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The Ordered and Disordered Phases of Three Unsymmetrical Cyclic Nitramines: (I), 1,3-Dinitro-1,3-diazacyclohexane; (II), 1,3-Dinitro-1,3-diazacycloheptane; (III), 1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane

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Abstract

(I): $C_4H_8N_4O_4$, M_r = 176·13, monoclinic, $P2_1/c$, a = 6·63 (1), b = 21·39 (2), c = 6·06 (1) Å, β = 120·0 (1)°, V = 744·26 Å^3, Z = 4, D_x = 1·572, D_m = 1·570 g cm^{-3} by flotation in benzene/bromoform, F(000) = 368·0, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·31 cm^{-1}, T = 290 K, R = 0·056 for 811 unique observed reflexions. (II): $C_5H_{10}N_4O_4$, M_r = 190·16, monoclinic, $P2_1/n$, a = 8·738 (8), b = 11·20 (1), c = 8·383 (7) Å, β = 90·1 (1)°, V = 820·41 Å^3, Z = 4, D_x = 1·539, D_m = 1·528 g cm^{-3} by flotation in benzene/carbon tetrachloride, F(000) = 400·0, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·24 cm^{-1}, T = 290 K, R = 0·056 for 829 unique observed reflexions. (III): $C_4H_8N_6O_5$, M_r = 220·15, monoclinic, Pc, a = 11·30 (1), b = 6·34 (1), c = 12·23 (1) Å, β = 102·4 (1)°, V = 855·74 Å^3, Z = 4, D_x = 1·709, D_m = 1·707 g cm^{-3} by flotation in carbon tetrachloride/bromoform, F(000) = 456·0, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·45 cm^{-1}, T = 290 K, R = 0·037 for 1985 unique observed reflexions. NNO_2 groups are planar to within 0·025 Å in all three structures, C atoms deviate up to 0·478 Å from these planes. Molecules of (I) and (II) are dish shaped (both NO_2 groups on same side of ring), both molecules in (III) are overall chairlike (NO_2 groups on opposite sides of ring). Plastically crystalline above transition temperatures, sparse data consistent with body-centred-cubic structures with a = 7·5 (1), 7·7 (1), 7·8 (1) Å for (I), (II) and (III) respectively. Thermodynamic data, ΔH, ΔS, ΔV for the transitions are reported. The ordered to plastic transformations are discussed in relation to the crystal structures reported for the ordered phases.

Introduction

The three related compounds (I), (II) and (III) (1,3-dinitro-1,3-diazacyclohexane, 1,3-dinitro-1,3-diaza-

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Table 1. *Summary of data-collection and refinement parameters*

	(I)	(II)	(III)
Independent molecules	1	1	2
2θ range cell dimensions (°)	10–40	10–40	10–45
Setting axis	*a*	*c*	*b*
2θ maximum (°)	50	50	55
Range *h*	0 to 8	10 to 10	−14 to 14
Range *k*	0 to 25	0 to 13	0 to 8
Range *l*	−6 to 6	0 to 8	−16 to 15
Crystal size (mm)	0·25 × 0·15 × 0·1	0·2 × 0·18 × 0·12	0·2 × 0·2 × 0·1
Reflexions measured	1403	1454	2325
Number unique	1288	1440	2324
Number used	811	829	1985
Parameters refined	149	165	286 (2 blocks)
R_{int}	0·012	0·002	–
R	0·056	0·056	0·037
wR	0·076	0·033	0·045
Δ/σ less than	0·015	0·015	0·03
S	1·17	2·44	2·04
Q	5·4	5·0	6·9
Final ΔF map (e Å^{-3}) min.	−0·28	−0·32	−0·22
max.	+0·20	+0·30	+0·24
Weight = $A/[\sigma^2(F) + BF^2]$ A	1·14	5·49	2·82
B	0·0034	0·000019	0·00020

Table 2. *Fractional atomic coordinates and* U_{eq} *values* (Å^2)

$$U_{\text{eq}} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
1,3-Dinitro-1,3-diazacyclohexane, (I)				
C(1)	0·0540 (7)	0·6037 (2)	−0·1722 (7)	0·058 (3)
C(2)	0·2506 (7)	0·6842 (2)	−0·0797 (9)	0·062 (4)
C(3)	0·4264 (6)	0·6429 (2)	0·1261 (8)	0·061 (4)
C(4)	0·3584 (7)	0·5750 (2)	0·0750 (9)	0·061 (4)
N(1)	0·0185 (5)	0·6693 (1)	−0·1202 (6)	0·062 (3)
N(2)	0·1207 (5)	0·5659 (1)	0·0318 (6)	0·054 (3)
N(3)	0·1001 (7)	0·5634 (1)	0·2486 (7)	0·065 (3)
N(4)	−0·1452 (5)	0·7139 (2)	−0·1886 (5)	0·059 (3)
O(1)	0·2723 (7)	0·5477 (2)	0·4462 (6)	0·101 (4)
O(2)	−0·0917 (6)	0·5726 (1)	0·2235 (7)	0·087 (4)
O(3)	0·3441 (5)	0·6975 (2)	−0·2574 (6)	0·080 (3)
O(4)	−0·0798 (5)	0·7688 (1)	−0·1667 (5)	0·075 (3)
1,3-Dinitro-1,3-diazacycloheptane, (II)				
C(1)	−0·0896 (5)	0·6457 (4)	0·1534 (5)	0·033 (4)
C(2)	0·0264 (6)	0·6666 (4)	0·4465 (4)	0·042 (5)
C(3)	0·0074 (6)	0·7979 (4)	0·4558 (5)	0·046 (5)
C(4)	−0·0666 (7)	0·8721 (4)	0·3274 (5)	0·046 (5)
C(5)	0·0019 (6)	0·8641 (4)	0·1639 (5)	0·044 (5)
N(1)	0·0435 (4)	0·7567 (3)	0·0757 (3)	0·034 (3)
N(2)	0·0057 (4)	0·7484 (4)	0·0761 (3)	0·042 (4)
N(3)	0·0050 (3)	0·6153 (3)	0·2881 (3)	0·028 (3)
N(4)	0·1545 (4)	0·5885 (3)	0·2565 (4)	0·043 (3)
O(1)	−0·0314 (4)	0·6620 (3)	0·1565 (3)	0·072 (4)
O(2)	0·0824 (3)	0·8320 (3)	−0·1269 (3)	0·049 (3)
O(3)	0·1877 (3)	0·5766 (3)	0·1147 (3)	0·057 (3)
O(4)	0·2405 (3)	0·5751 (3)	0·3694 (4)	0·067 (3)
1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane, (III)				
C(11)	0·8474 (3)	0·6955 (5)	0·8654 (3)	0·038 (3)
C(12)	0·8993 (3)	1·0456 (5)	0·7775 (3)	0·034 (1)
C(13)	1·0331 (3)	0·7994 (5)	0·6970 (3)	0·035 (2)
C(14)	0·9918 (3)	0·5941 (5)	0·7423 (3)	0·036 (2)
N(11)	0·8690 (0)	0·6048 (4)	0·7639 (0)	0·036 (1)
N(12)	0·8578 (2)	0·9280 (4)	0·8647 (2)	0·034 (1)
N(13)	1·0200 (2)	0·9803 (4)	0·7667 (2)	0·034 (1)
N(14)	0·7726 (3)	0·6024 (4)	0·6724 (2)	0·042 (2)
O(11)	0·7943 (2)	0·5437 (5)	0·5841 (2)	0·061 (2)
O(12)	0·6729 (2)	0·6525 (5)	0·6887 (3)	0·058 (2)
N(15)	0·8309 (3)	1·0429 (5)	0·9456 (2)	0·047 (2)
O(13)	0·7926 (2)	0·9379 (5)	1·0159 (2)	0·058 (2)
N(16)	1·1152 (2)	1·0430 (4)	0·8495 (2)	0·035 (1)
O(14)	1·2148 (2)	0·9677 (4)	0·8483 (2)	0·047 (1)
O(15)	1·0950 (2)	1·1735 (4)	0·9163 (2)	0·049 (1)
C(22)	0·3666 (3)	0·5178 (5)	0·0213 (3)	0·035 (2)
C(21)	0·3290 (3)	0·8685 (5)	0·1185 (3)	0·038 (2)
C(24)	0·5008 (3)	0·9424 (5)	0·0208 (3)	0·039 (3)
C(23)	0·5282 (3)	0·7405 (6)	−0·0364 (3)	0·038 (2)
N(23)	0·4220 (2)	0·6027 (4)	0·0650 (2)	0·034 (1)
N(22)	0·2870 (2)	0·6673 (4)	0·0604 (2)	0·031 (1)
N(21)	0·4557 (2)	0·9001 (4)	0·1221 (2)	0·037 (1)
N(26)	0·3559 (2)	0·5999 (4)	−0·1719 (2)	0·035 (1)
O(24)	0·3954 (2)	0·6989 (4)	−0·2429 (2)	0·049 (1)
O(25)	0·2635 (2)	0·4922 (4)	−0·1991 (2)	0·046 (1)
N(25)	0·1702 (3)	0·6262 (5)	0·0357 (3)	0·044 (2)
O(23)	0·1068 (2)	0·7588 (5)	0·0688 (2)	0·054 (2)
N(24)	0·5374 (2)	0·8336 (5)	0·2155 (2)	0·041 (2)
O(21)	0·6441 (2)	0·8403 (5)	0·2110 (2)	0·057 (2)
O(22)	0·4972 (3)	0·7775 (5)	0·2969 (2)	0·059 (2)

cycloheptane and 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane respectively), have been reported (Bell & Dunstan, 1966*a*,*b*) to undergo optically birefringent to isotropic phase changes at tempertures somewhat below their melting points. Two of them, (I) and (II) were studied using differential scanning carloimetry (DSC) by Hall (1971) who identified the high-termperature phases as being of the plastic mesophase type. Other similar cyclic nitramines, in particular 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) of known crystal structure and higher molecular symmetry do not undergo this type of phase change. The present investigation sought to compare the crystal structures of the compounds with those of RDX and HMX in the context of their ability to form plastic phases.

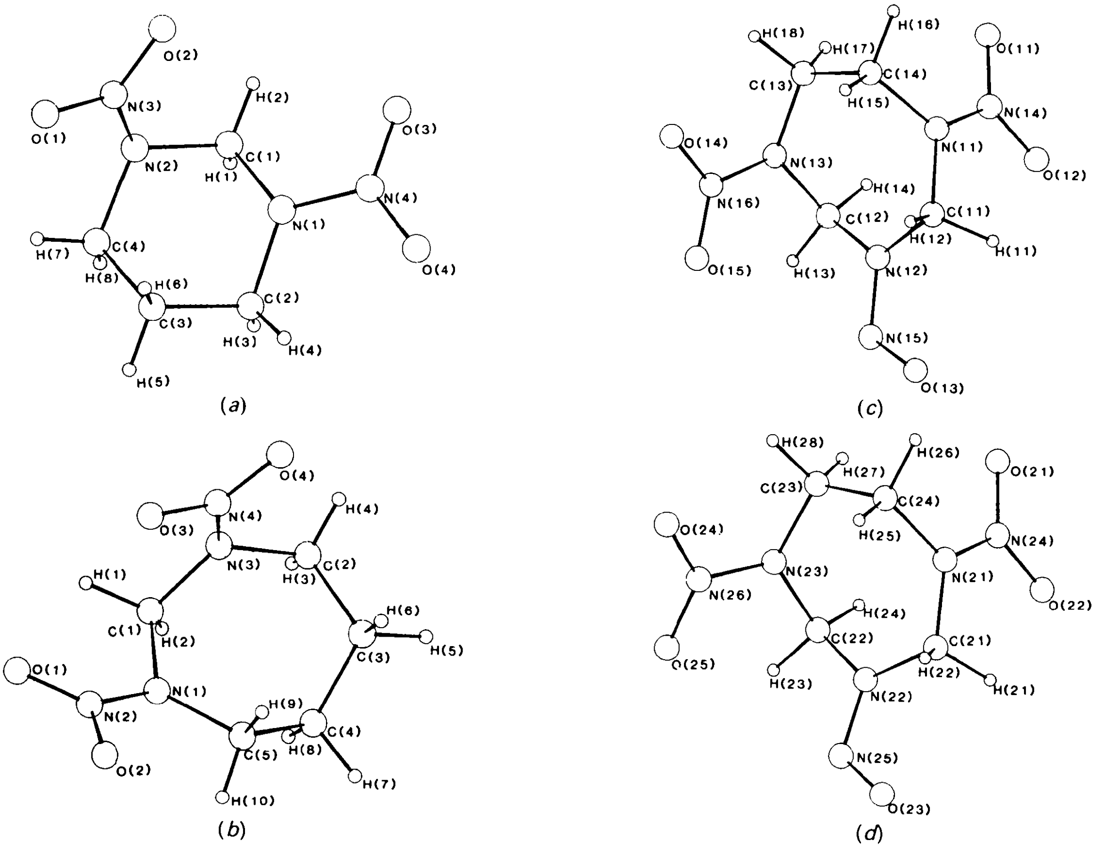
Experimental

Ambient-temperature investigation

As far as possible uniform conditions were used for data collection on the three title compounds. Table 1 summarizes these conditions and the figures of merit relating to the structure determination. Cell dimensions, initially from Weissenberg photographs [λ(Cu $K\alpha$) = 1·542 Å], were refined from setting angles of 20 reflexions in the ranges given in Table 1, on a STADI-2 two-circle diffractometer (graphite-monochromatized Mo $K\alpha$ radiation). This was also used for measurement of intensities from crystals of the sizes tabulated. In each case a standard was measured every 20 reflexions, intensity variation (< 10%) was corrected by linear interpolation. Measurements were made with a variable ω scan, $2\theta'$ fixed ($2\theta'$ is the projection of 2θ onto the equatorial plane for equi-inclination Weissenberg geometry), stationary background count. No absorption corrections made, Lp correction and data reduction using *SHELX*76 (Sheldrick, 1976). The structures were solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Least-squares refinement used F data for which $F > 6\sigma(F)$, full matrix for (I) and (II), two blocks alternately for (III). Positions and U_{ij} of C, N and O atoms refined. For H atoms, positions and U_{iso} of (I) and (II) were refined as were U_{iso} of (III), but positions for the latter were at coordinates calculated with C—H = 1·08 Å. For these and other calculations *SHELX76* was used. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are given in Table 2,* bond distances and angles in Table 3, the molecules with atomic labelling are shown in Fig. 1. The modes of molecular packing, including unit cells, of the three compounds are shown in Fig. 2.

High-temperature investigation

Crystals were mounted about known axes on fibres or in capillaries and heated by a stream of hot air maintained at constant temperature to within one degree. A Weissenberg instrument was found to be convenient for recording the patterns with Cu $K\alpha$ radiation. The behaviour of all three compounds with respect to increase of temperature was similar, no change in Weissenberg pattern was observed, until abruptly, the pattern disappeared when the transition temperature was reached. Stationary film patterns then showed polycrystalline rings, rarely of discrete spots and usually smooth and fairly sharp. Only two rings were observed for (I) and (III) and three for (II), the spacings indicated either simple or body-centred-cubic structures. Later evidence favoured the latter, the spacings were indexed as 110, 200 [and 220 for (II)], giving cubic unit cells of 7·5 (1), 7·7 (1) and 7·8 (1) Å respectively for (I), (II), and (III). Usually the transformed specimens could be cooled metastably to room temperature giving the same pattern for a period of a few hours. The high-temperature phases could also be produced by cooling from the melt. Once, exceptionally, a Weissenberg pattern of the mesophase of (II) was obtained from a crystal set originally in the low-temperature form about *b*, four reflexions 110, 200, 220 and 310 of a body-centred-cubic crystal rotated around *c* could be indexed. The crystal was poorly formed with the photograph showing an ω spread of approximately 10°. The material was contained in a capillary which may have induced orientation in the transformed crystal.



(*a*) (*c*) (*b*) (*d*)

Fig. 1. Molecules with atomic labelling: (*a*) 1,3-dinitro-1,3-diazacyclohexane; (*b*) 1,3-dinitro-1,3-diazacycloheptane; (*c*) 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane, molecule 1; (*d*) 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane, molecule 2.

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* Lists of structure factors, H-atom coordinates, anisotropic vibrational factors and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54257 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°)

1,3-Dinitro-1,3-diazacyclohexane, (I)

C(1)—N(1)	1·466 (5)	N(1)—N(4)	1·345 (4)
C(1)—N(2)	1·446 (5)	N(2)—N(3)	1·388 (4)
C(2)—N(1)	1·467 (5)	N(3)—O(1)	1·218 (4)
C(2)—C(3)	1·497 (5)	N(3)—O(2)	1·219 (4)
C(3)—C(4)	1·507 (5)	N(4)—O(3)	1·219 (4)
C(4)—N(2)	1·475 (5)	N(4)—O(4)	1·236 (4)
N(1)—C(1)—N(2)	108·3 (3)	N(4)—N(1)—C(1)	119·0 (3)
N(1)—C(2)—C(3)	109·0 (3)	N(4)—N(1)—C(2)	121·0 (3)
C(2)—C(3)—C(4)	111·7 (3)	N(2)—N(3)—O(1)	117·0 (3)
C(3)—C(4)—N(2)	110·3 (3)	N(2)—N(3)—O(2)	117·7 (4)
C(4)—N(2)—C(1)	114·0 (3)	O(1)—N(3)—O(2)	125·1 (4)
N(3)—N(2)—C(1)	114·5 (3)	N(1)—N(4)—O(3)	118·1 (4)
N(3)—N(2)—C(4)	116·1 (3)	N(1)—N(4)—O(4)	117·0 (3)
C(1)—N(1)—C(2)	116·7 (3)	O(3)—N(4)—O(4)	124·8 (3)

1,3-Dinitro-1,3-diazacycloheptane, (II)

C(1)—N(1)	1·461 (4)	N(1)—N(2)	1·347 (3)
C(1)—N(3)	1·438 (4)	N(3)—N(4)	1·367 (4)
C(2)—C(3)	1·502 (6)	N(2)—O(1)	1·223 (4)
C(2)—N(3)	1·473 (4)	N(2)—O(2)	1·228 (4)
C(3)—C(4)	1·505 (6)	N(4)—O(3)	1·232 (4)
C(4)—C(5)	1·499 (5)	N(4)—O(4)	1·217 (4)
C(5)—N(1)	1·466 (5)		
N(1)—C(1)—N(3)	113·1 (3)	C(1)—N(3)—N(4)	116·6 (3)
N(3)—C(2)—C(3)	113·0 (3)	C(2)—N(3)—N(4)	116·1 (3)
C(2)—C(3)—C(4)	114·8 (4)	N(1)—N(2)—O(1)	119·4 (4)
C(3)—C(4)—C(5)	116·7 (4)	N(1)—N(2)—O(2)	116·8 (4)
C(4)—C(5)—N(1)	113·7 (4)	O(1)—N(2)—O(2)	123·8 (3)
C(5)—N(1)—C(1)	123·3 (3)	N(3)—N(4)—O(3)	115·9 (3)
C(5)—N(1)—N(2)	116·5 (3)	N(3)—N(4)—O(4)	117·8 (3)
C(1)—N(1)—N(2)	116·8 (3)	O(3)—N(4)—O(4)	126·2 (4)
C(1)—N(3)—C(2)	120·5 (3)		

1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane, (III)

Molecule 1		Molecule 2	
C(11)—N(11)	1·436 (4)	C(21)—N(21)	1·438 (4)
C(11)—N(12)	1·479 (4)	C(21)—N(22)	1·487 (4)
C(12)—N(12)	1·458 (4)	C(22)—N(22)	1·457 (4)
C(12)—N(13)	1·458 (4)	C(22)—N(23)	1·442 (4)
C(13)—C(14)	1·527 (5)	C(23)—C(24)	1·521 (5)
C(13)—N(13)	1·456 (4)	C(23)—N(23)	1·465 (4)
C(14)—N(11)	1·469 (3)	C(24)—N(21)	1·463 (4)
N(14)—N(11)	1·384 (3)	N(24)—N(21)	1·371 (3)
N(14)—O(11)	1·216 (4)	N(24)—O(21)	1·220 (4)
N(14)—O(12)	1·227 (4)	N(24)—O(22)	1·232 (4)
N(15)—N(12)	1·316 (4)	N(25)—N(22)	1·315 (4)
N(15)—O(13)	1·237 (4)	N(25)—O(23)	1·228 (4)
N(16)—N(13)	1·368 (3)	N(26)—N(23)	1·360 (3)
N(16)—O(14)	1·225 (3)	N(26)—O(24)	1·230 (4)
N(16)—O(15)	1·219 (4)	N(26)—O(25)	1·226 (3)
N(11)—C(11)—N(12)	111·4 (3)	N(21)—C(21)—N(22)	110·3 (3)
N(12)—C(12)—N(13)	112·0 (2)	N(22)—C(22)—N(23)	113·2 (2)
N(13)—C(13)—C(14)	112·4 (3)	N(23)—C(23)—C(24)	112·0 (3)
C(13)—C(14)—N(11)	113·6 (2)	C(23)—C(24)—N(21)	112·2 (3)
C(14)—N(11)—C(11)	121·2 (2)	C(24)—N(21)—C(21)	121·7 (2)
C(14)—N(11)—N(14)	117·7 (2)	C(24)—N(21)—N(24)	117·9 (2)
C(11)—N(11)—N(14)	116·9 (2)	C(21)—N(21)—N(24)	118·1 (3)
C(11)—N(12)—C(12)	123·6 (3)	C(21)—N(22)—C(22)	124·0 (2)
C(11)—N(12)—N(15)	121·0 (3)	C(21)—N(22)—N(25)	118·8 (3)
C(12)—N(12)—N(15)	115·4 (3)	C(22)—N(22)—N(25)	117·1 (2)
C(12)—N(13)—C(13)	119·5 (2)	C(22)—N(23)—C(23)	120·6 (2)
C(12)—N(13)—N(16)	116·9 (2)	C(22)—N(23)—N(26)	117·6 (2)
C(13)—N(13)—N(16)	119·9 (2)	C(23)—N(23)—N(26)	119·4 (3)
N(11)—N(14)—O(11)	116·6 (3)	N(21)—N(24)—O(21)	116·6 (3)
N(11)—N(14)—O(12)	117·2 (3)	N(21)—N(24)—O(22)	117·6 (3)
O(11)—N(14)—O(12)	126·2 (3)	O(21)—N(24)—O(22)	125·8 (3)
N(12)—N(15)—O(13)	113·4 (3)	N(22)—N(25)—O(23)	114·6 (3)
N(13)—N(16)—O(14)	117·2 (3)	N(23)—N(26)—O(24)	117·6 (2)
N(13)—N(16)—O(15)	117·6 (2)	N(23)—N(26)—O(25)	117·4 (3)
O(14)—N(16)—O(15)	125·2 (2)	O(24)—N(26)—O(25)	124·9 (2)

Optical properties

Single crystals of the three compounds were examined using a hot stage under the polarizing microscope. Quite sharply, at the transition temperature the bright birefringent colour of the low-temperature form was replaced by darkness moving as a front across the crystal. Suitable temperature manipulation could reverse the process causing the single crystal to regrow provided a small fragment of the original remained to nucleate the growth. Once the whole sample had transformed to the high-temperature phase, cooling would yield a polycrystalline mass, often spherulitic, of the low-temperature form, sometimes after considerable delay.

Thermodynamic investigation

Calorimetric measurements were made using a Perkin Elmer 1B differential scanning calorimeter. For each of the compounds a major endotherm was observed at the transition temperature and a much smaller one at the melting point. The results are summarized in Table 4. For (I) the enthalpy changes are in significant agreement with those of Hall (1971)

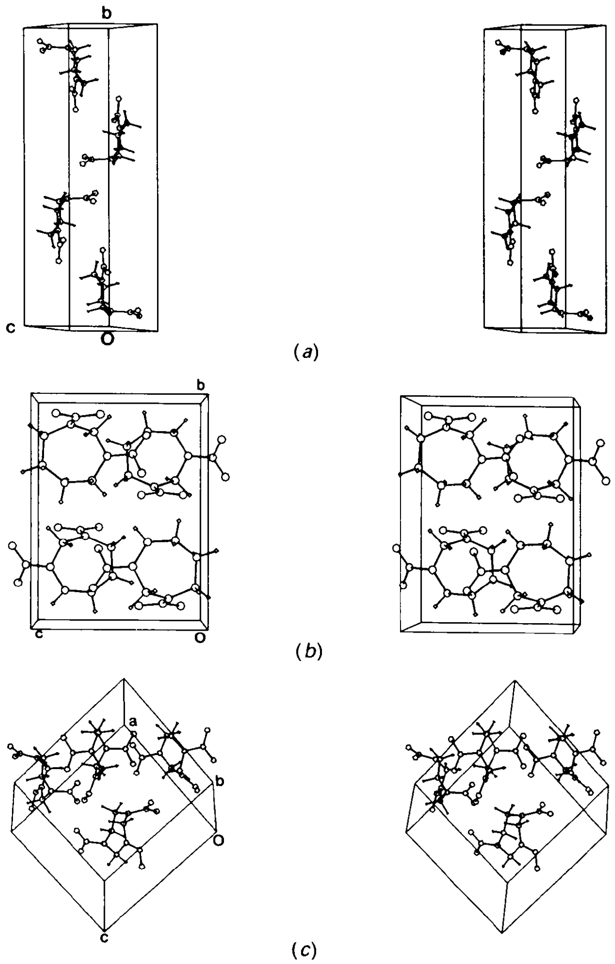


Fig. 2. Molecular packing showing unit cells: (*a*) 1,3-dinitro-1,3-diazacyclohexane projected on (100); (*b*) 1,3-dinitro-1,3-diazacycloheptane projected on (100); (*c*) 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane projected on (111).

Table 4. *Thermal data*

	(I)	(II)	(III)
Transition temperature (K)	343	369	404
Melting point (K)	354	374	440
$\Delta H_{\rm trans}$ (kJ mol^{-1})	15·8 (1)	21·8 (2)	25·7 (3)
$\Delta H_{\rm fusion}$ (kJ mol^{-1})	2·97 (4)	2·8 (1)	2·9 (2)
$\Delta S_{\rm trans}$ (J K^{-1} mol^{-1})	46·0 (3)	58·9 (6)	63·6 (8)
$\Delta S_{\rm fusion}$ (J K^{-1} mol^{-1})	8·4 (1)	7·5 (3)	6·6 (5)
ΔV transition (Å^3 molecule^{-1})	13·2	17·0	–
V ordered (298) (Å^3 molecule^{-1})	186·1	205·1	213·9
V plastic ($T_{\rm trans}$) (Å^3 molecule^{-1})	211	228	237

who gave only approximate values for the enthalpy changes in (II) and did not investigate (III).

Volume changes accompanying the phase transitions were made using a dilatometer which was a modification of one previously described (Howell & Stubley, 1969). After careful evacuation the material (100–200 mg) was sealed under mercury. No reliable measurements could be made in the case of (III) as a slight amount of gas was produced from the decomposition resulting from the higher temperature involved. The results are included in Table 4.

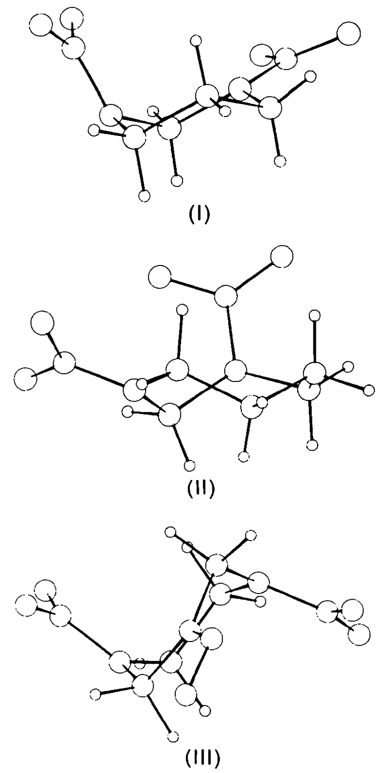
Discussion

Ambient-temperature structures

In all three compounds the NNO_2 groups are planar to within 0·025 Å, the $CCNNO_2$ (nitramine) groups are however only approximately planar, in common with all nitramines [except dimethylnitramine which lies on a mirror plane (Krebs, Mandt, Cobbledick & Small, 1979)]. This is mainly a consequence of non-planarity of the bonds around the amine N atoms. Over all the eight different nitramine groups in the three present compounds, the mean deviation of the C atoms from the NNO_2 planes is 0·259 Å (least 0·019, most 0·478 Å). A feature of the molecule are the O···H intramolecular interactions shown by the distances which are all in the narrow range 2·13 to 2·44 Å (mean value 2·30 Å). Similar values are found in other nitramine structures such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) where they are considered to impart rigidity to the molecule as revealed by careful analysis of the neutron diffraction U_{ij} values (Choi & Prince, 1972). The inference is drawn that in the present three compounds the molecules may also be described as rigid.

The molecule of (I) has some features in common with RDX (Choi & Prince, 1972) in which two of the NNO_2 groups are inclined at 62° to the plane of the C atoms and the third group at 18°. In (I) the plane C(1)C(2)C(4) is inclined at 15·9 (3)° to the plane N(1)N(4)O(3)O(4) and at 71·5 (3)° to the plane N(2)N(3)O(1)O(2). This difference is partly a result of the bonds around N(2) being more pyramidal, mean angle 114·9°, than those around N(1), mean angle 118·9°, the same situation also exists in the RDX molecule. In both structures the N—N bond length decreases when the amine N atom is more planar, in (I) for the more planar group N(1)—N(4) = 1·345 (4) Å and for the other N(2)—N(3) = 1·388 (4) Å [the relevant distances in RDX are 1·351 (3) (most planar), 1·392 (3), 1·398 (3) Å]. In (I) the decrease in N—N distance in the more planar NNO_2 group is compensated by an increase of one of the N—O distances, a feature also present in RDX. The C—C distances in (I), 1·497 (5), 1·507 (5) Å, are significantly shorter than the mean, 1·536 Å, of 2814 values between sp^3-bonded C atoms in cyclohexane derivatives tabulated by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987). There are no intermolecular distances between heavy atoms in (I) shorter than 3·13 Å.

In the molecule of (II) the ring atoms C(1), C(2), C(3) and C(5) are planar to within 0·067 Å with N(1), N(3) 0·098 (4) and 0·677 (4) Å respectively above that plane and C(4) 0·754 (4) Å below. The inclination of N(1)N(2)O(1)O(2) to this plane is 28·4 (4)° and that of N(3)N(4)O(3)O(4) is 92·7 (4)°. Compared with (I) there is less difference between the mean angles around N(1) and N(3) 118·9 and 117·7° respectively and a correspondingly smaller difference between N(1)—N(2), 1·347 (3) and N(3)—N(4), 1·367 (4) Å. The mean C—C distance, 1·502 Å,


(I)

(II)

(III)

Fig. 3. Molecules of the title compounds, viewed along the ring planes.

is again less than the mean value for cyclohexane derivatives. A notable feature of (II) is the increase of the endocyclic angles at the C atoms, mean value 114·3 compared with 109·8° in (I). The shortest intermolecular distance is 3·02 Å between O atoms.

The two crystallographically unrelated molecules in (III) have closely similar bond distances and angles, Table 3. The ring conformations also show close similarities; in molecule 1, N(12), C(11), C(14) and N(13) are coplanar to within 0·064 (4) Å with C(13), N(11), C(12), 0·336 (4), 0·605 (4) and 0·652 (4) Å respectively above that plane; in molecule 2, N(22), C(21), C(24) and N(23) are coplanar to within 0·011 (4) Å with C(23), N(21), C(22), respectively 0·360 (4), 0·627 (4) and 0·608 (4) Å above the plane. The mean angles at the amine N atoms are closer to 120° than in (I) or (II), being, at N(11), N(12), N(13) respectively 118·6, 120·0, 118·8° and at N(21), N(22), N(23) respectively 119·2, 120·0, 119·2°. In these molecules the mean angles at the C atoms, 112·4° in 1 and 111·9° in 2, are nearer to the tetrahedral value than in (II). The inclinations of the nitro and nitroso groups to the mean plane of the four ring atoms previously defined are: for N(11)N(14)O(11)O(12), N(13)N(16)O(14)O(15), N(12)N(15)O(13), 80·3 (3), 65·6 (3) and 24·9 (3)° respectively and for N(21)N(24)O(21)O(22), N(23)N(26)O(24)O(25), N(22)N(25)O(23), 77·4 (3), 57·3 (3) and 34·7 (3)° respectively. The inclinations of the nitro groups defined by N(14), N(24) are in the opposite sense relative to the ring atoms compared with the groups defined by N(16), N(15), N(26), N(25), thereby imparting to both molecules in (III) an overall chairlike shape compared with the cup or dish shape of the molecules of RDX, (I) and (II), Fig. 3. Intermolecular contacts between N(26)···O(22), 2·946 (4) Å in *c*-glide-related molecules of the same type and C(12)···O(21), 2·913 (4) Å between molecules of different types, have values which in other structures, *e.g.* RDX, have been considered to be 'short'. In spite of the differences of environment the two molecules in (III) are closely similar in shape, further evidence possibly of their rigidity.

High-temperature structures

The optical isotropy of the high-temperature phases of the title compounds indicates that they are cubic. The rather meagre diffraction patterns would accord with either simple or body-centred lattices. Simple cubic can be eliminated since the measured spacings interpreted on this basis would give molar volumes considerably less than the molar volumes of the low-temperture ordered crystals. The high-temperature structures are therefore most likely body-centred cubic, this is confirmed in the case of (II) by the Weissenberg pattern.

With two molecules per unit cell the necessary symmetry can only be achieved by disorder of some type, *e.g.* by having 48 alternative orientations of the unsymmetrical molecules involved. The entropy change associated with the change from a single molecular orientation in the low-temperature phase to 48 at the high temperature would be $R\ln48$ (32·2 J K^{-1} mol^{-1}) using the method of Guthrie & McCullough (1961). This is considerably less than any of the observed entropy changes (Table 4), suggesting that further effects such as free or hindered rotation are important entropy contributions in these three structures. The highly disordered nature of these phases (plastic crystals) is confirmed by the limited angular range of their diffraction patterns (high thermal-vibration factors) and the low entropies of fusion. These latter entropies are of the order of R (8·31 J K^{-1} mol^{-1}) for all three compounds indicating that on melting only the positional order is lost and three degrees of translational freedom gained, rotational freedom in the plastic crystals having already been achieved. Comparatively little structural information can be derived from the limited diffraction data.

Phase transitions

Crystals which have been described as plastic vary considerably in their degree of disorder. At one extreme adamantane (Nordman & Schmidtkons, 1965) has high molecular symmetry and only two alternative orientations are required to achieve the site symmetry in the face-centred-cubic structure, 39 unique reflexions have been measured and detailed structure investigation is possible; there is correspondingly a low entropy of transition (16·2 J K^{-1} mol^{-1}). Similarly in 1-fluoroadamantane (Amoureux, Bee & Sauvajol, 1982) with lower symmetry, 116 reflexions have been measured (59 significantly) and a model involving eight 'equilibrium' orientations derived. The present three compounds represent the other extreme of plastic crystalline behaviour, *i.e.* no molecular symmetry and extensive disorder required to simulate cubic site symmetry. It is of interest to compare the crystal structues and molecular shapes of the present three compounds with those of the closely related nitramines, RDX and HMX, melting points 479, 552 K (with decomposition) respectively, which do not show plastic premelting phase changes (both of these compounds are of technical importance as propellants and have been extensively investigated, it is unlikely that any significant range of plastic behaviour has been overlooked). HMX is polymorphic showing two molecular conformations, the shape relevant to this discussion is that found in the delta form (Cobbledick & Small, 1974), stable from 433 K to the melting point. This molecule which also occurs in some other polymorphic modifications and in intermolecular complexes has effectively *mm* symmetry. RDX has molecular symmetry *m*, which is noncrystallographic but fairly exact. Higher molecular symmetry is one factor which would favour plastic crystallinity as fewer molecular orientations would be required to achieve cubic site symmetry. In this instance symmetry differences therefore would operate against plastic crystal behaviour in the title compounds compared with RDX and HMX.

Other factors considered important in plastic crystallinity (Timmermans, 1961; Hall, 1971) are, a 'globular' shape without projecting groups, absence of strong intermolecular forces and a degree of flexibility of the molecule leading to a more compact shape at higher temperature. Differences in flexibility between RDX, HMX on the one hand and (I), (II), (III), suggested by Hall (1971), are unlikely to be significant as the similarity of shape and the existence of intramolecular $O\cdots H$ interactions point to equal rigidity in all five compounds. Molecular shape and mode of packing remain as the most important factors. Profiles of the van der Waals molecular envelopes are compared in Fig. 4; it will be noted that the three title compounds, although by no means spherical show no great eccentricity and may be described as approximately globular in spite of their asymmetry. On the other hand the profile of the HMX molecule is somewhat more elongated, a feature which together with an unusually close $C\cdots O$ intermolecular approach (2·89 Å), could account for the absence of a plastic phase. The overall profile of the RDX molecule is similar to those of the title compounds except that it is markedly cup-shaped. In the crystal, pairs of centrosymmetrically related RDX molecules interlock in a manner which involves use of the quite deep central depression, thereby making reorientation difficult.

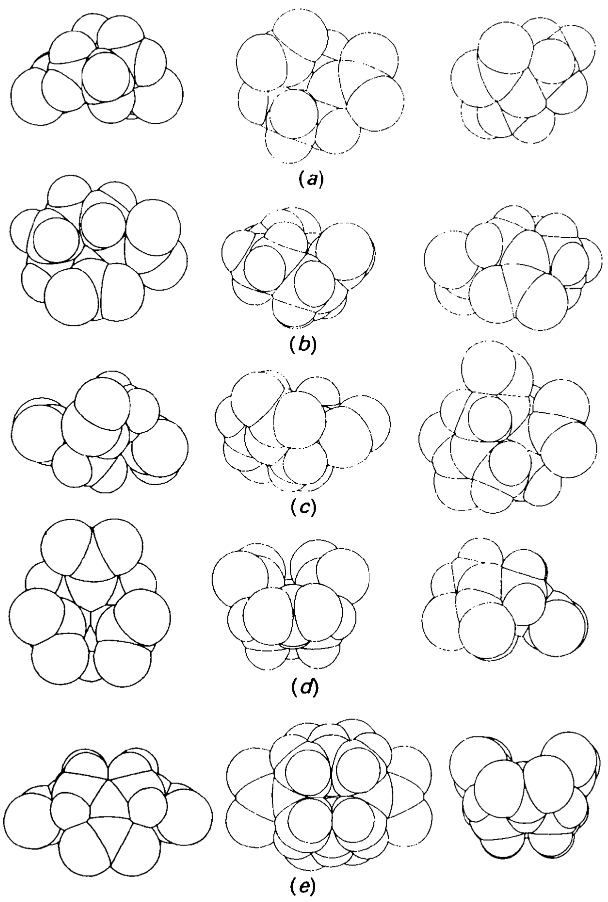


Fig. 4. Profiles of van der Waals envelopes of molecules with radii, C = 1·5, N = 1·5, O = 1·4, H = 1·2 Å. Three approximately orthoganol projections (including the most eccentric) of each molecule are shown: (*a*) 1,3-dinitro-1,3-diazacyclohexane (I); (*b*) 1,3-dinitro-1,3-diazacycloneptane (II); (*c*) 1,5-dinitro-3-nitroso-1,3,5-triazacycloheptane (III); (*d*) 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX); (*e*) 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).

Moreover the pairs of molecules are involved in two short $N\cdots O$ interactions (2·990 Å), the low-temperature ordered structure of RDX is thus rendered particularly stable. In the structues of the three title compounds, this interlocking effect is absent on account of the more compact shapes of the molecules and their more open modes of crystal packing, (Fig. 2), enabling rotation and escape of the molecules from their immediate environment.

In conclusion, the investigation does not provide any single decisive reason explaining the existence of stable plastic crystal forms of the title compounds compared with the closely similar RDX and HMX. The presence of polar groups or weak intermolecular forces do not appear to inhibit plastic crystallinity. The most important factor may be the mode of molecular packing in the ordered phase.

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Transferability of Deformation Densities among Related Molecules: Atomic Multipole Parameters from Perylene for Improved Estimation of Molecular Vibrations in Naphthalene and Anthracene

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Abstract

Earlier crystallographic refinements of naphthalene and anthracene against X-ray data recorded at five and six temperatures, respectively, have been repeated with atomic charge-deformation parameters transferred from a low-temperature study of perylene. Inclusion of these parameters causes the in-plane molecular translation amplitudes to decrease, and those normal to the plane to increase, with respect to values obtained with the spherical-atom model. The revised translation tensors are systematically smaller than those predicted by published lattice-dynamical calculations but the librations agree somewhat better. Their temperature dependence shows no anomalous behavior and accords qualitatively with the simplified model of Cruickshank [*Acta Cryst.* (1956), **9**, 1005–1009].

Introduction

In fitting a set of model parameters to experimental data, as in crystal structure refinement, it is often advantageous to reduce the flexibility of the model by fixing those parameters that are better known, from theory or previous experiments, than they can be determined from the observed data. Thus, for macromolecular structures yielding low-resolution X-ray data, it is routine to simplify the structural model by constraining bond lengths and angles or fixing the geometry of such groups as phenyl substituents. Even the use of atomic scattering factors calculated for spherical atoms constitutes such a simplification. This practice has the great advantage that the structure factors can be calculated by summation over the atoms, with a few parameters per atom, rather than by integration over the electron density. However, it is well known that the spherical-atom approximation may produce severe systematic errors in the refined atomic parameters (Ruysink & Vos, 1974; Hirshfeld, 1976). A powerful way to eliminate such errors is to refine electron deformation (multipole) parameters together with the atomic coordinates and displacement parameters (Stewart, 1976; Hansen & Coppens, 1978; Hirshfeld, 1991), but such a refinement requires highly accurate and extensive X-ray data. What if the data available are inadequate for such a treatment? One possibility is to set the deformation parameters at their most likely values, estimated either from theoretical electron density distributions or from multipole analyses of chemically related molecules.

The present study is an initial attempt in this direction. Its specific aim is to improve the temperature-dependent anisotropic displacement parameters (ADP's) of naphthalene between 92 and 239 K and of anthracene between 94 and 295 K that were derived by conventional least-squares analyses from X-ray data of moderate resolution (Brock &

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