

**Crystallographic Studies of the HMX Analogs 3,3,7,7-Tetranitro-1,5-dinitroso-1,5-diazacyclooctane,  $C_6H_8N_8O_{10}$ , 1,3,3,7,7-Pentanitro-5-nitroso-1,5-diazacyclooctane,  $C_6H_8N_8O_{11}$ , and 1,3,3,5,7,7-hexanitro-1,5-diazacyclooctane,  $C_6H_8N_8O_{12}$**

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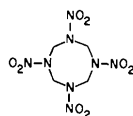
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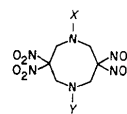
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**Abstract.**  $C_6H_8N_8O_{10}$ :  $M_r = 352.2$ , *Pbca*,  $a = 10.695$  (4),  $b = 10.607$  (3),  $c = 11.575$  (4) Å,  $Z = 4$ ,  $V = 1313.1$  Å<sup>3</sup>,  $D_x = 1.781$  Mg m<sup>-3</sup>, *Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 0.1586$  mm<sup>-1</sup>,  $F(000) = 720$ ,  $T = 294$  K,  $R = 0.051$ , 1131 unique data.  $C_6H_8N_8O_{11}$ :  $M_r = 368.2$ , *Pbca*,  $a = 10.955$  (3),  $b = 10.418$  (3),  $c = 11.756$  (3) Å,  $Z = 4$ ,  $V = 1341.7$  Å<sup>3</sup>,  $D_x = 1.823$  Mg m<sup>-3</sup>, *Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 0.1643$  mm<sup>-1</sup>,  $F(000) = 722$ ,  $T = 294$  K,  $R = 0.055$ , 1040 unique data.  $C_6H_8N_8O_{12}$ :  $M_r = 384.2$ , *Pbca*,  $a = 11.289$  (4),  $b = 10.205$  (2),  $c = 11.880$  (3) Å,  $Z = 4$ ,  $V = 1368.6$  Å<sup>3</sup>,  $D_x = 1.864$  Mg m<sup>-3</sup>, *Cu Kα*,  $\lambda = 1.5418$  Å,  $\mu = 1.562$  mm<sup>-1</sup>,  $F(000) = 784$ ,  $T = 294$  K,  $R = 0.037$ , 1117 unique data. The substances are isostructural. The  $C_6H_8N_8O_{10}$  and  $C_6H_8N_8O_{11}$  structures show some disorder of the N-linked nitroso and nitro groups. The molecules have a chair conformation similar to that of  $\beta$ -HMX. Various aspects of the molecular conformation and crystal packing are discussed.

**Introduction.** Perhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, better known as HMX (I), is one of the most important energetic nitramines, being utilized extensively in explosives and solid rocket propellants. Four solid polymorphs are known, called  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -HMX, of which the  $\beta$ -isomer is the stable room-temperature form. The crystal structures of the  $\alpha$ -,  $\beta$ -, and  $\delta$ -HMX's are known (Cady, Larson & Cromer, 1963; Choi & Boutin, 1970; Cobbleddick & Small, 1974). The eight-membered ring in the  $\beta$ -isomer exists in a chair conformation, while a chair–chair or crown conformation is found in the  $\alpha$ - and  $\delta$ -forms. In this paper, we report the crystal structures of three HMX analogs (II–IV), and compare the molecular conformations with each other and with  $\beta$ -HMX.



(I)



(II), X = Y = NO

(III), X = NO, Y = NO<sub>2</sub>

(IV), X = Y = NO<sub>2</sub>

**Experimental.** Samples of (II)–(IV) were supplied by Drs Dorothy Cichra and Horst Adolph at the Naval Surface Weapons Center, Silver Spring, MD. The two nitroso derivatives were X-rayed at the Naval Research Laboratory while the hexanitro compound was studied at the University of Maryland.  $D_m$  values were not determined. Table 1 summarizes the experimental data for the three compounds. The three structures were solved with the *MULTAN80* system of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by minimization of  $\sum w(F_o - F_c)^2$  with full-matrix least-squares techniques;  $w = 1/\sigma^2(F)$ . Anisotropic temperature factors were used for the C, N and O atoms. H atoms from  $\Delta\rho$  maps. In the case of (II) and (III), the H atoms were given the same temperature factors as the C atoms to which they were bonded, whereas in (IV), the H atoms were refined with independent isotropic temperature factors. No corrections for absorption or secondary extinction. The atomic coordinates and temperature factors are listed in Tables 2–4.\*

\* Anisotropic temperature factors, H-atom coordinates, bond lengths and angles involving H atoms, and lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38777 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The crystals are isostructural and the molecules lie on centers of symmetry ( $\frac{1}{2}, 0, 0$ ) coincident with the centers of the eight-membered rings. This position requires that the N-linked NO and NO<sub>2</sub> groups in (III) be disordered. Additionally, the NO groups in (II) show an apparent rotational disorder about the N—N bond, such that the resulting substituent appears like a lop-sided NO<sub>2</sub> group. Refinement of (II) and (III) in  $P2_12_12_1$ , which places no symmetry restrictions on the molecules and does not require the *a priori* presumption of disorder, gave results that were consis-

tent with the disordered model in  $Pbca$ . No constraints were placed on the occupancies of the disordered O atoms in (II) and (III) in the least-squares calculations. That is, the occupancies were not required to add to 1.0 in the case of (II), or to 1.5 in the case of (III), but rather these variables were permitted to refine independently. The sums of the occupancies obtained for (II) [0.857 (9) + 0.170 (10) = 1.027 (13)] and for (III) [0.960 (9) + 0.562 (9) = 1.522 (13)] are not significantly different from the 'ideal' values. The occupancies obtained for (III), the nitroso-nitro analog, suggest the presence of some small degree of nitroso-group rotational disorder similar to that found in (II).

The structures of (II)–(IV) are so similar that individual *ORTEP* drawings (Johnson, 1965) are not included in this paper. Rather, we show *ORTEP* drawings of (IV) and  $\beta$ -HMX in Figs. 1 and 3 to illustrate the similarities of these molecules. An additional view of (IV) is given in Fig. 2 to illustrate the chair conformation of the eight-membered ring in these compounds.

Molecular-fit calculations (Nyburg, 1974) for the eight-membered rings in (II)–(IV) gave r.m.s. deviations of 0.009 Å for (II) *vs* (IV) and 0.003 Å for (III) *vs*

Table 1. *Experimental data*

	(II)	(III)	(IV)
Diffractometer	Nicolet P3/F	Nicolet P3/F	Picker FACS-I
Monochromator	Graphite	Graphite	Graphite
No. of reflections to determine lattice parameters	15	23	12
$2\theta_{\max}$	49.5°	49.0°	126.9°
<i>hkl</i> range			
<i>h</i>	0–12	0–11	0–13
<i>k</i>	0–12	–11–0	0–13
<i>l</i>	0–13	–12–9	–11–11
Standard reflections	10,0,0(3.0%)	600(2.5%)	004(3.0%)
(maximum <i>I</i> deviation from average)	0,10,0(1.8%)	080(3.9%)	414(0.9%)
	0,0,10(2.8%)	008(3.1%)	024(3.5%)
Total data measured	1409	1985	2571
No. of unique data*	1131	1040	1117
No. with <i>I</i> > 3σ( <i>I</i> )*	1000	745	1087
<i>R</i>	0.051	0.055	0.037
<i>wR</i>	0.060	0.038	0.042
<i>S</i>	2.85	1.81	12.1
Average, maximum shift/error ratio	0.025, 0.377	0.100, 0.717	0.022, 0.792
Minimum, maximum height in final difference map	0.33, 0.34 e Å <sup>-3</sup>	–0.28, 0.28 e Å <sup>-3</sup>	–0.22, 0.22 e Å <sup>-3</sup>
Atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974)		
Computer programs	NRL in-house programs; least squares: Busing <i>et al.</i> (1975)		Stewart, Machin, Dickinson, Ammon, Heck & Flack (1976)
Computer	Texas Instruments Advanced Scientific Computer		UNIVAC 1100/82

\* Excluding systematically absent data.

Table 2. *Fractional coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for (II)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C(2)	0.3664 (2)	–0.0097 (2)	–0.0952 (2)	0.0334 (8)
C(3)	0.4389 (2)	–0.1314 (2)	–0.1193 (2)	0.0291 (8)
C(4)	0.5586 (2)	–0.1530 (2)	–0.0507 (2)	0.0331 (8)
N(1)	0.3768 (1)	0.0345 (1)	0.0228 (1)	0.0285 (6)
N(2)	0.3061 (3)	–0.0133 (2)	0.1061 (2)	0.051 (1)
N(3)	0.3513 (2)	–0.2455 (2)	–0.1048 (2)	0.0390 (8)
N(4)	0.4716 (2)	–0.1390 (2)	–0.2487 (2)	0.0377 (6)
O(1)†	0.2492 (2)	–0.1064 (2)	0.0810 (2)	0.064 (1)
O(2)‡	0.307 (2)	0.010 (2)	0.183 (2)	0.084 (8)
O(3)	0.3831 (2)	–0.3298 (2)	–0.0418 (1)	0.0635 (8)
O(4)	0.2550 (2)	–0.2421 (1)	–0.1595 (1)	0.0598 (8)
O(5)	0.4890 (1)	–0.2438 (2)	–0.2866 (2)	0.0607 (8)
O(6)	0.4843 (2)	–0.0427 (2)	–0.3015 (2)	0.0708 (9)

† Occupancy = 0.857 (9).

‡ Occupancy = 0.17 (1).

Table 3. *Fractional coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for (III)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C(2)	0.3692 (3)	–0.0128 (3)	–0.0938 (3)	0.030 (1)
C(3)	0.4388 (2)	–0.1378 (3)	–0.1147 (3)	0.026 (1)
C(4)	0.5566 (3)	–0.1561 (3)	–0.0470 (3)	0.031 (1)
N(1)	0.3825 (2)	0.0348 (2)	0.0224 (2)	0.026 (1)
N(2)	0.3078 (4)	–0.0119 (3)	0.1040 (4)	0.046 (1)
N(3)	0.3552 (2)	–0.2539 (3)	–0.0975 (3)	0.038 (1)
N(4)	0.4693 (2)	–0.1488 (2)	–0.2427 (3)	0.036 (1)
O(1)†	0.2512 (2)	–0.1079 (3)	0.0792 (3)	0.064 (1)
O(2)‡	0.3026 (5)	0.0404 (6)	0.1887 (6)	0.070 (3)
O(3)	0.3876 (2)	–0.3380 (2)	–0.0338 (2)	0.063 (1)
O(4)	0.2600 (2)	–0.2526 (2)	–0.1505 (2)	0.053 (1)
O(5)	0.4925 (2)	–0.2558 (2)	–0.2764 (3)	0.058 (1)
O(6)	0.4724 (2)	–0.0527 (3)	–0.2981 (3)	0.073 (1)

† Occupancy = 0.960 (9).

‡ Occupancy = 0.562 (9).

Table 4. *Fractional coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>) for (IV)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C(2)	0.3712 (2)	–0.0149 (2)	–0.0902 (2)	0.021 (3)
C(3)	0.4387 (2)	–0.1423 (2)	–0.1122 (2)	0.019 (2)
C(4)	0.5541 (2)	–0.1597 (2)	–0.0458 (2)	0.023 (3)
N(1)	0.3869 (1)	0.0345 (2)	0.0237 (1)	0.0203 (9)
N(2)	0.3115 (2)	–0.0114 (2)	0.1045 (2)	0.033 (1)
N(3)	0.3574 (2)	–0.2608 (2)	–0.0920 (1)	0.025 (2)
N(4)	0.4638 (2)	–0.1547 (2)	–0.2390 (1)	0.026 (2)
O(1)	0.2543 (2)	–0.1094 (2)	0.0804 (1)	0.037 (4)
O(2)	0.3103 (2)	0.0455 (2)	0.1942 (1)	0.040 (4)
O(3)	0.3899 (2)	–0.3452 (2)	–0.0281 (2)	0.047 (3)
O(4)	0.2640 (1)	–0.2599 (2)	–0.1426 (2)	0.026 (3)
O(5)	0.4914 (2)	–0.2641 (2)	–0.2708 (1)	0.050 (4)
O(6)	0.4576 (2)	–0.0586 (2)	–0.2968 (1)	0.072 (4)

(IV). A similar calculation for  $\beta$ -HMX *vs* (IV) gave an r.m.s. deviation of 0.136 Å, which is small when one considers that the comparison involves the tetrazocine and diazocine eight-membered rings. Calculations for all the C, N and O atoms in (II)–(IV), with the exception of the N-linked nitroso and nitro groups, gave r.m.s. deviations of 0.148 Å for (II) *vs* (IV) and 0.037 Å for (III) *vs* (IV). The smaller deviations found in the (III) *vs* (IV) calculations undoubtedly reflect that the molecules differ by only one O atom whereas there is a two-O difference between (II) and (IV).

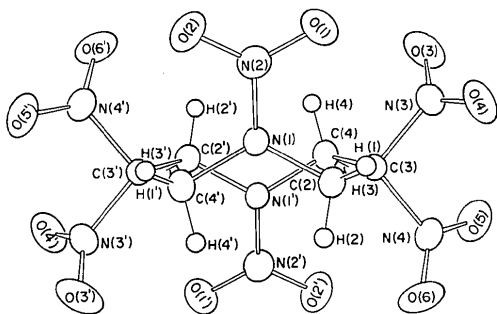


Fig. 1. ORTEP drawing of (IV) edge on to the eight-membered ring. The C, N and O atoms are drawn as 50% boundary ellipsoids and the H's are represented as 0.1 Å spheres.

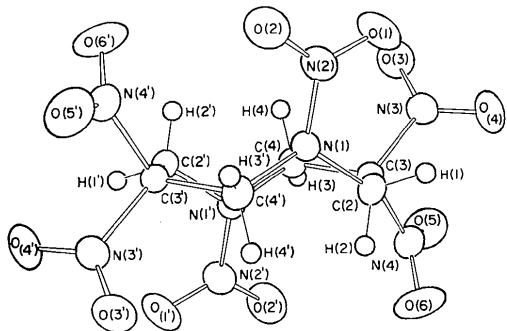


Fig. 2. ORTEP drawing of (IV) to illustrate the chair conformation of the ring.

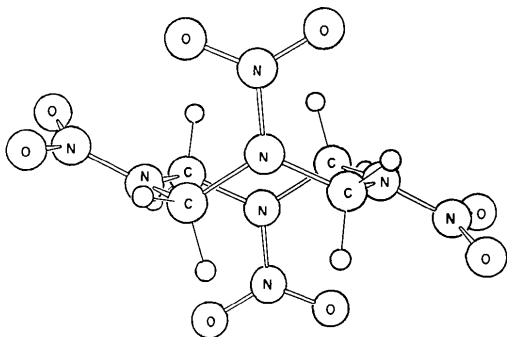


Fig. 3. ORTEP drawing of  $\beta$ -HMX (I) edge on to the eight-membered ring. The atoms are represented as spheres.

Brill & Reese (1980) have reported a detailed analysis of the intra- and intermolecular interactions in the  $\alpha$ -,  $\beta$ - and  $\delta$ -HMX's. They described the cross-ring interactions in  $\beta$ -HMX in terms of a strong transannular attraction between N(1) and C(4) at 2.78 Å which was offset in part by a 2.77 Å N(1)···N(5) repulsion. Elongation of the ring decreased the N(3)···N(7) repulsion at 3.94 Å. Structures (II)–(IV) show similar patterns of transannular distances with [N(1)···C(2'), N(1)···C(8')], [N(1)···N(1') and C(3)···C(3')] values of: (II), [2.883 (3), 2.908 (2)], 2.785 (2), 4.136 (3); (III), [2.856 (4), 2.874 (4)], 2.726 (3), 4.160 (4); (IV), [2.849 (3), 2.858 (3)], 2.707 (2), 4.178 (3) Å. The variation in the N(1) substituents from di-NO to NO, NO<sub>2</sub> to di-NO<sub>2</sub> would be expected to produce increasing amounts of positive charge on N(1) and lead to concomitant increases in the transannular repulsions and N(1)···N(1') distances in (II)–(IV). Since the observed N(1)···N(1') distances actually decrease, it is suggested that these transannular effects are relatively unimportant in determining the overall shape of the eight-membered ring.

Bond lengths, valence angles and some torsion angles for the three structures are given in Table 5. These values are quite similar, with the obvious exception of the *N*-nitroso and *N*-nitro regions. Several of the lengths and angles clearly reflect the increase in O substitution from (II) to (IV) as well as the NO/NO<sub>2</sub> disorder in (III). For example, the N(1)–N(2) distance of 1.352 (5) Å in (III) is approximately the mean of the 1.326 (3) Å in (II) and 1.366 (2) Å in (IV). The exocyclic bond angles at N(1) [C(2)–N(1)–N(2) and C(4')–N(1)–N(2)] are similar in (IV) at 117.3 (2) and 117.1 (2)°, but become progressively more unequal in (III) and (II). Although the direction of the distortion is one which presumably allows the nitroso O atom a little more room, the effect on the associated nonbonded intramolecular contacts is barely perceptible. The torsion angles underscore the conformational similarities in the three compounds.

Bond lengths and angles in the N–N=O region of (II) are very similar to those reported in *N*-nitrosodimethylamine (V) (Krebs & Mandt, 1975), with the exception of the N–O distances of 1.195 (3) Å in (II) *vs* 1.260 (6) Å in (V). Thermal effects could be responsible for some of the difference since the X-ray data were obtained at 294 K for (II) *vs* 143 K for (V). Krebs & Mandt (1975) argued that the N–N and N–O distances in (V) reflect a substantial contribution of the (CH<sub>3</sub>)<sub>2</sub>N<sup>+</sup>=N–O<sup>−</sup> canonical form to the resonance hybrid.

Bond lengths and angles in the N–NO<sub>2</sub> region of (IV) are within the range of values reported in other nitramines. The largest variation is in the reported N–N distances, *ca* 1.35–1.40 Å. In *N,N*-dimethylnitramine (VI) (Filhol, Bravic, Rey-Lafon & Thomas, 1980), the N–N distances of 1.323 (3) Å and average

N—O distances of 1.238 (5) Å suggest that canonical form  $R_2N^+=NO_2^-$  makes a larger contribution to the resonance hybrid than in other nitramines.

While the conformations of the N(1)-linked NO and NO<sub>2</sub> groups are fixed by mesomeric interactions of the type  $R_2N-NO_2 \leftrightarrow R_2N^+=NO_2^-$ , the C-linked NO<sub>2</sub> conformations are arranged to provide as much distance as possible for the various O...O contacts. The effective location of the highest-occupancy O atoms [O(1)'s] in (II) and (III) on only one side of N(2) can be related to a combination of intra- and intermolecular interactions. In (IV), for example, the shortest intramolecular contacts between O(1) and the C(3)—NO<sub>2</sub> oxygen atoms are O(1)...O(4) = 3.065 (3) and O(1)...O(3) = 3.130 (Å), whereas the corresponding O(2) distances are O(2)...O(6') = 2.893 (3) and O(2)...O(5') = 3.289 (3) Å. From these data, it seems

probable that avoidance of the O(2)...O(6') contact is the major intramolecular factor favoring the O(1) sites in (II) and (III). Because the three compounds are isostructural, the increase in the molecular sizes by an O atom from (II) to (III) and from (III) to (IV) would be expected to produce a concomitant change in the unit-cell volumes. The anticipated volume change is observed (*Abstract*), but one finds that while the *a* and *c* dimensions increase there is a decrease in *b* of ca 0.2 Å from (II) to (III) to (IV). While the expansion of the *a* and *c* dimensions can be readily rationalized on the basis of additional intermolecular repulsion in (III) and (IV), the contraction of *b* would appear to suggest that extra intermolecular attractions, with major components along *b*, are present in these structures. The crystal packing diagrams [a diagram for (IV) is shown in Fig. 4] contain no pattern of close contacts that can rationalize the shortening in *b*. The majority of intermolecular contacts increase from (II) to (IV), and there are only a few interactions which actually decrease. Not unexpectedly, the largest intermolecular contact differences are found in the region of the disordered nitro groups. The values, for example, of the O(1)...O(3)( $\frac{1}{2}-x, \frac{1}{2}+y, z$ ) distances are 3.554, 3.461, 3.403 Å in (II)–(IV). Here it is probable that the O(1)...O(3) decrease is a result and not a cause of the *b* contraction since the observed distances are appreciably larger than the 2.8 Å O...O van der Waals distance. Additionally, the interaction is a repulsion, not an attraction.

Table 5. Bond lengths (Å), valence angles (°), torsion angles (°) and *e.s.d.*'s (in parentheses) for (II)–(IV)

Primed atoms are related to the original atoms by a center of symmetry at  $\frac{1}{2}, 0, 0$ .

	(II)	(III)	(IV)
N(1)—C(2)	1.448 (3)	1.462 (4)	1.454 (3)
N(1)—N(2)	1.326 (3)	1.352 (5)	1.366 (2)
N(1)—C(4')	1.470 (2)	1.457 (4)	1.465 (3)
C(2)—C(3)	1.532 (3)	1.529 (4)	1.530 (3)
N(2)—O(1)	1.195 (3)	1.213 (5)	1.224 (3)
N(2)—O(2)	0.92 (2)	1.136 (8)	1.214 (3)
C(3)—C(4)	1.523 (3)	1.528 (4)	1.533 (3)
C(3)—N(3)	1.540 (3)	1.530 (4)	1.537 (3)
C(3)—N(4)	1.540 (3)	1.546 (5)	1.538 (3)
N(3)—O(3)	1.203 (3)	1.206 (4)	1.205 (3)
N(3)—O(4)	1.209 (3)	1.216 (3)	1.214 (3)
N(4)—O(5)	1.210 (3)	1.209 (3)	1.219 (3)
N(4)—O(6)	1.198 (3)	1.195 (4)	1.200 (3)
C(2)—N(1)—N(2)	121.3 (2)	118.7 (3)	117.3 (2)
C(2)—N(1)—C(4')	121.3 (1)	121.7 (2)	121.7 (2)
C(4')—N(1)—N(2)	115.8 (2)	116.7 (3)	117.1 (2)
N(1)—C(2)—C(3)	113.9 (2)	112.9 (3)	113.1 (2)
N(1)—N(2)—O(1)	115.5 (2)	115.8 (4)	116.4 (2)
N(1)—N(2)—O(2)	126 (1)	118.6 (4)	117.3 (2)
O(1)—N(2)—O(2)	117 (2)	125.5 (5)	126.2 (2)
C(2)—C(3)—C(4)	117.2 (2)	116.4 (3)	115.7 (2)
C(2)—C(3)—N(3)	109.5 (2)	110.7 (2)	110.2 (2)
C(2)—C(3)—N(4)	109.6 (2)	109.1 (3)	109.2 (1)
C(4)—C(3)—N(3)	109.7 (2)	109.8 (3)	109.6 (2)
C(4)—C(3)—N(4)	108.0 (2)	108.4 (2)	109.7 (2)
N(3)—C(3)—N(4)	101.7 (2)	101.5 (2)	101.4 (1)
C(3)—N(3)—O(3)	118.5 (2)	118.7 (2)	118.6 (2)
C(3)—N(3)—O(4)	116.0 (2)	115.9 (3)	115.8 (2)
O(3)—N(3)—O(4)	125.5 (2)	125.4 (3)	125.6 (2)
C(3)—N(4)—O(5)	115.8 (2)	115.6 (3)	115.2 (2)
C(3)—N(4)—O(6)	118.5 (2)	118.3 (3)	118.9 (2)
O(5)—N(4)—O(6)	125.6 (2)	126.0 (4)	125.9 (2)
C(3)—C(4)—N(1')	112.4 (2)	112.4 (3)	112.2 (2)
C(4')—N(1)—C(2)—C(3)	113.5 (2)	115.5 (3)	115.7 (2)
N(1)—C(2)—C(3)—C(4)	-31.5 (3)	-31.7 (4)	-30.7 (3)
C(2)—C(3)—C(4)—N(1')	-32.1 (3)	-30.8 (4)	-31.6 (3)
C(3)—C(4)—N(1')—C(2')	113.1 (2)	114.7 (3)	115.9 (2)
C(3)—C(2)—N(2)—N(2)	-81.8 (2)	-84.4 (3)	-87.1 (2)
C(2)—N(1)—N(2)—O(1)	11.1 (3)	13.9 (5)	15.0 (3)
N(1)—C(2)—C(3)—N(3)	94.4 (3)	94.4 (3)	94.3 (2)
N(1)—C(2)—C(3)—N(4)	-155.0 (2)	-154.7 (2)	-155.1 (2)
C(2)—C(3)—N(3)—O(3)	-127.2 (3)	-127.2 (3)	-126.2 (2)
C(2)—C(3)—N(4)—O(5)	-155.6 (2)	-160.0 (2)	-163.4 (2)

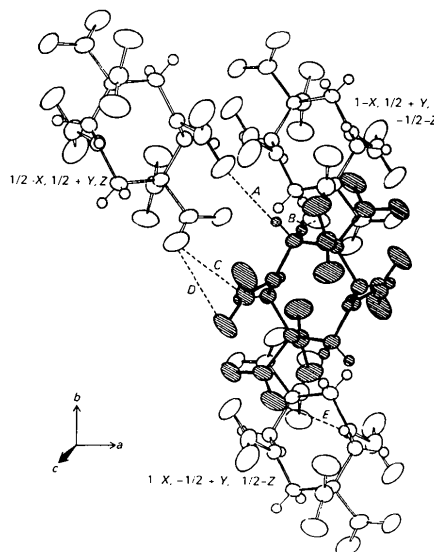


Fig. 4. Packing drawing for (IV) down the *c* axis. The center of the outlined molecule is at  $\frac{1}{2}, 0, 0$ . The capital letters refer to intermolecular contacts (Å) listed in order for (II), (III), and (IV) below: A (H...O), 2.376, 2.345, 2.345; B (H...O), 2.260, 2.277, 2.279; C (N...O), 3.289, 3.239, 3.244; D (O...O), 3.544, 3.461, 3.403; E (O...H), 2.455, 2.364, 2.364.

There are a few O...H contacts which decrease from (II) to (IV): H(3)...O(1)( $\frac{1}{2} - x, \frac{1}{2} + y, z$ ) = 2.376 (II), 2.345 (III), 2.345 (IV); O(5)...H(2)( $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$ ) = 2.455 (II), 2.386 (III), 2.364 Å (IV). These are likely to be weak interactions and, again, may be the result rather than the cause of the *b* contraction. It would be expected, however, that the amount of positive charge on H should increase from (II) to (IV) as a result of the enhanced electron-withdrawing ability of NO<sub>2</sub> vs NO. Some recent *ab initio* molecular-orbital calculations (similar to a minimum 6-3G basis set; Hariharan, Koski, Kaufman, Miller & Lowrey, 1982) on the HMX's have reported charges on H close to +0.3. This charge magnitude could lead to substantial Coulombic interactions of H atoms with the electron-rich O atoms. For example, the Coulombic energy of an H<sup>0.3+</sup> interacting with an O<sup>0.3-</sup> at a 2.4 Å distance (assuming a crystal dielectric constant of 3.0) is about 16 kJ mol<sup>-1</sup>.\* This is an appreciable interaction and C-H...O interactions may in fact be responsible for the *b* contraction.

We have also examined the possibility that the *b* contraction could have resulted from a slight shortening of the molecules more-or-less parallel to the *b* direction, or to a small molecular reorientation giving rise to an effective decrease in the *b* component. There are no significant differences in these aspects of the structures.

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\* Crystal potential-energy-function calculations with the program *WMIN* (Busing, 1981) have given O and H charges of -0.187 and +0.105, respectively. The corresponding Coulombic energy is 10 kJ mol<sup>-1</sup>.

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## The Structure of Two Polymorphs of *N*-(2-Ammonioethyl)carbamate, C<sub>3</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>

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**Abstract.** Form I:  $M_r = 104.1$ , orthorhombic, *Pna*2<sub>1</sub>,  $a = 12.799$  (9),  $b = 4.846$  (2),  $c = 8.285$  (5) Å,  $V = 513.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.35$  g cm<sup>-3</sup>, *Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 1.05$  cm<sup>-1</sup>,  $F(000) = 223.94$ , room temperature.  $R = 0.0443$ , 594 unique observed reflections. Form II:  $M_r = 104.1$ , monoclinic, *P2<sub>1</sub>/a*,  $a = 7.589$  (4),  $b = 8.130$  (7),  $c = 7.812$  (6) Å,  $\beta = 95.76$  (5)°,  $V = 479.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.44$  g cm<sup>-3</sup>,

*Mo Kα*,  $\lambda = 0.71069$  Å,  $\mu = 1.12$  cm<sup>-1</sup>,  $F(000) = 223.94$ , room temperature.  $R = 0.0812$ , 452 unique observed reflections. The two distinct crystalline forms result from a conformational difference along the ethylenediamine chain. Both crystalline forms can be obtained from 95% ethanol solutions. Customarily, the molecule is prepared from absolute methanol which yields form I.