

## The Crystal Structure of Cyclotrimethylene-trinitramine

BY C. S. CHOI

*Feltman Research Laboratory, Picatinny Arsenal, Dover, N. J. 07801, U.S.A., and Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234, U.S.A.*

AND E. PRINCE

*Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234, U.S.A.*

(Received 10 April 1972 and in revised form 24 May 1972)

The structure of cyclotrimethylene-trinitramine (RDX),  $C_3H_6N_6O_6$ , has been refined from single-crystal neutron-diffraction data. The final weighted  $R$  index for 836 independent reflections is 0.021. The compound crystallizes in the orthorhombic space group  $Pbca$ ,  $a = 13.182$  (2),  $b = 11.574$  (2),  $c = 10.709$  (2) Å,  $Z = 8$ . The molecule consists of alternate  $CH_2$  and  $N-NO_2$  groups in a puckered ring. The environment of the carbon atoms is essentially tetrahedral, and the  $N-NO_2$  groups are planar. The molecule possesses a plane of approximate mirror symmetry perpendicular to the plane defined by the three carbon atoms. The thermal motion may be described by rigid-body motion of the ring and separate rigid-body motion of the nitro groups.

### Introduction

The compound cyclotrimethylene-trinitramine,  $C_3H_6N_6O_6$ , also known as Cyclonite, or by the code designation RDX, is a well known explosive. There are two known polymorphic forms, designated RDX(I) and RDX(II) (McCrone, 1950). The structure of RDX(II) has not been determined because of the difficulty of obtaining and preserving well formed crystals, even for short periods, owing to its extreme instability. This paper describes the refinement of the structure of RDX(I); it will be referred to hereafter simply as RDX.

The crystal structure of RDX was first investigated by Hultgren (1936). He reported that it possesses orthorhombic symmetry, with eight molecules per unit cell and most probable space group  $V_h^{15}(Pbca)$ . A complete crystal morphology has been reported by McCrone (1950). The crystal structure of RDX was re-investigated by Harris & Reed (1959) using three-dimensional X-ray photographic data. They determined the complete crystal structure except for the hydrogen positions. The present study was undertaken to complete the crystal structure by determining the hydrogen positions and refining overall structural details.

### Experimental

The unit-cell dimensions were determined by a least-squares fit to scattering angles measured by X-ray diffraction. For this, the scattering angles ( $2\theta$ ) of the 30 most intense reflections having scattering angles in the range 35 to 60° were measured on an automated Picker 4-circle diffractometer with Mo  $K\alpha$  radiation monochromated by a pyrolytic graphite plate. The unit-cell dimensions thus obtained are,  $a = 13.182$  (2),  $b = 11.574$  (2),  $c = 10.709$  (2) Å, and  $D_x = 1.806$ . The observed

density is reported as  $D_m = 1.816$  (Federoff & Sheffield, 1966) and the melting point is 205°C (McCrone, 1950).

A crystal, approximately  $1.4 \times 1.2 \times 0.9$  mm, was used for this experiment. The crystal was mounted on a four-circle neutron diffractometer controlled by a computer (Alperin & Prince, 1970). The crystal was oriented with its  $a$  axis nearly, but not exactly, parallel to the  $\phi$  axis, in order to avoid systematic effects due to multiple diffraction. The diffraction intensities were measured by the procedure described by Prince (1972). With a neutron wavelength of 1.232 Å and a limiting  $2\theta$  angle of 100° there are 1590 independent reflections. The intensity at the peak position of each reflection was compared with the intensities at background positions on either side, and if the peak intensity ( $I_p$ ) did not exceed background ( $I_b$ ) by  $2\sigma$ , where  $\sigma$  is given by  $\sigma = (I_p + I_b)^{1/2}$ , the reflection was considered to be unobserved. 836 of the 1590 independent reflections had observable intensities. The intensities of all observed reflections were converted to relative structure factors and each was assigned a standard deviation,  $\sigma_F$ , based on counting statistics. The calculated linear absorption coefficient is  $1.2 \text{ cm}^{-1}$ , assuming an effective incoherent scattering cross-section for hydrogen of  $42 \times 10^{-24} \text{ cm}^2$  (Rush, Taylor & Havens, 1962). The maximum variation in  $F$  due to absorption is less than  $\pm 0.8\%$ . This was considered to be negligible, and no absorption corrections were made.

The positional parameters for the heavy atoms, as determined by Harris & Reed (1959), were used to compute signs for  $F_o$  and  $(F_o - F_c)$  Fourier syntheses. All hydrogen atom positions were determined from the difference synthesis. Three cycles of least-squares refinement with the program *RFINE* (Finger, 1968) with isotropic temperature factors, gave a weighted  $R$  index  $\{wR = [\sum w(s|F_o| - |F_c|)^2 / \sum wF_c^2]^{1/2}$  where  $s$  is the scale factor and  $w = 1/\sigma_F^2\}$  of 0.093. The refinement was continued

with anisotropic temperature factors for all atoms. An isotropic secondary extinction parameter,  $S$ , was included in the refinement, using the formula (Zachariasen, 1968)  $F_{\text{cor}} = |F_c|(1 + S\beta F_c^2)^{-1/4}$ , where  $\beta$  is a parameter proportional to the Lorentz factor. The final value of  $S$  was  $0.484 \times 10^{-3}$  for  $\beta = 1/\sin 2\theta$ . The two strongest reflections, 102 and 200, with calculated extinction factors of 0.7282 and 0.7275 respectively, were omitted from the final stage of refinement because of severe extinction. The final discrepancy indices were  $wR = 0.021$  and  $R = 0.039$  for all observed reflections except the two strongest reflections. The largest parameter shift in the last cycle was less than 0.01 of the standard deviation. The final least-squares parameters are given in Table 1, and the observed and calculated structure factors are listed in Table 2. There was no observable trend in the values of the function  $1/s \sum_s w(|F_o| - |F_c|)^2$ ,

where  $s$  is the number of reflections in a subset, for subsets of the observed reflections divided according to ranges of  $F$  and  $\sin \theta/\lambda$ . The difference Fourier map obtained after final least-squares refinement was featureless.

### Discussion

The heavy atom positions obtained in the present work all agree well with those reported in the previous X-ray study of Harris & Reed (1959), with differences of less than 0.02 Å in bond length and 0.8° in bond angle. The interatomic distances and angles in the RDX molecule, as obtained in the present study, are given in Table 3. The molecule of RDX consists of three N-NO<sub>2</sub> groups linked to three methylene groups alternately to form a puckered, six-membered C-N ring (see Figs. 1 and 2). The N(1)-NO<sub>2</sub> group is essentially

Table 1. Final least-squares parameters for the structure of RDX

Thermal parameters are the coefficients,  $B_{ij}$  (Å<sup>2</sup>), in the form  $\exp[-\frac{1}{4}(B_{11}a^2h^2 + B_{22}b^2k^2 + B_{33}c^2l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$ .

The estimated standard deviations are in parentheses.

	$x/a$ ( $\times 10^4$ )	$y/b$ ( $\times 10^4$ )	$z/c$ ( $\times 10^4$ )	$B_{11}$ ( $\times 10^2$ )	$B_{22}$ ( $\times 10^2$ )	$B_{33}$ ( $\times 10^2$ )	$B_{12}$ ( $\times 10^2$ )	$B_{13}$ ( $\times 10^2$ )	$B_{23}$ ( $\times 10^2$ )
C(1)	1839 (3)	3578 (3)	4400 (3)	322 (15)	297 (13)	206 (14)	-70 (13)	-69 (11)	7 (12)
C(2)	503 (2)	2440 (2)	3395 (3)	233 (15)	145 (11)	344 (13)	8 (13)	-1 (13)	-17 (11)
C(3)	1487 (2)	3813 (3)	2159 (3)	252 (14)	332 (16)	175 (14)	-34 (13)	34 (11)	-31 (12)
N(1)	1761 (2)	4360 (2)	3330 (2)	267 (8)	266 (8)	251 (9)	-109 (8)	1 (8)	0 (8)
N(2)	877 (2)	2996 (2)	4537 (2)	295 (9)	210 (8)	250 (9)	14 (8)	33 (8)	9 (7)
N(3)	536 (1)	3222 (2)	2329 (2)	211 (9)	228 (8)	274 (9)	15 (8)	-35 (7)	-37 (7)
N(4)	2260 (2)	5379 (2)	3346 (2)	217 (8)	241 (9)	348 (10)	-55 (8)	79 (9)	-26 (9)
N(5)	155 (2)	3525 (2)	5294 (2)	455 (14)	322 (10)	256 (10)	157 (10)	104 (9)	77 (9)
N(6)	-333 (2)	3875 (2)	2078 (2)	284 (11)	306 (10)	316 (10)	72 (9)	-72 (9)	-53 (8)
O(1)	2270 (3)	5932 (3)	2388 (4)	566 (23)	330 (17)	407 (19)	-122 (18)	82 (17)	68 (16)
O(2)	2649 (3)	5687 (3)	4338 (4)	342 (16)	330 (17)	417 (19)	-86 (15)	-13 (16)	-131 (14)
O(3)	-693 (3)	3142 (4)	5262 (4)	333 (21)	718 (26)	426 (20)	138 (21)	153 (17)	156 (19)
O(4)	454 (4)	4271 (3)	5990 (3)	894 (32)	381 (21)	258 (16)	251 (22)	57 (20)	-53 (15)
O(5)	-1121 (3)	3534 (4)	2504 (4)	246 (16)	572 (25)	584 (25)	44 (17)	-62 (16)	22 (21)
O(6)	-236 (4)	4691 (4)	1390 (4)	644 (27)	441 (23)	415 (20)	185 (21)	-91 (20)	62 (18)
H(1)	2401 (6)	2944 (7)	4226 (7)	372 (33)	532 (36)	564 (37)	-14 (30)	-128 (31)	141 (32)
H(2)	2013 (6)	4068 (6)	5244 (6)	762 (43)	560 (37)	270 (29)	-201 (34)	-127 (29)	-59 (28)
H(3)	-261 (5)	2117 (6)	3540 (6)	371 (34)	433 (33)	597 (35)	-146 (29)	-18 (31)	16 (27)
H(4)	1015 (5)	1728 (5)	3192 (7)	464 (30)	263 (26)	594 (37)	89 (27)	-16 (27)	-114 (27)
H(5)	2052 (5)	3166 (6)	1917 (6)	314 (28)	602 (37)	524 (37)	46 (30)	80 (25)	-225 (30)
H(6)	1440 (6)	4432 (7)	1413 (7)	637 (44)	602 (39)	363 (35)	-170 (35)	17 (28)	108 (31)

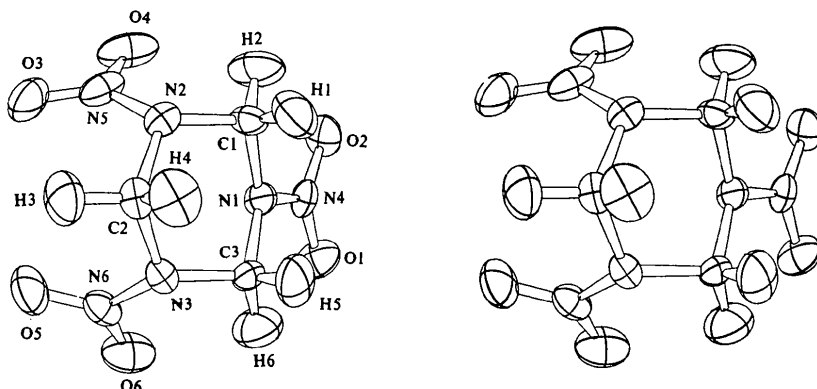


Fig. 1. RDX molecule showing a stereoscopic pair viewed from top of the molecular ring.

coplanar but the N(2)-NO<sub>2</sub> and N(3)-NO<sub>2</sub> groups are slightly bent. The distances of atoms from the best fit mean plane of each N-NO<sub>2</sub> group are given in Table 4. The bond lengths and bond angles of the N(1)-

NO<sub>2</sub> and N(3)-NO<sub>2</sub> groups are very similar but the configuration of the N(1)-NO<sub>2</sub> group is quite different. For the N(1)-NO<sub>2</sub> group, the N-N distance is shorter by approximately 0.04 Å, and the C-N-N angles are

Table 2. Observed and calculated structure factors for RDX

Unobserved reflections are indicated by an asterisk.

2 451* 472	1 62 -67	H*11,1	4 121 111	4 58 55	3 74* 26	7 130 121	4 237 55	10 243 242	12 134 145	12 82* 70	H*3,9	2 78* -20
4 394 -96	2 311 -313	1 121 117	5 64* -95	5 80* -95	4 132* -127	8 72* 67	5 347 346	11 72* 0	13 84 83	H*1,7	1 290 300	3 73* 61
6 103 -96	4 362 -362	3 73 78	6 198 83	6 45* -119	6 45* -119	10 75* 60	7 120 -121	13 182* 2		H*2,8	3 75* -77	2 104 -90
8 345 -139	5 100 103	4 321 322	8 71* -51	8 235 236	0 89* 49*	11 77* -30	8 71 50	0 80 77		H*3,7	5 106 139	4 94 -103
10 335 -331	6 256 257	5 154 -190	9 69* -71	9 93 113	0 93* 49*	12 39* 52	0 44* 45*	2 71* -63		H*4,8	3 136 139	6 115 -120
12 72* -11	7 326 -332	6 71 71	10 207 209	10 74* 71	1 38* 9	13 124 122	2 155* -164	3 341 -339	3 106 -310		4 129 139	7 97* -37
14 154 -136	8 177 -184	7 315 -135	11 157 168	11 31* 31	2 73* 73	14 182 182	3 167 -164	4 105 -96	5 174 -186		5 136 136	8 153 -144
16 42* -39	9 89 76	8 38* 36	12 108 95	12 223 -220	3 178 179	15 216 -159	4 368 40	5 331 331	6 72* -3		6 129 137	9 179 -198
H*1,0	10 109 -111	9 37* -18	13 38* -34	13 176 -185	4 182 -166	2 131 -132	5 78* -15	6 358 40	7 216 -216		7 151 151	8 183 -182
2 295 -286	12 207 -59	10 30* 30	14 40* -22	15 70* 73	5 194 -185	6 104 -112	7 203 203	8 164 -166	9 232 218		8 79* -11	11 77* 16
4 248 -272	14 234 -246	0 131 128	1 118 -118	H*4,3	6 143 132	6 271 271	1 64* 50	2 165 -166	3 125 112		9 80* 64	10 79* -42
6 238 -286	16 234 -246	2 135 79	2 70* -69	0 63* 4	7 193 -184	8 79* -37	3 221 245	4 75* -72	5 114 -118		11 81 83	12 37* -38
8 191 -410	18 78* -28	3 154 -140	3 135 -140	4 272 264	4 272 264	5 138 -83	6 78* -15	7 101 -77	8 114 -114		12 79* 58	1 176 -181
12 339 36	H*3,1	4 370 -40	5 65* -58	5 243 238	5 243 238	6 185 -155	7 101 -77	8 114 -114	9 125 -125		13 80* 6	2 91 89
14 78* 208	H*3,1	6 30* -30	7 65* -65	8 252 254	8 252 254	9 60* -42	10 149 139	11 39* -38	12 80* -80		H*3,8	3 133 -126
16 80* 33	2 119 -132	5 80* -70	6 252 254	6 60* -42	14 81* 25	15 70* -22	16 78* 78	17 78* 78	18 80* -80		H*4,7	4 82* 94
0 197 204	4 247 247	7 162 169	8 249 250	9 60* -28	15 41* 13	16 80* -80	17 78* 78	18 80* -80	19 100 107		H*5,6	5 371 -358
2 516 -529	6 65* 59	8 69* 8	9 80* -78	10 75* -80	11 75* -80	12 80* -80	13 80* -80	14 80* -80	15 100 107		H*6,5	6 89 88
4 482 485	8 65* 59	10 75* -80	11 75* -80	12 80* -80	13 80* -80	14 80* -80	15 100 107	16 100 107	17 100 107		H*7,4	7 70* -56
6 150 172	8 124 -126	1 76* 49	2 68* -68	3 79* -79	4 89* -89	5 99* -99	6 109* -109	7 119* -119	8 129* -129		H*8,3	8 70* -56
8 330 335	4 37* -61	2 77* -88	3 77* 85	4 77* 85	5 77* 85	6 77* 85	7 77* 85	8 77* 85	9 77* 85		H*9,2	9 70* -56
10 71 36	10 268 267	3 77* 85	4 77* 85	5 77* 85	6 77* 85	7 77* 85	8 77* 85	9 77* 85	10 77* 85		H*10,1	10 70* -56
12 37* 36	11 526 -521	4 78* -86	5 78* -86	6 78* -86	7 78* -86	8 78* -86	9 78* -86	10 78* -86	11 78* -86		H*11,0	11 70* -56
14 62* -94	12 164 151	5 150 171	6 150 171	7 150 171	8 150 171	9 150 171	10 150 171	11 150 171	12 150 171		H*12,0	12 70* -56
16 137 -143	13 81* -7	6 75* 18	7 75* 18	8 75* 18	9 75* 18	10 75* 18	11 75* 18	12 75* 18	13 75* 18		H*13,0	13 70* -56
H*3,0	15 78* -70	8 103 101	9 103 101	10 103 101	11 103 101	12 103 101	13 103 101	14 103 101	15 103 101		H*14,0	14 70* -56
2 76 91	H*3,0	0 166 -163	1 174 174	2 174 174	3 174 174	4 174 174	5 174 174	6 174 174	7 174 174		H*15,0	15 70* -56
4 416 446	H*4,1	0 166 -163	1 174 174	2 174 174	3 174 174	4 174 174	5 174 174	6 174 174	7 174 174		H*16,0	16 70* -56
6 275 288	0 369 -368	2 38* -18	3 38* -18	4 38* -18	5 38* -18	6 38* -18	7 38* -18	8 38* -18	9 38* -18		H*17,0	17 70* -56
8 115 -110	4 132 135	5 132 135	6 132 135	7 132 135	8 132 135	9 132 135	10 132 135	11 132 135	12 132 135		H*18,0	18 70* -56
10 351 347	2 73 -61	3 73 -61	4 73 -61	5 73 -61	6 73 -61	7 73 -61	8 73 -61	9 73 -61	10 73 -61		H*19,0	19 70* -56
12 591 -56	3 193 -169	H*2,2	0 92 81	1 92 81	2 92 81	3 92 81	4 92 81	5 92 81	6 92 81		H*20,0	20 70* -56
14 101 68	4 275 -250	5 275 -250	6 275 -250	7 275 -250	8 275 -250	9 275 -250	10 275 -250	11 275 -250	12 275 -250		H*21,0	21 70* -56
H*4,0	5 64* 9	6 64* 9	7 64* 9	8 64* 9	9 64* 9	10 64* 9	11 64* 9	12 64* 9	13 64* 9		H*22,0	22 70* -56
0 482 -81	7 307 -309	2 248 237	3 248 237	4 248 237	5 248 237	6 248 237	7 248 237	8 248 237	9 248 237		H*23,0	23 70* -56
2 121 -128	8 99* -106	4 74 -67	5 74 -67	6 74 -67	7 74 -67	8 74 -67	9 74 -67	10 74 -67	11 74 -67		H*24,0	24 70* -56
4 282 289	5 242 242	6 242 242	7 242 242	8 242 242	9 242 242	10 242 242	11 242 242	12 242 242	13 242 242		H*25,0	25 70* -56
6 356 -356	10 115 107	7 64* -56	8 64* -56	9 64* -56	10 64* -56	11 64* -56	12 64* -56	13 64* -56	14 64* -56		H*26,0	26 70* -56
8 137 -127	11 102 118	12 102 118	13 102 118	14 102 118	15 102 118	16 102 118	17 102 118	18 102 118	19 102 118		H*27,0	27 70* -56
10 120 130	12 130 130	13 130 130	14 130 130	15 130 130	16 130 130	17 130 130	18 130 130	19 130 130	20 130 130		H*28,0	28 70* -56
12 74* 61	13 76* 66	14 76* 66	15 76* 66	16 76* 66	17 76* 66	18 76* 66	19 76* 66	20 76* 66	21 76* 66		H*29,0	29 70* -56
14 163 162	15 126 129	16 126 129	17 126 129	18 126 129	19 126 129	20 126 129	21 126 129	22 126 129	23 126 129		H*30,0	30 70* -56
H*5,1	2 102 -102	3 102 -102	4 102 -102	5 102 -102	6 102 -102	7 102 -102	8 102 -102	9 102 -102	10 102 -102		H*31,0	31 70* -56
4 244 -237	1 214 214	2 214 214	3 214 214	4 214 214	5 214 214	6 214 214	7 214 214	8 214 214	9 214 214		H*32,0	32 70* -56
6 154 -63	3 64* -57	4 64* -57	5 64* -57	6 64* -57	7 64* -57	8 64* -57	9 64* -57	10 64* -57	11 64* -57		H*33,0	33 70* -56
8 37* 44	4 500 497	5 500 497	6 500 497	7 500 497	8 500 497	9 500 497	10 500 497	11 500 497	12 500 497		H*34,0	34 70* -56
10 177 175	5 187 -184	6 187 -184	7 187 -184	8 187 -184	9 187 -184	10 187 -184	11 187 -184	12 187 -184	13 187 -184		H*35,0	35 70* -56
12 149 137	6 136 132	7 136 132	8 136 132	9 136 132	10 136 132	11 136 132	12 136 132	13 136 132	14 136 132		H*36,0	36 70* -56
H*6,0	7 82* -82	8 82* -82	9 82* -82	10 82* -82	11 82* -82	12 82* -82	13 82* -82	14 82* -82	15 82* -82		H*37,0	37 70* -56
0 63* -71	9 140 136	10 140 136	11 140 136	12 140 136	13 140 136	14 140 136	15 140 136	16 140 136	17 140 136		H*38,0	38 70* -56
2 241 249	5 242 242	6 242 242	7 242 242	8 242 242	9 242 242	10 242 242	11 242 242	12 242 242	13 242 242		H*39,0	39 70* -56
4 95 -109	11 78* 60	12 78* 60	13 78* 60	14 78* 60	15 78* 60	16 78* 60	17 78* 60	18 78* 60	19 78* 60		H*40,0	40 70* -56
6 67* 51	13 80* 80	14 80* 80	15 80* 80	16 80* 80	17 80* 80	18 80* 80	19 80* 80	20 80* 80	21 80* 80		H*41,0	41 70* -56
8 123 120	14 78* -27	15 78* -27	16 78* -27	17 78* -27	18 78* -27	19 78* -27	20 78* -27	21 78* -27	22 78* -27		H*42,0	42 70* -56
10 122 -116	15 42* -12	16 42* -12	17 42* -12	18 42* -12	19 42* -12	20 42* -12	21 42* -12	22 42* -12	23 42* -12		H*43,0	43 70* -56
14 39* 121	H*7,0	0 271 -277	1 271 -277	2 271 -277	3 271 -277	4 271 -277	5 271 -277	6 271 -277	7 271 -277		H*44,0	44 70* -56
H*7,0	1 108 103	2 108 103	3 108 103	4 108 103	5 108 103	6 108 103	7 108 103	8 108 103	9 108 103		H*45,0	45 70* -56
4 163 -160	2 241 233	3 241 233	4 241 233	5 241 233	6 241 233	7 241 233	8 241 233	9 241 233	10 241 233		H*46,0	46 70* -56
6 108 -104	3 67* -51	4 67* -51	5 67* -51	6 67* -51	7 67* -51	8 67* -51	9 67* -51	10 67* -51	11 67* -51		H*47,0	47 70* -56
8 71* 68	4 81 80	5 81 80	6 81 80	7 81 80	8 81 80	9 81 80	10 81 80	11 81 80	12 81 80		H*48,0	48 70* -56
10 123 120	14 78* -27	15 78* -27	16 78* -27	17 78* -27	18 78* -27	19 78* -27	20 78* -27	21 78* -27	22 78* -27		H*49,0	49 70* -56
12 78* 43	15 42* -12	16 42* -12	17 42* -12	18 42* -12	19 42* -12	20 42* -12	21 42* -12	22 42* -12	23 42* -12		H*50,0	50 70* -56
H*8,0	0 271 -277	1 271 -277	2 271 -277	3 271 -277	4 271 -277	5 271 -277	6 271 -277	7 271 -277	8 271 -277		H*51,0	51 70* -56
2 92 72	1 108 103	2 108 103	3 108 103	4 108 103	5 108 103	6 108 103	7 108 103	8 108 103	9 108 103		H*52,0	52 70* -56
4 163 -160	2 241 233	3 241 233	4 241 233	5 2								

larger by more than  $3^\circ$ . The mean plane of the N(1)-NO<sub>2</sub> group is inclined to the plane defined by the three carbon atoms by only  $18^\circ$ , but the N(2)-NO<sub>2</sub> and N(3)-NO<sub>2</sub> planes are both inclined by  $62^\circ$ . Thus the trigonal molecular symmetry, which might be expected in the free RDX molecule, is not observed in the crystalline state, but there is a pseudo mirror plane passing through the atoms N(4), N(1), C(2), H(3), and H(4). These atoms are essentially coplanar with the plane defined by  $0.1869x - 0.1101y + 0.9762z = 3.3648$ . The atomic distances from the pseudo mirror plane and the inclination angles of the interatomic vectors between the two pseudo mirror symmetric atoms are summarized in Table 5. Only oxygen atoms show significant departures from the mirror symmetric positions. All the pseudosymmetry-related bond lengths and angles in a molecule agree within two standard deviations, with the exception of the N-N-C angles, which disagree by at most  $1.5^\circ$ .

Table 3. *Interatomic distances and angles in RDX*

## (a) Distances

C(1)-N(1)	1.464 (4) Å	N(1)-N(4)	1.351 (3) Å
C(1)-N(2)	1.443 (4)	N(2)-N(5)	1.392 (3)
C(2)-N(3)	1.468 (4)	N(3)-N(6)	1.398 (3)
C(2)-N(3)	1.458 (4)		
C(3)-N(3)	1.440 (4)	N(4)-O(1)	1.209 (5)
C(3)-N(1)	1.450 (4)	N(4)-O(2)	1.233 (4)
		N(5)-O(3)	1.203 (5)
C(1)-H(1)	1.058 (10)	N(5)-O(4)	1.207 (5)
C(1)-H(2)	1.092 (8)	N(6)-O(5)	1.201 (5)
C(2)-H(3)	1.085 (8)	N(6)-O(6)	1.205 (5)
C(2)-H(4)	1.087 (7)		
C(3)-H(5)	1.088 (8)		
C(3)-H(6)	1.075 (9)		

## (b) Angles

N(1)-C(1)-N(2)	107.8 (2)°	C(3)-N(1)-C(1)	115.1 (2)°
N(1)-C(1)-H(1)	109.9 (4)	C(3)-N(1)-N(4)	120.9 (2)
N(1)-C(1)-H(2)	110.0 (4)	C(1)-N(1)-N(4)	119.7 (2)
N(2)-C(1)-H(1)	108.0 (4)	N(1)-N(4)-O(1)	117.2 (3)
N(2)-C(1)-H(2)	110.0 (5)	N(1)-N(4)-O(2)	117.8 (3)
H(1)-C(1)-H(2)	111.0 (6)	O(1)-N(4)-O(2)	125.0 (3)
N(2)-C(2)-N(3)	111.7 (2)	C(1)-N(2)-C(2)	114.6 (2)
N(2)-C(2)-H(3)	110.1 (4)	C(1)-N(2)-N(5)	117.1 (2)
N(2)-C(2)-H(4)	106.9 (4)	C(2)-N(2)-N(5)	116.6 (2)
N(3)-C(2)-H(3)	110.7 (4)	N(2)-N(5)-O(3)	117.2 (3)
N(3)-C(2)-H(4)	107.2 (4)	N(2)-N(5)-O(4)	116.8 (3)
H(3)-C(2)-H(4)	110.1 (6)	O(3)-N(5)-O(4)	125.7 (4)
N(3)-C(3)-N(1)	108.4 (2)	C(2)-N(3)-C(3)	114.8 (2)
N(3)-C(3)-H(5)	107.4 (4)	C(2)-N(3)-N(6)	117.5 (2)
N(3)-C(3)-H(6)	111.1 (4)	C(3)-N(3)-N(6)	115.6 (2)
N(1)-C(3)-H(5)	109.6 (4)	N(3)-N(6)-O(5)	117.3 (3)
N(1)-C(3)-H(6)	111.3 (5)	N(3)-N(6)-O(6)	117.0 (3)
H(5)-C(3)-H(6)	108.8 (6)	O(5)-N(6)-O(6)	125.5 (4)

The methylene groups have essentially tetrahedral configurations, with the bond angles in the range of  $109.5 \pm 2^\circ$ , and the H-C-H planes perpendicular to the N-C-N planes. The C-H bonds range from 1.06 to 1.09 Å. When corrections for the thermal vibrations are applied by the riding model, they increase to between 1.09 and 1.13 Å.

Table 4. *The atomic distances from the best-fit mean planes of N-NO<sub>2</sub> groups*

The mean planes are:

$$\begin{aligned} 0.8473x - 0.4601y - 0.2654z &= -1.2993 && \text{for N(1)-NO}_2 \\ 0.2116x - 0.6696y + 0.7120z &= 1.3744 && \text{for N(2)-NO}_2 \\ -0.1646x - 0.5725y - 0.8032z &= -4.2606 && \text{for N(3)-NO}_2. \end{aligned}$$

	N(1)-NO <sub>2</sub>	N(2)-NO <sub>2</sub>	N(3)-NO <sub>2</sub>
N(1)	-0.002		
N(4)	0.008		
O(1)	-0.003		
O(2)	-0.003		
N(2)		0.007	
N(5)		-0.026	
O(3)		0.010	
O(4)		0.009	
N(3)			0.006
N(6)			-0.022
O(5)			0.008
O(6)			0.008
C(1)	0.198	-0.280	
C(2)		-0.536	-0.386
C(3)	0.316		-0.446

Table 5. *Atomic distances from the pseudo mirror plane*

Atoms in plane		Symmetry-related atom pair			
Distances		Distances		Angle	
N(4)	-0.005 Å	C(1)···C(3)	-1.23 Å	1.23 Å	90°
N(1)	0.006	N(2)···N(3)	-1.21	1.21	90
C(2)	0.003	N(5)···N(6)	-1.76	1.77	89
H(3)	-0.002	O(2)···O(1)	-1.10	1.07	87
H(4)	-0.002	O(3)···O(5)	-1.56	1.47	88
		O(4)···O(6)	-2.46	2.57	89
		H(1)···H(5)	-1.27	1.26	90
		H(2)···H(6)	-2.09	2.10	90

One hydrogen atom in each methylene group is always located very close to oxygen atoms of adjacent nitro groups on both sides, with the distances ranging from 2.22 to 2.30 Å. The C···O intramolecular distances are also short, ranging from 2.63 to 2.68 Å. Although the C-H···O angles,  $99 \pm 1^\circ$ , are much smaller than those in conventional hydrogen bonds, the oxygen atoms of the nitro-groups are bound tightly to the molecular ring by strong O···H as well as O···C inter-

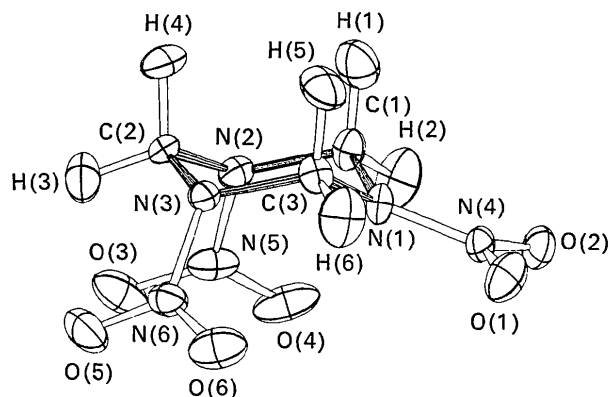


Fig. 2. Side view of the RDX molecule.

actions and tend to form approximately planar C<sub>2</sub>N-NO<sub>2</sub> groups. Consequently, we may expect to find some degree of rigidity in the RDX molecule. The rigid body motion analysis by the method of Schomaker & Trueblood (1968) was applied to all the heavy atoms of the molecule, as shown in Table 6. The r.m.s. DELTA  $U(I, J)$  was 0.008 Å<sup>2</sup> and the e.s.d. of the DELTA  $U(I, J)$  was 0.009. The disagreement with rigid-body molecular motion was greatest for the nitro group atoms. When the rigid-body analysis was applied to the ring atoms alone, the agreement was excellent; the r.m.s. DELTA  $U(I, J)$  was 0.0013 Å<sup>2</sup> and the e.s.d. of the DELTA  $U(I, J)$  was 0.0019. These facts may suggest that each nitro group possesses an independent libration superimposed upon the molecular libration, as is observed in the other nitro compounds, cyclotetramethylene tetranitramine (Choi & Boutin, 1970) and *s*-trinitrobenzene (Choi & Abel; 1972). The principal axis of the largest molecular libration lies almost exactly on the pseudo mirror plane, and has inclination angles of 34° with the N(1)-N(4) bond and 56° with both the other N-N bonds. Rigid body motion analysis of the nitro group alone is not possible because of the indeterminacy which occurs in the case of planar groups with five or fewer atoms. However, an investigation of the thermal ellipsoids of the nitro-group atoms shows clear evidence of rigid body motion, as shown in Table 7. We define Cartesian coordinate axes (radial, normal, and tangent) to which we refer the directions of the largest root-mean-square displacements,  $R_3$ , separately for each atom. For each atom of a nitro group, the radial axis is directed from the ring nitrogen to which the nitro group is attached toward that atom, and the normal axis is perpendicular to both the radial axis and the O...O vector of the nitro group. The normal axis, as defined above, is approximately normal to the best fit mean plane of the N-NO<sub>2</sub> group, with angular deviations of less than 1.5° for all three groups. The largest thermal vibration amplitudes occur in the directions of tangential axes for all atoms except O(1) and O(5), where they are in the normal direction. The direction of the least vibration amplitude is always along the radial axis. This is consistent with rigid-body motion of the nitro group with two dominant modes, one about the normal axis passing through the ring nitrogen atom and the other about a radial axis somewhere near the N-N bond.

Table 7. Principal axes of the thermal ellipsoids and orientations of the longest axes

	$R_1$	$R_2$	$R_3$	Radial	Normal	Tangent	$B$
N(4)	0.142 (4) Å	0.177 (3) Å	0.225 (3) Å	91°	73°	163°	2.69 Å <sup>2</sup>
O(1)	0.170 (6)	0.238 (5)	0.282 (6)	95	31	120	4.34
O(2)	0.156 (7)	0.218 (6)	0.257 (5)	86	73	163	3.63
N(5)	0.161 (4)	0.167 (4)	0.277 (4)	96	87	7	3.44
O(3)	0.167 (6)	0.226 (6)	0.329 (6)	96	100	12	4.93
O(4)	0.158 (7)	0.207 (6)	0.356 (6)	87	91	3	5.11
N(6)	0.164 (4)	0.181 (3)	0.234 (3)	92	86	176	3.02
O(5)	0.170 (6)	0.269 (6)	0.276 (6)	76	164	82	4.67
O(6)	0.183 (7)	0.246 (6)	0.310 (6)	88	107	163	5.00

Table 6. Rigid-body motion analysis

(a) Rigid-body motion applied for all heavy atoms

$$T = \begin{pmatrix} 0.028 & 0.0009 & 0.0030 \\ & 0.0284 & -0.0005 \\ & & 0.0226 \end{pmatrix} \quad L = \begin{pmatrix} 0.0031 & -0.0004 & 0.0010 \\ & 0.0064 & 0.0004 \\ & & 0.0039 \end{pmatrix}$$

Principal axes of L (°) and their direction cosines

4.6	-0.0700	0.9883	0.1352
3.8	-0.5736	0.0711	-0.8160
2.8	-0.8161	0.1347	0.5620

Displacements of libration axes from the center of mass (Å)

$L_{1,2} = 0.057$	$L_{1,3} = -0.261$
$L_{2,1} = -0.424$	$L_{2,3} = -0.490$
$L_{3,1} = -0.505$	$L_{3,2} = -0.705$

(b) Rigid-body motion applied for ring atoms alone

$$T = \begin{pmatrix} 0.0216 & 0.0015 & 0.0020 \\ & 0.0206 & -0.0042 \\ & & 0.0248 \end{pmatrix} \quad L = \begin{pmatrix} 0.0068 & 0.0013 & 0.0009 \\ & 0.0086 & -0.0023 \\ & & 0.0083 \end{pmatrix}$$

Principal axes of L (°) and their direction cosines

6.0	0.0988	0.7505	-0.6535
5.1	0.7722	0.3563	0.5260
4.0	0.6276	-0.5566	-0.5443

Displacements of libration axes from the center of mass (Å)

$L_{1,2} = -0.289$	$L_{1,3} = 0.163$
$L_{2,1} = -0.088$	$L_{2,3} = -0.512$
$L_{3,1} = 0.229$	$L_{3,2} = -0.025$

There are several short intermolecular distances in RDX. Those considered to be the most significant are shown in Fig. 3.

It may be interesting to compare the crystal structure of RDX with those of both  $\alpha$ - and  $\beta$ -HMX (cyclotetramethylene-tetranitramine) (Cady, Larson & Cromer, 1963; Choi & Boutin, 1970), in view of the close similarity in chemical composition and explosive nature. The bond lengths and angles of RDX agree well with those of  $\alpha$ - and  $\beta$ -HMX, except for the C-N-C angles, which are approximately 8° smaller in RDX than in HMX. In both compounds, the N-NO<sub>2</sub> group planes are bound tightly to the molecular ring by strong O...H as well as O...C interactions. The conformation of the N-NO<sub>2</sub> group attachment to the molecular ring in RDX is very similar to that of  $\alpha$ -HMX. Very short intermolecular distances occur in both compounds.

## References

- ALPERIN, H. A. & PRINCE, E. (1970). *J. Res. Natl. Bur. Stand. C74*, 89.

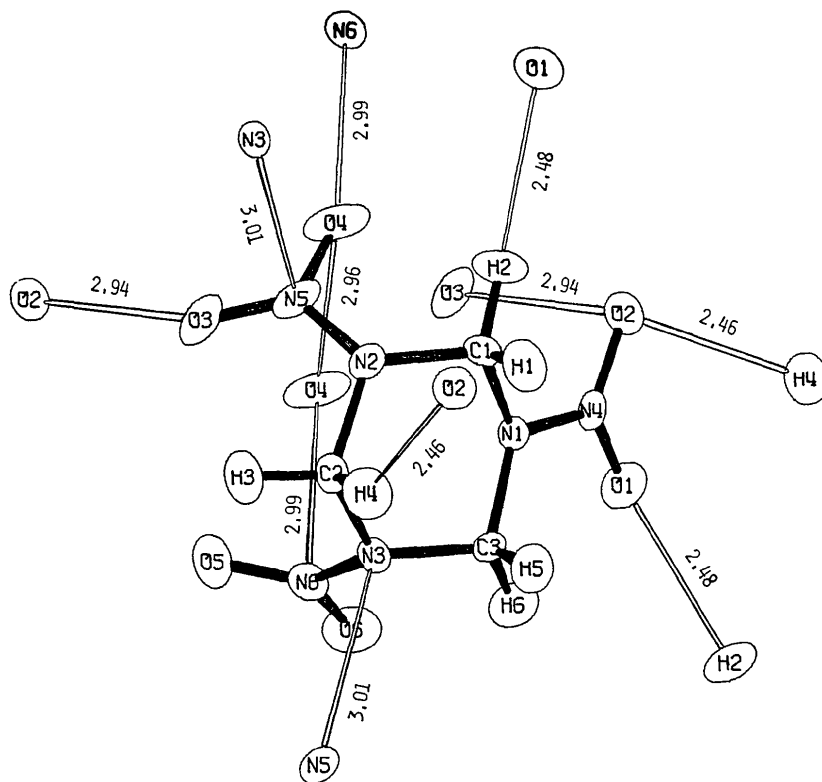


Fig. 3. A diagram of the RDX molecule and some atoms of neighboring molecules showing short intermolecular distances.

CADY, H. H., LARSON, A. C. & CROMER, D. T. (1963). *Acta Cryst.* **16**, 617.

CHOI, C. S. & ABEL, J. E. (1972). *Acta Cryst.* **B28**, 193.

CHOI, C. S. & BOUTIN, H. P. (1970). *Acta Cryst.* **B26**, 1235.

FEDOROFF, B. T. & SHEFFIELD, O. E. (1966). *Encyclopedia of Explosives and Related Items*, Vol. 3. Picatinny Arsenal, Dover, N.J.

FINGER, L. W. (1968). *Computer Programs for Least-Squares Refinement, Fourier Summation, and Error Calculations*. Geophysical Laboratory, Carnegie Institute of Washington, Washington, D.C.

HARRIS, P. M. & REED, P. T. (1959). AFOSR-TR-59-165 Ohio State University Research Foundation, Columbus, Ohio.

HULTGREN, R. (1936). *J. Chem. Phys.* **4**, 84.

MCCRONE, W. C. (1950). *Anal. Chem.* **22**, 954.

PRINCE, E. (1972). *J. Chem. Phys.* **56**, 4352.

RUSH, J. J., TAYLOR, T. I. & HAVENS, W. W. JR (1962). *J. Chem. Phys.* **37**, 234.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212.