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The absolute configuration of *N*-methylrhoeagenine iodide.*

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The absolute configuration of *N*-methylrhoeagenine iodide has been determined using the anomalous scattering of the iodine atoms; it is in agreement with that deduced by chemical methods.

Introduction

The crystal structure of *N*-methylrhoeagenine iodide has been determined by X-ray diffraction techniques (Huber, 1970). The effects of anomalous dispersion were ignored in the earlier X-ray study, and the organic cation was shown in the absolute configuration proposed by Santavy, Kaul, Hruban, Dolejs, Hanus, Blaha & Cross (1965). Santavy, Hrbek & Blaha (1967) reported further attempts to confirm this absolute configuration by comparing the optical rotatory dispersion (ORD) curves of rhoeadine and related substances with the ORD curves of the phthalideisoquinoline alkaloids. These results were consistent with their previous findings, giving added support for (*R*, *R*) absolute configuration (in the notation of Cahn, Ingold & Prelog, 1956) of the two asymmetric centres at the junction of the dihydropyran and azacycloheptene rings in rhoeagenine. However, conclusions based on such analogies are not always reliable and an X-ray determination of the absolute configuration seemed desirable (Santavy, 1971).

Experimental

The intensities of 25 pairs of reflexions showing relatively large anomalous dispersion effects were measured by visual comparison with a calibrated intensity scale. The equi-inclination Weissenberg photographs on which these intensities were recorded had been obtained during the earlier X-ray study. The pairs of reflexions chosen for intensity measurement all had fairly similar spot shapes. Care was taken to ensure that the indexing conformed to a right-handed system (Peerdeman & Bijvoet, 1956). The data were corrected for Lorentz and polarization factors, but not for absorption or extinction.

Structure factors were calculated using the final parameters from the earlier structure determination. The observed and calculated structure factor ratios are given for each of the 25 pairs of reflexions in Table 1. The anomalous scattering coefficients used for iodine were those of Cromer (1965): $\Delta f' = -1\cdot03$, $\Delta f'' = 6\cdot68$. Scattering-factor values were those of Hanson, Herman, Lea & Skillman (1964) for C, N and O, and of Cromer & Waber (1965) for I^-.

Results

For each pair of reflexions, the ratio of observed structure factors differs from unity in the same direction as the ratio of calculated structure factors. There can be no doubt, therefore, that the absolute configuration is given correctly by the final parameters of the earlier X-ray study, referred to a right-handed axial system. Using the previous numbering scheme, the absolute configuration can thus be expressed as 5*R*, 6*R*, 9*S*. This result unambiguously confirms the proposal of Santavy *et al.* (1965) and is also in full agreement with the work of Klötzer, Teitel & Brossi (1971) who have achieved the total synthesis of rhoeadine.

Table 1. *Observed and calculated structure factor ratios*

h_1	k_1	l_1	h_2	k_2	l_2	$F_o(h_1k_1l_1)/$ $F_o(h_2k_2l_2)$	$F_c(h_1k_1l_1)/$ $F_c(h_2k_2l_2)$
1	1	7	1	1	−7	1·06	1·12
1	1	11	1	1	−11	1·12	1·19
1	1	17	1	1	−17	1·41	1·29
1	3	15	1	3	−15	1·73	1·76
1	3	20	1	3	−20	0·82	0·76
1	7	4	1	−7	4	1·73	2·08
2	2	11	2	2	−11	1·42	1·53
2	2	14	2	2	−14	1·73	2·63
2	2	15	2	2	−15	0·82	0·85
2	2	19	2	2	−19	0·71	0·69
2	4	10	2	4	−10	1·29	1·44
2	4	13	2	4	−13	1·32	1·29
2	6	4	2	6	−4	1·35	1·61
2	10	1	2	10	−1	0·73	0·76
3	1	12	3	1	−12	1·15	1·22
3	1	14	3	1	−14	1·22	1·17
3	3	17	3	3	−17	0·53	0·43
4	2	18	4	2	−18	1·56	1·35
4	8	1	4	−8	1	0·66	0·48
4	10	9	4	−10	9	1·73	2·74
5	1	9	5	1	−9	1·15	1·19
5	1	16	5	1	−16	0·76	0·90
5	5	2	5	5	−2	0·76	0·84
7	1	7	7	1	−7	0·50	0·72
7	3	11	7	3	−11	0·65	0·73

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