47. *Crystal Structure and Configuration of the Isomeric Azobenzenes.*

By J. Monteath Robertson.

Ordinary (*trans-*) azobenzene crystallises in the monoclinic system and two almost planar centrosymmetrical molecules (which may not be identical) contribute to the asymmetric unit. The structure is briefly described and the mean dimensions of the molecule are given. *cis-*Azobenzene, recently isolated by Hartley, is orthorhombic, and the molecule has a two-fold axis of symmetry. The complete structure is deduced from absolute intensity measurements, by trial with various models, and the molecular dimensions are given. The benzene rings are now rotated by 50° from the planar positions. Other changes in the molecular dimensions with respect to the *trans*-form are related to this distortion. The form of analysis employed for the *cis*-structure may be useful in dealing with other molecules which exhibit axial symmetry.

Preliminary work on the crystal structure of ordinary azobenzene (Robertson, Prasad, and Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187) shows its similarity to the structures of the dibenzyl series (Robertson and Woodward, *ibid.*, 1937, *A*, **162**, 568; 1938, *A*, **164**, 436) and is sufficient to establish the *trans*-configuration of the molecule. A detailed *X*-ray analysis, giving more exact dimensions of the molecule, is now being carried out. The results are briefly summarised in this paper, and the structure is compared with that of the recently isolated *cis*-form of azobenzene (Hartley, J., 1938, 633). Dr. Hartley has kindly supplied the material for the present investigation.

trans-Azobenzene crystallises in the monoclinic system, space group $C_{2h}^5 (P2_1/a)$, with four centrosymmetrical molecules in the unit cell. As in the stilbene structure, successive layers of molecules are oppositely inclined to the (001) plane, and the asymmetric unit of the crystal $(C_{12}H_{10}N_2)$ consists of two half molecules (benzene ring and nitrogen atom), one of which is contributed by each of the two layers. The complete structure may then be derived by the operation of the symmetry elements on this unit. A general view of the two layers of molecules is shown by the model in Plate I.

The positions of all the atoms in the structure have been determined by successive Fourier analyses of quantitative intensity data. As in the case of stilbene, slightly different dimensions are derived for the two molecules which contribute to the asymmetric crystal unit. One molecule is also found to be almost exactly planar, while in the other the N=N bond is inclined at about 15° to the planes of the benzene rings. (The rings themselves are always parallel, because the molecule as a whole has a centre of symmetry.) It is possible that the observed differences in dimensions between the two molecules may be accounted for by errors in the analysis; the 15° departure from the planar form is, however rather too large to be explained in this way, and the possibility of one molecule existing in some excited state with respect to the other must be borne in mind. A detailed discussion of the structure, with co-ordinates of the atoms and orientations of the molecules, will be given elsewhere. For the present purpose of comparison with *cis*-azobenzene the mean dimensions obtained for the *trans*-molecule are indicated in Fig. 1.

FIG. 1.
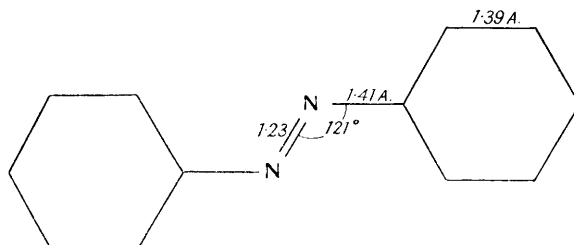
Mean dimensions of trans-*azobenzene molecule. Distances estimated to be within* ± 0·03 A. *The* N=N *bond may be inclined by from* 0° *to* 15° *to the planes of the benzene rings.*

FIG. 2.
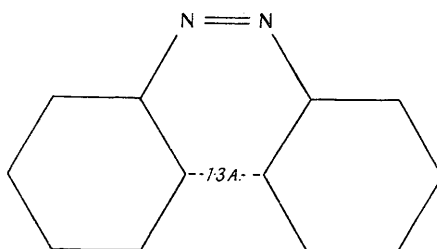
The dimensions found correspond with the values to be expected for this .type of structure. The C–N link, between the benzene ring and the N=N double bond, shows a considerable contraction from the normal value of 1·47 A. deduced from the covalent radii of carbon and nitrogen. This indicates that an excited structure such as (I) must make a considerable contribution to the normal state of the molecule. This contribution will facilitate conversion into the *cis*-form by rotation about the N–N link.
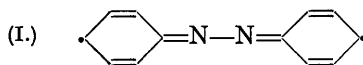

The crystal structure of *cis*-azobenzene is quite different. The system is orthorhombic, and the space group $D_{2h}^{14}(Pbcn)$. Again there are four molecules in the unit cell, and the molecule possesses an element of symmetry, but in this case it is a dyad axis. This change in molecular symmetry agrees with the assignment of the *cis*-configuration; a centre of symmetry would not be possible but a dyad axis is quite in keeping with the accepted stereochemistry.

There are no outstanding features in the X-ray spectra of *cis*-azobenzene, and to proceed with the analysis it is necessary in this case to test possible models and orientations until the intensities can be explained. Starting from the approximately planar *trans*-model (Fig. 1), if the N=N bond is rotated by 180°, we obtain the model of Fig. 2, where non-

bonded atoms in neighbouring benzene rings approach each other to within about 1·3 A. This is clearly impossible from the known steric requirements of such atoms, and in the actual model there must be a considerable rotation of the benzene rings about the " single " bonds connecting them to the nitrogen atoms. The resultant deviation of the molecules from the planar form may be expected to diminish any contribution made by the structure (I) which is conditioned by the benzene ring and the two nitrogen atoms being approximately coplanar. One result may be a certain lengthening of the C–N links towards the normal value of 1·47 A., and another, some diminution in the ease of reversion to the *trans*-form otherwise to be expected. Again, the mutual repulsion of the benzene rings will very likely tend to increase the N=N–C angle beyond the value of 121° observed in the *trans*-form.

These considerations indicate the kind of structure to be expected, and it is found that the best agreements with the observed intensities are obtained with the model shown in Fig. 3, where the benzene rings are rotated from the perpendicular position by 40° (or from the planar position of Fig. 2 by 50°). The clearance between the ortho-carbon atoms on

FIG. 3.
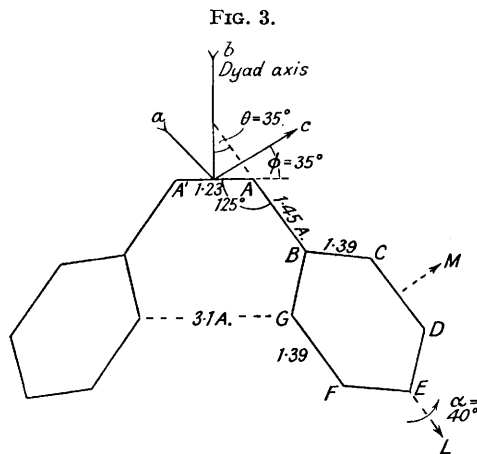
cis-*Azobenzene molecule in relation to the crystal axes. Dimensions estimated to be within about ± 0·04 A., and angles to within ± 4°.*

the benzene rings is now about 3·1 A. Uncertainties in the dimensions are probably greater than for the *trans*-form, because, owing to the complex grouping of the molecules in the crystal, it has not yet been possible to refine the results by an application of the Fourier series method. But the agreements obtained between the calculated and observed structure factors (Table III) indicate that the deductions made about the structure are substantially correct.

The general disposition of the molecules in the crystal is shown in Plate II. They are situated on two-fold rotation axes, which are parallel to the *b* crystal axis and are indicated by the upright supports in the photograph. The benzene rings of the end molecules are directed downwards, and those of the centre molecules upwards. The resulting structure is fairly compact, and the density (1·21₃) is practically the same as in the *trans*-form (1·21₇). The minimum distances of approach between the nitrogen atoms of one molecule and the carbon atoms of its neighbours are between 3·4 and 3·5 A., and the carbon–carbon minima are about 3·6 A.

EXPERIMENTAL.

cis-Azobenzene, > 99% pure by photometric tests, m. p. 71·4° by quick plunging, was supplied by Dr. Hartley (*loc. cit.*). Well-formed single crystals were obtained by allowing a petrol (b. p. 40—60°) solution to evaporate slowly from open vessels in the dark at 0°. When free from solvent, the dark red, rather thick plates appear to be quite stable at room temperatures in subdued light, and also during exposure to *X*-rays.
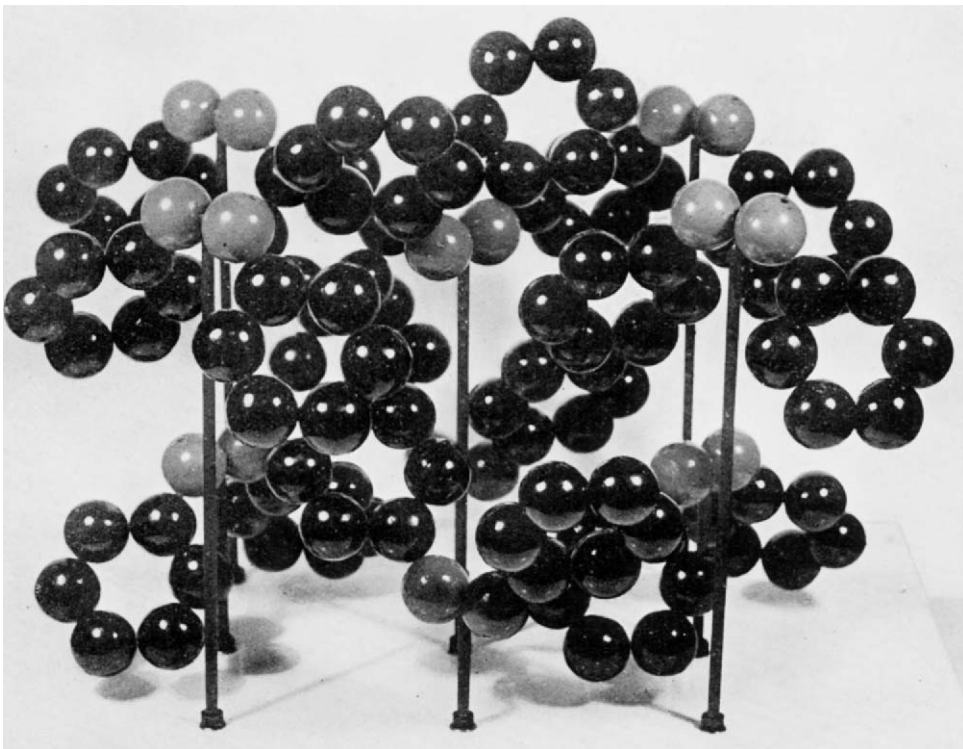
Rotation and moving-film photographs were taken with filtered Cu-*K*α radiation. The

PLATE I.
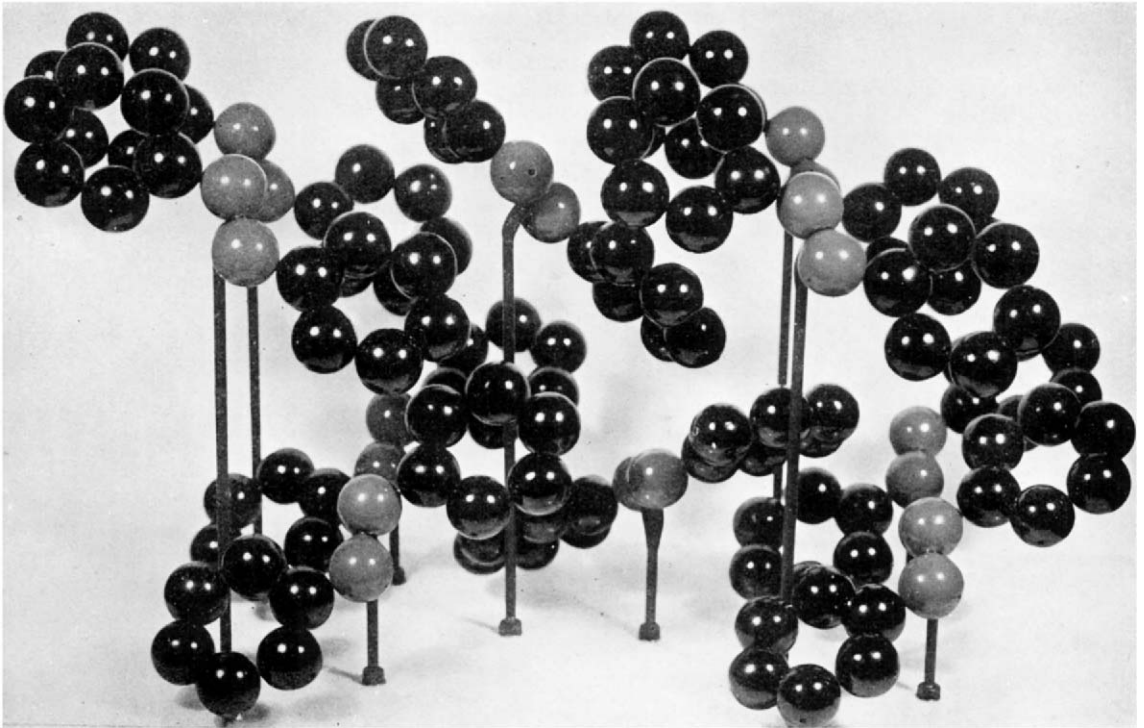
trans-*Azobenzene*.

PLATE II.

cis-*Azobenzene*.

orthorhombic crystals were found to have $a = 7.57 \pm 0.01$, $b = 12.71 \pm 0.03$, $c = 10.30 \pm 0.02$ A., giving a unit cell of volume 991 A.³, and, on the basis of 4 molecules of $C_{12}H_{10}N_2$ per unit cell, a calculated density of 1.213. The ($hk0$) reflexions are absent when ($h + k$) is odd, ($0kl$) when k is odd, and ($h0l$) when l is odd. The space group is therefore D_{2h}^{14} (*Pbcn*). As eight asymmetric units are required to complete the symmetry, the molecule of $C_{12}H_{10}N_2$ must itself possess two-fold symmetry, which in this space group can be either a two-fold axis or a centre. The structure analysis shows that the molecular symmetry in this case is a two-fold axis, parallel to the b crystal axis.

The intensities of the reflexions were recorded photographically on moving films, from specimens weighing 0.1—0.22 mg., which were completely immersed in the X-ray beam. The films were measured on an integrating photometer. As the specimens used had fairly uniform cross-sections, relative absorption corrections were not applied. Absolute values of the reflexions were obtained from a specimen weighing 0.219 mg. by comparison with a diamond standard on the two-crystal moving-film spectrometer (Robertson, *Phil. Mag.*, 1934, **18**, 729). The absolute absorption correction factor in this case, for a path of 0.55 mm. in the crystal, and $\mu = 6.87$ per cm. for $\lambda = 1.54$, is given by $e^{\mu t} = 1.46$.

Analysis of the Structure.—The asymmetric crystal unit of *cis*-azobenzene consists of half a chemical molecule, represented by the atoms lettered A to G in Fig. 3. The complete unit cell contains eight of these units (four molecules) derived from the standard one by certain symmetry operations. For example, in Fig. 3, the unlettered half of the molecule can be derived from the lettered half by a rotation of 180° about the dyad axis. A complete enumeration of the symmetry elements, co-ordinates of equivalent positions, and formulæ for calculating the structure amplitudes in this space group (*Pbcn*) are given in the International Tables for Determination of Crystal Structure (London : Bell and Sons, 1935) ; see also Lonsdale, " Structure Factor Tables " (London : Bell and Sons, 1936).

We require to find the co-ordinates of the atoms A ... G with respect to the crystal axes a, b, and c and an origin which is most conveniently chosen at a centre of symmetry at $(0, y, c/4)$ with respect to the dyad axis of Fig. 3. The structure is thus defined by 21 parameters in the most general case. But for testing a model of the type shown in Fig. 3, the parameters may be conveniently reduced to 4, two of which, θ and α, refer to the shape of the molecule itself. θ gives the inclination of the L molecular axis (ABE) to the dyad symmetry axis b, and defines the N=N–C valency angle. α gives the rotation of the benzene ring about the N–C bond, starting from the position in which the plane of the ring is perpendicular to the plane containing the atoms $A'AB$ (plane of diagram in Fig. 3). ϕ then defines the rotation of the model as a whole about the b crystal axis, and is the angle between the N=N bond and the c crystal axis. The final parameter, y_0, is required to define the height of the intersection of the L molecular axis and the dyad symmetry axis above the centre of symmetry which we have chosen as origin.

The co-ordinates of the atoms are most conveniently obtained by combining the dimensions of the model which is being tested with the direction cosines of the molecular axes L and M with respect to the crystal axes a, b, and c. These direction cosines are denoted by $\cos \chi_L$, $\cos \psi_L$, $\cos \omega_L$, $\cos \chi_M$, etc., and are given in terms of the above parameters by the relations

$$\cos \chi_L = \sin \theta \sin \phi \qquad \cos \chi_M = \cos \phi \cos \alpha - \sin \phi \sin \alpha \cos \theta$$
$$\cos \psi_L = \cos \theta \qquad \cos \psi_M = \sin \alpha \sin \theta$$
$$\cos \omega_L = \sin \theta \cos \phi \qquad \cos \omega_M = -\sin \phi \cos \alpha - \cos \phi \sin \alpha \cos \theta$$

For the model illustrated in Fig. 3, the co-ordinates with respect to the molecular axes are given in Table I, and those with respect to the crystal axes and centre of symmetry as origin are given by

$$x = L \cos \chi_L + M \cos \chi_M$$
$$y = L \cos \psi_L + M \cos \psi_M + y_0$$
$$z = L \cos \omega_L + M \cos \omega_M + c/4$$

TABLE I.

Co-ordinates : Molecular Axes ; Origin on Dyad Axis.

Atom.	A.	B.	C.	D.	E.	F.	G.
L (A.)	1.07	2.52	3.22	4.61	5.30	4.61	3.22
M (A.)	0	0	1.20	1.20	0	−1.20	−1.20

The parameters θ, α, ϕ, and y_0 can be varied independently, and various configurations tested against the absolute determinations of the structure factors, $F(hkl)$. To some extent this can be

done systematically. For example, only a small range of values for θ (the N=N–C valency angle) is probable. For a given θ value, the $(0k0)$ structure factors, involving only the y co-ordinates, depend almost entirely on y_0, and only to a minor extent on α. The other axial structure factors, $(h00)$ and $(00l)$, are very sensitive to changes in α and ϕ, but independent of y_0.

The agreements finally obtained between the calculated and observed structure factors are listed in Table III, where average atomic scattering factors for hydrocarbons (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 109) are employed, the nitrogen atoms being weighted with respect to the carbon atoms in the ratio of 6 to 5, and no account being taken of the hydrogen atoms. The shape and dimensions of the model employed are given in Table I and Fig. 3. Its orientation and position in the crystal are defined by the following parameter values and derived angles :

$$\theta = 35° ; \ \alpha = 40° ; \ \phi = 35° ; \ y_0 = 43° \ (1\cdot52 \text{ A.})$$

$$
\begin{array}{lll}
\chi_L = 71° & \chi_M = 71° & \chi_N = 27\tfrac{1}{2}° \\
\psi_L = 35° & \psi_M = 68\tfrac{1}{2}° & \psi_N = 116° \\
\omega_L = 62° & \omega_M = 150\tfrac{1}{2}° & \omega_N = 81\tfrac{1}{2}°
\end{array}
\right\} \text{(normal to benzene ring)}
$$

The co-ordinates of the atoms are given in Table II.

TABLE II.

cis-Azobenzene : co-ordinates with respect to crystal axes; centre of symmetry as origin.

	Atom (cf. Fig. 3).	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
A	N	0·35	17°	2·40	68°	3·08	107½°
B	C	0·83	39½	3·58	101½	3·76	131½
C	CH	1·45	69	4·60	130	3·04	106
D	CH	1·91	90½	5·74	162½	3·69	129
E	CH	1·74	83	5·86	166	5·07	177
F	CH	1·12	53½	4·85	137½	5·79	202½
G	CH	0·67	31½	3·71	105	5·14	179½

TABLE III.

Measured and calculated values of the structure factor (absolute scale).

hkl.	$\sin\theta$ ($\lambda = 1\cdot54$).	F, meas.	F, calc.	hkl.	$\sin\theta$ ($\lambda = 1\cdot54$).	F, meas.	F, calc.	hkl.	$\sin\theta$ ($\lambda = 1\cdot54$).	F, meas.	F, calc.
200	0·203	39	−42	102	0·183	55	+61	2, 10, 0	0·640	24	+28
400	0·406	12	+ 3	202	0·253	5	−18	310	0·313	20	+46
600	0·609	21	−21	302	0·340	7	− 3	330	0·355	48	−43
020	0·121	45	−42	402	0·433	11	−14	350	0·430	4	+ 4
040	0·242	3	+ 4	502	0·530	19	+24	370	0·523	5	+ 5
060	0·363	11	+ 9	602	0·628	<13	−11	390	0·625	< 7	+ 9
080	0·484	28	−16	104	0·315	47	−53	3, 11, 0	0·733	< 7	− 7
0, 10, 0	0·605	< 7	+ 1	204	0·363	7	+ 5	420	0·425	25	+39
002	0·149	19	+18	304	0·428	12	−12	440	0·473	< 6	+ 9
004	0·299	24	+21	404	0·505	14	+ 6	460	0·545	7	+ 8
006	0·448	36	+38	504	0·590	<12	− 1	480	0·635	12	−17
008	0·597	< 9	+ 9	604	0·680	<12	− 1	4, 10, 0	0·733	9	−16
								510	0·513	8	− 8
022	0·193	29	+29	110	0·118	16	−25	530	0·540	3	−10
024	0·323	5	− 6	130	0·208	24	+17	550	0·595	10	+19
042	0·285	21	+26	150	0·320	3	+ 4	570	0·663	16	−22
044	0·385	8	− 5	170	0·435	6	+ 7	590	0·748	< 7	+11
062	0·393	27	−18	190	0·555	22	−24	620	0·623	< 7	0
064	0·470	17	+18	1, 11, 0	0·673	12	+19	640	0·658	9	−23
082	0·508	< 8	+ 4	220	0·238	96	−81	660	0·713	< 7	+ 3
084	0·570	< 9	− 3	240	0·318	25	+10				
0, 10, 2	0·625	<10	+ 4	260	0·418	10	+ 8				
0, 10, 4	0·675	<10	+ 5	280	0·525	< 6	−11				
0, 12, 2	0·745	10	− 10								

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