

The Crystal Structure of Dinitropentamethylenetetramine (DPT)

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The crystal structure of dinitropentamethylenetetramine, or DPT, $C_5H_{10}N_6O_4$, has been studied by using three-dimensional X-ray (Mo $K\alpha$) diffraction data. The unit cell is monoclinic $P2_1/c$, with $a = 9.345$ (5), $b = 8.284$ (5), $c = 11.566$ (5) Å, $\beta = 105.6$ (1)° and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares methods to a final $R = 0.035$, $R_w = 0.037$. The two N-NO₂ groups in a DPT molecule are planar, with the two nitramine carbons out of the plane. The molecule has approximate mirror symmetry bisecting each of the two nitro groups.

Introduction

The cyclic nitramine 3,7-dinitro-1,3,5,7-tetraazabicyclo-[3,3,1]nonane, $C_5H_{10}N_6O_4$, or dinitropentamethylenetetramine (DPT) is an intermediate in the synthesis of the well-known explosives, cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX), and has an impact sensitivity lower than that of HMX and RDX. The DPT molecule has both the eight-membered C-N ring of HMX and the six-membered C-N ring of the RDX molecule. Recently the ^{15}N - ^{15}N nuclear spin coupling constants were measured using ^{15}N -labeled DPT (Bulusu, Autera & Axenrod, 1973), which indicated a conformational similarity to RDX rather than to HMX. The crystal structure of DPT was determined by X-ray diffraction for comparison with those of both HMX and RDX.

Experimental

The crystal used was an approximate ellipsoid with irregular surfaces, $0.4 \times 0.2 \times 0.2$ mm. Preliminary investigation by precession photographs with Mo $K\alpha$ radiation determined the space group to be monoclinic $P2_1/c$. $P2_1/c$ cell dimensions, together with the orientation matrix, were obtained by a least-squares fit of 15 high-intensity reflections with scattering angles over 30° in 2θ which were measured on a single-crystal diffractometer. The crystal data are summarized in Table 1.

The intensities were measured by θ - 2θ continuous scan using an automated three-circle diffractometer equipped with a Si(Li) solid-state detector (Hubbard, 1970). The scan speed of the 2θ angle was 4° min^{-1} and the background counts were measured for 15 s at the beginning and end of the scan. The scan ranges were determined by the relation $\Delta(2\theta) = 2.8 + \tan \theta$. In total, 5140 reflections in the entire $+h$ hemisphere were

Table 1. Crystal data for DPT

Chemical formula	$C_5H_{10}N_6O_4$
Space group	$P2_1/c$
Systematic absences	$h0l$ for $l \neq 2n$ $0k0$ for $k \neq 2n$
Cell dimensions	$a = 9.345$ (5) Å $b = 8.284$ (5) $c = 11.566$ (5) $\beta = 105.6$ (1)°
Cell volume	862.5 Å ³
Z	4 molecules
μ (Mo $K\alpha$)	0.97 cm ⁻¹ (based on μ/ρ by Cromer & Liberman, 1970)
D_x	1.682 g cm ⁻³
D_m	1.67 (3) g cm ⁻³
λ (Mo $K\alpha$)	0.71069 Å
$F(0,0,0)$	456

investigated. The observed intensities were adjusted to compensate for the intensity changes of the three standard reflections which were measured after every 50 reflections during the data collection. The two equivalent sets of reflections in the hemisphere (hkl and $h\bar{k}l$) were merged into a unique set of 2518 reflections, of which 1098 were unobserved according to the criterion $I \geq 3\sigma(I)$ for an observed reflection. The standard deviation of the observed intensity was defined as $\sigma(I) = [I + B + (KI)^2]^{1/2}$, where I and B are peak and background intensity respectively, and K is a constant (0.025 in this case). The agreement index between the two sets of equivalent reflections, $\sum \{2|F_o(hkl) - F_o(h\bar{k}l)| / [F_o(hkl) + F_o(h\bar{k}l)]\}$, was 0.028. Absorption corrections for a sphere were applied by using program *DMERGE* (Schroeder & Dickens, 1974). The minimum calculated transmission factor was 0.957. The observed intensities were then corrected for Lorentz and polarization effects to obtain structure amplitudes. Scattering factors for the neutral atoms were taken from Cromer & Mann (1968).

Structure determination and refinement

The structure amplitudes were converted to quasi-normalized structure factors (E) by using the *DATFIX* program of the X-RAY system (Stewart, 1970). A set of phases (signs) was assigned to 189 reflections out of 196 reflections with E larger than 1.5 by combined use of the programs *SIGMA2* and *PHASE* of the X-RAY system. The latter program treats the output of the *SIGMA2* search by a direct solution of product equations using a multi-symbolic technique. A subsequent E map, based on these phases, revealed all the heavy atom positions correctly. The positions were used as input to the least-squares refinement using the program *RFINE* written by L. W. Finger of the Carnegie Institute of Washington.

The full-matrix least-squares refinements for heavy atoms reduced the R index [$R = \sum(|F_o| - |F_c|) / \sum |F_o|$] to 7.7% after 3 cycles with isotropic thermal parameters followed by 3 cycles with anisotropic parameters. At this stage, the positions of all hydrogen atoms were located from $\Delta F(F_o - F_c)$ Fourier synthesis. The structure was further refined with isotropic thermal parameters for hydrogen atoms and anisotropic parameters for all other atoms. Isotropic secondary extinction corrections (Zachariasen, 1968) were applied in the last stage of refinement. The four strongest reflections (111, $21\bar{3}$, $11\bar{1}$, and 002), which had secondary extinction correction factors ($F_{\text{corr}}/F_{\text{cal}}$) ranging from 0.86 to 0.91, were excluded from the final refinements. The function minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma(I)^{-2}$. In the final cycle, the

R indices for all the observed reflections were $R = 0.035$ and $R_w = 0.037$ where $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. The average shift/error for all parameters was essentially zero, the maximum being 0.02. The secondary extinction parameters, γ^* in $F_{\text{corr}} = F_c(1 + \beta\gamma^*|F_c|^2)^{-1/4}$, was refined to 0.41×10^{-4} cm. The difference Fourier map calculated after the final cycle of refinement showed several small electron-density peaks localized near the middle of each C-N bond with the peak height less than $0.3 \text{ e } \text{Å}^{-3}$. The atomic parameters from the final cycle are given in Table 2.†

Discussion of the structure

The DPT molecule consists of a puckered eight-membered C-N ring with a methylene group bridging between N atoms at the two valley points of the C-N ring, and two nitro groups attached to the N atoms at the two opposing peaks of the ring, as shown in Fig. 1. The molecule contains two six-membered rings joined by means of two common bonds, N(2)-C(5)-N(4), with a nitro group attached to each ring. The two N-NO₂ groups are both essentially planar as shown in Table 3. The largest deviation of atoms in the N-NO₂ group from their mean plane is 0.01 Å for the N(1)-NO₂ group and 0.016 Å for the N(3)-NO₂ group. The two

† A list of structure amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30373 (12 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final least-squares parameters for the structure of DPT

Thermal parameters for heavy atoms have the form $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. Positional parameters are $\times 10^4$ for heavy atoms, $\times 10^3$ for hydrogen atoms. Thermal parameters are $\times 10^2$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	650 (2)	-285 (2)	1985 (2)	192 (7)	203 (6)	297 (7)	19 (6)	61 (6)	0 (6)
C(2)	2409 (2)	1918 (2)	2117 (2)	263 (7)	176 (6)	287 (7)	10 (6)	55 (6)	15 (6)
C(3)	4439 (2)	163 (3)	3286 (2)	240 (8)	285 (8)	289 (8)	-7 (6)	-36 (6)	18 (6)
C(4)	2721 (2)	-2055 (2)	3249 (1)	239 (8)	204 (6)	221 (7)	15 (6)	22 (6)	35 (5)
C(5)	2203 (2)	564 (2)	3884 (2)	375 (9)	262 (7)	207 (7)	21 (7)	78 (6)	-23 (6)
N(1)	1710 (2)	-1653 (2)	2057 (1)	211 (6)	171 (5)	221 (5)	8 (4)	17 (4)	-9 (4)
N(2)	1395 (2)	1083 (2)	2668 (1)	253 (6)	184 (5)	229 (6)	20 (5)	70 (5)	-13 (4)
N(3)	3750 (2)	959 (2)	2114 (1)	216 (6)	223 (5)	284 (6)	5 (5)	49 (5)	24 (5)
N(4)	3375 (2)	-586 (2)	3832 (1)	300 (6)	230 (6)	194 (5)	4 (5)	5 (5)	2 (4)
N(5)	1307 (2)	-2863 (2)	1258 (1)	250 (6)	224 (6)	243 (6)	-33 (5)	89 (5)	-27 (5)
N(6)	3691 (2)	81 (2)	1082 (1)	260 (6)	256 (6)	318 (6)	13 (5)	112 (5)	55 (5)
O(1)	1935 (2)	-4178 (1)	1514 (1)	432 (7)	208 (5)	379 (6)	46 (5)	75 (5)	-44 (5)
O(2)	368 (2)	-2575 (2)	307 (1)	326 (6)	352 (6)	252 (5)	-16 (5)	-17 (5)	-47 (4)
O(3)	4581 (2)	-1024 (2)	1152 (1)	413 (7)	378 (7)	474 (8)	155 (6)	171 (6)	27 (6)
O(4)	2802 (2)	499 (2)	147 (1)	405 (7)	439 (7)	262 (5)	84 (6)	80 (5)	44 (5)
H(1)	23 (2)	-1 (2)	111 (2)	206 (4)					
H(2)	-13 (2)	-67 (2)	233 (2)	87 (4)					
H(3)	191 (2)	219 (2)	131 (2)	94 (4)					
H(4)	282 (2)	290 (2)	263 (2)	122 (4)					
H(5)	491 (3)	105 (3)	379 (2)	267 (5)					
H(6)	514 (3)	-66 (3)	314 (2)	214 (5)					
H(7)	349 (2)	-282 (2)	313 (2)	137 (4)					
H(8)	217 (2)	-259 (2)	373 (2)	168 (4)					
H(9)	151 (2)	1 (2)	424 (2)	131 (4)					
H(10)	273 (2)	156 (2)	436 (2)	195 (4)					

carbon atoms adjacent to each N-NO₂ group are out of the mean plane (by approximately 0.48 and 0.16 Å for the C atoms of the N(1)-nitramine group and 0.44 and 0.46 Å for those of the N(3)-nitramine group). The average torsion angles about the N-N bond involving each carbon atom with the two oxygen atoms in a nitramine group are 19 and 7° for the N(1)-nitramine group, and 17 and 18° for the N(3)-nitramine group, as shown in Fig. 2. Thus, the entire nitramine group (N-NO₂ and two adjacent C atoms) is bent in such a way that the dihedral angle between the N-NO₂ group plane and the C-N-C plane in each nitramine group is approximately 26° for the N(1) group and approximately 34° for the N(3) group.

Table 3. The atomic distances from the best-fit mean planes of the N-NO₂ groups

$0.8621x + 0.2786y - 0.4234z = -0.5284$ for the N(1)-NO₂ group

O(1)	0.003 Å	C(1)	-0.482 Å
O(2)	0.003	C(4)	-0.157
N(5)	-0.010	H(1)	-0.106
N(1)	0.003	H(7)	0.372
		H(2)	-1.454
		H(8)	-1.0845

$0.7530x + 0.6256y - 0.2039z = 2.1565$ for the N(3)-NO₂ group

O(3)	0.006 Å	C(2)	-0.443 Å
O(4)	0.006	C(3)	-0.463
N(6)	-0.016	H(4)	0.119
N(3)	0.005	H(5)	0.100
		H(3)	-0.284
		H(6)	-0.326

The DPT molecule has pseudo-mirror symmetry about the mean plane through N(5), N(1), C(5), N(3), and N(6). These atoms are coplanar within 0.02 Å deviations from their mean plane, $0.6337x - 0.5597y + 0.5340z = 2.5972$. The distances of atoms from the pseudo-mirror plane are given in Fig. 2. Atoms of a pair related by the pseudo-symmetry are approximately equidistant from the pseudo-mirror plane, with the deviation less than 0.035 Å for all the heavy atoms in the molecule. The pseudo-mirror symmetry is also indicated by the bond lengths; bond pairs related by pseudo-symmetry are equal within two e.s.d.'s, except the pair N(1)-C(1) and N(1)-C(4), which differ by 0.008 Å or by 4 e.s.d.'s. The bond angles of the pseudo-symmetric pairs also agree within 1°. The bond lengths and angles are given in Fig. 3 and Table 4. The two nitro groups in the molecule are different in N-N bond length; the N-N bond of the N(5) nitro group is 1.35 Å, which is approximately 0.04 Å shorter than that of the N(6) nitro group. The C-N bonds in both the nitramine groups, N(1)-C and N(3)-C, are approximately 1.49 Å which is about 0.02 to 0.04 Å longer than the other C-N bonds in the molecular ring, N(2)-C and N(4)-C bonds. The angles between the four bonds of each methylene group are 109.5 ± 6.0 ; indicating a slightly distorted tetrahedral arrangement. The O-N-O angles of both the nitro groups are approximately 124° and all of the C-N-C angles of the four nitrogens in the

molecular ring are within the range between 109 and 114°, with the exception of the C(1)-N(1)-C(4) angle which is 118°.

The torsion angles about the ring bonds of the two six-membered C-N rings in the molecule range from 38 to 59° with an average of 48°, as shown in Fig. 2. Among the ring torsion angles, those about the two C(5)-N bonds (which are common to both rings) are comparatively very large, with an average of 57°, and those about the nitramine C-N bonds, which are not

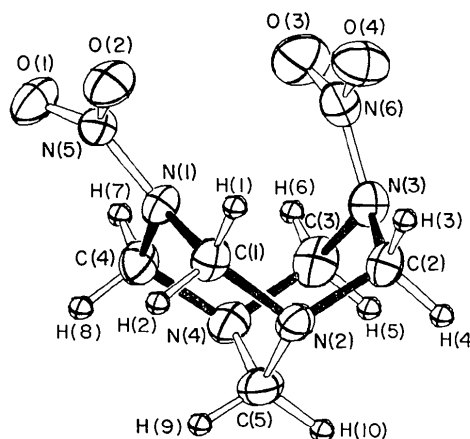


Fig. 1. A molecule of DPT with thermal ellipsoids scaled to enclose 50% probability. The isotropic hydrogen atoms are scaled down to an arbitrary small size.

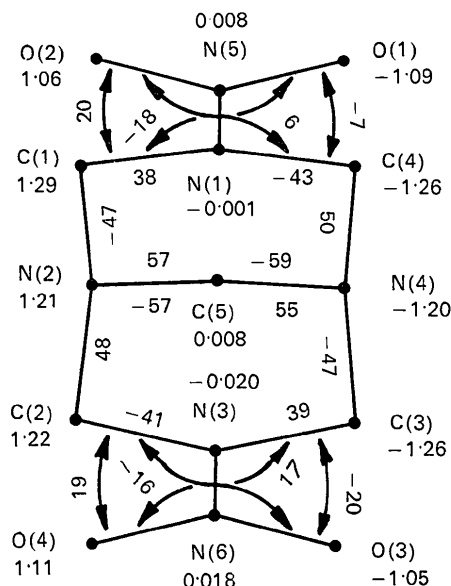


Fig. 2. A schematic diagram to illustrate the pseudo-mirror symmetry of the DPT molecule. The atomic distances from the pseudo-mirror plane are shown in Å. The torsion angles are given in (°). For each ring bond of the two six-membered rings, the torsion angle defined by the two adjacent ring bonds is written next to the bond. The torsion angles about the N-N bond involving the two C atoms with the two O atoms in each nitramine group are defined as indicated by double-headed arrows.

Table 4. Bond lengths (Å) and angles (°) involving the hydrogen atoms

C(1)-H(1)	1.01 (2)	C(4)-H(7)	0.99 (2)
C(1)-H(2)	0.97 (2)	C(4)-H(8)	0.97 (2)
C(2)-H(3)	0.95 (2)	C(3)-H(6)	0.99 (2)
C(2)-H(4)	1.02 (2)	C(3)-H(5)	0.97 (2)
C(5)-H(9)	0.97 (2)		
C(5)-H(10)	1.04 (2)		
N(1)-C(1)-N(2)	110.4 (1)	N(1)-C(4)-N(4)	109.2 (1)
N(1)-C(1)-H(1)	107.5 (12)	N(1)-C(4)-H(7)	108.5 (11)
N(1)-C(1)-H(2)	106.5 (11)	N(1)-C(4)-H(8)	109.5 (12)
N(2)-C(1)-H(1)	111.7 (12)	N(4)-C(4)-H(7)	111.8 (11)
N(2)-C(1)-H(2)	109.8 (11)	N(4)-C(4)-H(8)	110.1 (12)
H(1)-C(1)-H(2)	110.9 (16)	H(7)-C(4)-H(8)	107.7 (16)
N(2)-C(2)-H(3)	109.6 (11)	N(3)-C(3)-H(6)	106.8 (12)
N(2)-C(2)-H(4)	108.3 (10)	N(3)-C(3)-H(5)	103.0 (13)
N(3)-C(2)-H(3)	108.4 (11)	N(4)-C(3)-H(6)	110.2 (12)
N(3)-C(2)-H(4)	104.2 (10)	N(4)-C(3)-H(5)	108.6 (14)
H(3)-C(2)-H(4)	112.9 (15)	H(6)-C(3)-H(5)	114.2 (18)
N(2)-C(5)-H(9)	108.2 (11)	N(4)-C(5)-H(9)	107.5 (11)
N(2)-C(5)-H(10)	108.8 (11)	N(4)-C(5)-H(10)	106.3 (12)
H(9)-C(5)-H(10)	115.5 (16)		

involved with the C(5)-N bonds, are much smaller with an average of 40°. This may be indicative of intramolecular steric strain for this type of twin-ring conformation. The torsion angles for the molecules of other similar cyclic nitramine compounds, RDX (Choi &

Prince, 1972) and α -HMX (Cady, Larson & Cromer, 1963), were calculated for the purpose of comparison. The torsion angles about the ring C-N bonds of the former ranged from 44 to 53° with an average of 48°, and those of the latter from 52 to 65° with an average of 58°. The average torsion angles about each N-N bond involving the two C atoms with the two O atoms were 11, 17 and 17° respectively for the three nitramine groups of the RDX molecule, and 3 and 6° respectively for the two nitramine groups of the α -HMX molecule. The corresponding torsion angles of the DPT molecule average 48° for the ring bonds, 13° for the N(1)-nitramine group and 18° for the N(3)-nitramine group, showing rather closer similarity to those of RDX than to those of α -HMX. The bond lengths and angles of the nitramine groups in the DPT molecule are also compared with those of RDX, α -HMX, and β -HMX (Choi & Boutin, 1970), as shown in Table 5. The C-N bonds of both the nitramine groups in the DPT are approximately 0.02 to 0.05 Å longer than the corresponding C-N bonds of the RDX and HMX's. The C-N-C angles of these nitramine groups, 115.6° average, are considerably smaller than those of HMX but they agree well with those of the RDX molecule, indicating a similar ring conformation with the latter.

Table 5. The bond lengths and angles of the nitramine groups in the cyclic nitramine compounds, DPT, RDX, α -HMX and β -HMX

Molecule	N-O (Å)	N-O (Å)	N-N (Å)	N-C (Å)	N-C (Å)	O-N-O (°)	C-N-C (°)
DPT	1.232 (2)	1.235 (2)	1.347 (2)	1.485 (2)	1.493 (2)	123.9 (2)	118.2 (1)
	1.225 (2)	1.223 (2)	1.386 (2)	1.485 (2)	1.490 (2)	124.3 (2)	113.2 (2)
RDX	1.209 (5)	1.233 (4)	1.351 (3)	1.450 (4)	1.464 (4)	125.0 (3)	115.1 (2)
	1.203 (5)	1.207 (5)	1.392 (3)	1.443 (4)	1.468 (4)	125.7 (4)	114.6 (2)
	1.201 (5)	1.205 (5)	1.398 (3)	1.440 (4)	1.458 (4)	125.5 (4)	114.8 (2)
α -HMX	1.21 (1)	1.24 (1)	1.35 (1)	1.44 (1)	1.45 (1)	125 (2)	124 (1)
	1.22 (1)	1.23 (1)	1.37 (1)	1.45 (1)	1.47 (1)	125 (2)	120 (2)
β -HMX	1.222 (8)	1.233 (8)	1.354 (5)	1.448 (7)	1.471 (6)	125.9 (6)	122.4 (4)
	1.204 (8)	1.210 (8)	1.373 (5)	1.437 (6)	1.455 (6)	126.7 (5)	123.8 (4)

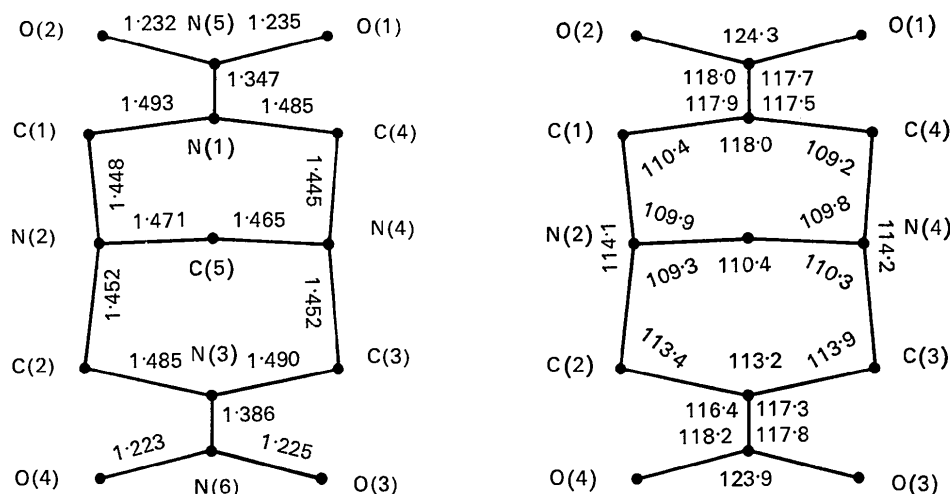


Fig. 3. The bond lengths and angles between non-hydrogen atoms. The estimated standard deviations are 0.002 Å for the bond lengths and 0.2° or less for the bond angles.

Table 6. Short intramolecular atomic distances (Å) with e.s.d.'s in parentheses

N(1)···N(3)	2·873 (2)
N(1)···N(6)	2·808 (2)
O(1)···C(4)	2·621 (2)
O(2)···C(1)	2·676 (2)
O(3)···C(3)	2·694 (2)
O(4)···C(2)	2·674 (2)
O(1)···H(7)	2·33 (2)
O(2)···H(1)	2·34 (2)
O(3)···H(6)	2·23 (2)
O(4)···H(3)	2·25 (2)

The DPT molecule is rather overcrowded, with many short intramolecular atomic distances, as shown in Table 6. The intramolecular atomic distances N(1)···N(6) and N(1)···N(3) are 2·808 (2) and 2·873 (2) Å respectively, considerably shorter than the sum of the van der Waals contact distances between two nitrogen atoms (3·0 Å). The oxygen atoms of each nitramine group are attracted strongly to the adjacent methylene group to give O···C distances ranging from 2·62 to 2·69 Å and O···H distances ranging from 2·23 to 2·34 Å. This strong intramolecular attraction may be attributable partly to C–H···O hydrogen bonding and also partly to the electrostatic interaction as demonstrated by the calculated charge distribution for several RDX-type conformers. The molecular orbital calculations by Orloff, Mullen & Rauch (1970) indicate a relatively high positive charge on the carbon atoms and a negative charge on the oxygen atoms. This charge distribution is consistent with the strong intramolecular and intermolecular C···O interactions observed not only in the DPT and RDX crystals but also other similar nitramine compounds. There are several short intermolecular C···O distances, ranging from 3·2 to 3·3 Å, in the DPT crystal. Among them C(2)–H(3)···O(2) ($-x, -y, -z$) and C(3)–H(5)···O(3) ($-x, \frac{1}{2}+y, \frac{1}{2}-z$) may be weak hydrogen bonds. The observed C···O and H···O distances and C–H···O angles are 3·31, 2·25 Å, and 151° for the former and 3·30, 2·46 Å, and 145° for the latter.

The rigid-body thermal motion of the DPT molecule was analyzed by the method of Schomaker & Trueblood (1968). The r.m.s. $\delta U(I, J)$ was 0·0036 Å² and the e.s.d. of the $\delta U(I, J)$ was 0·0041 for the rigid-body motion based on all heavy atoms. The average values of $U(I, J)$'s were approximately 0·032 Å² for C–N ring atoms and about 0·046 Å² for the nitro group oxygens. The $\delta U(I, J)$'s of the O atoms in the rigid body were significantly larger than those of other atoms, which indicates that the nitro group possesses segmental motion superimposed upon the molecular rigid-body motion. When the four oxygen atoms were omitted from the rigid body, the r.m.s. $\delta U(I, J)$ and its e.s.d. were reduced to 0·0019 Å² and 0·0023 respectively, without any appreciable changes in the translation (T) and libration (L) motion. This fact suggests that the oxygen atoms of each nitro group undergo a consider-

able amount of independent segmental motion, probably an oscillation about the N–N bond of each group. The rigid-body motions obtained from all heavy atoms are given in Table 7. The amplitudes of the libration motion are rather small, ranging from 4·9 to 2·7°. Consequently the effect of libration on bond length is also small, not more than 0·006 Å for all the bonds involved. Specifically, correction for librational motion increases each N–O bond length by 0·004 Å, N(1)–N(5) by 0·004 Å and N(3)–N(6) by 0·005 Å. Among the ten C–N ring bonds, C(1)–N(2), C(2)–N(2), C(3)–N(4) and C(4)–N(4) which are closer to the mass center of the molecule are increased by 0·004 Å and the other six C–N bonds are increased by 0·005 Å.

Table 7. Rigid-body thermal motion of the DPT molecule

$$T = \begin{pmatrix} 0\cdot0273 & 0\cdot0052 & 0\cdot0060 \\ & 0\cdot0246 & 0\cdot0011 \\ & & 0\cdot0227 \end{pmatrix}$$

$$L = \begin{pmatrix} 0\cdot0028 & 0\cdot0006 & -0\cdot0003 \\ & 0\cdot0046 & -0\cdot0004 \\ & & 0\cdot0024 \end{pmatrix}$$

Principal axes of L(°) and their direction cosines (orthogonal)

4·0	-0·3102	-0·9339	0·1779
3·0	-0·8437	0·3566	0·4013
2·7	-0·4381	-0·0256	-0·8985

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

$L_{1,2} =$	0·430	$L_{1,3} =$	0·013
$L_{2,1} =$	0·180	$L_{2,3} =$	-0·553
$L_{3,1} =$	-0·010	$L_{3,2} =$	0·700

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