

owing to the effect of conjugation between the oxygen and the benzene ring (Spek, Kojić-Prodić & Labadie, 1984). This conjugation could be justified by the coplanarity of the ether oxygen O(1) with the benzene ring [O(1)—C(5)—C(6)—C(7), -179.9 (2); O(1)—C(5)—C(4)—C(9), 178.2 (2) $^\circ$] which causes an enlargement of the angle O(1)—C(5)—C(4), 123.9 (1) $^\circ$, and narrowing of the angle O(1)—C(5)—C(6), 113.6 (1) $^\circ$. Similar observations were noted in the solid-state structures of a variety of compounds incorporating the pyran ring (Cantrell & Hockstein, 1982; Cantrell, Stalzer & Becker, 1974; Ponnuswamy & Trotter, 1984) and anisole moiety (Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979). The C(5)—O(1)—C(1), C(4)—C(3)—C(2) angles reflect the ring strain due to the neighbouring sp^2 atoms (Gzella, Jaskólski, Rychlewska & Kosturkiewicz, 1984).

The conformation of the dihydropyran ring is a modified half-chair distorted toward the *d,e* diplanar arrangement (Valente, Santarsiero & Schomaker, 1979). The corresponding asymmetry parameter (Duax, Weeks & Rohrer, 1976) $\Delta C_2[C(1)—C(2)] = 19.7^\circ$.

On account of fusion strains the benzene ring [atoms C(4) to C(9)] common to the naphthalene and benzopyran groups deviates from planarity [$\sum(\Delta/\sigma)^2 = 360$]; maximum deviations from the plane are 0.019 (1), -0.015 (1), 0.013 (2) Å for C(4), C(5) and C(7) respectively.

The molecular packing projected on the *bc* plane is illustrated in Fig. 2. There is a shortened intramolecular distance C(10)⋯O(2), 2.864 (3) Å. C(10)—H, 0.98 (2); O(2)⋯H, 2.19 (2) Å; angle C(10)—H⋯O(2), 125.5 (15) $^\circ$ which corresponds, according to the geometrical characteristics, to a weak C—H⋯O hydrogen bond (Taylor & Kennard, 1982; Berkovitch-

Yellin & Leiserowitz, 1984; Dvorkin, Malinowsky, Simonov, Andronati, Kuzmina & Yavorsky, 1985).

One of us (KR) thanks CSIR (India) for the award of a Senior Research Fellowship.

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Ethyl 3-Phenyl-4*H*-pyrazolo[3,2-*c*][1,4]benzothiazine-2-carboxylate (I) and 4-[Chloro(ethoxycarbonyl)methyleneamino]-2-methylene-2,3-dihydro-4*H*-1,4-benzothiazine 1,1'-Dioxide (II)

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(Received 4 December 1985; accepted 3 April 1986)

Abstract. (I): C₁₉H₁₆N₂O₂S, $M_r = 336.4$, monoclinic, $P2_1/c$, $a = 9.686$ (2), $b = 7.660$ (2), $c = 21.989$ Å,

$\beta = 98.31$ (2) $^\circ$, $V = 1614.3$ (6) Å³, $Z = 4$, $D_m = 1.37$, $D_x = 1.384$ Mg m⁻³; $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.20$ mm⁻¹, $F(000) = 704$, room temperature, $R = 0.045$, $wR = 0.031$ for 2299 observed reflections

† Deceased.

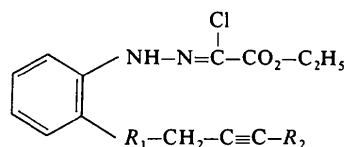
Table 1. Details of data collection and structure refinement

(a) Data Collection	(I)	(II)
Crystal size (mm)	0.25 × 0.18 × 0.17	0.28 × 0.20 × 0.15
Cell-parameter determination:		
number; range of reflections (°)	24; 10–14	24; 19–24
Range <i>h</i>	–11, 11	0, 10
<i>k</i>	0, 9	–11, 11
<i>l</i>	–26, 26	–13, 13
<i>θ</i> (°)	0.0–27.5	0.0–27.5
Standard reflections: number;		
variation of intensity (%)	2; 3	3; 2
Number of intensity measurements	5671	3350
Number of unique reflections	2836	3350
Merging <i>R</i> for equivalent <i>hkl</i>	0.026	
(b) Refinement		
Number of refined reflections	2299; <i>I</i> > 0.5σ(<i>I</i>)	3017; <i>I</i> > 0
<i>R</i>	0.045	0.039
<i>wR</i>	0.031	0.039
<i>S</i>	1.06	1.32
Weighting scheme; <i>a</i> *	0.0004	0.000225
(Δσ) _{max} in last cycle	<0.01	<0.01
Δρ in final difference Fourier map (e Å ^{–3})	0.2	0.3
Extinction coefficient <i>g</i> (× 10 ⁷)	67 (5)	14 (1)

$$* w = 4F_o / [\sigma^2(F_o^2) + aF_o^4].$$

[*I* > 0.5σ(*I*)]. (II): C₁₃H₁₃ClN₂O₄S, *M_r* = 328.8, triclinic, *P*1̄, *a* = 8.359 (1), *b* = 8.885 (2), *c* = 11.125 (1) Å, α = 101.97 (1), β = 109.28 (1), γ = 101.68 (2)°, *V* = 729.4 (2) Å³, *Z* = 2, *D_m* = 1.48, *D_x* = 1.497 Mg m^{–3}, λ(Mo *K*α) = 0.71069 Å, μ = 0.41 mm^{–1}, *F*(000) = 340, room temperature, *R* = 0.039, *wR* = 0.039 for 3017 observed reflections (*I* > 0). In spite of the remarkable differences in bond lengths, bond angles and torsion angles, the six-membered heterocyclic rings have a twisted conformation in both compounds. No π delocalization was found in the ethylene, methylamino and ethoxycarbonyl groups in (II). The fused benzene rings in both compounds are not strictly planar.

Introduction. The hydrazone (IIIa), by thermal reaction in boiling benzene and triethylamine, gives (I) as main product (Bruchè, Garanti & Zecchi, 1984). Under the same conditions, (IIIb) gives a compound similar to (I) and (II) and its 3-methylene isomer as by-products (Garanti & Zecchi, 1985).



(IIIa) *R*₁ = S, *R*₂ = C₆H₅

(IIIb) *R*₁ = SO₂, *R*₂ = H

The present X-ray study was carried out to confirm the structure of the main product (I) and to elucidate the nature of the compound (II), whose NMR spectra were not understood. In fact the knowledge of the structures of all the products is essential to understand the reaction mechanism.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters for non-H atoms

(I)	$B_{eq} = \frac{8\pi^2}{3} \text{trace } \bar{U}$			<i>B_{eq}</i> (Å ²)
	<i>x</i>	<i>y</i>	<i>z</i>	
S	0.39985 (6)	0.46256 (8)	0.89552 (2)	4.15 (2)
O(1)	0.3222 (1)	0.3681 (2)	0.58296 (5)	3.75 (4)
O(2)	0.5439 (1)	0.4536 (2)	0.60135 (5)	4.28 (4)
N(1)	0.5091 (2)	0.3613 (2)	0.78019 (6)	2.88 (4)
N(2)	0.5482 (2)	0.3796 (2)	0.72385 (6)	3.03 (4)
C(1)	0.3107 (2)	0.3197 (3)	0.83648 (9)	3.56 (7)
C(2)	0.3682 (2)	0.3483 (3)	0.77783 (8)	2.79 (5)
C(3)	0.6098 (2)	0.3489 (2)	0.83359 (8)	2.78 (5)
C(4)	0.7435 (2)	0.2915 (3)	0.82963 (9)	3.41 (6)
C(5)	0.8410 (2)	0.2803 (3)	0.8819 (1)	4.17 (7)
C(6)	0.8046 (3)	0.3269 (3)	0.9379 (1)	4.64 (7)
C(7)	0.6711 (3)	0.3815 (3)	0.94237 (9)	4.21 (7)
C(8)	0.5710 (2)	0.3923 (3)	0.89025 (8)	3.31 (6)
C(9)	0.3098 (2)	0.3566 (3)	0.71720 (7)	2.65 (5)
C(10)	0.4278 (2)	0.3759 (3)	0.68553 (7)	2.61 (5)
C(11)	0.1584 (2)	0.3449 (3)	0.69447 (7)	2.72 (5)
C(12)	0.1053 (2)	0.2264 (3)	0.64911 (9)	3.25 (6)
C(13)	–0.0377 (2)	0.2141 (3)	0.6303 (1)	4.17 (7)
C(14)	–0.1288 (3)	0.3184 (4)	0.6565 (1)	4.64 (7)
C(15)	–0.0780 (2)	0.4346 (3)	0.7017 (1)	4.12 (7)
C(16)	0.0640 (2)	0.4489 (3)	0.72075 (9)	3.28 (6)
C(17)	0.4399 (2)	0.4041 (3)	0.61944 (8)	2.90 (5)
C(18)	0.3241 (2)	0.3938 (4)	0.51730 (8)	3.96 (7)
C(19)	0.1815 (3)	0.3505 (6)	0.4857 (1)	5.4 (1)
(II)				
Cl	–0.45304 (6)	–0.16677 (5)	–0.20659 (4)	4.72 (1)
S	–0.24184 (5)	0.30413 (5)	–0.40969 (3)	3.342 (8)
O(1)	–0.2524 (2)	0.1497 (2)	–0.4884 (1)	4.60 (3)
O(2)	–0.2471 (2)	0.4316 (2)	–0.4698 (1)	5.57 (3)
O(3)	–0.1204 (1)	0.0464 (1)	0.15731 (9)	3.49 (2)
O(4)	–0.3842 (1)	–0.1417 (1)	0.0731 (1)	3.97 (3)
N(1)	–0.2122 (1)	0.1691 (1)	–0.1780 (1)	2.64 (2)
N(2)	–0.1959 (1)	0.1168 (1)	–0.0690 (1)	2.62 (2)
C(1)	–0.4035 (2)	0.2734 (2)	–0.3426 (1)	3.13 (3)
C(2)	–0.3925 (2)	0.1429 (2)	–0.2774 (1)	3.33 (3)
C(3)	–0.0630 (2)	0.2937 (2)	–0.1586 (1)	2.38 (3)
C(4)	0.0880 (2)	0.3442 (2)	–0.0404 (1)	2.91 (3)
C(5)	0.2351 (2)	0.4621 (2)	–0.0248 (2)	3.63 (4)
C(6)	0.2386 (2)	0.5340 (2)	–0.1230 (2)	4.07 (4)
C(7)	0.0923 (2)	0.4859 (2)	–0.2401 (2)	3.79 (4)
C(8)	–0.0571 (2)	0.3655 (2)	–0.2590 (1)	2.76 (3)
C(9)	–0.5185 (2)	0.3562 (3)	–0.3539 (2)	5.06 (5)
C(10)	–0.2922 (2)	–0.0130 (2)	–0.0700 (1)	2.81 (3)
C(11)	–0.2722 (2)	–0.0449 (2)	0.0610 (1)	2.83 (3)
C(12)	–0.0930 (2)	0.0293 (2)	0.2897 (2)	3.86 (4)
C(13)	0.0803 (3)	0.1451 (3)	0.3840 (2)	5.04 (5)

Table 3. Bond distances (Å) for non-H atoms

(I)			
S–C(1)	1.818 (2)	S–C(8)	1.763 (2)
O(1)–C(17)	1.325 (2)	O(1)–C(18)	1.460 (2)
O(2)–C(17)	1.196 (2)	N(1)–N(2)	1.354 (2)
N(1)–C(2)	1.361 (2)	N(1)–C(3)	1.417 (2)
N(2)–C(10)	1.337 (2)	C(1)–C(2)	1.493 (3)
C(2)–C(9)	1.372 (2)	C(3)–C(4)	1.382 (3)
C(3)–C(8)	1.393 (3)	C(4)–C(5)	1.381 (3)
C(5)–C(6)	1.377 (3)	C(6)–C(7)	1.376 (4)
C(7)–C(8)	1.392 (3)	C(9)–C(10)	1.429 (2)
C(9)–C(11)	1.482 (2)	C(10)–C(17)	1.491 (2)
C(11)–C(12)	1.391 (3)	C(11)–C(16)	1.399 (3)
C(12)–C(13)	1.390 (3)	C(13)–C(14)	1.378 (4)
C(14)–C(15)	1.373 (3)	C(15)–C(16)	1.382 (3)
C(18)–C(19)	1.491 (4)		
(II)			
Cl–C(10)	1.740 (1)	S–O(1)	1.435 (1)
S–O(2)	1.431 (2)	S–C(1)	1.749 (2)
S–C(8)	1.750 (1)	O(3)–C(11)	1.319 (2)
O(3)–C(12)	1.459 (2)	O(4)–C(11)	1.199 (2)
N(1)–N(2)	1.363 (1)	N(1)–C(2)	1.482 (2)
N(1)–C(3)	1.411 (2)	N(2)–C(10)	1.261 (2)
C(1)–C(2)	1.492 (3)	C(1)–C(9)	1.313 (3)
C(3)–C(4)	1.398 (2)	C(3)–C(8)	1.406 (2)
C(4)–C(5)	1.379 (2)	C(5)–C(6)	1.380 (3)
C(6)–C(7)	1.372 (2)	C(7)–C(8)	1.393 (2)
C(10)–C(11)	1.504 (2)	C(12)–C(13)	1.485 (2)

Experimental. D_m by flotation in dilute K_2HgI_4 solution. Details of data collection and refinement in Table 1. Intensity data collected with Enraf-Nonius CAD-4 diffractometer, graphite-monochromated $Mo K\alpha$ radiation, $\omega/2\theta$ scan technique, variable rate 2–12° min^{-1} . Correction for Lorentz and polarization, not for absorption. Structures solved using direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971); H atoms from Fourier synthesis. Full-matrix least-squares refinement of scale factor, secondary-extinction parameter g (Larson, 1967, equation 3), anisotropic heavy atoms and isotropic H atoms; quantity minimized $\sum w(|F_o| - |F_c|)^2$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs Enraf-Nonius (1979) *SDP*, *ORTEP* (Johnson, 1965) and various in-house programs for refinement and geometrical analysis running on a Gould 32/97 computer.

Discussion. The final positional parameters and their e.s.d.'s are given in Table 2.* Tables 3 and 4 report bond distances and angles respectively. Fig. 1 shows a

* Lists of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42980 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Bond angles (°) for non-H atoms

(I)			
C(1)–S–C(8)	97.1 (1)	C(17)–O(1)–C(18)	116.0 (2)
N(2)–N(1)–C(2)	112.6 (2)	N(2)–N(1)–C(3)	121.0 (2)
C(2)–N(1)–C(3)	126.4 (2)	N(1)–N(2)–C(10)	103.9 (2)
S–C(1)–C(2)	109.3 (2)	N(1)–C(2)–C(1)	118.4 (2)
N(1)–C(2)–C(9)	107.7 (2)	C(1)–C(2)–C(9)	133.9 (2)
N(1)–C(3)–C(4)	120.5 (2)	N(1)–C(3)–C(8)	118.9 (2)
C(4)–C(3)–C(8)	120.6 (2)	C(3)–C(4)–C(5)	120.1 (2)
C(4)–C(5)–C(6)	119.7 (2)	C(5)–C(6)–C(7)	120.5 (2)
C(6)–C(7)–C(8)	120.6 (2)	S–C(8)–C(3)	120.6 (2)
S–C(8)–C(7)	120.9 (2)	C(3)–C(8)–C(7)	118.5 (2)
C(2)–C(9)–C(10)	103.4 (2)	C(2)–C(9)–C(11)	125.0 (2)
C(10)–C(9)–C(11)	131.6 (2)	N(2)–C(10)–C(9)	112.4 (2)
N(2)–C(10)–C(17)	115.3 (2)	C(9)–C(10)–C(17)	132.2 (2)
C(9)–C(11)–C(12)	121.7 (2)	C(9)–C(11)–C(16)	120.0 (2)
C(12)–C(11)–C(16)	118.2 (2)	C(11)–C(12)–C(13)	120.5 (2)
C(12)–C(13)–C(14)	120.5 (2)	C(13)–C(14)–C(15)	119.7 (2)
C(14)–C(15)–C(16)	120.5 (2)	C(11)–C(16)–C(15)	120.7 (2)
O(1)–C(17)–O(2)	123.8 (2)	O(1)–C(17)–C(10)	112.2 (2)
O(2)–C(17)–C(10)	124.0 (2)	O(1)–C(18)–C(19)	106.7 (2)
(II)			
O(1)–S–O(2)	118.3 (1)	O(1)–S–C(1)	107.3 (1)
O(1)–S–C(8)	109.6 (1)	O(2)–S–C(1)	112.1 (1)
O(2)–S–C(8)	110.4 (1)	C(1)–S–C(8)	97.0 (1)
C(11)–O(3)–C(12)	115.7 (2)	N(2)–N(1)–C(2)	118.6 (1)
N(2)–N(1)–C(3)	113.4 (1)	C(2)–N(1)–C(3)	123.5 (1)
N(1)–N(2)–C(10)	124.8 (1)	S–C(1)–C(2)	111.2 (1)
S–C(1)–C(9)	121.8 (2)	C(2)–C(1)–C(9)	127.0 (2)
N(1)–C(2)–C(1)	112.8 (1)	N(1)–C(3)–C(4)	120.6 (1)
N(1)–C(3)–C(8)	121.6 (1)	C(4)–C(3)–C(8)	117.7 (1)
C(3)–C(4)–C(5)	119.9 (1)	C(4)–C(5)–C(6)	121.9 (2)
C(5)–C(6)–C(7)	119.2 (2)	C(6)–C(7)–C(8)	120.0 (2)
S–C(8)–C(3)	119.4 (1)	S–C(8)–C(7)	119.4 (1)
C(3)–C(8)–C(7)	121.2 (1)	Cl–C(10)–N(2)	128.4 (1)
Cl–C(10)–C(11)	113.1 (1)	N(2)–C(10)–C(11)	118.5 (2)
O(3)–C(11)–O(4)	125.7 (1)	O(3)–C(11)–C(10)	111.8 (1)
O(4)–C(11)–C(10)	122.5 (2)	O(3)–C(12)–C(13)	107.5 (1)

projection of the molecules with the numbering scheme which is the same for the benzothiazole skeleton in both compounds.

The different hybridization of C(1) and C(2) makes the six-membered heterocyclic rings quite different from each other. The most relevant differences are: bond lengths N(1)–C(2) and S–C(1), 1.361 (2) and 1.818 (2) in (I) vs 1.482 (2) and 1.749 (2) Å in (II); bond angles N(1)–C(2)–C(1) [118.4 (2) vs 112.8 (2)°] and C(2)–N(1)–C(3) [126.4 (2) vs 123.5 (1)°]; torsion angles around bonds S–C(1), C(1)–C(2) and C(2)–N(1) (see Table 5). In spite of these differences, the conformation of this ring is twisted in both molecules with a local pseudo-twofold axis running through the middle point of the S–C(1) bond. The puckering coordinates (Cremer & Pople,

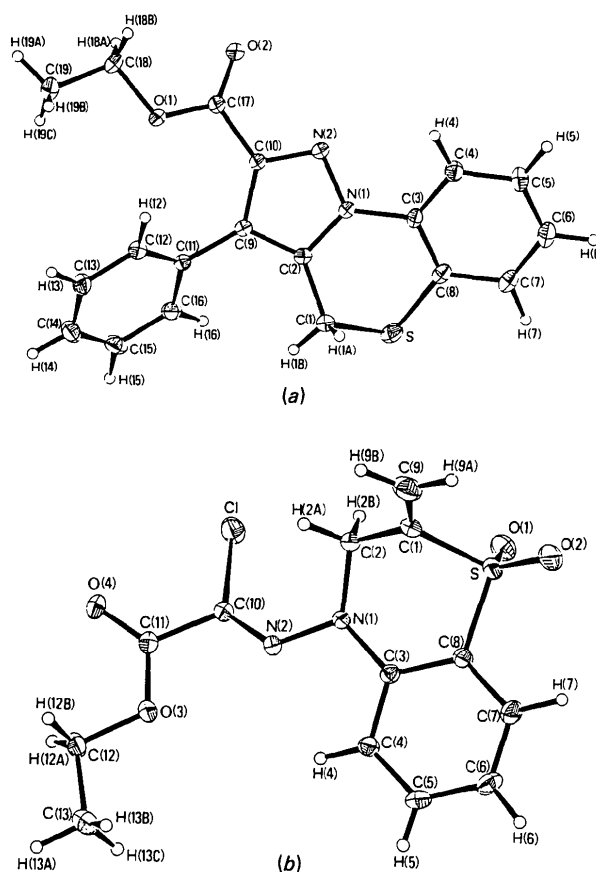


Fig. 1. (a) Compound (I); (b) compound (II). Thermal ellipsoids for heavy atoms are drawn at 20% of probability level; H atoms are not to scale.

Table 5. Torsion angles (°) in the thiazine ring

	(I)	(II)	(I)	(II)
C(1)–C(2)–N(1)–C(3)	0.6 (3)	–7.0 (2)	C(3)–C(8)–S–C(1)	36.8 (2)
C(2)–N(1)–C(3)–C(8)	–26.2 (3)	–22.9 (2)	C(8)–S–C(1)–C(2)	–55.9 (2)
N(1)–C(3)–C(8)–S	–0.3 (3)	2.2 (2)	S–C(1)–C(2)–N(1)	43.9 (2)
				53.0 (2)

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

Both crystal structures are stabilized by intermolecular hydrogen bonds. In (I) the strongest ones are: H(1A)⋯O(2) ($1-x, -\frac{1}{2}+y, \frac{3}{2}-z$) $2.38(2) \text{ \AA}$, C(1)–H(1A)⋯O(2) $150(2)^\circ$ and H(14)⋯O(2) ($-1+x, y, z$) $2.52(2) \text{ \AA}$, C(14)–H(14)⋯O(2)

$152(2)^\circ$; in (II) the most important ones are H(2A)⋯O(4) ($-1-x, -y, -z$) $2.42(2) \text{ \AA}$, C(2)–H(2A)⋯O(4) $168(1)^\circ$ and H(12B)⋯O(1) ($x, y, 1+z$) $2.49(2) \text{ \AA}$, C(12)–H(12B)⋯O(1) $139(1)^\circ$.

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

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(Received 2 December 1985; accepted 29 April 1986)

Abstract. C₅H₇N₅O₈, $M_r = 261.11$, orthorhombic, *Pbca*, $a = 10.328(2)$, $b = 15.657(3)$, $c = 23.713(4) \text{ \AA}$, $V = 3834.5 \text{ \AA}^3$, $Z = 16$, $D_x = 1.809 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha_1) = 0.70926 \text{ \AA}$, $\mu = 1.63 \text{ cm}^{-1}$, $F(000) = 2112$, 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 NO₂ 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^{-3} 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 CH₂Cl₂. Product melted at 388 K, significantly higher than 374–375 K reported by Doddi *et al.* (1979). Pale orange crystals grown from CH₂Cl₂. Crystal dimensions $0.28 \times 0.54 \times 0.90 \text{ mm}$. CAD-4 diffractometer, θ – 2θ scans. θ scan range $(0.8 + 0.34 \tan\theta)^\circ$. Scan speed 1.0 to $8.2^\circ \text{ min}^{-1}$. Background first and last one-sixth of scan range. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell: 25 reflections, $15 \leq 2\theta^\circ$. No absorption corrections. $\sin\theta/\lambda_{\text{max}} = 0.594 \text{ \AA}^{-1}$. 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,

* This work was performed under the auspices of the US Department of Energy.

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