organic papers

Urotropine–2,2,3,3-tetramethylcyclopropane-carboxylic acid (1/1)

Hai Feng, Hui-Min Zhang, Bing Tu and Zhi-Min Jin*

College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

Correspondence e-mail: zimichem@sina.com

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.081
wR factor = 0.209
Data-to-parameter ratio = 14.6

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

In the crystal structure of the title compound, $C_6H_{12}N_4 \cdot C_8H_{14}O_2$, neutral molecules of urotropine and 2,2,3,3-tetramethylcyclopropanecarboxylic acid are linked together by an O—H···N hydrogen bond.

Comment

It is known that urotropine (UTP) often forms hydrogen-bonded adducts with phenols and carboxylic acids. The structures of a number of such adducts, *e.g.* UTP–resorcinol (Ng *et al.*, 2002), UTP–*p*-nitrophenol (Ng, Hu *et al.*, 2001), UTP–3,5-dinitrosalicylic acid (Ng, Naumov *et al.*, 2001), UTP–Co(H$_2$O)$_6$-fumarate (Konar *et al.*, 2003), and UTP–phloroglucinol, UTP–methyl 3,4-dihydroxybenzoate and UTP–4-hydroxybenzoic acid (Ghosh *et al.*, 2005), have been published. Here we report the synthesis and crystal structure of the title compound, (I), a molecular complex of UTP with 2,2,3,3-tetramethylcyclopropanecarboxylic acid (TMCA).


(I)
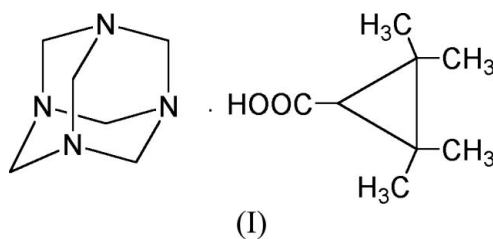
As shown in Fig. 1, the crystal structure of compound (I) is built of neutral molecules of UTP and TMCA, held together by an O—H···N hydrogen bond (Table 2). The O1···N3 distance is close to those observed in UTP–3,5-dinitrosalicylic acid [2.655 (7) Å; Ng, Naumov *et al.*, 2001] and UTP–4-hydroxybenzoic acid [2.670 Å; Ghosh *et al.*, 2005]. The C7—O1 and C7—O2 distances in the TMCA molecule (Table 1) are similar to the corresponding C—O distances in the carboxylic acid groups in UTP–3,5-dinitrosalicylic acid [1.326 (3) and 1.217 (3) Å; Ng, Naumov *et al.*, 2001] and tris(2-benzimidazylmethyl)amine-4-nitrobenzoic acid [1.298 (3) and 1.222 (3) Å; Ji *et al.*, 2000].

In addition to the O—H···N bond linking the UTP and TMCA molecules, there are two short intermolecular distances in the structure of (I) (Table 2). These interactions (Fig. 2) may also contribute to the stabilization of the structure.

Experimental

A mixture of urotropine (1 mmol, 0.14 g) and 2,2,3,3-tetramethyl-cyclopropanecarboxylic acid (1 mmol, 0.14 g) was dissolved in water
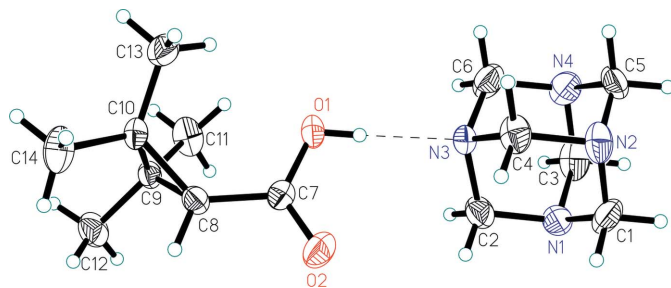
Figure 1
The asymmetric unit of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines.
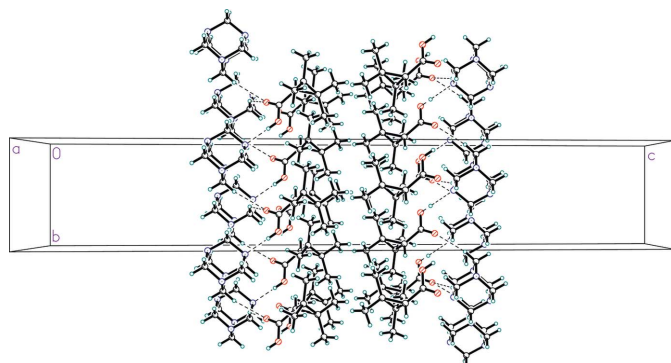
Figure 2
The packing diagram of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

(20 ml), heated to 363 K and stirred for 30 min. The reaction mixture was then cooled to room temperature and colourless crystals of (I) were collected after 25 d.

Crystal data

$C_8H_{14}O_2 \cdot C_6H_{12}N_4$	$Z = 8$
$M_r = 282.39$	$D_x = 1.228$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.2439$ (14) Å	$\mu = 0.08$ mm^{-1}
$b = 7.0715$ (9) Å	$T = 293$ (2) K
$c = 42.491$ (6) Å	Block, colourless
$\beta = 96.881$ (2)°	$0.25 \times 0.19 \times 0.16$ mm
$V = 3055.9$ (7) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	7802 measured reflections
	2758 independent reflections
φ and ω scans	2320 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$R_{int} = 0.028$
$T_{min} = 0.969$, $T_{max} = 0.980$	$\theta_{max} = 25.2°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0906P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.081$	$+ 2.4269P]$
$wR(F^2) = 0.209$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.24$	$(\Delta/\sigma)_{max} < 0.001$
2758 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
189 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.307 (4)	N2—C1	1.451 (4)
O2—C7	1.208 (3)	N2—C5	1.455 (4)
C7—C8	1.473 (4)	N2—C4	1.458 (4)
C8—C9	1.533 (4)	N3—C4	1.469 (4)
C8—C10	1.533 (4)	N3—C6	1.475 (4)
C9—C10	1.501 (4)	N3—C2	1.478 (4)
N1—C1	1.450 (4)	N4—C3	1.451 (5)
N1—C2	1.455 (4)	N4—C5	1.458 (5)
N1—C3	1.463 (5)	N4—C6	1.461 (4)
C7—O1—H1	108 (3)	C7—C8—C10	127.7 (2)
O2—C7—O1	122.2 (3)	C9—C8—C10	58.62 (17)
O2—C7—C8	120.3 (3)	C10—C9—C8	60.71 (18)
O1—C7—C8	117.6 (2)	C9—C10—C8	60.67 (17)
C7—C8—C9	126.1 (2)		

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O1—H1$\cdots$N3	0.92 (4)	1.76 (4)	2.670 (3)	172 (3)
C5—H5$B\cdots$O2^i	0.97	2.53	3.464 (4)	162
C6—H6$A\cdots$O2^{ii}	0.97	2.45	3.228 (4)	137

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

The H atom of the carboxylic O—H group (H1) was located in a difference Fourier map and refined in an isotropic approximation [O1—H1 = 0.92 (4) Å]. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms at C—H distances of 0.96 (methyl), 0.97 (methylene) and 0.98 Å (methine), with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2000). *SMART* (Version 5.618), *SADABS* (Version 2.05), *SAINT* (Version 6.02a) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Ghosh, K., Datta, M., Frohlich, R. & Ganguly, N. C. (2005). *J. Mol. Struct.* **737**, 201–206.

Ji, B. M., Du, C. X., Zhu, Y. & Ding, K. L. (2000). *J. Chem. Crystallogr.* **30**, 783–788.

Konar, S., Zangrando, E. & Chaudhuri, N. R. (2003). *Inorg. Chim. Acta*, **355**, 264–271.

Ng, S. W., Hu, S. Z., Hanna, J. V., Raj, S. S. S., Fun, H.-K., Razak, I. A., Wojciechowski, G. & Brzezinski, B. (2001). *J. Mol. Struct.* **595**, 189–194.

Ng, S. W., Naumov, P., Drew, M. G. B., Wojciechowski, G. & Brzezinski, B. (2001). *J. Mol. Struct.* **595**, 29–37.

Ng, S. W., Naumov, P., Ibrahim, A. R., Fun, H.-K., Chantrapromma, S., Wojciechowski, G., Brzezinski, B. & Hanna, J. V. (2002). *J. Mol. Struct.* **609**, 89–95.

Sheldrick, G. M. (1997). *SHELXL97*. Version 97-1. University of Göttingen, Germany.