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Refinement of azulene assuming rigid-body thermal motion. By G. S. PAWLEY,* Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A.

Introduction

Azulene presents a special computation problem, owing to the disordered nature of the molecules in the crystals (Robertson, Shearer, Sim & Watson, 1962). There are two non-centrosymmetric molecules in the unit cell, space group $P2_1/a$, which must each occupy a symmetry centre. This can only occur by a statistical arrangement of molecules in two orientations related by centrosymmetry. The main difficulties encountered in the refinement of the crystal structure follow from the high interactions between the positional and thermal parameters of pairs of atoms which approach each other (statistically) closer than the resolution of the measurements. Interpretation of the results of refinement is then difficult because there is no formal way of assigning the atoms to the correct molecule.

For azulene Robertson et al. chose the molecule with the most sensible bond lengths. They then analysed the anisotropic temperature factors for rigid body vibrations and obtained results similar to those with naphthalene.

The purpose of the present study was to re-examine the assumptions made by Robertson et al. and then to attempt methods which avoid some of these assumptions. The study was not encouraging in that it casts doubt on the results of any investigation with disorder, but it is thought that the methods reported will give physically meaningful results for ordered structures.

Re-examination of previous results

Independently both Hirshfeld, Sandler & Schmidt (1963) and Pawley (1962, 1963) have proposed a method of examining the anisotropic temperature factors of non-centrosymmetrical molecules for rigid body vibrations without assuming knowledge of the origin of the mean square rotational tensor ω. The latter author gives preliminary results for azulene. As mentioned above, there is difficulty in assigning atomic coordinates for a single molecule; there are in fact eight possibilities described in detail by Robertson et al. All eight were analysed by this least-squares rigid-body method. Two gave equally good results, and the other six were much poorer. This suggested that the choice was reduced to two, the molecule of Robertson et al., and the molecule with all ambiguous pairs interchanged. The latter molecule

had insignificantly poorer bond lengths, whereas the other six were again much poorer. The two 'possible' molecules had identical planarity, or aplanarity, while the remaining six were all more planar. It was therefore thought that the choice of the correct molecule was not certain.

Rigid body refinement

The crystal structure refinement procedure described by Pawley (1964) has been applied to azulene. The parameters varied were the scale factor, the six components of both T and ω, the origin of ω and the thirty position parameters for the carbon atoms. Hydrogen atoms were repositioned at the end of each cycle 1·09 Å from their bonded carbon atoms away from the centre of the appropriate ring. During the course of refinement the customary R index varied quite rapidly:

Before cycle	R (%)	
1	999·0	(scale factor blunder)
2	31·0	
3	9·3	
4	7·7	
5	7·1	
6, 7, 8	6·9	

with the final R value of 6·9% corresponding to 6·5% without unobservables. This is identical with the final R value obtained by Robertson et al. The largest shift of any parameter in the last cycle was 0·1 e.s.d., and refinement was thought to be complete. It was previously thought that R would be somewhat larger than 6·5% owing to the parameter constraints, but this only applies if the constraints represent approximations which are not entirely valid for the measurements under investigation.

The advantages of the rigid body refinement are:

(a) Reduction of computer time (each cycle took less than $\frac{1}{2}$ min on the IBM 7090).

(b) Fewer cycles necessary.

(c) More accurate tensors T and ω.

(d) Removal of positional and thermal parameter interactions.

(e) Removal of close pair ambiguity.

The last arises from the fact that as the origin of ω is allowed to vary, the temperature factors for any atom depend on its relationship to this origin, and therefore

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to its position in the molecule. The method requires all the atoms to belong to the same molecule so that no choice of molecule is necessary after refinement is complete. The molecule resulting from the refinement has the coordinates of Table 1, anisotropic temperature factors of Table 2, and bond lengths and angles as in

Table 1. *Final carbon fractional coordinates and their average errors*

	x/a	y/b	z/c	σ
A	0·1443	0·0406	0·3394	0·011 Å
B	0·1670	0·2089	0·2062	0·019
C	0·0682	0·1185	0·0493	0·004
D	0·0530	0·2298	−0·1082	0·004
E	−0·0356	0·1611	−0·2735	0·014
F	−0·1370	−0·0318	−0·3126	0·013
G	−0·1621	−0·1940	−0·2150	0·022
H	−0·1099	−0·2362	−0·0323	0·004
I	−0·0075	−0·0985	0·0854	0·004
J	0·0472	−0·1382	0·2624	0·013

Fig. 1. The mean-square translational and rotational tensors and their errors were

$$\mathbf{T} = \begin{bmatrix} 4\cdot48 & 0\cdot23 & 0\cdot07 \\ & 4\cdot43 & -0\cdot13 \\ & & 6\cdot33 \end{bmatrix} \qquad \sigma(\mathbf{T}) = \begin{bmatrix} 0\cdot15 & 0\cdot08 & 0\cdot09 \\ & 0\cdot09 & 0\cdot10 \\ & & 0\cdot09 \end{bmatrix}$$
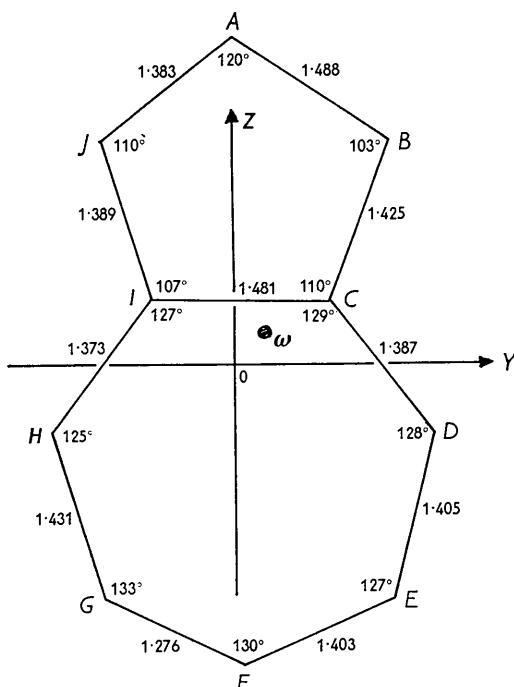

Fig. 1. The azulene molecule, showing the origin of the tensor ω. The shaded area gives the error. The inertia axes Y and Z intersect at O, which is almost coincident with the crystal-symmetry centre. Bond lengths and angles are included.

Table 2. *Final carbon anisotropic temperature factors; from* $\exp\left(-10^{-4}\sum_{ij} h_i h_j b_{ij}\right)$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
A	233	495	212	−6	40	34
B	192	332	253	−55	42	−9
C	166	236	217	−3	55	2
D	194	282	250	42	75	16
E	240	472	223	57	64	48
F	245	554	225	−51	26	25
G	218	414	293	−105	34	−20
H	192	258	311	−32	68	−20
I	174	242	232	13	63	6
J	221	376	243	69	75	37

in units of 10^{-2} Å^2, and

$$\omega = \begin{bmatrix} 27\cdot0 & 2\cdot8 & 2\cdot7 \\ & 13\cdot1 & 0\cdot0 \\ & & 8\cdot7 \end{bmatrix} \qquad \sigma(\omega) = \begin{bmatrix} 0\cdot8 & 0\cdot7 & 1\cdot6 \\ & 0\cdot8 & 0\cdot6 \\ & & 2\cdot6 \end{bmatrix}$$

in (degrees)^2. Fig. 1 shows the final centre of ω, which is displaced $-0\cdot03 \pm 0\cdot14$ Å from the molecule plane.

Conclusion

Very little of significance can be obtained from this analysis. The molecule deduced by Robertson et al. had atomic positions closest to those of Table 1, though many discrepancies far exceed the standard deviations for the statistically close pairs. The interactions between the positional coordinates of these pairs is still of course very high, much higher than any interaction with a thermal parameter. Although these latter interactions have been removed, the former still invalidate the bond length results involving these atoms.

The coordinates of the origin of ω bear no resemblance to those obtained for any of the eight previously possible molecules. However as the interactions of these parameters with the others was not high, the present results are thought to be significant. Libration occurs about a point in the plane of the molecule $0\cdot35 \pm 0\cdot07$ Å from the centre of gravity of the molecule and the crystal symmetry centre, which are nearly coincident.

The ordered structure in the space group Pa failed to refine below 24%, once more confirming the disordered structure.

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