Structure of the Nematogenic Compound 5,8-Dihydro-6,7-dimethyl-1,4-naphthalenediyl Bis(4-ethoxybenzoate), $C_{30}H_{30}O_6$

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Abstract. $M_r = 486 \cdot 5$, triclinic, $P\bar{1}$, $a = 11 \cdot 176$ (2), $b = 12 \cdot 020$ (1), $c = 10 \cdot 433$ (2) Å, $\alpha = 81 \cdot 54$ (1), $\beta = 98 \cdot 64$ (1), $\gamma = 112 \cdot 66$ (1)°, $V = 1272 \cdot 7$ Å³, $Z = 2$, $D_x = 1 \cdot 27$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1 \cdot 5418$ Å, $\mu = 0 \cdot 630$ mm⁻¹, $F(000) = 516$, $T = 293$ K. Final $R = 0 \cdot 052$ for 2524 observed reflections. The molecule adopts an optimum stretched form. The carboxylic groups are nearly parallel to their neighbouring benzene rings but they are approximately perpendicular to the central dihydronaphthalene group. The molecules are arranged in the crystal in a parallel-imbricated packing mode, which is typical of nematogenic compounds.

Introduction. The present X-ray structure analysis is part of a series of investigations of mesogenic compounds in their crystalline state (Baumeister, Hartung & Jaskólski, 1982). The title compound forms a nematic mesophase in the range 491 to 518 K. Such thermal behaviour is somewhat surprising when the chemical formula is considered since the rather large lateral extension of the bicyclic central part of the molecule is, to a certain degree, inconsistent with the classical model of rod-shaped molecules commonly accepted for mesogenic compounds. For this reason, it seemed to be useful to have an exact knowledge about both the molecular structure and the packing of the molecules in the crystal which is a precursor of the liquid-crystalline phase.
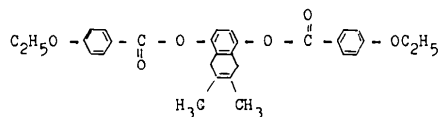
Experimental. Title compound first prepared by Zaschke (1980, unpublished work); Weissenberg and oscillation photographs indicated triclinic symmetry and gave approximate cell dimensions, precise lattice parameters obtained from a least-squares refinement of the setting angles of 15 counter reflections; intensity data measured on a Syntex $P2_1$ four-circle diffractometer, crystal of dimensions $0 \cdot 3 \times 0 \cdot 3 \times 0 \cdot 3$ mm, θ–2θ variable scan, Cu $K\alpha$ radiation, graphite monochromator, range of hkl $0,\overline{13},\overline{11}$ to $12,11,10$; of the total 3318 independent reflections collected ($\sin\theta/\lambda < 0 \cdot 55$ Å⁻¹), 2524 classified as observed with $I > 2 \cdot 5\,\sigma(I)$ and used in structure analysis; corrections applied for Lorentz and polarization effects but not for absorption.

Although the E-value statistics strongly indicated an inversion centre, direct methods (*SHELX* 76, Sheldrick, 1976) failed to solve the structure in the space group $P\bar{1}$. The direct methods approach was only successful after lowering the symmetry (*cf.* Sasvári, Simon & Párkányi, 1975). Starting from a structural fragment derived from a Patterson map the structure was solved in space group $P1$ and could then be refined in $P\bar{1}$ (after appropriate shifting of the origin).

Full-matrix least-squares refinement and a difference electron density map revealed the positions of all atoms; refinement of the complete structure with anisotropic non-H atoms and isotropic H atoms (their temperature factors fixed at the values equal to those of their carrier atoms) converged at $R = 0 \cdot 052$; unit weights used throughout refinement; ratio of max. LS shift to error = $0 \cdot 87$; max. and min. heights in final difference Fourier map $0 \cdot 204$ and $-0 \cdot 147$ e Å⁻³; all calculations performed on an ESER 1040 computer of the Halle University using programs *SHELX* 76, *PRARA* (Jaskólski, 1980) and *GEOME* (Jaskólski, 1981).

Discussion. Final atomic parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2.*

Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2, \times 10^3)$ *for the non-*H *atoms*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha).$$

	x	y	z	U_{eq}
C(1)	−4427 (4)	−4215 (4)	6807 (4)	78
C(2)	−3125 (3)	−3359 (3)	6421 (3)	62
C(3)	−1916 (2)	−2976 (2)	4575 (3)	51
C(4)	−1945 (3)	−3292 (3)	3353 (3)	64
C(5)	−973 (3)	−2618 (3)	2600 (3)	64
C(6)	52 (2)	−1616 (2)	3016 (3)	49
C(7)	94 (3)	−1303 (2)	4253 (3)	53
C(8)	−896 (3)	−1988 (3)	5037 (3)	55
C(9)	1031 (3)	−928 (3)	2104 (3)	57
C(10)	2887 (2)	823 (2)	1713 (3)	50
C(11)	4034 (2)	611 (2)	1829 (2)	45
C(12)	5013 (2)	1361 (2)	1063 (2)	45
C(13)	4799 (3)	2301 (2)	238 (2)	50
C(14)	3663 (3)	2502 (3)	128 (3)	62
C(15)	2674 (3)	1742 (3)	873 (3)	62
C(16)	6265 (3)	1172 (3)	1129 (3)	52
C(17)	6431 (3)	188 (2)	2093 (3)	53
C(18)	5497 (3)	−523 (2)	2832 (2)	56
C(19)	4222 (3)	−399 (2)	2754 (3)	59
C(20)	7726 (3)	76 (4)	2130 (4)	72
C(21)	5635 (5)	−1535 (5)	3797 (5)	89
C(22)	6684 (3)	4052 (3)	−37 (3)	53
C(23)	7790 (2)	4665 (2)	−812 (2)	45
C(24)	7971 (3)	4221 (3)	−1882 (3)	56
C(25)	9055 (3)	4853 (3)	−2551 (3)	61
C(26)	9964 (2)	5932 (2)	−2148 (3)	51
C(27)	9794 (1)	6381 (3)	−1068 (3)	55
C(28)	8723 (3)	5744 (3)	−418 (3)	53
C(29)	11304 (4)	6242 (3)	−3853 (4)	71
C(30)	12585 (4)	7123 (4)	−4258 (5)	88
O(1)	−2956 (2)	−3693 (2)	5229 (2)	64
O(2)	1064 (2)	−1238 (2)	1071 (2)	87
O(3)	1917 (2)	116 (2)	2538 (2)	55
O(4)	5795 (2)	3036 (2)	−545 (2)	52
O(5)	6541 (2)	4391 (2)	941 (2)	72
O(6)	11055 (2)	6628 (2)	−2739 (2)	66

Table 2. *Bond lengths* (Å) *and angles* (°) *for the bicyclic central part of the molecule*

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C(10)–C(11)	1·385 (3)	C(12)–C(16)	1·492 (4)
C(11)–C(12)	1·393 (3)	C(16)–C(17)	1·486 (5)
C(12)–C(13)	1·391 (4)	C(17)–C(18)	1·333 (4)
C(13)–C(14)	1·367 (4)	C(18)–C(19)	1·478 (4)
C(14)–C(15)	1·389 (5)	C(19)–C(11)	1·496 (4)
C(15)–C(10)	1·378 (5)	C(17)–C(20)	1·498 (5)
		C(18)–C(21)	1·502 (7)
C(10)–C(11)–C(19)	121·0 (2)	C(11)–C(12)–C(16)	121·1 (2)
C(10)–C(11)–C(12)	118·4 (2)	C(12)–C(16)–C(17)	116·7 (2)
C(11)–C(12)–C(13)	118·3 (2)	C(16)–C(17)–C(20)	113·6 (3)
C(13)–C(12)–C(16)	120·7 (2)	C(16)–C(17)–C(18)	122·1 (3)
C(12)–C(13)–C(14)	122·9 (2)	C(17)–C(18)–C(21)	123·0 (3)
C(13)–C(14)–C(15)	119·0 (3)	C(17)–C(18)18)–C(19)	122·9 (3)
C(14)–C(15)–C(10)	118·5 (3)	C(18)–C(19)–C(11)	116·7 (2)
C(15)–C(10)–C(11)	122·9 (2)	C(19)–C(11)–C(12)	120·6 (2)
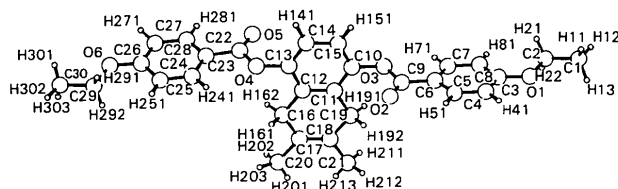
Fig. 1. *PLUTO* (Motherwell, 1978) plot of the molecule.

Atomic numbering and the molecular geometry are shown in Fig. 1. The molecule is characterized by an optimum stretched form and is, apart from the bicyclic central part, nearly centrosymmetric. The benzene rings are roughly coplanar with the ethoxy groups (interplanar angles 8·1 and 2·9°; here, as well as in the following discussion, the first value refers to the right half of the molecule in Fig. 1). An interesting aspect of the molecular structure is the orientation of the carboxylic groups with respect to their neighbouring ring systems. The torsion angles C(5)–C(6)–C(9)–O(2) −7·1 (4), C(28)–C(23)–C(22)–O(5) −2·5 (4), C(9)–O(3)–C(10)–C(15) 94·4 (3) and C(22)–O(4)–C(13)–C(14) 89·9 (3)° indicate that the carboxylic groups are nearly parallel to the C-bonded rings and nearly perpendicular to the O-bonded rings. As a result the two wing groups are roughly parallel to each other but approximately perpendicular to the bicyclic central part of the molecule.

From theoretical conformational analysis and from a survey of experimental torsion angles, Birner, Kugler, Simon & Náray-Szabó (1982) stated that for substituted phenyl benzoates there exists a large number of significantly different conformations with about the same energy. The experimental C—C [corresponding to C(5)–C(6)–C(9)–O(2)] and O—C [corresponding to C(9)–O(3)–C(10)–C(15)] torsion angles varied in the ranges 0 to 17° and 51 to 90°, respectively, and they were influenced predominantly by packing forces. The extreme values of 0 and 90° were found in the crystal of 4′-cyanophenyl 4-*n*-pentoxybenzoate (Baumeister, Hartung, Gdaniec & Jaskólski, 1981), where the molecules possessed exact *m* symmetry. All values for the bond lengths and angles within the two ethoxybenzoyloxy groups are in good agreement with those reported in the literature.

The dihydronaphthalene bicyclic ring system may be formally considered as consisting of a benzene ring and a 1,4-cyclohexadiene ring. The dimensions of the benzene ring are quite normal; it is only somewhat stretched in the direction perpendicular to the molecular long axis (*cf.* the corresponding C—C—C angles in Table 2). But the denotation of the other ring as a 1,4-cyclohexadiene is not in accordance with the observed bond lengths and angles (*cf.* Table 2): the C(17)–C(18) distance corresponds exactly to the standard value for an isolated C—C double bond whereas the C(11)–C(12) distance is typical of a C—C bond in an aromatic system. The ring is slightly folded along the C(16)–C(19) line and the two halves make an angle of 177·5°. Also the endocyclic torsion angles [0·8 (3), −2·9 (3), 2·4 (3), 0·2 (4), −2·3 (3), 1·8 (3)° listed counter-clockwise and beginning with C(19)–C(11)–C(12)–C(16)] indicate a slight folding.

The crystal structure contains centrosymmetric molecule pairs with partial overlap of the dihydronaphthalene groups (Fig. 2). These pairs are shifted with respect to one another by half the molecular length so
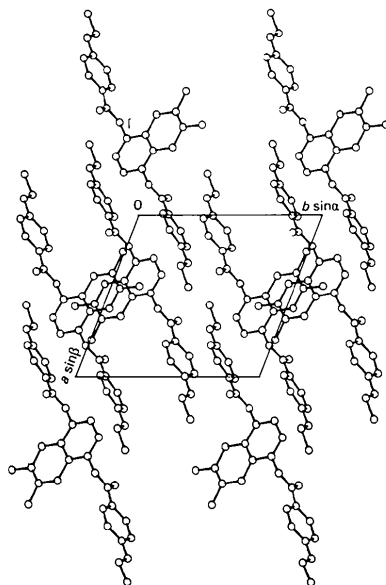
Fig. 2. Crystal structure projected along [001].

that parallel-imbricated molecular packing is achieved, which is generally considered to be a prerequisite for a compound to form a nematic phase. It allows a transformation into the liquid-crystalline phase without drastic changes in the orientation and arrangement of the molecules by melting. All non-H intermolecular distances are greater than the sum of the van der Waals radii.

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Méthyl-4 Diphényl-2,3 Hexahydro-1,3,3a,4,5,9b Naphto[1,2-c]pyrroletricarboxylate-1,1,3a Triméthylique et Méthyl-5 Diphényl-2,3 Hexahydro-1,3,3a,4,5,9b Naphto[1,2-c]pyrroletricarboxylate-1,1,3a Triméthylique, $C_{31}H_{31}NO_6$: Deux Pyrrolidines Obtenues par Cycloaddition Dipolaire-1,3

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Abstract. 4-Methyl compound: $M_r = 514$, monoclinic, $P2_1/c$, $a = 9.123$ (3), $b = 20.264$ (4), $c = 14.625$ (3) Å, $\beta = 94.22$ (3)°, $Z = 4$, $D_x = 1.26$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.0947 mm^{-1}, $R_w = 0.052$ for 3497 reflections, $T = 293$ K, $F(000) = 1088$. 5-Methyl compound: $M_r = 514$, monoclinic, $P2_1/c$, $a = 10.142$ (3), $b = 19.631$ (2), $c = 13.226$ (4) Å, $\beta = 107.31$ (4)°, $Z = 4$, $D_x = 1.36$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.1015 mm^{-1}, $R_w = 0.046$ for 3045 reflections, $T = 293$ K, $F(000) = 1088$. To discuss the diastereoselectivity of the cycloaddition reaction, the X-ray analysis of these two compounds was necessary.