1975) for the ring S, C(1), C(2), N(1), C(3), C(8) are $Q = 0.626$ (2) Å, $\varphi = 28.8$ (2)°, $\theta = 65.1$ (2)° in (I) and $Q = 0.642$ (2) Å, $\varphi = 34.5$ (2)°, $\theta = 63.3$ (1)° in (II). The fused benzene ring is not strictly planar, $Q = 0.017$ (2) and 0.014 (2) Å in (I) and (II) respectively. The pyrazole group [$Q = 0.005$ (2) Å] and the adjacent phenyl ring [$Q = 0.007$ (2) Å] in (I) are more nearly planar; the dihedral angle between these two rings is 50.9 (1)°. In (II) three double bonds are strongly localized on C(1)=C(9) [1.313 (3) Å], N(2)=C(10) [1.261 (2) Å] and C(11)=O(4) [1.199 (2) Å]; the non-bonding interaction N(2)···H(4) [2.31 (2) Å] produces the remarkable difference between the angles C(2)—N(1)—N(2) and C(3)—N(1)—N(2), 118.6 (1) and 113.4 (1)° respectively.

Both crystal structures are stabilized by intermolecular hydrogen bonds. In (I) the strongest ones are: H(1A)···O(2) (1−x, $−\frac{1}{2}+y$, $\frac{3}{2}−z$) 2.38 (2) Å, C(1)—H(1A)···O(2) 150 (2)° and H(14)···O(2) (−1+x, y, z) 2.52 (2) Å, C(14)—H(14)···O(2)

152 (2)°; in (II) the most important ones are H(2A)···O(4) (−1−x, −y, −z) 2.42 (2) Å, C(2)—H(2A)···O(4) 168 (1)° and H(12B)···O(1) (x, y, 1+z) 2.49 (2) Å, C(12)—H(12B)···O(1) 139 (1)°.

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Structure of 1-Methyl-2,3,4,5-tetranitropyrrole, a Possible High-Density Explosive*

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Abstract. $C_5H_3N_5O_8$, $M_r = 261.11$, orthorhombic, *Pbca*, $a = 10.328$ (2), $b = 15.657$ (3), $c = 23.713$ (4) Å, $V = 3834.5$ Å³, $Z = 16$, $D_x = 1.809$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu = 1.63$ cm⁻¹, $F(000) = 2112$, room temperature, final $R = 0.054$ for 2212 observed reflections [$I > 3\sigma(I)$] out of 3063 measured independent reflections. Bond lengths and angles are within normal range and are very similar for the two independent molecules. The rings of both molecules are planar. A small systematic increase in C—N bond length from 1.426 to 1.464 Å is present as the torsion angles of the NO_2 groups increase from about 6 to 80°.

Introduction. The detonation pressure of an explosive is proportional to the square of the crystal density. Therefore, in searching for better explosives, high density is one of the desired properties. Stine (1981) has devised an empirical method of density prediction based on the additivity of characteristic atomic volumes. As part of a program aimed at finding insensitive, high-performance explosive molecules we have prepared 1-methyl-2,3,4,5-tetranitropyrrole (I) and now report its crystal structure. Stine's (1981) method gives 1.83 g cm⁻¹ for the density of (I), in good agreement with D_x.

Experimental. (I) prepared according to procedure of Doddi, Mencarelli, Razzini & Stegel (1979) except that the product was extracted from the undiluted nitration mixture with CH_2Cl_2. Product melted at 388 K, significantly higher than 374–375 K reported by Doddi *et al.* (1979). Pale orange crystals grown from CH_2Cl_2. Crystal dimensions 0.28 × 0.54 × 0.90 mm. CAD-4 diffractometer, θ–2θ scans. θ scan range (0.8 + 0.34 tanθ)°. Scan speed 1.0 to 8.2° min⁻¹. Background first and last one-sixth of scan range. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell: 25 reflections, $15 \leq 20° \theta$. No absorption corrections. Sin $\theta/\lambda_{max} = 0.594$ Å⁻¹. Index range $0 \leq h \leq 11$, $0 \leq k \leq 18$, $0 \leq l \leq 28$. Standard reflections 400, 008, max. variation 1%. Structure solved by *MULTAN* (Germain,

Table 1. *Final least-squares parameters for* (I) (*positional parameters* $\times 10^4$, *equivalent isotropic* U_{eq} $\times 10^2$)

$$U_{eq}(\text{Å}^2) = \tfrac{1}{3}\Sigma U_{ii}.$$

	Molecule 1				Molecule 2			
	x	y	z	U_{eq}	x	y	z	U_{eq}
C(1)	2775(3)	1917(3)	1031(1)	3.5(4)	4193(3)	0566(2)	2725(1)	3.1(4)
C(2)	2952(4)	2787(3)	1053(2)	4.1(4)	3849(3)	1358(2)	2915(2)	3.3(4)
C(3)	3906(4)	2977(3)	0654(2)	4.1(4)	3123(3)	1225(2)	3407(2)	3.4(4)
C(4)	4243(3)	2230(3)	0404(2)	4.0(4)	3038(3)	0358(2)	3485(2)	3.6(4)
C(5)	3615(5)	0647(3)	0497(2)	5.3(5)	3862(5)	-0988(3)	2957(2)	4.9(5)
N(1)	1899(3)	1411(2)	1372(2)	4.7(4)	4969(3)	0343(2)	2242(2)	4.2(4)
N(2)	2250(4)	3395(3)	1382(2)	5.5(4)	4156(3)	2161(2)	2665(1)	4.2(4)
N(3)	4357(4)	3832(3)	0501(2)	5.8(4)	2608(4)	1878(2)	3784(1)	4.6(4)
N(4)	5231(4)	2119(3)	-0010(2)	5.4(4)	2279(3)	-0065(3)	3907(1)	4.6(4)
N(5)	3537(3)	1563(2)	0638(1)	3.6(4)	3711(3)	-0047(2)	3063(1)	3.3(3)
O(1)	1148(3)	0938(2)	1120(2)	7.1(4)	5962(3)	-0030(3)	2341(1)	7.4(4)
O(2)	1940(3)	1503(3)	1870(1)	7.7(5)	4587(4)	0525(2)	1782(1)	7.1(4)
O(3)	1225(4)	3158(3)	1592(2)	8.4(5)	4914(4)	2168(2)	2279(1)	6.8(4)
O(4)	2680(5)	4096(3)	1436(2)	9.2(5)	3623(3)	2787(2)	2848(2)	7.4(4)
O(5)	3752(4)	4211(2)	0155(2)	9.0(5)	3357(4)	2205(2)	4102(2)	8.0(4)
O(6)	5295(4)	4105(3)	0753(2)	9.2(5)	1473(3)	2053(3)	3746(1)	7.3(4)
O(7)	5817(4)	2760(3)	-0133(2)	8.4(5)	1877(3)	0381(2)	4283(1)	6.8(4)
O(8)	5402(4)	1425(3)	-0228(2)	8.3(5)	2062(3)	-0829(2)	3858(2)	7.0(4)
H(1)	3119	0513	0145	8(2)	4507	-1222	3234	15(3)
H(2)	3240	0293	0812	8(2)	4236	-1072	2569	11(2)
H(3)	4533	0467	0439	20(4)	3029	-1281	2992	17(4)

Type II isotropic extinction parameter = 2.1 (5) $\times 10^{-6}$ mm (Larson, 1969).

Table 2. *Bond lengths* (Å) *and angles* (°) *in* (I)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(1)-C(2)	1.374(6)	1.366(5)	C(5)-N(5)	1.474(5)	1.503(5)
C(2)-C(3)	1.399(6)	1.404(5)	N(1)-O(1)	1.228(5)	1.203(5)
C(3)-C(4)	1.356(6)	1.373(5)	N(1)-O(2)	1.190(5)	1.196(4)
C(4)-N(5)	1.389(5)	1.373(5)	N(2)-O(3)	1.227(5)	1.204(5)
C(1)-N(5)	1.341(5)	1.346(5)	N(2)-O(4)	1.192(5)	1.205(5)
C(1)-N(1)	1.449(5)	1.440(5)	N(3)-O(5)	1.189(5)	1.195(4)
C(2)-N(2)	1.428(6)	1.426(5)	N(3)-O(6)	1.216(5)	1.208(4)
C(3)-N(3)	1.464(5)	1.458(5)	N(4)-O(7)	1.208(5)	1.205(4)
C(4)-N(4)	1.428(5)	1.434(5)	N(4)-O(8)	1.215(5)	1.222(5)
C(2)-C(1)-N(1)	127.1(4)	128.8(3)	C(4)-N(5)-C(5)	127.8(3)	128.9(3)
C(2)-C(1)-N(5)	111.0(3)	110.8(3)	C(1)-N(1)-O(1)	116.9(4)	115.9(4)
N(1)-C(1)-N(5)	121.9(4)	120.4(3)	C(1)-N(1)-O(2)	117.7(4)	119.0(3)
C(1)-C(2)-C(3)	106.2(3)	106.2(3)	O(1)-N(1)-O(2)	125.4(4)	125.1(4)
C(1)-C(2)-N(2)	127.8(4)	127.3(3)	C(2)-N(2)-O(3)	117.3(4)	117.9(3)
C(3)-C(2)-N(2)	125.8(4)	126.5(3)	C(2)-N(2)-O(4)	118.9(4)	117.8(4)
C(2)-C(3)-C(4)	107.0(4)	107.0(3)	O(3)-N(2)-O(4)	123.8(5)	124.3(4)
C(2)-C(3)-N(3)	125.9(4)	126.9(3)	C(3)-N(3)-O(5)	117.4(4)	116.7(4)
C(4)-C(3)-N(3)	126.8(4)	126.0(4)	C(3)-N(3)-O(6)	117.0(4)	117.9(4)
C(3)-C(4)-N(4)	126.1(4)	125.8(4)	O(5)-N(3)-O(6)	125.6(4)	125.4(4)
C(3)-C(4)-N(5)	109.9(3)	109.0(3)	C(4)-N(4)-O(7)	115.0(5)	115.9(4)
N(4)-C(4)-N(5)	123.9(4)	124.9(4)	C(4)-N(4)-O(8)	120.4(4)	119.0(4)
C(1)-N(5)-C(4)	105.9(3)	107.0(3)	O(7)-N(4)-O(8)	124.6(4)	125.0(4)
C(1)-N(5)-C(5)	126.4(3)	124.1(3)			

	d(C···O) (Å)	d(H···O) (Å)	$\angle$C-H···O (°)
C(5)-H(1)···O(15)	3.34	2.48	143.5
C(5)-H(3)···O(15)	3.43	2.51	153.4
C(10)-H(4)···O(6)	3.18	2.46	129.4
C(10)-H(6)···O(12)	3.21	2.27	162.9

Main & Woolfson, 1971). Least-squares refinement minimized $\Sigma w(\Delta F)^2$, $w = [\sigma_c^2(F) + 0.015F^2]^{-1}$. H atoms poorly defined in ΔF Fourier but located by applying distance constraints so that C—H distance *ca* 1.0 Å and N—C—H angles *ca* tetrahedral (Waser, 1963). Scale factor, isotropic type II extinction parameter (Larson, 1969), positional parameters, anisotropic thermal parameters for heavy atoms and isotropic thermal parameters for H atoms refined, $R = 0.054$, $wR = 0.085$, $S = 3.2$, $\sigma_c^2(F)$ based on counting statistics, final $(\Delta/\sigma)_{max} = 0.09$. Final ΔF Fourier synthesis $-0.26 \leq \rho \leq 0.29$ e Å^{-3}. Scattering factors f, f' and f'' from *International Tables for X-ray Crystallography* (1974). Calculations on CDC-7600 using the Los Alamos Crystal Structure System developed primarily by A. C. Larson.*

Discussion. Final parameters are listed in Table 1. The numbering scheme for a molecule is shown in Fig. 1. Bond lengths and angles for the two independent molecules are given in Table 2. A stereo drawing of the eight molecules in the unit cell is shown in Fig. 2. Both molecular rings are nearly parallel to the {102} planes.

There is a small, systematic lengthening of the C—N bond as the angle between the ring plane and the NO_2 plane increases. This relationship is shown in Fig. 3. Resonance structures can be drawn which give some double-bond character to these C—N bonds. The bond

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43020 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
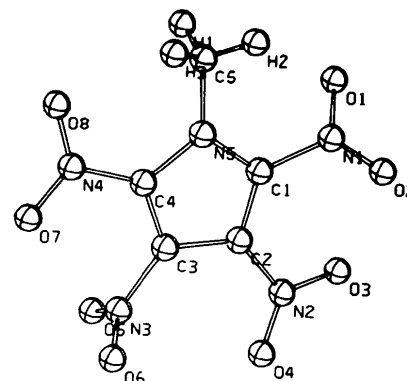

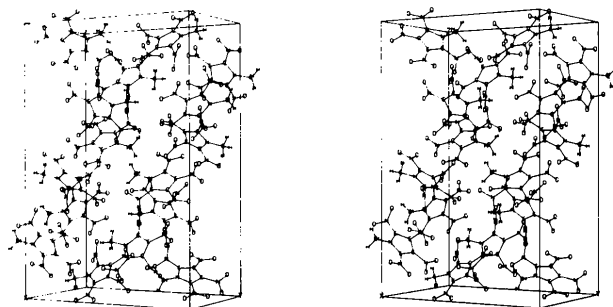Fig. 1. Drawing of molecule in order to define the atom numbering that is used.

Fig. 2. Stereo drawing showing the packing of the eight molecules of (I) in the unit cell. The origin is at the lower left, rear.
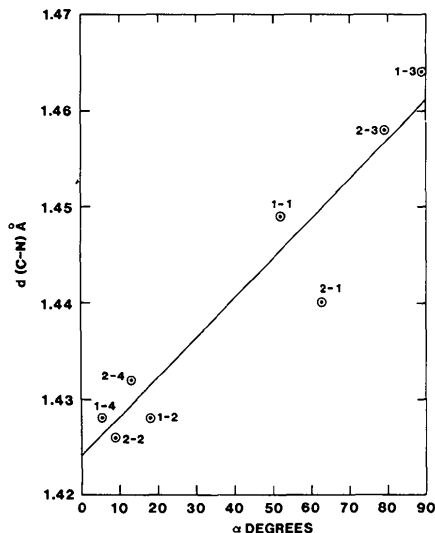
Fig. 3. C—N bond length *versus* torsion angle of the NO_2 group. The points are labeled 'molecule-group'. The least-squares line $d = 1\cdot424 + 0\cdot000409\alpha$ is drawn.

order would be a maximum if the NO_2 group were coplanar with the ring and a minimum with the NO_2 group at 90° from the ring. In a study of the conformations of a large number of nitro-substituted

aromatic rings Holden & Dickenson (1977) found no correlation between C—N distances and torsion angles.

The existence of C—H$\cdots$O hydrogen bonds has been noted by Sutor (1962). Such bonds could exist in the present structure and possible intermolecular hydrogen bonds are listed in Table 2. O$\cdots$H distances less than $2\cdot7$ Å are plotted as dotted lines in Fig. 2.

It is unusual, though hardly rare, to find two molecules in the asymmetric unit. There are, however, no close intermolecular contacts which suggest a dimer as the packing unit.

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Structure and Conformation of *cyclo*(-L-Phenylalanyl-L-prolyl-D-alanyl-), Form II of a Synthetic Cyclic Hexapeptide

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Abstract. $C_{34}H_{42}N_6O_6.5H_2O$, $M_r = 720\cdot8$, monoclinic, $P2_1$, $a = 13\cdot475$ (1), $b = 9\cdot361$ (2), $c = 15\cdot226$ (1) Å, $\beta = 100\cdot77$ (2)°, $Z = 2$, $V = 1887$ Å^3, $D_x = 1\cdot269$ g cm^{-3}, D_m not measured, $\lambda(Cu\,K\alpha) = 1\cdot5418$ Å, $\mu = 7\cdot5$ cm^{-1}, $F(000) = 772$, $R = 0\cdot044$, $wR = 0\cdot049$ for 2979 reflections $[I > 2\sigma(I)]$, 4232 unique reflections measured. The synthetic cyclic hexapeptide *cyclo*(-L-Phe-L-Pro-D-Ala-)$_2$ crystallizes in

two forms. Form I, crystallized from Me_2SO/H_2O mixture $[a = 18\cdot730$ (2), $b = 9\cdot239$ (1), $c = 21\cdot544$ (2) Å, $\beta = 95\cdot17$ (2)°, $Z = 4$, $V = 3713$ Å^3], contains two hexapeptide molecules and eight water molecules in the asymmetric unit [Kartha, Bhandary, Kopple, Zhu & Go (1984). *J. Am. Chem. Soc.* **106**, 3844–3850], while form II, crystallized from $H_2O/$MeOH/NaSCN solution, contains one hexapeptide molecule and five water molecules in the asymmetric unit. The conformation of the hexapeptide molecule

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* Deceased 18 June 1984.