L'anion fait apparaître deux liaisons B—F longues (1,39 Å de moyenne), celles situées dans le plan de symétrie cristallographique, et deux liaisons courtes, de 1,27 Å. L'angle que forment entre elles les liaisons courtes, 113,5°, est significativement différent de la valeur tétraédrique. De telles dissymétries de l'anion BF_4^- ont été déjà souvent observées sans qu'une explication évidente puisse être avancée. Il semble exclu, en tout cas, d'invoquer ici les contacts entre cations et anions puisque, comme on le voit à la Fig. 1, chacun des atomes de fluor a un groupement méthyle dans son voisinage immédiat, et cela à une distance de 3,31 Å, tout à fait normale. Il fait toutefois remarquer que les mouvements d'agitation thermique des atomes de l'anion sont considérablement plus importants que ceux des atomes du cation.

Les longueurs des liaisons du cation sont mentionnées à la Fig. 2. Elles appellent les commentaires suivants.

(1) La distance C(4)—C(5), 1,34 Å, est inférieure de manière significative aux autres distances du cycle benzénique qui ne s'écartent pas, quant à elles, de leur valeur moyenne, 1,40 Å, compte tenu de la précision des résultats (les écarts-type calculés ne dépassent pas 0,01 Å pour les distances interatomiques).

(2) La triple liaison C(7)≡C(8) est également très courte: 1,15 Å, au lieu de la valeur classique de 1,20 Å; au vu de la proximité des liaisons raccourcies C(4)—C(5) et C(7)—C(8) dans l'empilement cristallin (Fig. 1) on pourrait penser qu'il faut chercher dans des perturbations intermoléculaires sévères la cause des écarts observés mais, curieusement, l'action réciproque de la triple liaison sur une des liaisons benzéniques conduit au raccourcissement, et donc au renforcement, de l'une et l'autre. L'existence d'une interaction importante entre molécules superposées, au niveau des deux liaisons que nous venons de mentionner, est corroborée par l'examen des constantes d'agitation thermique; les valeurs de B_{22}, traduisant les déplacements parallèlement à l'axe b, sont sensiblement moins élevées pour les atomes proches d'une ligne passant par C(4) et C(9), ligne qui apparaît ainsi comme un axe de libration de torsion; dans ce mouvement, les déplacements des atomes des deux liaisons en contact étroit se trouvent réduit au minimum.

(3) Les distances C(9)—N(10) et C(9)—O(13) sont normales pour des liaisons qui peuvent être considérées comme partiellement doubles si l'on écrit les formes de résonance dans lesquelles la charge positive du cation est sur l'azote ou sur l'oxygène, à côté de celle où le charge est portée par C(9).

Les auteurs remercient le Professeur Viehe et le Dr Baum de leur avoir soumis ce problème et fourni les cristaux. JPD marque sa gratitude au Fonds National (Belge) de la Recherche Scientifique pour le mandat dont il bénéficie.

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Acta Cryst. (1977). B**33**, 1624–1627

A Photodimer of 1,1′-Trimethylene-3,3′-dipropylbisthymine

BY E. SKRZYPCZAK-JANKUN, H. MAŁUSZYŃSKA, Z. KAŁUSKI AND K. GOLANKIEWICZ

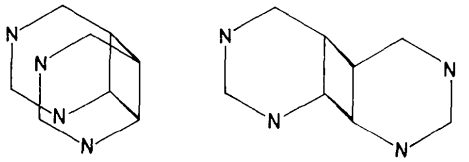
Chemistry Department, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 *Poznań, Poland*

(*Received* 20 *December* 1976; *accepted* 11 *January* 1977)

Abstract. $C_{19}H_{28}N_4O_4$, orthorhombic, space group $Pn2_1a$, $a = 16{\cdot}907\,(3)$, $b = 10{\cdot}757\,(2)$, $c = 10{\cdot}637\,(2)$ Å, $D_m = 1{\cdot}29$, $Z = 4$, $D_x = 1{\cdot}29$ g cm^{-3}. The structure was solved by direct methods and refined to $R(F) = 0{\cdot}064$ for 1015 symmetry-independent reflexions. The internal cyclobutane-type photodimer has the *cis–syn* configuration. The cyclobutane ring is puckered with a dihedral angle of 164·8°. The torsion angles about the bonds C(5)—C(5′) and C(6)—C(6′) are 10·4 and 10·6° respectively. The pyrimidine residues are not planar. The diazacycloheptane ring has a slight twist-chair conformation.

Introduction. This work forms part of an X-ray study on the conformation and structural properties of the photodimers of uracil and thymine derivatives. The title compound is the second analogue of thymidylyl(3′,5′)-thymidine (TpT) to be studied by X-ray analysis. The *cis–syn* geometry of the molecule was predicted by spectroscopic and chemical methods (Golankiewicz & Zasada-Parzyńska, 1974). The possible *trans–syn* isomer could not be detected, even in traces.

Clear colourless crystals, tabular (100), were obtained from ethyl alcohol solution. The systematic absences indicated space group *Pnma* or $Pn2_1a$. Cell constants were refined and intensity data determined from a crystal 0·25 × 0·25 × 0·05 mm with an automated Syntex $P2_1$ four-circle diffractometer, Mo *Ka* radiation and graphite monochromator. A standard reflexion was monitored after every 15 reflexions and did not show any intensity decrease during 60 h of X-ray exposure. 1361 unique reflexions were recorded up to $2\theta = 45°$



cis–syn *trans–syn*

Table 1. *Fractional atomic coordinates* (×10⁴) *with e.s.d.'s in parentheses*

	x	y	z
N(1)	2225 (5)	575	1975 (8)
N(3)	3528 (5)	864	1179 (8)
N(1′)	2170 (4)	1248	4518 (8)
H(3′)	3413 (5)	2288	4458 (8)
O(2)	2477 (4)	2050 (9)	509 (7)
O(4)	4526 (5)	−464 (10)	1573 (7)
O(2′)	2246 (4)	3291 (9)	4906 (8)
O(4′)	4541 (4)	1340 (10)	3914 (8)
C(2)	2713 (6)	1182 (13)	1197 (10)
C(4)	3863 (7)	−107 (12)	1822 (11)
C(5)	3374 (6)	−690 (12)	2864 (11)
C(6)	2481 (6)	−396 (10)	2814 (10)
C(2′)	2581 (8)	2313 (14)	4660 (11)
C(4′)	3849 (7)	1258 (14)	4131 (11)
C(5′)	3435 (7)	−4 (11)	4156 (11)
C(6′)	2519 (6)	53 (12)	4239 (10)
C(7)	1360 (6)	889 (12)	1998 (10)
C(8)	1113 (6)	1800 (12)	2991 (10)
C(7′)	1294 (5)	1346 (14)	4309 (10)
C(9)	3514 (7)	−2105 (12)	2896 (11)
C(10)	4014 (6)	1522 (12)	198 (11)
C(11)	3965 (7)	985 (17)	−1149 (12)
C(12)	4450 (7)	1719 (14)	−2048 (10)
C(9′)	3834 (6)	−712 (12)	5269 (11)
C(10′)	3848 (7)	3508 (13)	4610 (11)
C(11′)	3995 (9)	4165 (14)	3373 (16)
C(12′)	3332 (10)	4479 (16)	2563 (14)
H(1)	2130	−1190	2720
H(2)	2290	−645	4860
H(3)	1010	90	2070
H(4)	1199	1310	1055
H(5)	510	2090	2899
H(6)	1440	2720	2850
H(7)	1030	440	4440
H(8)	1050	1990	5030
H(9)	3230	−2550	3560
H(10)	4149	−2215	3084
H(11)	3368	−2456	2007
H(12)	3630	−1620	5000
H(13)	3619	−395	6167
H(14)	4469	−601	5237
H(15)	4620	1550	520
H(16)	3830	2520	190
H(17)	4150	30	−1040
H(18)	3320	990	−1370
H(19)	4390	3310	5160
H(20)	3480	4100	5260
H(21)	4450	3640	2860
H(22)	4350	5010	3550

Table 2. *Bond lengths* (Å) *and valency angles* (°) *with e.s.d.'s in parentheses*

	Unprimed	Primed
N(1)–C(2)	1·339 (14)	1·349 (15)
N(1)–C(6)	1·440 (12)	1·444 (13)
N(1)–C(7)	1·502 (13)	1·501 (11)
N(3)–C(2)	1·419 (13)	1·424 (16)
N(3)–C(4)	1·371 (14)	1·372 (15)
N(3)–C(10)	1·506 (14)	1·513 (14)
O(2)–C(2)	1·252 (15)	1·222 (17)
O(4)–C(4)	1·214 (15)	1·195 (14)
C(4)–C(5)	1·519 (17)	1·527 (19)
C(5)–C(6)	1·543 (15)	1·553 (16)
C(5)–C(9)	1·540 (19)	1·561 (17)
C(7)–C(8)	1·501 (17)	1·515 (16)
C(10)–C(11)	1·547 (18)	1·514 (21)
C(11)–C(12)	1·487 (19)	1·453 (23)
C(5)–C(5′)	1·564 (17)	
C(6)–C(6′)	1·592 (15)	

	Unprimed	Primed
C(2)–N(1)–C(6)	123·5 (8)	124·7 (9)
C(2)–N(1)–C(7)	120·1 (8)	117·6 (8)
C(6)–N(1)–C(7)	116·4 (8)	115·8 (8)
C(2)–N(3)–C(4)	125·3 (8)	125·7 (9)
C(2)–N(3)–C(10)	115·2 (8)	116·6 (9)
C(4)–N(3)–C(10)	118·6 (8)	117·7 (9)
N(1)–C(2)–N(3)	119·2 (9)	118·4 (1·0)
N(1)–C(2)–O(2)	121·9 (1·0)	121·1 (1·1)
N(3)–C(2)–O(2)	118·8 (1·0)	120·4 (1·1)
N(3)–C(4)–C(5)	116·9 (1·0)	117·7 (1·0)
N(3)–C(4)–O(4)	120·9 (1·1)	120·9 (1·1)
C(5)–C(4)–O(4)	122·0 (1·1)	121·2 (1·1)
C(4)–C(5)–C(6)	115·0 (1·0)	115·1 (1·0)
C(4)–C(5)–C(5)	114·2 (1·0)	115·8 (1·0)
C(5)–C(5)–C(6)	89·9 (8)	90·1 (9)
C(4)–C(5)–C(9)	109·9 (1·0)	104·4 (9)
C(6)–C(5)–C(9)	110·8 (9)	114·0 (9)
C(5)–C(5)–C(9)	115·9 (1·0)	117·7 (1·0)
N(1)–C(6)–C(5)	117·6 (8)	117·0 (9)
N(1)–C(6)–C(6)	112·4 (8)	116·7 (9)
C(5)–C(6)–C(6)	89·5 (8)	88·5 (8)
N(1)–C(7)–C(8)	115·4 (9)	111·1 (9)
C(7)–C(8)–C(7′)	112·6 (9)	
N(3)–C(10)–C(11)	115·9 (1·0)	113·1 (1·0)
C(10)–C(11)–C(12)	111·6 (1·1)	119·8 (1·3)

with a θ–2θ scan technique. 1015 reflexions with $I > 1{\cdot}96\sigma(I)$ were considered as observed. No absorption corrections were applied [μ_1(Mo $K\alpha$) = 1·0 cm^{-1}].

The statistical distribution of the $|E|$'s indicated the space group $Pn2_1a$, The structure was solved by direct methods with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and refined by the full-matrix least-squares method to R = 0·072 for all non-hydrogen atoms. Of the 28 H atoms the positions of two were taken from a difference map and those for 20 were calculated assuming a C–H distance of 1·08 Å. The six remaining atoms, belonging to the terminal atoms in the propyl substituents, were not found. H atoms were assigned B values equal to those of the atoms to which they were bonded and their parameters were included in the calculation but were not refined. Full-matrix least-squares refinement converged to $R_w = \Sigma\, w^{1/2}|F_o - F_c|/\Sigma\, w^{1/2}|F_o| = 0{\cdot}054$ with a corresponding $R(F)$ = 0·064.* The quantity minimized was $\Sigma\, w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$. The atomic scattering factors were from *International Tables for X-ray Crystallography* (1962). Because of the space group and the storage capacity of the computer (CDC6000 type CYBER72 and NOVA1200) the refinement was carried out keeping the y coordinates constant for a chosen group of atoms. A different set of atoms was held constant in different cycles. Final positional parameters are given in Table 1 and the bond distances and angles in Table 2.

Discussion. The X-ray analysis confirmed the *cis–syn* configuration of 3PrThy[1(CH$_2$)$_3$1′]3′PrThy (abbreviation proposed by Cohn, Leonard & Wang, 1974), Fig. 1. The same configuration was found for Thy[1(CH$_2$)$_3$1′]Thy (Leonard, Golankiewicz, McCredie, Johnson & Paul, 1969); however, the conformations of these two compounds are different. In contrast to 1,1′-trimethylenebisthymine the photodimer of the 3,3′-substituted derivative has a puckered cyclobutane ring with an average dihedral angle of 164·8°. As a result of the puckering the heterocyclic rings are twisted. The six-membered rings are rotated with respect to each other by about 10·5°. A measure of the 'twist' is the average value of the torsion angles

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32438 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

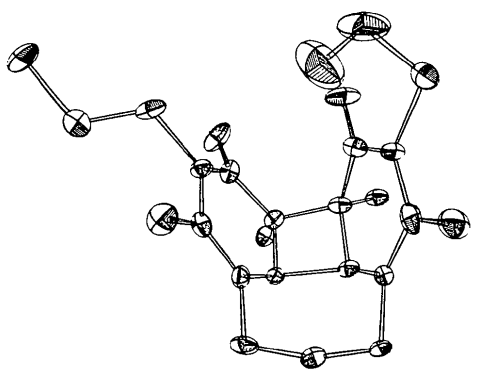


Fig. 1. The molecule of 3PrThy[1(CH$_2$)$_3$1′]3′PrThy. Thermal ellipsoids are drawn at the 40% probability level.

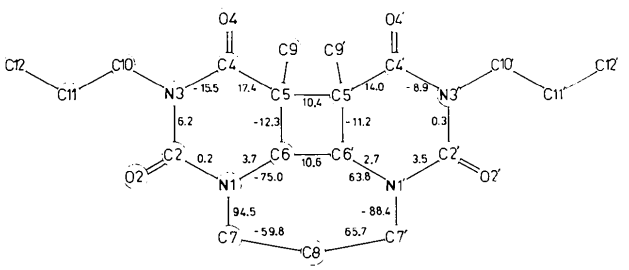


Fig. 2. Atom-numbering system and the torsion angles around the rings in the molecule.

Table 3. *Dihedral angles and twist angles in photodimers of uracil and thymine derivatives*

Photodimer	Dihedral angle of cyclobutane ring	Twist angle of pyrimidine residues
Thy[1(CH$_2$)$_3$1′]Thy	178°	0°
3PrThy[1(CH$_2$)$_3$1′]3′PrThy	164·8	10·5
6MeUra[]6′MeUra.H$_2$O	162	16·5
Thy$_3$.H$_2$O	173·5	5·8
1,3DiMeThy[]1′,3′diMeThy	153	26

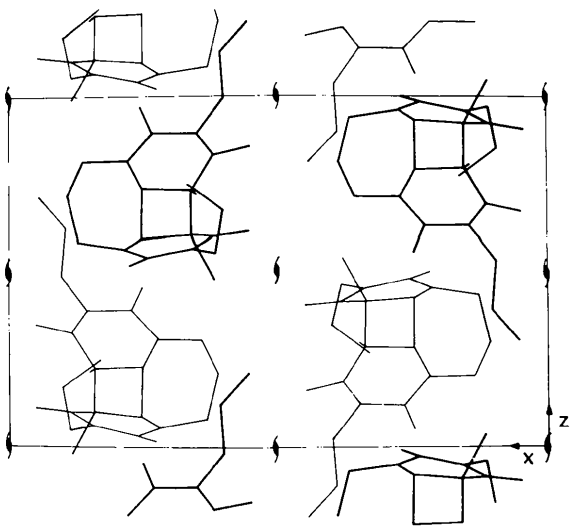


Fig. 3. Packing diagram viewed along **b**.

C(4)C(5)C(5′)C(4′) and N(1)C(6)C(6′)N(1′). The diazacycloheptane ring has a slight twist-chair conformation. All torsion angles around the rings are given in Fig. 2.

A similar geometry was found for the *cis–syn* photodimers of 6-methyluracil (Gibson & Karle, 1971) and thymine trimer (Flippen & Karle, 1971) (Table 3). However, the molecule of the known *cis–syn* photodimer of 1,3-dimethylthymine with substituted N atoms is much more distorted (Camerman & Camerman, 1970).

The bond lengths and angles in the molecule agree well with those for the dimers reported to date (Birnbaum, 1972 and references cited therein; Leonard *et al.*, 1969; Bremner, Warrener, Adman & Jensen, 1971; Cheng, Hornby, Wong-Ng, Nyburg & Weinblum, 1976).* The short lengths of the bonds C(11)–C(12), C(11′)–C(12′) are probably due to the thermal motion. The intramolecular distance C(9)···C(9′) is only 2·98 Å. The crystal packing is shown in Fig. 3.

* A full list of bond lengths and valency angles of all *cis–syn*, *cis–anti*, *trans–syn*, and *trans–anti* photodimers published to date is available from the authors.

We wish to thank Dr T. Głowiak for the data collection.

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Acta Cryst. (1977). B**33**, 1627–1630

N-(*N*-Piperidylacetyl)piperidinium Perchlorate

BY MARIUSZ JASKÓLSKI, MARIA GDANIEC AND ZOFIA KOSTURKIEWICZ

Laboratory of X-ray Crystallography, Institute of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

(*Received* 14 *December* 1976; *accepted* 11 *January* 1977)

Abstract. $C_{12}H_{23}N_2O_5Cl$, orthorhombic, *Pbca*; a = 18·699 (2), b = 15·456 (2), c = 10·302 (1) Å, V = 2977 Å^3; Z = 8, D_m = 1·39, D_c = 1·39 g cm^{-3}; μ(Cu $K\alpha$) = 24·8 cm^{-1}. R = 0·074 for 1672 observed reflexions. The cations are hydrogen bonded and form dimers, each dimer occupying a centre of symmetry.

Introduction. *N*-(*N*-Piperidylacetyl)piperidine is one of various model compounds investigated by Professor M. Wiewiórowski in his study of intramolecular catalysis. The crystals of *N*-(*N*-piperidylacetyl)piperidinium perchlorate were prepared and supplied by him.

Photographs showed systematic absences 0*kl* for *k* odd, *h*0*l* for *l* odd, *hk*0 for *h* odd. Precise unit-cell-constant determination (by least-squares fit of the setting angles of 15 reflexions) and intensity measurements were carried out on a Syntex $P2_1$ four-circle computer-controlled diffractometer using a crystal with dimensions 0·10 × 0·28 × 0·33 mm. Graphite-monochromatized Cu radiation and a variable θ–2θ scan were used. 2328 independent reflexions were collected in a 2θ range up to 114° and, of these, 1673 had $I > 1{\cdot}96\sigma(I)$ and were used in all calculations with the exception of the most intense reflexion, 400, which was excluded from the final stages of least-squares refinement. Structure factors were obtained from the intensities in the usual fashion. No absorption or extinction corrections were applied. The structure was solved by standard heavy-atom Patterson and Fourier methods. An electron density map calculated on the basis of only the Cl atom revealed the positions of all non-hydrogen atoms of the cation and a number of peaks around the Cl atom, the four highest of which were interpreted as O atoms. Attempts to locate the perchlorate group in