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Structure of the Nematogenic Compound 6-Hexylamino-1,2,4,5-tetrazin-3-yl 4-Pentyloxybenzoate, $C_{20}H_{29}N_5O_3$

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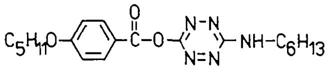
Abstract. $M_r = 387{\cdot}5$, triclinic, $P\bar{1}$, $a = 11{\cdot}646$ (1), $b = 13{\cdot}468$ (2), $c = 7{\cdot}321$ (1) Å, $\alpha = 103{\cdot}51$ (1), $\beta = 106{\cdot}26$ (1), $\gamma = 79{\cdot}59$ (1)°, $V = 1063{\cdot}7$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}21$, $D_m = 1{\cdot}17$ (2) g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 6{\cdot}0$ cm^{-1}, $F(000) = 416$, $T = 293$ K, final $R = 0{\cdot}054$ for 2293 observed reflections. The almost fully stretched molecule shows normal bond lengths and angles. The plane of the bridging carboxylic group is inclined to those of the benzene and tetrazine rings by 12·1 and 76·3°, respectively. Two of the hexyl-chain torsion angles are in the *gauche* region. The molecules are packed with their long axes parallel.

Introduction. This paper continues a series of structural investigations on mesogenic compounds carried out in our laboratory (Rapthel, Hartung & Jaskólski, 1983). It reports an X-ray analysis of the title compound,



abbreviated HTPB, which forms a nematic mesophase in the range 336 to 341 K. In particular we were interested in the details of the molecular conformation of HTPB in order to compare it with the conformational behaviour of mesogenic phenyl benzoates (Baumeister, Brandt, Hartung & Jaskólski, 1983). Moreover, a principal aim of our studies in the field of crystalline mesogenic compounds is to obtain molecular-packing schemes in the solid as a starting point for the discussion of the solid–mesophase relationships.

Experimental. HTPB first synthesized by Zaschke & Enzenberg (1980). Red prisms. Density measured by flotation method. Crystal 0·5 × 0·3 × 0·25 mm. Syntex $P2_1$ diffractometer, Cu $K\alpha$ radiation, graphite monochromator. Lattice parameters from least-squares refinement of the setting angles of 15 reflections. $2\theta \leq 115°$, h,k,l range $\bar{12}$, $\bar{14}$, 0 to 12, 14, 7. Check reflections $\bar{3}21$ and $\bar{1}\bar{2}1$ [intensity variations 3·27–3·47 (3) $\times 10^5$ and 3·78–3·97 (3) $\times 10^5$, respectively]. Total of 2802 independent reflections, 2304 observed [$I \geq 1{\cdot}96\sigma(I)$]. Lp correction. Absorption and extinction ignored. Direct methods (*SHELX*76, Sheldrick, 1976). Anisotropic full-matrix least-squares refinement. H (from difference electron density map) isotropic. 11 F_o with large $||F_o| - |F_c||/\sigma(F)$ omitted in last cycle. Final $R = 0{\cdot}054$; unit weights used throughout refinement. $(\Delta/\sigma)_{\max} = 0{\cdot}03$. Max. and min. heights in final $\Delta\rho$ map 0·204 and $-0{\cdot}153$ e Å^{-3}. All calculations performed on ESER 1040 computer of Halle University using programs *SHELX*76, *PRARA* (Jaskólski, 1980), *GEOME* (Jaskólski, 1981*a*) and *PLANE* (Jaskólski, 1981*b*).

Discussion. Final atomic parameters are listed in Table 1.* Selected bond lengths and angles are given in Table 2. Atomic numbering and molecular geometry can be seen from Fig. 1. The molecule has a stretched form, which is generally required for compounds forming liquid crystals. This nearly linear shape is preserved in spite of the rather unusual conformation of the hexylamino group, which is not fully staggered but includes two *gauche* conformations and is characterized by the following torsion angles: C(14)–N(5)–C(15)–C(16) $-177{\cdot}1$ (4), N(5)–C(15)–C(16)–C(17) 70·3 (4), C(15)–C(16)–C(17)–C(18) $-178{\cdot}0$ (3), C(16)–C(17)–C(18)–C(19) $-66{\cdot}1$ (4) and C(17)–C(18)–C(19)–C(20) $-175{\cdot}9$ (4)°. This effect is accompanied by an alternation of bond lengths within the hexyl group (*cf.* Table 2). Also striking is the rather short C(14)–N(5) distance.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles, selected torsion angles and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38990 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	U_{eq}
C(1)	6051 (4)	7354 (3)	−4881 (6)	102 (2)
C(2)	5624 (3)	7397 (3)	−3105 (5)	73 (2)
C(3)	4880 (3)	6551 (3)	−3296 (5)	67 (1)
C(4)	4425 (3)	6606 (3)	−1539 (5)	68 (1)
C(5)	3710 (3)	5746 (2)	−1750 (5)	65 (1)
C(6)	2568 (3)	5246 (2)	90 (5)	58 (1)
C(7)	2269 (3)	5427 (2)	1842 (5)	61 (1)
C(8)	1595 (3)	4787 (2)	2193 (4)	58 (1)
C(9)	1194 (3)	3961 (2)	785 (4)	52 (1)
C(10)	1466 (3)	3804 (2)	−983 (5)	64 (1)
C(11)	2150 (3)	4443 (3)	−1338 (5)	67 (1)
C(12)	501 (3)	3238 (2)	1110 (5)	57 (1)
C(13)	−20 (3)	2731 (2)	3614 (4)	58 (1)
C(14)	−929 (3)	1605 (2)	5034 (4)	51 (1)
C(15)	−2427 (3)	1393 (3)	6609 (5)	69 (1)
C(16)	−2707 (3)	612 (3)	7584 (5)	73 (2)
C(17)	−1824 (3)	500 (3)	9453 (5)	79 (2)
C(18)	−2080 (4)	−321 (3)	10419 (5)	83 (2)
C(19)	−3189 (4)	−79 (3)	11072 (6)	92 (2)
C(20)	−3350 (4)	−874 (4)	12137 (6)	102 (2)
N(1)	562 (2)	1795 (2)	3714 (4)	61 (1)
N(2)	84 (2)	1199 (2)	4430 (4)	58 (1)
N(3)	−1535 (2)	2540 (2)	4797 (4)	56 (1)
N(4)	−1034 (3)	3119 (2)	4068 (4)	63 (1)
N(5)	−1369 (2)	1034 (2)	5866 (4)	58 (1)
O(1)	3277 (2)	5916 (2)	−48 (3)	72 (1)
O(2)	−16 (2)	2589 (2)	−48 (3)	76 (1)
O(3)	539 (2)	3389 (2)	3064 (3)	67 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for the tetrazine ring and the hexylamino group*

N(1)—N(2)	1·323 (4)	C(14)—N(5)	1·328 (5)
N(2)—C(14)	1·354 (4)	N(5)—C(15)	1·444 (5)
C(14)—N(3)	1·351 (4)	C(15)—C(16)	1·525 (6)
N(3)—N(4)	1·329 (5)	C(16)—C(17)	1·485 (5)
N(4)—C(13)	1·302 (5)	C(17)—C(18)	1·554 (7)
C(13)—N(1)	1·327 (4)	C(18)—C(19)	1·458 (6)
		C(19)—C(20)	1·527 (7)

O(3)—C(13)—N(1)	116·6 (3)	C(14)—N(5)—C(15)	122·6 (3)
O(3)—C(13)—N(4)	115·8 (3)	N(5)—C(15)—C(16)	112·3 (3)
N(1)—C(13)—N(4)	127·5 (4)	C(15)—C(16)—C(17)	113·2 (3)
C(13)—N(1)—N(2)	116·4 (3)	C(16)—C(17)—C(18)	113·5 (3)
N(1)—N(2)—C(14)	117·4 (2)	C(17)—C(18)—C(19)	115·3 (3)
N(2)—C(14)—N(3)	124·2 (3)	C(18)—C(19)—C(20)	113·1 (4)
C(14)—N(3)—N(4)	116·7 (3)		
N(3)—N(4)—C(13)	117·4 (3)		
N(2)—C(14)—N(5)	117·6 (3)		
N(3)—C(14)—N(5)	118·1 (3)		

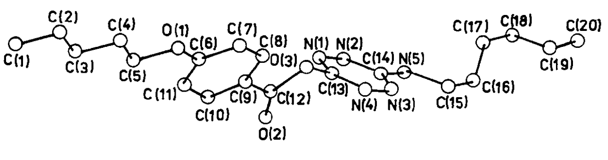

Fig. 1. Molecular structure of HTPB with atom-numbering scheme.

The benzene ring is almost coplanar with the pentyloxy group (interplanar angle 2·8°). The orientation of the carboxylic group with respect to the neighbouring ring systems can be described by the torsion angles τ_1[C(10)—C(9)—C(12)—O(2)] −11·2 (4), τ_2[C(9)—C(12)—O(3)—C(13)] −176·7 (3) and τ_3[C(12)—O(3)—C(13)—N(1)] 76·7 (3)° and corresponds to the results of experimental and theoretical investigations on the conformational behaviour of substituted phenyl benzoates (Birner, Kugler, Simon & Náray-Szabó, 1982; Baumeister, Brandt, Hartung & Jaskólski, 1983). The agreement of the HTPB values for τ_1 and τ_2 with the ranges valid for phenyl benzoates is an expected and rather trivial result whereas the value for τ_3 confirms the statement of the above-mentioned authors about the consequences of the conjugation of the lone electron pair at O(3) with the π-electron system of the aromatic ring. The angle between the plane of the carboxylic group and the tetrazine ring is influenced mainly by this conjugation and, to a certain degree, by packing forces, since there is no steric hindrance in contrast to the case of a benzene ring with its H atom in *ortho* position to the carboxylic group.

The tetrazine ring has the usual dimensions. As in the unsubstituted heterocycle (Bertinotti, Giacomello & Liquori, 1956), the N—C—N angles [mean 125·8 (22)°] are considerably greater than the N—N—C angles [mean 117·0 (5)°]. The distances of atoms from the tetrazine least-squares plane [N(1) −0·008 (3), N(2) −0·020 (3), N(3) −0·019 (3), N(4) −0·010 (3), C(13) 0·024 (3), C(14) 0·034 (3) Å] indicate a very slight but significant deviation from planarity towards a boat conformation. The molecular parallelism observed in the crystal structure (Fig. 2) is generated by the action of the inversion centres and translations of the space group $P\bar{1}$. The molecules are

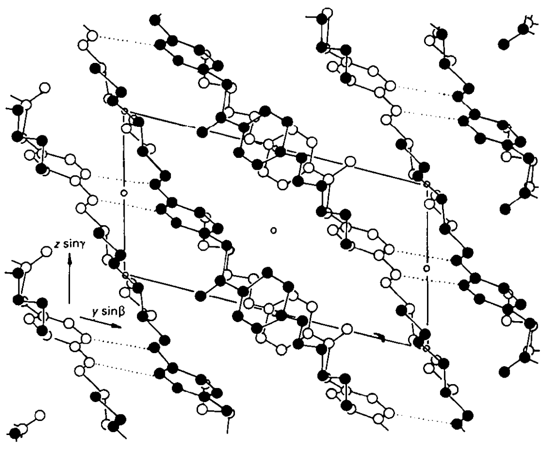

Fig. 2. Packing of the HTPB molecules viewed down the x axis (the intermolecular hydrogen bonds are marked by dotted lines).

arranged in sheets parallel to (021) and the sheets are related by the inversion centres at $z = 0{\cdot}5$. Molecules from neighbouring sheets are bonded *via* N(5)—H(N5)···N(2) hydrogen bridges and form dimers across the centre of symmetry. The N—H···N bond has the following geometry: N(5)—H(N5) 0·79 (2), H(N5)···N(2) 2·31 (3), N(5)···N(2) 3·094 (4) Å, N(5)—H(N5)···N(2) 171 (2)°. There is no indication of any other hydrogen bond and all intermolecular distances between non-hydrogen atoms are greater than the sum of the corresponding van der Waals radii.

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Structure of 11,14,27,30,35,38,43,46-Octaoxa-1,8,17,24-tetraazapentacyclo-[22.8.8.$8^{8,17}$.$2^{3,6}$.$2^{19,22}$]dopentaconta-3,5,19,21,49,51-hexaene,* $C_{40}H_{64}N_4O_8$, a Tricyclic Macrocycle Featuring Two [18]-N_2O_4 Binding Subunits and Two Benzene Bridges

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Abstract. $M_r = 728{\cdot}98$, $P\bar{1}$, $a = 8{\cdot}823\,(3)$, $b = 8{\cdot}813\,(4)$, $c = 13{\cdot}859\,(3)$ Å, $\alpha = 87{\cdot}40\,(1)$, $\beta = 84{\cdot}05\,(1)$, $\gamma = 85{\cdot}19\,(1)°$, $V = 1067{\cdot}3$ Å^3, $Z = 1$, $D_x = 1{\cdot}134$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}0735$ mm^{-1}, $F(000) = 396$, $T = 293$ K, final $R = 0{\cdot}048$ for 2124 observed reflections. The title compound is a tricyclic cryptand with an internal cavity defined by two parallel 18-membered [$C_{12}H_{24}N_2O_4$] macrocyclic units bridged by two parallel phenyl rings. The structure is consistent with the results obtained for a similar compound with two naphthalene bridges. However, the conformation of the macrocyclic subunit differs significantly from that of the free monocyclic analogue.

Introduction. An intriguing feature of the tricyclic cryptands containing two binding subunits is their ability to encapsulate diammonium salts and to form dinuclear metal complexes. Even more fascinating is the possibility of inserting one or several anions in the central cavity of the dinuclear complex (Lehn, 1980). These new coordination processes depend primarily on the rigidity of the cryptand, on the dimension of its central cavity and on the size of each binding subunit. Some of these parameters can be accurately determined following a crystallographic analysis. We have thus investigated the crystal structure of the title compound, a tricyclic macrocycle containing two [18]-N_2O_4 macrocyclic binding subunits, hereafter designated as compound (I). While this work was in progress, a short description of the structure of a similar ligand with two naphthalene bridges [hereafter designated as compound

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* Note that the preferred IUPAC numbering used in the nomenclature of the title compound differs slightly from the numbering used elsewhere in this paper.

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