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X-ray structure of 1,3-adamantane dicarbonamide

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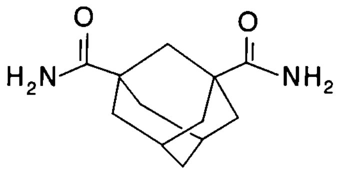
The X-ray crystal structure of 1,3-adamantane-dicarbonamide† has been determined. Colourless, cube shaped crystals of $C_{12}H_{18}N_2O_2$ crystallize in the monoclinic space group C2/c (#15) with cell dimensions $a = 7 \cdot 934(3)$, $b = 15 \cdot 543(3)$, $c = 9 \cdot 404(2)$ Å; $\beta = 93.63°$; $V = 1157.4(5)$ Å^3 and $Z = 4$. 1074 unique reflections with $I_{net} > 2.00\sigma(I)$ on refinement afforded values of $R = 0.039$ and $R_w = 0.040$.

KEY WORDS: Adamantane, dicarbonamide, structure.

Introduction

The preparation of small molecules that bear more than one heterocyclic moiety is an area of current interest among chemists working with inorganic rings.[1] We have shown that adamantane based nitrile sulphides $[R{-}C{\equiv}N{-}S]$ can be used to prepare a number of heterocycles with delocalized π systems.[2] To extend this development to multi-heterocyclic systems we have prepared the title compound, which is a crucial precursor to these studies and determined its solid state structure.

The structures of disubstituted adamantane molecules have rarely been reported.[3] The investigation of various carboxylic acid derivatives of adamantane has led to important insights into the structure and packing of hydrogen bonded network solids.[4] The title compound has been reported previously[5] but has not been reported in many synthetic schemes.[6] The structure of this compound has not been described.



Structure 1. 1,3-adamantane dicarbonamide.

Experimental

The title compound was prepared from 1,3-adamantane dicarbonylchloride [which was prepared from 1,3-adamantanedicarboxylic acid (Aldrich) according to ref. 7 and purified by sublimation] using a variation of the preparation described in ref. 5. Thus, 120 ml of 30% ammonium hydroxide was stirred in a 250 ml three neck flask and cooled in an ice-water bath. The dicarbonylchloride [6.4 g] was slowly added and the reaction mixture heated to reflux for 3 hr. The reaction mixture was cooled to room temperature and the precipitated white product was isolated by filtration and washed with water. The crude product was recrystallized from 100 ml of a 10:1 water:ethanol mixture to give colorless cube shaped crystals of the title compound [5.1 g, 94%, mp. 254–256°C]. The title compound is insoluble in most organic solvents and is only slightly soluble in water and ethanol but is reasonably soluble in dimethyl sulfoxide. IR (KBr plates, Nujol mull; cm^{-1}): 3399, 3350, 3278, 3211, 1693, 1644, 1608. NMR (^{1}H, $(CD_3)_2SO$, ppm): 6.993/6.996 (NH_2), 2.038, 1.768, 1.685, 1.578; (^{13}C, $(CD_3)_2SO$, ppm): 178.9 (C=O), 40.2, 39.5, 38.9, 38.0, 27.9.

X-ray crystallography

A single crystal (irregular shape) was mounted on a thin glass fiber and diffraction data were collected on a Rigaku AFC6S diffractometer. Experimental param-

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Table 1. Crystallographic data for 1,3-adamantane dicarbonamide

Compound	$C_{10}H_{14}(C(O)NH_2)_2$	μ_{calc}, cm^{-1}	0.82
Color	colorless	Scan type	$\omega/2\theta$
Formula wt.	222.29	Radiation	MoK_α
Crystal system	monoclinic	Max. Xtal Dimensions, mm	0.300 × 0.300 × 0.230
Space group	C2/c	Scan width	1.52 × 0.30 tan θ
Temp. °C	26 ± 1	2θ range, °	6 – 50.1
Cell constants[a]		Unique reflections	1074
a, Å	7.934(3)	Reflections observed[b]	764
b, Å	15.543(3)	Computer programs	TEXSAN-TEXRAY
c, Å	9.404(2)	Structure solution	Direct Methods
β, °	93.63(2)	Number of parameters	102
Vol., Å^3	1157.4(5)	G.O.F.	2.21
F(000)	480	R	0.039
Z	4	R_w	0.040
D_{calc}, gcm^{-3}	1.276	Final Diff. map (e/Å^3)	0.16

[a] Least squares refinement of $((\sin\theta)/\lambda)^2$ for 21 reflections $\theta > 18$.
[b] $I > 2.00\sigma(I)$. Corrections: Lorentz polarization and secondary extinction (coefficient: 0.63311×10^{-6}).

eters are presented in Table 1. Lattice constants were obtained from 22 centered reflections (38.37° ≤ 2θ ≤ 47.69°). The structure was solved by direct methods[8] and refined using the TEXSAN crystallographic software package of Molecular Structure Corporation.[9] Scattering factors were taken from *International Tables for X-Ray Crystallography*[10] and corrected for anomalous dispersion. All non-H atoms were refined anisotropically. The hydrogen atoms were located from difference maps generated at various stages during the

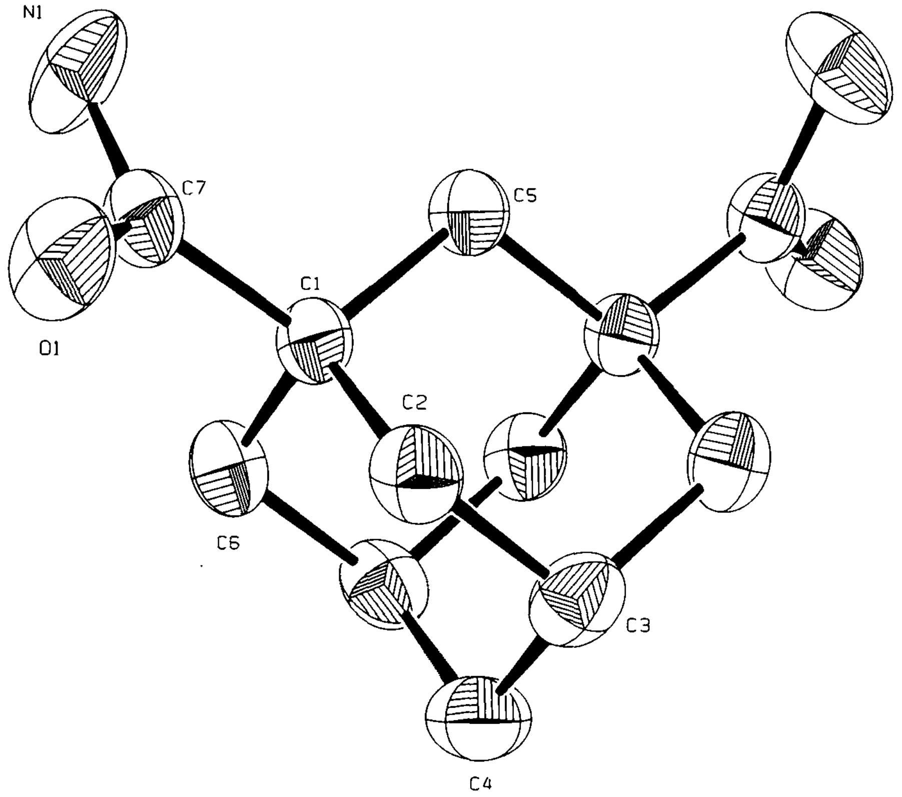

Fig. 1. ORTEP[11] diagram and atom numbering scheme of 1,3-adamantane dicarbonamide.

refinement and their isotropic thermal parameters were set 20% greater than those of the bonding partners (at the time of inclusion). The position of the hydrogen atoms were refined as there was sufficient data and no abnormal shifts resulted. The final least squares cycle was calculated with 34 atoms and 102 parameters and afforded $R = \Sigma(F_o - F_c)^2/\Sigma F_o = 0.039$, $R_W = \Sigma[W(F_o - F_c)^2/\Sigma(WF_o^2)]^{1/2} = 0.040$.

Results and discussion

ORTEP[11] perspective views of the title compound are presented in Figs. 1 and 2. Fractional atomic coordinates and listings of important bond lengths and angles are presented in Tables 2 and 3, respectively.

The observed structure [bond distances and angles] of the adamantane moiety in the title compound is not significantly different [$\Delta D \leq 3\sigma$] from that reported for 1,3-adamantane dicarbonylchloride.[3] The structure of the diacid chloride reveals a crystallographic mirror plane while the title compound has a two fold axis. The structure of the carbonyl moieties in the title compound [O1–C7 = 1.235(2) Å, C1–C7 = 1.525(2) Å, O1–C7–C1 = 121.1(2)°] is significantly different from the related diacid chloride of adamantane [O–C = 1.177(5) Å, C–C = 1.517(5) Å, O–C–C = 128.4(3)°][3] or the tetracid of adamantane [O–C = 1.216(1) Å, C–C = 1.523(1) Å, O–C–C = 123.26(10)°].[4] These differences in structure may be due to the difference in electronegativity of the substituent groups [Cl/OH vs H_2N], π bonding availability or hydrogen bonding to the groups. The diacid chloride does not show any hydrogen bonding but has long range contacts similar to those

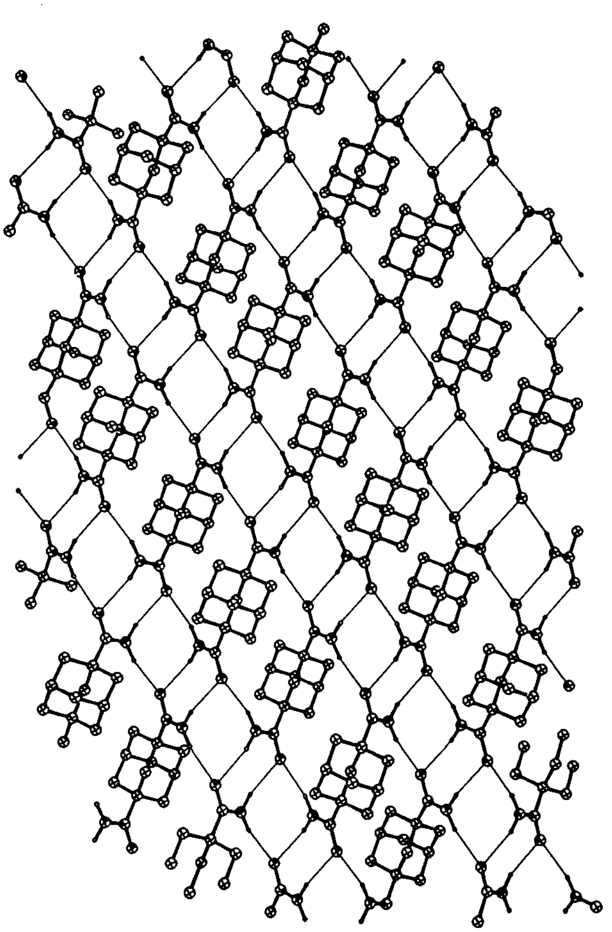

Fig. 2. ORTEP[11] view of 1,3-adamantane dicarbonamide showing the two dimensional network.

Table 2. Final fractional atomic coordinates x, y, and z and $B_{(eq)}$ for 1,3-adamantane dicarbonamide

Atom	x	y	z	B (eq)
O(1)	0.6835(2)	0.0651(1)	0.4617(1)	4.26(7)
N(1)	0.6694(2)	−0.0202(1)	0.6507(2)	4.6(1)
C(1)	0.8681(2)	0.1004(1)	0.6664(2)	2.53(8)
C(2)	0.9592(3)	0.1578(1)	0.5633(2)	3.08(9)
C(3)	1.0885(3)	0.2148(1)	0.6460(2)	3.3(1)
C(4)	1.0000	0.2718(2)	3/4	3.9(1)
C(5)	1.0000	0.0439(2)	3/4	2.7(1)
C(6)	0.7797(2)	0.1580(1)	0.7733(2)	3.2(1)
C(7)	0.7332(2)	0.0466(1)	0.5851(2)	2.95(8)

Table 3. Intramolecular bond distances (Å) and angles (°) for 1,3-adamantane dicarbonamide

Distances

atom	atom	distance	atom	atom	distance
O(1)	C(7)	1.235(2)	C(1)	C(7)	1.525(2)
N(1)	C(7)	1.326(2)	C(2)	C(3)	1.530(3)
C(1)	C(2)	1.533(3)	C(3)	C(4)	1.524(3)
C(1)	C(5)	1.542(2)	C(3)	C(6)	1.533(3)
C(1)	C(6)	1.547(3)			

Angles

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(5)	108.8(1)	C(2)	C(3)	C(6)	109.5(2)
C(2)	C(1)	C(6)	108.9(2)	C(4)	C(3)	C(6)	110.1(2)
C(2)	C(1)	C(7)	110.2(1)	C(3)	C(4)	C(3)	108.9(2)
C(5)	C(1)	C(6)	108.6(1)	C(1)	C(5)	C(1)	110.7(2)
C(5)	C(1)	C(7)	112.1(2)	C(1)	C(6)	C(3)	109.4(2)
C(6)	C(1)	C(7)	108.1(1)	O(1)	C(7)	N(1)	120.8(2)
C(1)	C(2)	C(3)	110.1(2)	O(1)	C(7)	C(1)	121.1(2)
C(2)	C(3)	C(4)	110.0(2)	N(1)	C(7)	C(1)	118.2(2)

seen in interhalogen compounds while the tetracid has two strong hydrogen bonds to each substituent group. The carbon-nitrogen bond [C7-N1 = 1.326(2) Å] in the title compound is approximately the distance expected for a C(sp^2)-N(sp^2) bond.[12]

The substituent groups in the title compound have torsion angles [O1-C7-C1-C5 = −137.2(2)°] that place the groups out of the mirror plane of the adamantane group. The pattern and length of the hydrogen bonds in the dicarbonamide [O1-H1A = 2.09(3) Å, O1-H1B = 2.12(3) Å] is similar to those seen in urea derivatives.[13] The rigid adamantane group prevents intramolecular hydrogen bonding from occurring therefore according to Etter's Rules the molecules must form intermolecular bonds between the best proton donors and acceptors featuring three center bonds to the carbonyl groups.[13] The net effect of these hydrogen bonds is to create a two dimensional sheet of monomer units with rows of adamantane groups alternating above and below the plane (Fig. 2) held together by the hydrogen bonds.

Acknowledgments

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References

1. Steudel, R. (Ed.) *The Chemistry of Inorganic Ring Systems* Elsevier: Amsterdam, 1992.
2. Bridson, J.N.; Copp, S.B.; Schriver, M.J.; Zhu, S.; Zaworotko, M.J. *Can. J. Chem.* **1994,** *72*, 1143–1153.
3. Leser, J.; Rabinovich, D. *Acta Cryst.* **1978,** *B34*, 2264-2269.
4. Ermer, O. *J. Amer. Chem. Soc.* **1988,** *110*, 3747–3754.
5. Prelog, V.; Seiwerth. *Chem. Ber.* **1941,** *74*, 1769.
6. Novakov, I.A.; Kulev, I.A.; Radchenko, S.S.; Birznieks, K.A.; Boreko, E.I.; Vladyko, G.V.; Korobchenko, L.V. *Khim.-Farm. Zh.* **1987,** *21*, 454–458. Morozov, P.A.; Morozova, N.K.; Il'yasov, A.V. *Zh. Strukt. Khim.* **1983,** *24*, 127–128. Shvekhgeimer, G.A.; Kuz'micheva, L.K. *Khim. Geterotsikl. Soedin.* **1976,** 1654–1657.
7. Furniss, B.S.; Hannaford, A.J.; Smith, P.W.G.; Tatchell, A.R. *Vogel's Textbook of Practical Organic Chemistry* (5th ed.); John Wiley and Sons: New York, 1989.
8. Gilmore, C.J. *J. Appl. Cryst.* **1984,** *17*, 42–46, Beurskens, P.T. DIRDIF technical report 1984/1, Nijmegen, 1984.
9. TEXSAN—TEXRAY, Structure Analysis Package, Molecular Structure Corporation, 1985.
10. Cromer, D.T.; Waber, J.T. *International Tables for X-Ray Crystallography* Vol. IV; The Kynoch Press: Birmingham, 1974, Table 2.2A.
11. Johnson, C.K. ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, TN, 1976.
12. March, J. *Advanced Organic Chemistry* (3rd Ed.) John Wiley and Sons: New York, 1985; p. 19, and references therein.
13. Etter, M.C.; Urbanczyk-Lipkowska, Z.; Zia-Ebrahimi, M.; Panunto, T.W. *J. Amer. Chem. Soc.* **1990,** *112*, 8415–8426.