Structure of 1,3,5,7-Tetranitro-3,7-diazabicyclo[3.3.0]octane. Structure Solution from Molecular Packing Analysis

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Abstract

The structure was solved with the molecular packing program *MOLPAK*, starting with a molecular mechanics-geometry optimized model of an isolated molecule. The best predicted crystal structures from the *MOLPAK* procedure were subjected to lattice energy refinement with the *WMIN* program. The *MOLPAK/WMIN*-predicted crystal structure, whose cell parameters were closest to the experimental values, gave an initial R of 0.48 for the 173 data to $\theta = 25°$. Four cycles of least-squares refinement of x, y, z and U gave an R of 0.27 for the 277 data to $\theta = 30°$. Final $R = 0.038$, $wR = 0.044$. There are no unusual intermolecular distances and crystal packing is normal.

1. Introduction

Nitro- and nitramine-containing compounds are important as potential high-energy density materials. Poly-nitropolycyclic 'cage' compounds (Marchand, 1988, 1989) are of particular interest, because of the molecular energy content associated with ring strain. In this connection, 1,3,5,7-tetranitro-3,7-diazabicyclo[3.3.0]-octane (I) has been synthesized recently at Geo-Centers/ARDEC, starting with 3,7-ditosyl-3,7-di-aza-1,5-cyclooctanedione *via* a transannular cyclization reaction (Dave, Forohar, Axenrod, Qi, Yazdekhasti & Yazdekhasti, 1994). A search of the literature revealed only one example of the 3,7-diazabicyclo[3.3.0]octane ring system (Altman, Babad, Itzchaki & Ginsburg, 1966) and no polynitrated examples. Therefore, it was of

interest to examine the structural features of the compound.

The structure solution was achieved by an *ab initio* molecular packing procedure that has been under development in our laboratory over the last several years.

2. Experimental

Experimental details are given in Table 1.* Refinement was by full-matrix least-squares; minimization of $\Sigma\{[1/\sigma^2(F_o)](F_o - F_c)^2\}$; anisotropic temperature factors for C, N and O; H atoms initially positioned from the C-atom framework and refined with individual isotropic temperature factors.

The majority of the crystallographic calculations were performed with the *TEXSAN* (Molecular Structure Corporation, 1989) program system on DEC VAX-Station II and 3100 computers; structure solution with the molecular packing program *MOLPAK* (Holden, Du & Ammon, 1993) was carried out on an IBM *RS6000* model 390 workstation. Fig. 1 was drawn with the *Chem3D* program (Cambridge Scientific Computing, 1993a) and labeled with the *CHEMDRAW* program (Cambridge Scientific Computing, 1993b) on an Apple MacIntosh IIx workstation and printed on an Apple LaserWriter IINTX. Fig. 2 was created with the *ORTEP* (Johnson, 1976) subprogram of *TEXSAN*; the *PLOTMD* program (Luo, Ammon & Gilliland, 1989) was used to display the drawing on a VAXStation monitor, add labels and prepare a print file for a Hewlett Packard Laser-Jet II printer.

3. Discussion

The structure was solved with the use of an *ab initio* crystal structure prediction procedure. The procedure and programs have been described in detail (Holden, Du &
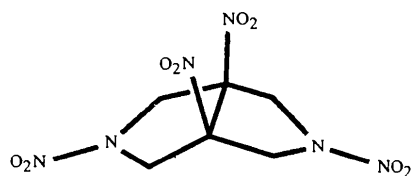
(I)

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* A list of observed and calculated structure factors has been deposited with the IUCr (Reference: FG0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

Crystal data

Chemical formula	$C_6H_8N_6O_8$
Chemical formula weight	292.16
Cell setting	Monoclinic
Space group	$P2_1/c$
a (Å)	11.559 (2)
b (Å)	8.018 (1)
c (Å)	11.697 (2)
β (°)	98.01 (1)
V (Å^3)	1073.5 (3)
Z	4
D_x (Mg m^{-3})	1.807
Radiation type	Cu $K\alpha$
Wavelength (Å)	1.54178
No. of reflections for cell parameters	29
θ range (°)	51.2–72.8
μ (mm^{-1})	1.43
Temperature (K)	223
Crystal form	Irregular section of plate
Crystal size (mm)	0.16 × 0.13 × 0.06
Crystal color	Colorless

Data collection

Diffractometer	Siemens *R3m/V*
Data collection method	$\theta/2\theta$ scans
Absorption correction	None
No. of measured reflections	1676
No. of independent reflections	1537
No. of observed reflections	1118
Criterion for observed reflections	$I > 3\sigma(I)$
R_{int}	0.012
θ_{max} (°)	56.1
Range of h, k, l	$-11 \rightarrow h \rightarrow 12$
	$-8 \rightarrow k \rightarrow 8$
	$-12 \rightarrow l \rightarrow 12$
No. of standard reflections	3
Frequency of standard reflections (min)	60
Intensity decay (%)	−2.2

Refinement

Refinement on	F
R	0.038
wR	0.044
S	2.06
No. of reflections used in refinement	1118
No. of parameters used	214
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.03F_o)^2]$
$(\Delta/\sigma)_{max}$	0.03
$\Delta\rho_{max}$ (e Å^{-3})	0.23
$\Delta\rho_{min}$ (e Å^{-3})	−0.24
Extinction method	Zacharisen (1968)
Extinction coefficient	0.7 (1) × 10^{-5}
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Computer programs

Data collection	*P3/PC* (Siemens, 1989a)
Cell refinement	*P3/PC* (Siemens, 1989a)
Data reduction	*XDISK* (Siemens, 1989b)
Structure solution	*MOLPAK* (Holden, Du & Ammon, 1993)
Structure refinement	*TEXSAN* (Molecular Structure Corporation, 1989)

Ammon, 1993) and only a brief outline will be given here. Investigations of the molecular coordination environments in a number of triclinic to orthorhombic

crystal structures with one molecule per asymmetric unit have revealed common patterns in the coordination geometries for each of the space groups. The coordination for $P2_1/c$ pertinent to this determination is illustrated in Fig. 1. There are three well defined coordination geometries for $P2_1/c$, which have been given the codes AK, AI and AM. The molecular packing program *MOLPAK* (Holden, Du & Ammon, 1993) was written to reconstruct the various geometries starting with
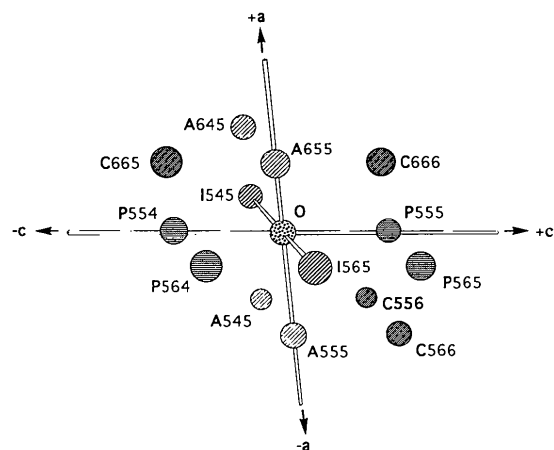

Fig. 1. Coordination sphere for a $P2_1/c$ structure (*MOLPAK* AI category), which illustrates the 14 molecules surrounding a central molecule (O). The I, A, C and P designations refer to the symmetry operations x, y, z; $-x, \frac{1}{2} + y, \frac{1}{2} - z$; $-x, -y, -z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$, respectively. The three-digit number following each capital letter is similar to an *ORTEP* translation code. For example, P564 refers to a molecule (relative to O) at $(x, \frac{1}{2} - y, \frac{1}{2} + z) + (0, +1, -1) = (x, \frac{3}{2} - y, z - \frac{1}{2})$. This coordination is characterized by IU's along the b axis (coincident with I545→I565) and two sets of PU's (P555 and P554; P565 and P564) in the bc plane.
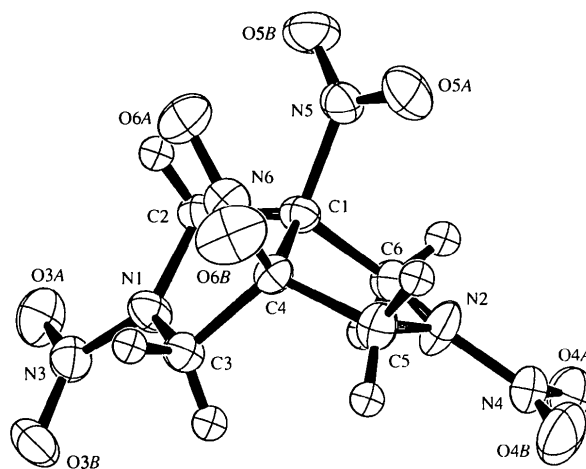

Fig. 2. *ORTEP* (Johnson, 1965) drawing. The C, N and O atoms are shown as 50% ellipsoids and the H atoms are drawn as spheres with $B = 1.5$ Å^2.

models for the compounds of interest. *MOLPAK* uses a rigid-body model of the compound (the search probe) to build a number of packing arrangements (possible crystal structures) with the predetermined coordination geometry. All unique orientations of the search probe (with respect to fixed Cartesian axes) are examined and the molecules are fit together, in the appropriate coordination geometry, with a repulsion-only potential function. The best (smallest volume) of the *MOLPAK* packing arrangements are refined with the *WMIN* procedure (Busing, 1981).

The extent of planarity of the nitramine amino nitrogen was a major region of uncertainty in obtaining a suitable search probe for the *MOLPAK* procedure. A search of the Cambridge Structural Database revealed nitramine nitrogen planarities (sum of the three angles at N) ranging from 293 (N in a three-membered ring) to 338 (four-membered ring), 354 (five-membered ring) or 360° (no ring). There were no examples of molecules with the 1-nitroazacyclopentane moiety. Geometry optimization of models with the AM1 semi-empirical molecular orbital procedure (Dewar, Zoebisch, Healy & Stewart, 1985; Stewart, 1994) gave N planarities from 343 to 348°. Three conformations were produced: (IIa) both nitramine nitro groups away from the C-nitro groups (down in I); (IIb) both toward the C-nitro groups (up); (IIc) one up and one down. Conformation (IIa) had the most extreme shape. None of these conformations lead to a solution of the structure and these trials will not be discussed further.

We previously found that geometry optimization of the R_2N CO_2^- moiety with the molecular mechanics ($MM2^*$) force field in the *MACROMODEL* program (Still, 1994) led to flat amino N's (360° angle sum). In the present case, a model was constructed with CO_2 in place of the two nitramine NO_2 groups; the geometry was optimized with *MACROMODEL* and the C atoms in the CO_2 groups replaced by N (360° planarity). No further optimization was performed. This search probe led ultimately to a structure solution. A least-squares fit of the 12 central C and N atoms in the search probe to the refined X-ray model gave an r.m.s. deviation of 0.153 Å (maximum deviation for a nitro O atom was 0.594 Å). In a retrospective examination of the search probe geometry, an initial model was subjected to complete geometry optimization with the *ab initio* 6-31G* basis set and the *Gaussian92* program system (Frisch, Trucks, Schlegel, Gill, Johnson, Wong, Foresman, Robb, Head-Gordon, Replogle, Gomperts, Andres, Raghavachari, Binkley, Gonzalez, Martin, Fox, Defrees, Baker, Stewart & Pople, 1993), and a least-squares fit to the X-ray model gave a 12-atom r.m.s. deviation of 0.064 Å (maximum deviation of 0.349 Å for a nitro O atom); the sums of angles at the amino N atoms were 360°.

Ideally, a complete *MOLPAK* space group search (presently coded for $P1$, $P\bar{1}$, $P2_1$, $P2_1/c$, $C2/c$, $P2_12_12_1$, $Pca2_1$, $Pna2_1$ and $Pbca$) followed by *WMIN* refinement (force-field crystal structure refinement by lattice energy

Table 2. *Comparison of the cell constants from the X-ray and predicted structures**

	X-ray (Å)	Δ_1 (%)	Δ_2 (%)	Δ_3 (%)
a (Å)	11.559	−0.8	−1.2	−1.5
b (Å)	8.018	8.4	2.2	4.4
c (Å)	11.697	0.1	0.5	0.7
β (°)	98.01	−6.1	0.2	−2.1

* X-ray = experimental cell constants. Δ_1, Δ_2 and Δ_3 give per cent differences between the predicted and experimental unit-cell parameters [% = 100 × (predicted − X-ray)/X-ray]. Nos. 1, 2 and 3 refer to calculations with the molecular mechanics-derived, X-ray and 6-31G* basis set optimized structure search probes, respectively.

minimization) of the best of the *MOLPAK*-generated structures should point to the 'correct' structure as that with the lowest lattice energy. In tests with known crystal structures, in which the search probe was identical to the X-ray structure model, the predicted (correct) crystal structure was always among the lowest energy structures, but it did not necessarily have the lowest energy. We attribute this to either (1) the simple form of the *WMIN* algorithm and quality of the parameterization and/or (2) the discovery of an unknown more stable polymorph. The most likely reason for the energy discrepancy is (1) in most instances. In cases in which an *ab initio* model is used as the search probe, the correct structure may not be among the lowest energy-predicted crystal structures. When an experimental space group and unit-cell parameters are known, the best *MOLPAK/WMIN*-generated crystal structure is that which gives the closest agreement with these data.

The present *MOLPAK/WMIN* calculations were restricted to the three $P2_1/c$ coordination geometries AI, AK and AM. All unique orientations of the search probe (C—H bond lengths and geometries and nitro group N—O bond lengths were 'idealized' to standard values of Csp^3—H = 1.098 and N—O = 1.22 Å) were examined for each of the coordination geometries; the orientations were created by rotation in an Eulerian system over the range 180° in 10° increments for each axis for a total of $19^3 = 6859$ orientations. Each orientation was converted into a hypothetical crystal structure with the appropriate coordination geometry and a repulsion-only force field. The 25 smallest volume *MOLPAK* packing arrangements were refined with the *WMIN* procedure (lattice energy minimization), which adjusts the unit-cell constants and the orientation and position of the search probe. In the present case the correct structure was not identified by the lowest *WMIN*-calculated lattice energy, but by a comparison of the experimental and calculated reduced cell parameters. These data are summarized in Table 2. The rather high lattice energy must be associated with the 'approximate' search probe structure, since similar *MOLPAK/WMIN* calculations with a search probe based on the refined X-ray structure gave a lower lattice energy by approxi-

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\mathring{A}^2)$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.2965 (2)	0.4004 (4)	0.7226 (2)	0.073 (1)
C2	0.3825 (3)	0.5310 (4)	0.6937 (2)	0.078 (2)
C3	0.2177 (2)	0.5111 (4)	0.5348 (2)	0.079 (2)
C4	0.1794 (2)	0.4300 (3)	0.6429 (2)	0.068 (2)
C5	0.1173 (3)	0.2614 (4)	0.6233 (3)	0.096 (2)
C6	0.3277 (3)	0.2218 (4)	0.6917 (3)	0.089 (2)
N1	0.3375 (2)	0.5583 (3)	0.5729 (2)	0.085 (2)
N2	0.2146 (2)	0.1480 (3)	0.6525 (2)	0.114 (2)
N3	0.4006 (2)	0.6351 (3)	0.5014 (2)	0.093 (2)
N4	0.2065 (3)	−0.0138 (3)	0.6226 (2)	0.129 (2)
N5	0.2834 (2)	0.4027 (3)	0.8493 (2)	0.099 (2)
N6	0.1010 (2)	0.5546 (3)	0.6932 (2)	0.094 (2)
O3A	0.4998 (2)	0.6816 (3)	0.5407 (2)	0.124 (2)
O3B	0.3547 (2)	0.6503 (3)	0.4006 (2)	0.125 (2)
O4A	0.2976 (2)	−0.0956 (3)	0.6411 (2)	0.161 (2)
O4B	0.1100 (2)	−0.0661 (3)	0.5825 (2)	0.186 (2)
O5A	0.1983 (2)	0.3290 (3)	0.8761 (2)	0.157 (2)
O5B	0.3592 (2)	0.4701 (3)	0.9149 (2)	0.142 (2)
O6A	0.1458 (2)	0.6533 (3)	0.7649 (2)	0.124 (2)
O6B	−0.0020 (2)	0.5516 (3)	0.6524 (2)	0.160 (2)

Table 4. *Bond lengths* $(\mathring{A})$ *and angles* $(°)$

C1—C2	1.514 (4)	N4—O4B	1.222 (3)
N1—N3	1.334 (3)	C3—N1	1.446 (4)
C1—C4	1.552 (4)	N5—O5A	1.225 (3)
N2—N4	1.344 (4)	C4—C5	1.533 (4)
C1—C6	1.532 (4)	N5—O5B	1.209 (3)
N3—O3A	1.232 (3)	C4—N6	1.521 (4)
C1—N5	1.511 (4)	N6—O6A	1.215 (3)
N3—O3B	1.230 (3)	C5—N2	1.450 (4)
C2—N1	1.452 (4)	N6—O6B	1.220 (3)
N4—O4A	1.235 (4)	C6—N2	1.449 (4)
C3—C4	1.540 (4)		
C2—C1—C4	107.7 (2)	N2—N4—O4A	116.1 (3)
C2—N1—N3	121.8 (2)	C1—C4—C5	107.8 (2)
C2—C1—C6	114.2 (2)	N2—N4—O4B	117.3 (3)
C3—N1—N3	120.8 (2)	C1—C4—N6	112.6 (2)
C2—C1—N5	111.7 (2)	O4A—N4—O4B	126.6 (3)
C5—N2—C6	117.1 (2)	C3—C4—C5	115.6 (2)
C4—C1—C6	102.4 (2)	C1—N5—O5A	116.0 (3)
C5—N2—N4	121.3 (3)	C3—C4—N6	107.1 (2)
C4—C1—N5	112.9 (2)	C1—N5—O5B	117.7 (3)
C6—N2—N4	120.3 (3)	C5—C4—N6	110.2 (2)
C6—C1—N5	107.6 (2)	O5A—N5—O5B	126.2 (3)
N1—N3—O3A	117.9 (2)	C4—C5—N2	100.7 (2)
C1—C2—N1	99.5 (2)	C4—N6—O6A	118.4 (2)
N1—N3—O3B	116.5 (2)	C1—C6—N2	103.0 (2)
C4—C3—N1	103.3 (2)	C4—N6—O6B	115.9 (2)
O3A—N3—O3B	125.6 (2)	C2—N1—C3	117.3 (2)
C1—C4—C3	103.4 (2)	O6A—N6—O6B	125.5 (3)

mately $17\,kJ\,mol^{-1}$. The range of *WMIN*-calculated lattice energies for the 25 hypothetical crystal structures based on the molecular mechanics-derived model was -144.9 to $-177.7\,kJ\,mol^{-1}$ (correct structure was $-153.2\,kJ\,mol^{-1}$), the corresponding values based on an X-ray search probe were -149.5 to $-173.2\,kJ\,mol^{-1}$ ($-170.4\,kJ\,mol^{-1}$) and the values for the 6-31G* basis set optimized model were -139.5 to $-177.4\,kJ\,mol^{-1}$ ($-166.68\,kJ\,mol^{-1}$).

Placement of the hypothetical crystal structure into the experimental unit cell required changing the fractional coordinates (see Table 3) to account for differences between the predicted and experimental cell parameters. An initial structure factor calculation for the 173 data to $\sin\theta/\lambda$ of 0.274 ($\theta = 25°$) gave $R = 0.48$, $wR = 0.61$. Several cycles of least-square refinement of the x, y, z and U parameters with the 277 data to $\sin\theta/\lambda$ of 0.324 ($\theta = 30°$) gave $R = 0.27$, $wR = 0.36$. Structure refinement was completed in the usual manner.

An *ORTEP* drawing is shown in Fig. 2 and bond lengths and angles are given in Table 4. The structure is the first example of a molecule containing the 1-nitro-1-azacyclopentane moiety with four sp^3 hybridized C atoms. The sums of angles at the two amino N atoms are 358.1 and 359.8°. The crystal packing is normal. There are no intermolecular distances less than the appropriate van der Waals contact values.

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