

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; Cobble Dick & 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), $C_7H_5N_3O_3S$

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Abstract. $M_r = 187.17$, monoclinic, $P2_1/c$, $a = 9.815$ (2), $b = 14.699$ (4), $c = 5.098$ (2) Å, $\beta = 90.41$ (3)°, $V = 735.5$ (4) Å³, $Z = 4$, $D_m = 1.71$, $D_x = 1.690$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 3.66$ mm⁻¹, $F(000) = 384$, room temperature, final $R = 0.051$ 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 $\sim 0.5 \times 0.2 \times 0.05$ mm, Hülgner & Watts computer-controlled four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, $\omega/2\theta$ scan technique ($2\theta_{\text{max}} = 140^\circ$, $-12 \leq h \leq 12$, $0 \leq k \leq 18$, $0 \leq l \leq 7$), cell dimensions by least-squares refinement of the setting angles of 24 reflections with

$40 < 2\theta < 50^\circ$; two standard reflections (040, 202) measured after every 50 reflections showed a 0.47 and 0.02% variation in intensity respectively (overall e.s.d.'s are 0.55 and 0.60%); 1481 reflections measured, 1325 unique reflections ($R_{\text{int}} = 0.021$, 312 contributing reflections), 1056 observed reflections with $I > 3\sigma(I)$, Lp corrections, absorption correction by the method of North, Phillips & Mathews (1968) with values between 0.692 and 0.986, scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) (for H), scattering factor for S corrected for anomalous dispersion [International Tables for X-ray Crystallography, 1974].

Structure solved with *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981) with the S-atom position obtained from a sharpened Patterson synthesis as input. Refinement with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) by full-matrix least squares on F , first with isotropic temperature factors and then anisotropically. H atoms located in ΔF synthesis, and included in refinement with B equal to B_{overall} but not refined. Final $R = 0.051$, $wR = 0.066$ and $S = 0.065$, $w = (100 + |F_o| + 0.006|F_o|^2 + 0.01|F_o|^3)^{-1}$, $(\Delta/\sigma)_{\text{av}} = 0.007$, $(\Delta/\sigma)_{\text{max}} = 0.03$, $\Delta\rho = -0.50-0.35 \text{ e } \text{Å}^{-3}$ (rejection ratio = 0.3).

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The structure with atomic-numbering scheme is depicted in Fig. 1. Bond lengths and angles are listed in Table 2. Where in niridazole (Peeters, Blaton & De Ranter, 1984) the thiazole ring was non-planar, probably due to packing forces, the thiazole ring in aminitrozole is almost exactly planar [$\Delta_{\text{max}} \text{C}(5) = -0.006 \text{ Å}$]. Compared to niridazole most bond lengths and angles are the same within experimental error. The differences in the bonds C(4)–C(5) [1.340 (5); 1.372 (6), the second value always refers to niridazole], C(5)–N(6) [1.430 (5); 1.408 (5)], C(2)–N(9) [1.368 (4); 1.350 (5)] and N(9)–C(10) [1.378 (4); 1.400 (5) Å] suggest less interaction of the nitro and the amido group with the thiazole ring in aminitrozole. This can also be concluded from the dihedral angles between the least-squares planes through these planar groups [2.9 (3) and 4.3 (1) against 1 (1) and 1.5 (9)° in niridazole].

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s of the refined parameters in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
S(1)	4110 (1)	-1546 (1)	-880 (2)	3.18 (2)
C(2)	4567 (3)	-905 (2)	1814 (7)	2.85 (8)
N(3)	3609 (3)	-399 (2)	2859 (6)	3.27 (8)
C(4)	2413 (3)	-505 (2)	1505 (8)	3.39 (9)
C(5)	2505 (3)	-1091 (2)	-499 (7)	3.13 (9)
N(6)	1427 (3)	-1331 (2)	-2269 (6)	3.58 (9)
O(7)	1660 (3)	-1891 (2)	-3962 (6)	4.63 (8)
O(8)	321 (3)	-948 (2)	-1969 (7)	5.65 (10)
N(9)	5859 (3)	-922 (2)	2842 (6)	3.06 (7)
C(10)	6910 (3)	-1414 (2)	1763 (8)	3.24 (9)
C(11)	8225 (4)	-1359 (3)	3202 (9)	3.85 (11)
O(12)	6709 (2)	-1840 (2)	-251 (5)	4.14 (7)

Table 2. Bond lengths (Å) and bond angles (°)

S(1)–C(2)	1.723 (3)	C(5)–N(6)	1.430 (4)
S(1)–C(5)	1.724 (3)	N(6)–O(7)	1.215 (4)
C(2)–N(3)	1.315 (4)	N(6)–O(8)	1.233 (4)
C(2)–N(9)	1.368 (4)	N(9)–C(10)	1.378 (4)
N(3)–C(4)	1.366 (4)	C(10)–C(11)	1.482 (5)
C(4)–C(5)	1.340 (5)	C(10)–O(12)	1.219 (4)
C(2)–S(1)–C(5)	86.0 (1)	C(4)–C(5)–N(6)	125.9 (3)
S(1)–C(2)–N(3)	116.7 (2)	C(5)–N(6)–O(7)	118.2 (3)
S(1)–C(2)–N(9)	122.0 (2)	C(5)–N(6)–O(8)	117.2 (3)
N(3)–C(2)–N(9)	121.2 (3)	O(7)–N(6)–O(8)	124.6 (3)
C(2)–N(3)–C(4)	110.2 (3)	C(2)–N(9)–C(10)	123.4 (3)
N(3)–C(4)–C(5)	113.4 (3)	N(9)–C(10)–C(11)	115.2 (3)
S(1)–C(5)–C(4)	113.7 (2)	N(9)–C(10)–O(12)	119.3 (3)
S(1)–C(5)–N(6)	120.4 (2)	C(11)–C(10)–O(12)	125.5 (3)

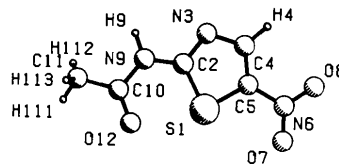


Fig. 1. Perspective view [PLUTO78 (Motherwell & Clegg, 1978)] of the molecule with atomic-numbering scheme.

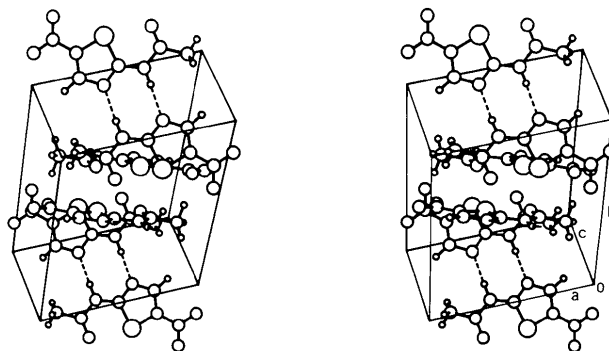


Fig. 2. Stereoscopic packing diagram [PLUTO78 (Motherwell & Clegg, 1978)] with hydrogen bonds shown as broken lines.

* Lists of structure factors, anisotropic thermal parameters, coordinates, bond lengths and bond angles involving H and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42072 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A packing diagram is shown in Fig. 2. The molecules form a dimer around the inversion center at $(\frac{1}{2}, 0, \frac{1}{2})$ through N(9)–H(9)···N(3) hydrogen bonds [N(9)···N(3)ⁱ = 2.972 (5), H(9)···N(3)ⁱ = 2.047 Å, \angle N(9)–H(9)···N(3)ⁱ = 161.9°, symmetry code (i) 1–x, –y, 1–z]. An intermolecular distance of 2.445 Å between O(8) and H(4ⁱⁱ) [symmetry code (ii) –x, –y, –z] stabilizes the crystal structure in the a direction. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

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Structural Investigation of the Triaryl Derivatives of the Group V Elements. IX.* Structure of Triphenylamine, C₁₈H₁₅N

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Abstract. $M_r = 245.2$, monoclinic, Bb , $a = 15.655$ (5), $b = 22.257$ (7), $c = 15.807$ (5) Å, $\gamma = 91.04$ (2)°, $V = 5507$ (3) Å³, $Z = 16$, $D_m = 1.18$, $D_x = 1.18$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.64$ cm⁻¹, $F(000) = 2080$, $T = 297$ K, $R = 0.036$ for 2902 reflections. The mean values for N–C bonds and CNC angles are 1.419 (6) Å and 119.6 (7)°, respectively. Four independent molecules in the crystal are related pairwise by the supersymmetry elements. The structural parameters of triphenylamine (TPHA) molecules are compared with those of a series of triaryl derivatives of the Group V elements.

Introduction. The structural investigation of the triaryl derivatives of N subgroup elements Ar₃X, where X = N, P, As, Sb and Bi, is of special interest for the solution of the problem of the possibility of the interaction between the lone electron pair (l.e.p.) of the hetero-atom X and π electrons of adjoining aromatic systems ($p\pi$ conjugation).

The character of the l.e.p. in Ar₃X is mostly influenced by the molecular conformation and also by the value of the bond angle CXC. These values in Ar₃X compounds can vary significantly (according to the

state of the valence electrons s^2p^3 of the Group V elements) from $\sim 90^\circ$ (σ bonds C–X are formed by the p orbitals of X) to $\sim 120^\circ$ (σ bonds are formed by sp^2 orbitals of X), and the character of the l.e.p. can vary from s^2 to p^2 . The greater the contribution of the p state in the l.e.p. orbital the more probable is an overlapping of this orbital with π orbitals of aromatic rings or its donation to the highest occupied molecular orbital (HOMO) of the corresponding compound.

Therefore, structural investigations of such compounds are important for both prediction and estimation of the intramolecular electronic interactions and for the calculation of different molecular parameters.

In continuation of a series of structural investigations of the triaryl derivatives of the Group V elements (Sobolev, Chetkina, Romm & Guryanova, 1976; Sobolev, Romm, Belsky & Guryanova, 1979, 1980; Sobolev & Belsky, 1981; Sobolev, Romm, Belsky, Syutkina & Guryanova, 1981; Sobolev, Romm, Chernikova, Belsky & Guryanova, 1981; Sobolev, Belsky, Chernikova & Akhmadulina, 1983; Sobolev, Belsky & Romm, 1983; Sobolev, Belsky, Romm & Guryanova, 1983) we report here the crystal and molecular structure of triphenylamine and summarize some results on the structures Ar₃X from the point of view of the steric influence on molecular conformation. [The

* Part VIII: Sobolev, Belsky, Chernikova & Akhmadulina (1983).