

Fig. 3. Molecular packing diagram viewed along the *c* axis.

The pyrimidine and imidazole rings of the caffeine molecule are planar and the dihedral angle between them is 1.6 (1) and 2.6 (1)° for molecules *A* and *B*, respectively; the dihedral angle between them is 67.0 (2)° in the free molecule (Sutor, 1958).

**Intermolecular bonds and molecular packing.** Molecular packing in the crystal is shown in Fig. 3. Three hydrogens are available for hydrogen bonding in each molecule, two from the aryl amino nitrogen and one from the sulfonamido nitrogen. But H(42)*A* and H(41)*B* do not participate in hydrogen bonding.

*Acta Cryst.* (1991). C47, 580–584

## Structure of an Adenine Tetrafluoroborate Salt

BY AIDEEN C. M. YOUNG AND JOHN C. DEWAN\*

*Department of Chemistry, New York University, New York, NY 10003, USA*

AND ANTHONY J. EDWARDS

*Department of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, England*

(Received 26 January 1990; accepted 2 May 1990)

**Abstract.** Adenine–adeninium tetrafluoroborate–water (1/1/2),  $C_5H_5N_5 \cdot C_5H_6N_5^+ \cdot BF_4^- \cdot 2H_2O$ ,  $M_r = 394.10$ , monoclinic,  $P2_1/m$ ,  $a = 5.358$  (1),  $b = 19.468$  (7),  $c = 7.905$  (2) Å,  $\beta = 104.75$  (2)°,  $V = 797.4$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.641$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.42$  cm<sup>-1</sup>,  $F(000) = 404$ ,  $T = 298$  K.

\* Author to whom correspondence should be addressed.

0108-2701/91/030580-05\$03.00

Table 3. Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	<i>D</i> ... <i>A</i>	H... <i>A</i>	<i>D</i> —H... <i>A</i>
N(4) <i>B</i> —H(42) <i>B</i> ...O(3) <sup><i>A</i></sup>	0.79 (3)	3.134 (3)	2.38 (3)	160.7 (2.6)
N(4) <i>A</i> —H(41) <i>A</i> ...O(3) <sup><i>B</i></sup>	0.79 (3)	3.195 (4)	2.45 (3)	159.3 (2.6)
N(1) <i>B</i> —H(1) <i>B</i> ...N(6) <sup><i>A</i></sup>	0.80 (3)	3.083 (3)	2.29 (3)	171.4 (2.3)
N(1) <i>A</i> —H(1) <i>A</i> ...N(6) <sup><i>B</i></sup>	0.81 (3)	2.978 (4)	2.17 (3)	172.0 (2.1)

Symmetry code: (i)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x, y, z$ ; (iv)  $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$ .

The hydrogen-bonding geometry (Table 3) shows weak hydrogen bonds having *D*...*A* lengths > 3.0 Å. The predominant intermolecular forces responsible for complex formation are therefore non-bonded interactions. The flat caffeine molecules are packed parallel to each other.

### References

- BASAK, A. K., MAZUMDAR, S. K. & CHAUDHURI, S. (1984). *Acta Cryst.* C40, 419–422.
- HIGUCHI, T. & LACH, J. L. (1954). *J. Am. Pharm. Assoc. Sci. Ed.* 43, 349–354.
- KÁLMÁN, A., CZUGLER, M. & ARGAY, G. (1981). *Acta Cryst.* B37, 868–877.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
- NAKAI, H., TAKASUKA, M. & SHIRO, M. (1984). *J. Chem. Soc. Perkin Trans. 2*, pp. 1459–1464.
- SHEFTER, E. & SACKMAN, P. (1971). *J. Pharm. Sci.* 60, 282–286.
- SHELDRIK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
- SUTOR, D. J. (1958). *Acta Cryst.* 11, 453–458.

Final  $R = 0.062$  for 1597 unique observed reflections with  $I_o > 2\sigma(I_o)$ . After consideration of various factors the structure was assigned as adenine and adeninium moieties in a 1:1 ratio, disordered over the one site. The  $BF_4^-$  anion and the two water molecules of crystallization lie on mirror planes. H atoms on C(2), N(6), C(8) and N(9) of adenine were located in difference-Fourier maps and were refined, but those

© 1991 International Union of Crystallography

on the water molecules could not be located and have been ignored. The site of protonation required for charge balance could be either N(1) of the adenine moiety or a water molecule of crystallization and has been assigned as the former, where the occupancy of that proton is 0.5. The adenine bases are hydrogen bonded together in two different modes found commonly in other adenine salts.

**Introduction.** In an attempt to synthesize a complex between  $\text{Pb}^{\text{II}}$  and adenine, crystals were obtained that have subsequently been shown by X-ray analysis to be a hydrated adenine tetrafluoroborate salt. The crystals contain no  $\text{Pb}^{\text{II}}$ . Refinement was undertaken in space group  $P2_1/m$  and also in its non-centrosymmetric equivalent,  $P2_1$ . In space group  $P2_1$  there are two asymmetric units per unit cell, each consisting of two adenine moieties, one  $\text{BF}_4^-$  anion and two water molecules of crystallization. In space group  $P2_1/m$  there are four asymmetric units per cell and each is composed of one adenine moiety, one half  $\text{BF}_4^-$  anion and two half water molecules of crystallization. The  $\text{BF}_4^-$  anion and both water molecules lie on mirror planes. Charge-balance considerations require that the structure be mono-protonated at some position. In space group  $P2_1/m$  charge balance could be achieved either by the presence of a half proton on the N(1) of adenine, giving a disordered structure, or a half proton on one of the two half water molecules in the asymmetric unit, giving  $\text{H}_3\text{O}^+$ . In space group  $P2_1$  protonation of one of the two adenine groups or one of the two water molecules in the asymmetric unit is also required for charge neutrality. Assignment of a full proton to N(1) of both adenine groups would disrupt the overall charge balance, unless one water molecule was actually a hydroxyl group. This is an unlikely situation in a solution at pH 3.25 and one that we have not considered further. When considering the protonation of one adenine, both ordered and disordered structures are possible in  $P2_1$ . In the ordered structure the asymmetric unit would contain one adenine and one adeninium group in separate sites. In the disordered structure, the adenine and adeninium groups would occupy the same sites with half occupancy. Refinement in  $P2_1$  suggested the disordered structure and refinement has, therefore, been completed in  $P2_1/m$ . The considerations pertaining to the choice of space group and protonation site are discussed below.

**Experimental.** Crystals were obtained by the following method.  $\text{Pb}(\text{NO}_3)_2$  (0.25 g, 0.75 mmol), adenine (0.306 g, 2.26 mmol) and  $\text{NaBF}_4$  (0.5 g, 4.55 mmol) were each dissolved in water (25 ml). The three solutions were mixed and heated to  $\sim 363$  K for 15 min. The resulting white precipitate was

Table 1. *Atom coordinates and isotropic temperature factors ( $\text{\AA}^2$ )*

$$B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or <i>B</i> <sub>eq</sub>
N(1)	-0.0852 (3)	0.3612 (1)	0.3670 (2)	3.30 (7)
N(3)	-0.3631 (4)	0.4292 (1)	0.1492 (2)	3.64 (8)
N(6)	0.3240 (4)	0.3931 (1)	0.5257 (3)	3.75 (8)
N(7)	0.2089 (4)	0.5280 (1)	0.3163 (2)	3.46 (7)
N(9)	-0.1692 (4)	0.5395 (1)	0.1184 (2)	3.54 (8)
C(2)	-0.3052 (4)	0.3735 (1)	0.2439 (3)	3.64 (9)
C(4)	-0.1734 (4)	0.4762 (1)	0.1890 (3)	3.08 (8)
C(5)	0.0620 (4)	0.4691 (1)	0.3118 (3)	2.98 (8)
C(6)	0.1094 (4)	0.4078 (1)	0.4057 (3)	3.06 (8)
C(8)	0.0604 (5)	0.5678 (1)	0.1987 (3)	3.59 (9)
O(1)	-0.0825 (5)	0.25	0.5611 (4)	4.7 (1)
O(2)	0.4826 (6)	0.25	0.6935 (4)	6.4 (2)
B(1)	0.1209 (8)	0.25	0.0600 (5)	3.9 (1)
F(1)	0.2456 (5)	0.25	0.2350 (3)	5.7 (1)
F(2)	-0.1403 (5)	0.25	0.0345 (4)	8.9 (2)
F(3)	0.1947 (5)	0.3061 (1)	-0.0162 (3)	9.2 (1)
H(1)†	-0.07 (1)	0.314 (3)	0.449 (7)	5 (1)
H(2)	-0.433 (5)	0.336 (2)	0.216 (3)	3.6 (5)
H(8)	0.119 (5)	0.612 (1)	0.168 (3)	4.1 (6)
H(61)	0.460 (6)	0.424 (2)	0.562 (4)	4.8 (6)
H(62)	0.343 (6)	0.354 (2)	0.571 (4)	5.2 (7)
H(9)	-0.289 (5)	0.557 (2)	0.038 (4)	4.3 (6)

† Occupancy = 0.5.

filtered and discarded and the filtrate allowed to evaporate slowly in air. Colorless X-ray quality crystals grew within four days. The pH of the solution was 3.25. A rational synthesis of the compound has not been attempted.

Details of the crystallography are as follows. Colorless block-shaped crystal, dimensions  $0.75 \times 0.31 \times 0.26$  mm, monoclinic, space group  $P2_1/m$  (no. 11), Rigaku AFC-6S four-circle diffractometer, data collected at room temperature. The crystal-to-detector distance was 285 mm, monochromated  $\text{Mo K}\alpha$  radiation was employed with a 1.0 mm diameter incident-beam collimator,  $\omega/2\theta$  scan technique, variable scan width where  $\Delta\omega = (1.30 + 0.30 \tan \theta)^\circ$ , scan rate  $4^\circ \text{ min}^{-1}$  in  $\omega$ . Weak reflections with  $F < 10\sigma(F)$  were rescanned a maximum of four times and counts accumulated, stationary background counts were recorded at each side of the reflection. The ratio of peak:background counting time was 2:1. Lattice parameters were from 25 reflections having  $30.0 < 2\theta < 31.9^\circ$ . An empirical absorption correction was applied using *DIFABS* (Walker & Stuart, 1983) with transmission factors ranging between 0.77 and 1.18. The absorption correction was applied to the structure after isotropic refinement of all atoms, excluding hydrogen. Three intensity standards measured every 150 data showed no decay. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) followed by difference-Fourier syntheses. The total of 2089 reflections was measured to  $2\theta = 55.1^\circ$  ( $h$  0 $\rightarrow$ 6,  $k$  0 $\rightarrow$ 24,  $l$  -10 $\rightarrow$ 9) with 1900 being unique. Equivalent reflections were averaged ( $R_{\text{int}} = 0.044$ ) and the 1597 having  $I_o > 2\sigma(I_o)$  were used in the

Table 2. *Interatomic distances (Å) and angles (°) involving the non-H atoms*

N(1)—C(2)	1.345 (3)	N(9)—C(4)	1.354 (3)
N(1)—C(6)	1.357 (3)	N(9)—C(8)	1.350 (3)
N(3)—C(2)	1.309 (3)	C(4)—C(5)	1.389 (3)
N(3)—C(4)	1.345 (3)	C(5)—C(6)	1.394 (3)
N(6)—C(6)	1.322 (3)	B(1)—F(1)	1.374 (5)
N(7)—C(5)	1.386 (3)	B(1)—F(2)	1.362 (5)
N(7)—C(8)	1.312 (3)	B(1)—F(3)	1.354 (3)
C(2)—N(1)—C(6)	121.7 (2)	C(4)—C(5)—C(6)	117.9 (2)
C(2)—N(3)—C(4)	112.0 (2)	N(1)—C(6)—N(6)	119.7 (2)
C(5)—N(7)—C(8)	103.5 (2)	N(1)—C(6)—C(5)	115.2 (2)
C(4)—N(9)—C(8)	106.6 (2)	N(6)—C(6)—C(5)	125.1 (2)
N(1)—C(2)—N(3)	126.7 (2)	N(7)—C(8)—N(9)	114.0 (2)
N(3)—C(4)—N(9)	127.9 (2)	F(1)—B(1)—F(2)	111.5 (3)
N(3)—C(4)—C(5)	126.4 (2)	F(1)—B(1)—F(3)	109.0 (2)
N(9)—C(4)—C(5)	105.8 (2)	F(2)—B(1)—F(3)	109.8 (2)
N(7)—C(5)—C(4)	110.1 (2)	F(3)—B(1)—F(3')	107.5 (4)
N(7)—C(5)—C(6)	132.0 (2)		

structure refinement which was by full-matrix least squares on  $F$  (154 variables) using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). The final data-to-parameter ratio was 10.37. All non-H atoms were refined anisotropically. H atoms of the adenine moiety were located and refined isotropically. Problems relating to the assignment of a proton on N(1) of adenine are discussed in detail below. H atoms on the water molecules could not be located and have consequently been ignored. Neutral-atom scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). Final  $R = 0.062$ ,  $wR = 0.085$ ,  $GOF = 3.81$ . Weights were given by  $w = 4F_o^2/\sigma^2(F_o^2)$ . In the final cycle the maximum LS shift/e.s.d. was 0.001. The final difference-Fourier map maximum and minimum peaks were 0.36 and  $-0.44 \text{ e } \text{Å}^{-3}$ , respectively. Table 1 gives atomic positional parameters, Table 2 bond lengths and angles and Table 3 lists possible hydrogen-bonding interactions. Fig. 1 depicts the hydrogen bonding between adenine moieties along with the atom-labeling scheme.\*

**Discussion.** The structure has been refined, and is reported, in space group  $P2_1/m$ , but was also refined in the non-centrosymmetric equivalent space group  $P2_1$ . The *DIFABS* absorption correction was applied in both cases after full isotropic refinement of all atoms, excluding hydrogen. H atoms on C(2), N(6), C(8) and N(9) were located in difference-Fourier maps but those on the water molecules could not be

\* Lists of thermal parameters, structure factors, bond distances and angles including H atoms, intermolecular distances and least-squares-planes data and a complete description of the structure determination have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53236 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Possible hydrogen-bonding interactions (< 3.4 Å); O(1) and O(2) are water molecules of crystallization*

N(3)···N(9 <sup>i</sup> )	2.903 (3)	F(1)···C(2 <sup>v</sup> )	3.390 (3)
N(6)···N(7 <sup>ii</sup> )	2.931 (3)	F(2)···O(2 <sup>vi</sup> )	2.928 (4)
O(1)···N(1)	2.652 (3)	F(2)···C(2)	3.170 (3)
O(1)···N(1 <sup>iii</sup> )	2.652 (3)	F(2)···N(1)	3.360 (3)
O(1)···O(2)	2.941 (4)	F(3)···C(8 <sup>vii</sup> )	2.995 (3)
O(1)···O(2 <sup>iv</sup> )	2.787 (4)	F(3)···N(9 <sup>viii</sup> )	3.107 (3)
O(2)···N(6)	3.110 (3)	F(3)···C(2')	3.213 (3)
O(2)···N(6 <sup>iii</sup> )	3.110 (3)	F(3)···O(2 <sup>viii</sup> )	3.262 (4)
F(1)···N(1)	3.140 (3)		

Symmetry code: (i)  $-1-x, 1-y, -z$ ; (ii)  $1-x, 1-y, 1-z$ ; (iii)  $+x, \frac{1}{2}-y, +z$ ; (iv)  $-1+x, +y, +z$ ; (v)  $1+x, +y, +z$ ; (vi)  $-1+x, +y, -1+z$ ; (vii)  $-x, 1-y, -z$ ; (viii)  $+x, +y, -1+z$ .

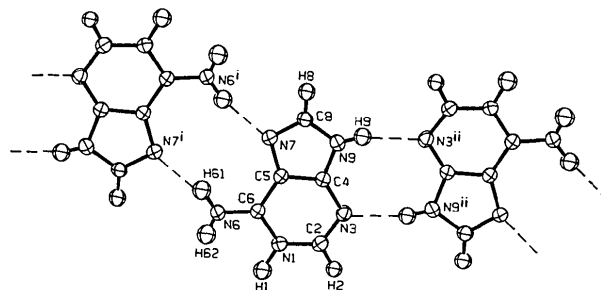


Fig. 1. ORTEP diagram (Johnson, 1976) showing the infinite chain of hydrogen-bonded adenine moieties along with the atom-labeling scheme and 30% probability thermal ellipsoids. For symmetry codes see Table 3.

located. The structure refined to an  $R$  factor of 0.065 in  $P2_1/m$ , with full shifts being applied, and to the same  $R$  factor in space group  $P2_1$ , where it was necessary to apply half shifts. Both refinements were carried out with no proton assigned to N(1) of adenine. When a proton of occupancy 0.5 was assigned to adenine N(1) in space group  $P2_1/m$ , the  $R$  factor dropped from 0.065 to 0.062,  $wR$  from 0.090 to 0.085, and the  $GOF$  from 4.01 to 3.81. The charge on each  $\text{BF}_4^-$  anion must be balanced by a single positive charge to achieve charge neutrality. This could be accomplished either by protonation of an adenine ring or protonation of a water molecule of crystallization. The usual site of protonation of adenine is at N(1) which has a  $pK_a$  value of 4.15. Protonation would be expected in the pH range 2–4.5 (Ts'o, 1974). Several structures have been reported that contain adenine protonated at N(1) (Hingerty, Einstein & Wei, 1981; Kistenmacher & Shigematsu, 1974; Langer & Huml, 1978; Langer, Huml & Lessinger, 1978; Langer, Huml & Zachova, 1979).

Voet & Rich (1970) note that sites of protonation on a purine or pyrimidine base can be readily inferred from a consideration of bond angles and bond distances. Specifically, the internal ring angle at an N atom in a six-membered heterocyclic ring will average  $118.6 (14)^\circ$  when the N atom is not protonated

and  $123.0(4)^\circ$  when that N has an extra-annular attachment, such as a proton. This is supported by several structural studies (Hingerty, Einstein & Wei, 1981; Iwasaki, 1974; Kistenmacher & Shigematsu, 1974; Langer & Huml, 1978; Langer, Huml & Lessinger, 1978; Langer, Huml & Zachova, 1979). Furthermore, the average internal ring angles at C(2) and C(6), which are adjacent to N(1), are  $129.1(15)$  and  $117.3(16)^\circ$ , respectively, in a non-protonated pyrimidine and these angles are expected to each decrease by  $\sim 4^\circ$  on N(1) protonation.

In the present structure, in space group  $P2_1$ , if one adenine group is protonated while the other is not this should be manifested in very different ring angles within the two adenine groups in the asymmetric unit. The internal ring angles at N(1), C(2) and C(6) of both adenine groups in space group  $P2_1$  are as follows. For the first adenine ring the angles are  $120.1(5)$ ,  $125.7(5)$  and  $116.8(4)^\circ$ , while for the second ring the angles are  $122.7(5)$ ,  $128.5(5)$  and  $114.2(4)^\circ$ . A comparison of these ring angles with those for protonated and non-protonated pyrimidines (Hingerty, Einstein & Wei, 1981; Langer, Huml & Lessinger, 1978; Voet & Rich, 1970) shows that in the present case it is not possible to decide whether either adenine group is protonated or not. The value of  $120.1(5)^\circ$  at N(1) of the first adenine ring is midway between the values for protonated and non-protonated adenine rings. The value of  $125.7(5)^\circ$  at C(2) is characteristic of the protonated pyrimidine while the value of  $116.8(4)^\circ$  at C(6) is closer to what would be expected for a non-protonated pyrimidine. For the second adenine ring, angles of  $122.7(5)$  and  $114.2(4)^\circ$  at N(1) and C(6), respectively, are indicative of a protonated pyrimidine, while the  $128.5(5)^\circ$  angle at C(2) suggests a non-protonated pyrimidine. These results are not consistent with the existence of one adenine and one adeninium group in separate sites in the asymmetric unit of the structure in space group  $P2_1$ , and instead are suggestive of a disordered structure. The possibility remains that one of the two water molecules in the asymmetric unit is protonated. H atoms on the water molecules could not be located in difference-Fourier maps, however, making it impossible to say anything definitive regarding the likelihood of an  $H_3O^+$  species. Since the observed geometric differences between both adenine groups in  $P2_1$  are not thought to constitute an asymmetry in the structure, refinement has been completed in space group  $P2_1/m$ .

The three H atoms on the adenine ring and the two H atoms on the exocyclic amino group were the five strongest peaks ( $0.5$  to  $0.7 e \text{ \AA}^{-3}$ ) on final difference-Fourier maps in space group  $P2_1/m$  and were located at distances of  $0.83$ – $1.12 \text{ \AA}$  from their respective heavy atoms. A peak of  $0.3 e \text{ \AA}^{-3}$  (no. 22 in this list) was  $1.12 \text{ \AA}$  distant from N(1), the most

probable site of protonation on adenine. This peak, being much weaker than the five peaks that were assigned as H atoms, could not confidently be ascribed to a proton – at least not a proton with full occupancy. Geometric considerations in  $P2_1/m$  are also inconclusive. The internal ring angles at N(1), C(2) and C(6) are  $121.7(2)$ ,  $126.7(2)$  and  $115.2(2)^\circ$ , respectively, again falling approximately midway between the average values reported by Voet & Rich (1970) for those angles in protonated and non-protonated adenine-containing compounds. They are also the averages of those values given above for these angles in the two adenine groups in space group  $P2_1$ . These crystallographic results support a situation in which the structure is disordered. We have settled on a description of the structure whereby a proton is located on N(1) of adenine but with an occupancy of  $0.5$ . This would be consistent with the low intensity of the peak near N(1) on the difference-Fourier map.

The second possibility, mentioned above, is that charge balance could be achieved if one of the water molecules were protonated instead of an adenine group, giving the formula  $2C_5H_5N_5 \cdot H_3O^+ \cdot BF_4^- \cdot H_2O$ . As in space group  $P2_1$ , the H atoms on the water molecules could not be located in difference-Fourier maps in  $P2_1/m$ . Peaks appearing at  $\sim 1 \text{ \AA}$  from the water O atoms were refined as H atoms but the refinement was unsuccessful. Also, attempts to assign plausible hydrogen-bonding schemes involving the water molecules were inconclusive. Therefore, while protonation of a water molecule of crystallization remains a possibility, the structure has been assigned as  $C_5H_5N_5 \cdot C_5H_6N_5^+ \cdot BF_4^- \cdot 2H_2O$ .

The adenine bases are hydrogen bonded together *via* two different modes of base pairing, first *via* hydrogen bonds of the type N(9)—H $\cdots$ N(3) and second *via* N(6)—H $\cdots$ N(7), thereby forming an infinite hydrogen-bonded chain (Fig. 1). The N(3) $\cdots$ N(9) and N(6) $\cdots$ N(7) distances are  $2.903(3)$  and  $2.931(3) \text{ \AA}$ , respectively. These two hydrogen-bonding modes have also been observed in other structures (Hingerty, Einstein & Wei, 1981; Langer, Huml & Lessinger, 1978). Details of possible hydrogen-bonding interactions are given in Table 3.

Funds to purchase the X-ray diffraction equipment were provided by NSF CHE 87-11307.

#### References

- HINGERTY, B. E., EINSTEIN, J. R. & WEI, C. H. (1981). *Acta Cryst.* B37, 140–147.
- IWASAKI, H. (1974). *Chem. Lett.* pp. 409–410.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KISTENMACHER, T. J. & SHIGEMATSU, T. (1974). *Acta Cryst.* B30, 166–168.

- LANGER, V. & HUML, K. (1978). *Acta Cryst.* B34, 1157–1163, 1881–1884.
- LANGER, V., HUML, K. & LESSINGER, L. (1978). *Acta Cryst.* B34, 2229–2234.
- LANGER, V., HUML, K. & ZACHOVA, J. (1979). *Acta Cryst.* B35, 1148–1152.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- SHELDRIK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- TS'O, P. O. P. (1974). *Basic Principles in Nucleic Acid Chemistry*, edited by P. O. P. Ts'o, Vol. I, pp. 453–584. New York: Academic Press.
- VOET, D. & RICH, A. (1970). *Prog. Nucleic Acid Res. Mol. Biol.* 10, 183–265.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

*Acta Cryst.* (1991). C47, 584–587

## Pyramidalization in a Hexachloronorborene Derivative

BY WILLIAM H. WATSON\* AND RAM P. KASHYAP

*Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129 USA*

AND BENJAMIN F. PLUMMER

*Department of Chemistry, Trinity University, San Antonio, Texas 78212 USA*

(Received 30 April 1990; accepted 18 June 1990)

**Abstract.** 7,8,9,10,11,11-Hexachloro-7,10-dihydro-7,10-methanofluoranthene, (1),  $C_{17}H_6Cl_6$ ,  $M_r = 422.95$ , monoclinic,  $P2_1/c$ ,  $a = 14.814$  (8),  $b = 8.623$  (2),  $c = 14.206$  (4) Å,  $\beta = 111.22$  (3)°,  $V = 1691.6$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.660$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 10.16$  cm<sup>-1</sup>,  $F(000) = 840$ ,  $T = 295$  K,  $R = 0.0488$  for 3186 reflections. The molecule is composed of a naphthalene ring system joined to a hexachloronorborene molecule forming an acenaphthylene moiety. The acenaphthylene system is planar (0.005 Å r.m.s. deviation); however, the  $C(sp^2)$  atoms of the two double bonds in norbornene are pyramidalized with substituents bent away from the methano bridge in the *endo* direction. The  $C(sp^2)$  atoms associated with the naphthalene ring fusion exhibit pyramidalization angles of 5.1 (3)° while the  $C(sp^2)$  atoms substituted by Cl have pyramidalization angles of 2.4 (4)°.

**Introduction.** Most derivatives of *anti*-sesquinorborene (2) exhibit planar geometries around the olefinic C atoms (Watson, Galloy, Bartlett & Roof, 1981; Paquette, Hayes, Charumilind, Bohm, Gleiter & Blount, 1983; Gajhede, Jorgensen, Kopecky, Watson & Kashyap, 1985); however, the *exo*-4-nitrophenylmaleimide derivative (Ermer & Bodecker, 1983) exhibits a pyramidalization of 13.2 (3)° indicating a rather low barrier to the bending mode. In these papers the pyramidalization is reported either as the deviation of the interplanar angle from 180° or

as  $\chi$ , the deviation from planarity of the dihedral angles about the  $sp^2$  C atoms (Ermer & Mason, 1982). The olefinic C atoms of *syn*-sesquinorborene (3) and derivatives are considerably pyramidalized and exhibit deformation angles of 16–18° (Watson, Galloy, Bartlett & Roof, 1981; Hagenbuch, Vogel, Pinkerton & Schwarzenbach, 1981). Derivatives containing additional saturation at the ethano bridge exhibit slightly larger angles (Paquette, Green, Gleiter, Schaefer & Gallucci, 1984) with derivative (4) exhibiting a deformation angle of 22.1 (2)° (Watson, Galloy, Grossie, Bartlett & Combs, 1984). Recently, a *syn*-sesquinorborene with *spiro* fusion at the two methano C atoms was shown to have a deformation angle of 32.4° (Paquette & Shen, 1990). This deformation is enhanced by steric interactions of the spiro groups and the strained double bond is sterically shielded from reactants. Relief of angle strain about the central double bond is thought to be a major driving force in the pyramidalization; however, derivatives with bicyclo[2.2.1] (Paquette, Carr, Charumilind & Blount, 1980) (5) and bicyclo[3.2.1] (Paquette, Hsu, Gallucci, Korp, Bernal, Kravetz & Hathaway, 1984) (6) frameworks were found to have distortion angles of 9.3–11.8°. Recently, a neutron diffraction study of (7) (Ermer, Bell & Mason, 1989) found a 7.4 (2)° pyramidalization for the  $\pi$  bond which is larger than predicted by theory (Burkert, 1981; Spanget-Larsen & Gleiter, 1982; Ermer, Bodecker & Preut, 1984; Wipff & Morokuma, 1980; Rondan, Paddon-Row, Caramella & Houk, 1981). When the  $\pi$  bond in norbornene results from fusion

\* Author to whom correspondence should be addressed.