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Azinobis(ethylidyne-*p*-phenylene) Dipropionate, $C_{22}H_{24}N_2O_4$

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Abstract. $M_r = 380{\cdot}4$, monoclinic, $P2_1/c$, $a = 19{\cdot}836\,(3)$, $b = 5{\cdot}450\,(1)$, $c = 24{\cdot}068\,(3)$ Å, $\beta = 128{\cdot}37\,(15)°$, $V = 2040\,(4)$ Å^3, $Z = 4$, $D_m =$ (flotation) $= 1{\cdot}23$, $D_x = 1{\cdot}23$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 6{\cdot}6$ cm^{-1}, $F(000) = 808$, $T = 298$ K, $R = 0{\cdot}055$ for 875 observed independent reflections. The independent structural unit is formed by two crystallographically unrelated half-molecules. Both crystallographically independent molecules assume an almost planar conformation, the phenyl rings being slightly rotated with respect to the average molecular plane.

Introduction. The mesogenic character of the rigid molecular group $R = -(p\text{-}C_6H_4)-C(-CH_3)=N-N=C(-CH_3)-(p\text{-}C_6H_4)-$ has been observed both in low-molecular-weight homologues of the title compound (Roviello & Sirigu, 1976) and in linear polymers with formula $[-OOC-(CH_2)_n-COOR-]_x$ (Roviello & Sirigu, 1975). The title compound itself exhibits an enantiotropic nematic phase between 378 and 438 K. Most of the compounds mentioned exhibit mesomorphism of nematic type. Only low-molecular-weight esters with formula $CH_3(CH_2)_n-COO-R-OOC-(CH_2)_nCH_3$ exhibit smectic (although monotropic) mesomorphism for $n > 8$.

We are interested in elaborating structural models for the nematic phase of the polymers mentioned. As far as we know no structural investigation concerning the molecular group R was available before now. Therefore for a correct evaluation of the relevant molecular parameters (particularly the torsion angles around the $-C-C_6H_4-$ bond) the title compound was chosen for a complete structural study.

Experimental. The title compound has been prepared according to a procedure already described (Roviello & Sirigu, 1976). Single crystals (thin yellow platelets $0{\cdot}5 \times 0{\cdot}2$ mm) suitable for X-ray studies were obtained by evaporation of ethanol–chloroform solutions. Lattice parameters obtained from the angular coordinates of 25 accurately centered strong reflections in the range $20° < 2\theta < 60°$ by means of least-squares fitting. Enraf–Nonius CAD-4 automated single-crystal diffractometer, 2θ–ω scan mode, max. $\sin\theta/\lambda = 0{\cdot}56$ Å^{-1}, $-16 \le h \le 16$, $-6 \le k \le 0$, $0 \le l \le 26$, Ni-filtered Cu $K\alpha$ radiation. Two standard reflections every 2 h showed only random deviations. 3021 independent reflections collected. Corrections for Lorentz and polarization factors were applied. No correction for absorption. 2146 reflections having $I < 3\sigma(I)$ not considered for refinement. Structure solved with program *MULTAN* (Germain, Main & Woolfson, 1971). The Fourier map calculated with the highest combined figure of merit given by *MULTAN* showed all non-H atoms of the two independent half-molecules. Refinement (on F) was carried out by the full-matrix least-squares method with all non-H atoms. Coordinates for H atoms were defined on stereochemical grounds. The positions of the H atoms of the methyl groups of the $-C(-CH_3)=N-N=C(-CH_3)-$ group were defined on the basis of a F_o-F_c Fourier map. Isotropic thermal factors equal to those of the carrier atoms were assigned to the H atoms. Refinement carried out with anisotropic thermal parameters for all non-H atoms yielded $R = 0{\cdot}055$, $R_w = 0{\cdot}062$, $S = 2{\cdot}3$. Refinement was continued with weights $w = 1/\sigma^2(F_o)$ until $(\Delta/\sigma)_{\max}$ for the atomic coordinates was less than $0{\cdot}2$. The difference Fourier map in the final stage of refinement showed no maxima higher than $0{\cdot}2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs from Enraf–Nonius (1981) *Structure Determination Package.*

Discussion. Fractional atomic coordinates and thermal parameters for the two crystallographically independent

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

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

$B_{\rm eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$(Å^2)
O(1*A*)	0·6144 (3)	0·048 (1)	0·7776 (2)	6·6 (2)
O(2*A*)	0·7005 (3)	−0·275 (1)	0·8227 (2)	7·8 (2)
N(*A*)	0·5072 (3)	−0·017 (1)	0·9751 (2)	5·6 (2)
C(1*A*)	0·6907 (4)	−0·324 (2)	0·6999 (3)	6·8 (3)
C(2*A*)	0·6492 (4)	−0·118 (2)	0·7089 (3)	5·5 (3)
C(3*A*)	0·6596 (4)	−0·134 (2)	0·7760 (3)	5·2 (3)
C(4*A*)	0·6088 (4)	0·057 (2)	0·8330 (3)	5·3 (3)
C(5*A*)	0·5599 (5)	−0·115 (2)	0·8350 (3)	6·0 (3)
C(6*A*)	0·5459 (4)	−0·095 (2)	0·8843 (3)	5·7 (3)
C(7*A*)	0·6438 (4)	0·247 (2)	0·8792 (3)	6·0 (3)
C(8*A*)	0·6325 (4)	0·265 (2)	0·9304 (3)	5·9 (3)
C(9*A*)	0·5816 (4)	0·099 (2)	0·9321 (3)	5·0 (2)
C(10*A*)	0·5639 (4)	0·126 (2)	0·9844 (3)	4·7 (2)
C(11*A*)	0·6138 (4)	0·317 (2)	1·0420 (3)	6·6 (3)
O(1*B*)	0·1182 (3)	0·599 (1)	0·3404 (2)	6·2 (2)
O(2*B*)	0·2042 (3)	0·266 (1)	0·3836 (2)	8·4 (2)
N(*B*)	0·0071 (3)	0·490 (1)	0·0323 (2)	6·1 (2)
C(1*B*)	0·1900 (5)	0·224 (2)	0·4937 (3)	8·8 (3)
C(2*B*)	0·1495 (4)	0·426 (2)	0·4419 (3)	6·8 (3)
C(3*B*)	0·1628 (4)	0·413 (2)	0·3873 (3)	5·8 (3)
C(4*B*)	0·1097 (4)	0·600 (2)	0·2771 (3)	5·0 (2)
C(5*B*)	0·0621 (4)	0·417 (2)	0·2277 (3)	5·7 (3)
C(6*B*)	0·0470 (4)	0·432 (2)	0·1640 (3)	5·5 (3)
C(7*B*)	0·1441 (4)	0·793 (2)	0·2660 (3)	5·5 (3)
C(8*B*)	0·1278 (4)	0·800 (1)	0·2007 (3)	5·6 (3)
C(9*B*)	0·0806 (4)	0·623 (1)	0·1496 (3)	4·6 (2)
C(10*B*)	0·0648 (4)	0·639 (1)	0·0802 (3)	4·7 (3)
C(11*B*)	0·1132 (4)	0·817 (2)	0·0700 (3)	8·4 (3)

half-molecules are given in Table 1. The parameters of the molecular structure are shown in Table 2. The lettering is shown in Fig. 1.*

The structural parameters of the two crystallographically independent half-molecules are substantially equivalent within experimental errors. The N—N, N—C(10) and C(9)—C(10) bond lengths, as well as the N—N—C(10) bond angles are very close to the values found for analogous compounds, *e.g.* benzalazine (Burke-Laing & Laing, 1976) and salicylaldehyde azine (Arcovito, Bonamico, Domenicano & Vaciago, 1969).

The trigonal bond geometry around C(10) is rather distorted. The N—C(10)—C(9) bond angle is significantly smaller than the corresponding angles in benzalazine (122·5°) and salicylaldehyde azine [121·6 (2)°]. This feature, together with a relatively large value for the bond angle N—C(10)—C(11) is produced by the steric interaction between atoms N′ and C(11) [N′··· C(11) = 2·71 (1), 2·69 (1) Å].

The atomic group C(9)—C(10)[—C(11)]=N—N=C(10)[—C(11)]—C(9) is planar. The entire *R* group, however, is not planar. This is a significant difference with respect to the substantial planarity found for the previously mentioned analogues. The N—C(10)—C(9)—C(8) torsion angles of 170·9 (19) and −167·5 (18)° indicate that the phenyl rings are slightly rotated with respect to the plane of the $-C(-CH_3)=N-N=C(-CH_3)-$ group. This feature appears to be related to the need to increase the distance between the phenyl ring and the adjacent $-CH_3$ group [C(8)··· C(11) = 2·94 (1), 2·98 (1) Å].

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

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

C(1*A*)—C(2*A*)	1·48 (1)	C(1*B*)—C(2*B*)	1·47 (1)
C(2*A*)—C(3*A*)	1·50 (1)	C(2*B*)—C(3*B*)	1·49 (1)
C(3*A*)—O(2*A*)	1·17 (1)	C(3*B*)—O(2*B*)	1·19 (1)
C(3*A*)—O(1*A*)	1·35 (1)	C(3*B*)—O(1*B*)	1·36 (1)
C(4*A*)—O(1*A*)	1·41 (1)	C(4*B*)—O(1*B*)	1·42 (1)
C(4*A*)—C(5*A*)	1·37 (1)	C(4*B*)—C(5*B*)	1·38 (1)
C(4*A*)—C(7*A*)	1·35 (1)	C(4*B*)—C(7*B*)	1·37 (1)
C(5*A*)—C(6*A*)	1·38 (1)	C(5*B*)—C(6*B*)	1·37 (1)
C(6*A*)—C(9*A*)	1·39 (1)	C(6*B*)—C(9*B*)	1·39 (1)
C(7*A*)—C(8*A*)	1·39 (1)	C(7*B*)—C(8*B*)	1·39 (1)
C(8*A*)—C(9*A*)	1·37 (1)	C(8*B*)—C(9*B*)	1·38 (1)
C(9*A*)—C(10*A*)	1·51 (1)	C(9*B*)—C(10*B*)	1·50 (1)
C(10*A*)—C(11*A*)	1·51 (1)	C(10*B*)—C(11*B*)	1·49 (1)
C(10*A*)—N(*A*)	1·27 (1)	C(10*B*)—N(*B*)	1·288 (7)
N(*A*)—N(*A*)′	1·41 (1)	N(*B*)—N(*B*)′	1·402 (8)

C(3*A*)—O(1*A*)—C(4*A*)	120 (1)	C(1*B*)—C(2*B*)—C(3*B*)	114 (1)
C(1*A*)—C(2*A*)—C(3*A*)	113 (1)	C(2*B*)—C(3*B*)—O(2*B*)	127 (1)
C(2*A*)—C(3*A*)—O(2*A*)	128 (1)	C(2*B*)—C(3*B*)—O(1*B*)	108 (1)
C(2*A*)—C(3*A*)—O(1*A*)	110 (1)	O(1*B*)—C(3*B*)—O(2*B*)	124 (2)
O(1*A*)—C(3*A*)—O(2*A*)	122 (2)	C(5*B*)—C(4*B*)—C(7*B*)	123 (1)
C(5*A*)—C(4*A*)—C(7*A*)	120 (2)	C(5*B*)—C(4*B*)—O(1*B*)	119 (1)
C(5*A*)—C(4*A*)—O(1*A*)	119 (1)	C(3*B*)—O(1*B*)—C(4*B*)	119 (1)
C(7*A*)—C(4*A*)—O(1*A*)	120 (1)	C(7*B*)—C(4*B*)—O(1*B*)	118 (1)
C(4*A*)—C(5*A*)—C(6*A*)	120 (1)	C(4*B*)—C(5*B*)—C(6*B*)	119 (1)
C(5*A*)—C(6*A*)—C(9*A*)	120 (1)	C(5*B*)—C(6*B*)—C(9*B*)	121 (1)
C(4*A*)—C(7*A*)—C(8*A*)	120 (1)	C(4*B*)—C(7*B*)—C(8*B*)	117 (1)
C(7*A*)—C(8*A*)—C(9*A*)	120 (1)	C(7*B*)—C(8*B*)—C(9*B*)	123 (1)
C(6*A*)—C(9*A*)—C(8*A*)	119 (1)	C(6*B*)—C(9*B*)—C(8*B*)	118 (1)
C(6*A*)—C(9*A*)—C(10*A*)	120 (1)	C(6*B*)—C(9*B*)—C(10*B*)	121 (1)
C(8*A*)—C(9*A*)—C(10*A*)	121 (1)	C(8*B*)—C(9*B*)—C(10*B*)	121 (1)
C(9*A*)—C(10*A*)—C(11*A*)	118 (1)	C(9*B*)—C(10*B*)—C(11*B*)	121 (1)
N(*A*)—C(10*A*)—C(9*A*)	116 (1)	N(*B*)—C(10*B*)—C(9*B*)	114 (1)
N(*A*)—C(10*A*)—C(11*A*)	126 (2)	N(*B*)—C(10*B*)—C(11*B*)	125 (1)
N(*A*)′—N(*A*)—C(10*A*)	113 (1)	N(*B*)′—N(*B*)—C(10*B*)	113 (1)

C(1*A*)—C(2*A*)—C(3*A*)—O(1*A*)	−175 (1)	C(1*B*)—C(2*B*)—C(3*B*)—O(1*B*)	176 (1)
C(1*A*)—C(2*A*)—C(3*A*)—O(2*A*)	6 (3)	C(1*B*)—C(2*B*)—C(3*B*)—O(2*B*)	−3 (3)
C(2*A*)—C(3*A*)—O(1*A*)—C(4*A*)	175 (1)	C(2*B*)—C(3*B*)—O(1*B*)—C(4*B*)	−170 (1)
O(2*A*)—C(3*A*)—O(1*A*)—C(4*A*)	−6 (3)	C(4*B*)—O(1*B*)—C(3*B*)—O(2*B*)	9 (3)
C(3*A*)—O(1*A*)—C(4*A*)—C(5*A*)	−71 (2)	C(3*B*)—O(1*B*)—C(4*B*)—C(5*B*)	66 (1)
C(6*A*)—C(5*A*)—C(4*A*)—O(1*A*)	−173 (2)	C(6*B*)—C(5*B*)—C(4*B*)—O(1*B*)	174 (1)
C(10*A*)—C(9*A*)—C(8*A*)—C(7*A*)	−176 (2)	C(10*B*)—C(9*B*)—C(8*B*)—C(7*B*)	180 (2)
C(11*A*)—C(10*A*)—C(9*A*)—C(6*A*)	171 (2)	C(11*B*)—C(10*B*)—C(9*B*)—C(6*B*)	−169 (2)
N(*A*)—C(10*A*)—C(9*A*)—C(6*A*)	−9 (3)	N(*B*)—C(10*B*)—C(9*B*)—C(6*B*)	11 (3)
N(*A*)′—N(*A*)—C(10*A*)—C(9*A*)	−179 (1)	N(*B*)′—N(*B*)—C(10*B*)—C(9*B*)	180 (1)
N(*A*)′—N(*A*)—C(10*A*)—C(11*A*)	0 (3)	N(*B*)′—N(*B*)—C(10*B*)—C(11*B*)	0 (3)

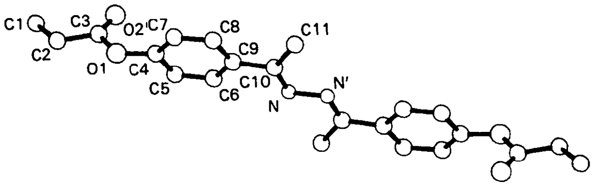

Fig. 1. Model molecule for the title compound. The two independent half-molecules in the unit cell are numbered in the same manner but with *A* and *B* denomination.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39871 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

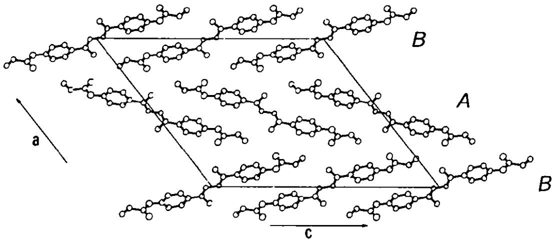

Fig. 2. Crystal packing of the title compound viewed along [010].

The crystal packing is shown in Fig. 2. It may be described by an ...*ABAB*... sequence of molecular layers piled along **b** × **c**. Each layer contains only crystallographically related molecules. Within each layer the molecules are packed with their long axes parallel to each other and tilted by +75° (layer *A*) or −75° (layer *B*) with respect to **b** × **c**.

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Stereochemical Studies of Oligomers. XV.* Structure of 2-Methyl-1,4-butanediyl Dibenzoate, $C_{19}H_{20}O_4$

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Abstract. $M_r = 312\cdot4$, triclinic, $P\bar{1}$, $a = 13\cdot211\ (3)$, $b = 8\cdot059\ (2)$, $c = 8\cdot704\ (2)$ Å, $\alpha = 114\cdot57\ (4)$, $\beta = 97\cdot98\ (3)$, $\gamma = 91\cdot57\ (3)°$, $V = 830\cdot9\ (5)$ Å^3, $Z = 2$, $D_x = 1\cdot25$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot5418$ Å, $\mu = 6\cdot70$ cm^{-1}, $F(000) = 332$, room temperature, $R = 0\cdot062$ for 2056 observed reflections. The conformation of the chain is *trans–trans–gauche* without any variation with respect to that of the unmethylated derivative. The planar carboxylic groups are tilted by 2·3 (1) and 2·5 (1)° with respect to their phenyl rings which have normal bond lengths and angles.

Introduction. In preceding papers of this series the influence of methyl groups, attached to the aliphatic chain, on the conformation of this type of derivative was extensively examined (Bocelli & Grenier-Loustalot, 1982*a,b*, 1983*a,b,c,d*, 1984*b,c*, 1985). In particular, the structure analyses of derivatives with ethanediyl chains clearly showed that the presence of one methyl group moves the conformation away from a *trans* arrangement (Bocelli & Grenier-Loustalot, 1983*a,b,c,d*, 1984*b*). This result seems instead to be contradicted by the analysis of derivatives with propanediyl chains (Bocelli & Grenier-Loustalot, 1985). Furthermore the conformations of derivatives with a butanediyl chain and with 1,4-dimethyl groups also seem to be influenced by the presence of chlorine atoms on the rings (Bocelli & Grenier-Loustalot, 1984*c*).

It may be interesting to know which type of conformational changes occur when the methyls are not on the extremities of the chain and this is the goal of the present analysis.

Experimental. White crystals recrystallized from methanol, prism, 0·14 × 0·11 × 0·04 mm, Siemens AED single-crystal diffractometer equipped with a General Automation Jumbo 220 computer, Ni-filtered Cu *Kα* radiation, cell parameters from angular values of 24

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* Part XIV: Bocelli & Grenier-Loustalot (1985).

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