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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

The space group of azulene.
By G. A. SIM, *Chemistry Department, The University, Glasgow, W. 2, Scotland.*

1. Introduction

There has been considerable controversy about the space group of azulene. The absent X-ray spectra indicate the centrosymmetric space group $P2_1/a$ and with only two non-centrosymmetric molecules in the unit cell this implies a disordered structure. A comparison of the entropies of azulene and naphthalene (Günthard, 1949) provides support for the possibility of disorder in the azulene crystal.

Two independent investigations of the crystal structure of azulene (Robertson & Shearer, 1956; Takeuchi & Pepinsky, 1956), however, led to an ordered arrangement of molecules in the non-centrosymmetric space group Pa with apparently satisfactory agreement between calculated and observed structure amplitudes in the principal zones. This choice of space group was supported by a study (Bernal, 1956) of the morphology of azulene crystals. Moreover Robertson & Shearer applied the $N(z)$ statistical test (Howells, Phillips & Rogers, 1950) to the $(h0l)$ intensity data and obtained results indicating an acentric distribution of intensities and hence supporting the assignment of Pa as the correct space group.

Subsequent refinement of the crystal structure, however, using full three-dimensional intensity data, showed that the ordered arrangement of molecules gives substantially poorer agreement between calculated and observed structure amplitudes than does a disordered centrosymmetric arrangement based on $P2_1/a$ as space group, the percentage discrepancies being 22·4 for the ordered structure and 13·5 for the disordered structure (Robertson, Shearer, Sim & Watson, 1958).

At a time when the alternative structures gave about equally good agreement between calculated and observed structure amplitudes, the actual overall percentage discrepancies being 21·4 and 22·4 for the centrosymmetrical and non-centrosymmetrical structures, respectively, the application of intensity statistics to the determination of the space group of azulene was reinvestigated with a view to providing evidence in favour of one or other of the molecular arrangements. It was found, in fact, that the intensity distribution obtained from the three-dimensional crystal data definitely favours the disordered structure.

2. Procedure

The X-ray spectra were divided into five groups with $\sin \theta = 0·35 - 0·45, \ldots, 0·75 - 0·85$, a total of 423 reflections being involved. In each group $\langle |F_o|^2 \rangle$ was obtained and used to derive values of $z = |F_o|^2/\langle |F_o|^2 \rangle$. Values of $_{obs.}N(z)$ for $z = 0·1, 0·2, \ldots, 2·0$ were calculated and the five values for each z were then averaged to yield the final values listed in Table 1, allowance being made for the different number of spectra in each group. As five independent results were used to derive each final $_{obs.}N(z)$ value it was possible to calculate a standard deviation for each such value. These standard deviations

are listed also in Table 1. The $_{obs.}N(z)$ results in Table 1 agree more closely with the centric $_{\bar{1}}N(z)$ distribution of Howells *et al.* than with the acentric $_{1}N(z)$ distribution.

Table 1. *The distribution of values of $|F|^2$ for azulene*

z	obs.$N(z)$	σ	calc. $_{\bar{1}}N(z)$	σ	calc. $_{1}N(z)$	σ
0	0·000		0·000		0·000	
0·1	0·225	0·012	0·232	0·015	0·102	0·011
0·2	0·326	0·022	0·340	0·010	0·210	0·012
0·3	0·390	0·021	0·404	0·012	0·288	0·021
0·4	0·440	0·018	0·454	0·011	0·355	0·014
0·5	0·485	0·016	0·506	0·008	0·409	0·012
0·6	0·527	0·013	0·551	0·009	0·475	0·003
0·7	0·574	0·011	0·584	0·015	0·525	0·010
0·8	0·615	0·010	0·619	0·019	0·563	0·014
0·9	0·655	0·010	0·655	0·021	0·610	0·017
1·0	0·695	0·003	0·690	0·023	0·648	0·020
1·2	0·740	0·006	0·733	0·016	0·728	0·008
1·4	0·775	0·004	0·775	0·010	0·771	0·008
1·6	0·809	0·007	0·779	0·009	0·804	0·006
1·8	0·849	0·007	0·827	0·008	0·827	0·009
2·0	0·868	0·005	0·851	0·004	0·863	0·007

Although these results appeared fairly conclusive it was felt that a much more direct test of the two alternative structures was desirable and this was achieved by repeating the calculations detailed above but with values of $|F_c|$ for the two alternative structures replacing values of $|F_o|$. The results, denoted by $_{calc. \bar{1}}N(z)$ and $_{calc. 1}N(z)$ for the disordered and ordered structures, respectively, are listed in Table 1 along with the appropriate standard deviations.

3. Discussion

An examination of the results listed in Table 1 shows that the differences between values of $_{obs.}N(z)$ and of $_{calc. \bar{1}}N(z)$, when compared with the appropriate standard deviations, can not be regarded as significant. On the other hand the differences between values of $_{obs.}N(z)$ and of $_{calc. 1}N(z)$ must be highly significant. These results provide strong evidence for the centrosymmetric disordered crystal structure attributed to azulene.

It is interesting that an examination of the statistical distribution of $|F_c|^2$ values should have provided a clear indication of which of the alternative structures is the more acceptable at a stage of refinement at which it was not possible to decide on the basis of the agreement between observed and calculated structure amplitudes that one structure was clearly correct and the other incorrect. If the problem of alternative structures should occur again it would seem worthwhile to repeat this type of analysis to distinguish the structure more likely to be correct.

An advantage possessed by this procedure for deciding between alternative space groups is that in the case of a molecule possessing one or more 'heavy' atoms and/or any appreciable degree of symmetry the necessity for deciding which of the many theoretical $N(z)$ distributions should be selected for comparison with the $_{obs.}N(z)$ distribution is avoided. Moreover sampling errors arising from the grouping adopted for the intensity data will be common to the $_{calc.}N(z)$ and $_{obs.}N(z)$ distributions and so will not normally cause trouble.

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Unit-cell dimensions and space groups of some optically active oxims.

By H. A. J. OONK and J. B. HULSCHER, *Laboratorium v. Kristalchemie, Rijksuniversiteit, Catharijnesingel 51, Utrecht, the Netherlands*

The oxims in question are camphoroxim, with its hydrochloride and hydrobromide, and carvoxim.

From systematic absences on Weissenberg photographs (Cu $K\alpha$-radiation) the following space groups are found:

Carvoxim	$P2_1$	$Z = 2$
Camphoroxim	$P2_1$	$Z = 2$
Camphoroximhydrochloride	$P2_12_12_1$	$Z = 4$
Camphoroximhydrobromide	$P2_1$	$Z = 2$

The unit-cell dimensions of these compounds were determined from Weissenberg photographs, calibrated with NaCl-powder. The results are tabulated below and agree with the data given by Groth.

The structure analyses of carvoxim and camphoroxim are in progress.

	a	b	c	β
	in Å ± 0·02 Å			± 0·1°
Carvoxim	10·17	11·64	8·54	100·8°
Camphoroxim	12·17	11·82	7·19	99·7
Camphoroxim HCl	21·15	6·96	7·44	—
Camphoroxim HBr	10·39	7·09	7·68	99·3

	a	:	b	:	c	β
	from X-rays					
Carvoxim	0·874	:	1	:	0·734	100·8°
Camphoroxim	1·021	:	1	:	0·608	99·7
Camphoroxim HCl	3·039	:	1	:	1·069	—
Camphoroxim HBr	1·465	:	1	:	1·083	99·3

	a	:	b	:	c	β
	Groth					
Carvoxim	0·8739	:	1	:	0·3667	100° 54'
Camphoroxim	1·0252	:	1	:	0·6073	99° 42'
Camphoroxim HCl						
Camphoroxim HBr	1·4699	:	1	:	1·0796	99° 19'