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The 1:1 adduct of hexamethylenetetramine (HMT) with racemic *trans*-1,2-cyclohexanedicarboxylic acid (CDA)

Ramaiyer Venkatraman,[a] Paresh Chandra Ray[a] and Frank R. Fronczek[b]*

[a]Department of Chemistry, Jackson State University, Jackson, MS 39217, USA, and [b]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA
Correspondence e-mail: ffroncz@lsu.edu

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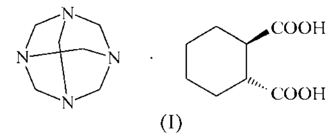
Hexamethylenetetramine and *rac-trans*-1,2-cyclohexanedicarboxylic acid crystallize in a 1:1 ratio as a neutral molecular adduct, $C_6H_{12}N_4 \cdot C_8H_{12}O_4$. Two dicarboxylic acid molecules and two tetramine molecules form a hydrogen-bonded ring, in the shape of a rhombus, which lies on a crystallographic twofold axis bisecting the two diacid molecules. The O—H···N hydrogen bonds have lengths 2.6808 (19) and 2.6518 (19) Å, and, in each ring, both acid molecules have the same handedness.

Comment

Hexamethylenetetramine ($C_6H_{12}N_4$, also known as hexamine and urotropine, and abbreviated as HMT) forms one-, two- and three-dimensional structures with dicarboxylic acids and phenols (Gaillard *et al.*, 1996, 1998; Hostettler *et al.*, 1999; Lough *et al.*, 2000; Coupar, Ferguson *et al.*, 1997; Coupar, Glidewell & Ferguson, 1997; Mak, 1965; Jordan & Mak, 1970). These self-assembled co-crystalline molecular adducts of HMT with dicarboxylic acids are usually interconnected by hydrogen bonds, with the N atoms of HMT acting as acceptors and the carboxyl H atoms as donors. Similarly, HMT with alkanedioic acids [HOOC–$(CH_2)_n$–COOH] forms 1:1 crystalline adducts with rich phase diagrams. Trimesic acid (benzene-1,3,5-tricarboxylic acid), with its three carboxylic acid groups, has been extensively used in the creation of highly ordered co-crystalline solids. Shan *et al.* (2003) used a range of bases, including HMT, with cyclohexane-1,3-*cis*,5-*cis*-tricarboxylic acid to form supramolecular motifs. In the present study, we used racemic *trans*-1,2-cyclohexanedicarboxylic acid, CDA, with the possibility of double deprotonation, to bind with HMT to form similar co-crystalline solids. Pale-yellow rectangular prisms of the title adduct, (I), resulted on mixing hot ethanol solutions of HMT and CDA (in 1:1 molar ratio) and evaporating the mixture at room temperature. Unlike other systems involving HMT and dicarboxylic acids, we have found only one stoichiometric co-crystal of HMT with CDA. In this report, we present the crystal structure of this adduct, (I).



(I)

The asymmetric unit of the co-crystal of CDA and HMT consists of one HMT molecule in a general position and two CDA molecules lying on a crystallographic twofold axis. The one independent COOH group on each CDA molecule forms a hydrogen bond with an N atom on the HMT molecule, and the twofold axis thus forms a hydrogen-bonded rhombus with formula $(CDA)_2(HMT)_2$ (Fig. 1). Details of the hydrogen bonds, which are essentially linear, are given in Table 2. Although the crystal is racemic, both CDA molecules in any given hydrogen-bonded rhombus have the same handedness.

There is a mismatch in number between the two strong hydrogen-bond donors on CDA and the total of six acceptors (four N atoms on HMT and two C═O groups on CDA), so formation of the hydrogen-bonded rhombus precludes any extended hydrogen-bonding network. In the absence of such a network, weaker C—H···O and C—H···N interactions involve the remaining acceptors. These are also detailed in Table 2, which shows that all C—H donors are HMT CH_2 groups. The two excess HMT N atoms each accept one C—H···N interaction, and each CDA C═O group accepts two C—H···O interactions. These weaker interactions allow the

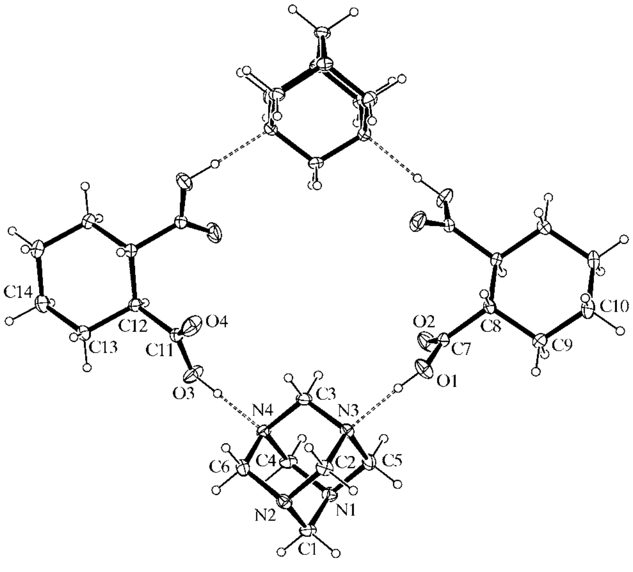


Figure 1
The hydrogen-bonded ring of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related to labelled atoms by a horizontal twofold axis at $(1 - x, 1 - y, z)$.

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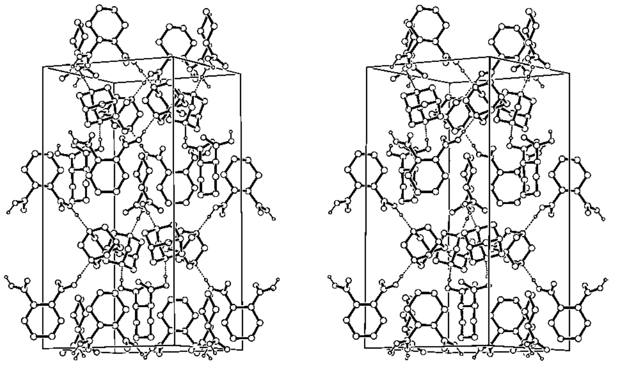

Figure 2
A stereoview of the unit cell of (I). The origin is bottom center (background), with c vertical and b nearly horizontal.

perching of two HMT molecules above and below each rhombus. This results in alternating layers of HMT and CDA molecules each $\frac{1}{4}$ translation along the polar c axis, as shown in Fig. 2.

The space group for (I) is uncommon, being reported for approximately 0.1% of the entries in the Cambridge Structural Database (Version 5.25; Allen, 2002). In their analysis of space-group frequencies, Brock & Dunitz (1994) found that twofold axes in this space group are usually occupied, with 18 of 24 structures in their sample having $Z' = \frac{1}{2}$.

Experimental

All reagents and solvents used were commercially available and used as received without further purification. An ethanol solution (15 ml) of CDA (0.172 g, 1.0 mmol) was added to a stirred solution (5 ml) of HMT (0.100 g, 1.0 mmol) and the reaction mixture stirred for 1 h. The resulting colorless solution was allowed to stand in air at room temperature for 2 d, yielding colorless crystals of (I) suitable for X-ray analysis. IR spectra for the product were obtained in the 4000–400 cm^{-1} range from KBr pellets on a Nicolet Nexus 670 FT–IR spectrophotometer. (The –OH stretching frequency ν_{OH} around 3560 cm^{-1} is very broad compared with the sharp –OH band in the spectrum for CDA. Similarly, the sharp bands of –CN stretching and –NCN bond + ring deformation around 1440 and 1540 cm^{-1} are also found to become one broad band in the adduct.)

Crystal data

$C_6H_{12}N_4 \cdot C_8H_{12}O_4$
$M_r = 312.37$
Orthorhombic, *Aba*2
$a = 11.990$ (3) Å
$b = 11.814$ (3) Å
$c = 22.606$ (6) Å
$V = 3202.1$ (14) Å^3
$Z = 8$
$D_x = 1.296$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3171 reflections
$\theta = 2.5$–33.1°
$\mu = 0.10$ mm^{-1}
$T = 102$ K
Rectangular prism, colorless
0.25 × 0.25 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer (with an Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
17 655 measured reflections
3119 independent reflections
2652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 33.1°$
$h = -18 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -34 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.097$
$S = 1.04$
3119 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.5607P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

O1—C7	1.322 (2)	N2—C6	1.468 (2)
O2—C7	1.214 (2)	N2—C1	1.480 (2)
O3—C11	1.323 (2)	N3—C3	1.476 (2)
O4—C11	1.213 (2)	N3—C2	1.483 (2)
N1—C4	1.464 (2)	N3—C5	1.494 (2)
N1—C5	1.466 (2)	N4—C3	1.476 (2)
N1—C1	1.483 (2)	N4—C6	1.481 (2)
N2—C2	1.464 (2)	N4—C4	1.485 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N3	0.88 (3)	1.80 (3)	2.6808 (19)	175 (3)
O3—H3O···N4	0.93 (3)	1.72 (3)	2.6518 (19)	177 (3)
C1—H1*A*···O4^{i}	0.99	2.54	3.435 (2)	150
C1—H1*B*···O2^{ii}	0.99	2.40	3.317 (2)	153
C2—H2*A*···O2^{ii}	0.99	2.56	3.436 (2)	147
C3—H3*A*···N2^{iii}	0.99	2.58	3.487 (2)	152
C3—H3*B*···N1^{iv}	0.99	2.48	3.355 (2)	147
C4—H4*A*···O4^{i}	0.99	2.48	3.388 (2)	152

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

The absolute structure could not be determined, and Friedel equivalents were averaged. H atoms on C atoms were treated as riding in idealized positions, with C—H distances in the range 0.95–0.99 Å, depending on atom type. The coordinates of H atoms on O atoms were refined (see Table 2). Displacement parameters for all H atoms were assigned as $U_{iso}(H) = 1.2U_{eq}$ of the attached atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1744). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.

Coupar, P. I., Ferguson, G., Glidewell, C. & Meehan, P. R. (1997). *Acta Cryst.* C**53**, 1978–1980.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Gaillard, V. B., Chapuis, G., Dusek, M. & Petříček, V. (1998). *Acta Cryst.* A**54**, 31–43.

Gaillard, V. B., Paciorek, W., Schenk, K. & Chapuis, G. (1996). *Acta Cryst.* B**52**, 1036–1047.

Hostettler, M., Birkedal, H., Gaillard, M., Chapuis, G., Schwarzenbach, D. & Bonin, M. (1999). *Acta Cryst.* B**55**, 448–458.

Jordan, T. H. & Mak, T. C. W. (1970). *J. Chem. Phys.* **52**, 3790–3794.

Lough, A. J., Wheatley, P. S., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 261–272.

Mak, T. C. W. (1965). *J. Chem. Phys.* **43**, 2799–2805.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Shan, N., Bond, A. D. & Jones, W. (2003). *New J. Chem.* **27**, 365–371.

Sheldrick, G. (1997). *SHELXL*97. University of Göttingen, Germany.