

RESEARCH ARTICLES

Further experiments using other physical techniques for *in situ* study of kinetics are in progress.

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RESEARCH COMMUNICATIONS

Crystal structure of the mesogenic compound *trans*-4-propylcyclohexyl-4-(*trans*-4-propylcyclohexyl) benzoate

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It is of interest to study the effects of structural changes due to additional atoms on the physical properties of compounds of a homologous series. We have earlier reported¹ the structure of the nematogenic compound *trans*-4-propylcyclohexyl-4-(*trans*-4-ethylcyclohexyl) benzoate (TPEB). In this paper we report the crystal structure of the next higher member of a homologous series, *trans*-4-propylcyclohexyl-4-(*trans*-4-propylcyclohexyl) benzoate (TPPB).

Good single crystals of TPPB were obtained by slow-evaporation technique using acetone as solvent. X-ray diffraction intensity data were collected on an Enraf Nonius diffractometer using Mo K_α radiation. A ω -2 θ scanning mode was employed, and Lorentz and polarization corrections were applied.

The structure was solved by direct methods using MULTAN80 (ref. 2) with $E > 1.537$. The phase set with best combined figure of merit was used for computing the E map. This map gave only a partial structure showing the benzene ring and C=O. Karle recycling of this fragment failed to develop the structure any further. Hence this fragment was assumed to be correctly oriented but wrongly positioned. Repositioning was

carried out, whereupon the full molecule was generated. Full-matrix and block-diagonal least-squares refinement was carried out using the LSTSQ-NRCVAX (ref. 3) program. Refinement with isotropic thermal parameters converged R to 0.3264, and refinement with anisotropic thermal parameters reduced it to 0.240. The hydrogen atoms were generated manually, but were not included in the refinement. The last least-squares cycle was calculated with 65 atoms, 235 parameters and 1360 out of 1363 reflections. Unit weights were used. The final residuals are $R_f = 0.240$ and $R_w = 0.238$ (where $R_f = \Sigma(F_o - F_c)/\Sigma F_o$, $R_w = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$), and the maximum shift/sigma ratio 0.070. The maximum and minimum electron-density peaks in the final difference map were +1.07 and -0.85 e Å⁻³ respectively. The computational work was carried out on a Wipro PC-AT 386/387 using the NRCVAX structure determination package³. The high residuals are due to the nonavailability of sufficient number of reflections with $I > 2\sigma(I)$ as the data set was poor.

Figure 1 shows the numbering scheme of the molecule projected on the best plane. Atomic coordinates and thermal parameter data have been submitted as supplementary material to the journal. Tables 1 and 2 give the bond lengths and angles and torsion angles for non-hydrogen atoms. The bond distances and angles are in good agreement with the standard values and those of TPEB. The equation for the best plane of the molecule is $4.58(3)X + 8.67(6)Y + 4.18(12)Z = 2.546(21)$. The equations for the best planes of the two cyclohexane cores and the benzene ring are $0.73(9)X - 8.73(8)Y + 9.71(11)Z = 4.07(14)$, $-2.33(8)X -$

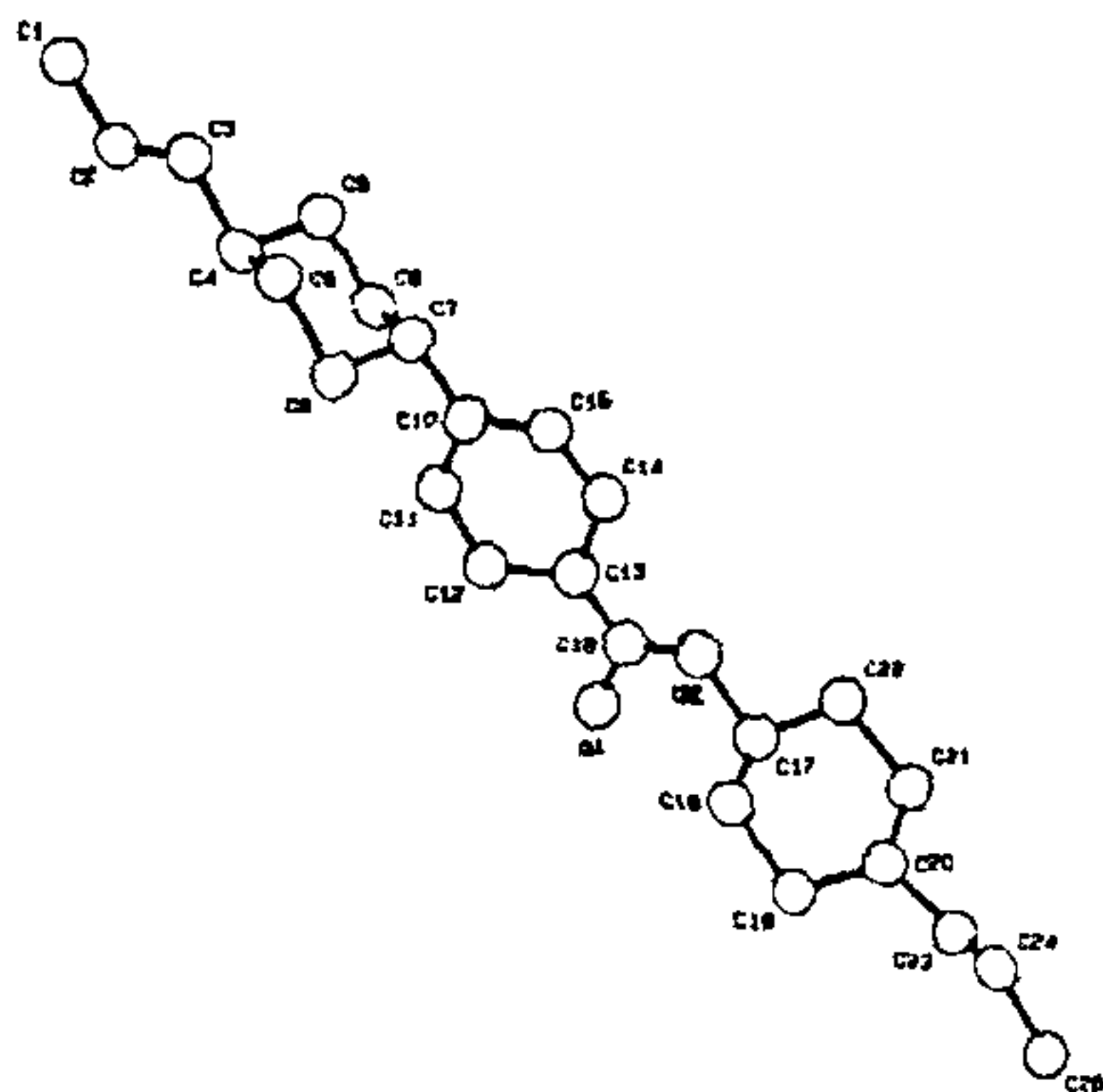


Figure 1. Projection of TPPB on the best plane.

$2.06(12)Y + 13.736(3)Z = 1.36(4)$, and $-4.93(6)X + 6.11(9)Y + 8.55(11)Z = 1.77(9)$ respectively.

The central phenyl ring makes angles of $96.3(9)^\circ$ and $51.5(9)^\circ$ with the mean planes of the two cyclohexane rings. The latter make an angle of $45.2(9)^\circ$. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.995(2) \text{ \AA}$, $b = 11.186(2) \text{ \AA}$, $c = 13.739(3) \text{ \AA}$, $\alpha = 101.28(2)^\circ$, $\beta = 107.96(3)^\circ$, $\gamma = 91.38(2)^\circ$, $Z = 2$, $D_c = 1.078 \text{ mg m}^{-3}$. Figure 2 shows the packing of the molecules. Imbricated packing of molecules is observed down the z axis, a mixture of imbrication and layering down the y axis, and strong layering down the x axis. The clearing point, which is higher for this homologue with respect to TPEB, can be accounted for by the layering of the

Table 1. Bond lengths and bond angles of nonhydrogens in TPPB

O(1)-C(16)	1.25(3)	C(11)-C(12)	1.41(3)
O(2)-C(16)	1.32(3)	C(12)-C(13)	1.50(3)
O(2)-C(17)	1.547(23)	C(13)-C(14)	1.47(3)
C(1)-C(2)	1.66(4)	C(13)-C(16)	1.39(3)
C(2)-C(3)	1.42(5)	C(14)-C(15)	1.36(3)
C(3)-C(4)	1.76(4)	C(17)-C(18)	1.37(3)
C(4)-C(5)	1.50(4)	C(17)-C(22)	1.58(4)
C(4)-C(9)	1.62(4)	C(18)-C(19)	1.64(3)
C(5)-C(6)	1.72(3)	C(19)-C(20)	1.52(4)
C(6)-C(7)	1.65(4)	C(20)-C(21)	1.43(4)
C(7)-C(8)	1.63(4)	C(20)-C(23)	1.64(3)
C(7)-C(10)	1.60(3)	C(21)-C(22)	1.73(3)
C(8)-C(9)	1.71(3)	C(23)-C(24)	1.02(5)
C(10)-C(11)	1.36(3)	C(24)-C(25)	1.60(5)
C(10)-C(15)	1.41(3)		
Bond angles (degrees)			
C(16)-O(2)-C(17)	116.7(17)	C(12)-C(13)-C(16)	115.6(19)
C(1)-C(2)-C(3)	104(3)	C(14)-C(13)-C(16)	124.5(19)
C(2)-C(3)-C(4)	100(3)	C(13)-C(14)-C(15)	117.5(19)
C(3)-C(4)-C(5)	99.8(18)	C(10)-C(15)-C(14)	123.1(19)
C(3)-C(4)-C(9)	99.1(22)	O(1)-C(16)-O(2)	121.4(22)
C(5)-C(4)-C(9)	103.4(19)	O(1)-C(16)-C(13)	122.1(21)
C(4)-C(5)-C(6)	107.4(18)	O(2)-C(16)-C(13)	113.2(20)
C(5)-C(6)-C(7)	95.7(22)	O(2)-C(17)-C(18)	111.7(16)
C(6)-C(7)-C(8)	110.5(21)	O(2)-C(17)-C(22)	98.6(14)
C(6)-C(7)-C(10)	101.4(21)	C(18)-C(17)-C(22)	115.0(19)
C(8)-C(7)-C(10)	102.1(19)	C(17)-C(18)-C(19)	113.1(20)
C(7)-C(8)-C(9)	97.1(18)	C(18)-C(19)-C(20)	102.0(23)
C(4)-C(9)-C(8)	102.7(23)	C(19)-C(20)-C(21)	119.7(20)
C(7)-C(10)-C(11)	123.5(19)	C(19)-C(20)-C(23)	110.2(23)
C(7)-C(10)-C(15)	115.9(19)	C(21)-C(20)-C(23)	105.3(25)
C(11)-C(10)-C(15)	120.5(17)	C(20)-C(21)-C(22)	113.6(21)
C(10)-C(11)-C(12)	122.6(18)	C(17)-C(22)-C(21)	101.1(21)
C(11)-C(12)-C(13)	116.4(22)	C(20)-C(23)-C(24)	129(3)
C(13)-C(14)-C(15)	119.3(17)	C(23)-C(24)-C(25)	123(5)

The last digit in each case is ESD.

structure and also the plausibility of the existence of an anomalous smectic phase^{4,5} as in 4-4'-bis(pentyl-oxyazoxy)benzene. The lower melting point of TPPB can be accounted for by the reduced dipole-dipole

Table 2. Torsion angles (degrees) of nonhydrogens in TPPB

C17-O2-C16-O1	12.2(10)	C17-O2-C16-C13	172.2(22)
C16-O2-C17-C18	-90.4(17)	C16-O2-C17-C22	148.3(20)
C1-C2-C3-C4	171.3(33)	C2-C3-C4-C5	-151.5(32)
C2-C3-C4-C9	103.1(27)	C3-C4-C5-C6	-179.4(23)
C9-C4-C5-C6	-77.4(17)	C3-C4-C9-C8	179.2(24)
C5-C4-C9-C8	76.8(18)	C4-C5-C6-C7	70.2(17)
C5-C6-C7-C8	-71.5(17)	C5-C6-C7-C10	-179.2(24)
C6-C7-C8-C9	75.3(18)	C10-C7-C8-C9	-177.5(24)
C6-C7-C10-C11	65.2(16)	C6-C7-C10-C15	-113.3(20)
C8-C7-C10-C11	-48.9(14)	C8-C7-C10-C15	132.6(21)
C7-C8-C9-C4	-70.8(17)	C7-C10-C11-C12	-172.1(21)
C15-C10-C11-C12	6.3(11)	C7-C10-C15-C14	173.6(20)
C11-C10-C15-C14	-4.9(10)	C10-C11-C12-C13	-6.8(9)
C11-C12-C13-C14	6.1(10)	C11-C12-C13-C16	-165.9(24)
C12-C13-C14-C15	-4.9(10)	C16-C13-C14-C15	166.3(23)
C12-C13-C16-O1	-11.6(11)	C12-C13-C16-O2	-171.4(24)
C14-C13-C16-O1	177.0(25)	C14-C13-C16-O2	17.1(9)
C13-C14-C15-C10	4.3(9)	O2-C17-C18-C19	179.2(19)
C22-C17-C18-C19	-69.5(15)	O2-C17-C22-C21	175.9(21)
C18-C17-C22-C21	57.0(15)	C17-C18-C19-C20	59.3(15)
C18-C19-C20-C21	-53.5(15)	C18-C19-C20-C23	-175.8(25)
C19-C20-C21-C22	53.7(15)	C23-C20-C21-C22	178.3(24)
C19-C20-C23-C24	-134.5(41)	C21-C20-C23-C24	95.1(37)
C20-C21-C22-C17	-46.5(14)	C20-C23-C24-C25	161.2(40)

The last digit in each case is ESD

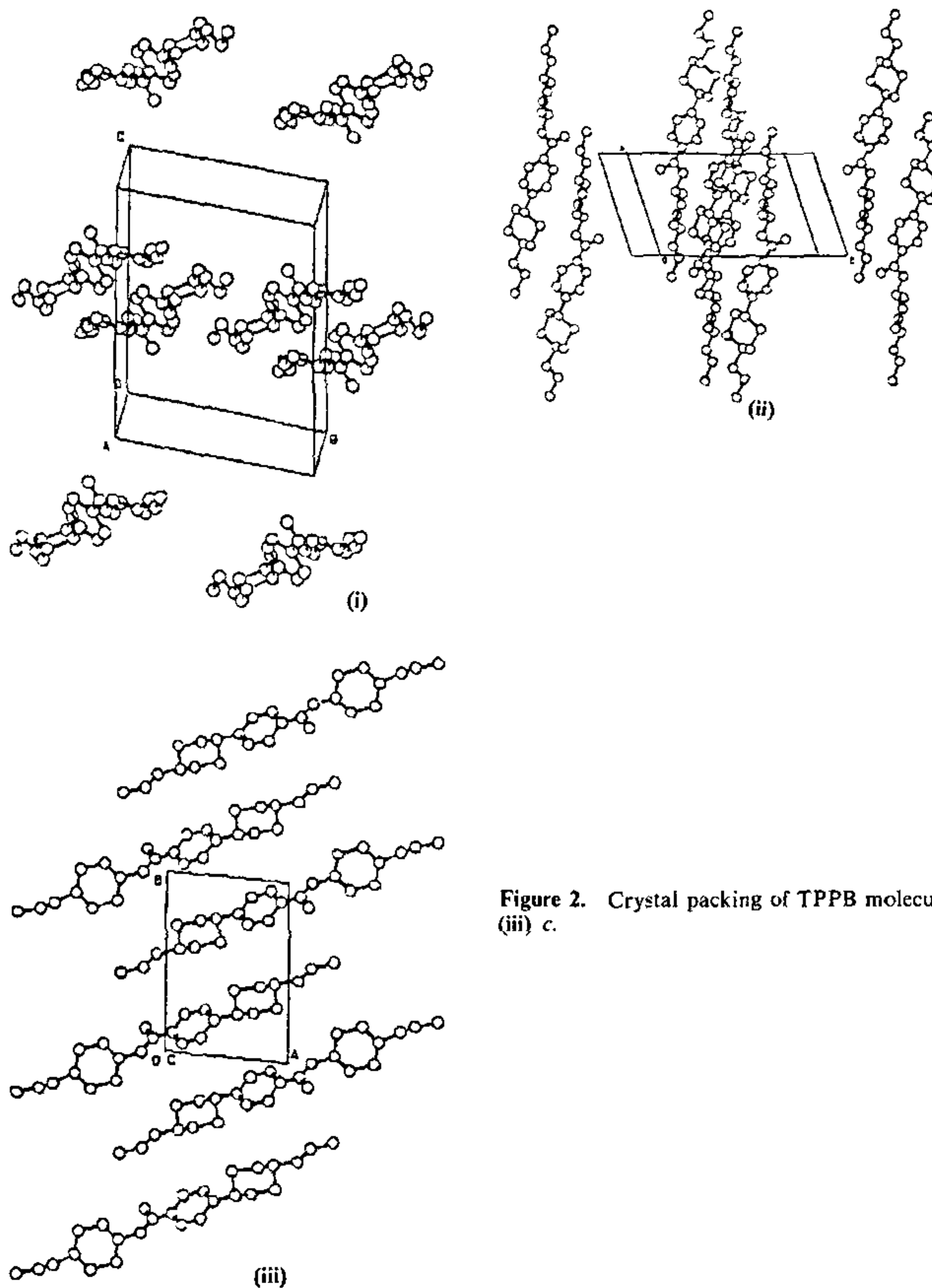


Figure 2. Crystal packing of TPPB molecules down (i) *a*, (ii) *b*, and (iii) *c*.

interaction of $-C=O-$ dipole induced by the conformational changes in the ring system.

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