78. *Bond Lengths and Resonance in the* cis-*Azobenzene Molecule.*

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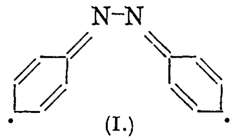
Refinements have been made in the determination of the crystal structure of *cis*-azobenzene, by applying the Fourier series method of analysis. Steric effects prevent the molecule from being coplanar, the two benzene rings being rotated so that the distance between the *o*–*o*′ carbon atoms is 3·34 A. This departure from coplanarity leads to a suppression of the resonance, as is shown by the values found for the N–N and C–N distances. The analysis also indicates a slight distortion of the molecule, so that the C–N bonds are not quite directed from the centres of the benzene rings, this slight distortion also no doubt being due to steric repulsion.

IN a previous paper (Robertson, J., 1939, 232) a trial *X*-ray analysis of the *cis*-azobenzene structure was described. The arrangement of the molecules in the crystal and their orientation and dimensions were deduced from a series of absolute intensity measurements. In this preliminary analysis, however, the structure was described in terms of four parameters and it was not feasible to test possible variations in individual bond lengths and angles. This has now been carried out by applying the Fourier series method of analysis to one of the principal zones of structure factors, whereby a fairly good resolution of the separate atoms is obtained, as can be seen from the contour map in Fig. 1.

Such a study is of considerable interest in the case of *cis*-azobenzene, because steric factors prevent the molecule from assuming a normal coplanar configuration. One would expect, therefore, that resonance with structures of the type (I) would largely be inhibited, since such structures containing double bonds adjacent to the benzene rings require the molecule to be planar. If the resonance is suppressed, there should be a measurable alteration in some of the bond lengths as compared with those found in *trans*-azobenzene.



(I.)

Such cases of suppression of resonance by steric effects are now well established, both from measurements of electric dipole moments (Birtles and Hampson, J., 1937, 10; Ingham and Hampson, J., 1939, 981; Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310) and also from an examination of chemical properties (Baddeley, *Nature*, 1939, **144**, 444; Brown, Widiger, and Letang, *J. Amer. Chem. Soc.*, 1939, **61**, 2597; Spitzer and Wheland, *ibid.*, 1940, **62**, 2995).

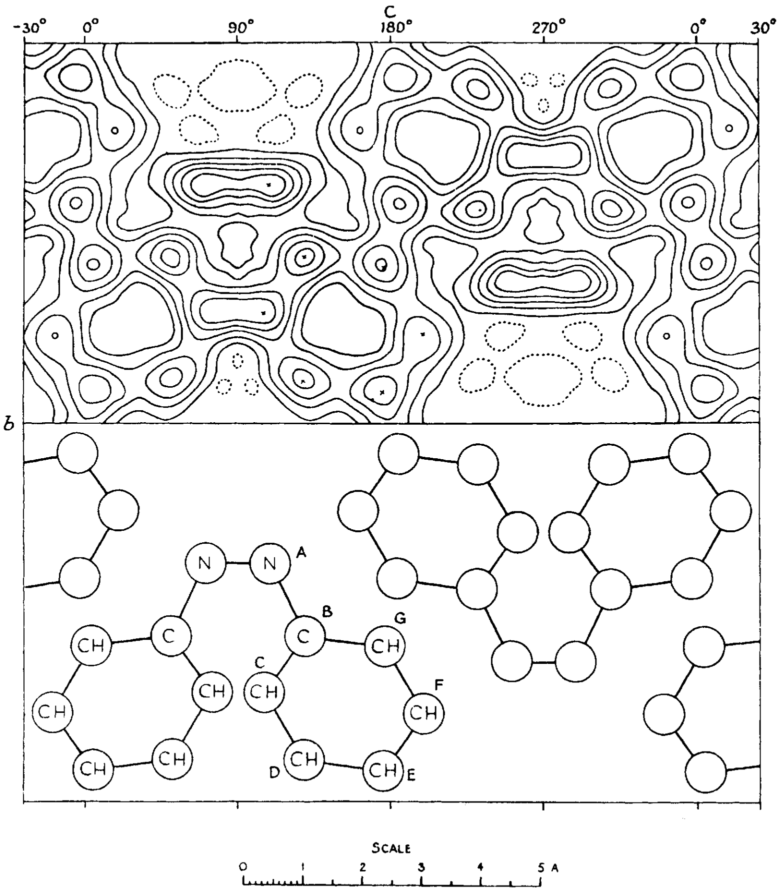
The results of our present analysis are given in the contour map of Fig. 1 which shows a portion of the structure in normal projection along the *a* axis. There are some imperfections in the Fourier series, due in part to difficulties in making accurate intensity measurements, but all the atoms in the ring are resolved and the positions of their centres can be estimated with some certainty.

The orientation and dimensions of the molecule have been obtained by inscribing the projection of a regular hexagon on the ring atoms to give the best fit at all points, and then deducing the inclinations of certain lines or axes by calculation from the observed foreshortening in the projection. The final figures have been checked by recalculation of the structure factors from the new co-ordinates and comparison against the observed values for the zone under investigation (0*kl*); but the other zones, (*h*0*l*) and (*hk*0), have also been utilised to obtain a final adjustment of the atomic positions in the direction normal to the projection plane.

The dimensions finally obtained for the molecule are shown in Fig. 2, which represents its projection along the *a* crystal axis. The dimensions are probably correct to about ± 0·03 A., and within these limits the benzene ring appears to be a regular planar hexagon of normal size, but rotated out of the plane containing the two nitrogen atoms by 56° (90° — 34°). The clearance between the two benzene rings (distance between the atoms marked C) is 3·34 A. The distance between the two nitrogen atoms has the almost normal double-bond value of 1·23 A. (the accuracy here is rather low), and the carbon–nitrogen distance (AB) is 1·46 A.

The latter value is of interest because it comes near to the normal C–N single-bond distance of 1·47 A., showing that the contribution of C=N double-bond structures to the resonance hybrid must be quite small. This is conditioned by the steric effects which prevent the molecule from assuming a planar configuration. This C–N distance should be contrasted with that of 1·41 A. found in *trans*-azobenzene (Robertson, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398) where the molecules are nearly planar.

FIG. 1.

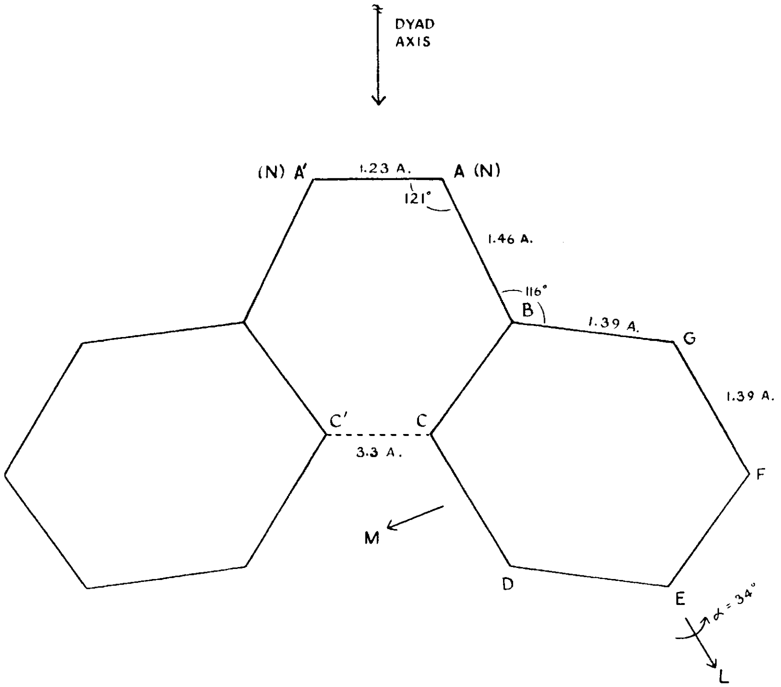


cis-Azobenzene. *Projection along* a *axis. Contour levels at unit intervals (electrons per* A., *one-electron line dotted). The map is extended to* 30° *(or* 1/12 *of a translation) beyond the edge of the unit cell on each side, the origin being taken at a centre of symmetry marked* 0°. *There are dyad screw axes at* 90° *and at* 270°.

An interesting distortion of the valency angles is also found in the *cis*-azobenzene molecule, and as this effect is somewhat greater than the estimated experimental error it is probably real. The N–N–C angle of 121° is practically normal and the same as that found in *trans*-azobenzene (*loc. cit.*). But the C–N bond emerging from the benzene ring is bent by about 5° or 6° from its normal direction (the direction of the *L* molecular axis). The distortion is about 4° towards the atom marked G (Fig. 2), combined with a movement of about 4° out of the plane of the benzene ring. The result of this distortion is to give a maximum clearance between the atoms of the two benzene rings while keeping them as nearly coplanar as possible and at the same time retaining the N–N–C valency angle at about 121°. There seems little doubt that this distortion results from the repulsion between the atoms marked C on the two benzene rings, the C . . . C distance of 3·34 A.

being brought rather below the minimum van der Waals approach distance for non-bonded aromatic carbon atoms.

FIG. 2.



Dimensions of cis-*azobenzene molecule. Projection along* a *axis.*

EXPERIMENTAL.

Crystal Data.—*cis*-Azobenzene, $C_{12}H_{10}N_2$; $M = 182$; m. p. 71·4°; density, calc., 1·213; orthorhombic bipyramidal, $a = 7{\cdot}57 \pm 0{\cdot}01$, $b = 12{\cdot}71 \pm 0{\cdot}03$, $c = 10{\cdot}30 \pm 0{\cdot}02$ A., $(hk0)$ halved when $(h + k)$ is odd, $(0kl)$ when k is odd, and $(h0l)$ when l is odd. Space group D_{2h}^{14} (*Pbcn*). Four molecules per unit cell. Molecular symmetry, dyad axis, parallel to b. Volume of the unit cell = 991 A.^{3}. Absorption coefficient for X-rays ($\lambda = 1{\cdot}54$) = $\mu = 6{\cdot}87$ per cm. Total number of electrons per unit cell = $F(000) = 384$.

The reflections were recorded photographically, and intensity measurements carried out on an integrating photometer. Details of the specimens used have already been given (J., 1939, 232). After the usual corrections had been applied, and the F values put on an absolute scale by calibration with a diamond standard, a double Fourier series was set up from the $(0kl)$ structure factors, the coefficients being given in Table I.

TABLE I.

Values and signs of F(0kl) *used in Fourier summation.*

					l →					
↑ k	0	1	2	3	4	5	6	7	8	9
0	+384	—	+19	—	+24	—	+36	—	—	—
2	− 45	+27	+29	−10	− 5	−18	− 7	—	—	—
4	+ 3	+18	+21	− 8	− 8	− 7	+13	—	+14	—
6	+ 11	+ 6	−27	+42	+17	—	—	—	—	+14
8	− 28	—	—	−10	—	+12	−13	—	—	—
10	—	+12	—	—	—	—	—	—	—	—
12	− 7	−20	−10	—	—	—	—	—	—	—

The signs attached to these coefficients were determined from the trial analysis already described (*loc. cit.*). Subsequent recalculation of the structure factors from the final co-ordinates (Table II) shows two small changes in these signs, for the (040) and the (083) plane.

TABLE II.

Measured and calculated values of the structure factors (calculated from the co-ordinates given in Table III).

hkl.	*F*, meas.	*F*, calc.	*hkl.*	*F*, meas.	*F*, calc.	*hkl.*	*F*, meas.	*F*, calc.	*hkl.*	*F*, meas.	*F*, calc.
200	39	−40	044	8	−11	0, 10, 6	<10	− 2	170	6	+10
400	12	+14	045	7	− 9	0, 12, 1	20	−21	190	22	−26
600	21	−20	046	13	+23	0, 12, 2	10	−13	1, 11, 0	12	+15
020	45	−40	047	< 8	+ 8	0, 12, 3	<10	+ 1	220	96	−74
040	3	− 1	048	14	+24	102	55	+65	240	25	+11
060	11	+11	049	<10	− 4	202	5	−11	260	10	+13
080	28	−23	061	6	+ 8	302	7	− 9	280	< 6	−10
0, 10, 0	< 9	+ 1	062	27	−21	402	11	−21	2, 10, 0	24	+30
0, 12, 0	7	−25	063	42	+48	502	19	+22	310	20	+30
002	19	+18	064	17	+21	602	<13	−12	330	48	−45
004	24	+27	065	< 8	− 4	104	47	−46	350	4	+ 7
006	36	+45	066	< 8	+ 1	204	7	+ 4	370	5	+ 4
008	< 9	+ 5	067	<10	+ 7	304	12	− 7	390	< 7	+ 9
00, 10	< 8	+ 5	068	<11	− 8	404	14	+12	3, 11, 0	< 7	− 1
021	27	+25	069	14	+24	504	<12	− 1	420	25	+31
022	29	+31	081	< 8	−15	604	<12	− 6	440	< 6	0
023	10	−10	082	< 8	+ 3	106	< 9	− 2	460	7	+14
024	5	− 4	083	10	+ 9	206	<10	− 6	480	12	−18
025	18	−23	084	< 9	− 1	306	<12	− 8	4, 10, 0	9	−18
026	7	− 5	085	12	+ 8	406	<12	+11	510	8	+ 7
027	< 8	− 6	086	13	−19	506	13	+20	530	3	−10
028	< 9	+ 4	087	<10	+ 2	108	<12	+ 8	550	10	+16
029	<10	+12	0, 10, 1	12	+15	208	<13	− 9	570	16	−23
02, 10	<10	− 7	0, 10, 2	<10	+ 8	308	<13	− 2	590	< 7	+ 7
041	18	+23	0, 10, 3	<10	− 8	110	16	−20	620	< 7	− 2
042	21	+21	0, 10, 4	<10	+ 4	130	24	+15	640	9	−12
043	8	−12	0, 10, 5	<10	− 7	150	3	+ 2	660	< 7	+ 2

Corrections for these changes have not been made in the present projection, because their effect is small, but the changes should be noted in any future refinement of this analysis.

The results of the summation are plotted in the contoured diagram of Fig. 1. The estimated positions of the atom centres are indicated by small crosses for one half molecule, and these were derived (for the benzene ring) by inscribing the projection of a regular hexagon on the contoured diagram in such a way as to secure the best average centres for all the atoms. Small random errors are in this way eliminated, although the process does not take account of any real distortion in the regularity of the benzene ring, if such a distortion should exist. This seems unlikely, and apparent deviations from regularity are probably to be ascribed to various errors, chiefly incompleteness in the Fourier series.

The orientations of the benzene rings relative to the crystal axes were then deduced in the following way. χ_L, ψ_L, ω_L, χ_M, ψ_M, and ω_M denote the real angles which the molecular axes *L* and *M* (compare Fig. 2) make with the *a*, *b*, and *c* crystal axes. ζ_L and ζ_M are the angles measured on the projection between the *L* and *M* axes and the projected *b* crystal axis. y_0 is the distance of the intercept of the *L* molecular axis with the dyad axis below the centre of symmetry chosen as origin for the co-ordinates (marked 0° at the top of Fig. 1). R_{CG} is the assumed real distance between the atoms C and G, and r_{CG} is this distance actually measured on the projection.

Careful measurement of the projection then leads to the following values:

$\zeta_M = 110{\cdot}8^\circ\ (69{\cdot}2^\circ)$ $\quad R_{CG} = 2{\cdot}406$ A. (assumed)
$\zeta_L = 30{\cdot}0^\circ$ $\quad r_{CG} = 2{\cdot}18$ A.
$y_0 = 1{\cdot}624$ A.

Assuming a regular planar hexagon, we have the following relations :

(1) $\cos^2\chi_L + \cos^2\psi_L + \cos^2\omega_L = 1$ $\quad$ (4) $\cos\omega_M = \cos\psi_M \tan\zeta_M$
(2) $\cos^2\chi_M + \cos^2\psi_M + \cos^2\omega_M = 1$ $\quad$ (5) $\cos\omega_L = \cos\psi_L \tan\zeta_L$
(3) $\cos\chi_L \cos\chi_M + \cos\psi_L \cos\psi_M + \cos\omega_L \cos\omega_M = 0$ $\quad$ (6) $\sin\chi_M = r_{CG}/R_{CG}$

These equations lead to the following values for the orientation of the benzene ring :

$\chi_M = 65{\cdot}0^\circ$ $\quad \cos\chi_M = 0{\cdot}4226$ $\quad \chi_L = 71{\cdot}0^\circ$ $\quad \cos\chi_L = 0{\cdot}3251$
$\psi_M = 71{\cdot}2^\circ$ $\quad \cos\psi_M = 0{\cdot}3217$ $\quad \psi_L = 35{\cdot}0^\circ$ $\quad \cos\psi_L = 0{\cdot}8189$
$\omega_M = 147{\cdot}9^\circ$ $\quad \cos\omega_M = -0{\cdot}8473$ $\quad \omega_L = 61{\cdot}8^\circ$ $\quad \cos\omega_L = 0{\cdot}4730$

In the previous trial analysis (*loc. cit.*) the structure was defined in terms of four parameters, *viz.*, θ, the inclination of L to the dyad axis; α, the rotation of the benzene ring about the N–C bond from the position perpendicular to the plane of the nitrogen atoms; ϕ, the angle between the N$\equiv$N bond and the c crystal axis; and y_0, defined above. The new values for these parameters are now as follows :

$$\cos\theta = \cos\psi_L = 0\cdot8189 \qquad \theta = 35\cdot0^\circ \qquad \alpha = 34\cdot0^\circ$$
$$\cos\phi = \cos\omega_L/\sin\psi_L = 0\cdot8240 \qquad \phi = 34\cdot5^\circ \qquad y_0 = 1\cdot624\text{ A.}$$
$$\sin\alpha = \cos\psi_M/\sin\psi_L = 0\cdot5600$$

To interpret the results of the present Fourier analysis (Fig. 1) it is necessary, however, to modify the simple model used in the previous trial analysis. The atom A (nitrogen) is not accurately collinear with the atoms B and E of the benzene ring, but is so displaced that AB makes an angle of about 4° with the L molecular axis in the projection. Several recalculations of the ($h0l$) and the ($hk0$) structure factors show also that the best agreements with the observed values are obtained when the bond AB is further inclined to the plane of the benzene ring by about 4°. The molecular dimensions resulting from these movements are indicated in Fig. 2.

With these adjustments the final co-ordinates obtained for all the atoms with respect to the crystal axes and the centre of symmetry as origin are given in Table III.

TABLE III.

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

Atom (cf. Fig. 2).		x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
A	N	0·261	12·4°	2·355	66·7°	3·100	108·3°
B	C	0·880	41·9	3·574	101·2	3·703	129·4
C	CH	1·614	76·8	4·531	128·3	3·011	105·2
D	CH	2·065	98·2	5·666	160·5	3·668	128·2
E	CH	1·784	84·9	5·850	165·7	5·016	175·3
F	CH	1·049	49·9	4·892	138·5	5·708	199·5
G	CH	0·598	28·4	3·757	106·4	5·051	176·5

The agreements obtained when the structure factors are recalculated from the above co-ordinates are shown in Table II. The discrepancies between the observed and the calculated values are still considerable for some planes, but the improvement achieved as a result of the Fourier analysis is shown by the following figures for the three principal zones, which express the total discrepancies as a percentage of the total measured F values.

	$0kl$.	$h0l$.	$hk0$.
Original trial structure	24·0	18·8	36·3
Present Fourier analysis	19·1	14·1	28·2

The remaining discrepancies are probably due to inaccurate intensity measurements, to the absence of any allowance for anisotropic thermal vibrations, and to failure to locate the best mean atomic positions.

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