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References

- BURROWS, B. F., TURNER, W. B. & WALKER, E. R. H. (1975). *J. Chem. Soc. Perkin I*. In the press.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst. A* **27**, 368–376.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY 70 System of Crystallographic Programs, Univ. of Maryland.

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1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN)

BY A. SANTORO

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

C. S. CHOI

Feltman Research Laboratory, Picatinny Arsenal, Dover, N.J. 07801, U.S.A. and Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.

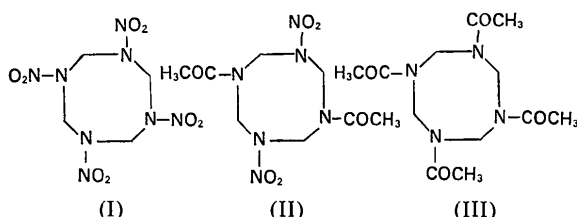
AND J. E. ABEL

Feltman Research Laboratory, Picatinny Arsenal, Dover, N.J. 07801, U.S.A.

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Abstract. $C_8H_{14}N_6O_6$, monoclinic, $P2_1/c$, $a=7.422(1)$, $b=13.253(2)$, $c=6.156(1)$ Å, $\beta=103.38(1)^\circ$, $Z=2$, $D_x=1.636$, $D_m=1.63$ g cm $^{-3}$, $F(000)=304$. X-ray intensities were measured with Mo $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations to final R and R_w values of 4.1 and 4.8%, respectively, for 1149 observed reflections.

Introduction. Tetraazacyclooctane derivatives are important intermediates in the synthesis of cyclotetramethylenetetranitramine (I), also known as HMX, which is a well known explosive and a by-product in the manufacture of cyclotrimethylenetrinitramine (RDX). One such derivative, 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (II), hereafter referred to as DADN, is obtained in good yields from 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane without formation of triazine products (Yoshida, Sen & Thyagarajan, 1973; Siele, Warman & Gilbert, 1974).



Chemically, DADN is closely related to HMX and to its tetraacetyl analog, 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane, also known as TAT (III). All these compounds are based on the same eight-mem-

bered C–N ring, but the side groups vary from compound to compound. The presence of two –NO₂ and two –COCH₃ groups suggests that many important structural features in DADN must be different from those found in the α , β and δ modifications of HMX and in the stable phase of TAT (Eiland & Pepinsky, 1955; Cady, Larson & Cromer, 1963; Choi & Boutin, 1970; Cobble-dick & Small, 1974; Choi, Abel, Dickens & Stewart, 1973). The X-ray study of DADN, therefore, was undertaken not only to provide information necessary for the characterization of the compound, but also to permit a comparison of the packing and of the molecular configuration of DADN with those of the previously determined structures.

Colorless crystals of DADN were obtained by evaporation of a benzene solution. Crystal symmetry and approximate lattice parameters were determined from zero- and upper-level precession photographs. The 2θ angles of 12 strong reflections in the range 20–45° were measured with a diffractometer using Mo $K\alpha$ radiation ($\lambda=0.710688$ Å) and the cell parameters were refined by least-squares analysis.

A plate-like crystal of approximate dimensions 0.2 × 0.35 × 0.5 mm was mounted on a three-circle diffractometer equipped with a Si(Li) solid-state detector (Hubbard, 1973). Intensities were measured with the 2θ scan method for all the reflections in a hemisphere with 2θ up to 55° with Mo $K\alpha$ radiation. In total, 3064 reflections were measured. Intensities which were less than four times the standard deviation were considered ‘unobserved’. Equivalent reflections were merged into a unique set of 1342 reflections of which 193 were unobserved (the agreement index of equivalent reflections was 0.025). The observed in-

Table 1. *Final least-squares parameters for the structure of DADN*

The values of the fractional coordinates and of the temperature factors are multiplied by 10^4 for the heavy atoms. For the hydrogen atoms the positional parameters and the isotropic temperature factors are multiplied by 10^3 and by 10, respectively. Numbers in parentheses are standard deviations in the last significant digits. The anisotropic temperature factor has the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1345 (2)	-1081 (1)	507 (2)	131 (3)	30 (1)	173 (4)	9 (1)	38 (3)	0 (1)
C(2)	1457 (2)	658 (1)	2414 (2)	166 (3)	31 (1)	131 (3)	7 (1)	19 (3)	2 (1)
C(3)	1673 (2)	1469 (1)	-1145 (2)	151 (3)	25 (1)	172 (4)	-5 (1)	39 (3)	2 (1)
C(4)	3734 (2)	1471 (1)	-343 (3)	148 (3)	49 (1)	259 (5)	-20 (1)	40 (3)	2 (2)
N(1)	2105 (2)	-396 (1)	2353 (2)	128 (2)	31 (1)	157 (3)	6 (1)	6 (2)	10 (1)
N(2)	655 (2)	1009 (1)	189 (2)	124 (2)	25 (1)	134 (3)	-1 (1)	18 (2)	4 (1)
N(3)	2914 (2)	-794 (1)	4365 (2)	126 (2)	45 (1)	178 (4)	10 (1)	18 (2)	23 (1)
O(1)	3474 (2)	-1663 (1)	4462 (2)	213 (3)	49 (1)	292 (4)	39 (1)	4 (3)	34 (1)
O(2)	3102 (2)	-223 (1)	5982 (2)	249 (3)	63 (1)	149 (3)	18 (1)	6 (2)	6 (1)
O(3)	878 (2)	1835 (1)	-2916 (2)	192 (3)	49 (1)	193 (3)	6 (1)	50 (2)	36 (1)

tensities were corrected for Lorentz and polarization factors but no absorption correction was applied because of the small linear absorption coefficient of the material ($\mu = 1.51 \text{ cm}^{-1}$).

The structure amplitudes were converted to normalized structure factors (*E*) by the *NORMSF* program of the X-RAY system (Stewart, 1972). Intensity statistics confirmed the center of symmetry in the structure. A set of signs was assigned to 194 reflections with *E* larger than 1.0 by the *PHASE* program of the X-RAY system. An *E* map calculated with these signs revealed the heavy-atom positions correctly. These positions were used in the initial stages of least-squares refinement by the *RFINE* program (Finger, 1972).

Full-matrix least-squares refinement of the heavy atoms, first with isotropic and then with anisotropic temperature factors, gave a conventional *R* of about 12% [$R = \sum(|F_o| - |F_c|) / \sum F_o$]. The function minimized was $\sum w(|F_o| - |F_c|)^2$, in which the weights *w* were those calculated from counting statistics. At this stage, the positions of all the hydrogen atoms were located in a difference Fourier synthesis. The structure was then refined by including the hydrogen atoms with isotropic thermal parameters. Secondary extinction corrections (Zachariasen, 1968) were applied in the last stages of

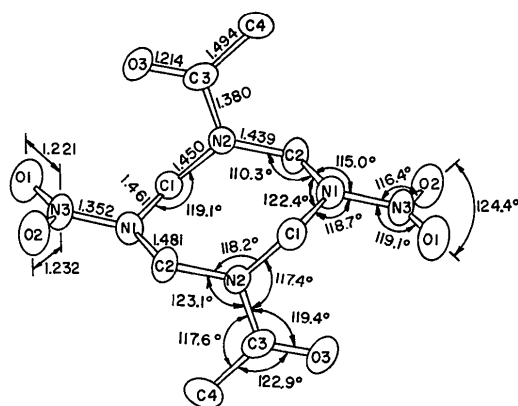


Fig. 1. View of a molecule of DADN with thermal ellipsoids and unique bond distances and angles (the estimated standard deviations are 0.002 Å for the bond distances and 0.1° for the bond angles).

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	185 (3)	-93 (1)	-81 (3)	15 (3)
H(2)	172 (2)	-175 (1)	102 (3)	11 (3)
H(3)	251 (3)	107 (1)	317 (3)	17 (3)
H(4)	50 (3)	69 (1)	333 (3)	23 (4)
H(5)	423 (3)	164 (2)	-161 (5)	48 (6)
H(6)	427 (3)	83 (2)	24 (4)	38 (5)
H(7)	411 (4)	197 (2)	68 (5)	49 (6)

refinement. Five of the strongest reflections (10 $\bar{2}$, 020, 040, 11 $\bar{1}$, 21 $\bar{1}$) were heavily affected by extinction and were omitted from subsequent calculations.

After the final cycle of refinement the *R* values for all the observed reflections were *R* = 0.041 and *R_w* = 0.048 where $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. The maximum and the average shift/error were 0.07 and 0.01, respectively. The final atomic parameters are given in Table 1.*

Discussion. As there are two molecules in the unit cell of DADN the symmetry $\bar{1}$ of the space group is also a symmetry operation of the molecule. The shortest intermolecular distances (≤ 3.5 Å) between heavy atoms range from 3.14 to 3.38 Å for C-O contacts and from 3.07 to 3.30 Å for N-O contacts, with two O-O distances of 3.34 and 3.37 Å. These lengths are comparable with those found in TAT (Choi, Abel, Dickens & Stewart, 1973) and are slightly longer than those found in α -, β - and δ -HMX (Cady, Larson & Cromer, 1963; Choi & Boutin, 1970; Cobbleddick & Small, 1974). The shortest H...O intermolecular distances, which range from 2.55 to 2.75 Å, are significantly longer than those reported for β -HMX (range 2.36–2.59 Å) and for δ -HMX (range 2.32–2.67 Å).

As mentioned above, the molecule of DADN is centrosymmetrical. The same molecular symmetry and the same 'twisted-chair' configuration have been found in β -HMX, in contrast to the α and δ modifi-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31001 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

cations of HMX and to the stable phase of TAT in all of which the molecular shape is 'boat' like and consistent with an exact or an approximate twofold symmetry operation. A perspective view of the DADN molecule is given in Fig. 1 with the unique bond distances and angles. In Fig. 2(a) the short non-bonded intramolecular distances are indicated.

Because of the molecular symmetry, the four carbon atoms of the C-N ring are exactly coplanar. The same is true, of course, for the four ring nitrogen atoms. The planes of the carbon atoms and of the nitrogen atoms form a dihedral angle of 30.8° (the value of the corresponding angle for β -HMX is 29.7°). The heavy atoms in the acetyl group $-\text{COCH}_3$ and those in the nitro group $-\text{NO}_2$ are coplanar with the ring nitrogen atoms to which they are attached (the mean deviation of the atoms from the best fit plane is 0.004 \AA for the acetyl group and 0.007 \AA for the nitro group). The ring carbon atoms adjacent to N(2) are 0.16 and 0.12 \AA away from the best-fit plane through the acetyl group atoms. These deviations are larger than those found in the structure of TAT in which they range from 0.06 to 0.12 \AA . In the case of the nitro group, the C(1) atom deviates 0.41 \AA and the C(2) atom 0.04 \AA from the best-fit plane through the atoms of the group. These distances are not unusual, but are in fact quite close to those found for one of the two nitro groups of β -HMX. The plane of the acetyl group and that of the ring nitrogen atoms form an angle of 53.8° , while the corresponding angle for the nitro group is 41.0° .

The bond distances and angles found in the present study agree closely with those determined for α -, β - and δ -HMX and for TAT. As in the case of TAT, the C-O bond length (1.214 \AA) shows that it is a double bond and the C(acetyl)-N bond length (1.380 \AA) shows partial double bonding. The value of 1.494 \AA for the C-C distance is also somewhat shorter than a simple C-C single bond (the corrections on the bond distances due to thermal motion are around 0.003 \AA , i.e. less than twice the standard deviation).

The shortest non-bonded intramolecular distances are 2.54 , 2.82 , 2.87 , 2.84 , 3.00 , and 3.16 \AA for C-O, C-N, C-C, N-N, N-O and O-O contacts, respectively. There are also two short H-O distances of 2.22 and 2.45 \AA . The distance N(2)-N(2') of 2.84 \AA shows that the molecule is considerably contracted along this direction, in agreement with the results reported for β -HMX (the distance N(1)-N(1') is 3.88 \AA).

The torsional angles about the bonds of the DADN molecule are indicated in Fig. 2(b). The angles about the ring bonds range from 19.8 to 65.2° and agree to within 5° with the corresponding values found in the structure of β -HMX. These values show a considerable twisting of the eight-membered ring in the two compounds.

References

CADY, H. H., LARSON, A. C. & CROMER, D. T. (1963). *Acta Cryst.* **16**, 617-623.

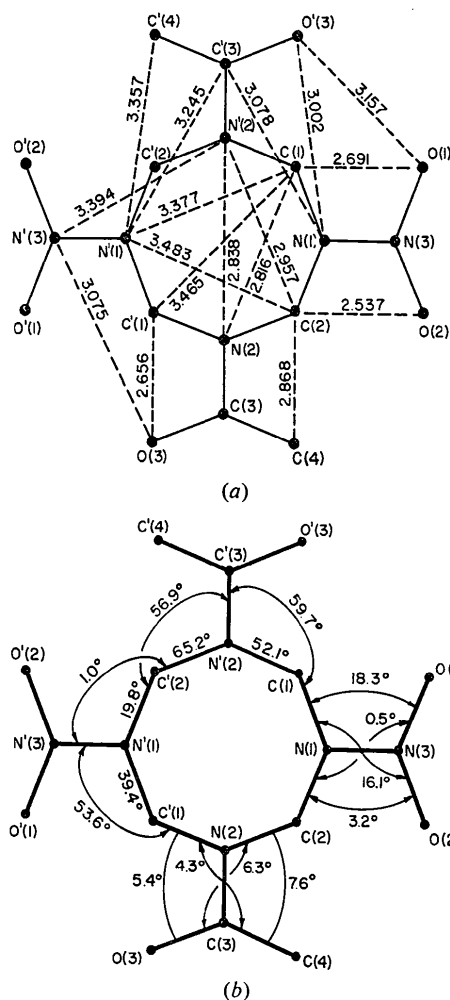


Fig. 2. Schematic illustration of the DADN molecule with (a) short non-bonded intramolecular distances, (b) torsional angles about the bonds (the angles written on ring bonds are torsional angles within the ring).

CHOI, C. S., ABEL, J. E., DICKENS, B. & STEWART, J. M. (1973). *Acta Cryst.* **B29**, 651-656.

CHOI, C. S. & BOUTIN, H. P. (1970). *Acta Cryst.* **B26**, 1235-1240.

COBBLEDICK, R. E. & SMALL, R. W. H. (1974). *Acta Cryst.* **B30**, 1918-1922.

EILAND, P. F. & PEPINSKY, R. (1955). *Z. Kristallogr.* **106**, 273-298.

FINGER, L. (1972). *RFINE. A Fortran Computer Program for Structure-Factor Calculations and Least-Squares Refinement of Crystal Structures*. Geophysical Laboratory, Carnegie Institution of Washington. Unpublished.

HUBBARD, C. R. (1973). Abstract F11, Amer. Cryst. Assoc. Winter Meeting, Univ. of Florida, Gainesville, Florida.

SIELE, V. I., WARMAN, M. & GILBERT, E. E. (1974). *J. Heterocyclic Chem.* **11**, 237-239.

STEWART, J. M. (1972). X-RAY System. Technical Report TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

YOSHIDA, H., SEN, G. & THYAGARAJAN, B. S. (1973). *J. Heterocyclic Chem.* **10**, 725-730.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212-216.