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Structures of Di-*p*-tolyl Terephthalate ($C_{22}H_{18}O_4$) and 1,4-Phenylene Di-*p*-toluate ($C_{22}H_{18}O_4$)

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Abstract. Di-*p*-tolyl terephthalate (CA), $M_r = 346{\cdot}2$, monoclinic, $C2/m$, $a = 7{\cdot}920$ (1), $b = 8{\cdot}957$ (1), $c = 13{\cdot}017$ (1) Å, $\beta = 98{\cdot}425$ (6)°, $V = 913{\cdot}4$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}259$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 6{\cdot}6$ cm^{-1}, $F(000) = 364$, $T = 298$ K, $R = 0{\cdot}056$ for 673 reflections. 1,4-Phenylene di-*p*-toluate (CB), $M_r = 346{\cdot}2$, monoclinic, $P2_1/c$, $a = 6{\cdot}127$ (3), $b = 7{\cdot}555$ (1), $c = 19{\cdot}360$ (4) Å, $\beta = 102{\cdot}39$ (3)°, $V = 875{\cdot}4$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}313$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 6{\cdot}9$ cm^{-1}, $F(000) = 364$, $T = 298$ K, $R = 0{\cdot}054$ for 905 reflections. Consistent with their mesogenic properties, molecules CA and CB have a strongly anisometric shape. A common feature of their crystal packing is the almost parallel orientation of their molecular axes; layers in this direction are formed in CA but not in CB. The torsion angle C10—C9—O1—C8 of CB is 76·2 (4)° while the corresponding angle for CA is ~90°, owing to different conformations.

Introduction. The title compounds are both mesogenic. They are characterized by the atomic groups $A =$ —φ—OOC—φ—COO—φ— and $B =$ —φ—COO—φ—OOC—φ— (—φ— = *p*-phenylene) that have been extensively utilized in the synthesis of low-molecular-weight mesogenic compounds (Dewar & Goldberg, 1970; Schroeder & Bristol, 1973; Kelker & Hatz, 1980) and polymeric (Lenz, 1985) mesogenic compounds.

The detailed examination of the relationship between molecular structure and mesogenic properties of a number of compounds containing groups *A* or *B* has indicated that quite a relevant role is played by the stereochemical nature of the atomic groups linked to *A* or *B*; for instance, structures of the type *R*—OOC—*A*—COO—*R* are more frequently smectogenic while nematic phases are given preferentially by structures *R*—COO—*A*—OOC—*R*. In addition, systematic differences in the mesophasic properties have been observed between *A*- and *B*-type compounds containing identical terminal groups (Dewar & Goldberg, 1970), since *A*-type compounds exhibit higher nematic to isotropic liquid transition temperatures. To a first approximation, electric polarizability and steric hindrance appear to be the relevant factors, the latter being probably less effective.

The title compounds have been chosen for a complete structural study in order to detect molecular structure and packing differences in a pair of nematogenic *A*- and *B*-type compounds containing terminal groups that have moderate effects on the electronic structure of the molecular cores.

Experimental. The title compounds were prepared by condensation of terephthaloyl chloride with *p*-cresol (CA) and *p*-toluoyl chloride with hydroquinone (CB). The reactions were carried out at room temperature using 1,2-dichloroethane as solvent and equimolar amounts of triethylamine as the catalyst and HCl acceptor. After precipitation and recrystallization from methanol the nature and the purity of the compounds were controlled by TLC, ^{1}H NMR and IR methods. The phase behaviour was examined by DSC and polarizing microscopy. Compound CA melts at 473·3 K to a nematic liquid (mobile schlieren

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texture) with a 145 J g^{-1} transition enthalpy and isotropizes at 492·3 K (3·71 J g^{-1} transition enthalpy).

Compound CB starts melting at 504·1 K. Melting and isotropization DSC endotherms are not resolved but the mesophasic nature of the liquid and the upper limit of the isotropization transition (507·3 K) are easily detected by polarizing microscopy. The nematic nature of the mesophase is indicated by the mobile schlieren texture also observed for CB. The total enthalpic change for the two phase transition is 143 J g^{-1}.

Single crystals suitable for X-ray diffraction studies were obtained for both compounds by slow evaporation of ethanol–chloroform solutions. CA 0·5 × 0·3 × 0·15 mm and CB 0·4 × 0·4 × 0·15 mm.

The lattice parameters were obtained by least-squares fitting from the angular coordinates of 25 accurately centered reflections in the range $17 < 2\theta < 30°$. For the collection of the diffraction intensity data an Enraf–Nonius CAD-4 automated single-crystal diffractometer was utilized in the 2θ–ω scan mode with Ni-filtered Cu $K\alpha$ radiation. Reflections were measured within the following ranges: $-8 \le h \le 8$, $0 \le k \le 10$, $0 \le l \le 14$ for CA, $-6 \le h \le 6$, $0 \le k \le 8$, $0 \le l \le 21$ for CB with a maximum value for $\sin\theta/\lambda = 0{\cdot}56$ Å^{-1} for both compounds. Two standard reflections every 2 h showed only random deviations.

728 reflections for CA and 1156 reflections for CB were measured. Corrections were made for Lorentz and polarization factors but not for absorption. 673 reflections (74 refined parameters) for CA and 905 reflections (118 refined parameters) for CB were used for refinement. Reflections with $I < 3\sigma(I)$ were considered unobserved.

The structures were solved by use of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The Fourier maps calculated with the highest combined figure of merit showed part of the non-H atoms for both compounds. Structure-factor calculations and successive Fourier maps showed all non-H atoms. Refinement (on F) was performed by full-matrix least squares on all non-H atoms. The coordinates of the H atoms were defined on a stereochemical basis and, for the methyl groups, from the $F_o - F_c$ Fourier map. The H atoms were included in the calculations at the beginning of the anisotropic refinement and their positions were redefined in the last structure-factors calculation. Corrections for secondary extinction were applied for CA [$g = 6{\cdot}32\,(1) \times 10^{-5}$].

The refinement, carried out with anisotropic thermal parameters for all non-H atoms, was continued with weighting factors $w = 1/\sigma^2(F_o)$ until $(\Delta/\sigma)_{max}$ for the atomic coordinates was less than 0·2. The final difference Fourier maps showed no maxima higher than 0·2 e Å^{-3}. $R = 0{\cdot}056$, $wR = 0{\cdot}073$ for CA; $R = 0{\cdot}054$, $wR = 0{\cdot}069$ for CB.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

E.s.d.'s, in units of the last significant figure, are given in parentheses. $B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
CA				
C1	0·2185 (4)	0	0·4634 (2)	5·63 (8)
C2	0·3370 (3)	0	0·3821 (2)	4·01 (6)
C3	0·3916 (2)	0·1327 (2)	0·3431 (1)	4·39 (4)
C4	0·4978 (2)	0·1339 (2)	0·2674 (1)	4·22 (4)
C5	0·5476 (3)	0	0·2305 (2)	3·83 (5)
C6	0·8181 (3)	0	0·1755 (2)	3·59 (5)
C7	0·9091 (3)	0	0·0832 (2)	3·57 (5)
C8	1·0858 (3)	0	0·1004 (2)	4·35 (6)
C9	0·8229 (3)	0	−0·0175 (2)	4·42 (6)
O1	0·6464 (2)	0	0·1484 (1)	4·81 (4)
O2	0·8866 (2)	0	0·2637 (1)	4·56 (4)
CB				
C1	0·3111 (6)	0·4111 (5)	0·0571 (2)	4·89 (8)
C2	0·2828 (5)	0·3969 (4)	0·1323 (1)	3·77 (7)
C3	0·4419 (5)	0·3121 (4)	0·1836 (2)	4·10 (7)
C4	0·4192 (5)	0·3032 (4)	0·2529 (2)	3·87 (7)
C5	0·2387 (4)	0·3832 (4)	0·2734 (1)	3·08 (6)
C6	0·0788 (5)	0·4691 (5)	0·2225 (2)	3·86 (7)
C7	0·0998 (5)	0·4736 (5)	0·1528 (2)	4·05 (7)
C8	0·2255 (5)	0·3746 (4)	0·3480 (2)	3·54 (7)
C9	0·0391 (5)	0·4907 (4)	0·4332 (1)	3·73 (7)
C10	0·1900 (5)	0·5759 (5)	0·4853 (2)	4·40 (8)
C11	−0·1507 (5)	0·4137 (4)	0·4473 (2)	4·19 (8)
O1	0·0686 (3)	0·4870 (3)	0·3636 (1)	4·48 (5)
O2	0·3377 (3)	0·2818 (3)	0·3926 (1)	4·63 (5)

Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV); programs were from Enraf–Nonius (1979) *Structure Determination Package*.

Discussion. The final positional and thermal parameters are reported in Table 1 for both compounds. Table 2 contains the molecular structure parameters. A picture of the molecules is given in Fig. 1.*

Coherent with their mesogenic properties, the molecules of compounds CA and CB have a strongly anisometric shape with an elongated axis of 18·5 Å measured between the C atoms of the terminal methyl groups. A common feature of their crystal packing is the almost parallel orientation of these long molecular axes. The two compounds exhibit, however, significant differences both in the crystal packing and in some conformational parameters.

In CA, the terephthalate group, strictly planar, lies on the mirror planes at $y = 0$ and $y = \frac{1}{2}$ and is orthogonal to the plane containing the p-methylphenyl group. The mirror symmetry is pre-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52993 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsional angles* (°)

E.s.d.'s, in units of the last significant figure, are given in parentheses.

CA

C1—C2	1·514 (7)	C6—C7	1·489 (7)
C4—C5	1·371 (5)	C5—O1	1·415 (6)
C7—C9	1·386 (8)	C3—C4	1·387 (6)
C6—O2	1·196 (6)	C7—C8	1·384 (8)
C2—C3	1·387 (5)	C6—O1	1·353 (7)
C1—C2—C3	121·0 (2)	C2—C3—C4	121·4 (4)
C3—C4—C5	118·5 (4)	C4—C5—O1	118·9 (3)
C7—C6—O1	112·1 (4)	C7—C6—O2	124·8 (5)
O1—C6—O2	123·1 (5)	C6—C7—C8	117·8 (5)
C6—C7—C9	122·2 (5)	C8—C7—C9	120·0 (5)
C5—O1—C6	116·7 (4)		
C4—C3—C2—C1	−178·9 (2)	C5—C4—C3—C2	0·5 (3)
C6—O1—C5—C4	91·5 (2)	O1—C5—C4—C3	175·8 (2)

CB

C1—C2	1·507 (8)	C6—C7	1·384 (7)
C3—C4	1·380 (8)	C8—O1	1·364 (6)
C5—C8	1·465 (8)	C2—C7	1·393 (7)
C9—C11	1·379 (8)	C5—C6	1·392 (7)
C9—O1	1·399 (6)	C9—C10	1·374 (8)
C2—C3	1·390 (8)	C8—O2	1·207 (6)
C4—C5	1·390 (7)		
C1—C2—C3	121·0 (5)	C1—C2—C7	120·8 (6)
C3—C2—C7	118·2 (5)	C2—C3—C4	121·1 (5)
C3—C4—C5	120·5 (5)	C4—C5—C6	119·0 (5)
C4—C5—C8	118·5 (5)	C6—C5—C8	122·6 (5)
C5—C6—C7	120·2 (5)	C2—C7—C6	121·1 (5)
C5—C8—O1	112·4 (5)	C5—C8—O2	126·0 (5)
O1—C8—O2	121·5 (5)	C8—O1—C9	118·0 (4)
O1—C9—C10	120·7 (5)	O1—C9—C11	118·1 (5)
C10—C9—C11	121·1 (5)		
C4—C3—C2—C1	178·3 (3)	C5—C4—C3—C2	−1·7 (5)
C5—C6—C7—C2	−1·7 (5)	C6—C5—C4—C3	1·4 (5)
C6—C7—C2—C1	−176·6 (3)	C6—C7—C2—C3	1·4 (5)
C7—C2—C3—C4	0·3 (5)	C7—C6—C5—C4	0·3 (5)
C8—C5—C4—C3	−178·2 (3)	C8—C5—C6—C7	179·8 (3)
O1—C8—C5—C4	167·5 (3)	O1—C8—C5—C6	−12·1 (4)
O2—C8—C5—C6	168·3 (3)	C9—O1—C8—C5	179·7 (3)
C9—O1—C8—O2	−0·7 (4)	C10—C9—O1—C8	76·2 (4)
C11—C9—O1—C8	−106·7 (3)		

served for the methyl groups only on a statistical basis as detected on the $F_o - F_c$ Fourier map.

Molecules are packed together on the *ac* crystallographic plane (Fig. 2*a*) with their elongation axes very closely parallel to the $\mathbf{a}-\mathbf{c}$ vector. The closest packing of the terephthalate molecular cores occurs among molecules forming layers parallel to the *ab* plane. Therefore, the molecular elongation axis is largely tilted with respect to the interlayer distance vector.

A view of the crystal packing along the molecular elongation axis C2–C2′ is shown in Fig. 2(*b*). A fairly regular quasihexagonal packing of 'molecular columns' is apparent.

In CB, there is an inversion center at the 1,4-phenylenedioxy group. The *p*-methylbenzoate group is not planar. The dihedral angle between the plane containing the carboxy group and that containing the *p*-methylphenylene is 12·7 (5)°.

CA and CB molecules are also different in the conformation of —φ—COO—φ—. In fact, while the torsion angle C10—C9—O1—C8 of CB is 76·2 (4)°, the corresponding parameter of CA departs from 90° by a small, hardly significant amount. As a consequence, the dihedral angle between the two *p*-phenylene groups is 62·1 (1)° in CB and 90° in CA.

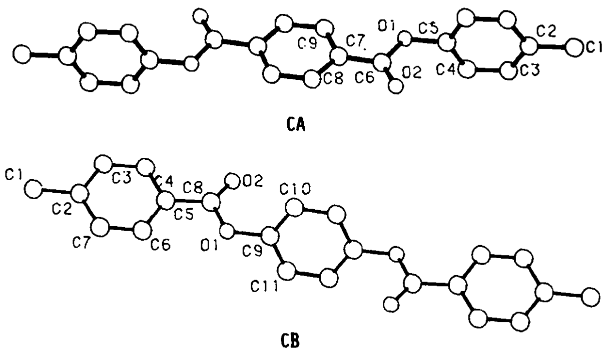
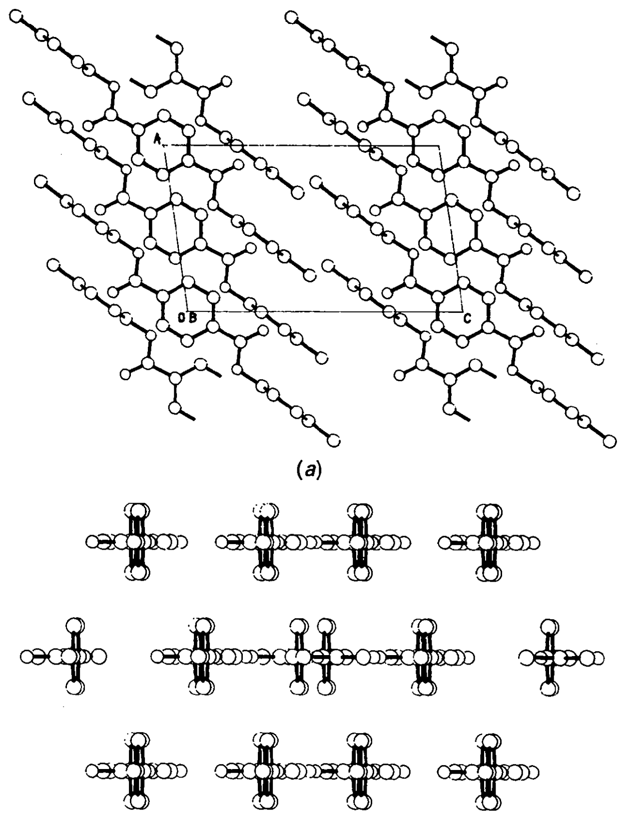


Fig. 1. Molecules CA and CB.



(*a*)

(*b*)

Fig. 2. Crystal packing of CA (*a*) on the *ac* plane; (*b*) along the molecular elongation axis.

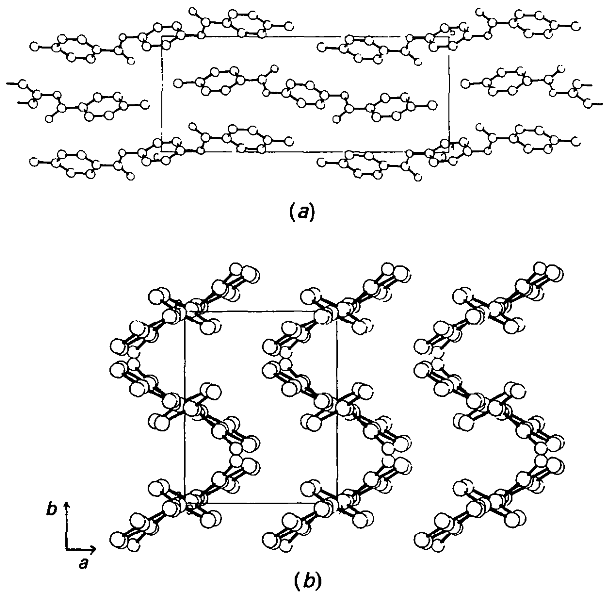


Fig. 3. Crystal packing of CB viewed (*a*) along **a**; (*b*) along the crystallographic *c* axis.

The molecules of CB pack together with a quasi-parallel orientation of the elongation axes but, at variance with CA, a large molecular intercalation occurs along that direction and no layers are formed (Fig. 3*a*). A view of the crystal packing along the crystallographic *c* axis is shown in Fig. 3(*b*) giving evidence of the packing differences with respect to CA.

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Structure of 3-Benzoyl-1,1,2-tricyano-3-(1-pyridinio)-2-propen-1-ide

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Abstract. $C_{18}H_{10}N_4O$, $M_r = 298$, monoclinic, $P2_1/c$, $a = 9{\cdot}8958$ (8), $b = 15{\cdot}3406$ (19), $c = 10{\cdot}5753$ (11) Å, $\beta = 111{\cdot}803$ (7)°, $V = 1490{\cdot}6$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}329$, $D_m = 1{\cdot}315$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}027$ cm^{-1}, $F(000) = 616$, $T = 293$ K. The structure was solved by direct methods and refined to $R = 0{\cdot}041$ for 1997 independent reflections. The negative charge is delocalized in the planar conjugated ylide fragment C(3)═C(2)—C(1)(CN)$_2$ with the positive charge located on the N atom of the pyridinium ring. The planes of the Py$^+$ and Ph substituents are rotated relative to the ylide plane by 107·5 and 60·9° respectively. Such orientation of the carbonyl group relative to the dicyanomethylide fragment, which is due to a number of shortened intramolecular contacts, is unfavourable for the cyclization of the compound studied.

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Introduction. The title compound (I) was obtained by the reaction of tetracyanoethylene with benzoylpyridiniomethylide; the latter is formed as a result of interaction of triethylamine with a methanol solution of *N*-phenylacylpyridinium bromide. In contrast to the earlier-studied pyridinium ylides (Tominaga, Motokawa, Shiroshita & Hosomi, 1987), ylide (I) does not undergo, on heating, cyclization to the corresponding pyran or pyridine (depending on the reaction conditions).

An X-ray structural study of ylide (I) has been carried out in order to elucidate the peculiarities of its structure and the reasons for its inertness in cyclization.

Experimental. Prismatic ruby-coloured crystals were obtained on recrystallization of the salt (I) from ethanol. Density measured by flotation. One of the crystals, 0·3 × 0·3 × 0·4 mm in size, was used for the

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