0·27 (1) Å out of the plane through the three bonded atoms. The departure from the tetrahedral value may be explained by the ring strain. The observed N(1)—N(2) bond length of 1·41 (1) Å is very close to that found in the related compound diacetylhydrazine (Shintani, 1960) and falls within the range of distances observed for this bond in analogous systems (Jensen & Lingafelter, 1961; Karle & Karle, 1965). Packing is due mainly to van der Waals interactions and all intermolecular contacts agree with those predicted from radii-sum rules. The F2TD2 crystal structure, as viewed down **b**, is presented in Fig. 4.

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Structure of 1,3,5,7-Tetranitroadamantane,* $C_{10}H_{12}N_4O_8$

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Abstract. $M_r = 316{\cdot}23$, tetragonal, $P\bar{4}2_1c$, $a = b = 7{\cdot}874$ (2), $c = 10{\cdot}552$ (2) Å, $V = 654{\cdot}2$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}605$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}24$ mm^{-1}, $F(000) = 328$, $T = 300$ K. Final $R = 0{\cdot}027$ for 296 independent observed reflections. The molecule lies on a crystallographic $\bar{4}$ axis coincident with the axis through opposing secondary C atoms in the adamantane cage. The nitro groups are rotated approximately 15° from a symmetrical eclipsed position with the adjacent cage bonds to the C atoms on the $\bar{4}$ axis. The crystal symmetry is identical to that of the low-temperature form of the unsubstituted adamantane.

Introduction. The title compound (TNA) was provided by G. Sollott who first synthesized the material (Sollott & Gilbert, 1980). This compound was investigated as a part of a continuing program to examine the structures of high-density polynitro organic compounds. It is one of a series of nitroadamantanes examined (George & Gilardi, 1983) to provide a library of observed structural parameters for energetic organic substituents. These are used to evaluate and modify semi-empirical parameters used to predict the properties of nitro-organic compounds by methods of quantum chemistry or conformational energy analysis.

Experimental. Clear 0·65 × 0·65 × 0·75 mm crystal, m.p. 634–636 K. Automatic Picker four-circle diffractometer upgraded with Krisel Control automation, diffracted-beam graphite monochromator, Cu $K\alpha$. 20 centered reflections within $40 \le 2\theta \le 82°$ used for measuring lattice parameters. No absorption correction applied. $(\sin\theta/\lambda)_{\max} = 0{\cdot}56$ Å^{-1}, range of hkl: $0 \le h \le 6$, $-8 \le k \le 8$, $-11 \le l \le 11$; standards 220, $2\bar{2}0$ and 245 with maximum variation of 2, 2, and 4%, respectively over data collection; $\theta/2\theta$ scan mode, scan width 2°, scan rate a function of the count rate; 1854 reflections measured, 296 unique, $R_{\text{int}} = 0{\cdot}029$, 296 observed with $I \ge 2\sigma(I)$. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), H atoms located in difference maps; final refinement by full-matrix least-squares program *ORXFLS*3 (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1975), function minimized $\sum w(|F_o|-|F_c|)^2$ where $w = 1/\sigma^2(F_o)$; standard deviation of the observed structure factor is $\sigma^2_F = QI/4\text{Lp}\,[(\sigma_I/I)^2 + (\sigma_Q/Q)^2]$ where Lp is the Lorentz–polarization factor, Q is the attenuation factor used when source is attenuated for intense peaks, σ_I/I includes a counting statistics term and a term proportional to the intensity for random instrumental errors (0·02 in this work) (Gilardi, 1973). 63 parameters refined: all atom coordinates, anisotropic

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* Adamantane is tricyclo[3.3.1.1^{3,7}]decane.

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Table 1. *Fractional coordinates and isotropic thermal factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
C(1)	−0·1469 (3)	−0·0522 (3)	−0·0823 (2)	2·84
C(2)	−0·2057 (3)	0·0956 (3)	0·0006 (2)	3·03
C(9)	0·0000	0·0000	−0·1690 (3)	3·20
N	−0·2987 (3)	−0·1044 (3)	−0·1639 (2)	3·72
O(1)	−0·4140 (3)	−0·1789 (3)	−0·1110 (2)	5·06
O(2)	−0·2990 (3)	−0·0674 (3)	−0·2744 (2)	6·06
H(2*A*)	−0·242 (3)	0·192 (4)	−0·052 (2)	2·2 (6)
H(2*B*)	−0·298 (3)	0·064 (3)	0·054 (2)	1·7 (6)
H(9)	−0·029 (3)	0·100 (3)	−0·227 (2)	1·3 (5)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·528 (3)	C(1)–N	1·529 (3)
C(1)–C(9)	1·531 (3)	O(1)–N	1·216 (3)
C(1)–C(8)	1·539 (3)	O(2)–N	1·203 (3)
C(2)–C(1)–C(9)	111·5 (2)	C(1)–N–O(1)	117·1 (2)
C(8)–C(1)–C(9)	110·3 (2)	C(1)–N–O(2)	118·8 (3)
C(8)–C(1)–C(2)	110·9 (2)	O(1)–N–O(2)	124·1 (3)
C(2)–C(1)–N	106·9 (2)	C(1)–C(2)–C(3)	106·4 (2)
C(8)–C(1)–N	108·0 (2)	C(1)–C(9)–C(5)	106·6 (2)
C(9)–C(1)–N	109·1 (2)		

temperature factors for non-H atoms, isotropic temperature factors for H; $R = 0·027$, $wR = 0·031$, $S = 1·38$. $(\Delta/\sigma)_{\rm max} = 0·01$. Final difference Fourier $\Delta\rho$ excursions 0·14 and −0·09 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 lists the refined coordinates and isotropic B values;* bond distances and angles are given in Table 2. One complete TNA molecule is displayed in Fig. 1 prepared with the aid of *ORTEP* (Johnson, 1965).

TNA crystallizes in the same space group as the low-temperature form of adamantane (Nordman & Schmitkons, 1965), with the $\bar{4}$ axis directed along the tetragonal c axis. The molecule is positioned so that two of the opposing secondary C atoms of the adamantane cage lie on the $\bar{4}$ axis with the origin midway between them as shown in Fig. 1. The $\bar{4}$ operation on the atoms in the asymmetric unit, C(1), C(2), C(9), N, O(1), O(2), H(2*A*), H(2*B*) and H(9), generates a complete molecule. The carbon cage atoms of the molecular units projected on to the ab plane form squares whose edges make an angle of 19·6° with the a or b axes. The orientation of the NO$_2$ group with respect to the adamantane cage is defined by the torsion angles O(1)–N–C(1)–C(2) = −72·7 (3), O(2)–N–C(1)–C(2) = 105·9 (3), O(1)–N–C(1)–C(9) = 166·6 (2) and O(2)–N–C(1)–C(9) = −14·8 (3)°. Intermolecular contacts are normal van der Waals interactions with nearest contacts of O(1)···H(9)′ = 2·48 (2) and O(1)···C(2)′ = 3·284 (4) Å.

The adamantane cage in TNA and the compounds which follow is only slightly distorted from ideal. The average C–C distance in TNA is 1·533 Å, 1·536 Å for the low-temperature form of adamantane (Donohue & Goodman, 1967), and 1·525 Å for both 2-bromo-2-nitroadamantane and 2,2-dinitroadamantane (George & Gilardi, 1983). The average $\angle C_tC_sC_t$'s are 106·5, 108·9, 110·3 and 110·5° and the average $\angle C_sC_tC_s$'s are 110·9, 108·8, 109·1 and 108·9°, respectively, for the previously cited compounds. The subscripts denote secondary and tertiary atoms. The C–N distance is 1·529 (3) Å and the O–N–O angle is 124·1 (3)°. While the C–N bond is long compared to C–N bonds in other bonding environments (1·4–1·5 Å, Sutton, 1965), it is similar to those observed in 2-bromo-2-nitroadamantane, 1·538 (7) Å, and 2,2-dinitroadamantane, 1·560 (5) and 1·555 (5) Å (George & Gilardi, 1983). The C–N bond lengths and O–N–O valence angles observed are consistent with the results of statistical analyses of alicylic nitro compounds which shows a correlation of these parameters; an increase in the O–N–O angle is generally accompanied by an increase in C–N bond length (Sadova & Vilkov, 1982).

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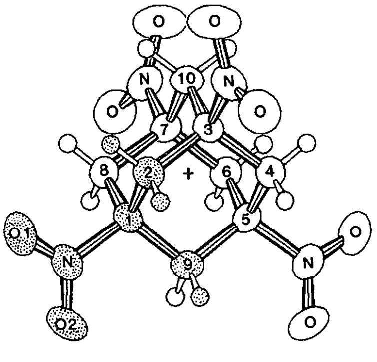

Fig. 1. Perspective view of a molecule of TNA. Only the shaded atoms are independent; C(3),C(5), and C(7) are equivalent to C(1); C(4),C(6), and C(8) are equivalent to C(2); and C(10) is equivalent to C(9). The atoms in the group labeled N,O(1),O(2) are independent, the other NO$_2$ groups are equivalent. The origin is located midway between C(9) and C(10) on the c axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39016 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Novel and Reproducible Polymorph (*Z*) of the Histamine H_2-Receptor Antagonist Cimetidine, $C_{10}H_{16}N_6S$

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Abstract. $M_r = 252\cdot34$, $P2_1/c$, $a = 7\cdot283\,(2)$, $b = 10\cdot808\,(2)$, $c = 18\cdot281\,(3)$ Å, $\beta = 118\cdot18\,(2)°$, $V = 1268\cdot4\,(5)$ Å^3, $D_x = 1\cdot321$ Mg m^{-3}, $Z = 4$, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 0\cdot24$ mm^{-1}, $F(000) = 536$, $T = 295\,(2)$ K, $R = 0\cdot034$ for 1733 unique reflexions. The crystal structure of a novel polymorph (*Z*) of cimetidine is compared with that of *A* reported by Hädicke, Frickel & Franke [*Chem. Ber.* (1978), **111**, 3222–3232]. Its bond distances and angles (except three angles) agree well with the corresponding ones observed in polymorph *A*. However, due to the full rearrangement (*i.e.* geometrical isomerization) of the guanidine moiety, their conformations differ markedly; *e.g.* the intramolecular bond distance $N(2)\cdots N(4) = 2\cdot881\,(2)$ Å of form *A*, which corresponds to a strong hydrogen bond, increased to $7\cdot382\,(3)$ Å. Consequently, the hydrogen bonding of *Z* also differs significantly from that of *A*.

Introduction. The efficacious histamine H_2-receptor antagonist cimetidine [*N*-cyano-*N*′-methyl-*N*″-(2-{[(5-methyl-1*H*-imidazol-4-yl)methyl]thio}ethyl)guanidine] is known to exhibit rich polymorphism, *e.g.* three crystal modifications are mentioned by Bavin, Sly, Tovey & Ward (1976). The existence of further polymorphs is assumed by Kojić-Prodić, Kajfez, Belin, Toso & Sunjić (1979) on the basis of IR spectra and X-ray powder diagrams. However, owing to the coprecipitation of these polymorphs neither recipes for their reproducible preparations, nor descriptions of their structures could be provided. Only the crystal structure of the modification already used in human pharmacotherapy (hereinafter polymorph *A*) has been reported so far (Hädicke, Frickel & Franke, 1978). Consequently, it is of primary importance to describe the preparation and the crystal structure of a novel cimetidine polymorph termed *Z* which in contrast to the other hardly reproducible ones can be prepared from aqueous solution in unique form. Since the sand-like *Z* form of cimetidine adsorbs only a low amount of water it is a rather profitable intermediate in the industrial production of the registered form *A*.

Experimental. Crystals of polymorph *Z* prepared as follows: 20 g cimetidine mixed with 40% (v/v) methanol/water solution; from the well stirred suspension a homogenous solution was obtained by adding 7 ml of CH_3COOH; after cleaning and filtering this solution cimetidine was precipitated with NH_4OH at 283 K (pH = 9); crystals were filtered and dried; m.p. 414–416 K. Crystal $0\cdot1 \times 0\cdot12 \times 0\cdot22$ mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Cell constants by least squares using 25 reflexions, $20° \leq 2\theta \leq 30°$. Systematic absences *h*

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