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The Structure of a Dinucleoside Monophosphate Having a High-*anti* Conformation: 8,2'-*S*-Cyclo-2'-thioadenylyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine (A^spA^s) Hydrochloride

BY SATOSHI FUJII, KENSAKU HAMADA, REIKO MIURA, SEIICHI UESUGI, MORIO IKEHARA
AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, Yamadaoka 1–6, Suita, Osaka 565, Japan

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Abstract

The crystal and molecular structure of 8,2'-*S*-cyclo-2'-thioadenylyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine (A^spA^s) hydrochloride, $2(\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_8\text{PS}_2^+\cdot\text{Cl}^-)\cdot 5\text{H}_2\text{O}$, has been determined by X-ray diffraction methods and refined to an *R* value of 0.078. A^spA^s crystallizes in the triclinic space group *P*1, with unit-cell

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dimensions: $a = 11.161(4)$, $b = 11.824(4)$, $c = 12.136(3)$ Å, $\alpha = 89.20(3)$, $\beta = 97.92(3)$ and $\gamma = 116.75(2)^\circ$; $Z = 1$, $D_m = 1.655(4)$, $D_x = 1.656$ g cm⁻³, $\sin \theta/\lambda = 0.595$ Å⁻¹. The molecular conformations of two independent A^spA^s molecules in an asymmetric unit are almost identical, and are both in the sharp 'bend' conformation. *i.e.* the rotation (ω' , ω) around the P–O bond is (g^- , t) rather than the preferred (g^- , g^-) or

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(g^+, g^+). These torsion angles concerning the sugar-phosphate backbone are quite distinct from those found in crystalline dinucleoside monophosphates so far determined by X-ray studies. There is no intramolecular base stacking or base pairing but strong intermolecular base stacking exists.

Introduction

Many theoretical, spectroscopic and X-ray structural studies concerning non-helical oligonucleotide conformations have been reported, and we describe here a new type of stable non-helical conformation first found in crystalline dinucleoside monophosphates.

The dinucleoside monophosphate 8,2'-*S*-cyclo-2'-thioadenylyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine ($A^s p A^s$), a derivative of ApA, is cyclized with an S atom between the 8-position of the purine base and the 2'-position of the sugar ring, and characterized by an unusual base-sugar orientation, a high-*anti* conformation. Therefore, it may possess an interesting structural feature, *i.e.* instead of having the right-handed stacking form found for the ApA molecule in aqueous solution, $A^s p A^s$ may tend to form the left-handed stacking form which we proposed from the results of CD measurements and energy calculations (Uesugi, Yasumoto, Ikehara, Fang & Ts'o, 1972; Fujii & Tomita, 1976).

In order to prove the left-handed stacking in the crystalline state and to obtain substantial information about the influences of the high-*anti* conformation on the molecular structure of nucleic acids, we have carried out the X-ray structure analysis of an $A^s p A^s$ crystal. The chemical structure and the numbering of the $A^s p A^s$ molecule are shown in Fig. 1.

Experimental

By slow evaporation of an acidic solution of $A^s p A^s$ which was synthesized by the method described

previously (Ikehara, Uesugi & Yasumoto, 1970), transparent prismatic crystals were obtained at 283 K.

The space group and preliminary cell dimensions were determined by precession and Weissenberg photographs and then the cell dimensions were refined by the least-squares procedure using the θ values of 32 reflections ($29^\circ < 2\theta < 38^\circ$; Mo $K\alpha$ radiation) measured by a diffractometer.

The intensities of 4976 independent reflections up to $2\theta = 50^\circ$ were collected on a Rigaku-Denki automatic four-circle diffractometer with Mo $K\alpha$ radiation. The ω - 2θ scanning technique was employed at a rate of 2° min^{-1} . The intensities of four standard reflections were measured for every 50 reflections of the data set; these indicated no deterioration during the run. Lorentz-polarization corrections were applied but no corrections were made for absorption. The observed density indicates that two independent $A^s p A^s$ molecules and some solvent molecules are in an asymmetric unit.

Structure determination and refinement

The initial attempt to solve the structure by the vector-superposition technique failed. The structure was then solved by combination of direct methods (*MULTAN* 78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and successive Fourier techniques. Except for four strong reflections, the calculated result showed that one set of phases had figures of merit which were definitely different from those of other sets. From an *E* map using this phase set, we could determine six heavy-atom (S and P) positions for the $A^s p A^s$ molecules. Successive Fourier syntheses revealed the four purine moieties and then the remaining non-H atoms. The refinement of the positional and isotropic temperature parameters was carried out by a full-matrix least-squares method and further refinements were by block-diagonal least squares with anisotropic temperature parameters. In this procedure, the matrices were calculated by dividing two independent molecules into two or four parts to reduce computer time. A difference Fourier synthesis revealed all the H atoms except for those of the five water molecules, which were included in the final refinement and the final *R* value dropped to 0.078. Throughout the refinement, each reflection was given a unit weight. The atomic scattering factors used were those cited in *International Tables for X-ray Crystallography* (1974). For all computations *UNICS* (1973) was used on the ACOS-700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and discussion

The two independent $A^s p A^s$ molecules in an asymmetric unit are designated $A^s(A)pA^s(B)$ -1 and $A^s(C)pA^s(D)$ -2, where (A) and (C) correspond to the

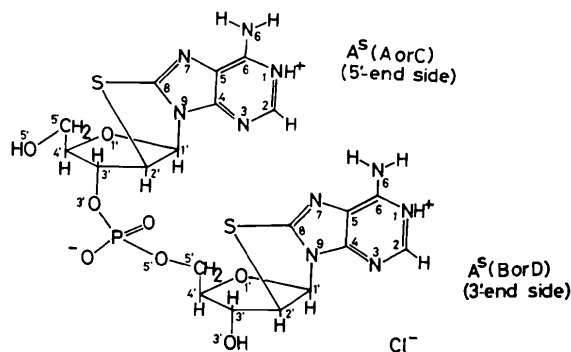


Fig. 1. Chemical structure of $A^s p A^s$.

Table 1. Atomic coordinates of non-H atoms ($\times 10^3$) and equivalent isotropic thermal parameters (\AA^2) for $\text{A}^{\text{s}}\text{pA}^{\text{s}}$

The B_{eq} values were calculated with Hamilton's (1959) formula. The standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
N(1)(A)	807 (12)	670 (12)	87 (12)	3.2 (2)
C(2)(A)	856 (15)	620 (15)	179 (17)	3.5 (2)
N(3)(A)	784 (12)	543 (11)	248 (12)	3.0 (2)
C(4)(A)	653 (13)	523 (12)	228 (12)	2.1 (2)
C(5)(A)	592 (14)	571 (14)	142 (13)	2.6 (2)
C(6)(A)	673 (16)	644 (13)	66 (14)	2.9 (2)
N(6)(A)	630 (15)	688 (14)	-21 (12)	3.9 (2)
N(7)(A)	457 (13)	531 (12)	152 (11)	2.9 (2)
C(8)(A)	437 (15)	461 (14)	240 (13)	2.7 (2)
N(9)(A)	551 (12)	452 (12)	287 (10)	2.6 (2)
C(1')(A)	538 (14)	363 (14)	373 (12)	2.4 (2)
C(2')(A)	386 (13)	300 (13)	390 (12)	2.1 (2)
C(3')(A)	336 (14)	158 (14)	351 (12)	2.6 (2)
C(4')(A)	448 (13)	157 (13)	297 (13)	2.3 (2)
C(5')(A)	429 (17)	144 (17)	172 (15)	3.6 (2)
O(1')(A)	570 (10)	269 (10)	345 (10)	3.0 (1)
S(A)	298 (4)	377 (4)	304 (4)	2.7 (1)
O(3')(A)	319 (10)	85 (10)	499 (9)	2.7 (1)
O(5')(A)	402 (14)	237 (12)	120 (11)	4.6 (2)
P(1)	174 (4)	17 (4)	488 (3)	2.5 (1)
O(L)(1)	192 (11)	-33 (11)	600 (9)	3.4 (2)
O(R)(1)	72 (11)	-74 (11)	400 (10)	3.7 (2)
N(1)(B)	78 (13)	458 (13)	32 (12)	3.1 (2)
C(2)(B)	141 (16)	533 (15)	124 (15)	3.2 (2)
N(3)(B)	108 (13)	510 (12)	224 (12)	3.2 (2)
C(4)(B)	1 (15)	398 (15)	226 (11)	2.5 (2)
C(5)(B)	-74 (15)	314 (14)	135 (14)	2.8 (2)
C(6)(B)	-29 (14)	349 (15)	33 (13)	2.7 (2)
N(6)(B)	-92 (15)	274 (14)	-61 (11)	3.7 (2)
N(7)(B)	-180 (12)	201 (12)	166 (10)	2.6 (2)
C(8)(B)	-166 (13)	224 (14)	274 (13)	2.3 (2)
N(9)(B)	-61 (13)	340 (11)	315 (10)	2.6 (2)
C(1')(B)	-34 (15)	364 (15)	436 (13)	2.8 (2)
C(2')(B)	-162 (14)	267 (15)	479 (12)	2.5 (2)
C(3')(B)	-109 (15)	229 (15)	590 (12)	2.6 (2)
C(4')(B)	26 (13)	240 (14)	569 (12)	2.2 (2)
C(5')(B)	18 (16)	115 (16)	526 (15)	3.2 (2)
O(1')(B)	70 (10)	336 (10)	485 (9)	2.8 (2)
S(B)	-253 (4)	132 (4)	377 (3)	2.6 (1)
O(3')(B)	-98 (12)	315 (13)	676 (10)	4.2 (1)
O(5')(B)	146 (10)	138 (10)	505 (10)	2.9 (2)
N(1)(C)	671 (14)	927 (13)	155 (11)	3.3 (2)
C(2)(C)	539 (17)	895 (16)	158 (13)	3.4 (2)
N(3)(C)	465 (13)	833 (12)	226 (12)	3.1 (2)
C(4)(C)	536 (15)	794 (15)	308 (12)	2.7 (2)
C(5)(C)	670 (15)	816 (13)	312 (12)	2.5 (2)
C(6)(C)	750 (16)	894 (15)	236 (14)	3.0 (2)
N(6)(C)	876 (14)	935 (14)	235 (12)	3.6 (2)
N(7)(C)	707 (12)	757 (12)	404 (11)	2.6 (2)
C(8)(C)	595 (14)	703 (15)	448 (13)	2.6 (2)
N(9)(C)	488 (12)	721 (12)	394 (11)	2.7 (2)
C(1')(C)	361 (15)	673 (14)	441 (13)	2.7 (2)
C(2')(C)	386 (13)	611 (13)	551 (12)	2.1 (2)
C(3')(C)	385 (15)	696 (13)	644 (13)	2.5 (2)
C(4')(C)	382 (16)	812 (13)	588 (14)	3.0 (2)
C(5')(C)	516 (17)	932 (15)	605 (15)	3.3 (2)
O(1')(C)	333 (11)	769 (10)	470 (9)	3.2 (1)
S(C)	550 (4)	605 (4)	559 (3)	2.5 (1)
O(3')(C)	261 (10)	628 (10)	689 (8)	2.5 (1)
O(5')(C)	623 (12)	923 (12)	571 (11)	4.3 (2)
P(2)	267 (4)	551 (4)	799 (3)	2.6 (1)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(L)(2)	125 (12)	475 (11)	817 (10)	3.8 (2)
O(R)(2)	359 (12)	639 (11)	892 (10)	3.9 (2)
N(1)(D)	989 (13)	732 (12)	630 (12)	3.1 (2)
C(2)(D)	895 (15)	638 (16)	558 (14)	3.1 (2)
N(3)(D)	799 (13)	535 (13)	587 (11)	3.0 (2)
C(4)(D)	803 (14)	527 (14)	698 (13)	2.4 (2)
C(5)(D)	897 (13)	618 (14)	780 (12)	2.2 (2)
C(6)(D)	994 (15)	724 (14)	743 (15)	3.0 (2)
N(6)(D)	1091 (14)	820 (14)	812 (13)	3.9 (2)
N(7)(D)	868 (12)	583 (12)	886 (12)	3.1 (2)
C(8)(D)	759 (15)	473 (14)	868 (11)	2.6 (2)
N(9)(D)	714 (12)	433 (12)	754 (10)	2.6 (2)
C(1')(D)	593 (14)	317 (13)	730 (12)	2.5 (2)
C(2')(D)	560 (13)	248 (13)	838 (13)	2.4 (2)
C(3')(D)	409 (15)	195 (13)	836 (12)	2.6 (2)
C(4')(D)	374 (14)	285 (14)	761 (12)	2.4 (2)
C(5')(D)	362 (17)	385 (15)	832 (14)	3.4 (2)
O(1')(D)	479 (10)	340 (11)	693 (10)	3.2 (2)
S(D)	658 (4)	368 (4)	957 (3)	3.0 (1)
O(3')(D)	348 (12)	67 (10)	784 (11)	4.2 (2)
O(5')(D)	327 (12)	462 (11)	754 (9)	3.4 (2)
Cl(1)	782 (5)	860 (4)	783 (4)	4.0 (1)
Cl(2)	84 (5)	119 (4)	74 (4)	3.9 (1)
O(W1)	60 (13)	851 (12)	36 (11)	4.5 (2)
O(W2)	708 (13)	16 (12)	937 (11)	4.3 (2)
O(W3)	431 (14)	-104 (12)	900 (12)	5.2 (2)
O(W4)	180 (15)	833 (14)	243 (12)	5.6 (2)
O(W5)	57 (21)	117 (21)	810 (16)	9.7 (4)

adenylyl part ('5'-end side nucleoside') and (B) and (D) to the adenosine part ('3'-end side nucleoside') of two $\text{A}^{\text{s}}\text{pA}^{\text{s}}$ molecules. The atomic coordinates are shown in Table 1.* The bond lengths and angles listed in Tables 2 and 3 respectively are in good agreement with those of related compounds.

Molecular conformation

Two independent $\text{A}^{\text{s}}\text{pA}^{\text{s}}$ molecules having similar conformation are shown in Fig. 2 (ORTEP drawing; Johnson, 1965), and the relevant torsion angles are summarized in Table 4. Both $\text{A}^{\text{s}}\text{pA}^{\text{s}}$ molecules form 'bend'-like structures in which the dihedral angles between two bases in the same molecule are $63.6(4)^\circ$ in $\text{A}^{\text{s}}\text{pA}^{\text{s}}-1$ and $59.4(4)^\circ$ in $\text{A}^{\text{s}}\text{pA}^{\text{s}}-2$. This 'bend' conformation is characterized by $(\omega', \omega) = (g^-, t)$, *gauche-trans* around the C(4')-C(5') bond at the 3'-end side nucleoside and C(2')-endo-like sugar puckerings at both end side nucleosides (see below). This conformation is quite different from all those found in the duplexes of crystalline dinucleoside monophosphates.

* Lists of structure factors, anisotropic thermal parameters for non-H atoms and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36377 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

It was suggested by energy calculations (Fujii & Tomita, 1976) that the (g^-, t) conformation for (ω', ω) affords a rather stable conformation not only for dinucleoside monophosphates but also for polynucleotides. Moreover, this 'bend' conformation might be important for preservation of the loop structure in polynucleotide chains, because it is found at G18, Gm34 and C56 in the loop region of the tRNA^{Phe} molecule (Jack, Ladner & Klug, 1976).

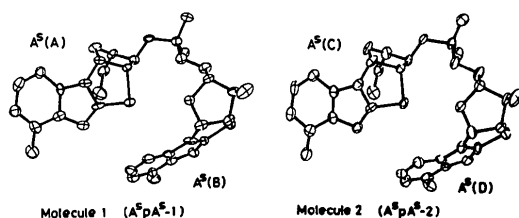


Fig. 2. ORTEP drawing of the molecular structure.

Table 2. Bond lengths (Å) with their *e.s.d.*'s in parentheses

	A ^s (A)	A ^s (B)	A ^s (C)	A ^s (D)
N(1)—C(2)	1.414 (21)	1.338 (20)	1.354 (22)	1.349 (20)
N(1)—C(6)	1.367 (20)	1.308 (20)	1.400 (21)	1.368 (19)
C(2)—N(3)	1.283 (21)	1.301 (20)	1.235 (21)	1.289 (21)
N(3)—C(4)	1.359 (17)	1.327 (19)	1.393 (20)	1.352 (19)
C(4)—C(5)	1.415 (19)	1.398 (21)	1.382 (21)	1.400 (19)
C(4)—N(9)	1.364 (18)	1.373 (19)	1.347 (19)	1.363 (18)
C(5)—C(6)	1.387 (21)	1.386 (21)	1.400 (21)	1.354 (20)
C(5)—N(7)	1.383 (19)	1.419 (19)	1.420 (19)	1.387 (18)
C(6)—N(6)	1.305 (22)	1.362 (21)	1.269 (21)	1.359 (20)
N(7)—C(8)	1.324 (20)	1.318 (18)	1.304 (19)	1.312 (19)
C(8)—N(9)	1.370 (19)	1.382 (19)	1.379 (19)	1.419 (19)
C(8)—S	1.703 (15)	1.732 (14)	1.743 (15)	1.734 (15)
N(9)—C(1')	1.453 (19)	1.459 (20)	1.467 (19)	1.424 (19)
C(1')—C(2')	1.554 (20)	1.531 (21)	1.573 (20)	1.534 (20)
C(1')—O(1')	1.371 (17)	1.416 (18)	1.360 (18)	1.440 (18)
C(2')—C(3')	1.570 (20)	1.546 (21)	1.538 (20)	1.503 (20)
C(2')—S	1.848 (14)	1.843 (16)	1.850 (14)	1.877 (14)
C(3')—C(4')	1.494 (19)	1.521 (21)	1.522 (22)	1.530 (20)
C(3')—O(3')	1.434 (17)	1.424 (20)	1.429 (17)	1.459 (19)
C(4')—C(5')	1.507 (22)	1.532 (21)	1.524 (24)	1.539 (22)
C(4')—O(1')	1.456 (17)	1.475 (17)	1.479 (20)	1.426 (17)
C(5')—O(5')	1.380 (22)	1.391 (19)	1.359 (21)	1.440 (21)
O(3')—P	1.586 (10)		1.612 (11)	
O(5')—P		1.617 (11)		1.616 (12)
P—O(L)		1.502 (12)		1.470 (12)
P—O(R)		1.481 (12)		1.480 (13)

Table 4. Torsion angles (°) with their *e.s.d.*'s in parentheses

Notation	Designation	A ^s (A)p-1	pA ^s (B)-1	A ^s (C)p-2	pA ^s (D)-2
χ	C(8)—N(9)—C(1')—O(1')	117.2 (14)	96.3 (15)	117.0 (14)	101.1 (14)
ψ	C(3')—C(4')—C(5')—O(5')	57.1 (18)	177.4 (12)	57.1 (19)	180.7 (12)
ψ'	O(3')—C(3')—C(4')—C(5')	139.6 (13)	150.3 (13)	141.0 (13)	147.0 (12)
ω	O(3')—P—O(5')—C(5')	—	171.9 (10)	—	173.8 (11)
ω'	C(3')—O(3')—P—O(5')	301.1 (10)	—	303.9 (10)	—
ϕ'	C(4')—C(3')—O(3')—P	209.0 (9)	—	209.8 (10)	—
ϕ	C(4')—C(5')—O(5')—P	—	165.6 (9)	—	163.4 (10)
Furanose ring					
τ_0	C(4')—O(1')—C(1')—C(2')	23.1 (14)	—8.0 (15)	20.0 (15)	—4.7 (14)
τ_1	O(1')—C(1')—C(2')—C(3')	—6.7 (14)	24.9 (15)	—6.3 (14)	19.7 (14)
τ_2	C(1')—C(2')—C(3')—C(4')	—11.2 (13)	—31.8 (14)	—8.7 (14)	—26.1 (14)
τ_3	C(2')—C(3')—C(4')—O(1')	24.3 (13)	27.0 (14)	19.6 (15)	23.4 (14)
τ_4	C(3')—C(4')—O(1')—C(1')	—30.1 (14)	—12.5 (14)	—25.4 (16)	—11.8 (15)

Possible helical structures could be constructed by proper combination of ω' , ω , ψ , and sugar puckering. The helical parameters calculated from the observed bond lengths, bond angles, and torsion angles in this crystal (helical pitch 6.1 Å, angular rotation 92° and displacement of the P atom from helix axis 2.4 Å)

Table 3. Bond angles (°) with their *e.s.d.*'s in parentheses

	A ^s (A)	A ^s (B)	A ^s (C)	A ^s (D)
C(2)—N(1)—C(6)	121.5 (13)	122.7 (14)	123.2 (14)	122.3 (13)
N(1)—C(2)—N(3)	126.2 (15)	125.9 (14)	129.1 (16)	124.7 (15)
C(2)—N(3)—C(4)	111.4 (13)	112.0 (13)	110.9 (14)	113.3 (13)
N(3)—C(4)—C(5)	128.2 (12)	126.5 (14)	125.6 (14)	126.4 (13)
N(3)—C(4)—N(9)	127.0 (12)	128.7 (14)	127.5 (13)	127.2 (13)
C(5)—C(4)—N(9)	104.8 (11)	104.8 (13)	106.8 (13)	106.4 (12)
C(4)—C(5)—C(6)	117.1 (13)	116.5 (13)	120.5 (14)	116.9 (13)
C(4)—C(5)—N(7)	110.1 (12)	112.0 (13)	110.3 (13)	111.7 (12)
C(6)—C(5)—N(7)	132.9 (14)	131.5 (13)	129.1 (13)	131.3 (13)
N(1)—C(6)—C(5)	115.4 (14)	116.3 (14)	110.4 (13)	116.5 (13)
N(1)—C(6)—N(6)	120.2 (14)	121.8 (14)	120.9 (14)	120.3 (13)
C(5)—C(6)—N(6)	124.5 (15)	121.9 (14)	128.7 (15)	123.2 (14)
C(5)—N(7)—C(8)	104.9 (12)	101.5 (12)	102.1 (12)	103.0 (12)
N(7)—C(8)—N(9)	112.4 (13)	115.2 (12)	115.1 (13)	114.4 (13)
N(7)—C(8)—S	132.9 (12)	131.2 (11)	132.0 (12)	132.6 (12)
N(9)—C(8)—S	114.6 (11)	113.5 (10)	112.8 (10)	112.9 (10)
C(4)—N(9)—C(8)	107.7 (12)	106.4 (12)	105.7 (12)	104.5 (11)
C(4)—N(9)—C(1')	133.7 (12)	136.3 (13)	134.4 (12)	138.8 (12)
C(8)—N(9)—C(1')	118.0 (12)	116.9 (12)	119.6 (12)	116.6 (12)
N(9)—C(1')—C(2')	106.0 (11)	105.4 (12)	105.0 (11)	108.9 (11)
N(9)—C(1')—O(1')	113.3 (12)	111.4 (12)	111.8 (12)	110.7 (11)
C(2')—C(1')—O(1')	108.1 (11)	105.3 (12)	107.8 (12)	104.6 (11)
C(1')—C(2')—C(3')	102.9 (11)	104.4 (12)	104.0 (11)	106.4 (11)
C(1')—C(2')—S	109.3 (9)	108.8 (10)	109.8 (9)	107.2 (9)
C(3')—C(2')—S	113.2 (9)	111.9 (10)	112.7 (9)	112.2 (10)
C(2')—C(3')—C(4')	105.0 (11)	102.8 (12)	106.1 (12)	103.1 (11)
C(2')—C(3')—O(3')	107.7 (11)	107.9 (12)	107.4 (11)	106.6 (12)
C(4')—C(3')—O(3')	110.4 (11)	113.6 (12)	108.6 (12)	111.3 (12)
C(3')—C(4')—C(5')	118.1 (12)	113.2 (12)	115.1 (13)	110.7 (12)
C(3')—C(4')—O(1')	105.3 (11)	104.8 (11)	104.5 (12)	106.7 (11)
C(5')—C(4')—O(1')	114.1 (11)	110.4 (11)	112.1 (13)	112.3 (12)
C(4')—C(5')—O(5')	113.6 (14)	107.9 (12)	116.0 (14)	105.8 (14)
C(1')—O(1')—C(4')	110.5 (10)	112.6 (10)	111.9 (12)	112.2 (11)
C(8)—S—C(2')	91.2 (7)	90.3 (7)	91.5 (7)	91.3 (7)
C(3')—O(3')—P	119.3 (9)		116.9 (9)	
C(5')—O(5')—P		117.8 (9)		118.5 (10)
O(3')—P—O(5')	100.0 (5)		100.5 (6)	
O(3')—P—O(L)	107.0 (6)		106.1 (6)	
O(3')—P—O(R)	111.5 (6)		110.2 (6)	
O(5')—P—O(L)		108.4 (6)		110.9 (7)
O(5')—P—O(R)		111.7 (6)		111.9 (7)
O(L)—P—O(R)		116.7 (7)		116.0 (7)

indicate the base moieties protruding out from the helix axis. But this conformation does not belong to either an 'extended' or an 'open' form. Hingerty (1979) noted that the 'bend' conformation with $(\omega', \omega) = (g^-, t)$ could be built. This (g^-, t) conformation may correspond to that of the GpC fragment in Z_1 -DNA (Wang, Quigley, Kolpak, van der Marel, van Boom & Rich, 1981) where $(\omega', \omega) = (291, 223^\circ)$, if the torsion angle ω is slightly distorted from the ideal *trans* form.

Sugar conformation

The sugar puckerings at the 5'-end side and the 3'-end side in two independent molecules are C(4')-endo, and C(3')-exo respectively, which are both C(2')-endo-like conformations. The C(4')-endo conformation is frequently found in the cyclonucleosides and nucleotides so far determined by X-rays, and the displacement of the C(4') atom from the remaining four atoms in the furanose ring, 0.41 (2) for A^s(A) or 0.35 (2) Å for A^s(C), is rather small (Table 5). Therefore it is possible to have *gauche-gauche* orientation around the C(4')-C(5') bond. If not, the short contacts between the O(5') atom and the base moiety are fixed at the high-*anti* region, and prevent the adoption of the *gauche-gauche* orientation but allow the *gauche-trans* or *trans-gauche* orientation. In fact, 8,2'-*S*-cyclo 3'-AMP (K. Tomita, to be published) and 8,2'-*S*-cyclo 5'-AMP (Tanaka, Fujii, Fujiwara & Tomita, 1979) having C(4')-endo sugar puckerings take the *gauche-trans* orientation.

On the other hand, the C(3')-exo conformation found in the 3'-end side nucleoside is unusual for cyclonucleosides or cyclonucleotides fused at the 2'-position of the sugar. The displacement of the C(3') atom from the best plane of the remaining four atoms of the ring [0.47 (2) for A^s(B) or 0.40 (2) Å for A^s(D)] causes a large distortion from the ideal envelope-type puckering and may influence the planarity of the adjacent fused ring [C(2')-C(1')-N(9)-C(8)-S]. As listed in Table 5, planes VI and VIII for newly fused *S*-cyclo moieties at the 3'-end side are rather distorted with large deviations of C(1') and C(2'), in opposite directions. Although this fused ring has rather weak π -bond character, it might be easily influenced by puckering of the adjacent furanose ring. The difference between the torsion angles at the 5'-end side, 117.2 (14) [A^s(A)] or 117.0 (14)° [A^s(C)], and those at the 3'-end side, 96.3 (15) [A^s(B)] or 101.1° [A^s(D)], apparently depends on the magnitudes of the deviations of C(1') and C(2') from the fused ring. The dihedral angles between the purine and furanose planes fall in the small range 66.1 to 69.9°.

Hydrogen bonding

The hydrogen bonds are listed in Table 6. All the hydrogen-donor atoms participate in hydrogen bond-

Table 5. *Plane equations and deviations (Å) of atoms from the best plane through several parts of the molecule*

Asterisks indicate atoms included in the calculation of the best plane.

	A ^s (A)	A ^s (B)	A ^s (C)	A ^s (D)
Purine moiety				
Plane	I	II	III	IV
N(1)	0.01 (2)*	0.02 (2)*	-0.02 (2)*	-0.03 (2)*
C(2)	0.06 (2)*	0.01 (2)*	-0.03 (2)*	-0.01 (2)*
N(3)	-0.01 (1)*	-0.01 (2)*	-0.00 (2)*	0.00 (2)*
C(4)	-0.01 (2)*	-0.01 (2)*	0.03 (2)*	0.03 (2)*
C(5)	-0.05 (2)*	-0.03 (2)*	-0.00 (2)*	0.04 (2)*
C(6)	0.02 (2)*	-0.01 (2)*	0.06 (2)*	0.01 (2)*
N(6)	-0.14 (2)	-0.00 (2)	0.18 (2)	0.01 (2)
N(7)	0.02 (2)*	0.00 (1)*	-0.02 (2)*	-0.01 (1)*
C(8)	0.02 (2)*	-0.02 (2)*	-0.01 (2)*	-0.03 (2)*
N(9)	-0.02 (1)*	-0.00 (2)*	0.01 (1)*	-0.00 (1)*
C(1')	-0.22 (2)	0.14 (2)	0.14 (2)	-0.07 (2)
C(2')	-0.32 (2)	-0.17 (2)	0.23 (2)	0.17 (2)
S	0.02 (1)	0.13 (1)	-0.10 (1)	-0.10 (1)
S-cyclo moiety				
Plane	V	VI	VII	VIII
C(8)	-0.09 (2)*	-0.07 (2)*	0.10 (2)*	0.08 (2)*
N(9)	0.03 (2)*	-0.02 (2)*	-0.03 (2)*	0.02 (2)*
C(1')	0.04 (2)*	0.16 (2)*	-0.06 (2)*	-0.14 (2)*
C(2')	-0.07 (2)*	-0.19 (2)*	0.09 (2)*	0.13 (2)*
S	0.01 (1)*	0.01 (1)*	-0.01 (1)*	-0.01 (1)*
Sugar moiety				
Plane	IX	X	XI	XII
C(1')	0.05 (2)*	-0.06 (2)*	0.04 (2)*	-0.03 (2)*
C(2')	-0.03 (2)*	0.03 (2)*	-0.03 (2)*	0.02 (2)*
C(3')	0.03 (2)*	-0.47 (2)	0.02 (2)*	-0.40 (2)
C(4')	0.41 (2)	-0.03 (2)*	0.35 (2)	-0.02 (2)*
O(1')	-0.02 (1)*	0.03 (1)*	-0.02 (2)*	0.02 (1)*
C(5')	1.83 (3)	1.34 (2)	1.78 (2)	1.78 (2)

Plane equations of the best planes: *X*, *Y*, and *Z* refer to the orthogonal coordinate system (Å) with *X* along **a**, *Y* along **b*** × **a** and *Z* along **c***.

Plane	Equation
I	-0.222 <i>X</i> + 0.778 <i>Y</i> + 0.568 <i>Z</i> - 4.889 = 0.0
II	0.879 <i>X</i> - 0.447 <i>Y</i> + 0.167 <i>Z</i> + 3.533 = 0.0
III	-0.183 <i>X</i> + 0.799 <i>Y</i> + 0.573 <i>Z</i> - 8.401 = 0.0
IV	0.890 <i>X</i> - 0.456 <i>Y</i> + 0.031 <i>Z</i> - 2.366 = 0.0
V	-0.159 <i>X</i> + 0.691 <i>Y</i> + 0.705 <i>Z</i> - 5.056 = 0.0
VI	0.894 <i>X</i> - 0.402 <i>Y</i> + 0.195 <i>Z</i> + 3.300 = 0.0
VII	-0.055 <i>X</i> + 0.813 <i>Y</i> + 0.580 <i>Z</i> - 8.700 = 0.0
VIII	0.910 <i>X</i> - 0.408 <i>Y</i> + 0.079 <i>Z</i> - 3.054 = 0.0
IX	0.187 <i>X</i> - 0.223 <i>Y</i> + 0.957 <i>Z</i> - 4.180 = 0.0
X	-0.229 <i>X</i> + 0.656 <i>Y</i> + 0.719 <i>Z</i> - 6.747 = 0.0
XI	0.787 <i>X</i> + 0.617 <i>Y</i> + 0.025 <i>Z</i> - 4.083 = 0.0
XII	-0.045 <i>X</i> + 0.838 <i>Y</i> + 0.543 <i>Z</i> - 7.038 = 0.0

Dihedral angles (°) between planes

I/V	9.1 (4)	III/VII	7.4 (4)
I/II	63.6 (4)	III/IV	59.4 (4)
I/IX	69.6 (6)	III/XI	68.8 (6)
II/VI	3.1 (4)	IV/VIII	4.0 (4)
II/X	68.0 (5)	IV/XII	66.1 (5)

Table 6. *Hydrogen-bond distances (Å) with their e.s.d.'s in parentheses*

Donor	Acceptor	Donor	Acceptor	Donor	Acceptor
N(1)(A)—O(W1 ^{II})	2.822 (18)	N(6)(C)—O(R)(1 ^{VI})	2.809 (18)	O(W2)—Cl(1 ^{IX})	3.086 (14)
N(6)(A)—O(R)(2 ^{III})	2.858 (19)	N(6)(C)—Cl(2 ^{VI})	3.236 (15)	O(W2)—O(W3 ^I)	2.727 (19)
N(6)(A)—Cl(1 ^{III})	3.237 (16)	O(5')(C)—Cl(1 ^I)	3.198 (13)	O(W3)—O(R)(2 ^{IX})	2.756 (19)
O(5')(A)—Cl(2 ^I)	3.144 (14)	N(1)(D)—O(L)(1 ^{VI})	2.738 (17)	O(W3)—O(3')(D ^I)	2.871 (19)
N(1)(B)—O(L)(2 ^{III})	2.721 (17)	N(6)(D)—O(W1 ^{VII})	2.837 (19)	O(W4)—O(R)(1 ^{VIII})	2.849 (19)
N(6)(B)—O(W2 ^{IV})	2.847 (19)	N(6)(D)—O(3')(D ^{VI})	3.098 (19)	O(W4)—N(3)(C ^I)	3.217 (20)
N(6)(B)—O(3')(B ^{III})	3.200 (19)	O(3')(D)—O(L)(1 ^I)	2.574 (17)	O(W5)—Cl(1 ^X)	3.177 (22)
O(3')(B)—O(L)(2 ^I)	2.730 (17)	O(W1)—Cl(2 ^{VIII})	3.092 (14)	O(W5)—Cl(2 ^{XI})	3.184 (22)
N(1)(C)—O(W2 ^I)	2.843 (19)	O(W1)—O(W4 ^I)	2.742 (20)		

Symmetry code

(i) x, y, z ; (ii) $1 + x, y, z$; (iii) $x, y, -1 + z$; (iv) $-1 + x, y, -1 + z$; (v) $x, 1 + y, -1 + z$; (vi) $1 + x, 1 + y, z$; (vii) $1 + x, y, 1 + z$; (viii) $x, 1 + y, z$; (ix) $x, -1 + y, z$; (x) $-1 + x, -1 + y, z$; (xi) $x, y, 1 + z$.

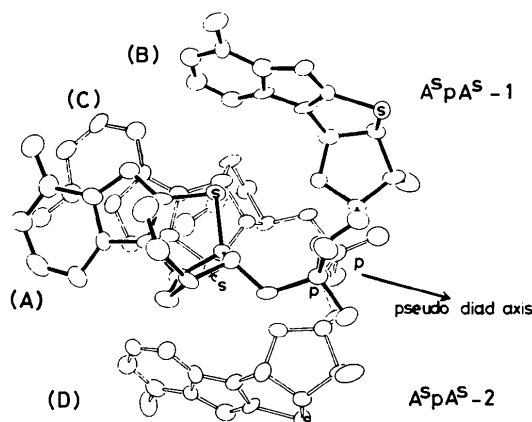


Fig. 3. Intermolecular stacking between $A^s p A^s-1$ and $A^s p A^s-2$. The pseudo diad axis is shown with an arrow.

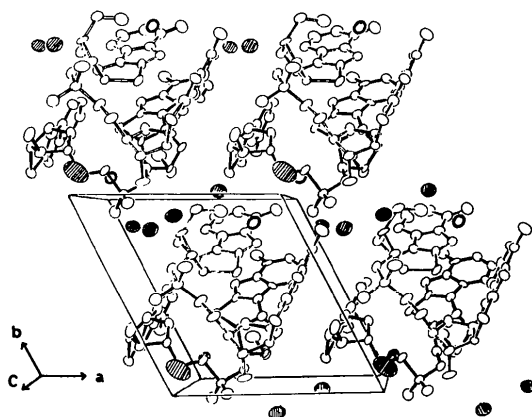


Fig. 4. Molecular packing viewed perpendicular to (001) plane. Water molecules are shown by hatched ellipsoids. Chloride ions are indicated with heavy circles. The atoms in $A^s p A^s-2$ molecules are connected by solid bonds.

ing, and the hydrogen-bonding schemes of the $A^s p A^s-1$ and $A^s p A^s-2$ molecules are very similar with a few exceptions: the N(3) [$A^s(C)$] and O(3') [$A^s(D)$] in $A^s p A^s-2$ are used as hydrogen acceptors, but those in $A^s p A^s-1$ are not. The O(3') atom at the 3'-end side

nucleoside [$A^s(B)$ or $A^s(D)$] participates in hydrogen bonds with N(6), and O(L) (1) or O(L) (2); the latter also strongly bonds to N(1) [$A^s(B)$ or $A^s(D)$] of the same purine moiety.

The crystalline waters $W(1)$ and $W(2)$ have similar environments, but waters $W(3)$ and $W(4)$ have different environments, *i.e.* $W(3)$ is strongly bound to O(R) (2), O(3') [$A^s(D)$] and O(W2), but $W(4)$ is strongly connected only with O(R) (1) and O(W1), and the hydrogen bond with N(3) [$A^s(C)$] is very weak.

Base stacking and molecular packing

There is no intramolecular base stacking but strong intermolecular base stacking is found between the base moieties at the 5'-end sides of $A^s p A^s-1$ and $A^s p A^s-2$ with an average distance of 3.4 Å, as shown in Fig. 3. Overlapping occurs between imidazole rings and also between the fused rings involving the S atoms in a manner related to the presence of the pseudo diad axis (see Fig. 3), but the base moiety at the 3'-end side has no stacking.

Therefore, two $A^s p A^s$ molecules form a stable pair with strong intermolecular stacking in the crystal lattice. Fig. 4 shows the molecular packing viewed perpendicular to the (001) plane. It is apparent that the water molecules and chloride ions are allowed to fill the space in the crystalline lattice.

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X-ray Structure and Crystal Packing Analysis of Triphenylchloromethane*

BY A. DUNAND AND R. GERDIL†

Département de Chimie Organique et Laboratoire de Radiocristallographie, Université de Genève, 30 quai Ernest Ansermet, 1211 Genève, Switzerland

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Abstract

$\text{C}_{19}\text{H}_{15}\text{Cl}$ is trigonal, space group $P\bar{3}$, with $a = 13.998$ (2), $c = 13.202$ (4) Å, $V = 2240.2$ Å³, $Z = 6$, $D_m = 1.26$, $D_x = 1.240$ Mg m⁻³, $F(000) = 876$, $\mu = 0.225$ mm⁻¹. The final R and R_w , based on 905 reflections, are 0.038 and 0.025 respectively. The molecules lie in special positions on the crystallographic threefold axes. They are associated in pairs and form two distinct $\text{Ph}_3\text{C}-\text{Cl}\cdots\text{Cl}-\text{CPh}_3$ head-to-head arrangements characterized by long C–Cl bonds and short $\text{Cl}\cdots\text{Cl}$ contacts. The shortest $\text{Cl}\cdots\text{Cl}$ distance (3.210 Å) is about 0.3 Å smaller than the sum of the van der Waals radii. For the sake of comparison, the lattice energy was computed using two different sets of Buckingham potential functions. The effects of including electrostatic terms were also investigated. These calculations account satisfactorily for all the salient features of the crystal packing. Analysis of the thermal motion showed that the rigid-body approximation holds reasonably well for the triphenylchloromethane molecule.

Introduction

Triphenylchloromethane (TPCM) was first described by Hemilian (1874). The continuous interest in its molecular conformation goes back to the early chemistry of free radicals (Gomberg, 1900). Young (1931) measured the cell parameters for the triclinic and trigonal forms. Wang & Lu (1944) examined the isomorphous trigonal forms of TPCM and triphenylbromomethane and concluded that these molecules lie in special positions on the crystallographic threefold axes. Further studies by Landais (1953) and Stora & Poyer (1966) revealed the presence of short $\text{Br}\cdots\text{Br}$ intermolecular contacts in triphenylbromomethane crystals. Spurred on by these preliminary accounts we have carried out the structure analyses of TPCM and triphenylbromomethane (Dunand & Gerdil, 1981) to obtain comparative information on short halogen–halogen interactions (Dunand, 1977; Dunand & Gerdil, 1976*b*). Both structures display linear $\text{C}-\text{X}\cdots\text{X}-\text{C}$ arrangements with long C–X bonds and unusually short $\text{X}\cdots\text{X}$ contacts. The influence of the crystallization conditions on the formation of trigonal and/or triclinic TPCM crystals, as well as the geometrical relationship between the respective lattices,

* (Chloro)triphenylmethane.

†To whom correspondence should be addressed.