The PPN cation is bent at the central N atom, 137·4 (2)°, and is staggered about the P···P vector, having a 'mean torsion angle' (Glidewell & Liles, 1981) of 51·9 (1)°. There is a weak intramolecular quasi-graphitic packing of rings 3 and 5 [centroid–centroid distance 4·466 (6) Å, dihedral angle 24·8 (4)°], but a much stronger intermolecular one between rings 2 and 5[4·178 (4) Å, 7·8 (4)°] with ring 5 at ($\frac{1}{2}-x, -\frac{1}{2}+y, z$), where ring n comprises C(n1–n6) and a centroid–centroid distance $\leq$ 4·7 Å is considered significant (Welch, 1974). Full details of these interactions have been deposited as Table 6, and Fig. 2 reproduces the contents of one unit cell in a view nearly along the a axis, looking towards (100).

We thank the SERC for support, the Department of Chemistry, University of Edinburgh, for a vacation scholarship (DAR), and Dr D. Reed for the NMR spectrum.

References

Andrews, S. J., Robb, D. A. & Welch, A. J. (1983). To be published.
Andrews, S. J., Welch, A. J., Jacobsen, G. B. & Morris, J. H. (1982). *J. Chem. Soc. Chem. Commun.* pp. 749–750.
Arunchaiya, M. & Morris, J. H. (1983). To be published.
Craven, B. N. & Sabine, T. M. (1966). *Acta Cryst.* **20**, 214–219.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Glidewell, C. & Liles, D. C. (1981). *J. Organomet. Chem.* **212**, 291–300.
Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Roberts, P. & Sheldrick, G. M. (1976). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.
Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Welch, A. J. (1974). PhD Thesis, Univ. of London, England.

Acta Cryst. (1983). C**39**, 882–887

Structural Studies of Intermediates in Antibiotic Synthesis. I. The Structures of Penicillin Sulfoxide Rearrangement Products: 2,3,5,6-Tetrahydro-5-hydroxymethyl-6,6-dimethyl-1,3-dioxo-8-[(phenylacetyl)amino]-1*H*-imidazo[5,1-*c*][1,4]thiazine (I), $C_{17}H_{19}N_3O_4S$, and 2,3,5,6-Tetrahydro-6,6-dimethyl-1,3-dioxo-8-[(phenylacetyl)amino]-1*H*-imidazo[5,1-*c*]-[1,4]thiazine-5-carboxylic Acid (II), $C_{17}H_{17}N_3O_5S$

By T. E. Haran

Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

A. Nudelman

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

and Z. Shakked*

Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

(*Received* 10 *June* 1982; *accepted* 20 *December* 1982)

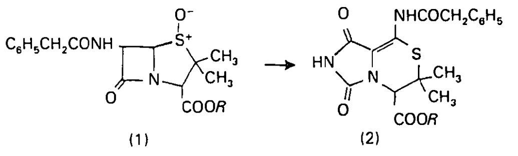
Abstract. (I): $M_r = 361$, $P\bar{1}$, $a = 8{\cdot}888$ (10), $b = 9{\cdot}556$ (2), $c = 11{\cdot}483$ (7) Å, $\alpha = 116{\cdot}85$ (5), $\beta = 103{\cdot}69$ (8), $\gamma = 94{\cdot}27$ (6)°, $Z = 2$, $V = 826{\cdot}8$ Å^3, $D_m = 1{\cdot}45$, $D_x = 1{\cdot}448$ g cm^{-3}, graphite-monochromated Mo $K\alpha$, $\mu = 1{\cdot}78$ cm^{-1}, $T = 83$ K, $F(000) = 380$, $R = 0{\cdot}07$ for 3172 observed reflexions. (II): $M_r = 375$, $P2_1$, $a = 7{\cdot}332$ (1), $b = 14{\cdot}608$ (1), $c = 8{\cdot}371$ (2) Å, $\beta = 107{\cdot}98$ (2)°, $Z = 2$, $V = 889{\cdot}5$ Å^3, $D_m = 1{\cdot}40$, $D_x = 1{\cdot}398$ g cm^{-3}, graphite-monochromated Cu $K\alpha$, $\mu = 18{\cdot}03$ cm^{-1}, $T = 293$ K, $F(000) = 392$, $R = 0{\cdot}04$ for 1732 observed reflexions. The two compounds, obtained from a rearrangement reaction of a penicillin sulfoxide, display the novel 2,3,5,6-tetrahydro-1*H*-imidazo[5,1-*c*][1,4]thiazine bicyclic ring system. The abnormal behavior of the hydroxymethyl carbon in (I) indicates a possible chemical disorder. In both crystals the molecules are held together by means of intermolecular hydrogen bonds and van der Waals interactions.

---

* Incumbent of the Hugo Ramniceanu Career Development Chair. To whom correspondence should be addressed.

0108-2701/83/070882-06$01.50

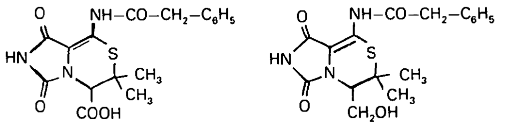
Introduction. The chemical transformation of a fermentation-produced penicillin into cephalosporin is very important in view of the commercial value of cephalosporin derivatives of improved antibiotic activity. The first practical chemical rearrangement of a penicillin sulfoxide to a cephalosporin was described by Morin and co-workers (Morin, Jackson, Mueller, Lavagnino, Scanlon & Andrews, 1963,1969). A conceivable alternative method is to start from a penicillin sulfilimine, as the chemistry of sulfilimines is similar to that of sulfoxides. An attempt has been made to obtain penicillin sulfilimines by the reaction of penicillin sulfoxide esters (1) with ethoxycarbonyl isocyanate (Nudelman, Haran & Shakked, 1981). The attempted reaction (scheme 1) failed to yield penicillin sulfilimine. Several possible structures which could concur with the spectral data (NMR, MS, IR) of the product were considered, but (2) was not among them, as this ring system was unprecedented in the chemical literature. The purpose of the X-ray analysis was to establish the structure of the novel product (2).



(1) (2)

Scheme (1)

Hydrogenolysis of (2) ($R = p$-nitrobenzyl) gave the acid (3), except in one case where unexpected further reduction to the alcohol (4) took place (scheme 2). Moreover, this alcohol underwent racemization in the course of the reaction. We have determined the structure of both the acid and the alcohol products of the hydrogenolysis reaction.



(3) (4)

Scheme (2)

Based on the X-ray analysis, a proposed mechanism for the rearrangement reaction has been described (Nudelman, Haran & Shakked, 1981).

Experimental. (I) and (II) recrystallized from acetone/ether; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation at 83 K for (I), Cu $K\alpha$ at 293 K for (II); Lorentz and polarization corrections, no absorption correction; $\sin\theta_{\max}/\lambda$ 0·704 Å^{-1} for (I), 0·630 Å^{-1} for (II); 3582 independent reflections for (I), 1756 for (II); 3172 observed [$F_o > 3\sigma(F_o)$] reflections for (I), 1732 for (II). The alcohol structure (I) was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). An E map calculated from the 499 strongest E values revealed all the non-hydrogen atoms in the structure. The structure was refined by least squares using the *SHELX*76 system (Sheldrick, 1976). The positions of the H atoms were determined from a difference Fourier synthesis. After further refinement with anisotropic temperature factors for all heavy atoms and isotropic temperature factors for H atoms, the final R factor was 0·070. The acid structure (II) was also solved by *MULTAN*. An E map calculated with the 499 strongest E values revealed 20 non-hydrogen atoms. The remaining six non-hydrogen atoms were located from a difference Fourier map. The structure was refined in the same manner as described for (I), and the final R factor was 0·038. Unit weights were used in the refinement of both structures. Scattering factors were from *International Tables for X-ray Crystallography* (1974).

Discussion. The results for the alcohol molecule (I) are given in Tables 1 and 2, and for the acid molecule (II) in Tables 3 and 4.* Figs. 1 and 2 show perspective views of the two molecules and the numbering schemes. The packing arrangements are shown in Figs. 3 and 4.

Table 1. *Atom coordinates* ($\times 10^4$) *and* U_{eq}(Å^2 $\times 10^3$) *for* (I)

The value of U_{eq} for S(7) is multiplied by 10^4. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C(1)	10227 (4)	4115 (5)	5828 (4)	14 (3)
N(2)	11295 (4)	3486 (4)	5148 (3)	15 (3)
C(3)	10554 (5)	2115 (5)	3883 (4)	16 (3)
N(4)	8972 (4)	1833 (4)	3804 (3)	15 (3)
C(5)	7671 (5)	667 (5)	2641 (4)	16 (3)
C(6)	6479 (5)	40 (5)	3156 (4)	18 (3)
S(7)	5567 (1)	1668 (1)	4166 (1)	155 (6)
C(8)	7273 (4)	3160 (5)	5213 (4)	14 (3)
C(9)	8695 (4)	3046 (5)	4964 (4)	14 (3)
O(10)	10509 (3)	5333 (3)	6946 (3)	17 (1)
O(11)	11205 (3)	1362 (4)	3045 (3)	21 (1)
C(12)	7310 (5)	−679 (5)	4018 (5)	24 (3)
C(13)	5060 (5)	−1200 (5)	1960 (5)	26 (3)
C(14)	7441 (5)	6719 (5)	9143 (4)	18 (3)
C(15)	8949 (5)	7691 (5)	9644 (4)	21 (3)
C(16)	10099 (6)	7741 (6)	10724 (5)	27 (3)
C(17)	9746 (6)	6818 (6)	11316 (5)	31 (4)
C(18)	8251 (6)	5841 (6)	10818 (5)	29 (3)
C(19)	7104 (5)	5796 (5)	9744 (4)	23 (3)
C(20)	6188 (5)	6613 (5)	7946 (4)	19 (3)
C(21)	5884 (5)	5025 (5)	6655 (4)	16 (3)
O(22)	4554 (3)	4252 (4)	5896 (3)	22 (2)
N(23)	7227 (4)	4518 (4)	6379 (3)	15 (3)
C(24)	6834 (3)	1334 (4)	1887 (3)	2 (1)
O(25)	7816 (4)	1610 (4)	1127 (3)	25 (2)

---

* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, coordinates and isotropic thermal parameters for hydrogen atoms, torsion angles and hydrogen-bond distances for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38287 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (I)

N(2)—C(1)	1·372 (6)	C(9)—C(1)	1·456 (5)
C(10)—C(1)	1·234 (4)	C(3)—N(2)	1·400 (4)
N(4)—C(3)	1·385 (5)	C(11)—C(3)	1·216 (5)
C(5)—N(4)	1·447 (4)	C(9)—N(4)	1·408 (5)
C(6)—C(5)	1·534 (7)	C(24)—C(5)	1·405 (6)
S(7)—C(6)	1·850 (4)	C(12)—C(6)	1·530 (8)
C(13)—C(6)	1·539 (5)	C(8)—S(7)	1·745 (3)
C(9)—C(8)	1·362 (6)	N(23)—C(8)	1·393 (5)
C(15)—C(14)	1·399 (6)	C(19)—C(14)	1·397 (8)
C(20)—C(14)	1·507 (6)	C(16)—C(15)	1·387 (7)
C(17)—C(16)	1·392 (9)	C(18)—C(17)	1·392 (7)
C(19)—C(18)	1·382 (7)	C(21)—C(20)	1·514 (5)
O(22)—C(21)	1·226 (4)	N(23)—C(21)	1·374 (6)
C(25)—C(24)	1·459 (6)		

C(9)—C(1)—N(2)	106·0 (3)	C(10)—C(1)—N(2)	127·0 (3)
O(10)—C(1)—C(9)	127·0 (4)	C(3)—N(2)—C(1)	111·6 (3)
N(4)—C(3)—N(2)	105·9 (3)	O(11)—C(3)—N(2)	125·5 (4)
O(11)—C(3)—N(4)	128·6 (3)	C(5)—N(4)—C(3)	127·9 (3)
C(9)—N(4)—C(3)	110·3 (3)	C(9)—N(4)—C(5)	121·0 (3)
C(6)—C(5)—N(4)	109·1 (4)	C(24)—C(5)—N(4)	112·4 (4)
C(24)—C(5)—C(6)	106·3 (3)	S(7)—C(6)—C(5)	110·7 (3)
C(12)—C(6)—C(5)	109·6 (4)	C(12)—C(6)—S(7)	110·6 (3)
C(13)—C(6)—C(5)	111·4 (4)	C(13)—C(6)—S(7)	103·7 (3)
C(13)—C(6)—C(12)	110·8 (4)	C(8)—S(7)—C(6)	99·2 (2)
C(9)—C(8)—S(7)	122·6 (3)	N(23)—C(8)—S(7)	120·1 (3)
N(23)—C(8)—C(9)	117·2 (3)	N(4)—C(9)—C(1)	106·0 (3)
C(8)—C(9)—C(1)	127·9 (3)	C(8)—C(9)—N(4)	126·1 (3)
C(19)—C(14)—C(15)	119·2 (4)	C(20)—C(14)—C(15)	121·4 (5)
C(20)—C(14)—C(19)	119·3 (4)	C(16)—C(15)—C(14)	120·5 (5)
C(17)—C(16)—C(15)	119·7 (4)	C(18)—C(17)—C(16)	120·1 (5)
C(19)—C(18)—C(17)	120·2 (6)	C(18)—C(19)—C(14)	120·2 (4)
C(21)—C(20)—C(14)	112·6 (4)	O(22)—C(21)—C(20)	123·4 (4)
N(23)—C(21)—C(20)	114·6 (3)	N(23)—C(21)—C(22)	122·0 (3)
C(21)—N(23)—C(8)	125·9 (3)	O(25)—C(24)—C(5)	107·9 (3)

Table 3. *Atom coordinates* ($\times 10^4$) *and* U_{eq}($\text{Å}^2 \times 10^3$) *for* (II)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	6815 (6)	−732 (3)	−114 (5)	35 (3)
N(2)	5860 (5)	−482 (3)	−1654 (4)	40 (2)
C(3)	4388 (7)	134 (4)	−1750 (5)	39 (3)
N(4)	4462 (5)	306 (3)	−195 (4)	35 (2)
C(5)	3086 (6)	853 (4)	289 (5)	37 (2)
C(6)	4189 (7)	1361 (4)	1865 (6)	43 (3)
S(7)	5207 (2)	515	3491 (1)	44 (1)
C(8)	6357 (6)	−205 (3)	2487 (5)	34 (2)
C(9)	5887 (6)	−228 (3)	872 (5)	33 (3)
C(10)	8175 (4)	−1269 (3)	338 (4)	40 (2)
C(11)	3272 (5)	452 (3)	−2963 (4)	54 (2)
C(12)	5793 (8)	1930 (4)	1578 (7)	56 (3)
C(13)	2882 (9)	1951 (4)	2523 (7)	57 (4)
C(14)	10944 (7)	−1993 (4)	4644 (6)	45 (3)
C(15)	12372 (8)	−1631 (5)	4131 (8)	58 (4)
C(16)	13135 (1)	−2131 (6)	3124 (9)	79 (6)
C(17)	12432 (1)	−3012 (7)	2641 (1)	80 (6)
C(18)	11000 (1)	−3383 (5)	3164 (8)	66 (5)
C(19)	10250 (8)	−2880 (4)	4140 (7)	54 (3)
C(20)	10114 (8)	−1455 (5)	5753 (6)	52 (4)
C(21)	8248 (7)	−959 (4)	4969 (6)	42 (3)
O(22)	7179 (6)	−735 (3)	5707 (4)	60 (3)
N(23)	7866 (5)	−761 (3)	3379 (4)	39 (2)
C(24)	1394 (7)	296 (4)	414 (6)	44 (3)
O(25)	43 (6)	627 (3)	698 (6)	79 (4)
O(26)	1512 (6)	−580 (3)	67 (6)	56 (3)

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (II)

N(2)—C(1)	1·360 (5)	C(9)—C(1)	1·451 (7)
C(10)—C(1)	1·234 (6)	C(3)—N(2)	1·388 (7)
N(4)—C(3)	1·365 (6)	O(11)—C(3)	1·213 (5)
C(5)—N(4)	1·448 (6)	C(9)—N(4)	1·403 (5)

Table 4 (*cont.*)

C(6)—C(5)	1·553 (6)	C(24)—C(5)	1·517 (7)
S(7)—C(6)	1·857 (5)	C(12)—C(6)	1·523 (9)
C(13)—C(6)	1·527 (9)	C(8)—S(7)	1·744 (5)
C(9)—C(8)	1·345 (6)	N(23)—C(8)	1·399 (6)
C(15)—C(14)	1·367 (9)	C(19)—C(14)	1·412 (8)
C(20)—C(14)	1·513 (9)	C(16)—C(15)	1·387 (11)
C(17)—C(16)	1·401 (13)	C(18)—C(17)	1·379 (13)
C(19)—C(18)	1·363 (10)	C(21)—C(20)	1·512 (7)
O(22)—C(21)	1·203 (7)	N(23)—C(21)	1·360 (6)
O(25)—C(24)	1·195 (7)	C(26)—C(24)	1·324 (7)

C(9)—C(1)—N(2)	104·9 (4)	O(10)—C(1)—N(2)	127·2 (5)
O(10)—C(1)—C(9)	127·8 (4)	C(3)—N(2)—C(1)	112·8 (4)
N(4)—C(3)—N(2)	105·5 (3)	O(11)—C(3)—N(2)	127·1 (5)
O(11)—C(3)—N(4)	127·4 (5)	C(5)—N(4)—C(3)	125·0 (3)
C(9)—N(4)—C(3)	110·6 (4)	C(9)—N(4)—C(5)	123·8 (4)
C(6)—C(5)—N(4)	107·7 (3)	C(24)—C(5)—N(4)	112·5 (4)
C(24)—C(5)—C(6)	114·0 (4)	S(7)—C(6)—C(5)	109·7 (4)
C(12)—C(6)—C(5)	109·4 (4)	C(12)—C(6)—S(7)	109·9 (3)
C(13)—C(6)—C(5)	112·8 (4)	C(13)—C(6)—S(7)	103·8 (4)
C(13)—C(6)—C(12)	111·1 (5)	C(8)—S(7)—C(6)	99·2 (2)
C(9)—C(8)—S(7)	122·3 (3)	N(23)—C(8)—S(7)	119·5 (3)
N(23)—C(8)—C(9)	118·1 (4)	N(4)—C(9)—C(1)	106·1 (4)
C(8)—C(9)—C(1)	128·3 (4)	C(8)—C(9)—N(4)	125·4 (4)
C(19)—C(14)—C(15)	119·5 (6)	C(20)—C(14)—C(15)	120·6 (5)
C(20)—C(14)—C(19)	119·9 (5)	C(16)—C(15)—C(14)	120·2 (6)
C(17)—C(16)—C(15)	119·5 (8)	C(18)—C(17)—C(16)	120·5 (8)
C(19)—C(18)—C(17)	119·4 (7)	C(18)—C(19)—C(14)	120·9 (6)
C(21)—C(20)—C(14)	116·5 (4)	O(22)—C(21)—C(20)	122·4 (4)
N(23)—C(21)—C(20)	115·9 (5)	N(23)—C(21)—O(22)	121·7 (4)
C(21)—N(23)—C(8)	124·7 (4)	O(25)—C(24)—C(5)	123·1 (5)
O(26)—C(24)—C(5)	112·9 (5)	O(26)—C(24)—O(25)	123·8 (5)

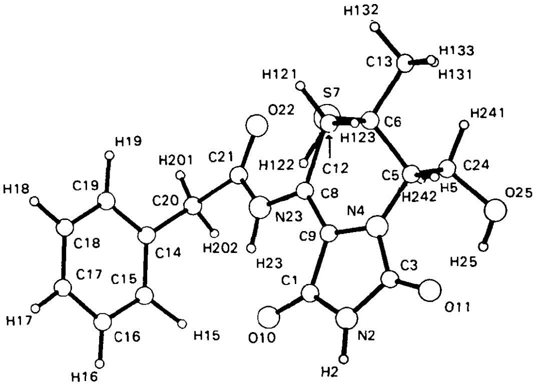


Fig. 1. A perspective view of molecule (I) showing the atom-numbering scheme.

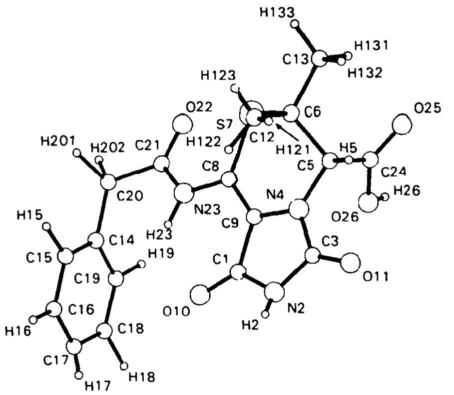


Fig. 2. A perspective view of molecule (II) showing the atom-numbering scheme.

Inspection of the thermal parameters of (I) showed normal behavior for all atoms except C(24), which had a non-positive-definite tensor of thermal motion. The difference map calculated for this structure revealed a considerable residual electron density (1·5 e Å^{-3}) at the position of C(24), as though the concerned atom should have a larger scattering power. Although the chemical analysis indicated that the alcohol molecule is the major product, we have carried out several structure factor calculation and refinement experiments by substituting the C by an N or an O, and also by a mixture of $>CH-CH_2OH$ with $>CH-OH$ or $>C=CH_2$. Normal temperature factors and a zero residual density, as well as a significant decrease in the R factor (0·070 to 0·054) were obtained when substituting the C by an O atom, that is a peroxide group instead of the hydroxymethyl group. It is very unlikely that this group is a peroxide, particularly in view of the chemical reaction conditions, and we are not able to offer a reasonable explanation at this stage. As mentioned earlier, the production of the racemic alcohol from the chiral ester (2) was totally unexpected, and therefore it is planned to perform a reaction which will yield deliberately the alcohol product. The comparison of the spectroscopic results (including X-ray analysis) of the old and new products may unravel the present mystery.

Molecular conformation. The important structural feature of the molecules is their novel ring system. It consists of a five-membered imidazolyl ring and a six-membered dihydrothiazine ring.

The five-membered imidazolyl rings are planar ($\sum d^2 = 0{\cdot}0007$, r.m.s.d = 0·012).* We performed a connectivity search on the Cambridge Crystallographic Database files for similar fragments and found that planar imidazolyl rings were observed in 1-*p*-bromophenyl-4,5-(1,2-*cis*-D-glucofurano)imidazolidine-2-thione (referred to as BGLFIT; Vega, Hernández-Montis & López-Castro, 1976) and in biotin-*c*3-indole (BIOIND; Paton, Liu & Paul, 1979). The other common conformations of single-bonded five-membered rings with two non-adjacent heteroatoms are the envelope and half-chair conformations. The envelope conformation was observed, for example, in 1-(*p*-chlorobenzyl)-2-(4,5-dihydro-2-imidazolyl)-1-nitrosohydrazine monohydrate (CNHYDM; Palenik, 1965), 2,3,5,6-tetrahydro-5-phenyl-1*H*-imidazo[1,2-*a*]-imidazole (IMAFEN; Lambert, Evrard & Durant, 1978) and [1,4]thiazino[4,3-*a*]benzimidazole (MCHTBI; Davidson, Murray, Preston & King, 1979). In these structures four atoms are nearly coplanar and the fifth atom is displaced significantly from the plane. The half-chair conformation, where two adjacent atoms are displaced in opposite directions from the plane defined by the other atoms, was observed, for example, in 3-methoxycarbonyl-9,9-dimethyl-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene 4-oxide (XTCNON; Guy & Hamor, 1974).

In the six-membered dihydrothiazine rings the five atoms N(4), C(5), S(7), C(8) and C(9) are approximately coplanar; C(6) is displaced from the mean plane by 0·77 Å. This conformation resembles that of XTCNON which has a similar dihydrothiazine ring skeleton. It may be mentioned here that the conformation of the dihydrothiazine ring in cephalosporins is different. In the structures of cephaloglycine and cephaloridine the S atom is displaced by 1·07 and 0·90 Å respectively from the mean plane of the other five atoms (Sweet & Dahl, 1970).

The dihydrothiazine ring is fused to the imidazolyl ring *via* the C(9) and N(4) atoms. N(4) was originally the β-lactam-ring N atom in the starting material. In active penicilins and cephalosporins the β-lactam N atom has a large pyramidal character. In cephaloglycin it is displaced by 0·22 Å from the plane of its substituents, and in cephaloridine by 0·24 Å. On the other hand, the β-lactam N atom of inactive cephalosporins is nearly planar (*e.g.* 0·065 Å deviation in phenoxymethyl-Δ-desacetoxycephalosporin; Sweet & Dahl, 1970). In (I) and (II) the N atom, N(4), is displaced by 0·074 and 0·062 Å respectively from the plane of C(3), C(5) and C(9), as in inactive cephalosporin compounds.

In both molecules the amido N atom, N(23), of the side chain forms an intramolecular hydrogen bond with O(10). The N(23)···C(10) distances are 2·80 and 2·83 Å, and the H(23)···C(10) distances are 1·95 and 2·14 Å for (I) and (II) respectively.

The conformational features of the two molecules are similar except for a different rotation around the C(20)—C(21) bond, where the corresponding torsion angles are 45·5 and 23·4° for (I) and (II) respectively. The phenyl ring is nearly perpendicular to the plane through C(14)—C(20)—C(21), as frequently observed in phenylalanine structures (*e.g.* Harada & Iitaka, 1974, 1977).

Bond lengths and angles. The four C—N bonds of the five-membered ring show an alternating pattern of short and long bond distances. The short bonds, C(1)—N(2) and C(3)—N(4), average to 1·366 and 1·375 Å respectively. The longer bonds, N(2)—C(3) and N(4)—C(9), average to 1·394 and 1·405 Å respectively.

The bond lengths involving the S atom, C(6)—S(7) and S(7)—C(8) (av. 1·854, 1·745 Å), are similar to those in MCHTBI and XTCNON which incorporate an analogous thiazine skeleton. The C—S bond adjacent to the C=C double bond is shorter than the one adjacent to the C—C single bond in all four molecules (I, II, MCHTBI, XTCNON).

The two side-chain C—N bonds, C(8)—N(23) and C(21)—N(23), are significantly different (av. 1·396 and 1·367 Å). The two adjacent C—C single bonds [C(14)—C(20), C(20)—C(21)] are similar (av. 1·510 and

---

* d = deviation from plane; r.m.s.d = $(\sum d^2/n)^{1/2}$; n = No. of atoms defining plane.

1·513 Å). The benzene-ring bond lengths average to 1·392 Å for (I) and 1·385 Å for (II). The smaller values of (II) probably result from the relatively large librational motion of the benzene rings in (II).

The bond lengths of the carboxyl group of (II) conform to the average values found in the literature for this group. The highly significant shortening and elongation of the C(5)—C(24) and C(24)—O(25) bonds in the alcohol [1·405 (6), 1·459 (6) Å)] is probably related to the ambiguity regarding the nature of C(24), as discussed above.

Angle 'widening' and 'shrinking' effects are observed in the imidazolyl ring of the two molecules. It results from the geometrical constraints imposed by the planar five-membered ring. The internal angles vary from 105 to 113° and they are all in the range of values observed for such systems in other structures (*e.g.* Paton, Liu & Paul, 1979). Larger values are observed in all the exocyclic angles of the imidazolyl ring.

The C(8)—S(7)—C(6) angle (av. 99·2°) in the two molecules is slightly larger than the corresponding angles in MCHTBI and in XTCNON (97·5 and 96·5° respectively). The S(7)—C(6)—C(5) and C(6)—C(5)—N(4) bond angles are close to the expected tetrahedral value (109·5°). The dihydrothiazine-ring internal angles at N(4), C(9) and C(8) agree with the values observed in XTCNON (av. 122·4, 125·8 and 122·5° respectively). The bond angles at the sp^3 atoms vary between 105·7 and 116·5°. The range observed for the sp^2 atoms is larger, 105·5 to 128·6°. The extreme values observed at C(9) probably result from the geometrical constraints of the ring system discussed earlier. The relatively large values of C(8)—N(23)—C(21) (av. 125·3°), probably result from the close interaction between S(7) and O(22).

Intermolecular interactions and packing arrangement. The packing arrangement of the alcohol molecule (I) is shown in Fig. 3. The molecules are arranged in centrosymmetric dimers. In the dimer the two imidazolyl rings are stacked one upon the other in an antiparallel manner with an interplanar distance of 3·5 Å. The dimer is held by two intermolecular hydrogen bonds involving the hydroxy and imidazolyl O atoms, O(25)—H(25)···O(10). Another intermolecular hydrogen bond involving the imidazolyl N and the side-chain O, N(2)—H(2)···O(22), links the dimers along the *a* axis. This arrangement leads to the formation of separate polar and hydrophobic regions. The polar species are arranged in infinite columns along the *a* axis and surrounded by hydrophobic regions formed by phenyl and methyl groups.

The intermolecular hydrogen bonds in (II) are between similar atoms as in (I): the O(26)—H(26)···O(10) hydrogen bond between the imidazolyl and the carboxyl O atoms, and the N(2)—H(2)···O(22) hydrogen bond between the side-chain amide O atom and the imidazolyl-ring N atom. However, the molecular packing of the chiral acid is different from that of the racemic alcohol. The first hydrogen bond links the molecules along the *a* axis (Fig. 4*a*) and the second links the molecules along the *c* axis (Fig. 4*b*). The separation into polar and hydrophobic regions is achieved here by a 'herring-bone' type of packing, *via* the twofold screw axes. The polar groups are arranged in infinite layers perpendicular to the *b* axis and interspaced by hydrophobic layers formed by the phenyl and methyl groups.

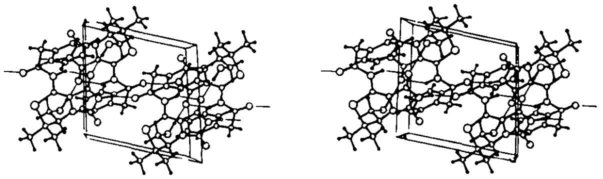


Fig. 3. Stereoscopic view of the packing arrangement of (I) viewed down the *c* axis.

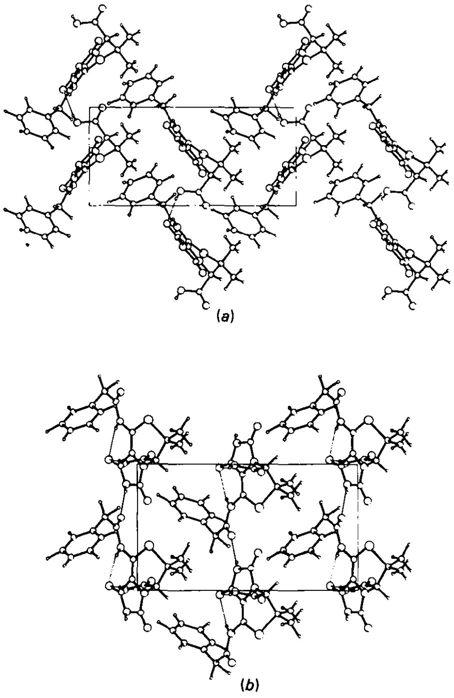


Fig. 4. Molecular packing of (II) viewed down (*a*) the *c* axis and (*b*) the *a* axis.

References

Davidson, A., Murray, I. E. P., Preston, P. N. & King, T. J. (1979). *J. Chem. Soc. Perkin Trans.* 1, pp. 1239–1245.

Guy, J. J. & Hamor, T. A. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 1133–1136.

Harada, Y. & Iitaka, Y. (1974). *Acta Cryst.* B**30**, 726–730.

Harada, Y. & Iitaka, Y. (1977). *Acta Cryst.* B**33**, 247–249.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Lambert, P., Evrard, G. & Durant, F. (1978). *Acta Cryst.* B**34**, 2654–2655.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MORIN, R. B., JACKSON, B. G., MUELLER, R. A., LAVAGNINO, E. R., SCANLON, W. B. & ANDREWS, S. L. (1963). *J. Am. Chem. Soc.* **85**, 1896–1897.

MORIN, R. B., JACKSON, E. G., MUELLER, R. A., LAVAGNINO, E. R., SCANLON, W. B. & ANDREWS, S. L. (1969). *J. Am. Chem. Soc.* **91**, 1401–1407.

NUDELMAN, A., HARAN, T. E. & SHAKKED, Z. (1981). *J. Org. Chem.* **46**, 3026–3029.

PALENIK, G. J. (1965). *Acta Cryst.* **19**, 47–56.

PATON, W. F., LIU, F.-T. & PAUL, I. C. (1979). *J. Am. Chem. Soc.* **101**, 1005–1013.

SHELDRICK, G. M. (1976). *SHELX76.* A program for crystal structure determination. Univ. of Cambridge, England.

SWEET, R. M. & DAHL, L. F. (1970). *J. Am. Chem. Soc.* **92**, 5489–5507.

VEGA, R., HERNÁNDEZ-MONTIS, V. & LÓPEZ-CASTRO, A. (1976). *Acta Cryst.* B**32**, 1363–1366.

Acta Cryst. (1983). C**39**, 887–888

1-Methyl-5-thia-1-thioniacyclooctane Iodide, $C_7H_{15}S_2^+.I^-$

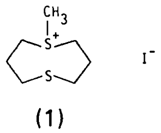
BY W. K. MUSKER, M. M. OLMSTEAD* AND M. H. GOODROW

Department of Chemistry, University of California, Davis, California 95616, *USA*

(*Received* 9 *December* 1982; *accepted* 16 *February* 1983)

Abstract. $M_r = 290{\cdot}23$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}736\,(2)$, $b = 12{\cdot}287\,(3)$, $c = 13{\cdot}046\,(4)$ Å, $V = 1079{\cdot}7\,(7)$ Å^3, $Z = 4$, D_m (298 K) = 1·77 (1), D_x(85 K) = 1·79 (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 32{\cdot}5$ cm^{-1}, $F(000) = 568$, $T = 85$ K. Final $R = 0{\cdot}020$ for 1447 unique reflections. The compound results from the reaction of 1,5-dithiacyclooctane and excess methyl iodide in diethyl ether. The S···S non-bonded distance of 3·259 (2) Å and C—S···S angle of 174·2 (1)° present in the cation suggest an intramolecular interaction.

Introduction. Certain sulfur-bonded derivatives of 1,5-dithiacyclooctane have been found to have relatively short transannular S···S contact distances in the range 3·121 (5)–3·271 (3) Å. These are 1-acetonyl-5-thia-1-thioniacyclooctane perchlorate (Johnson, Maier & Paul, 1970), 1,5-dithiacyclooctane diiodine adduct (Nichols, 1981) and *trans*-bis(1,5-dithiacyclooctane)tetrachlorotin(IV) (Olmstead, Williams & Musker, 1982). The structure of (1) was of interest in order to determine the transannular distance in the simple *S*-methyl derivative, in which the electronic effects of the derivative group would be minimal.



(1)

Experimental. Sticky, yellow crystals of title compound recovered directly from reaction mixture of methyl iodide and 1,5-dithiacyclooctane, no dialkylation product formed; D_m measured by flotation in $C_2H_2Br_4$/CCl_4; crystal of dimensions 0·37 × 0·42 × 0·75 mm selected for data collection, several others rejected due to twinning; Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus; lattice parameters computed from a least-squares fit of 12 reflections with $30° < 2\theta < 35°$; systematic absences for $h00$, $h = 2n+1$; $0k0$, $k = 2n+1$; $00l$, $l = 2n+1$ indicated space group $P2_12_12_1$ (No. 19); an empirical absorption correction assuming an ellipsoid applied with range of absorption correction factors 6·8–7·8; data collected to $2\theta_{\max} = 55°$ in positive octant with maximum indices h, k, l of 9, 16, 17 respectively; two check reflections showed less than a 2% average fluctuation during data collection; total of 1447 unique reflections measured of which nine having $F < 3\sigma(F)$ rejected; structure solved by Patterson and Fourier techniques, refined by full-matrix least squares (based on F) using $w = 1/[\sigma^2(F) + 0{\cdot}00008F^2]$; methyl H atoms located on a difference map and refined as a rigid body with the bonded C atom, allowing $U_{\rm iso}$ to vary; remaining H atoms placed at computed positions and assigned $U_{\rm iso} = 1{\cdot}2\,U_{\rm eq}$ (bonded C), refined using a riding model in which they contribute to the derivatives used in the least-squares procedure; non-H atoms assigned anisotropic thermal parameters, bringing total number of parameters to 94; in final cycle of refinement, maximum shift/e.s.d. −0·379 for overall scale and average shift/e.s.d. 0·037; final difference electron density map showed a maximum and minimum peak height of 0·39 and −0·80 e Å^{-3} respectively in vicinity of the I atom;

---

* To whom correspondence should be addressed.

0108-2701/83/070887-02$01.50