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2-Amino-5-[4-(octylamino)phenyl]cyclohepta-2,4,6-trien-1-one

Kanji Kubo,[a]* Taisuke Matsumoto,[b] Kouki Katahira[c] and Akira Mori[b]

[a]School of Dentistry, Health Sciences University of Hokkaido, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido 061-0293, Japan, [b]Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, and [c]Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

Correspondence e-mail: kubo-k@hoku-iryo-u.ac.jp

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.071
wR factor = 0.202
Data-to-parameter ratio = 16.3

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

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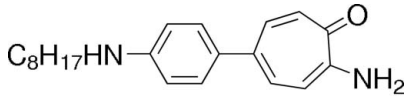
The title compound, also known as 2-amino-5-[4-(octylamino)phenyl]tropone, $C_{21}H_{28}N_2O$, contains two crystallographically independent molecules in the asymmetric unit. The NH_2 group of the 2-aminotropone unit and the NH group of the aminobenzene unit participate in intermolecular hydrogen bonding with the O atoms of neighbouring molecules. An intermolecular π–π interaction is observed in the crystal structure.

Comment

Self-assembled systems are of great significance, particularly for their potential application to nanomaterials such as liquid crystals and gelators (Kubo, Tsuji *et al.*, 2004). Numerous studies have been dedicated to the structural investigation and the determination of the molecular aggregation mechanisms. Troponoids, a remarkable class of non-benzenoid π-conjugated systems, have also been used as a building block of molecular assemblies such as liquid crystals and organogelators (Kubo, Mori *et al.*, 2004). Tropone and tropolone frequently play an important role as entities determining the specific properties of molecular assemblies.



(I)

Recently, we have prepared liquid crystals with a troponoid core such as tropone itself (Mori & Takeshita, 1995), nitrotropone (Kubo, Tsuruta *et al.*, 2002), bitropone (Kubo, Sutoh *et al.*, 2002), and phenyltropone (Mori *et al.*, 2002). The troponoid cores enhanced formation of smectic phases when compared with the corresponding benzenoids. The crystal structure analyses of some troponoid-core liquid crystals have been carried out (Yamamoto *et al.*, 2001; Kubo *et al.*, 2001,

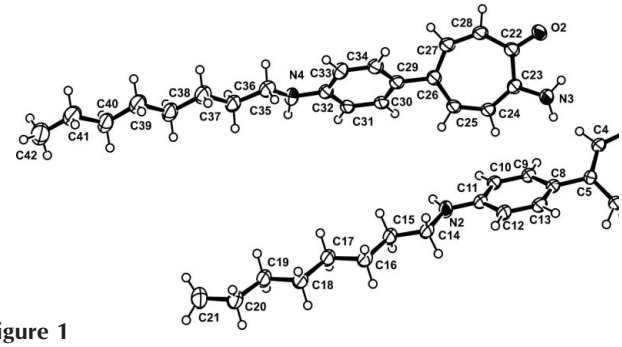


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids.

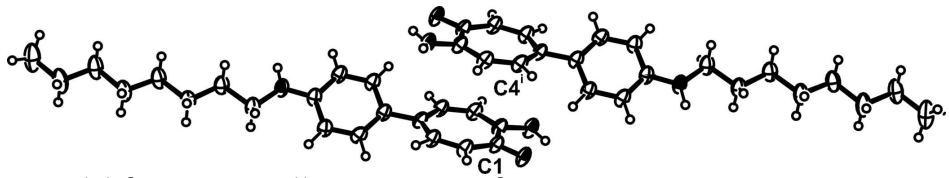


Figure 2
The π–π interaction of molecule (I*a*). [Symmetry code: (i) $-1-x, -y, 2-z$.]

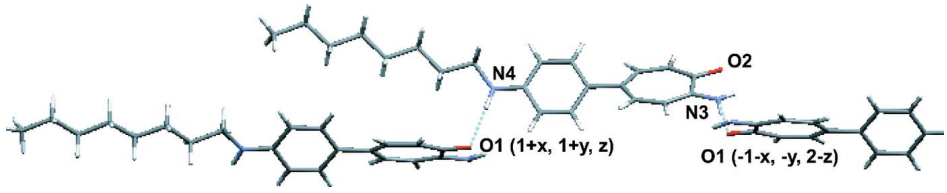


Figure 3
N—H···O interactions (dashed lines) for molecule (I*b*).

2005; Kubo, Sutoh *et al.*, 2002). These crystal structures involve intermolecular π–π interactions and intermolecular hydrogen bonds. We now report the crystal structure of 2-amino-5-[4-(octylamino)phenyl]tropone, (I), which was determined in order to elucidate the substituent effect of 5-phenyltropone on the crystal packing.

There are two molecules, (I*a*) and (I*b*), in the asymmetric unit (Fig. 1). In both, the octyl chain has an all-*trans* conformation, thus forming an almost planar zigzag; the deviations of atoms from the least-squares plane defined by atoms C14–C21 for (I*a*) and C34–C42 for (I*b*) are all within 0.045 (3) and 0.021 (3) Å, respectively. The planarity of the seven-membered ring is fairly good; the deviations of atoms from the least-squares plane defined by atoms C1–C7 for (I*a*) and C22–C28 for (I*b*) are within 0.013 (3) and 0.007 (3) Å. The C—C bond lengths of the seven-membered ring, apart from the C1—C2 and C22—C23 bonds, show no apparent bond alternation, in contrast to what has been observed for tropolone (Shimanouchi & Sasada, 1973), but similar to 2-amino-5-hexyloxytropone (Yamamoto *et al.*, 2001). The average value of the C—C bond lengths, apart from the C1—C2 and C22—C23 bonds, is 1.394 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 and C22—C23 bonds are significantly longer than all other bonds in the ring. The dihedral angles between the least-squares planes *A* (defined by atoms C1–C7) and *B* (defined by C8–C13) of (I*a*) and between the least-squares planes *C* (defined by C22–C28) and *D* (defined by C29–C34) of (I*b*) are 36.4 (1) and 38.1 (1)°, respectively, resembling those of 40.6 (2)° in 2-methoxy-5-(4-methoxyphenyl)cyclohepta-2,4,6-trien-1-one (Gulbis *et al.*, 1992), and distinct from that (0°) in biphenyl (Charbonneau & Delugeard, 1977).

An intermolecular π–π interaction between pairs of tropone planes (head-to-tail) is observed for (I*a*) (Fig. 2). The distances between the tropone planes are within the range associated with π–π interactions (3.3–3.8 Å; Prout *et al.*, 1973; Kubo *et al.*, 2001).

There is an intramolecular N—H···O hydrogen bond in the 2-aminotropone unit (Table 2). Furthermore the NH_2 group of the 2-aminotropone unit of (1*b*) and the NH group of the aminobenzene unit participate in N—H···O intermolecular hydrogen bonds. The N···O distances are close to the intermolecular N—H···O distance [N···O = 2.877 (4) Å] of 2-amino-5-hexyloxytropone (Yamamoto *et al.*, 2001). Thus, the crystal structure of (I) has intermolecular π–π interactions and intermolecular N—H···O hydrogen bonds.

Experimental

A hexamethylphosphoric triamide (3 ml) solution of 2-amino-5-(4-aminophenyl)tropone (40 mg, 0.19 mmol) and NaH (60%, 14 mg, 0.57 mmol) was stirred at 273 K for 1 h. 1-Bromohexane (75 mg, 0.46 mmol) was added and the reaction mixture was stirred at 333 K for 12 h. The mixture was poured into 2 *M* HCl and shaken with ethyl acetate. The organic layer was washed with saturated NaCl solution and dried over $MgSO_4$. The solvent was evaporated and the residue chromatographed on a silica-gel column (hexane–ethyl acetate, 5:1 (*v*/*v*) to give (I) (20 mg, 27%). Crystals of (I) were grown from hexane and ethyl acetate solution (1:1 *v*/*v*) by slow evaporation.

Crystal data

$C_{21}H_{28}N_2O$
M_r = 324.46
Triclinic, $P\overline{1}$
a = 7.691 (2) Å
b = 14.882 (4) Å
c = 16.948 (5) Å
α = 77.200 (14)°
β = 77.262 (14)°
γ = 80.658 (14)°
V = 1832.0 (9) Å^3
Z = 4
D_x = 1.176 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2903 reflections
θ = 3.1–27.5°
μ = 0.07 mm^{-1}
T = 123.1 K
Platelet, yellow
0.12 × 0.10 × 0.03 mm

Data collection

Rigaku Saturn diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.991, T_{max} = 0.998
22067 measured reflections
8302 independent reflections
3759 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -19 \rightarrow 19$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.202
S = 1.00
8285 reflections
508 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[0.0015F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Extinction correction: Larson (1970), equation 22
Extinction coefficient: 1.6 (6) × 10^2

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.279 (3)	C4—C5	1.391 (3)
O2—C22	1.274 (3)	C5—C6	1.418 (3)
N1—C2	1.345 (3)	C5—C8	1.482 (3)
N2—C11	1.362 (3)	C6—C7	1.375 (3)
N2—C14	1.451 (3)	C22—C23	1.473 (4)
N3—C23	1.352 (3)	C22—C28	1.423 (3)
N4—C32	1.385 (3)	C23—C24	1.389 (4)
N4—C35	1.439 (4)	C24—C25	1.382 (3)
C1—C2	1.472 (3)	C25—C26	1.397 (3)
C1—C7	1.414 (3)	C26—C27	1.404 (4)
C2—C3	1.382 (3)	C26—C29	1.486 (3)
C3—C4	1.390 (3)	C27—C28	1.379 (4)
C1···C3^{i}	3.570 (4)	C3···C1^{i}	3.570 (4)
C1···C4^{i}	3.459 (4)	C3···C7^{i}	3.591 (4)
C2···C4^{i}	3.522 (4)	C7···C3^{i}	3.591 (4)
O1—C1—C2	116.0 (2)	O2—C22—C23	117.0 (2)
O1—C1—C7	120.4 (2)	O2—C22—C28	120.0 (2)
C2—C1—C7	123.6 (2)	C23—C22—C28	123.0 (2)
N1—C2—C1	113.5 (2)	N3—C23—C22	112.9 (2)
N1—C2—C3	120.3 (2)	N3—C23—C24	120.4 (2)
C1—C2—C3	126.2 (2)	C22—C23—C24	126.7 (2)
C2—C3—C4	132.3 (2)	C23—C24—C25	132.3 (2)
C3—C4—C5	130.9 (2)	C24—C25—C26	130.6 (2)
C4—C5—C6	123.3 (2)	C25—C26—C27	123.6 (2)
C5—C6—C7	130.7 (2)	C26—C27—C28	131.4 (2)
C1—C7—C6	132.8 (2)	C22—C28—C27	132.4 (2)
C11—N2—C14—C15	−172.2 (2)	C18—C19—C20—C21	−179.7 (2)
C32—N4—C35—C36	−169.9 (2)	N4—C35—C36—C37	−174.9 (2)
N2—C14—C15—C16	179.9 (2)	C35—C36—C37—C38	−177.3 (2)
C14—C15—C16—C17	171.3 (2)	C36—C37—C38—C39	−179.0 (2)
C15—C16—C17—C18	178.8 (2)	C37—C38—C39—C40	−178.1 (2)
C16—C17—C18—C19	−179.2 (2)	C38—C39—C40—C41	179.2 (2)
C17—C18—C19—C20	−177.0 (2)	C39—C40—C41—C42	178.3 (2)

Symmetry code: (i) $-x-1, -y, -z+2$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.89 (3)	2.13 (2)	2.570 (2)	109 (2)
N2—H11···O2^{ii}	0.93 (3)	2.07 (3)	2.993 (3)	168 (2)
N3—H29···O2	0.87 (3)	2.11 (2)	2.579 (3)	113 (2)
N3—H30···O1^{i}	0.97 (3)	1.90 (3)	2.845 (3)	165 (3)
N4—H39···O1^{iii}	0.98 (3)	2.02 (3)	2.993 (4)	170 (2)

Symmetry codes: (i) $-x-1, -y, -z+2$; (ii) $x+1, +y, +z$; (iii) $x+1, +y+1, +z$.

H atoms bonded to C atoms were included in the refinement at calculated positions as riding atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atoms of the NH_2 and NH groups were located in a difference synthesis and refined isotropically. Some low-angle reflections were excluded from the refinement, as they were probably obscured by the beam-stop.

Data collection: *CRYSTALCLEAR* (Rigaku, 1999); cell refinement: *CRYSTALCLEAR*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *CrystalStructure*.

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