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## The Crystal Structure of the Azulene, *s*-Trinitrobenzene Complex

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The crystal is monoclinic  $P2_1/a$ , with  $Z=4$ . Unit-cell constants at  $-95^\circ\text{C}$  are  $a=16.39$ ,  $b=6.66$ ,  $c=13.77$  Å,  $\beta=96.10^\circ$ . The formula is  $\text{C}_{10}\text{H}_8\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_6$ .

The structure was determined from the three-dimensional Patterson synthesis, and refined by least-squares procedures. The structure is disordered, with about 7% of the azulene molecules adopting an alternative orientation, but this disorder did not seriously limit the accuracy of the analysis.

The azulene molecule is nearly planar, but the *s*-trinitrobenzene molecule is not. The  $\text{NO}_2$  groups are twisted out of the plane of the benzene nucleus by amounts which vary, and which are probably determined by molecular environment. The constituent molecules overlap each other with an average interplanar spacing of 3.33 Å, but two C-N contacts are found to have lengths of 3.30 Å.

### Introduction

The crystal structure of azulene has been shown by Robertson, Shearer, Sim & Watson to be disordered, with the result that the molecular geometry could not be accurately determined (1962). The present study of the complex azulene, *s*-trinitrobenzene was undertaken as a further attempt to determine the molecular geometry of azulene. Experience with the similar complexes of skatole and indole with *s*-trinitrobenzene suggested that the work would be useless unless carried out at a reasonably low temperature (Hanson, 1964). There could of course be no guarantee that the structure of the complex is free from disorder. Brown & Wallwork, in a brief account of the structure determination at room temperature, report that the azulene position is disordered to a degree which prevents reasonable refinement (1965). In the present analysis (at  $-95^\circ\text{C}$ ) it is found that about 7% of the azulene mole-

cules adopt an alternative orientation, but that this small degree of disorder does not appreciably limit the accuracy achieved.

### Experimental

*Crystal data at  $-95^\circ\text{C}$*

(Values in parentheses refer to measurements at room temperature).

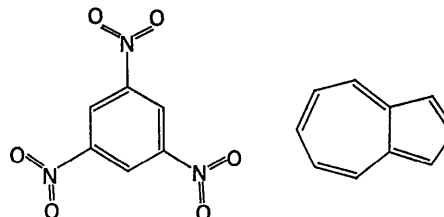


Fig. 1. Azulene, *s*-trinitrobenzene.

## Monoclinic

$$a = 16.39 (16.39) \pm 0.03 \text{ \AA}$$

$$b = 6.66 (6.80) \pm 0.01$$

$$c = 13.77 (13.99) \pm 0.02$$

$$\beta = 96.10 (95.86) \pm 0.05^\circ$$

$$V = 1500 (1551) \text{ \AA}^3$$

Formula  $C_{10}H_8, C_6H_3N_3O_6$ ; F.W. = 341.27

$$D_x \text{ (calculated density)} = 1.51 (1.46) \pm 0.01 \text{ g.cm}^{-3}$$

$$D_m \text{ (measured density)} = (1.46) \pm 0.02 \text{ g.cm}^{-3}$$

$$Z = 4$$

$$\mu = 11.8 \text{ cm}^{-1} \text{ (Cu } K\alpha)$$

Space group  $P2_1/a$  (from precession and Weissenberg photographs. Systematic absences  $h0l$  for  $h$  odd;  $0k0$  for  $k$  odd).

Molecular symmetry: none

The material crystallizes from toluene solution in the form of needles whose long axes are parallel to  $b$ . They appear blue-black, and shiny, by reflected light, but red by transmitted light. Crystals are frequently found to be twinned on (001). The material decomposes by loss of azulene at room temperature, particularly when exposed to X-rays. Specimens were therefore sealed in thin-walled fused-quartz capillaries in company with a small quantity of pure azulene.

Photographs taken at room temperature show considerable low-angle diffuse scattering. Corresponding photographs at  $-140^\circ\text{C}$  show this scattering concentrated in diffuse reflexions, some quite intense, with apparent indices  $h, k, l + \frac{1}{2}$ . The reason for this is not known, but the temperature-dependence of the phenomenon suggests that it does not result from disorder of the type it was hoped to avoid.

The unit-cell constants were measured with the General Electric XRD 5 spectrogoniometer and goniostat at room temperature and at  $-95^\circ\text{C}$ . In addition,  $b$  was measured over a range of temperatures, with results summarized in Fig. 2. This was done with the intention of using the crystal itself as a temperature indicator. The value of  $b$  (derived from the Bragg angle, which was in the range  $65$ – $69^\circ$ , of the intense 080 reflexion) was easily measured whenever necessary, giving a sensitive indication of the working temperature.

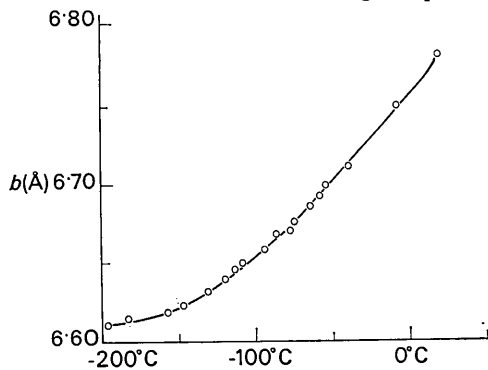


Fig. 2. Temperature dependence of  $b$ .

Relative intensities were measured on the spectrogoniometer and goniostat with a scintillation counter. Copper  $K\alpha$  radiation was used, and reasonable monochromatization was achieved by means of a  $K\beta$  filter and a reverter (pulse-height analyser). The moving-crystal moving-counter method of Furnas (1957) was used. Goniostat settings were precomputed.

It had originally been planned to measure the intensities at the convenient working temperature of  $-140^\circ\text{C}$ . However, routine checking revealed that the intensities of certain reflexions were very sensitive to small changes of temperature. The worst example noted was 080, for which a curve of intensity against temperature is given in Fig. 3. From this curve it can be seen that, at  $-140^\circ\text{C}$ , virtually no variation of temperature can be tolerated. It was obviously impracticable to investigate the temperature sensitivity of all the reflexions. However, a cursory examination of some of the sensitive ones showed that they behaved much like 080: maximum intensities occurred at about  $-95^\circ\text{C}$ , although the peaks were less sharp. The nature of the temperature-dependence of the structure is not known. It was decided, however, that the intensity data would have to be collected at  $-95^\circ\text{C}$ , with as little temperature fluctuation as could be managed.

The specimen was maintained in a stream of cold gaseous nitrogen, which was itself surrounded by an envelope of dry nitrogen at room temperature. The working temperature was raised to  $-95^\circ\text{C}$  by mixing with the cold stream a controlled flow of nitrogen at room temperature. Periodic checks on  $b$  indicated that the temperature fluctuation was held to  $\pm 3^\circ\text{C}$ .

The specimen used was a regular solid of dimensions  $0.3 \times 0.3 \times 0.5$  mm. It was mounted about the long axis, which was coincident with  $b$ . Of the 3333 accessible reflexions (those for which  $2\theta \leq 165^\circ$ ) significant counts were recorded for 2409. The range of observed intensities is about 1 to 15,000.

## Structure determination

The trial structure (which was very similar to those found for indole, and skatole,*s*-trinitrobenzene) was readily deduced from sections at  $V=0$  and  $V=\frac{1}{4}$  of the three-dimensional Patterson synthesis. The interpretation was initially equivocal with regard to the orientation (but not the position) of the azulene molec-

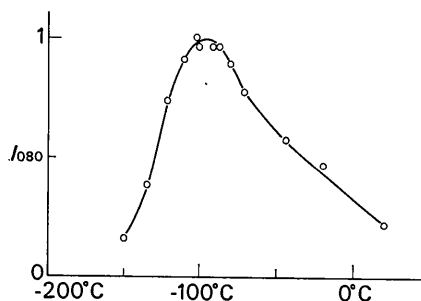


Fig. 3. Temperature dependence of  $I_{080}$ .

ule. However, attempted refinement soon confirmed that one orientation was at least predominant. Refinement, assuming this orientation, was continued with the structure-factor least-squares program of Mair (1963). This program uses the block-diagonal approximation with a  $3 \times 3$  matrix for the position parameters, and a  $6 \times 6$  matrix for the thermal parameters of each atom. The scale factor of observed structure amplitudes, and the overall isotropic temperature factor are refined in a  $2 \times 2$  matrix (Cruickshank, 1961). Schomaker's correction (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The weighting scheme used was

$$1/w = 1 + \{(F_o - 5F_T)/4F_T\}^2$$

where  $F_T$  is the nominal minimum value of  $F_o$ , in this case 3.2. This weighting scheme discriminated against the relatively inaccurate weak reflexions, and against the very strong ones, which were ultimately found to suffer somewhat from extinction. Reasonable positions and isotropic temperature factors were assumed for the hydrogen atoms, but were not refined. No convergence acceleration factors were applied. The scattering-factor curves of Freeman used were throughout (1959).

The structure converged rapidly, and at a late stage, when the agreement residual ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) had been reduced to 0.075, a three-dimensional difference synthesis was computed. The section of this synthesis in the plane of the azulene molecule is shown in Fig. 4(b). There are four anomalous peaks in this sect-

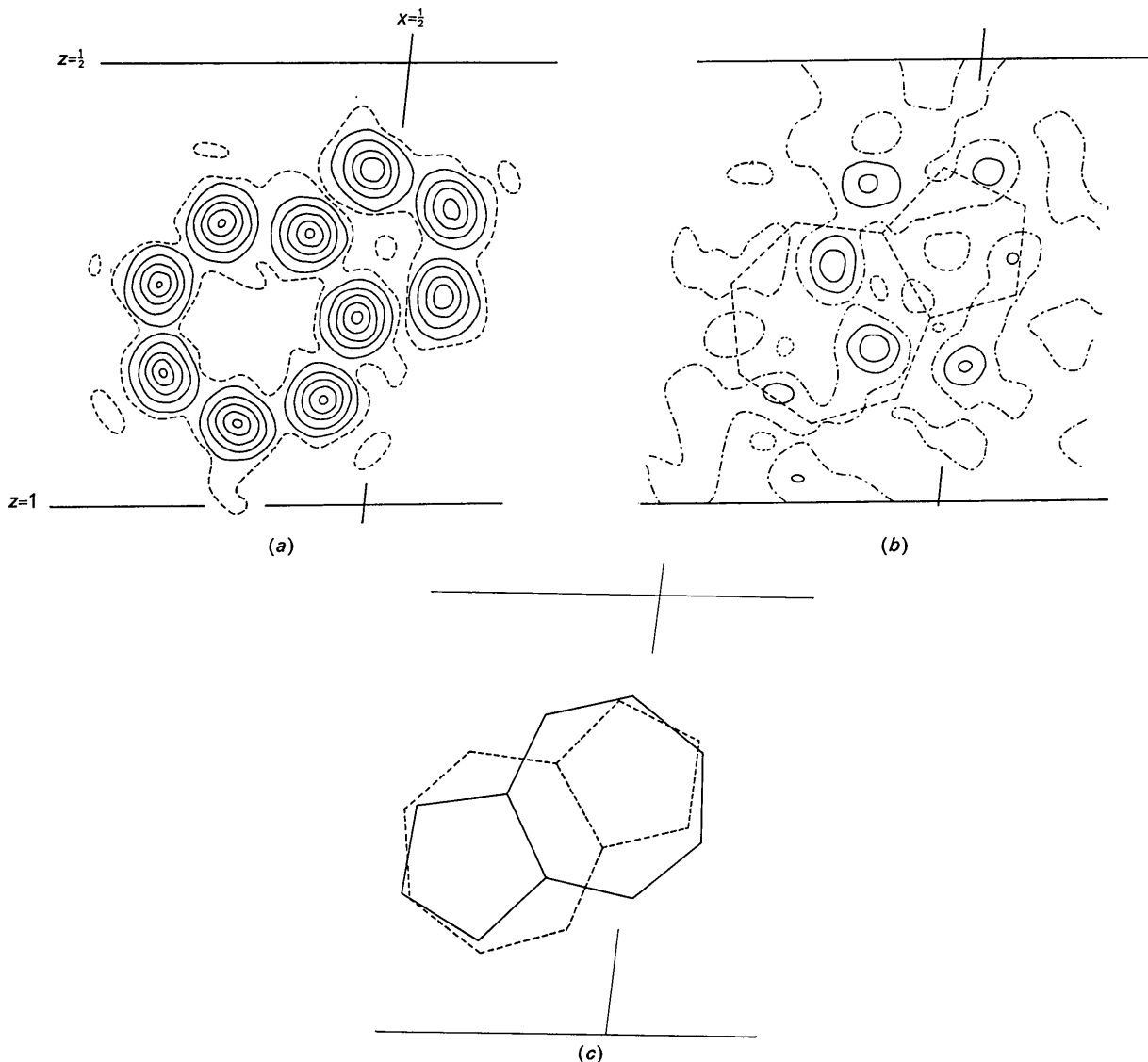


Fig. 4. (a) Section of  $F_o$  synthesis in plane of azulene molecule. Solid contours are at intervals of  $2 \text{ e.}\text{\AA}^{-3}$ , the lowest being  $2 \text{ e.}\text{\AA}^{-3}$ . The broken contour is at  $1 \text{ e.}\text{\AA}^{-3}$ . (b) Corresponding section of difference synthesis. Contours are at intervals of  $0.2 \text{ e.}\text{\AA}^{-3}$ ; solid contours are positive, broken contours are negative, chain contour is zero. Position of the predominant molecule is indicated in broken outline. (c) Interpretation of (b): the solid outline indicates the position of the alternative molecule.

ion, ranging in height from 0.45 to 0.55 e.Å<sup>-3</sup>. The estimated standard deviation of electron density is 0.11 e.Å<sup>-3</sup>, and these peaks are therefore significant. Moreover, they occur at some distance from any of the assumed atoms, and cannot be expected to disappear on further refinement. The proposed explanation is illustrated in Fig. 4(c): the structure is disordered, with the azulene molecule adopting the alternative orientation shown with a probability ultimately estimated at 7%. Only four atoms of this molecule appear in the difference map because the remaining six are effectively overlapped by those of the molecule in the assumed, predominant orientation. The positional and thermal parameters of the assumed atoms are adjusted by the refinement procedure in such a way as to reduce the residual electron density in their immediate vicinities. For comparison, the corresponding section of the  $F_0$

Fourier synthesis is given in Fig. 4(a); disorder could scarcely be inferred from this synthesis.

Refinement was continued on the assumption that the structure was so disordered. Molecules in both the predominant and alternative orientations (hereafter designated, for convenience, as the predominant and alternative molecules) were included in the structure-factor calculations, with appropriately adjusted scattering-factor curves. In order to avoid interaction between overlapping atoms, however, the parameters of the alternative molecule were not subjected to least-squares analysis. Instead, it was assumed that the alternative molecule was of the same shape, lay in the same plane, and was subject to the same modes of thermal motion as the predominant molecule. Its position, orientation, and probability of occurrence were deduced from difference maps.

Table 1. *Final parameters of non-hydrogen atoms*  $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z)$

Atom	$x$ $\times 10^5$	$y$ $\times 10^5$	$z$ $\times 10^5$	T.F. = exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$						$B_1$ (Å <sup>2</sup> )	$B_2$ (Å <sup>2</sup> )	$B_3$ (Å <sup>2</sup> )
				$\beta_{11}$ $\times 10^5$	$\beta_{22}$ $\times 10^5$	$\beta_{33}$ $\times 10^5$	$\beta_{12}$ $\times 10^5$	$\beta_{13}$ $\times 10^5$	$\beta_{23}$ $\times 10^5$			
<i>s</i> -Trinitrobenzene												
C(1)	12460	12359	17004	208	1300	260	-90	54	13	1.78	2.49*	2.19*
C(2)	17866	12010	25428	150	1255	273	-89	60	-2	1.43	2.14	2.26
C(3)	14432	12330	34148	190	1230	243	-81	40	-3	1.73	1.97*	2.32*
C(4)	6074	13160	34716	211	1174	364	-123	237	-153	1.34	3.53	2.01
C(5)	1077	13709	25964	130	1161	531	-60	97	-187	1.30	4.02	2.05
C(6)	4034	13161	17028	206	1351	374	-12	-100	-48	1.97	3.19	2.38
N(7)	15936	11786	7578	340	1673	241	-67	67	-32	1.77	3.70	2.93
N(8)	19970	11494	43285	291	2068	230	-29	19	1	1.76	3.08	3.69
N(9)	-7871	14929	26271	172	1520	853	-160	211	-396	1.60	6.62	2.62
O(10)	11122	12884	113	512	2944	231	462	-128	72	1.81	6.39*	4.40*
O(11)	23318	10151	7710	290	3478	338	-351	277	-222	1.44	3.72	6.45
O(12)	27148	8186	42767	214	5493	347	48	-94	70	2.01	3.02	9.75
O(13)	16937	13650	50826	493	5966	230	990	94	-402	1.50	4.63	11.42
O(14)	-10402	14548	34296	249	2741	974	-287	562	-625	1.49	8.45	4.44
O(15)	-12198	16452	18490	163	2719	1009	-81	-223	-75	1.55	8.05	4.84
Azulene (predominant orientation; weight 0.93)												
C(16)	29572	12219	85143	243	1460	387	-78	213	8	1.70	3.58	2.66
C(17)	37037	12864	91012	319	1560	241	-78	172	-62	1.41	3.70	2.75
C(18)	45001	13405	88253	231	1403	295	-61	-60	66	2.09	2.82*	2.37*
C(19)	47443	13434	78900	140	1211	349	11	41	41	1.48	2.67	2.10
C(20)	42096	13137	69419	233	1091	263	-8	139	-51	1.51	2.84	1.95
C(21)	33595	12554	68088	242	1275	295	-18	-43	-35	2.22	2.70	2.22
C(22)	28046	12186	75040	145	1513	416	-41	20	-49	1.58	3.21	2.59
C(23)	55487	13832	76548	159	1561	583	-56	117	183	1.62	4.50	2.68
C(24)	55423	13719	66493	270	1629	658	0	497	45	1.36	6.05	2.88
C(25)	47372	13422	62061	362	1499	346	61	356	-18	1.33	4.80	2.68
Azulene (alternative orientation; weight 0.07) (Parameters not refined by least squares)												
C(26)	55920	13880	67620	220	1502	465	0	235	0	1.70	3.97	2.68
C(27)	48580	13410	61500	311	1507	233	0	137	0	1.51	3.49	2.68
C(28)	40580	12940	63500	300	1308	300	0	-106	0	2.16	3.44	2.31
C(29)	37670	12800	72620	162	1141	286	0	-12	0	1.50	2.21	2.04
C(30)	42670	13140	82500	202	1141	210	0	52	0	1.50	2.21	2.04
C(31)	51170	13660	84380	278	1308	330	0	-130	0	2.16	3.44	2.31
C(32)	56920	13990	77750	144	1507	448	0	-56	0	1.51	3.49	2.68
C(33)	29500	12310	74500	142	1514	612	0	77	0	1.48	4.62	2.70
C(34)	29170	12320	84500	256	1622	662	0	473	0	1.36	5.95	2.89
C(35)	37000	12820	89500	358	1514	336	0	318	0	1.48	4.62	2.70

\* Corresponding directions not approximately parallel to, or normal to, the  $x-z$  plane.

Refinement of the disordered structure was considered to be complete after six cycles, as none of the coordinate shifts then exceeded 0.2 e.s.d.'s of atomic position. The final parameters for all atoms are given in Tables 1 and 2. It will be noted that the assumed isotropic temperature factors for the hydrogen atoms are appreciably less than the mean values of the atoms to which they are attached. This assumed behaviour is consistent with recent experience of the thermal motion of hydrogen atoms in similar structures (Sundaralingham & Jensen, 1963; Hanson, 1965).

Table 2. Assumed parameters of hydrogen atoms

Atom	$x$ $\times 10^4$	$y$ $\times 10^4$	$z$ $\times 10^4$	$B$ ( $\text{\AA}^2$ )
H(2)	2397	1136	2524	0
H(4)	378	1344	4114	0.25
H(6)	27	1356	1082	0.37
H(16)	2455	1188	8869	1.10
H(17)	3678	1289	9814	1.10
H(18)	4954	1370	9361	1.10
H(21)	3124	1237	6114	1.10
H(22)	2225	1180	7222	1.10
H(23)	6051	1414	8161	1.40
H(24)	6047	1406	6303	1.90
H(25)	4558	1329	5486	1.40

### Assessment of results

The agreement between observed and calculated structure amplitudes is reasonable, as indicated by the agreement summary (Table 3). It seems unnecessary to publish the table of  $F_o$  and  $F_c$ , but copies may be obtained from the National Science Library, National Research Council, Ottawa, Canada, giving reference to this paper. The final agreement residual, for observed reflexions only, is 0.060.

Table 3. Agreement summary

Category	Number of reflexions
1 ( $ \Delta F  \leq \frac{1}{2}F_T$ or $ \Delta F  \leq 0.1F_o$ )	2836
2 ( $\frac{1}{2}F_T <  \Delta F  \leq F_T$ or $0.1F_o <  \Delta F  \leq 0.2F_o$ )	433
3 ( $F_T <  \Delta F  \leq \frac{3}{2}F_T$ or $0.2F_o <  \Delta F  \leq 0.3F_o$ )	61
4 ( $\frac{3}{2}F_T <  \Delta F  \leq 2F_T$ )	3

$$\Delta F = |F_o| - |F_c|$$

$F_T$  = estimated minimum observable structure amplitude for reflexion concerned.

The final three-dimensional difference synthesis is satisfactorily featureless. Electron density anomalies of as much as  $\pm 0.3 \text{ e.}\text{\AA}^{-3}$  are found in regions occupied by some of the  $\text{NO}_2$  groups; these probably result from the intense, and presumably non-ellipsoidal thermal motion of the oxygen atoms. Elsewhere in the synthesis, the electron density does not exceed  $\pm 0.2 \text{ e.}\text{\AA}^{-3}$ .

The standard deviations of the coordinates of the atoms included in the least-squares analysis range from 0.0020 to 0.0037  $\text{\AA}$ ; these values were estimated from the least-squares results, and increased by 16% to allow for the probable effect of omitting the unobserved reflexions.

It is obvious that the parameters of the alternative molecule (including the probability of its occurrence) have not been determined with high accuracy. The possibility must be considered that residual errors may be prejudicial to the accuracy of the parameters of the predominant molecule. Comparison of the final parameters with those previously obtained for an ordered structure reveals that the effect of considering the alternative molecule is to cause coordinate shifts in the predominant molecule no greater than 0.016  $\text{\AA}$ , and bond length changes no greater than 0.014  $\text{\AA}$ . These effects, while appreciable, are sufficiently small to suggest that remaining errors in the parameters of the alternative molecule are unlikely to affect the parameters of the predominant molecule.

### Discussion of thermal motion

In Table 1, the magnitudes of the temperature factors along the principal axes of the vibration ellipsoids are

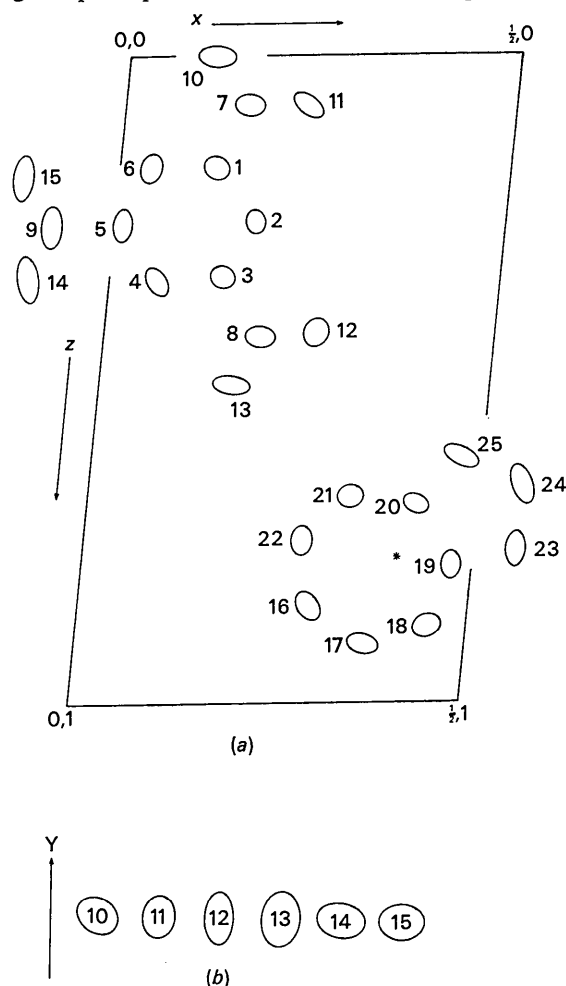


Fig. 5. (a) The thermal motion ellipsoids viewed along  $b$ ; the asterisk is the assumed centre of libration of the azulene molecule. (b) The thermal motion ellipsoids of the oxygen atoms, viewed along the directions of least thermal motion, from the periphery of the  $s$ -trinitrobenzene molecule.

given for each atom. The directions of least thermal motion (corresponding to  $B_1$ ) for all atoms lie within  $5^\circ$  of the  $x-z$  plane. The mean molecular planes are themselves almost parallel to this plane. With the exceptions noted in the table, the remaining principal directions (corresponding to  $B_2$  and  $B_3$ ) lie within  $10^\circ$  of, respectively, the  $x-z$  plane and its normal. (The exceptions among the carbon atoms are not important, as the differences between  $B_2$  and  $B_3$  for the exceptional atoms are fairly small, and the precise directions of the corresponding axes are not of much significance).

The vibration ellipsoids of all atoms, viewed along **b**, are sketched in Fig. 5(a). As a further aid in visualizing the thermal motion, the vibration ellipsoids of the oxygen atoms are also shown in Fig. 5(b), as they would appear viewed along the directions of least thermal motion from the periphery of the *s*-trinitrobenzene molecule.

For the azulene molecule it can be seen that the most important mode of thermal motion is a rigid-body libration in the molecular plane, about the point indicated. The r.m.s. amplitude of this libration is estimated to be about  $4.6^\circ$ ; the appropriate corrections, using the methods of Busing & Levy, have the effect of increasing all bond lengths by 0.32% (1964). Comp-

arison of the values of  $B_3$  suggests that there are also librations about axes in the molecular plane, but that these are too small to affect the bond lengths.

For the *s*-trinitrobenzene molecule also, the most obvious mode of thermal motion is a libration of the molecule as a whole, in its own plane. However, the centre of this libration does not coincide with the centre of gravity; it is in fact quite close to C(2). (It is interesting to note that libration about this point was also found in the complex indole, *s*-trinitrobenzene). The r.m.s. amplitude of the libration is estimated to be  $3.8^\circ$ , and the appropriate corrections lengthen all bonds by 0.22%. Additional thermal motion of the NO<sub>2</sub> groups is indicated by the high values of  $B_3$  for N(8) and for the oxygen atoms. For purpose of correcting the bond lengths, that part of the thermal anisotropy which cannot be attributed to rigid-body libration in the molecular plane is assumed to consist of two modes. The first, an out-of-plane libration of each NO<sub>2</sub> group about the adjacent carbon atom, has an appreciable effect only on the bond C(3)-N(8). The second, a riding motion (in the terminology of Busing & Levy) of each oxygen atom on the adjacent nitrogen atom, has a large effect on all the N-O bonds. The assumed model of non-rigid motion is undoubtedly oversimpli-

Table 4. Bond lengths

Bond		$l(\text{\AA})$ uncorrected	$\Delta l$ ( $\text{\AA} \times 1000$ )	$l(\text{\AA})$ corrected	Mean $l$ ( $\text{\AA}$ )	Mean e.s.d. ( $\text{\AA} \times 1000$ )
C(1)	C(2)	1.383	3	1.386	1.383	4
C(2)	C(3)	1.379	3	1.382		
C(3)	C(4)	1.381	3	1.384		
C(4)	C(5)	1.384	3	1.387		
C(5)	C(6)	1.370	3	1.373		
C(6)	C(1)	1.382	3	1.385		
C(1)	N(7)	1.472	6	1.478	1.480	3
C(3)	N(8)	1.472	9	1.481		
C(5)	N(9)	1.474	6	1.480		
N(7)	O(10)	1.230	20	1.250	1.243	3
N(7)	O(11)	1.213	22	1.235		
N(8)	O(12)	1.206	37	1.243		
N(8)	O(13)	1.206	45	1.251		
N(9)	O(14)	1.221	19	1.240		
N(9)	O(15)	1.225	16	1.241		
C(16)	C(22)	1.387	4	1.391	1.394	4
C(16)	C(17)	1.393	4	1.397		
C(17)	C(18)	1.398	4	1.402	1.398	4
C(21)	C(22)	1.389	4	1.393		
C(18)	C(19)	1.388	4	1.392	1.391	4
C(20)	C(21)	1.386	4	1.390		
C(19)	C(23)	1.391	4	1.395	1.400	4
C(20)	C(25)	1.400	4	1.404		
C(23)	C(24)	1.383	4	1.387	1.392	5
C(24)	C(25)	1.394	4	1.398		
C(19)	C(20)	1.493	5	1.498	1.498	4

fied, and possibly misleading. Consequently the corrections to the N–O bonds may well be viewed with some skepticism. The total corrections to all bonds are given in Table 4.

### Discussion of the structure

Details of molecular structure are given in Table 4 and Fig. 6. The azulene molecule is nearly planar, and makes an angle of about  $1.5^\circ$  with the  $x-z$  plane. The two end atoms C(16) and C(24), however, each lie at a distance of about  $0.0088 \text{ \AA}$  from the mean plane  $0.4039x - 6.6477y + 0.0263z + 0.6793 = 0$ , giving the molecule a slight boat shape. The departure from planarity is significant at the 1% level. Differences between chemically equivalent bond lengths are significant only at the 5% level.

Only the benzene nucleus of the *s*-trinitrobenzene molecule is planar. The  $\text{NO}_2$  groups are bent and twisted out of the plane by varying amounts, which are presumably fixed by the molecular environment. There are apparently significant differences between the N–O bond lengths; these probably result from the oversimplified treatment of thermal motion. The dif-

ference between the greatest and least C–C bond length is  $0.014 \text{ \AA}$ , a quantity which approaches significance at the 1% level. However, it is difficult to accept the reality of this difference.

The molecules overlap each other as shown in Fig. 7. The average interplanar separation is of course  $3.33 \text{ \AA}$ , and with two exceptions the intermolecular distances are greater than this. However, the distances between N(7) ( $x, 1+y, z$ ) and C(17) ( $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$ ), and between N(9) ( $x, y, z$ ) and C(23) ( $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$ ) are each  $3.30 \text{ \AA}$ . It is interesting that nitrogen atoms should be involved in each case. [N(8) is of course too far away to participate in such a contact]. It is difficult to say whether these distances represent attraction, or mere toleration. Distances between non-overlapping molecules are normal. Shortest distances are  $3.05 \text{ \AA}$  for O–O,  $3.35 \text{ \AA}$  for C–O, and  $3.90 \text{ \AA}$  for C–C.

A disturbing aspect of the analysis is the discovery of the alternative orientation of the azulene molecule in the unexpectedly small proportion of 7%. A still smaller degree of disorder (or the same degree in a less accurate analysis) might well have escaped detection. Moreover, the disorder in this case was discovered only because four of the atoms were well resolved. Otherwise

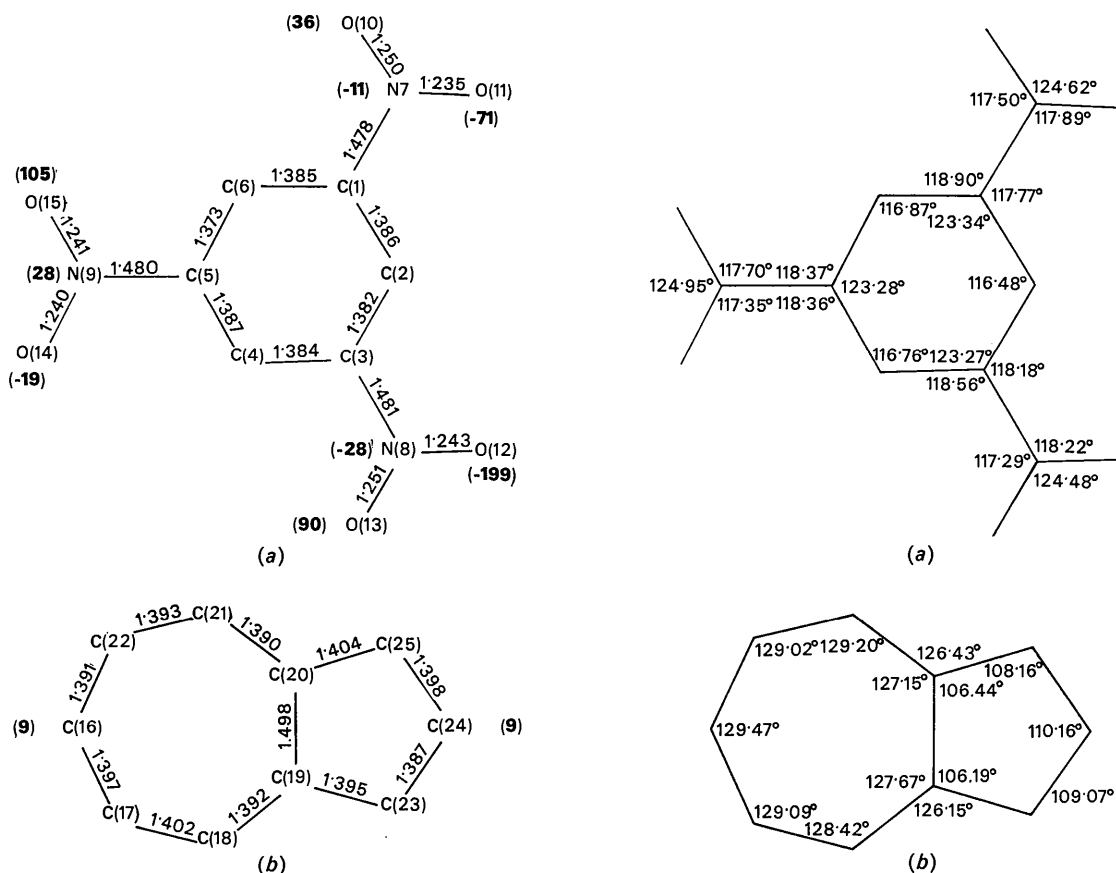


Fig. 6. (a) Bond lengths and angles in the *s*-trinitrobenzene molecule. The distances of nitrogen and oxygen atoms from the mean plane of the benzene nucleus are shown in  $\text{\AA} \times 1000$  (bold figures). The mean e.s.d. of angles is  $0.22^\circ$ . (b) Bond lengths and angles in the azulene molecule. The distances of C(16) and C(24) from the mean plane are shown in  $\text{\AA} \times 1000$  (bold figures). The mean e.s.d. of angles is  $0.25^\circ$ .

the disorder would presumably have been concealed by errors in the molecular geometry and thermal motion.

The specimen material was prepared by Mr Y. Lupien of the Division of Pure Chemistry. Computations were carried out on the IBM 1620 computer under the supervision of Dr F. R. Ahmed, using his programs and those of Dr G. A. Mair and Mrs M. E. Pippy. Drs Brown and Wallwork were kind enough to allow study of their paper before publication. The assistance of those mentioned, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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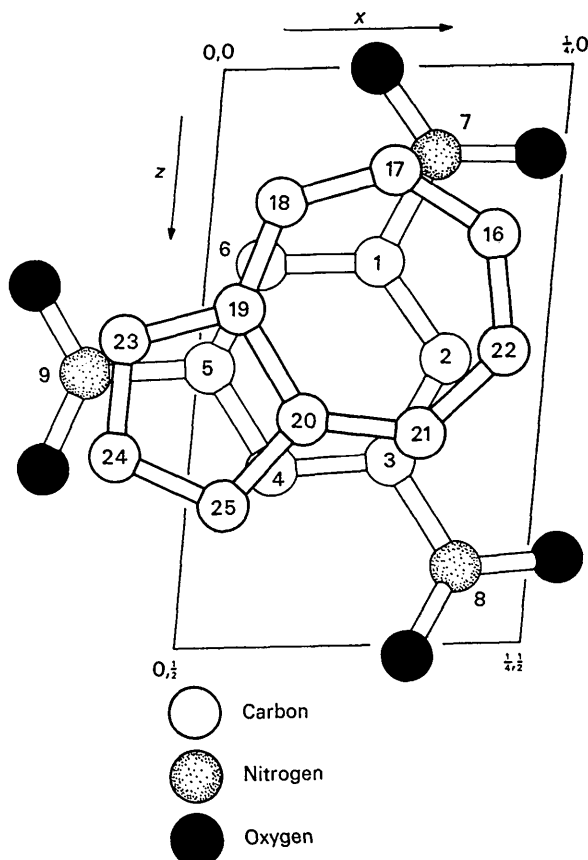


Fig. 7. Projection along *b* of the asymmetric unit, showing overlap.

*Acta Cryst.* (1965). **19**, 26

## Multiple Phase Formation in the Binary System $\text{Nb}_2\text{O}_5\text{--WO}_3$ .

### I. Preparation and Identification of Phases

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An equilibrium study at 1300–1400°C of the system  $\text{Nb}_2\text{O}_5\text{--}1\text{Nb}_2\text{O}_5\text{:}1\text{WO}_3$  led to the identification of five compounds in what had been previously reported as a region of solid solution. Three phases,  $\text{WNb}_{30}\text{O}_{78}$ ,  $\text{WNb}_{12}\text{O}_{33}$  and  $\text{W}_5\text{Nb}_{16}\text{O}_{55}$  are monoclinic, while the remaining two,  $\text{W}_3\text{Nb}_{14}\text{O}_{44}$  and  $\text{W}_8\text{Nb}_{18}\text{O}_{69}$ , are tetragonal. Each phase is characterized, and it is shown that the existence of not more than two of them could have been predicted by crystallochemical arguments.

### Introduction

We have recently discussed the crystal chemistry of niobium pentoxide and the compounds, related to it,

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that are formed when elements with about the same ionic radii, and of the same or lower valency, are substituted for niobium (Roth & Wadsley, 1965a). The structures all contain metal–oxygen octahedra forming sub-units or blocks of the  $\text{ReO}_3$ -type, of finite sizes in two dimensions but infinite in the third, which condense upon themselves by edge-sharing in such a way