

isotropy in the niobium thermal parameters may partly result from the laminar structure of this compound; however, that for the sulfur atoms should not be considered significant.

#### References

GAMBLE, F. R., DiSALVO, F. J., KLEMM, R. A. & GEBALLE, T. M. (1970). *Science*, **168**, 568–570.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

*International Tables for X-ray Crystallography*. (1962). Vol. III. Birmingham: Kynoch Press.

JELLINEK, F., BRAUER, G. & MULLER, H. (1960). *Nature, Lond.* **185**, 376–377.

JONES, R. E. JR, SHANKS, H. R., FINNEMORE, D. K. & MOROSIN, B. (1972). *Phys. Rev. B* **6**, 835–838.

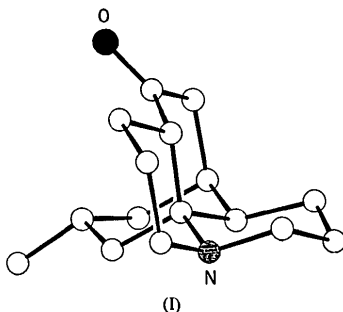
WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 1. New York: Interscience.

*Acta Cryst.* (1974). **B30**, 552

**The absolute configuration of lycopodine: a warning.** By D. ROGERS and A. QUICK, *Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England* and MAZHAR-UL-HAQUE, *Chemistry Department, Pahlavi University, Shiraz, Iran*

(Received 1 November 1973; accepted 15 November 1973)

Attention is drawn to the inability of the FC link in X-RAY 63 and 70 to allow correctly for dispersion. In one instance, lycopodine, use of these programs gave a significantly strong bias in favour of the wrong chirality. The chirality (I) is confirmed.



Lycopodine, one of numerous alkaloidal constituents of *Lycopodium lucidulum* Michx, has been assigned the structure and chirality (I) on the basis of extensive chemical work and a positive Cotton effect (Manske & Marion, 1946; Harrison & MacLean, 1960; Anet, 1960; Wiesner, Francis, Findlay & Valente, 1961; Burnell & Taylor, 1961). Recently, Ayer, Altenkirk, Burnell & Moins (1969) have reexamined the o.r.d. evidence for several members of this group of alkaloids, their salts, and derivatives. They found that lycopodine salts, epilycopodine and its salts, and the alkaloid L23 all have negative Cotton effects and that the structure of the o.r.d. curves is more complex than was realized when Wiesner *et al.* (1961) first assigned the chirality of annotinine and lycopodine. As the octant diagrams are not altered by protonation and are generally similar for all these compounds, they concluded that it was not safe to apply octant rules for carbonyl groups in this context until the large and obviously different contributions of N: and N<sup>+</sup> were properly understood, and they specifically queried whether (I) correctly depicted lycopodine. They adduced other items of indirect evidence and concluded, but with less confidence than before, that (I) was probably correct after all.

We have recently completed the determination of the crystal structure of lycopodine hydrochloride (which will be reported elsewhere), and as a byproduct have confirmed that (I) is correct. But because of a flaw in a well-known

computer program, we initially came to the opposite conclusion. The circumstances seem to us serious enough to justify a warning to crystallographers.

Lycopodine hydrochloride (C<sub>16</sub>H<sub>26</sub>NOCl) is orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with *a* = 7.606, *b* = 9.540, *c* = 21.371 Å, *Z* = 4. Of 1716 reflexions measured with Cu *K*α radiation on a Siemens diffractometer to *θ* = 70°, 1695 were observed, corrected for absorption, and, apart from eight zonal reflexions affected by extinction, were used to refine the structure to *R* ~ 0.05. Allowance for anomalous dispersion for the chloride ion was applied initially to all these reflexions for both possible molecular chiralities. *R*(+) , corresponding to configuration (I) was 0.0586, while *R*(-), from its enantiomorph, was 0.0559. Application of Hamilton's (1965) significance test shows that these figures are *strongly in favour of the enantiomorph of (I)* (at a confidence level ≥ 99.5%).

This conclusion led us to check every step, which revealed that a fault lay in the computer program used for calculating structure factors. This was the FC link in X-RAY 70 (Stewart, Kundell & Baldwin, 1963–1972). Subsequent tests have shown that both the X-RAY 63 and 70 versions of FC calculate structure factors correctly when the atomic scattering factors are real, but fail to allow correctly for the imaginary dispersion component. They give in fact *A*(+) + *iB*(-) for *Af*'', positive, and *A*(-) + *iB*(+) for *Af*'', negative. The X-RAY 72 version of FC, however, works correctly.

This was the first time we had attempted to use the *FC* link for this purpose. Previously the comparison had been done after refinement by *ORFLS* (in X-RAY 63) or *CRYLSQ* (in X-RAY 70). We have checked that each of these, though in different ways, correctly allows for dispersion, so none of our previous assignments need revision. (*ORFLS* on X-RAY 70 will only refine if not required to allow for dispersion.) Two reruns, using four cycles of *CRYLSQ* (in X-RAY 70) on all the non-zonal reflexions of lycopodine hydrochloride with  $\Delta f' = 0.33$  and  $\Delta f'' = \pm 0.72$ , produced trifling shifts of all parameters, but gave a very different result, [ $R(+)=0.059$ ,  $R(-)=0.077$ ] which represents a most emphatic confirmation of the chirality (I).

It is disconcerting to discover that an erroneous program could produce a strongly and *wrongly* biased result, and it is clear that crystallographers must avoid using the *FC* link in X-RAY 63 or 70 for this purpose. They should also check to see whether any chiralities they may have published were based on these versions of *FC*, or on some program that they have not personally checked rigorously.

*Acta Cryst.* (1974). B30, 553

**On the crystal structures of  $C_5H_{12}N^+HS^-$  and  $C_5H_{11}N \cdot HCl$ .** By J. K. DATTA GUPTA,\* *Saha Institute of Nuclear Physics, Calcutta-9, India*

(Received 23 October 1973; accepted 24 October 1973)

Crystal structures of piperidinium hydrogen sulphide and piperidine hydrochloride are found to be isomorphous.

Recently a paper has been published (Smail & Sheldrick, 1973) on the crystal and molecular structure of piperidinium hydrogen sulphide,  $C_5H_{12}N^+HS^-$ . A comparison of this structure with the piperidine hydrochloride structure, determined by Dattagupta & Saha (1970) and Rérat (1960), shows that they are isomorphous. Cell dimensions, space groups, fractional coordinates *etc.* of the two reported structures are given in Table 1 for easy comparison. Transformations to be made in one structure for comparison with the other are obvious.

\* Present address: Max-Planck-Institut für Metallforschung, 7 Stuttgart 1, Seestrass 75, Germany (BRD).

- References**
- ANET, F. A. L. (1960). *Tetrahedron Lett.* **20**, 13–17.  
 AYER, W. A., ALTENKIRK, B., BURNELL, R. H. & MOINAS, M. (1969). *Canad. J. Chem.* **47**, 449–455.  
 BURNELL, R. H. & TAYLOR, D. R. (1961). *Tetrahedron*, **15**, 173–182.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.  
 HARRISON, W. A. & MACLEAN, D. B. (1960). *Chem. Ind.* pp. 261–262 and references therein.  
 MANSKE, R. H. F. & MARION, L. (1946). *Canad. J. Res. (B)*, **24**, 57–62.  
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1963–1972). Compilers of various editions of the X-RAY Library System of Crystallographic Programs, Univ. of Maryland. *FC* occurs in the 63, 70 and 72 versions; *ORFLS* in 63 and 70; *CRYLSQ* in 70 and 72.  
 WIESNER, K., FRANCIS, J. E., FINDLAY, A. J. & VALENTE, Z. (1961). *Tetrahedron Lett.* **5**, 187–196.

In both structures the molecules are linked by N–H···S (N–H···Cl) type hydrogen bonds to form infinite chains, and the piperidine ring has a chair conformation with a crystallographic mirror plane through atoms S (Cl), N and C(3).

**References**

- DATTA GUPTA, J. K. & SAHA, N. N. (1970). *Indian J. Phys.* **44**, 561–564.  
 RÉRAT, C. (1960). *Acta Cryst.* **13**, 72–80.  
 SMAIL, E. J. & SHELDRIK, G. M. (1973). *Acta Cryst.* B**29**, 2027–2028.

Table 1. *Data relating to the two structures*

	Piperidinium hydrogen sulphide (Smail & Sheldrick, 1973)			Piperidine hydrochloride (Dattagupta & Saha, 1970)			
	$C_5H_{12}N^+HS^-$			$C_5H_{11}N \cdot HCl$			
Crystal system	Orthorhombic			Orthorhombic			
Space group	<i>Pmab</i>			<i>Pbcm</i>			
Cell dimensions	$a = 9.77 \text{ \AA}$ $b = 7.30$ $c = 9.84$			$a = 9.68 \text{ \AA}$ $b = 7.30$ $c = 9.67$			
Density	$D = 1.13 \text{ g cm}^{-3}$ $Z = 4$			$D = 1.14 \text{ g cm}^{-3}$ $Z = 4$			
	$10^4x$	$10^4y$	$10^4z$	$10^4x$	$10^4y$	$10^4z$	
S	2500	9632	3269	Cl	1733	363	2500
N	2500	5472	3645	N	1430	4572	2500
C(1)	3753	4641	3046	C(1)	1929	5404	1201
C(2)	3758	4901	1541	C(2)	3469	4967	1155
C(3)	2500	4140	905	C(3)	4081	5851	2500

In both structures the molecules are linked by N–H···S (N–H···Cl) type hydrogen bonds to form infinite chains, and the piperidine ring has a chair conformation with a crystallographic mirror plane through atoms S(Cl), N and C(3).