Table 3. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C1—C14	1·426 (2)	C9—C10	1·349 (3)
C1—N15	1·417 (2)	C10—C11	1·394 (3)
C1—C2	1·384 (2)	C11—C12	1·377 (2)
C2—C3	1·378 (4)	C12—C13	1·411 (2)
C3—C4	1·350 (4)	C13—C14	1·447 (2)
C4—C5	1·421 (3)	N15—C16	1·467 (2)
C5—C14	1·412 (2)	N15—C20	1·466 (2)
C5—N6	1·372 (3)	C16—C17	1·498 (3)
N6—N7	1·284 (3)	C17—O18	1·415 (3)
N7—C8	1·402 (2)	O18—C19	1·409 (3)
C8—C13	1·407 (2)	C19—C20	1·514 (4)
C8—C9	1·406 (3)	C16—H161	0·99 (2)
C2—H2	1·08 (3)	C16—H162	0·97 (2)
C3—H3	1·06 (3)	C17—H171	1·02 (2)
C4—H4	0·91 (3)	C17—H172	1·04 (2)
C9—H9	1·01 (2)	C19—H191	1·02 (3)
C10—H10	0·95 (2)	C19—H192	0·97 (3)
C11—H11	0·92 (3)	C20—H201	1·01 (3)
C12—H12	1·00 (2)	C20—H202	1·01 (2)

C2—C1—C14	119·0 (2)	C10—C11—C12	120·9 (2)
C2—C1—N15	121·2 (2)	C11—C12—C13	120·9 (1)
C14—C1—N15	119·8 (1)	C8—C13—C14	116·3 (1)
C1—C2—C3	122·2 (2)	C12—C13—C8	117·0 (1)
C2—C3—C4	120·3 (2)	C12—C13—C14	126·6 (1)
C3—C4—C5	119·9 (2)	C13—C14—C5	115·5 (1)
C4—C5—N6	115·3 (2)	C13—C14—C1	126·9 (1)
C4—C5—C14	120·6 (2)	C1—C14—C5	117·5 (1)
N6—C5—C14	124·2 (2)	C1—N15—C16	113·2 (1)
C5—N6—N7	120·4 (2)	C1—N15—C20	117·7 (1)
N6—N7—C8	120·1 (2)	C16—N15—C20	109·4 (1)
N7—C8—C9	116·0 (2)	N15—C16—C17	110·3 (2)
N7—C8—C13	123·1 (2)	C16—C17—O18	112·2 (2)
C9—C8—C13	120·8 (2)	C17—O18—C19	109·1 (2)
C8—C9—C10	120·7 (2)	O18—C19—C20	111·2 (2)
C9—C10—C11	119·7 (2)	C19—C20—N15	108·5 (2)
H2—C2—C1	117·1 (15)	H162—C16—N15	109·2 (12)
H2—C2—C3	120·6 (15)	H162—C16—C17	108·7 (12)
H3—C3—C2	126·7 (16)	H171—C17—C16	107·6 (13)
H3—C3—C4	113·1 (16)	H171—C17—O18	107·6 (14)
H4—C4—C3	127·9 (16)	H171—C17—H172	115·0 (19)
H4—C4—C5	112·2 (16)	H172—C17—C16	108·1 (13)
H9—C9—C8	114·8 (12)	H172—C17—O18	106·5 (13)
H9—C9—C10	124·4 (12)	H191—C19—O18	116·2 (16)
H10—C10—C9	120·4 (14)	H191—C19—C20	106·3 (16)
H10—C10—C11	119·9 (14)	H191—C19—H192	102·1 (22)
H11—C11—C10	120·6 (12)	H192—C19—O18	108·1 (17)
H11—C11—C12	118·5 (12)	H192—C19—C20	112·7 (17)
H12—C12—C11	118·4 (9)	H201—C20—N15	106·3 (14)
H12—C12—C13	120·5 (9)	H201—C20—C19	112·6 (14)
H161—C16—N15	109·5 (11)	H201—C20—H202	109·2 (19)
H161—C16—C17	109·9 (11)	H202—C20—N15	106·1 (13)
H161—C16—H162	109·2 (16)	H202—C20—C19	113·7 (13)

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Structure of 2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane (TNSU), an Energetic Spiro Bicyclic Nitramine

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Abstract. $C_7H_{12}N_8O_8$, $M_r = 336{\cdot}22$, monoclinic, $C2/c$, $a = 12{\cdot}831\,(3)$, $b = 10{\cdot}726\,(3)$, $c = 19{\cdot}644\,(5)$ Å, $\beta = 108{\cdot}13\,(2)°$, $V = 2569{\cdot}4$ Å^3, $Z = 8$, $D_x = 1{\cdot}739\ \mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}47\ \mathrm{cm^{-1}}$, $F(000) = 1392$, $T = 291$ K, $R = 0{\cdot}049$ for 1509 reflections with $|F_o| > 3\sigma(F)$. Both rings of TNSU have chair conformations with two of the nitramine groups equatorial and two axial. The geometry of the nitramine groups in TNSU, with average N—N bond lengths of 1·383 (5) Å, average N—O bond lengths of 1·219 (7) Å, and average C—N bond lengths of 1·462 (15) Å, is typical of

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related compounds. As seen in cyclotrimethylenetrinitramine (RDX) and other cyclic nitramines, but in contrast to cyclotetramethylenetetranitramine (HMX), the average value for the C—N—C angles in TNSU is 115·2 (4)°. The closest intermolecular contact distances [2·857 (5), 2·998 (5) Å] are approximate van der Waals distances for nitrogen—oxygen distances.

Introduction. Cyclic (poly)nitramines are widely used dense powerful, but relatively insensitive, energetic materials. We have a continuing program to both attempt to understand the interrelationships between molecular and crystal structures and energetic properties and to design and prepare new nitramines with improved properties. Cyclotrimethylenetrinitramine (RDX, Fig. 1) exhibits density, sensitivity and explosive performance typical of this class of compounds; it is the nitramine most commonly used as an explosive. However, the β-polymorph of cyclotetramethylenetetranitramine (HMX, Fig. 1) has an unexpectedly high density. The high density and consequently enhanced explosive performance of β-HMX provide the 'benchmark' against which all new energetic materials are measured.

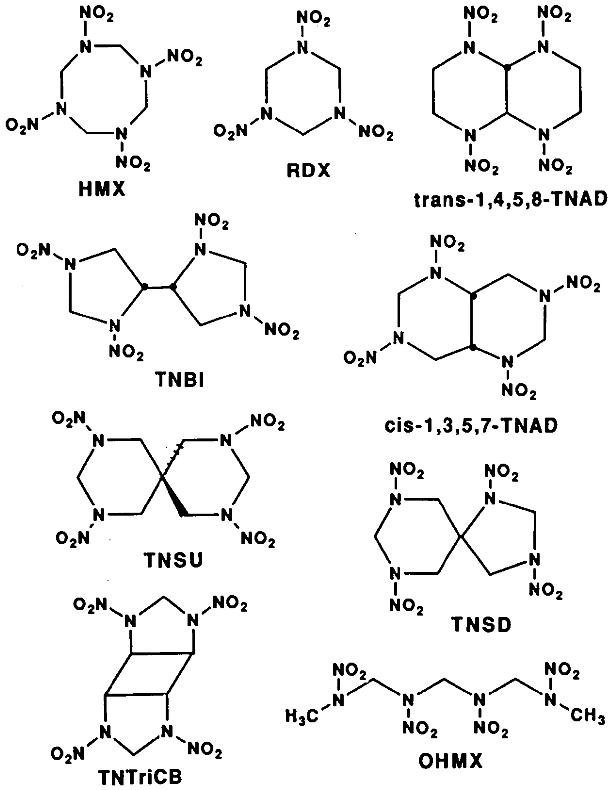

Fig. 1. Representations of nitramines discussed in Table 1 and the text.

Table 1. *Data for representative nitramine explosives*

	Density (g cm^{-3})^a	Impact sensitivity (cm)^b
Monocyclic		
β-HMX	1·92^c	18–26
RDX	1·81^d	25–28
Bicyclic		
$C_6H_{10}N_8O_8$ isomers		
trans-1,4,5,8-YNAD	1·84^e	35, 40
cis-1,3,5,7-TNAD	1·79^e	–^{f}
TNBI	1·71^e	
TNSD	1·71^e	50
TNSU $C_7H_{12}N_8O_8$	1·74	60
Tricyclic		
TNTriCB $C_6H_8N_8O_8$	1·83^g	
Acyclic		
OHMX $C_5H_{12}N_8O_8$	1·598^h	

Notes: (*a*) Densities by X-ray diffraction. (*b*) Height from which a falling 2·5 kg weight will cause detonation 50% of the time. Naval Weapons Center values on a BOM-type machine. (*c*) Bryden (1957); see also Cady, Larson & Cromer (1963). (*d*) Choi & Prince (1972). (*e*) Lowe-Ma (1987). (*f*) *trans*-1,3,5,7-TNAD has a sensitivity of 65 cm. (*g*) Lowe-Ma, unpublished work. (*h*) Oyumi, Brill & Rheingold (1987).

While the density of an explosive is, arguably, the most important single performance criterion for a new energetic material, its sensitivity to initiation by inadvertent stimuli determines its usability. Table 1 lists the densities and impact sensivities (where known) for a series of nitramines. (Structural diagrams are shown in Fig. 1.) This series, a small subset of known nitramines, was selected to exclude other functionality which might affect density, performance or sensitivity. TNSU (Fig. 1) is one of several new nitramines that have been synthesized as part of our on-going program to synthesize and characterize new energetic materials. As shown in Table 1, TNSU is much less sensitive to impact than β-HMX, indicating that it would be much safer to handle. However, density of TNSU is much lower, implying, consequently, poorer performance. (On this approximately logarithmic scale, a sensitive explosive such as lead azide would have an impact sensitivity in centimeters of slightly less than half that of β-HMX and TNT would have a value in centimeters about three times that of TNSU.) With the elusive goal of understanding key molecular and structural features that dominate the properties of energetic materials in general, and nitramines in particular, the crystal and molecular structure of TNSU has been determined. Each structure increases our data base of energetic materials that can be used in models to predict density and empirically calculate explosive properties.

Experimental. TNSU was synthesized as previously described (Willer, 1982; Willer & Atkins, 1984) and crystallized from dimethylformamide and water.

Although preliminary X-ray diffraction photographs indicated that many of the crystals were twinned, the thin platelet (~0·07 × 0·28 × 0·62 mm) selected for data collection did not appear to have any twinning. The unit-cell parameters were determined by a least-squares fit of 25 computer-centered reflections. The parameters for data collection on a Nicolet *R*3 were as follows: $2\theta/\theta$ scans for a 2θ range of 4 to 50° and minimum–maximum *hkl* values of *h*/0 to 17/, *k*/0 to 14/, *l*/ − 25 to 25/; scan range of $2\theta(\alpha_1) - 0{\cdot}95$ to $2\theta(\alpha_2) + 1{\cdot}05°$; ratio of total background counting time to scan time, of 1·0; variable scan speeds (2θ) of 2 to 6° min^{-1}; two check reflections, 333 and $80\overline{8}$ collected every 46 reflections, exhibited less than 4% variation overall. Intensity data were collected as for a primitive cell. Systematic absences are *hkl*, $h + k = 2n + 1$; *h*0*l*, $l = 2n + 1$; 00*l*, $l = 2n + 1$. The data were corrected for Lorentz and polarization effects but not for absorption. After merging there were 2262 unique reflections ($R_{\rm merge} = 0{\cdot}0061$) of which 1509 with $|F_o| > 3\sigma(F)$ were considered to be observed. All calculations were performed with *SHELXTL* programs (Sheldrick, 1984). With the inclusion of five reflections added to the default starting set, the first *E* map obtained from the multi-solution direct methods of *SHELXTL* yielded all of the non-H atoms. After initial refinement, all H atoms were observed on a difference Fourier map. During subsequent refinement, the H atoms were constrained to 'ride' on their adjacent C atoms with fixed geometry and 0·96 Å bond lengths but with unconstrained thermal parameters. All C, N and O atoms were refined anisotropically. Scattering factors internal to *SHELXTL* were used. The function minimized with *SHELXTL*'s blocked-cascade least-squares algorithm was $[\sum w(|F_o| - k|F_c|)^2]$ with $w = 1/[\sigma^2(F) + 0{\cdot}0025F^2]$. During the final cycles the largest shift-to-e.s.d. ratios were for the overall scale factor and were less than 0·5. The final difference Fourier map had peaks and troughs of $+0{\cdot}22$ to $-0{\cdot}26$ e Å^{-3}. Final *R* factor is 0·049, *wR* = 0·061 and goodness-of-fit is 1·16. Atomic coordinates are listed in Table 2. Bond lengths and angles for TNSU are given in Table 3.*

Table 2. *Atom coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	*U**
C(1)	1230 (3)	2648 (2)	6273 (2)	25 (1)
C(2)	1997 (2)	1845 (3)	5971 (2)	27 (1)
C(3)	3525 (2)	2097 (3)	7105 (2)	31 (1)
C(4)	1946 (2)	3496 (3)	6870 (2)	31 (1)
C(5)	493 (2)	1844 (3)	6561 (2)	27 (1)
C(6)	552 (2)	3514 (3)	5672 (2)	31 (1)
C(7)	− 1020 (2)	2090 (3)	5415 (2)	32 (1)
N(1)	2805 (2)	2809 (2)	7394 (1)	30 (1)
N(2)	2578 (2)	2266 (3)	7972 (2)	34 (1)
N(3)	2847 (2)	1244 (2)	6558 (1)	26 (1)
N(4)	3446 (2)	344 (2)	6346 (1)	30 (1)
N(5)	− 333 (2)	1241 (2)	5966 (1)	29 (1)
N(6)	− 924 (2)	304 (3)	6167 (1)	36 (1)
N(7)	− 311 (2)	2820 (3)	5131 (1)	30 (1)
N(8)	− 43 (3)	2319 (3)	4559 (2)	39 (1)
O(1)	3167 (2)	1437 (2)	8296 (1)	51 (1)
O(2)	1803 (2)	2713 (3)	8126 (1)	50 (1)
O(3)	3017 (2)	− 177 (2)	5779 (1)	46 (1)
O(4)	4357 (2)	92 (2)	6762 (1)	41 (1)
O(5)	− 558 (2)	− 119 (2)	6769 (1)	49 (1)
O(6)	− 1754 (2)	− 59 (3)	5722 (1)	57 (1)
O(7)	680 (2)	2823 (3)	4382 (1)	56 (1)
O(8)	− 607 (2)	1450 (3)	4236 (1)	55 (1)

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

Table 3. *Bond lengths* (Å) *and bond angles* (°)

C(1)—C(2)	1·559 (5)	C(1)—C(4)	1·541 (4)
C(1)—C(5)	1·513 (5)	C(1)—C(6)	1·541 (4)
C(2)—N(3)	1·468 (3)	C(3)—N(1)	1·444 (5)
C(3)—N(3)	1·473 (4)	C(4)—N(1)	1·453 (4)
C(5)—N(5)	1·463 (3)	C(6)—N(7)	1·476 (4)
C(7)—N(5)	1·477 (4)	C(7)—N(7)	1·439 (5)
N(1)—N(2)	1·384 (4)	N(2)—O(1)	1·212 (4)
N(2)—O(2)	1·225 (5)	N(3)—N(4)	1·376 (4)
N(4)—O(3)	1·214 (3)	N(4)—O(4)	1·230 (3)
N(5)—N(6)	1·388 (4)	N(6)—O(5)	1·216 (3)
N(6)—O(6)	1·213 (3)	N(7)—N(8)	1·382 (5)
N(8)—O(7)	1·215 (5)	N(8)—O(8)	1·228 (4)
C(2)—C(1)—C(4)	108·6 (3)	C(2)—C(1)—C(5)	111·7 (2)
C(4)—C(1)—C(5)	110·3 (3)	C(2)—C(1)—C(6)	108·2 (3)
C(4)—C(1)—C(6)	106·8 (2)	C(5)—C(1)—C(6)	111·1 (3)
C(1)—C(2)—N(3)	110·2 (2)	N(1)—C(3)—N(3)	108·1 (2)
C(1)—C(4)—N(1)	112·4 (2)	C(1)—C(5)—N(5)	109·6 (3)
C(1)—C(6)—N(7)	111·5 (2)	N(5)—C(7)—N(7)	108·3 (2)
C(3)—N(1)—C(4)	115·3 (3)	C(3)—N(1)—N(2)	115·0 (2)
C(4)—N(1)—N(2)	119·2 (3)	N(1)—N(2)—O(1)	119·0 (3)
N(1)—N(2)—O(2)	115·6 (3)	O(1)—N(2)—O(2)	125·3 (3)
C(2)—N(3)—C(3)	115·2 (2)	C(2)—N(3)—N(4)	114·7 (2)
C(3)—N(3)—N(4)	113·5 (2)	N(3)—N(4)—O(3)	117·7 (2)
N(3)—N(4)—O(4)	117·3 (2)	O(3)—N(4)—O(4)	125·0 (3)
C(5)—N(5)—C(7)	115·6 (2)	C(5)—N(5)—N(6)	114·6 (2)
C(7)—N(5)—N(6)	113·6 (2)	N(5)—N(6)—O(5)	117·9 (2)
N(5)—N(6)—O(6)	117·5 (3)	O(5)—N(6)—O(6)	124·6 (3)
C(6)—N(7)—C(7)	114·7 (3)	C(6)—N(7)—N(8)	117·4 (3)
C(7)—N(7)—N(8)	116·9 (3)	N(7)—N(8)—O(7)	117·8 (3)
N(7)—N(8)—O(8)	117·3 (3)	O(7)—N(8)—O(8)	124·7 (4)

Discussion. Based on the energetic characteristics of HMX and RDX, nitramine (> N—NO$_2$) moieties have been identified as being chemically stable but important to explosive properties and performance. Considering the geometric details of this functional group for the series of nitramines listed in Table 1 (Fig. 1) could help to determine if there are any molecular differences that are unique to HMX. Bond lengths and angles of the nitramines (Table 1, Fig. 1) used for comparison were taken from: Choi & Boutin (1970) for the neutron refinement of β-HMX; Cady, Larson & Cromer (1963), Cobbledick & Small (1974), and Main, Cobbledick & Small (1985) for the

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* Coordinates of 'riding' H atoms, anisotropic thermal parameters and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52475 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

α-, δ- and γ-HMX polymorphs, respectively; Choi & Prince (1972) for the neutron refinement of RDX; Lowe-Ma (1987) for *trans*-1,4,5,8-TNAD, TNSD, TNBI and *cis*-1,3,5,7-TNAD; Lowe-Ma (unpublished) for TNTriCB; Oyumi, Brill & Rheingold (1987) for OHMX. Features considered in the following discussion are the nitramine N—N bond length, N—O bond length, C(secondary)—N bond length, O—N—O bond angle and C—N—C bond angle.

For the 23 N—N bonds of the following cyclic nitramines, RDX, *trans*-1,4,5,8-TNAD, TNSD, TNBI, *cis*-1,3,5,7-TNAD, TNSU and TNTriCB, the mean N—N bond length was found to be 1·369 (22) Å. (For all the mean values given, the sample standard deviation is given in parentheses.) This is the same as 1·370 (16) Å found for the 14 N—N bonds in the α-, δ- and γ-HMX polymorphs. The linear OHMX has an average N—N bond length of 1·357 (5) Å. The two (unique) N—N bond lengths of β-HMX (1·354, 1·373 Å) encompass this range of mean N—N bond length values. Although HMX does not have an unusual N—N bond length relative to these nitramines, as compared to other organic molecules the mean N—N bond length for all of these nitramines is significantly shorter than the value, 1·420 (15) Å, expected for a three-coordinate pyramidal N bonded to three-coordinate planar N (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The mean nitramine bond length is more similar to the mean N—N bond length of 1·366 (19) Å observed in pyrazoles. This suggests that the N—N bond in these nitramines has some conjugated double-bond character. Hence, even though N—N bond-breaking is thought to be the first step in the decomposition of HMX (Melius, 1987), the nitramine N—N bond is not a particularly weak bond in the ground state. The nitramines considered here form a small subset of known nitramines. The mean N—N length observed for these nitramines may not be representative of N—N nitramine bond lengths in molecules with other functionalities or constraints. For the 26 N—N bonds in ten nitramine-containing molecules with other functionality that were listed in a recent report (Gilardi, George & Flippen-Anderson, 1987), the mean N—N bond length was found to be 1·380 (19) Å.

The C(secondary)—N and N—O bond lengths of HMX and the other nitramines of Fig. 1 are not unusual. From Allen *et al.* (1987) an average C(sp^3)—N(sp^3) bond has a mean value of 1·469 (14) Å. Piperidines have C—N bond lengths of 1·473 (13) Å. The mean C(secondary)—N bond length for the cyclic nitramines of Fig. 1, including the HMX polymorphs, is 1·454 (16) Å. The mean N—O bond length of 1·220 (13) Å for all of the cyclic nitramines considered here is the same as the mean N—O bond length, 1·218 (13) Å, observed in C—NO_2 groups (Allen *et al.*, 1987).

The δ-HMX polymorph (Cobbledick & Small, 1974) has a very wide variation in reported O—N—O angles, 121·3 to 127·1°, (along with the largest variation of any nitramine in N—O lengths, 1·187 to 1·250 Å), which may indicate poorer quality data. For the three HMX polymorphs other than β-HMX, the mean O—N—O angle is 125·1 (1·8)°; the O—N—O bond angles for β-HMX are 125·9 and 126·7° which are slightly larger numerically, but statistically the same. For all of the other cyclic nitramines, the mean O—N—O bond angle is 125·5 (5)°; for the linear OHMX the mean value is 125·2 (6)°. The most striking difference found among the nitramines of Fig. 1 is the difference in the C—N—C angles between those of the other cyclic nitramines and those of HMX. The values for the C—N—C angles of β-HMX are 122·4 and 123·8°. The mean value of the C—N—C angles for the other three HMX polymorphs is 121·2 (2·7)°. The mean C—N—C angle for just RDX and TNSU, which contain only six-membered rings without other constraints, is 115·0 (4)° for seven values ranging from 114·6 to 115·6°. For all of the cyclic nitramines (but excluding HMX), the mean C—N—C bond angle is 115·6 (2·2)°. However, except for HMX, the cyclic nitramines of Fig. 1 all contain five-membered or six-membered rings. These rings have put some constraint on the C—N—C angle of the nitramine

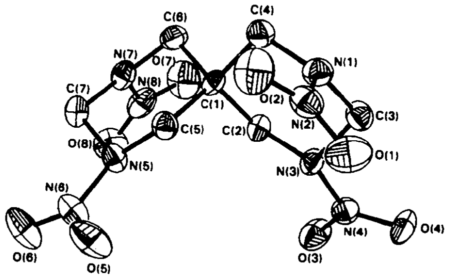

Fig. 2. TNSU plotted with 50% probability thermal ellipsoids.

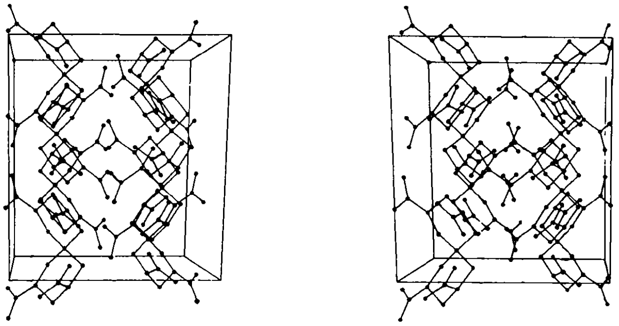

Fig. 3. Stereo packing plot of TNSU.

groups as the mean C—N—C angle in the acyclic 'linear chain' OHMX is 122·4°, which is the same as for HMX.

Both rings of TNSU have chair conformations. Torsion angles around the two six-membered rings range from |49·2| to |57·9|° with a mean (absolute) value of 53·8 (3·3)°. The value for an ideal chair conformation would be 60°. However, these values for TNSU are similar to the 55·9° observed in cyclohexane (Clark & McKervey, 1979). The molecule has a non-crystallographic pseudo twofold axis as shown in Fig. 2. TNSU has no unusually short intermolecular contact distances; a stereo packing plot is shown in Fig. 3. Its observed density at 1·74 g cm^{-3} is not anomalously large and is just slightly higher than the empirically predicted value of 1·67 g cm^{-3} (Cichra, Holden & Dickinson, 1980). Although TNSU is a fairly insensitive material (Table 1), its low density excludes it from consideration as a useful energetic material.

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Ester Méthylique de la Clométacine

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Abstract. Methyl 3-(4-chlorobenzoyl)-6-methoxy-2-methyl-1*H*-indole-1-acetate, $C_{20}H_{18}ClNO_4$, M_r = 371·814, orthorhombic, *Pcab*, a = 12·045 (5), b = 15·211 (8), c = 19·813 (6) Å, V = 3630·1 (30) Å^3, Z = 8, D_x = 1·36 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·3 mm^{-1}, $F(000)$ = 1480, room temperature, R = 0·050 for 1570 observed reflections. The *p*-chlorobenzoyl group and the acetate chain are on the same side of the indole group. This conformation explains the differences in therapeutic activity between the title compound and indomethacin, in which the lipophilic substituent is on one side and the acetate chain on the other side of the indole group.

Introduction. Alors que la clométacine (1) (Allais, Meir, Mathieu, Nomine, Peterfalvi, Deraedt, Chif-

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