LETTERS TO THE EDITORS

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Structure of Azulene

PREVIOUS work on the crystal structure of azulene[1] has shown that the apparent space group is $P2_1/a$ (C^5_{2h}) with two molecules in the unit cell. This implies a centrosymmetric molecule, which is in conflict with the chemical evidence. The two most likely explanations of this discrepancy are : (a) that the implied centre of symmetry is only statistically true, and is due to rotating molecules or a disordered structure ; or (b) that the absent spectra leading to the deduction of the space group $P2_1/a$ are accidental, and that the true space group is really of lower symmetry. Günthard[2] has discussed these possibilities, and in recent work[3] has shown that a comparison of the entropies of azulene and naphthalene (which has similar lattice dimensions) appears to confirm the presence of some disorder in the azulene crystal.

We have now made a further examination of the crystal structure of azulene and have obtained the cell dimensions $a = 7 \cdot 91 \pm 0 \cdot 02$, $b = 6 \cdot 00 \pm 0 \cdot 02$, $c = 7 \cdot 84 \pm 0 \cdot 02$ A., $\beta = 101° \ 30'$. This unit cell contains two molecules of $C_{10}H_8$ and the (h0l) reflexions are absent when h is odd. We have looked for the (0k0) spectra carefully up to the seventh order, giving long exposures on oscillation photographs, but have only been able to find (020) with F about $15 \cdot 5$ and (060) with F about $1 \cdot 7$. What appeared to be a weak (010) was observed with copper radiation, but this is probably spurious and could not be repeated with iron radiation.

So far our work is in good agreement with previous results and suggests the space group $P2_1/a$, although only two (0k0) reflexions can be recorded. To obtain further evidence we have applied the statistical tests of Wilson[4] and Howells[5] to the (h0l) spectra, and the results indicate quite strongly that the projection of the structure on (010) is non-centrosymmetrical. If this conclusion is accepted, it means that the (0k0) absences are accidental and that the space group is probably Pa (C^2_s) with two asymmetric molecules in the unit cell.

Proceeding on this assumption, a trial structure based on the chemical formula was postulated and refined by the method of difference syntheses. Good agreements were soon obtained for all the (h0l) spectra, and an electron-density projection of the structure on (010) is shown in Fig. 1. At this stage the average discrepancy between observed and calculated structure factors in the (h0l) zone is 11 per cent. The other zones also give substantial agreements and are being further refined.

The positions of the molecules in the unit cell are similar to those of the naphthalene structure[6], although the azulene molecules have a rather different orientation. Their position with respect to the glide plane is such as to create an almost exact halving of the (0k0) spectra ; but this halving is, of course, accidental in the sense that it is not necessarily imposed by the symmetry elements of the space group. From Fig. 1 it is seen that the molecular plane is steeply inclined to (010), as in the corresponding naphthalene structure, and this prevents clear resolution of all the atoms. Nevertheless, the form
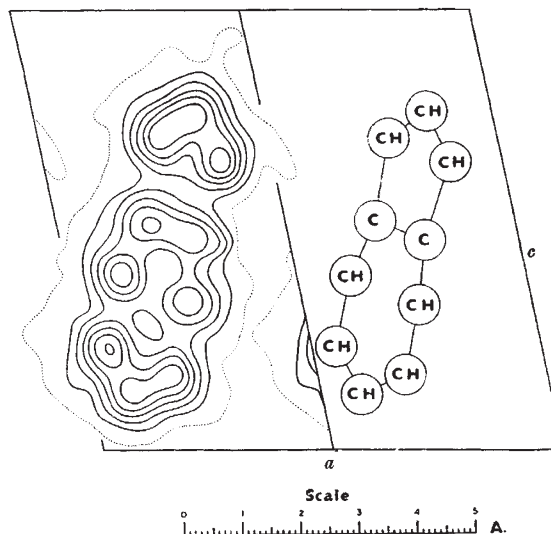

Fig. 1. Projection of the azulene structure on (010)

of the molecule, consisting of a fused five- and seven-membered ring system, can be clearly seen. Although some disorder may be present in the structure, it does not seem to be enough to prevent a full determination of the molecular structure by the X-ray method.

The peak values of the electron density are seen to vary in an interesting manner on the different atoms ; but neither these variations nor the variations of bond-length which can be obtained after allowing for the orientation are significant at the present stage of refinement. As the structure is non-centrosymmetric, it is expected that this refinement process will have to be carried quite far, probably with the use of full three-dimensional data, before really significant and chemically interesting results are obtained. This work is now proceeding.

We are indebted to Prof. Wilson Baker and to Dr. E. Clar for supplies of pure azulene.

J. MONTEATH ROBERTSON
H. M. M. SHEARER

Chemistry Department,
University of Glasgow.
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Radioactivity of Iron Meteorites by the Photographic Method

WE wish to present the preliminary results of a study of the α-radioactivity of iron meteorites by the method of nuclear emulsions.

The important work of Paneth's group[1] on the helium ages of iron meteorites shows uranium and thorium contents of $0 \cdot 1–1 \times 10^{-8}$ gm./gm. Davis's radium determinations on seven iron meteorites gave uranium equivalents of the same order of magnitude[2].

The meaning of the helium ages has been discussed by Urey[3,4]. He states that on thermodynamical