

The Crystal Structure of 3,7-Diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DAPT)

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.

A. SANTORO

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

AND J. E. ABEL

Feltman Research Laboratory, Picatinny Arsenal, Dover, N.J. 07801, U.S.A.

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The crystal structure of 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DAPT), $C_9H_{16}N_4O_2$, has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the monoclinic system with $a=6.183(2)$, $b=10.101(2)$, $c=17.037(4)$ Å, $\beta=101.78(4)^\circ$, space group $P2_1/c$, $D_x=1.353$, $D_m=1.34$ g cm $^{-3}$ and $Z=4$. The structure has been solved by direct methods and has been refined by least-squares analysis to a conventional R value of 0.052 ($R_w=0.04$) based on 1708 observed reflections. The molecule of DAPT has a twin-chair conformation similar to that of the molecule of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT). The heavy atoms of the acetamide groups are essentially coplanar with the ring carbon atoms adjacent to each group. The bicyclononane ring of the DAPT molecule possesses two pseudo-symmetry planes almost perpendicular to one another. Short intermolecular contacts of 3.28, 3.39 and 3.47 Å have been observed. The molecules having these contacts are stacked along the unique b axis to form a linear chain. The lateral links between chains are weak with contacts between heavy atoms longer than 3.5 Å.

Introduction

The compound 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane, hereinafter DAPT, is one of the intermediates in the synthesis of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, commonly called HMX (Yoshida, Sen & Thyagarajan, 1973; Siele, Warman & Gilbert, 1974). The crystal structures of the various modifications of HMX and of other key intermediates involved in the synthesis of HMX have been studied by several investigators, (a) α -HMX (Cady, Larson & Cromer, 1963), (b) β -HMX (Choi & Boutin, 1970), (c) δ -HMX (Cobbledick & Small, 1974), (d) TAT (1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane; Choi, Abel, Dickens & Stewart, 1973), (e) DADN (1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane; Santoro, Choi & Abel, 1975), (f) DPT (3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane; Choi & Bulusu, 1974).

Among the derivatives of 1,3,5,7-tetraazacyclooctane the changes in the substituent groups do not cause significant changes in the basic structure of the molecule (e.g. α -HMX, or δ -HMX, and TAT, β -HMX and DADN are isomorphous pairs). On the other hand other properties vary considerably (e.g. compounds with nitro groups are often highly explosive, while those with acetyl groups are stable).

Recently the structures of several bicyclo[3,3,1]-nonane derivatives have been reported; (a) 1-*p*-bromobenzenesulphonyloxymethyl-5-methylbicyclo[3,3,1]nonan-9-ol (BSBO) by Brown, Martin & Sim (1965), (b) 2-chlorobicyclo[3,3,1]nonan-9-one (CBNO)

by Webb & Becker (1967), (c) 1,7-dicarbomethoxy-3a,7-methano-3a*H*-decahydrocyclopentacyclooctane-2,10-dione (DCPCO) by Abola, Pletcher & Sax (1974) and (d) DPT. These studies have shown that the bicyclo[3,3,1]nonane system assumes a twin-chair conformation in all compounds except DCPCO, in which it has a partial boat-chair conformation and each of the two cyclohexane rings is severely distorted from the ideal geometry.

The determination of the crystal structure of DAPT was undertaken as part of a continuing effort to study the intermediates involved in the preparation of HMX and other explosives and to compare the structural features of the compound with those of related structures.

Experimental

Crystals of DAPT were grown by evaporation of a benzene solution. A crystal with approximate dimensions 0.3 × 0.3 × 0.4 mm was selected for the data col-

Table 1. *Crystal data for 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DAPT)*

Figures in parentheses are standard deviations on the last significant figure.

$C_9H_{16}N_4O_2$	$V=1041.6$ Å 3
Space group: $P2_1/c$	$Z=4$
$a=6.183(2)$ Å	$D_x=1.353$ g cm $^{-3}$
$b=10.101(2)$	$D_m=1.34$
$c=17.037(4)$	$\mu(\text{Mo } K\alpha)=1.07$ cm $^{-1}$
$\beta=101.78(4)^\circ$	$F(000)=456$

lection. Space group and approximate unit-cell dimensions were determined with the precession method. The cell dimensions were then refined by least-squares analysis to obtain the best agreement between the calculated and the observed 2θ angles of nine strong reflections. The crystal data are summarized in Table 1.

Intensities were measured with an automated three-circle X-ray diffractometer equipped with a Si(Li) solid state detector (Hubbard, 1973) by using the θ - 2θ scan and Mo $K\alpha$ radiation ($\lambda=0.710688$ Å). The scan range was determined with the relation $\Delta(2\theta)=2+\tan\theta$. 6103 reflections with $2\theta\leq 60^\circ$ were measured in the $+h$ hemisphere. Among these reflections 2978 were 'unobserved' according to the criterion $I\leq 3\sigma(I)$, where $\sigma=(I+B)^{1/2}$, I and B being the peak and background intensities respectively. Two standard reflections (21 $\bar{8}$ and 080) were periodically measured and no significant changes of their intensities were observed. Equivalent reflections were merged into a unique set of 3039 reflections of which 1331 were unobserved

(the agreement value between the equivalent reflections hkl and $h\bar{k}l$ was 0.023). Intensities were corrected for absorption by applying the correction for a sphere ($\mu=1.07$ cm $^{-1}$; μR ranges for our crystal from 0.015 to 0.02) and then for the Lorentz and polarization factors.

A set of normalized structure factors E was obtained by a least-squares fit of the isotropic bulk temperature factor to the Wilson plot. The signs of 202 strong reflections ($E\geq 1.4$) were determined by using the \sum_2 relations between the reflections with E larger than 1.0 (Stewart, 1972). An E map revealed all the positions of the non-hydrogen atoms correctly. The hydrogen atom positions were determined by a difference Fourier synthesis. The structure was refined by full-matrix least-squares calculations with anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms, using the program *RFINE* (Finger, 1972). The function minimized was $\sum w(F_o - |F_c|)^2$ with $w=[1.0 + \sigma(F)]^{-2}$. The standard deviation $\sigma(F)$ is based on counting statistics alone. The scattering factors used for the neutral atoms were those given by Cromer & Mann (1968). Secondary extinction corrections (Zachariasen, 1968) were applied in the refinement. The secondary extinction parameter γ^* in $F_{corr}=F_c(1+\beta\gamma^*|F_c|^2)^{1/4}$ was refined to 0.82×10^{-4} . Five of the strongest reflections (10 $\bar{2}$, 110, 012, 014, and 104) with high secondary extinction factors were excluded from the final stage of refinement. After the final cycle the conventional R values were $R=0.052$ and $R_w=0.04$. The maximum shift/error was 0.17 and the average shift was 0.01σ . A difference Fourier map calculated at the end of the refinement showed no significant residual electron density. The final least-squares parameters are given in Table 2.†

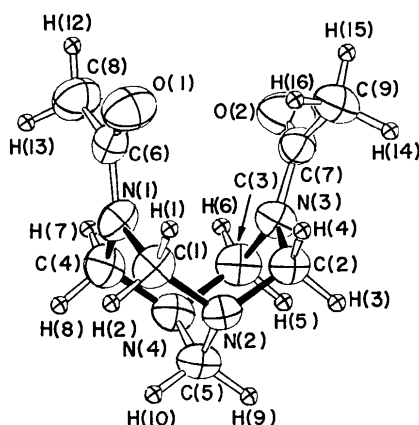


Fig. 1. Perspective view of the DAPT molecule with thermal ellipsoids.

Table 2. Final least-squares parameters for DAPT

The thermal parameters for the heavy atoms have the form

$$\exp \left[-\frac{1}{2} \{ B_{11}(a^*h)^2 + B_{22}(b^*k)^2 + B_{33}(c^*l)^2 + 2(B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl) \} \right].$$

Positional parameters for the heavy atoms are $\times 10^4$ and for H, $\times 10^3$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	9905 (3)	2034 (2)	4511 (2)	2.76 (8)	4.05 (10)	5.18 (12)	0.41 (7)	0.45 (8)	-0.14 (9)
C(2)	8427 (3)	885 (2)	3262 (1)	2.87 (8)	3.77 (10)	4.42 (11)	0.65 (7)	1.02 (8)	0.36 (8)
C(3)	4699 (3)	1711 (2)	3322 (1)	2.52 (8)	4.75 (11)	4.99 (12)	0.46 (8)	0.64 (8)	0.52 (9)
C(4)	6207 (4)	2850 (2)	4565 (2)	3.65 (9)	4.61 (11)	4.86 (12)	0.95 (8)	1.56 (8)	-0.03 (9)
C(5)	6886 (3)	551 (2)	4406 (1)	3.61 (9)	4.04 (10)	4.44 (11)	0.19 (8)	1.13 (8)	0.98 (9)
C(6)	8925 (4)	4296 (2)	4057 (1)	4.45 (10)	3.67 (10)	4.30 (11)	0.15 (8)	0.53 (9)	-0.67 (9)
C(7)	6591 (3)	2661 (2)	2333 (1)	4.21 (10)	3.47 (9)	3.69 (10)	-0.08 (8)	0.40 (8)	-0.06 (8)
C(8)	7234 (5)	5393 (3)	3921 (2)	6.06 (14)	4.08 (12)	6.62 (16)	0.96 (11)	1.44 (13)	0.58 (11)
C(9)	8589 (5)	2703 (3)	1956 (2)	5.97 (13)	5.41 (13)	4.48 (12)	-0.36 (10)	1.73 (11)	0.97 (11)
N(1)	8384 (3)	3170 (2)	4396 (1)	3.06 (7)	3.48 (8)	5.37 (10)	0.31 (6)	0.98 (7)	-0.41 (7)
N(2)	8927 (2)	834 (2)	4129 (1)	2.74 (6)	3.22 (7)	4.01 (9)	0.30 (6)	0.56 (6)	0.42 (6)
N(3)	6625 (2)	1816 (2)	2941 (1)	2.79 (7)	4.30 (8)	3.70 (8)	0.66 (6)	0.71 (6)	0.68 (7)
N(4)	5294 (2)	1625 (2)	4188 (1)	2.86 (7)	4.26 (9)	4.46 (9)	0.34 (6)	1.30 (6)	0.59 (7)
O(1)	728 (3)	4441 (2)	3875 (1)	5.00 (8)	5.34 (9)	8.36 (12)	-0.22 (7)	2.62 (8)	0.71 (8)
O(2)	4988 (3)	3363 (2)	2089 (1)	5.84 (9)	6.01 (9)	6.81 (10)	2.16 (7)	0.93 (8)	2.52 (8)

† A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31190 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (cont.)

	x	y	z	B
H(1)	119 (3)	230 (2)	428 (1)	2.6 (4)
H(2)	33 (3)	190 (2)	510 (1)	3.5 (5)
H(3)	790 (3)	-4 (2)	304 (1)	3.3 (5)
H(4)	977 (3)	112 (2)	308 (1)	2.4 (4)
H(5)	384 (3)	84 (2)	309 (1)	3.6 (5)
H(6)	379 (3)	250 (2)	315 (1)	2.7 (5)
H(7)	512 (3)	362 (2)	437 (1)	2.9 (5)
H(8)	638 (3)	272 (2)	517 (1)	4.0 (5)
H(9)	616 (3)	-35 (2)	413 (1)	3.8 (5)
H(10)	729 (3)	48 (2)	500 (1)	2.7 (5)
H(11)	588 (5)	508 (3)	351 (2)	8.7 (9)
H(12)	780 (4)	612 (3)	370 (1)	6.1 (7)
H(13)	675 (4)	558 (3)	442 (2)	7.7 (8)
H(14)	875 (4)	178 (3)	169 (2)	7.0 (7)
H(15)	828 (4)	334 (2)	155 (1)	5.3 (6)
H(16)	989 (5)	304 (2)	239 (2)	7.3 (8)

Description of the structure

The molecule of DAPT contains two six-membered C-N rings joined by a common N-C-N bridge, and an acetyl group attached to each ring. A perspective view of the molecule is shown in Fig. 1. A comparison with the molecule of DPT (Choi & Bulusu, 1974) shows that the molecular structures of DAPT and DPT are very similar.

Table 3. Atomic distances from various best fit mean planes (Å)

Mean plane of the C(6) acetamide group

Acetamide group	Distance (Å)	Adjacent atoms	Distance (Å)
C(6)	0.006	C(1)	0.071
C(8)	-0.002	C(4)	0.135
N(1)	-0.002		
O(1)	-0.002		

Mean plane of the C(7) acetamide group

Acetamide group	Distance (Å)	Adjacent atoms	Distance (Å)
C(7)	-0.003	C(2)	0.051
C(9)	0.001	C(3)	0.026
N(3)	0.001		
O(2)	0.001		

Bisecting plane through the atoms C(5), N(1) and N(3)

Ring atoms	Distance (Å)	Acetyl atoms	Distance (Å)
C(1)	1.22	C(6)	0.07
C(4)	-1.23	C(7)	-0.06
C(2)	1.24	C(8)	-1.23
C(3)	-1.24	C(9)	1.23
N(2)	1.20	O(1)	1.14
N(4)	-1.20	O(2)	-1.14

Bisecting plane through the atoms N(2), N(4) and C(5)

Ring atoms	Distance (Å)	Acetyl atoms	Distance (Å)
C(1)	-1.20	C(6)	-1.50
C(2)	1.23	C(7)	1.91
C(4)	-1.20	C(8)	-1.61
C(3)	1.23	C(9)	2.17
N(1)	-1.38	O(1)	-1.54
N(3)	1.46	O(2)	2.12

The bicyclononane ring of the DAPT molecule has two pseudo-symmetry planes, one defined by the atoms C(5), N(1) and N(3) (plane I) and the other by the atoms N(2), N(4) and C(5) (plane II). The atomic distances from these planes are given in Table 3. These distances are almost the same for each pseudo-symmetric pair, except for the N(1) and N(3) atoms which are affected by the tilt of the acetamide groups discussed below. Planes I and II are almost perpendicular to one another (dihedral angle = 89.9°). The pseudo-symmetry

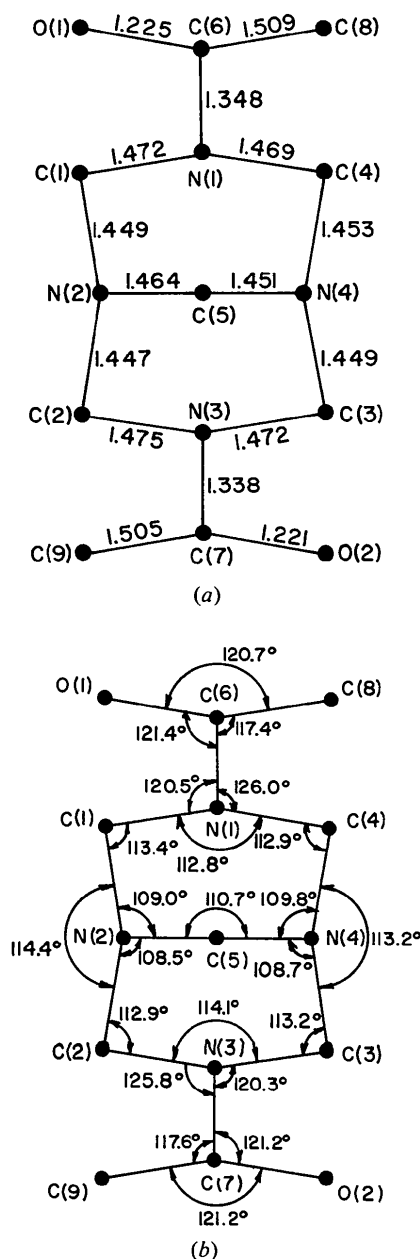


Fig. 2. Schematic illustration of the DAPT molecule with (a) bond distances and (b) bond angles. The estimated standard deviations are 0.003 Å for the bond distances and 0.2° for the bond angles.

$mm2$ of the bicyclononane ring is also shown by bond distances and angles and by the torsional angles (Figs. 2 and 3).

The heavy atoms in each acetamide group are coplanar as shown in Table 3. The two ring C atoms adjacent to each acetamide group are also very close to the planes of the acetamide groups, with displacements less than 0.14 Å for the N(1) group and less than 0.06 Å for the N(3) group (this result is also reflected by the small values of the torsional angles about the C–N bond of each group). Similar deviations have been found also in the structure of TAT and they are much smaller than those determined for the ring C atoms adjacent to the N–NO₂ groups in all the cyclic nitramine compounds studied. This result suggests that

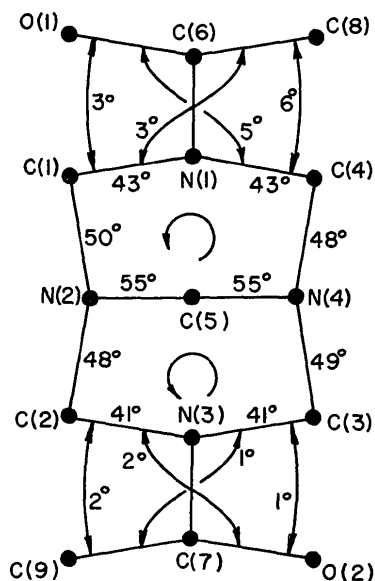


Fig. 3. Torsional angles in the DAPT molecule. The angles written on ring bonds are torsional angles within the six-membered ring.

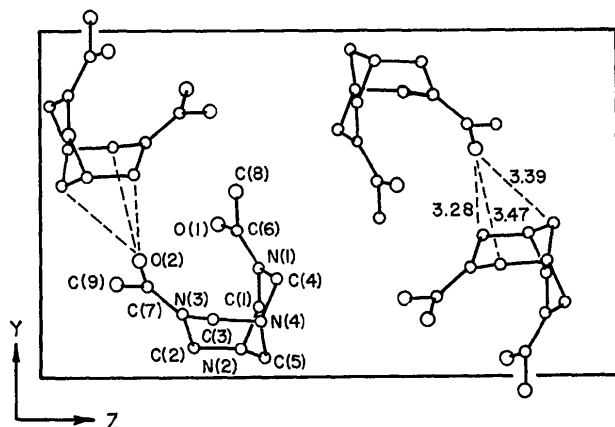


Fig. 4. Molecular packing in the structure of DAPT viewed perpendicularly to the (100) plane.

the non-planarity of the ring C atoms adjacent to the nitramine groups may be attributed to inherent electronic structure rather than to intramolecular steric hindrance.

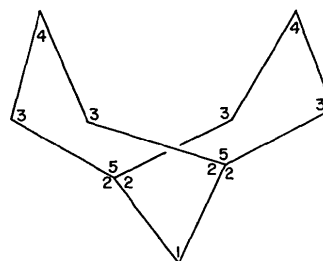
Bond lengths and angles of the acetamide groups of DAPT agree well with those of TAT and DADN. However, two bond angles involving the acetamide groups, *i.e.* C(1)–N(1)–C(4) and C(2)–N(3)–C(3), are approximately 5° smaller than the corresponding angles in the other two molecules. This result is a consequence of the fact that the ring conformation of the DAPT molecule is closer to that of cyclohexane than to that of cyclooctane. The dihedral angle between the mean planes of the two acetamide groups is 25.4°, *i.e.* about 4° larger than the corresponding angle between the planes of the N–NO₂ groups in the DPT molecule.

The dihedral angles between plane II and the planes of the C(7) and C(6) acetamide groups are 19.8 and 5.6° respectively, *i.e.* the C(7) acetamide group is tilted away from plane II more than the C(6) acetamide group. A similar situation, only more severe in degree, was found for the two nitro groups of DPT.

Bond distances and angles for the ring atoms of the DAPT and DPT molecules agree well, except for those involving the N atoms of the acetamide or nitramine groups. The bond angles of DAPT agree well also with those of BSBO, CBNO, and DCPCO, with a deviation from the mean value of less than 2° (Table 4).

Table 4. Bond angles of the bicyclo[3,3,1]nonane nucleus of DAPT compared with those of DPT, BSBO, CBNO and DCPCO

Angle	DAPT	DPT	BSBO	CBNO	DCPCO	Mean
1	110.7	110.4	111	112.3	111.9	111.3
2	109.0	109.9	109	108.7	106.3	
	108.5	109.3	109	107.9	107.3	
	108.7	110.3	109	108.1	106.0	
3	109.8	109.8	110	108.4	109.3	108.7
	113.4	110.4	113	114.6	113.8	
	112.9	113.4	115	113.5	116.5	
	112.9	113.9	115	114.0	114.6	
	113.2	109.2	112	115.2	116.1	113.6
4	112.8	118.0	116	113.4	109.7	
	114.1	113.2	114	112.7	114.7	112.0
5	114.4	114.1	112	114.9	115.7	
	113.2	114.2	113	115.8	113.2	114.1



The conformation of the bicyclo[3,3,1]nonane system of the DAPT and DPT molecules can be explained in terms of steric strains similar to those discussed by

previous authors for BSBO, CBNO and DCPCO. The separation between the atoms N(1) and N(3) and angles 5 (as designated in Table 4) are found to be 2.85 Å and 114 and 113.2°, respectively. These values are different from those that one would expect in a molecule with ideal chair conformation with tetrahedral angles [the distance between N(1) and N(3) would be 2.38 Å in such molecule assuming a C-N distance of 1.46 Å].

The conformation of the DAPT molecule is also different from that calculated by assuming for the cyclohexane rings the geometry predicted by Kitaigorodsky (1960) for the free molecule with angles between the ring atom bonds of 112°. For this theoretical geometry the predicted values for the N(1)-N(3) distance and for the angles 5 are 2.17 Å and 95.9°, *i.e.* quite different from the observed values.

As a result of the distortion the angles 2, as defined in Table 4, are smaller and the angles 3 and 5 are larger than the theoretical cyclohexane angle of 112°. This is true for the ring bond angles of other bicyclo[3,3,1]nonane systems as shown in Table 4. The dihedral angles between the mean plane through the atoms C(1), N(2), N(4) and C(4) and the two adjacent planes through the atoms N(1), C(1), C(4), and C(5), N(2), N(4) are 42.8 and 55.8°, respectively, and the dihedral angles between the mean plane through C(2), N(2), N(4) and C(3) and the two adjacent planes through N(3), C(2), C(3) and C(5), N(2), N(4) are 41.0 and 58.2°, respectively. The corresponding angles in the undistorted Kitaigorodsky model for cyclohexane should be 47.9°. Thus, the upper half of the chair is more flattened, and the lower half is puckered up more sharply in the distorted molecule than in the undistorted one.

The O atoms of both acetyl groups are very close to the adjacent methylene H atoms (≈ 2.27 Å). This may be an indication of intramolecular C-H...O hydrogen bonding.

Fig. 4 shows the packing of the DAPT molecule in the crystal. There are two short intermolecular C...O contacts between O(2) of a molecule and C(2) and C(5) of a neighboring molecule at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$. The distances O...H and O...C and the angles C-H...O are 2.38, 3.28 Å and 144.8°, respectively, for the C(2)-H(3)...O(2) contact, and 2.43, 3.39 Å and 147.2° for the C(5)-H(9)...O(2) contact. These values may indicate weak hydrogen bonding. The third short intermolecular distance occurs between the same pair of molecules. The molecules with these short contacts

are stacked along the unique *b* axis to form an infinite linear chain. The lateral links between the chains are comparatively weak, with intermolecular distances between heavy atoms longer than 3.5 Å.

A rigid body motion analysis (Schomaker & Trueblood, 1968) has been applied to the DAPT molecule with the hydrogen atoms excluded. The libration amplitudes about the three principal axes were 3.4, 2.6 and 1.1°. The effect of this libration on the bond lengths ranges from 0.006 to 0.004 Å, *i.e.* between two and three times the standard deviation.

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