data (the distances vary from 1.490 Å to 1.525 Å), when one considers the relatively high thermal parameters (Table II). Besides this, one finds that the presumed fully extended molecular form is documented by the fact that the C-atoms of both butyl groups are practically in plane with phenyl ring II. The calculated distances and angles in butyl group B deviate from normal values owing to the presence of somewhat higher thermal vibrations and the partial occupation of carbon atom positions.

The appropriate distances and angles for both central carboxylate groups are given in Table III. All values are of normal magnitude and comparable with known values for other phenyl benzoate structures.[14-17] The dihedral angles between the best planes through the phenyl groups are: I–II : 48.8°, II–III : 61.5° and I–III : 20.8°.

For the purpose of comparison between the suggested and the determined structure of DB-PBB, the torsion angles are tabulated in Table IV. It can be seen that the calculated angles, based on a theoretical conformational analysis, in principle agree with the data for the solid state excepting one of the t_3 angles, which surprisingly deviates in the sign ($-69.2°$ instead of $60°$). Thus the predicted molecular structure with respect to extension, i.e. for crystalline DB-PBB, relates to fully extended molecules. In agreement with the known interpretation, the values of t_1 (defined in Table IV) indicate that the π-bond of each carbonyl group is practically in plane with its respective relevant neighbouring phenyl ring. Likewise the torsional angles t_3

TABLE IV

Torsion angles

Atoms	Angle [°] this work	Angle [°] Ref. 11
Angle t_1		
C(9)[a]—C(8)—C(11)—O(1)	−4.7	0
C(14)—C(15)—C(18)—O(3)	−3.3	0
Angle t_2		
C(8)—C(11)—O(2)—C(12)	184.6	180
C(15)—C(18)—O(4)—C(19)	182.4	180
Angle t_3		
C(11)—O(2)—C(12)—C(17)	53.6	60
C(18)—O(4)—C(19)—C(20)	−69.2	60

[a] The numeration of the atoms does not correspond with Ref. 11.

of 53.6° and −69.2° also confirm the assumption of maximum conjugation between the lone electron pairs of oxygen atoms O(2) and O(4) with phenyl rings II and III respectively. The minor deviations of the experimental t_3-values as compared with the calculated angle of |60°| is probably a consequence of packing forces acting upon the molecule. We nevertheless must consider sixteen geometrical conformations of the molecule when $t_1 = 0°$, $t_2 = 180°$ and $t_3 = |60°|$. By assuming that some conformations are equivalent when a mirror plane acts on phenyl ring II, and taking the molecular dipole moment (as a result of the presence of the carboxylate group) into account, then one finds two different molecular forms. These conformations, namely *a* and *b*, are depicted in Figure 2 together with their calculated respective dipole moments, based on the known bond data[12,13] ($\mu_\perp = 1.68$ D and $\mu_\parallel = 0.89$ D respectively). In the solid crystalline state, version *a* has been shown to exist. As a result of a comparison between data obtained from dielectric measurements[3,10] and known values of the dipole moment of the carboxylate group,[12,13] Birner *et al.*[11] suggested the prevalence of conformation *b* (for the nematic liquid crystalline state). This means that additionally to the processes normally occurring at the melting point, one has to consider a conformational change in DB-PBB.

Molecular packing

The molecules related by the inversion center of symmetry lie collinear to each other in a head-to-tail manner. This arrangement is shown in

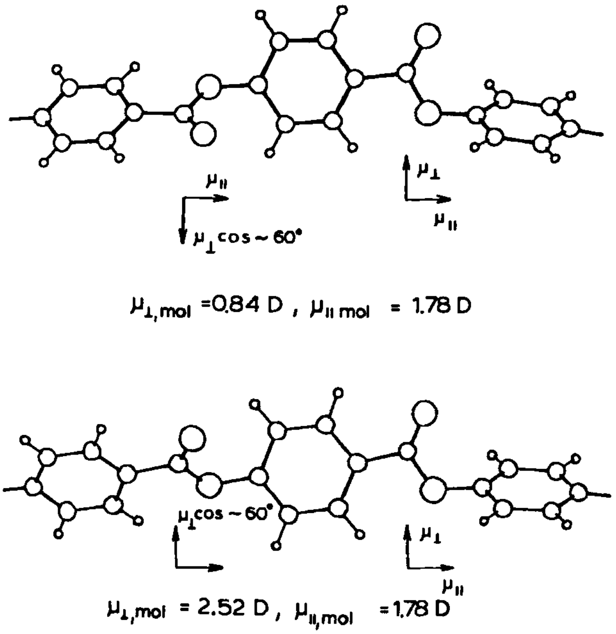

FIGURE 2 The two conformations of DB-PBB. Upper part: case *a*; lower part: case *b*.

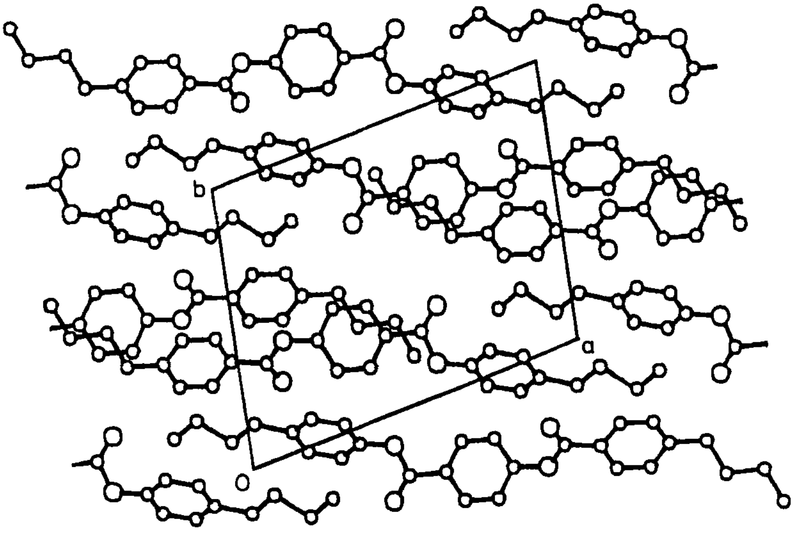

FIGURE 3 Projection perpendicular to the crystallographic (001)-plane.

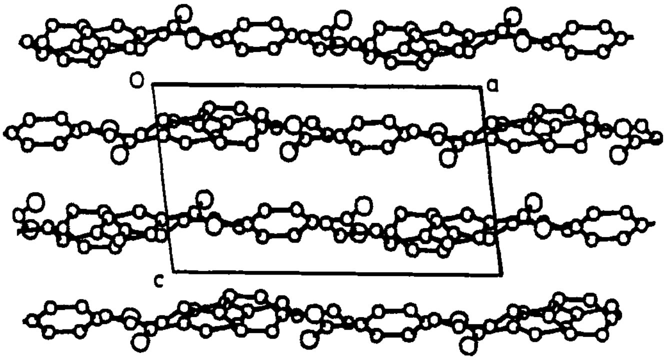

FIGURE 4 Projection perpendicular to the crystallographic (010)-plane.

Figure 3. As can be seen, the molecules are packed virtually parallel to the line (110). At the same time they extend over nearly two elementary cells along the *a*-axis; however, they form layers perpendicular to the *c*-axis in $c \sim \frac{1}{4}$ and $\sim \frac{3}{4}$ respectively. This stacking is demonstrated in Figure 4. Results of our investigations do not support the assumption of intermolecular contact between neighbouring molecules.

Thermal Properties

A selection of previous papers on DB-PBB and similar compounds[1,3,4,6-8] have mentioned a variety of temperatures for the melting point as well as for the clearing point. Thus the values varied between 76 °C[4] and 90 °C[3] for the former and from 177 °C[3] to 184.5 °C[8] for the latter. It therefore seems rather remarkable that none of the hitherto mentioned reports has concerned itself with the obvious discrepancies with regard to these two transition points.

Our own investigations with respect to the phase behaviour of DB-PBB showed that the compound melted to the nematic phase at 87 °C when analyzed by the DSC-method. This transition point was subsequently confirmed by thermal microscopy. The corresponding enthalpy of fusion was determined as 26.6 ± 1.0 kJ/mol. In addition to this, the DSC-thermograms were indicative of further transitions preceding the melting point by approximately 10 degrees, i.e., occurring at about 76 °C. The rather broad transition signal, as well as its magnitude, amounting to approximately 11 kJ/mol, suggests that solid state transitions and thus solid state polymorphism should also be considered for DB-PBB. This interpretation is also strongly supported by the changes in texture occurring at these temperatures when the compound is analyzed by thermal microscopy. At this point it should however be mentioned that additional changes in the texture are observable between 76 °C and 87 °C, but we have not been able to characterize these so far. Our investigations are therefore being continued to determine whether further transitions might occur and to secure evidence for the reversibility of the above-mentioned solid state transitions. With regard to the clearing point, this was determined as 176 °C and is in accordance with the lower values from the literature.

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