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Crystallographic data for heteratisine and some derivatives. By R. ANEJA and S. W. PELLETIER,
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Heteratisine was isolated from the roots of *Aconitum heterophyllum* by Jacobs & Craig (1942). Some of its chemistry (Aneja & Pelletier, unpublished) is markedly different from that of the other aconite alkaloids, largely owing to the presence of a lactone ring in its molecule. This structural feature has not been encountered in the aconites studied earlier.

We have prepared some derivatives of heteratisine and obtained preliminary X-ray crystallographic data for them, as also for the parent alkaloid (Table 1). The unit-cell dimensions were measured from precession photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The space groups were deduced from systematic absences and the fact that these compounds are optically active. The densities were measured by flotation, in aqueous cesium chloride for heteratisine and in mixtures of carbon tetrachloride and benzene for the hydrohalides.

Diffraction spots of the hydrobromide (II) and the hydroiodide showed tails, evidently due to disorder in

the growth of the crystals. Hydrobromide (I) was efflorescent and gradually crumbled to a powder on loss of solvent of crystallization. Moreover, its asymmetric unit contains two molecules. The crystals were, therefore, considered unsuitable for a complete structure analysis and no further work on these derivatives is contemplated.

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Table 1. *Crystal data for heteratisine and derivatives*

	Heteratisine	Heteratisine hydrobromide (I)	Heteratisine hydrobromide (II)	Heteratisine hydroiodide
Solvent of crystallization	Ethanol	Methanol	Acetonitrile	Ethanol
m.p.	267-69°	280-83°	272-74°	274-76°
$[\alpha]_D^{25}$ ($c = 1.0, \text{CH}_3\text{OH}$)	+40°	+24°	+26°	+19°
Mol. formula	$\text{C}_{22}\text{H}_{33}\text{O}_5\text{N}$	$\text{C}_{22}\text{H}_{34}\text{O}_5\text{NBr} \cdot 0.5\text{CH}_3\text{OH}$	$\text{C}_{22}\text{H}_{34}\text{O}_5\text{NBr}$	$\text{C}_{22}\text{H}_{34}\text{O}_5\text{NI}$
% C, H, N (found)	67.57, 8.60, 3.74	55.25, 7.42, 2.91	55.89, 7.26, 2.88	50.86, 6.44, 2.82
% C, H, N (calc.)	67.47, 8.50, 3.58	55.25, 7.55, 2.86	55.85, 7.25, 2.96	50.87, 6.60, 2.69
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
a (Å)	13.62	18.66	10.17	18.26
b (Å)	10.65	16.40	11.13	10.00
c (Å)	8.89	15.55	9.15	23.78
β	133° 18'	—	92° 23'	—
V (Å ³)	983.0	4758.6	1035.2	4342.2
Z	2	8	2	8
M	391.49	488.43	472.41	519.41
D_x (g.cm ⁻³)	1.322	1.362	1.515	1.570
D_m (g.cm ⁻³)	1.32	1.355	1.505	1.56
Space group	$P2_1$	$P2_12_12$	$P2_1$	$C222_1$

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Least-squares structure refinement assuming molecular rigidity. By G. S. PAWLEY, *Department of Chemistry, Harvard University, Cambridge, Massachusetts, U.S.A.*

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Cruikshank (1956) has shown how to treat the results of structure refinement to get the rigid-body translational and rotational components of the thermal vibration. The method neglects the effect of internal vibrations and assumes that the temperature factors for all the atoms depend solely on the rigid-body motion. Following this assumption we can write the structure factor equation

$$\mathbf{F}_h = c \sum_{i \text{ atoms}} f_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i) \times \exp(-\mathbf{h} \cdot \mathbf{A}^{-1} \cdot \{\mathbf{T} + \mathbf{V}_i \cdot \boldsymbol{\omega} \cdot \tilde{\mathbf{V}}_i\} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}}) = \sum_i \mathcal{F}_i \quad (1)$$

where

$\mathbf{h} = (h, k, l)$, the reflection indices,
 $\mathbf{x}_i = (x_i, y_i, z_i)$, the crystal coordinates for the i th atom,

$\mathbf{X}_i = \mathbf{A} \cdot \mathbf{x}_i$ is the transformation to an arbitrary orthogonal coordinate system in Å,

$$\mathbf{V}_i = \begin{bmatrix} 0 & -Z_i & Y_i \\ Z_i & 0 & -X_i \\ -Y_i & X_i & 0 \end{bmatrix}, \text{ an axial vector in tensor form,}$$

$\tilde{\mathbf{V}}_i$ is the transpose of the tensor \mathbf{V}_i ,

$$\tilde{\mathbf{h}} = \begin{pmatrix} h \\ k \\ l \end{pmatrix},$$

c is the scale factor,

\mathbf{T} is the mean-square translational tensor, and

ω is the mean-square rotational tensor.

Both \mathbf{T} and ω differ in units from those of Cruickshank by $2\pi^2$:

$$\mathbf{T} = 2\pi^2 \mathbf{T} \text{ (Cr.)}$$

If we let $\mathbf{B}_i = \mathbf{A}^{-1} \cdot \mathbf{V}_i$, then $\tilde{\mathbf{B}}_i = \tilde{\mathbf{V}}_i \cdot \tilde{\mathbf{A}}^{-1}$ and the second exponential of (1) can be written

$$\exp(-\mathbf{h} \cdot \mathbf{A}^{-1} \cdot \mathbf{T} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}} - \mathbf{h} \cdot \mathbf{B}_i \cdot \omega \cdot \tilde{\mathbf{B}}_i \cdot \tilde{\mathbf{h}})$$

If we have grounds for assuming that the rigid-body motions contribute predominantly to the temperature factors of all the atoms in the molecule, we can refine the crystal structure using as parameters the atomic coordinates and the components of \mathbf{T} and ω . Although this procedure will give a poorer reliability factor than the standard procedure with anisotropic temperature factors for each atom, due to the decrease in the number of parameters refined, the resulting tensors may, in some cases, have more meaning than those obtained by analysis of the anisotropic temperature factors.

Most of the partial differentials required for the least-squares analysis are straightforward, namely

$$\frac{\partial \mathbf{F}_h}{\partial c} = \frac{1}{c} \sum_i \mathcal{J}_i \quad (2)$$

$$\frac{\partial \mathbf{F}_h}{\partial T_{jk}} = - \sum_i \mathcal{J}_i \mathbf{h} \cdot \mathbf{A}^{-1} \cdot \frac{\partial \mathbf{T}}{\partial T_{jk}} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}} \quad (3)$$

$$= - \mathbf{F}_h \mathbf{h} \cdot \mathbf{A}^{-1} \cdot \frac{\partial \mathbf{T}}{\partial T_{jk}} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}} \quad (3')$$

(Equation (3') holds only when there is only one molecule in the unit cell.)

$$\frac{\partial \mathbf{F}_h}{\partial \omega_{jk}} = - \sum_i \mathcal{J}_i \mathbf{h} \cdot \mathbf{B}_i \cdot \frac{\partial \omega}{\partial \omega_{jk}} \cdot \tilde{\mathbf{B}}_i \cdot \tilde{\mathbf{h}} \quad (4)$$

Only the $\partial \mathbf{F}_h / \partial x_i$ give difficulty. If we write

$$\frac{\partial \mathbf{F}_h}{\partial x_i} \cong 2\pi i h \mathcal{J}_i \quad (7)$$

neglecting

$$- \mathbf{h} \cdot \mathbf{A}^{-1} \cdot \left\{ \frac{\partial}{\partial x_i} (\mathbf{V}_i \cdot \omega \cdot \tilde{\mathbf{V}}_i) \right\} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}} \mathcal{J}_i \quad (8)$$

the problem is considerably simplified. It is plausible to

argue that (8) is smaller than (7) as it represents the change in \mathbf{F}_h due to the alterations of the temperature factors for each atom with change in position of that atom in the molecule.

Thus far the theory only holds for centrosymmetrical molecules with the origins of the coordinate systems at the centre of symmetry. It has been shown (Pawley, 1963) that the best fit for \mathbf{T} and ω does not necessarily occur when the origin for ω is the centre of gravity of the molecule in the non-centrosymmetric case. We must therefore introduce three more parameters to be varied, the coordinates of the origin of ω . Let these be (ξ, η, ζ) in the arbitrary orthogonal system. We must now write

$$\mathbf{V}_i = \begin{bmatrix} 0 & -(Z_i - \zeta) & (Y_i - \eta) \\ (Z_i - \zeta) & 0 & -(X_i - \xi) \\ -(Y_i - \eta) & (X_i - \xi) & 0 \end{bmatrix} \quad (9)$$

All the above equations still hold, to which must be added

$$\frac{\partial \mathbf{F}_h}{\partial \xi} = - \sum_i \mathcal{J}_i \mathbf{h} \cdot \mathbf{A}^{-1} \cdot \left\{ \mathbf{V}_i \cdot \omega \cdot \frac{\partial \tilde{\mathbf{V}}_i}{\partial \xi} + \frac{\partial \mathbf{V}_i}{\partial \xi} \cdot \omega \cdot \tilde{\mathbf{V}}_i \right\} \cdot \tilde{\mathbf{A}}^{-1} \cdot \tilde{\mathbf{h}} \quad (10)$$

Now as

$$\frac{\partial \mathbf{V}_i}{\partial \xi} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix},$$

$$\frac{\partial \tilde{\mathbf{V}}_i}{\partial \xi} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix},$$

and as ω is symmetric,

$$\mathbf{V}_i \cdot \omega \cdot \frac{\partial \tilde{\mathbf{V}}_i}{\partial \xi} = \left(\frac{\partial \tilde{\mathbf{V}}_i}{\partial \xi} \cdot \omega \cdot \tilde{\mathbf{V}}_i \right)$$

and the computation is simplified.

We now have all the necessary expressions for a least-squares refinement. This will be programmed shortly. The first structure to be refined by this method is hoped to be azulene, which was last refined by Robertson, Shearer, Sim & Watson (1962) using standard procedures. This is chosen because the structure contains non-centrosymmetrical molecules in a centrosymmetric space group. The statistical arrangement proposed by Robertson *et al.* gives rise to atomic positions of very close proximity. The position and anisotropic temperature parameters for the close pairs of atoms interact giving large errors, as observed by Robertson *et al.* It is hoped that the parameters in the above method will not interact to the same degree and will give smaller errors.

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