organic papers

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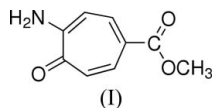kubo-k@hoku-iryo-u.ac.jp

Key indicators

Single-crystal X-ray study
$T = 153$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.109
Data-to-parameter ratio = 11.3

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

Methyl 4-amino-5-oxocyclohepta-1,3,6-triene-1-carboxylate

In the title compound, $C_9H_9NO_3$, the methoxycarbonyl group makes an angle of 18.59 (5)° with the seven-membered ring. The NH_2 group participates in intermolecular N—H···O hydrogen bonding with the O atoms of neighbouring molecules, and the crystal packing is consolidated by π–π, N—H···π and C—H···O interactions.

Comment

Molecular self-assembly often results in a number of thermodynamically interesting states, such as those of crystals, liquid crystals, gels, and colloids. Numerous studies have been dedicated to the structural investigation and the determination of molecular aggregation mechanisms (Kubo, 2004). Troponoids have been used as a building block of molecular assemblies such as liquid crystals (Kubo, Mori *et al.*, 2005). 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 tropolone and 2-aminotropone (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 cores such as tropone (Barrow *et al.*, 1973), tropolone (Shimanouchi & Sasada, 1973), 2-amino-5-hexyloxytropone (Yamamoto *et al.*, 2001), 5-cyano- and 5-nitrotropolones (Kubo *et al.*, 2001), 2-amino-5-[4-(octylamino)phenyl]tropone (Kubo, Matsumoto *et al.*, 2005) and 5-(acetyloxy)tropolone (Kubo, Yamamoto & Mori, 2006) have been determined. The crystal structure of 2-amino-5-[4-(octylamino)phenyl]tropone (Kubo, Matsumoto *et al.*, 2005) features intermolecular π–π interactions and N—H···O hydrogen bonding. We now report the crystal structure of 2-amino-5-methoxycarbonyltropone, (I), which was determined in order to elucidate the substituent effect of 2-aminotropone upon the crystal packing.

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), but similar to 2-amino-5-hexyloxytropone (Yamamoto *et al.*, 2001) and 2-amino-5-[4-(octylamino)phenyl]tropone (Kubo, Matsumoto *et al.*, 2005). The average value of the C—C bond lengths, apart from the C1—C2 bond, is 1.396 (2) Å, which agrees with that of
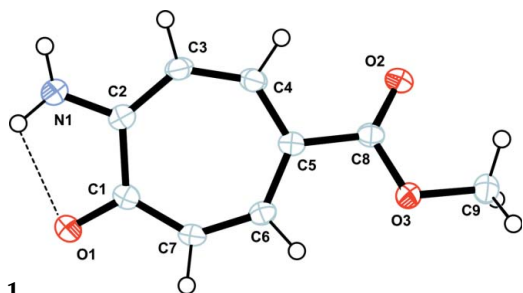
Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.
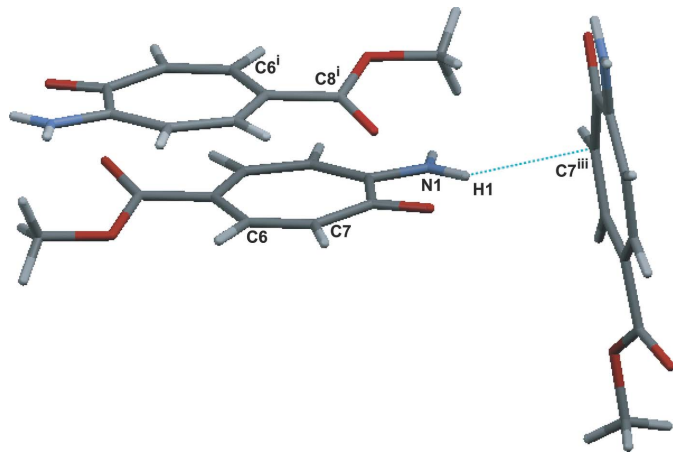

Figure 2
Intermolecular N—H···π and π–π interactions in (I) [symmetry codes: (i) $1 - x, -y, 1 - z$; (iii) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$].
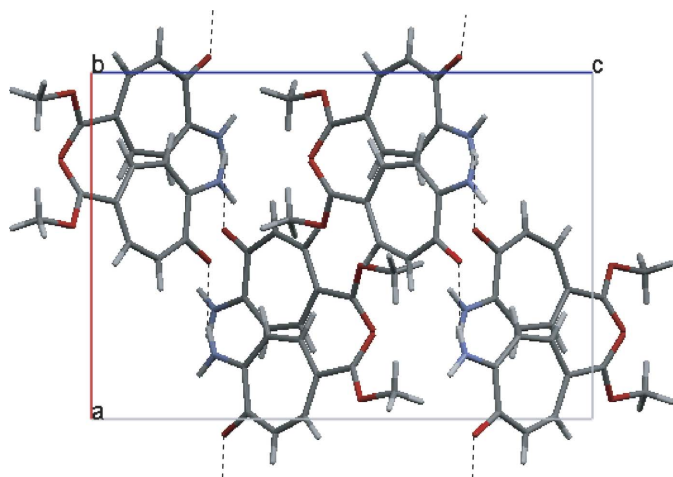

Figure 3
Packing diagram for (I), viewed down the b axis, with intermolecular hydrogen bonds shown as dashed lines.

tropolone [1.385 (4) Å] and the standard aromatic C—C bond length of 1.392 Å (Lide, 1990). The C1—C2 bond distance of 1.486 (2) Å is significantly longer than all other bonds in the ring. The dihedral angle between the least-squares plane A (defined by atoms C1–C7) and B (defined by atoms C8/C9/O2/O3) is 18.6 (1)°, which is close to the value of 6.9 (1)° in methyl p-aminobenzoate (Doriguetto et al., 2004).

Intermolecular π–π interactions occur in (I) between the tropone ring planes (Fig. 2). The C6···C6^i [symmetry code: (i)

$1 - x, -y, 1 - z$] separation is 3.313 (2) Å, which is within the range associated with π–π interactions (3.3–3.8 Å). This value is similar to that of the equivalent intermolecular separation in tropolone (3.42 Å; Shimanouchi & Sasada, 1973). There is an intramolecular N—H···O hydrogen bond in the 2-amino-tropone unit (Table 2 and Fig. 1). Furthermore, the NH_2 group participates in an N—H···O intermolecular hydrogen bond that serves to link molecules of (I) into infinite chains stretching along the a axis. Various intermolecular C—H···O interactions (Table 2) help to consolidate the crystal packing of (I). Similar interactions have been seen in related materials (Kubo, Yamamoto & Mori, 2006; Kubo, Fukeda et al., 2006). There is also an intermolecular N—H···π interaction (Table 2 and Fig. 3). The combination of all of the above intermolecular interactions builds up a three-dimensional network.

Experimental

Compound (I) was prepared by the methylation of 5-methoxy-carbonyltropolone with diazomethane and amination with aqueous ammonia (Hashimoto et al., 2003). Crystals of (I) were grown from an ethyl acetate/methanol solution (1:1 v/v) by slow evaporation.

Crystal data

$C_9H_9NO_3$	$Z = 8$
$M_r = 179.17$	$D_x = 1.468$ Mg m^{-3}
Orthorhombic, $Pbca$	Cu $K\alpha$ radiation
$a = 11.113$ (3) Å	$\mu = 0.94$ mm^{-1}
$b = 9.084$ (3) Å	$T = 153.1$ K
$c = 16.059$ (4) Å	Prism, yellow
$V = 1621.1$ (8) Å^3	$0.30 \times 0.24 \times 0.15$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	13745 measured reflections
ω scans	1443 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1348 reflections with $F^2 > 2\sigma(F^2)$
$T_{min} = 0.641$, $T_{max} = 0.868$	$R_{int} = 0.033$
	$\theta_{max} = 68.2°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.051P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 1.2779P]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1443 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
128 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: SHELXL97
	Extinction coefficient: 0.0034 (4)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.329 (2)	C3—C4	1.388 (2)
C1—C2	1.486 (2)	C4—C5	1.385 (2)
C1—C7	1.424 (2)	C5—C6	1.403 (2)
C2—C3	1.398 (2)	C6—C7	1.375 (2)
C9—O3—C8—C5	−178.79 (13)	C6—C5—C8—O2	162.11 (16)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N1—H1⋯O1	0.90 (2)	2.18 (2)	2.574 (2)	106 (2)
N1—H2⋯O1[iv]	0.87 (2)	2.20 (2)	3.029 (2)	159 (2)
N1—H1⋯C7[iii]	0.90 (2)	2.77 (2)	3.592 (2)	153 (2)
C3—H3⋯O1[iv]	0.95	2.51	3.341 (2)	146
C6—H5⋯O2[ii]	0.95	2.37	3.146 (2)	139
C9—H7⋯O1[v]	0.98	2.55	3.368 (2)	142
C9—H8⋯O3[v]	0.98	2.57	3.325 (2)	134

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

The H atoms of the NH$_2$ group were located in a difference map and refined; see Table 2 for distances. All C-bound H atoms were placed in idealized locations (C—H = 0.95–0.98 Å) and refined in the riding-model approximation, with $U_{iso}(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$ or $1.5U_{eq}$(methyl C).

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: *SHELXL97* (Sheldrick 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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