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2-Amino-5-hexyloxytropone

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.071
wR factor = 0.244
Data-to-parameter ratio = 20.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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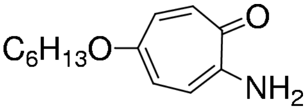
In the title compound, $C_{13}H_{19}NO_2$, the NH_2 group participates in intermolecular hydrogen bonding with the O atoms of neighbouring molecules. The shortest distance between the tropone planes exceeds 4.0 Å; this implies that π–π interaction between the tropone rings can hardly be among those factors which determine the crystal packing of this compound.

Comment

Troponoids, being a remarkable class of non-benzenoid π-conjugated systems, frequently play an important role as entities determining the specific properties of molecular assemblies. Recently, we have prepared liquid crystals with a tropone core, such as 5-hydroxytropolone and 2-amino-5-hydroxytropone (Mori & Takeshita, 1995; Mori *et al.*, 1997). The troponoid cores enhanced formation of smectic phases when compared with the corresponding benzenoids. We now report the crystal structure of 2-amino-5-hexyloxytropone, (I), which was determined in order to elucidate the substituent effect at the 2- and 5-positions of tropone on the crystal packing.



(I)

The hexyl chain has an all-*trans* conformation thus forming an almost planar zigzag; the deviations of atoms from the least squares plane defined by atoms C8–C13 are all within 0.063 (7) Å. The planarity of the seven-membered ring is fairly good; the deviations of atoms from the least squares plane defined by atoms C1–C7 are within 0.023 (4) Å. The C—C bond lengths of the seven-membered ring, apart from the C1—C2 bond, show no apparent bond alternation in contrast to what has been observed for tropolone (Shimanouchi & Sasada, 1973). The average value of the C—C bond lengths, apart from the C1—C2 bond, is 1.388 Å, which agrees with that of tropolone (1.385 Å) and the standard aromatic C—C bond length of 1.392 Å (Lide, 1990). The C1—C2 bond [1.474 (3) Å] is significantly longer than all other bonds in the ring; the same structural peculiarity had been noted in the tropolone structure.

The NH_2 group participates in an N1—H1$\cdots$O1 intermolecular hydrogen bond [N1$\cdots$O1^{i} 2.877 (4) Å; symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, z$]. The N$\cdots$O distance is close to the standard intermolecular N—H$\cdots$O distance [N$\cdots$O 2.89 Å; Kuleshova & Zorkii, 1981]. These hydrogen bonds link molecules of (I) into infinite chains stretching along the *a* axis of

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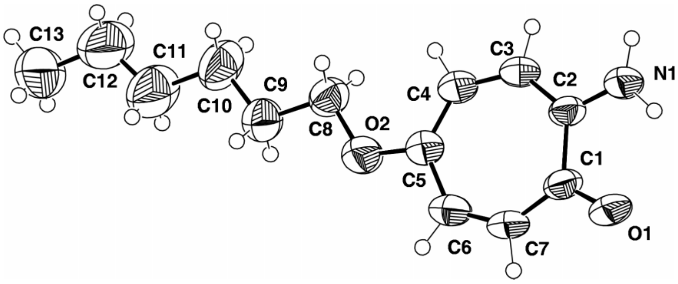

Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

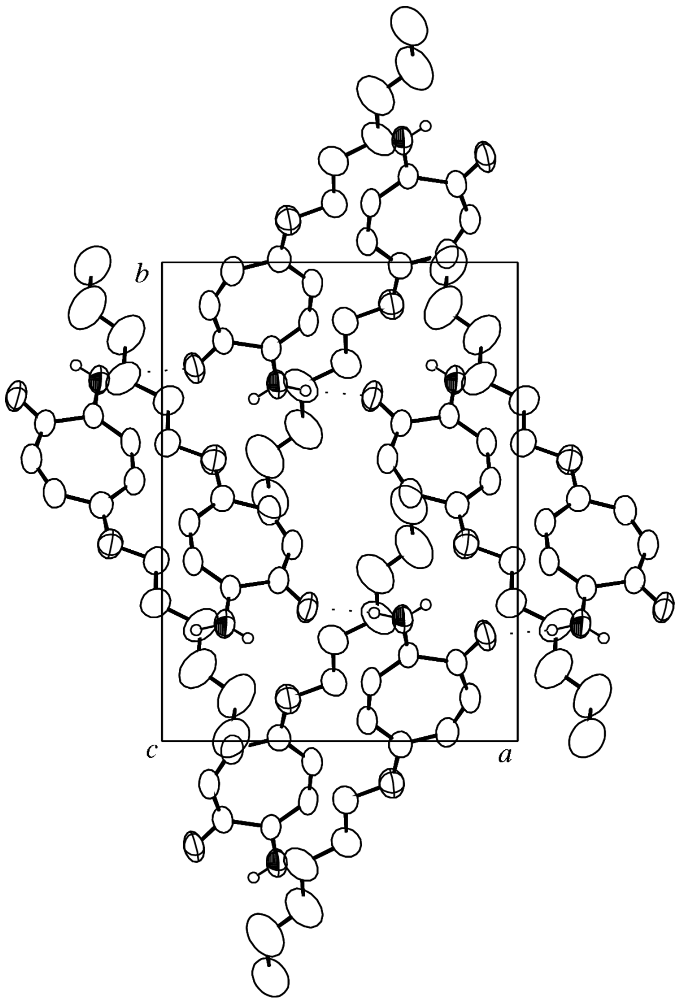

Figure 2
Packing diagram of (I) viewed down the *c* axis. The H atoms, except for NH_2, have been omitted for clarity. The ellipsoids with octant shading and ellipsoids with principal ellipses represent N and O atoms, respectively. Hydrogen bonds are shown as dotted lines.

the crystal. Another relatively short intermolecular contact, $N1\cdots O2^{ii}$ of 3.312 (4) Å [symmetry code: (ii) $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$], is much longer than the above-mentioned standard $N-H\cdots O$ hydrogen-bonding distance.

The distance between the tropone planes of neighbouring molecules in the crystal is greater than 4.0 Å, which is substantially longer than that in tropolone itself (3.715 Å; Shimanouchi & Sasada, 1973). This makes us believe that the π–π interaction can hardly be among those factors which determine the crystal packing of the title compound.

Experimental

A methanol (5 ml) solution of 5-hexyloxy-2-methoxytropone (0.327 g, 1.38 mmol) and aqueous ammonia (28%, 2 ml) was heated at 373 K for 12 h in a sealed tube. The mixture was extracted with chloroform (50 ml). The extract was dried over $MgSO_4$ and distilled *in vacuo* and the residue was chromatographed on a silica-gel column (hexane–ethyl acetate, 1:1 *v*/*v*) to give (I) (0.166 g, 54%). Single crystals of (I) were obtained by recrystallization from ethyl acetate.

Crystal data

$C_{13}H_{19}NO_2$
$M_r = 221.29$
Monoclinic, $P2_1/a$
$a = 10.7540$ (4) Å
$b = 13.9616$ (5) Å
$c = 8.9464$ (4) Å
$\beta = 104.9458$ (12)°
$V = 1297.80$ (9) Å^3
$Z = 4$
$D_x = 1.133$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.7$–18.2°
$\mu = 0.08$ mm^{-1}
$T = 296$ (2) K
Prism, yellow
$0.40 \times 0.37 \times 0.17$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.987$, $T_{max} = 1.000$
3274 measured reflections
3113 independent reflections
1461 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 28.0°$
$h = -14 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.071$
$wR(F^2) = 0.244$
$S = 1.03$
3113 reflections
153 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1195P)^2 + 0.2445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.340 (4)	C1—C7	1.423 (4)
N1—H1	0.89 (4)	C2—C3	1.385 (4)
N1—H2	0.84 (4)	C3—C4	1.382 (4)
O1—C1	1.250 (3)	C4—C5	1.376 (4)
O2—C5	1.367 (3)	C5—C6	1.409 (4)
C1—C2	1.474 (3)	C6—C7	1.353 (4)
C5—O2—C8—C9	180.0 (3)	C9—C10—C11—C12	173.7 (5)
O2—C8—C9—C10	178.7 (3)	C10—C11—C12—C13	−178.0 (5)
C8—C9—C10—C11	−179.0 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^{i}	0.89 (4)	2.00 (4)	2.877 (4)	172 (2)
N1—H2$\cdots$O2^{ii}	0.84 (4)	2.54 (3)	3.312 (4)	154 (2)

Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$.

H atoms bonded to C atoms were included in the refinement at calculated positions as riding models, with C—H set to 0.93 Å for aromatic, 0.96 Å for for CH_3 and 0.97 Å for CH_2. The H atoms of the NH_2 group were located in the difference synthesis and subsequently included in the refinement in an isotropic approximation.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL*97.

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