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Structure of the 1/1 Complex between Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), $C_4H_8N_8O_8$, and *N*-Methyl-2-pyrrolidinone (NMP), C_5H_9NO

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Abstract. HMX–NMP, $M_r = 395{\cdot}1$, hexagonal, $R\bar{3}c$, $a = 16{\cdot}607$ (4), $c = 31{\cdot}506$ (8) Å, $V = 7525{\cdot}2$ (38) Å^3, $Z = 18$, $D_x = 1{\cdot}570$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}28$ cm^{-1}, $F(000) = 3744$, $T = 298$ K, $R_F = 0{\cdot}085$ with a goodness-of-fit of 1·887 for those 1287 reflections with $F_o > 5\sigma(F_o)$ and 114 parameters. The structure of HMX–NMP consists of HMX molecules in the chair–chair ring conformation and twofold disordered NMP molecules, a situation comparable to that found for HMX–DMF. Bond distances and angles in HMX are regular and normal. The closest HMX–HMX contact is 3·016 (7) Å.

Introduction. The energetic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, $C_4H_8N_8O_8$, known as HMX, stoichiometrically cocrystallizes with a variety of organic molecules having appropriate size, shape, and polarity (George, Cady, Rogers & Rohwer, 1965; Selig, 1982). In fact, the physical and chemical properties of HMX might be tailored systematically by such dopants. A desire to learn how nitramines accommodate other molecules in their crystal lattice prompted us to determine the structure of HMX–*N*,*N*-dimethylformamide (DMF) (Haller, Rheingold & Brill, 1983) which had been reported earlier (Cobbledick & Small, 1975). However, our sample contained two distinctly different crystal habits, one of which matched the space group $R\bar{3}c$ (Cobbledick & Small, 1975), and the other of which had major violations to rhombohedral symmetry. Both structures were found to be very similar. Marsh (1984) believes them to be the same and we have not been able to resolve the problem satisfactorily. The structure of the 1/1 complex of hexahydro-1,3,5-trinitro-*s*-triazine with sulfolane has also recently been described (Haller, Brill & Rheingold, 1984). We expand this subject now with the structure of the 1/1 complex between HMX and *N*-methyl-2-pyrrolidinone (NMP).

Experimental. A crystal (0·26 × 0·32 × 0·38 mm) of HMX–NMP, grown by slow cooling of a saturated NMP solution of HMX, was epoxied to a glass fiber and coated with varnish to prevent solvent loss. Data collected on a Nicolet *R*3 automated diffractometer, graphite monochromator. 25 reflections used to refine orientation matrix. No absorption correction. Systematic absences are $hkil$: $-h + k + l = 3n + 1, 3n + 2$; $h\bar{h}0l$: $l = 2n + 1$; possible space groups $R\bar{3}c$ ($\bar{3}m$) and $R3c$; $R\bar{3}c$ chosen by E statistics and later confirmed by successful solution and refinement. 5833 reflections scanning ω ($3° \le 2\theta \le 43°$) at 3·5° min^{-1}; limits: $h = 0$–18, $k = 0$–±18, $l = 0$–±33; $R_{merge} = 0{\cdot}0212$; 2048 unique, 1287 observed with $F_o \ge 5\sigma(F_o)$; 114 parameters. 3 check reflections measured every 141 reflections, no decay. *SHELXTL* direct methods *SOLV* (Sheldrick, 1981). Blocked-cascade procedure.

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$R_F = 0.085$, $wR_F = 0.097$ with $w^{-1} = \sigma^2(F_o) + G|F_o|^2$, $G = 0.0020$. Nonhydrogen atoms of HMX anisotropic; positional parameters for the NMP atoms C(4) and C(7) fixed in final refinement due to insufficient resolution in diffraction data; H atoms located in idealized positions on C atoms; final GOF = 1·877; max. peak 0·32 e Å^{-3} in final difference map; $\Delta/\sigma = 0.07$; no secondary-extinction correction necessary. All form factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. HMX–NMP and HMX–DMF both possess $R\bar{3}c$ symmetry and contain ordered, thermally well behaved HMX molecules along with twofold disordered solvent molecules. The unit-cell dimensions of HMX–NMP are comparable to those of HMX–DMF [$a = 15.989$ (8), $c = 30.920$ (12) Å]. Because DMF and NMP differ in size and shape, the packing of the HMX molecules (Fig. 1) probably plays the predominant role in determining the unit-cell boundaries and motif. In fact, if only the HMX packing is considered, the two rhombohedral HMX solvates are isomorphous. Disordered DMF and NMP molecules fill the interstices. It is interesting to note that HMX–NMP has a second, as yet uncharacterized, polymorph which is unstable at room temperature with respect to transformation to this $R\bar{3}c$ structure (George, Cady, Rogers & Rohwer, 1965). The carbonyl O atom of the solvent molecule is positioned in the face of the tetrazocine ring opposite the NO_2 groups and is probably responsible for the gross orientation of the solvent relative to HMX.

* Fractional atomic coordinates of H atoms, anisotropic Gaussian amplitudes for non-hydrogen atoms, and calculated and observed structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42093 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

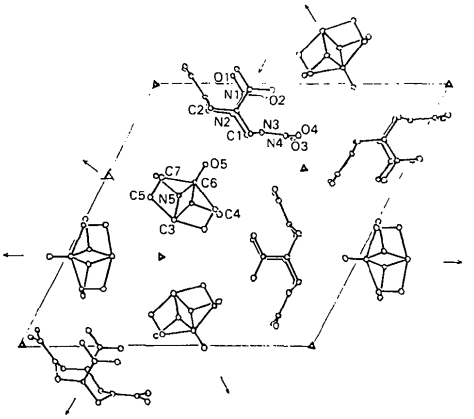

Fig. 1. The arrangement of HMX and disordered NMP viewed along the *c* axis.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U_{eq} or U_{iso}
C(1)	5288 (3)	819 (4)	2070 (2)	55 (3)*
C(2)	4400 (4)	−975 (4)	2141 (2)	55 (3)*
N(1)	3654 (3)	−111 (4)	1908 (1)	56 (3)*
N(2)	4462 (3)	−96 (3)	2021 (1)	52 (2)*
N(3)	5255 (3)	1282 (3)	2446 (1)	54 (2)*
N(4)	5346 (3)	2161 (3)	2413 (2)	71 (3)*
O(1)	2951 (3)	−864 (3)	1896 (1)	72 (2)*
O(2)	3726 (3)	647 (3)	1831 (1)	78 (2)*
O(3)	5386 (3)	2565 (3)	2739 (2)	92 (3)*
O(4)	5379 (3)	2452 (3)	2052 (2)	92 (3)*
C(3)	3333	−1983 (5)	4167	117 (6)*
C(4)	4583	−266	4278	60 (6)
C(5)	2114 (10)	−2234 (11)	4006 (4)	105 (4)
C(6)	3333	−514 (10)	4167	116 (4)
C(7)	2150	−1532	4050	172 (16)
N(5)	3050 (6)	−1318 (7)	4146 (3)	77 (3)
O(5)	3333	169 (3)	4167	90 (3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond distances* (Å) *and angles* (°) *for HMX in HMX–NMP*

C(1)–N(2)	1·460 (5)	C(1)–N(3)	1·426 (7)
C(2)–N(2)	1·460 (8)	C(2)–N(3a)	1·448 (6)
N(1)–N(2)	1·378 (8)	N(1)–O(1)	1·211 (5)
N(1)–O(2)	1·228 (9)	N(3)–N(4)	1·395 (8)
N(3)–C(2a)	1·448 (7)	N(4)–O(3)	1·211 (9)
N(4)–O(4)	1·228 (9)		

N(2)–C(1)–N(3)	112·3 (4)	N(2)–C(2)–N(3a)	111·2 (5)
N(2)–N(1)–O(1)	117·0 (6)	N(2)–N(1)–O(2)	116·0 (4)
O(1)–N(1)–O(2)	127·0 (6)	C(1)–N(2)–C(2)	125·0 (5)
C(1)–N(2)–N(1)	116·5 (5)	C(2)–N(2)–N(1)	117·9 (4)
C(1)–N(3)–N(4)	119·3 (5)	C(1)–N(3)–C(2a)	120·5 (5)
N(4)–N(3)–C(2a)	118·2 (5)	N(3)–N(4)–O(3)	117·7 (6)
N(3)–N(4)–O(4)	116·1 (6)	O(3)–N(4)–O(4)	126·1 (6)

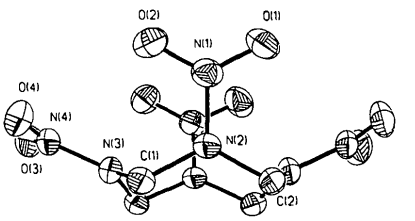

Fig. 2. An *ORTEP* plot (Johnson, 1965) of the HMX molecule (40% probability).

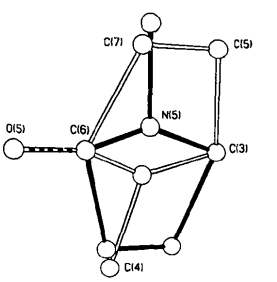

Fig. 3. The model used in the refinement of the disordered NMP molecule. Two orientations of NMP share atoms C(3), C(6) and O(5); these atoms lie on a crystallographic twofold rotational axis. The refined occupancies of the two rotationally related orientations are equal.

Table 1 gives the atomic coordinates for HMX–NMP. The bond distances and angles of HMX are regular and normal (Table 2) but those of NMP are, of course, affected by the disorder. Fig. 2 shows the HMX molecule and Fig. 3 the best behaved model for NMP. The model of NMP disorder is the best that can be done based on the electron density map. We realize that it is not very good and attribute the high R value to this difficulty. The tetrazocine ring of HMX adopts the chair–chair conformation resembling that in α-, γ-, and δ-HMX (Cady, Larson & Cromer, 1963; Goetz & Brill, 1979; Cobbledick & Small, 1974) and HMX–DMF. The chair ring conformation appears only in β-HMX (Eiland & Pepinsky, 1955; Choi & Boutin, 1970). The disorder of NMP precludes a description of its intermolecular contact distances. The closest HMX–HMX intermolecular distance is the interplane O(1)···C(2) contact at 3·016 (7) Å. All other intermolecular distances exceed 3·16 Å.

In conclusion, the two solvates of HMX that have so far been structurally characterized contain comparably packed HMX molecules interspaced with disordered solvent molecules. This is not surprising if the packing of HMX is mainly responsible for the overall crystal structure. Subtle differences in the disorder of the solvent molecules that do not significantly perturb the unit-cell parameters may contribute to the discrepancies regarding the space group of these HMX–solvate structures.

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Structure of *N*-(5-Nitro-2-thiazolyl)acetamide (Aminitrozole), $C_5H_5N_3O_3S$

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Abstract. $M_r = 187{\cdot}17$, monoclinic, $P2_1/c$, $a = 9{\cdot}815$ (2), $b = 14{\cdot}699$ (4), $c = 5{\cdot}098$ (2) Å, $\beta = 90{\cdot}41$ (3)°, $V = 735{\cdot}5$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}71$, $D_x = 1{\cdot}690$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 3{\cdot}66$ mm^{-1}, $F(000) = 384$, room temperature, final $R = 0{\cdot}051$ for 1056 observed reflections. The carbonyl moiety is *cis* to the S atom of the thiazolyl ring. The thiazole ring is almost exactly planar with the C atom bearing the nitro substituent showing the maximum deviation from the mean plane of −0·006 Å. The molecules form pairs through N(9)—H(9)···N(3) hydrogen bonds of 2·972 (5) Å around an inversion center.

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Introduction. 5-Nitro-substituted heterocyclic compounds show antibacterial and antiprotozoal properties. To obtain a better understanding of the quantitative structure–activity relationship studied in this laboratory (Verplanken, 1984), the crystal structure of aminitrozole has been determined.

Experimental. Crystals obtained at room temperature from a dimethylformamide solution. Density measured by flotation in *n*-heptane/bromoform, crystal ~0·5 × 0·2 × 0·05 mm, Hilger & Watts computer-controlled four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, $\omega/2\theta$ scan technique ($2\theta_{max} = 140°$, $-12 \le h \le 12$, $0 \le k \le 18$, $0 \le l \le 7$), cell dimensions by least-squares refinement of the setting angles of 24 reflections with