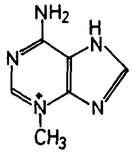
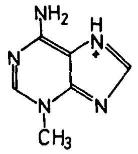
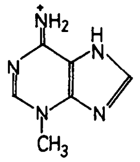
viewed down the *b* axis is illustrated in Fig. 1. The 3-methyladenine molecule takes a cationic form with N(7) protonated. The bond lengths and angles of the present structure together with those of related compounds are shown in Table 2. The observed bond lengths are consistent with those calculated for the predominant resonance structures (I)–(III). The charge-density distributions of N atoms calculated by using the *INDO* method (Pople & Segal, 1966) are −0·275, −0·051, −0·062, −0·269 and −0·185 e for N(1), N(3), N(7), N(9) and N(6), respectively.


(I)


(II)


(III)

The overall molecular dimensions of 3-methyladenine with N(7) protonated are significantly different from the standard values proposed for adenine (Taylor & Kennard, 1982) as well as those found in two 3-alkylated adenine derivatives, *cis*-diamminebis(3-methyladenine)platinum(II) (m^{3}A-Pt; Orbell, Solorzano, Marzilli & Kistenmacher, 1982) and 3-ethyladenine (e^3 A; Petersen & Furberg, 1975). The N(1)—C(2) and N(9)—C(4) bonds in 3-alkylated adenine derivatives are commonly shorter than those in adenine, whereas the N(3)—C(4) and N(7)—C(8) bonds are somewhat longer. Also the ring angles at N(3), N(9) and C(4) differ considerably from those of adenine. Some geometric differences are observed in the 3-alkylated adenine derivatives. The considerable changes occur at internal ring angles of N(7) and the ajacent C(5) and C(8) atoms. The variance is probably a direct result of the different environment about each N(7) atom. Indeed, the values in the 3-methyladenine with N(7) coordinated to a metal (m^{3}A-Pt) are intermediate between those of 3-methyladenine with N(7) protonated and free 3-ethyladenine (e^3 A). The nine-membered purine ring is essentially planar. The maximum deviation from the least-squares plane is 0·011 (4) Å for C(2). C(3) is displaced from this plane by 0·037 (5) Å. As shown in Fig. 1, the 3-methyladenine molecule is connected by three N—H···Cl type hydrogen bonds, forming an infinite hydrogen-bonded column along the *b* axis. The hydrogen-bonding distances are 3·086 (3) Å for N(7)···Cl^{i}, 3·277 (3) Å for N(6)···Cl^{i} [(i) $1-x$, $-\frac{1}{2}+y$, $1-z$] and 3·235 (3) Å for N(6)···Cl.

References

Brookes, P. & Lawley, P. D. (1964). *J. Cell. Comp. Physiol.* **64**, Suppl. 1, 111–128.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, 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.

Orbell, J. D., Solorzano, C., Marzilli, L. G. & Kistenmacher, T. J. (1982). *Inorg. Chem.* **21**, 2630–2636.

Petersen, C. S. & Furberg, S. (1975). *Acta Chem. Scand. Ser. B*, **29**, 37–40.

Pople, J. A. & Segal, G. A. (1966). *J. Chem. Phys.* **44**, 3289–3296.

Taylor, B. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 3209–3212.

UNICS (1979). *The Universal Crystallographic Computing System – Osaka.* Library of Programs, Computation Center, Osaka Univ.

Acta Cryst. (1987). C**43**, 1197–1200

Thermally Induced Acyl Migration in Salicylamides. 1. Structures of the Reactants, *O*-Acetylsalicylamide and *O*-Benzoylsalicylamide*

By K. Vyas, V. Mohan Rao† and H. Manohar‡

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, *India*

(*Received* 25 *November* 1985; *accepted* 10 *February* 1987)

Abstract. *O*-Acetylsalicylamide (I*a*), $C_9H_9NO_3$, $M_r = 179\cdot18$, monoclinic, $P2_1/c$, $a = 8\cdot155\,(5)$, $b = 8\cdot571\,(2)$, $c = 13\cdot092\,(3)$ Å, $\beta = 99\cdot54\,(5)°$, $V = 902\cdot4\,(6)$ Å^3, $Z = 4$, $D_m = 1\cdot31$, $D_x = 1\cdot319$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 1\cdot08$ cm^{-1}, $F(000) = 376$, $T = 295$ K, $R = 0\cdot076$ for 1604 reflections. *O*-Benzoylsalicylamide (I*b*), $C_{14}H_{11}NO_3$, $M_r = 241\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot423\,(1)$, $b = 5\cdot116\,(1)$, $c = 26\cdot424\,(2)$ Å, $\beta = 103\cdot97\,(1)°$, $V = 1236\cdot2\,(3)$ Å^3, Z

---

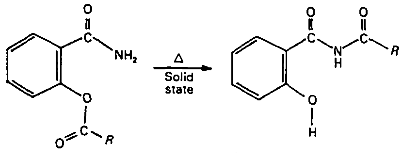
* Presented in part at the XIIth International Congress on Crystallography, Ottawa, 1981.

† Present address: Indian Explosives (Gomia), Giridih, Bihar-829112, India.

‡ Author to whom correspondence should be addressed.

= 4, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}296\ \text{g cm}^{-3}$, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 7{\cdot}71\ \text{cm}^{-1}$, $F(000) = 504$, $T = 295$ K, $R = 0{\cdot}050$ for 2115 reflections. The dihedral angles between the amide group and the benzene ring are 39·9° (I*a*) and 37·9° (I*b*), whereas between the acyl group and the benzene ring they are 78·1° (I*a*) and 93·4° (I*b*). The differences in the packing of the two structures are brought out in terms of the observed hydrogen-bonding patterns. Based on the crystallographic results, an intramolecular mechanism for the migration of the acyl group from the O to the N position is suggested in both compounds.

Introduction. The migration of the acyl group from the O to the N position is salicylamides attracted the attention of chemists as early as 1906 (McConnan & Thitherley, 1906). The rearrangement in the *O*-acetyl derivative was studied both in solution and in the solid state using spectroscopic and thermoanalytical techniques (Gordon, 1967). However, no crystallographic studies have been reported. X-ray crystallographic investigations of the acetyl and benzoyl derivatives have been undertaken with the aim of understanding this interesting solid-state reaction from the structural point of view. The reaction (I*a*)→(II*a*) takes place at ~373 K and (I*b*)→(II*b*) at ~393 K. In this paper, the structures of the reactants are reported; the following paper (Vyas, Mohan Rao & Manohar, 1987) presents structural details of the products of the reaction.



(I*a*) $R = CH_3$ (II*a*) $R = CH_3$
(I*b*) $R = C_6H_5$ (II*b*) $R = C_6H_5$

Experimental. Compounds prepared by acylation of salicylamide according to reported procedure (Gordon, 1967; McConnan & Thitherley, 1906). Experimental conditions and refinement details are listed in Table 1. Lp corrections, no absorption correction. Structures solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) for (I*a*) and *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (I*b*). H-atom positions from ΔF synthesis. (I*a*): full-matrix least-squares refinement on F using *UCLALS*1 (Gantzel, Sparks & Trueblood, 1961), with $w = (a + |F_o| + c|F_o|^2)^{-1}$ (Cruickshank, Bujosa, Lovell & Truter, 1961) where $a = 10{\cdot}0$ and $c = 0{\cdot}005$. H-atom positions (with $\beta = 5{\cdot}0$ Å^2) included in structure-factor calculations. (I*b*): full-matrix refinement on F using *SHELX*76 (Sheldrick, 1976), $w = [\sigma^2(F_o) + 0{\cdot}00065|F_o|^2]^{-1}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978) were used for diagrams. The relatively high R value (0·076) for compound (I*a*) is probably due to the poor quality of the crystals.

Table 1. *Experimental conditions and refinement details*

	(I*a*)	(I*b*)
Method of measuring D_m	Flotation (in aqueous KI)	Flotation (in aqueous KI)
Solvent used for crystallization	Ethyl acetate	Ethyl acetate
Crystal shape	Needles	Needles
Crystal size (mm)	0·6 × 0·3 × 0·2	0·55 × 0·27 × 0·20
Diffractometer	CAD-4	CAD-4
Radiation	Graphite-monochromatized Mo $K\alpha$	Nickel-filtered Cu $K\alpha$
Scan mode	$\omega/2\theta$	$\omega/2\theta$
No. of reflections for measuring lattice parameters, θ range (°)	25, 10–20	25, 10–40
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·70	0·63
Range of h	$0 \le h \le 11$	$0 \le h \le 11$
k	$0 \le k \le 12$	$0 \le k \le 6$
l	$-18 \le l \le 18$	$-33 \le l \le 33$
Standard reflections	$2\bar{1}\bar{1}$, 400	1,1,12, 1,2,18, $\bar{1}27$
Fluctuations (%)	<2	<2
No. of reflections measured	2970	3282
No. of unique observed reflections	1604 $[I > 3\sigma(I)]$	2115 $[F_o > 3\sigma(F_o)]$
R_{int}	0·045	0·038
No. of parameters	118	207
R, wR, S	0·076, 0·084, 2·47	0·050, 0·083, 1·95
$(\Delta\rho)_{\min}$, $(\Delta\rho)_{\max}$ (e Å^{-3})	−0·72, 0·10	−0·09, 0·07
$(\Delta/\sigma)_{\max}$	0·03	0·02

Discussion. Perspective views of the molecules with numbering schemes are shown in Fig. 1. Fig. 2 gives the bond lengths and angles involving non-H atoms, and positional coordinates for non-H atoms are given in Table 2.* Figs. 3 and 4 show the crystal packing for (I*a*) and (I*b*) respectively.

The C(7)—N(1) distances in both structures are typical of the amide group (Sasada, Takano & Kakudo, 1964) and indicate sp^2 hybridization of the amide N(1) atom. The carbonyl distances of ~1·23 and ~1·19 Å are characteristic of the amide (Sasada, Takano & Kakudo, 1964) and ester (Wheatley, 1964) groups respectively. The angles at C(1) in (I*a*) and (I*b*) (Fig. 2) reveal that the amide group is pushed away from the acyl group. This is indicated by the intramolecular contacts involving the C(7) atom, namely, C(7)···C(8) is 3·341 (5) Å in (I*a*) and 3·533 (3) Å in (I*b*). The angles around the acyl C(8) atom in both structures are considerably different from the trigonal angle of 120°. Similar observations have been made in an analysis on compounds containing acetoxy groups (Murthy & Venkatesan, 1985), such as aspirin (Wheatley, 1964) and 7-acetoxycoumarin (Gnanaguru, Ramasubbu,

---

* Lists of structure factors, anisotropic thermal parameters, intermolecular separations, H-atom positions and their isotropic temperature factors, bond lengths and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43698 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Venkatesan & Ramamurthy, 1985). This distortion can be explained on the basis of the greater repulsion due to the bonded pairs on the carbonyl bond than that due to the bonded pairs on the other two bonds. The dihedral angles between the amide group and the benzene ring are 39·9 (I*a*) and 37·9° (I*b*), whereas between the acyl group and the benzene ring they are 78·1 (I*a*) and 93·4° (I*b*) (e.s.d.'s ~0·3–0·5°).

In discussing the packing modes of the two structures the detailed analysis by Leiserowitz & Hagler (1983) on the secondary and tertiary structures of primary amides resulting from the interlinking of hydrogen-bonded rings (primary structure) is useful. The details of the hydrogen-bond parameters are given in Table 3. In both (I*a*) and (I*b*) hydrogen-bonded rings are formed between amide N(1) and amide O(1) atoms across centres of symmetry. However, in view of the differences in the formation of tertiary structures from these basic hydrogen-bonded rings, (I*a*) and (I*b*) exhibit striking contrast in their packing modes. In (I*a*) (Fig. 3), the 2_1 axis generates sheets of rings which are linked together by a second set of hydrogen bonds between the amide N(1) and acyl O(3) atoms. This results in a repeat distance of 8·57 Å along **b**, which is close to the value of 9·0 Å characteristic of the twofold screw axis motif for primary amides (Leiserowitz & Hagler, 1983). A similar situation is observed in the structure of the *β* form of *O*-acetamidobenzamide (Etter, 1983). On the

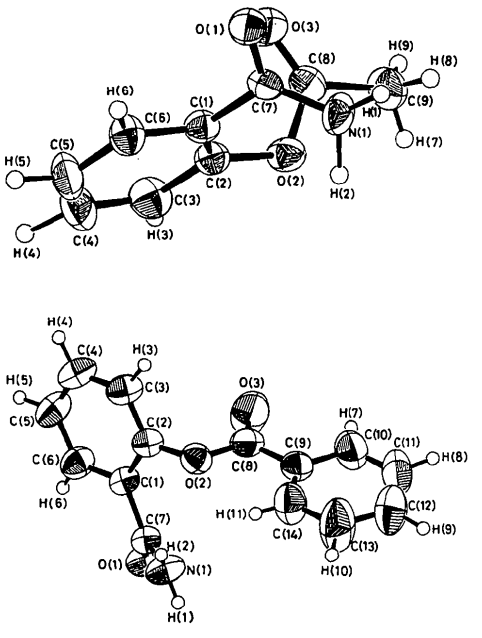


Fig. 1. Perspective views of molecules (I*a*) (top) and (I*b*) (bottom).

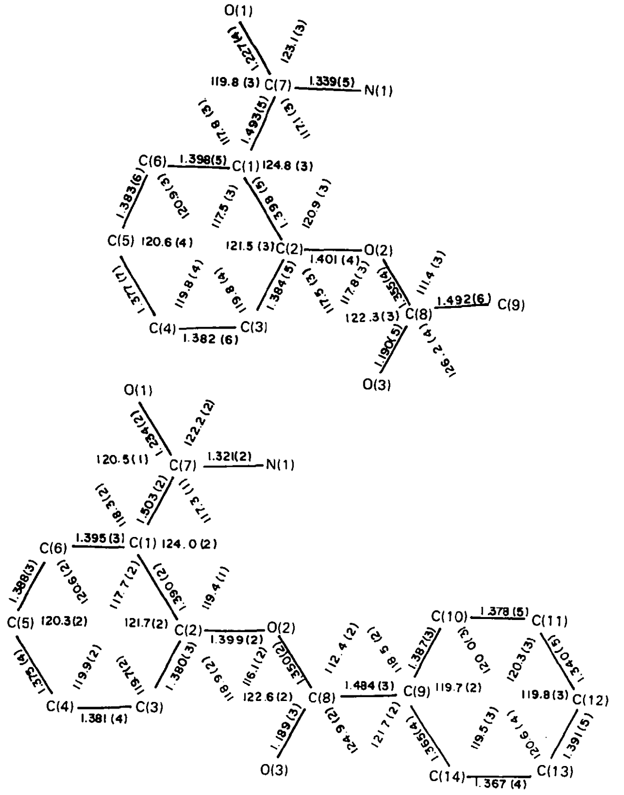


Fig. 2. Bond lengths (Å) and angles (°) of non-H atoms with the numbering scheme for (I*a*) (top) and (I*b*) (bottom). E.s.d.'s are in parentheses.

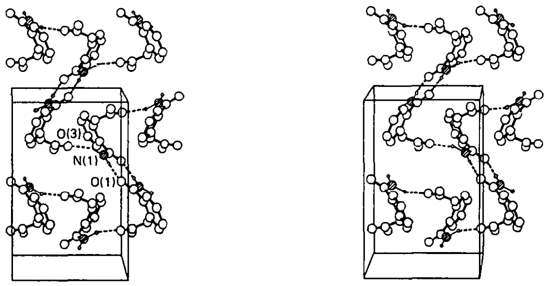


Fig. 3. Stereoscopic view along [100] of the unit cell of (I*a*): *b* axis horizontal; *c* axis vertical. Broken lines indicate hydrogen bonds.

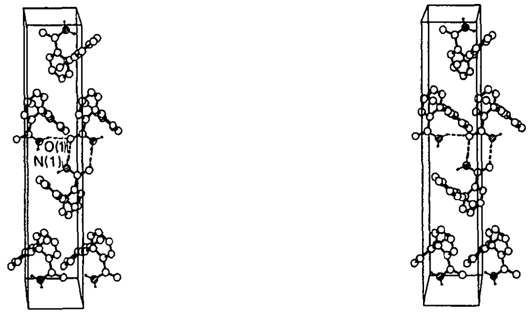


Fig. 4. Stereoscopic view along [100] of the unit cell of (I*b*): *b* axis horizontal; *c* axis vertical. Broken lines indicate hydrogen bonds.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors for non*-H *atoms in O-acetylsalicylamide* (I*a*) *and O-benzoylsalicylamide* (I*b*), *with e.s.d.'s in parentheses*

$$B_{\rm iso} = \tfrac{4}{3}\textstyle\sum_i\sum_j b_{ij}\mathbf{a}_i.\mathbf{a}_j;\ U_{\rm iso} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	(I*a*)				(I*b*)			
	x	*y*	*z*	$B_{\rm iso}$(Å^2×10)	*x*	*y*	*z*	$U_{\rm iso}$(Å^2×10^4)
O(1)	2111 (3)	−127 (3)	4639 (2)	34 (1)	4278 (2)	3227 (2)	9363 (1)	578 (5)
O(2)	600 (3)	2373 (3)	2011 (2)	32 (1)	5582 (1)	9126 (3)	8574 (1)	565 (4)
O(3)	924 (4)	−116 (4)	1590 (3)	51 (1)	6930 (2)	6162 (5)	8284 (1)	1122 (9)
N(1)	59 (4)	1575 (4)	4052 (3)	40 (1)	4814 (2)	7475 (3)	9485 (1)	600 (6)
C(1)	2735 (4)	1839 (4)	3504 (2)	27 (1)	3720 (2)	5962 (3)	8613 (1)	479 (5)
C(2)	2257 (4)	2453 (4)	2510 (2)	28 (1)	4320 (2)	7755 (4)	8328 (1)	526 (6)
C(3)	3377 (5)	3226 (5)	2003 (3)	39 (1)	3695 (3)	8236 (6)	7808 (1)	684 (7)
C(4)	5005 (5)	3417 (5)	2487 (4)	45 (1)	2444 (3)	6910 (5)	7560 (1)	769 (8)
C(5)	5506 (5)	2820 (6)	3465 (4)	44 (1)	1845 (3)	5085 (5)	7829 (1)	762 (8)
C(6)	4397 (4)	2019 (5)	3965 (3)	34 (1)	2479 (2)	4592 (4)	8351 (1)	636 (7)
C(7)	1601 (4)	1006 (4)	4106 (2)	27 (1)	4314 (2)	5448 (3)	9185 (1)	449 (5)
C(8)	47 (5)	995 (4)	1579 (3)	32 (1)	6864 (2)	8064 (5)	8536 (1)	630 (7)
C(9)	−1756 (5)	1071 (5)	1129 (3)	44 (1)	8144 (2)	9497 (4)	8851 (1)	613 (7)
C(10)					9532 (3)	8706 (7)	8826 (1)	852 (10)
C(11)					10747 (3)	9946 (8)	9124 (2)	977 (13)
C(12)					10594 (4)	11907 (9)	9443 (2)	1116 (15)
C(13)					9202 (4)	12738 (8)	9462 (2)	1222 (17)
C(14)					7986 (3)	11520 (6)	9170 (1)	832 (10)

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°) *in* (I*a*) *and* (I*b*)

	D—H···*A*	*D*—H	*D*···*A*	H···*A*	*DHA*
(I*a*)*	N(1)—H(1)···O(1$^{\rm i}$)	0·98	2·935 (4)	1·96	173
	N(1)—H(2)···O(3$^{\rm ii}$)	1·14	3·027 (5)	1·96	154
(I*b*)	N(1)—H(1)···O(1$^{\rm iii}$)	0·83 (3)	2·978 (4)	2·15 (3)	170 (3)
	N(1)—H(2)···O(1$^{\rm iv}$)	0·90 (3)	2·990 (2)	2·15 (3)	153 (2)

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

* E.s.d.'s for parameters involving H atoms are not provided, as the H atoms were not refined.

other hand, in (I*b*) (Fig. 4) two hydrogen-bonded rings, related by a unit translation along the **b** direction (short repeat distance of 5·12 Å), are interlinked by a second set of hydrogen bonds between amide N(1), and amide O(1) [instead of acyl O(3), as in (I*a*)]. This results in a ribbon parallel to the *b* axis. The 2_1 axis generates a similar ribbon resulting in a two-dimensional motif. In both structures, the tertiary structure is generated by translation along the *a* axis.

Some comments on the reaction. The reaction, in essence, involves bond formation between N(1) and C(8) and hence the contacts between these atoms are of relevance. In (I*a*), the intramolecular N(1)···C(8) contact is 3·274 (6) Å, whereas the intermolecular contacts with the screw- and glide-related molecules are 3·875 (5) and 3·911 (5) Å respectively. In (I*b*), the intramolecular contact is 3·528 (3) Å and no intermolecular contacts <5·0 Å are observed. In (I*a*), even though the intermolecular contacts are within the range in which solid-state reactions are known to occur (Paul & Curtin, 1973), the intramolecular separation is the smallest. Thus, based solely on crystallographic considerations, an intramolecular mechanism appears likely.

We thank Dr S. P. Sudhakara Rao for useful discussions. The help rendered by Dr N. C. Shivaprakash during data collection is gratefully acknowledged. One of the authors (KV) thanks the Department of Atomic Energy, India, for financial support.

References

CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. London: Pergamon Press.

ETTER, M. C. (1983). *J. Chem. Soc. Perkin Trans.* 2, pp. 115–121.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *UCLALS*1. Univ. of California.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

GNANAGURU, K., RAMASUBBU, N., VENKATESAN, K. & RAMAMURTHY, V. (1985). *J. Org. Chem.* **50**, 2337–2346.

GORDON, A. J. (1967). *Tetrahedron*, **23**, 863–870.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

LEISEROWITZ, L. & HAGLER, A. T. (1983). *Proc. R. Soc. London Ser. A*, **388**, 133–175.

MCCONNAN, J. & THITHERLEY, A. W. (1906). *J. Chem. Soc.* **89**, 1318–1339.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. A program for drawing crystal and molecular structures. Univ. of Cambridge, England.

MURTHY, G. S. & VENKATESAN, K. (1985). Personal communication.

PAUL, I. C. & CURTIN, D. Y. (1973). *Acc. Chem. Chem. Res.* **6**, 217–225.

SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Jpn*, **37**, 940–946.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

VYAS, K., MOHAN RAO, V. & MANOHAR, H. (1987). *Acta Cryst.* C**43**, 1201–1204.

WHEATLEY, P. J. (1964). *J. Chem. Soc.* pp. 6036–6048.