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The Crystal and Molecular Structure of Azulene

By J. Monteath Robertson, H. M. M. Shearer, G. A. Sim and D. G. Watson
Chemistry Department, The University, Glasgow, W. 2, Scotland

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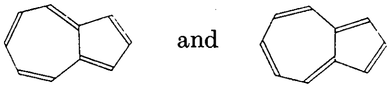
Azulene crystallizes in the monoclinic system with two molecules in a unit cell of dimensions

$$a = 7{\cdot}884,\ b = 5{\cdot}988,\ c = 7{\cdot}840\ \text{Å},\ \beta = 101°\ 33'.$$

The systematic absences indicate that the space group is $P2_1/a$ and, since the azulene molecule is not centrosymmetrical, this implies that the crystal structure is disordered. Attempts to surmount this difficulty by assuming that the space group is Pa and the $0k0$ halvings accidental led to an ordered crystal structure with reasonable agreement between calculated and observed structure amplitudes in the three principal zones. However difficulties were encountered in a three-dimensional refinement and the ordered structure based on Pa had to be rejected as incorrect. With a disordered crystal structure (space group $P2_1/a$) in which successive azulene molecules are subject to random reversal of direction satisfactory refinement was obtained and this structure must be essentially correct. Because of the close overlap of atoms the molecular dimensions obtained are of only limited accuracy, except possibly for the transannular bond which, at 1·483 Å, appears to be rather longer than the other bonds in the molecule.

1. Introduction

Azulene, $C_{10}H_8$, is an interesting hydrocarbon with aromatic properties. Its structure was first elucidated by Pfau & Plattner (1936) and has been generally represented by two Kekulé-type formulae,



A previous crystallographic investigation of azulene (Günthard, Plattner & Brandenberger, 1948) showed that the apparent space group is $P2_1/a$ (C_{2h}^5) with two molecules in the unit cell. As the azulene molecule is non-centrosymmetric, however, it follows that either the crystal structure is disordered or the absent spectra leading to the deduction of the space group $P2_1/a$ are accidental, the true space group being of lower symmetry. These alternatives have been discussed by Günthard (1949) who later showed (Günthard, 1955) that a comparison of the entropies of azulene and naphthalene provides support for the possibility of disorder in the azulene crystal.

Nevertheless, when the crystal structure of azulene was studied by Robertson & Shearer (1956) an ordered arrangement of molecules in the non-centrosymmetric space group Pa was deduced. The two molecules were placed with respect to the glide plane in such a way as to create an almost exact halving of the $0k0$ spectra and apparently satisfactory agreement was obtained between observed and calculated structure amplitudes in all the principal zones. Moreover when the N(z) statistical test (Howells, Phillips & Rogers, 1950) was applied to the $h0l$ reflexions an acentric distribution of intensities was indicated.

Further support for an ordered crystal structure based on Pa was provided at about the same time by an examination of the morphology of azulene crystals (Bernal, 1956) and by an independent crystal-structure analysis of azulene by Takeuchi & Pepinsky (1956). In the latter investigation satisfactory agreement between calculated and observed structure amplitudes was obtained for an ordered crystal structure almost identical with that proposed by Robertson & Shearer, whereas distinctly poorer agreement was obtained when disordered structures based on $P2_1/a$ were tested.

In spite of this, subsequent refinement by us of the ordered structure using full three-dimensional intensity data proved disappointing and even after a number of cycles of least-squares adjustment of positional and isotropic temperature parameters the discrepancy factor R could not be reduced below 0·224. This led us to re-examine the possibility that the space group might after all be $P2_1/a$, as indicated by the halvings, and the structure centrosymmetric and disordered. On this basis further refinement did indeed prove possible (Robertson, Shearer, Sim & Watson, 1958; Watson, 1959) and it must be concluded that the crystal structure is disordered as postulated earlier by Günthard.

2. Crystal data

Azulene, $C_{10}H_8$; M, 120·1; m.p. 99 °C.; d, calc. 1·174, found 1·175 g.cm.$^{-3}$.

Monoclinic,

$$a = 7{\cdot}884 \pm 0{\cdot}008,\ b = 5{\cdot}988 \pm 0{\cdot}008,\ c = 7{\cdot}840 \pm 0{\cdot}008\ \text{Å},\ \beta = 101°\ 33' \pm 20'.$$

Absent spectra, $h0l$ when h is odd; $0k0$ when k is odd.
Space group, $P2_1/a$ (C^5_{2h}).
Two molecules per unit cell.
Volume of unit cell, 362·6 Å^3.
Absorption coefficient for X-rays,

$$\lambda = 1{\cdot}542 \text{ Å}, \ \mu = 6{\cdot}06 \text{ cm.}^{-1}$$
$$F(000) = 136 \ .$$

From methanol diamond-shaped plates are obtained. The {110} and {001} faces are well developed and the a and b axes lie along the diagonals of the plate.

3. Experimental

Rotation, oscillation and moving-film photographic methods were used, with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). The unit-cell parameters were calculated from equatorial layer line Weissenberg photographs calibrated with sodium chloride powder lines. Two independent observers made the three-dimensional intensity survey by the visual estimation of reflexions on multiple-film (Robertson, 1943) equi-inclination Weissenberg photographs. The layer lines recorded and the dimensions of the crystals used are given in Table 1.

Table 1. *Layer lines recorded and dimensions of crystals used*

Layer lines	Cross-section × length along rotation axis (mm.)
$(0kl)-(5kl)$	0·66 × 0·69 × 0·82
$(h0l)-(h3l)$	0·48 × 0·51 × 0·80
$(hk0)-(hk5)$	0·63 × 0·66 × 0·54
$(hhl)-(h, h+5, l)$	0·60 × 0·66 × 1·02
$(0kl)-(2kl)$	0·16 × 0·12 × 0·51
$(h0l)-(h2l)$	0·18 × 0·18 × 0·54

The intensities of strong spectra were derived from small crystals rotated about the [100] and [010] axes and previously dipped in liquid air to reduce the effects of extinction. The intensities were corrected for Lorentz, polarization, and the rotation factors appropriate to upper layers (Tunell, 1939). Absorption corrections were obtained by calculating the mean path length for the ray through the crystal (Albrecht, 1939). Common reflexions in the different zones and layer lines served to correlate the data. In all 670 independent reflexions were measured. The standard deviation in structure amplitude for reflexions observed more than once was found to be approximately a constant percentage of the structure amplitude, with $\sigma(|F|) \approx 0{\cdot}07|F|$. A list of the observed $|F|$ values and the values calculated from the final coordinates is given in Table 14.

4. Structure determination

(*a*) *Ordered structure based on Pa*

Since the space group ($P2_1/a$) indicated by the systematic absences requires a disordered crystal structure it appeared desirable initially to investigate the possibility that the $0k0$ absences are accidental and that the true space group is Pa. As a first step the $N(z)$ statistical test (Howells, Phillips & Rogers, 1950) was applied to the $h0l$ spectra and the results suggested that the projection of the structure on (010) is non-centrosymmetrical. Accordingly a trial structure based on the chemical formula was postulated in which the two molecules were placed with respect to the glide plane in such a way that an almost exact halving of the $0k0$ planes was obtained. Good agreement was soon obtained between calculated and observed structure amplitudes for all the $h0l$ reflexions and further refinement of the atomic positions by Fourier and difference Fourier syntheses reduced the value of R for this zone to 0·11. The other zones also gave reasonable agreements and the ordered crystal structure appeared substantiated (Robertson & Shearer, 1956).

An electron-density projection of the structure on (010), based on these calculations for an ordered arrangement of molecules in Pa, is shown in Fig. 2(*a*).

After some further refinement by generalized projections, structure factors were calculated for all the 670 observed hkl reflexions. The value of R was 0·234. A least-squares refinement employing the three-dimensional data was then attempted with the help of Prof. R. Pepinsky and Dr V. Vand but after three cycles of calculations the value of R only decreased to 0·224 and it was obvious that there was something fundamentally wrong with the postulated crystal structure.

(*b*) *Disordered structure based on $P2_1/a$*

As the ordered crystal structure based on Pa could not be refined successfully the possibility was examined that the space group might after all be $P2_1/a$, as indicated by the systematic absences. The low value of R obtained for the $h0l$ data during the refinement of the ordered structure suggested that the orientation of the molecule must be essentially correct. Consequently the atomic coordinates deduced previously were referred to a new origin at the centre of the molecule which was taken to coincide with a centre of symmetry in $P2_1/a$, and the atoms were given half weight. This procedure postulates the superposition of two molecules, one in the original orientation and the other in the orientation related to this by inversion through the symmetry centre, and corresponds physically to a simple random reversal of direction of successive azulene molecules in the crystal. The resulting superposition of two molecules is illustrated in Fig. 1.

Structure factors for all the observed reflexions were calculated at the National Physical Laboratory and the resulting values of the discrepancy factor R compared (Table 2) with the values appropriate to the non-centrosymmetrical structure. The improvement was encouraging and further detailed refinement

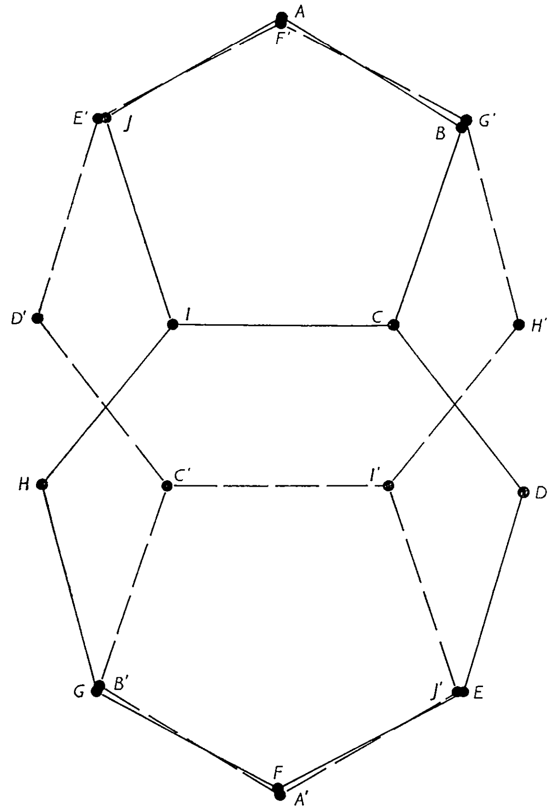


Fig. 1. Superposition of two azulene molecules.

(see below) soon proved that the centrosymmetrical model is essentially correct.

The disorder is of the same type as found in *p*-chlorobromobenzene (Hendricks, 1933; Klug, 1947) where the space group ($P2_1/a$) demands a centrosymmetrical molecule, and is also similar to that reported in 2-amino-4-methyl-6-chloropyrimidine (Clews & Cochran, 1948), though no space-group requirement is involved in this case. Other similar examples of disorder are provided by di-indenyliron (Trotter, 1958) and acepleiadylene (Hanson, 1960).

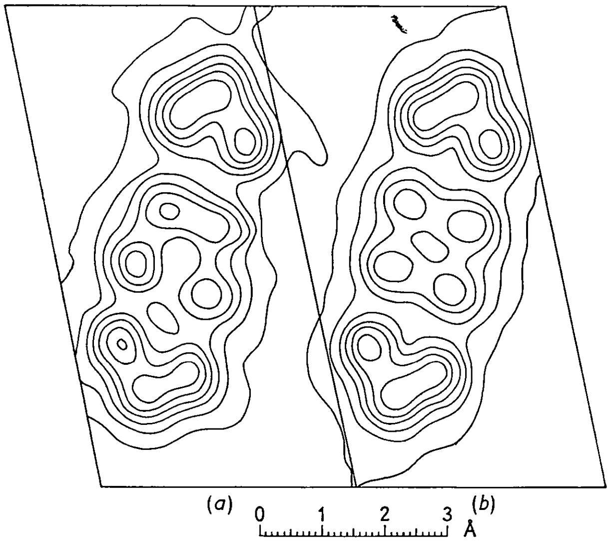


Fig. 2. Electron density projections on (010).

(*a*) Ordered structure in space group $P2a$.
(*b*) Disordered structure in space group $P2_1/a$.

Table 2. *Comparison of discrepancy factors* (R) *for space groups* $P2_1/a$ *and* Pa

	$P2_1/a$	Pa
$0kl$	0·149	0·200
$h0l$	0·102	0·115
$hk0$	0·181	0·142
hkl	0·204	0·224

An electron-density projection on (010) for the revised structure is shown in Fig. 2(*b*). The strong similarity between this and the electron-density projection shown in Fig. 2(*a*) is very marked and accounts for the good structure-factor agreement obtained for the non-centrosymmetrical ordered structure.

5. Intensity statistics

Before detailed refinement of the atomic positions and thermal vibrations was attempted various statistical tests were applied to the azulene intensities in an effort to obtain independent evidence in support of the disordered structure.

The $N(z)$ test of Howells *et al.* (1950) was found to give indeterminate results when its application to the $h0l$ data was reinvestigated (Watson, 1959). This is clearly a consequence of the limited number of data available for this zone (71 reflexions), necessitating the choice of rather large ranges of sin θ and introducing large sampling errors. When applied to some 423 three-dimensional data, however, the results agreed closely with the centric ${}_{\bar{1}}N(z)$ distribution of Howells *et al.* An even more conclusive indication of centrosymmetry was obtained when the theoretical $N(z)$ curves of Howells *et al.* were replaced by distributions based on values of $|F_c|^2$ for the alternative structures (Sim, 1960).

Supporting evidence resulted from the application of the variance test (Wilson, 1951) to the three-dimensional data. The experimental specific variance, 2·2, is slightly higher than the theoretical value, 2·0, for a centrosymmetric structure but this can be attributed to the random errors in the intensities.

6. Structure refinement

(*a*) *Isotropic diagonal least-squares refinement*

The first stage of the refinement process was performed for us by Prof. R. Pepinsky using the IBM 704 programme NY XRI. Unobserved reflexions were excluded from the analysis, so that 670 observational equations were available for the formation of the matrix of normal equations. Hydrogen atoms were included in the structure-factor calculations but refinement of positional parameters was confined to the carbon atoms. Individual isotropic temperature factors and the overall scale factor were also adjusted.

Eight cycles of least-squares analysis were carried out and the value of R fell from 0·210 to 0·135. The coordinates obtained are given in Table 3(a) and the corresponding bond lengths in Table 4(a).

(b) *Anisotropic block diagonal least-squares refinement*

When the Glasgow University DEUCE computer became available in 1958 a least-squares programme (Rollett, 1961) was used to obtain improved positional coordinates and anisotropic temperature factors. In this analysis 70 unobserved terms were included, each with a value equal to one-half of the minimum $|F|$ locally observable. Hydrogen contributions were included but only the parameters of the carbon atoms were refined. The weighting system employed was as follows:

$$|F_o| \le 8|F_{\text{min.}}|\,, \quad \sqrt{w} = |F_o|/8|F_{\text{min.}}|$$
$$|F_o| > 8|F_{\text{min.}}|\,, \quad \sqrt{w} = 8|F_{\text{min.}}|/|F_o|\,.$$

It would in theory be more correct to assign a separate weighting system to the unobserved reflexions but as they represent only 9% of the total data the above weighting system was applied to all the data. The atomic form factors employed in the structure-factor calculations were those of Berghuis *et al.* (1955) for carbon and those of McWeeny (1952) for hydrogen.

After seven rounds of calculations the bond lengths were examined and found to be rather irregular. Small shifts were then applied to atoms H and J in an effort to improve the situation. The revised atomic coordinates were then used as the starting point for further refinement and an additional five rounds of calculations reduced the value of R to 0·093. The coordinates and bond lengths obtained at this stage are shown in Tables 3(b) and 4(b) respectively.

(c) *Anisotropic full-matrix least-squares refinement*

The validity of applying least-squares programmes that neglect all or most of the off-diagonal terms is open to question in the case of a disordered crystal structure such as azulene where some of the effective interatomic distances are extremely small (compare Fig. 1). Accordingly we arranged for a number of cycles of refinement to be performed on the Oxford University MERCURY computer by Dr R. A. Sparks using his full-matrix least-squares programme. Three positional and six thermal parameters for each carbon atom and an overall scale factor, i.e. 91 parameters in all, were refined, the starting point being the results given by the isotropic diagonal least-squares refinement. The weighting system employed was

$$|F_o| \le 4|F_{\text{min.}}|\,, \quad \sqrt{w} = |F_o|/4|F_{\text{min.}}|$$
$$|F_o| > 4|F_{\text{min.}}|\,, \quad \sqrt{w} = 4|F_{\text{min.}}|/|F_o|\,.$$

After six rounds of calculations the hydrogen positions were adjusted to place the hydrogen atoms radially at 1·08 Å from the carbon atoms to which they are covalently bonded. Two further cycles of refinement were then carried out. The course of refinement is indicated in Table 5: the final value of R is 0·065. The calculations would have been terminated at cycle 4 but for the fact that the positional parameters were still showing shifts as large as 0·022 Å.

At this stage it is interesting to note that although the refinement process had apparently ceased when R reached 0·093 in the case of the anisotropic block diagonal least-squares method **6**(b), yet on application of the full matrix method the refinement process converged further to a value of R of 0·065. It would appear that the block diagonal treatment has led to an apparent solution which does not in fact represent the true minimum of R.

7. Coordinates and molecular dimensions

The final coordinates of the carbon atoms and the final anisotropic temperature-factor parameters are shown in Tables 3(c) and 6, respectively. The final bond lengths with their estimated standard deviations calculated from the full inverse matrix are given in Table 4(c). The final valency angles in the molecule are shown in Table 7. The deviations of the carbon atoms from the mean molecular plane, derived by the

Table 3. *Atomic coordinates*

(a) Isotropic diagonal least-squares method. (b) Anisotropic block-diagonal least-squares method.
(c) Anisotropic full matrix least-squares method

	(a)			(b)			(c)		
Atom	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
A	0·1396	0·0373	0·3273	0·1396	0·0367	0·3278	0·1438	0·0532	0·3300
B	0·1633	0·2021	0·2069	0·1628	0·2026	0·2076	0·1607	0·2036	0·2039
C	0·0683	0·1159	0·0500	0·0678	0·1153	0·0499	0·0682	0·1179	0·0500
D	0·0529	0·2294	−0·1096	0·0524	0·2279	−0·1080	0·0524	0·2301	−0·1083
E	−0·0372	0·1516	−0·2681	−0·0380	0·1515	−0·2697	−0·0303	0·1533	−0·2628
F	−0·1386	−0·0342	−0·3210	−0·1389	−0·0336	−0·3224	−0·1343	−0·0183	−0·3212
G	−0·1677	−0·2003	−0·2129	−0·1664	−0·2003	−0·2135	−0·1697	−0·1995	−0·2163
H	−0·1115	−0·2373	−0·0323	−0·1095	−0·2356	−0·0336	−0·1096	−0·2362	−0·0325
I	−0·0090	−0·0964	0·0838	−0·0084	−0·0976	0·0843	−0·0078	−0·0996	0·0856
J	0·0448	−0·1450	0·2675	0·0452	−0·1447	0·2648	0·0520	−0·1460	0·2705

Table 4. *Bond lengths*

(*a*) Isotropic diagonal least-squares method
(*b*) Anisotropic block-diagonal least-squares method
(*c*) Anisotropic full matrix least-squares method

	(*a*)	(*b*)	(*c*)
A–B	1·404 Å	1·406 Å	1·363 ± 0·027 Å
B–C	1·405	1·411	1·378 ± 0·019
C–D	1·407	1·394	1·395 ± 0·005
D–E	1·383	1·401	1·337 ± 0·034
E–F	1·384	1·379	1·337 ± 0·035
F–G	1·356	1·359	1·422 ± 0·026
G–H	1·414	1·408	1·440 ± 0·021
H–I	1·378	1·370	1·369 ± 0·007
I–J	1·447	1·422	1·459 ± 0·024
J–A	1·353	1·352	1·425 ± 0·032
C–I	1·457	1·457	1·483 ± 0·004

Table 5. *Course of refinement with full matrix least-squares method*

Cycle	R	$\Sigma w\Delta^2$
1	0·128	40·4
2	0·111	25·7
3	0·069	7·29
4	0·062	5·76
5	0·062	5·67
6	0·062	5·60
7	0·076	8·08
8	0·065	5·56

Table 6. *Final thermal parameters for carbon atoms*

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
A	0·0189	0·0490	0·0290	−0·0074	−0·0158	0·0121
B	0·0204	0·0265	0·0296	−0·0069	−0·0109	0·0058
C	0·0149	0·0229	0·0224	−0·0009	0·0002	0·0108
D	0·0198	0·0268	0·0250	0·0004	0·0060	0·0147
E	0·0199	0·0607	0·0244	0·0032	0·0097	0·0121
F	0·0286	0·0504	0·0172	0·0209	−0·0010	0·0039
G	0·0178	0·0574	0·0218	0·0018	−0·0222	0·0070
H	0·0182	0·0271	0·0288	−0·0011	−0·0046	0·0120
I	0·0164	0·0256	0·0220	0·0019	0·0027	0·0119
J	0·0205	0·0332	0·0204	0·0114	0·0081	0·0088

The temperature factor is expressed in the form
$\exp -(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl)$

Table 7. *Valency angles in the azulene molecule*

∠ *A–B–C*	106·1°	∠ *F–G–H*	129·2°
B–C–I	109·0	*G–H–I*	128·1
I–C–D	128·5	*H–I–C*	127·0
C–D–E	125·5	*C–I–J*	107·0
D–E–F	136·8	*I–J–A*	102·0
E–F–G	124·5	*J–A–B*	115·6

Table 8. *Deviations of carbon atoms from the mean molecular plane*

Atom	Deviation	Atom	Deviation
A	−0·037 Å	*F*	−0·022 Å
B	−0·013	*G*	−0·029
C	0·001	*H*	0·001
D	−0·007	*I*	0·001
E	0·051	*J*	0·054

method of Schomaker *et al.* (1959), are listed in Table 8.

8. Analysis of thermal motion

The vibrations of an atom in an anisotropic harmonic potential field may be represented by a symmetric tensor **U**, such that the mean square amplitude of vibration $\overline{u^2}$ in the direction of a unit vector **l** with components l_i is given by

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j \, .$$

In terms of rigid-body vibrations the motion of the molecule may be expressed as two symmetric tensors **T** and **ω**, each with six independent components (Cruickshank, 1956). **T** represents the translational vibrations of the mass centre and **ω** the angular oscillations about the centre.

For azulene molecular axes were chosen with OX_m through atoms *A* and *F*, OY_m perpendicular to OX_m and in the plane of the molecule, and OZ_m perpendicular to both OX_m and OY_m. The six independent U_{ij} values for each carbon atom, derived from the anisotropic temperature-factor parameters of Table 6 and referred to the molecular axes, are shown in Table 9 in the columns headed 'obs.'. The **T** and **ω** tensors are shown in Table 10; taking the square roots of the diagonal terms we find that the r.m.s. amplitudes of translational vibration in the directions of the molecular axes and the r.m.s. amplitudes of angular oscillation about the molecular axes are

along OX_m	0·26 Å	about OX_m	4·1°
along OY_m	0·21 Å	about OY_m	3·7°
along OZ_m	0·18 Å	about OZ_m	5·3°.

From the **T** and **ω** tensors the **U** tensor for each

Table 9. *Observed and calculated values of* U_{ij}
(In units of 10^{-2} Å^2)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{23}		U_{13}	
Atom	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	8·59	6·54	8·12	10·42	5·70	6·19	1·65	0·35	1·97	0·90	0·90	0·54
B	8·44	7·78	5·16	7·43	6·14	5·57	1·78	2·01	−0·37	0·46	0·21	0·56
C	6·95	7·02	3·89	4·81	3·68	3·79	0·12	0·46	0·40	0·36	0·27	0·47
D	8·07	8·76	4·39	4·83	4·61	4·83	−0·69	−0·65	0·41	0·45	0·44	0·21
E	7·88	7·84	9·32	7·46	6·20	5·50	−1·46	−1·82	2·64	0·84	−0·22	0·22
F	5·46	6·54	10·94	9·98	6·64	5·97	−1·18	−0·10	−1·11	0·90	0·57	0·43
G	6·26	7·74	10·56	7·74	5·16	5·71	1·70	2·07	1·72	0·51	1·07	0·54
H	8·70	7·75	4·99	4·82	4·47	4·25	0·75	0·67	0·21	0·34	0·39	0·43
I	7·00	6·99	4·42	4·82	3·78	3·75	−0·35	−0·21	0·40	0·42	0·33	0·41
J	6·57	7·66	6·45	7·74	4·70	5·53	−1·29	−1·77	−0·27	0·80	0·18	0·16

atom was calculated. The values of U_{ij} so derived are listed in Table 9 in the columns headed 'calc.'. The r.m.s. difference between the $U_{ij}^{\text{obs.}}$ and $U_{ij}^{\text{calc.}}$ values is 0·0105 Å^2, corresponding to an estimated standard deviation for the $U_{ij}^{\text{obs.}}$ of 0·0107 Å^2. The corresponding estimated standard deviations of the T_{ij} and ω_{ij} values are shown in Table 11.

The values of the **T** and **ω** tensors are rather similar to those of naphthalene (Cruickshank, 1957*a*), where the r.m.s. amplitudes of translational vibration in the directions of the molecular axes are 0·22, 0·20 and 0·19 Å and the r.m.s. amplitudes of angular oscillation about the molecular axes are 4·4°, 3·7° and 4·2°. In azulene as in naphthalene and anthracene (Cruickshank, 1957*b*) the greatest amplitude of translational vibration is along the long axis of the molecule.

Table 10. *Values of T_{ij} and ω_{ij}*

(T_{ij} in 10^{-2} Å^2 and ω_{ij} in deg.^{2})

$$\mathbf{T}=\begin{bmatrix} 6\cdot53 & 0\cdot12 & 0\cdot48 \\ & 4\cdot57 & 0\cdot37 \\ & & 3\cdot37 \end{bmatrix} \qquad \boldsymbol{\omega}=\begin{bmatrix} 17\cdot10 & 0\cdot45 & 2\cdot46 \\ & 13\cdot40 & -2\cdot63 \\ & & 27\cdot83 \end{bmatrix}$$

Table 11. *Values of $\sigma(T_{ij})$ and $\sigma(\omega_{ij})$*

($\sigma(T_{ij})$ in 10^{-2} Å^2 and $\sigma(\omega_{ij})$ in deg.^{2})

$$\sigma(\mathbf{T})=\begin{bmatrix} 0\cdot36 & 0\cdot34 & 0\cdot40 \\ & 0\cdot48 & 0\cdot48 \\ & & 0\cdot96 \end{bmatrix} \qquad \sigma(\boldsymbol{\omega})=\begin{bmatrix} 4\cdot10 & 1\cdot94 & 2\cdot57 \\ & 2\cdot32 & 1\cdot99 \\ & & 1\cdot95 \end{bmatrix}$$

9. Discussion

Because of the disorder in the crystal structure the overlap of atoms is very marked, the actual distances of separation for the various atom pairs being

$A\cdots F'$	0·228 Å		
$B\cdots G'$	0·111 Å	$D\cdots I'$	0·890 Å
$C\cdots H'$	0·803 Å	$E\cdots J'$	0·175 Å .

In an ordered crystal structure the molecular geometry can be settled in a perfectly unambiguous manner when the coordinates of the atoms are known, for there is a clear distinction between distances involving directly bonded atoms and those involving non-bonded atoms. In a disordered structure such as the present, on the other hand, where atom sites are separated by only a few tenths of an Ångström unit, the choice of the correct set of atoms to define the molecule may be difficult. In azulene, with three pairs of closely overlapping atoms, eight possible molecules,

ABCDEFGHIJ, *AG'CDEFB'HIJ*, *F'BCDJ'A'GHIE'*, etc.,

can be selected from the coordinates shown in Table 3(*c*) and the centrosymmetrically related set. A scrutiny of the bond lengths corresponding to the various possibilities indicated that the most acceptable molecule comprises the atoms *ABCDEFGHIJ*.

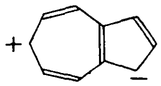
The atoms least affected by the overlap are *C*, *D*, *I* and *H*. As would be expected these are also the atoms showing the smallest displacements from the mean molecular plane (Table 8) and the atoms which yield bond lengths with smallest estimated standard deviations (Table 4(*c*)). In particular the transannular bond *CI* involving the two atoms most free from overlap has an e.s.d. of only 0·004 Å.

On the assumption that the symmetry of the azulene molecule is C_{2v}, weighted average lengths for the equivalent bonds were calculated from the data in Table 4(*c*) and are shown, with their estimated standard deviations, in Table 12. The transannular carbon–carbon bond (1·483 Å) is distinctly longer than the other carbon–carbon bonds which, at 1·383–1·413 Å, conform to the lengths generally found in aromatic compounds. In 2-amino-azulene (Takaki, Sasada & Nitta, 1959) a similar pattern is observed, the central carbon–carbon bond having a length of 1·52 Å while the other carbon–carbon bonds range from 1·37–1·41 Å.

Table 12. *Weighted average bond lengths and their estimated standard deviations*

A–B	1·391 ± 0·021 Å
B–C	1·413 ± 0·015
C–D	1·383 ± 0·004
D–E	1·401 ± 0·018
E–F	1·385 ± 0·021
C–I	1·483 ± 0·004

Theoretical studies of the azulene molecule by the method of molecular orbitals have been reported by, among others, Estelles & Alonso (1952) and Brown (1948). The results obtained by the latter are in agreement with those to be expected on the basis of the two Kekulé structures shown earlier, these being the most important forms with, in addition, a small contribution from dipolar forms such as



to account for the dipole moment of 1·0D measured by Wheland & Mann (1949). Accordingly the carbon–

Table 13. *The shorter intermolecular contacts*

$H\cdots D^{I}$	3·54 Å	$F\cdots J^{IV}$	3·85 Å
$H\cdots H^{II}$	3·59	$F\cdots A_{IV}$	3·86
$J\cdots D^{III}$	3·68	$G\cdots D^{I}$	3·86
$I\cdots D^{III}$	3·71	$A\cdots A^{V}$	3·88
$C\cdots D^{III}$	3·75	$E\cdots B^{III}$	3·92
$E\cdots A^{IV}$	3·76	$J\cdots E^{III}$	3·97
$A\cdots D^{III}$	3·77	$J\cdots A^{VI}$	3·97
$B\cdots D^{III}$	3·80	$A\cdots E^{III}$	3·99
$A\cdots J^{V}$	3·80		

The superscripts refer to the positions

I	x	$y-1$	z
II	$-x$	$-1-y$	$-z$
III	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$-z$
IV	x	y	$z-1$
V	$-x$	$-y$	$1-z$
VI	$\frac{1}{2}-x$	$y-\frac{1}{2}$	$1-z$

Table 14. *Measured and calculated structure factors*

h	k	ℓ	$10F_o$	$10F_c$
0	0	1	300	303
		2	140	-141
		3	198	200
		4	76	77
		5	59	-57
		6	30	-26
		7	23	-22
		8	13	-13
		9	06	06
2	0	-9	13	-13
		-8	11	11
		-7	56	52
		-6	18	-18
		-5	41	-36
		-4	69	60
		-3	40	-39
		-2	40	-30
		-1	565	570
		0	240	242
		1	180	-182
		2	108	109
		3	143	144
		4	54	-55
		5	95	-96
		6	71	-72
		7	25	-24
		8	07	07
		9	10	-07
4	0	-8	52	54
		-7	12	12
		-6	56	-58
		-5	21	20
		-4	53	50
		-3	75	-76
		-2	37	-32
		-1	38	-35
		0	64	-60
		1	43	40
		2	42	40
		3	32	-33
		4	51	-49
		5	54	-52
		6	28	-28
		8	11	-09
6	0	-9	18	19
		-8	12	12
		-7	31	-31
		-5	40	41
		-4	22	-24
		-3	74	-75
		-2	78	-79
		-1	29	-22
		0	49	43
		1	12	-13
		2	42	-41
		3	11	11
		4	10	-10
		5	17	14
8	0	-6	10	09
		-5	07	-06
		-4	22	-22
		-3	29	-28
		-2	12	-11
		-1	32	27
		0	05	-07
		1	37	-35
		2	19	18
		3	31	28
10	0	-2	07	04
0	1	1	07	-07
		2	25	-24
		3	33	32
		4	63	57
		5	14	-13
		6	76	-77
		7	51	-50
1	1	-8	17	-16
		-7	12	11
		-6	18	-16
		-5	55	-56
		-4	76	77
		-3	82	82
		-2	162	-164
		-1	276	278
		0	432	437
		1	134	-135
		2	03	06
		3	99	100
		4	29	-28
		5	51	-46
		6	14	-14
		7	23	-22
2	1	-9	06	-06
		-8	22	24
		-7	53	56
		-6	13	12
		-5	56	-56
		-4	20	-18
		-3	70	71
		-2	96	-97
		-1	478	-483
		0	305	-308
		1	65	65
		2	07	06
		3	40	-40
		4	03	-04
		5	11	-11
		6	24	-22
		9	10	-09
3	1	-9	12	-12
		-8	16	17
		-7	17	18
3	1	-6	46	-45
		-5	06	06
		-4	74	75
		-3	58	-58
		-2	37	33
		-1	195	197
		0	20	-24
		2	70	71
		3	08	-10
		4	37	-37
		5	20	-20
		6	30	-30
4	1	-6	15	-15
		-4	31	33
		-3	21	-24
		-2	186	-187
		-1	179	-181
		0	41	42
		1	33	33
		2	82	-82
		3	19	-19
		4	54	57
		5	36	36
		6	07	09
5	1	-9	07	06
		-8	21	24
		-7	15	-16
		-6	18	-19
		-5	35	31
		-4	08	-06
		-3	31	-31
		-2	28	25
		-1	15	-16
		0	14	13
		1	38	34
		2	21	-20
		3	18	-17
		5	23	-22
		6	10	-11
6	1	-9	07	-11
		-8	06	-08
		-7	05	08
		-5	10	-09
		-3	13	-13
		-2	33	-32
		-1	16	15
		0	24	25
		1	36	-36
		2	21	-21
		3	43	46
		4	43	45
		5	11	10
		6	03	01
7	1	-7	11	-11
		-4	21	-21
		-3	14	-14
		-2	21	-21
		-1	07	05
		0	14	18
		1	22	-21
		2	11	-11
		3	18	18
		4	06	-05
		5	11	-12
8	1	-6	15	-16
		-5	10	-10
		-4	20	20
		-3	20	17
		-2	04	04
		2	15	14
		3	13	13
9	1	-6	05	-06
		-5	12	-12
		-4	07	-07
		-3	14	-15
		-2	05	-06
		-1	10	10
		0	07	-09
		1	07	-06
		2	13	15
10	1	-2	05	-09
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		1	159	-161
		2	29	26
		3	88	89
		4	52	-49
		5	56	-50
		6	29	29
		7	07	04
		8	14	-13
1	2	-9	04	-05
		-8	05	05
		-7	55	51
		-6	38	35
		-5	29	-27
		-4	16	-17
		-3	37	40
		-2	07	-10
		-1	75	-76
		0	96	-97
		1	45	45
		2	18	18
		3	39	-40
		4	13	12
		5	06	06
		6	41	-42
		7	15	-15
		8	13	10
		9	04	-05
2	2	-9	05	-05
		-8	19	-18
		-7	10	-09
2	2	-6	39	-40
		-5	25	-24
		-4	82	82
		-3	16	12
		-2	106	-107
		-1	08	10
		0	54	-52
		1	10	10
		2	66	66
		3	57	-58
		4	46	-44
		5	57	61
		6	35	35
		7	12	-12
3	2	-9	05	02
		-8	20	24
		-7	31	31
		-5	30	-34
		-3	17	19
		-2	96	-97
		-1	196	-198
		0	27	-29
		1	85	86
		2	39	-43
		3	39	-43
		4	35	39
		5	14	15
		6	12	-11
		7	05	03
4	2	-9	10	-11
		-8	10	-11
		-7	14	-15
		-6	06	-05
		-5	35	32
		-4	06	-04
		-3	33	-32
		-2	109	110
		-1	91	92
		1	38	33
		2	13	-14
		3	30	-31
		4	34	39
		5	24	27
		6	13	-14
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		-8	05	06
		-7	11	11
		-6	05	-04
		-5	23	-22
		-4	06	-03
		-3	30	-29
		-2	124	-125
		-1	65	-61
		0	45	46
		1	20	-20
		2	50	-51
		3	25	28
		4	45	46
		5	07	07
6	2	-6	06	06
		-5	16	-16
		-4	21	-22
		-3	57	62
		-2	69	70
		-1	13	-07
		0	07	03
		1	16	17
		2	05	-05
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		5	19	-19
7	2	-8	03	04
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		-6	13	-14
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		-4	07	-03
		-3	22	-22
		-2	35	-35
		-1	06	-01
		1	19	-18
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		3	27	30
		4	12	13
8	2	-6	06	-07
		-5	18	-18
		-4	05	05
		-3	10	12
		-2	18	-19
		-1	09	-07
		0	16	15
		1	08	05
		3	11	-13
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		-3	11	-10
		-2	13	-11
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		2	05	09
0	3	1	21	20
		2	58	59
		3	34	-32
		4	28	-29
		5	28	27
		6	17	16
1	3	-9	05	05
		-8	08	-10
		-7	08	07
		-6	18	18
		-5	36	-33
		-4	22	-21
		-3	48	48
		-2	23	-21
		-1	104	-105
1	3	0	121	-122
		1	46	-50
		2	88	89
		3	10	-13
		4	70	-71
		5	32	34
		6	51	52
		7	08	-07
		8	06	-05
2	3	-9	04	04
		-8	06	05
		-7	05	05
		-6	07	06
		-5	15	16
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		3	40	-40
		4	34	35
		5	25	25
		6	16	-16
		8	04	04
3	3	-8	13	-13
		-7	07	-09
		-6	06	-05
		-5	07	03
		-4	07	-01
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		-2	12	-12
		-1	16	-14
		0	47	-48
		1	37	35
		2	13	13
		3	52	-56
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		5	57	61
		7	11	-12
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		-8	15	17
		-7	21	21
		-6	15	16
		-5	24	-25
		-4	39	-43
		-3	08	07
		-2	11	11
		-1	22	-24
		0	13	12
		1	05	-06
		2	21	-19
		3	22	24
		4	14	15
		5	25	-25
		6	11	-10
		7	06	07
5	3	-8	11	-12
		-6	15	15
		-5	05	-05
		-4	43	-43
		-3	15	13
		-2	68	68
		-1	08	-11
		0	21	-20
		1	20	20
		2	05	-02
		4	22	22
		6	05	-06
6	3	-8	10	12
		-7	12	11
		-6	11	-11
		-5	33	-31
		-4	14	-14
		-3	27	-26
		-2	68	-68
		-1	34	-33
		2	12	11
		3	11	11
		4	11	-11
		5	05	-03
7	3	-7	03	06
		-5	22	-22
		-3	45	47
		-2	07	07
		-1	28	-26
		0	12	12
		1	22	22
		3	05	-06
8	3	-6	07	-07
		-5	08	-07
		-4	16	-17
		-3	48	-45
		-2	33	-32
		2	08	11
		3	07	06
9	3	-4	11	13
		-3	05	05
		-2	08	-10
		0	12	13
0	4	0	04	01
		1	14	-12
		2	07	05
		3	10	-12
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		6	33	32
1	4	-8	07	07
		-7	12	-11
		-6	23	-25
		-5	21	20
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		-2	38	-37
		-1	43	51
		0	13	14
		1	16	17
		2	18	16
		3	23	-21
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		6	07	07
		7	06	-05
		8	04	-03
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		-7	20	20
		-6	24	25
		-5	12	-11
		-4	30	-30
		-3	13	-17
		-1	12	-13
		0	48	-52
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		3	13	-12
		4	07	-07
		5	22	24
		7	11	-11
3	4	-7	05	-07
		-6	16	16
		-5	26	24
		-4	38	-45
		-3	47	-51
		-2	45	46
		-1	43	40
		1	14	-15
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		5	14	-14
		6	08	-09
		7	04	05
4	4	-5	08	-09
		-4	23	-26
		-3	21	-22
		-2	18	-18
		-1	64	-64
		0	52	-54
		1	22	24
		2	18	18
		3	11	-12
		4	07	07
		5	10	12
5	4	-7	06	07
		-6	10	11
		-5	18	-17
		-4	25	-28
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6	4	-6	10	09
		-4	16	-15
		-2	20	-19
		-1	37	-36
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		1	21	19
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		-2	28	-25
		1	07	05
		2	10	11
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		-3	20	18
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		3	30	30
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		-6	23	20
		-5	16	14
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		-1	10	09
		1	39	-41
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		5	03	-04
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		-5	10	-10
		-4	12	-11
		-3	10	-10
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		1	17	-16
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		3	10	11
		6	04	02
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		0	15	-14
		2	13	13
		3	13	12
		4	04	01
5	5	-5	08	07
		-4	07	10
		-3	07	-06
		-2	25	-26
		-1	33	-31
		1	16	16
		3	05	-03
		4	10	09
6	5	-5	05	05
		-4	05	05
		-3	15	15
		-2	15	14
		-1	12	12
		0	04	-01
		2	08	10
		3	03	03
7	5	-1	04	05
		0	06	07
		1	05	-05
0	6	0	20	-22
		1	35	-37
		2	39	-37
		4	16	15
		5	06	05
1	6	-6	05	-04
		-4	05	-03
		-3	15	-14
		-2	09	09
		-1	17	18
		0	28	-29
		1	17	-18
		2	28	29
		3	18	20
		4	05	-02
		5	04	-04
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		-4	10	10
		-3	07	-09
		-2	18	-18
		-1	11	-11
		0	16	-17
		1	29	-30
		2	13	-13
		3	08	10
		4	11	12
3	6	-6	08	-09
		-5	10	09
		-4	08	09
		-3	08	06
		-2	10	10
		-1	13	-13
		0	07	-09
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4	6	-5	07	05
		-4	15	15
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		-2	04	03
		-1	07	09
		1	06	-05
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		4	06	06
5	6	-4	07	06
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6	6	-3	05	04
		-2	07	07
		-1	13	11
0	7	1	11	-12
		2	05	02
1	7	-4	13	15
		-3	16	13
		-2	06	-09
		-1	14	-14
		0	07	-07
		1	07	-05
		3	05	06
2	7	-4	05	04
		-3	17	15
		-2	28	26
		-1	16	18
		0	11	11
		1	22	19
		2	11	11
		3	05	-05
3	7	-2	04	-05
		-1	10	11
		0	11	11
		1	07	-07
		2	12	-11
4	7	-2	18	15
		-1	15	13
		0	21	21

carbon bonds, apart from the transannular bond, should have about 50% double-bond character (as in benzene) with lengths of about 1·39 Å, while the transannular bond should be predominantly single in character and distinctly longer than the others. The standard single-bond distance between carbon atoms in the sp^2 state of hybridization has been the subject of some controversy but has been estimated (Dewar

& Schmeising, 1959) as 1·479 Å, close to the values in butadiene, 1·483 Å, *p*-benzoquinone, 1·477 Å (Trotter, 1960) and benzoic acid, 1·48 Å (Sim, Robertson & Goodwin, 1955). Our estimate of 1·483 Å for the length of the transannular bond in azulene agrees closely with these values.

For the purpose of deriving the bond lengths shown in Table 12 the molecular symmetry was assumed to be C_{2v}. Nevertheless some of the differences between equivalent bonds in Table 4(*c*) are large and it is clear that the full matrix least-squares analysis has yielded a somewhat unsymmetrical molecule. Application of the χ^2 test, moreover, suggests that these differences are significant. A possible explanation would be that the centrosymmetrical relationship between the two possible orientations is not exact and that the space group is after all *Pa*, the asymmetric crystal unit consisting of two half-weight molecules free to move relative to one another. This, however, would necessitate the determination of another ninety parameters and as *R* has been reduced to a value of 0·065 on the basis of centrosymmetrical disorder (cf. the estimated standard deviation of $0{\cdot}07|F|$ in the observed structure amplitudes), it is difficult to believe that any further significant refinement is possible. The alternative, and preferable, explanation is that the standard deviations in bond lengths shown in Table 4(*c*) are underestimates and that the differences between equivalent bonds are insignificant, reflecting merely the difficulty of determining accurately positional and thermal parameters for atoms separated by only 0·1–0·2 Å. The differences between the positional parameters given by the three least-squares procedures used in this analysis (see Tables 3 and 4) emphasize the difficulty of obtaining completely satisfactory results when atomic overlap is marked. Even for the bond least affected by overlap, i.e. *CI*, there is a difference of 0·026 Å between the length given by the full matrix method and that given by the isotropic diagonal and anisotropic block-diagonal methods.

Table 13 illustrates that the disorder in the crystal structure does not lead to any unusual approach distances between molecules. The intermolecular contacts are all greater than 3·5 Å and correspond to normal van der Waals interactions.

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