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The Crystal and Molecular Structure of *trans*-2,2′-Dichloroazobenzene

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In a previous paper,[1] the dipole moment and spectral data of substituted azobenzenes have been presented. The dipole moment and the intensity of the π–π^* band are apparently reduced by the introduction of methyl groups into ortho position with respect to azo group. This has been interpreted as due to the reduced conjugation by the twisting of the molecule. In this connection, it became desirable to obtain information about the molecular structure of 2,2′-disubstituted azobenzene in crystal. Recently, the crystal and molecular structures of 4,4′-disubstituted azobenzenes were determined and it was found that the molecules are nearly planar.[2–4] However, for 2,2′-disubstituted ones, no such information is available as yet. This paper presents the three-dimentional X-ray structure analysis of 2,2′-dichloroazobenzene.

Experimental

2,2′-Dichloroazobenzene was prepared from *o*-chloroaniline,[5] and recrystallized by slow evaporation from a benzene–ligroin solution. The compound crystallized as red plates having a predominant (001) face.

Crystal data: $C_{12}H_8N_2Cl_2$; M=251.1; mp=138—139 °C, monoclinic, $a=13.651(8)$, $b=3.946(8)$, $c=11.626(4)$ Å, $\beta=114.40(3)°$, $U=570.4$ Å^3, $D_m=1.47$, $D_x=1.46$ g cm^{-3}, $Z=2$. Absorption coefficient for Cu$K\alpha$; $\mu=48.8$ cm^{-1}. $F(000)=256$.

Absent spectra: $h0l$ when h is odd and $0k0$ when k is odd. Space group is $P2_1/a$.

Using Cu$K\alpha$ radiation, multiple-film equi-inclination Weissenberg photographs were taken for the layers from $0kl$ to $9kl$ and from $h0l$ to $h2l$. A total of 995 independent nonzero reflections was recorded. The intensities were estimated visually. After Lorentz, polarization and spot-shape corrections were made, the intensities of various layers were adjusted to the same relative scale by making use of all the common reflections. The relative values were converted to an absolute scale by Wilson's method. No corrections were applied for absorption and extinction effects.

Structure Determination

In the space group $P2_1/a$, four is the minimum number of asymmetric units necessary to fulfill the symmetry operation, while there are only two molecules in the unit cell. Hence it must be that the molecules themselves are centrosymmetric, and occupy the position of a center of symmetry of the cell.

Approximate x,y,z parameters for all non-hydrogen atoms were easily determined from a three-dimensional Patterson map. The structure was refined by the block-diagonal least-squares method[6] with isotropic thermal parameters to an R value of 0.17 and with anisotropic ones to the R of 0.10. The difference Fourier synthesis showed the locations of all the four hydrogen atoms. Furthermore, six cycles of calculation were made with anisotropic thermal parameters for the non-hydrogen atoms and with isotropic thermal parameters (initially set at $B=3.5$ Å^2) for the hydrogen atoms using unit weight for all the observed reflections. The final R index was 0.087 for all the observed reflections. The final positional and thermal parameters are given in Table 1. The numerical calculations were performed with the aid of a HITAC 5020E computer of the Computer Center of the University of Tokyo, a FACOM 230—60 computer of the Data Processing Center of Kyoto University. The atomic scattering factors were taken from Ref. (7).

Results and Discussion

The bond lengths and angles are shown in Fig. 1. The average C–C bond length in the benzene ring is 1.389 Å. The bond angles in benzene ring range from 118.6 to 121.4°. The other bond lengths and angles are listed in Table 2, together with the corresponding bond lengths and angles of azobenzene and other related compounds. As shown in Table 2, the N=N, N–C and C–Cl bond lengths and the N=N–C

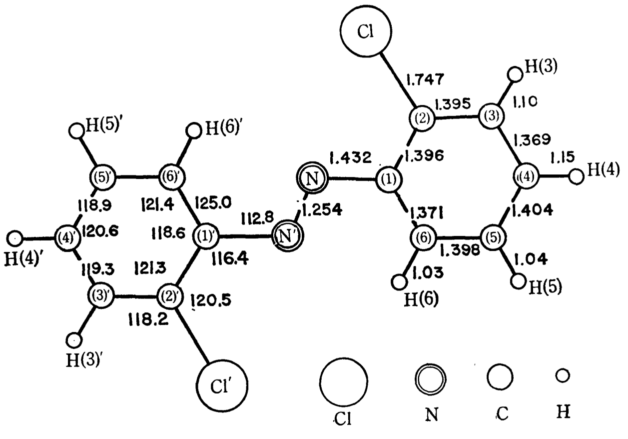

Fig. 1. Bond lengths and angles. Estimated standard deviations are 0.007—0.010 Å for lengths not involving H, 0.07 Å for C–H lengths and 0.5—0.7° for angles not involving H.

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Table 1. Final fractional atomic coordinates and their estimated standard deviations for the atoms in asymmetric unit, and isotropic thermal parameters for hydrogen atoms

	x	*y*	*z*	B_{iso}		*x*	*y*	*z*	B_{iso}
C(1)	0.1202(5)	−0.0415(16)	0.1391(5)		N	0.0093(4)	0.0129(15)	0.0573(4)	
C(2)	0.1516(5)	0.0436(15)	0.2659(5)		Cl	0.0591(1)	0.2175(5)	0.3176(1)	
C(3)	0.2571(5)	−0.0052(18)	0.3545(5)		H(3)	0.280(5)	0.068(17)	0.453(6)	1.0(14)
C(4)	0.3307(5)	−0.1447(18)	0.3165(6)		H(4)	0.419(5)	−0.207(18)	0.382(6)	1.3(14)
C(5)	0.3012(5)	−0.2333(19)	0.1896(6)		H(5)	0.353(5)	−0.328(16)	0.152(5)	0.6(12)
C(6)	0 1949(5)	−0.1817(17)	0.1029(5)		H(6)	0.175(5)	−0.260(17)	0.011(6)	1.6(14)

Anisotropic thermal parameters$^{a)}$ and estimated standard deviations ($\times 10^4$) for the non-hydrogen atoms

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	47(4)	443(41)	55(5)	−9(22)	43(7)	32(23)
C(2)	50(4)	368(39)	67(5)	−9(21)	62(8)	−13(24)
C(3)	50(4)	591(48)	52(5)	−27(24)	25(7)	45(26)
C(4)	53(4)	564(48)	79(6)	−23(25)	44(8)	63(29)
C(5)	58(4)	597(50)	81(6)	52(27)	55(8)	79(31)
C(6)	57(4)	543(46)	59(5)	14(25)	46(8)	41(26)
N	50(3)	593(40)	52(4)	12(20)	36(6)	−20(22)
Cl	53(1)	717(13)	62(1)	−10(7)	54(2)	−118(7)

a) Anisotropic temperature factors are of the form $\exp(-h^2B_{11}-k^2B_{22}-l^2B_{33}-hkB_{12}-hlB_{13}-klB_{23})$.

Table 2. Comparison of the bond lengths and angles between this compound and related compounds

	N=N	N–C	C–Cl	N–N–C	N–C(1)–C(6)	N–C(1)–C(2)
This compound	1.254 Å	1.432 Å	1.747 Å	112.8°	125.0°	116.4°
Azobenzene[8]	1.243	1.443	—	113.6	124.1	115.5
4,4′-Dimethylazobenzene[3]	1.244	1.433	—	113.8	128.8	112.6
4,4′-Dibromoazobenzene[2]	1.276	1.528	—	112.2	125.6	114.7
4,4′-Dichloroazobenzene[4]	1.252	1.443	1.737	112.6	125.9	114.2
N-5-Chlorosalicylideneaniline[9]	—	1.419	1.755	—	124.3	116.1
2-Chloro-*N*-salicylideneaniline[10]	—	1.421	1.737	—	121.2	120.2

Table 3. Deviation (Å) of atom from plane (1) and (2)

	Plane(1)	Plane(2)		Plane(1)	Plane(2)
C(1)	−0.017*	0.000*	C(6)	−0.001*	0.277
C(2)	−0.003*	−0.249	N	0.013*	0.000*
C(3)	−0.002*	−0.247	N′	−0.232	0.000*
C(4)	0.010*	0.029	Cl	0.001*	−0.585
C(5)	0.000*	0.286			

Least-squares plane is determined by the atoms with asterisk.
Dihedral angle between the two plane is 12.8°.
The numbering of each atom is the same as that in Fig. 1.

Table 4. Intermolecular contacts

Atom	Neighbour atom	Distance	Atom	Neighbour atom	Distance
(1) I···II			(4) II···IV		
C(4)	Cl	3.54 Å	H(3)	H(3)	2.55 Å
H(4)	Cl	3.02	H(3)	C(3)	3.01
(2) I···III			Cl	H(3)	3.00
Cl	H(3)	3.00	(5) III···IV		
H(3)	H(3)	2.55	Cl	H(4)	3.08
H(3)	C(3)	3.01	Cl	H(5)	3.08
(3) I···V					
Cl	Cl	3.95			
Cl	C(2)	3.63			

Perpendicular distance from benzene ring (I) to benzene ring (V) is 3.62 Å

Key for position of molecules
I: *x*, *y*, *z*; II: 1/2+*x*, 1/2−*y*, *z*; III: 1/2−*x*, 1/2+*y*, 1−*z*; IV: 1−*x*, −*y*, 1−*z*; V: *x*, 1+*y*, *z*

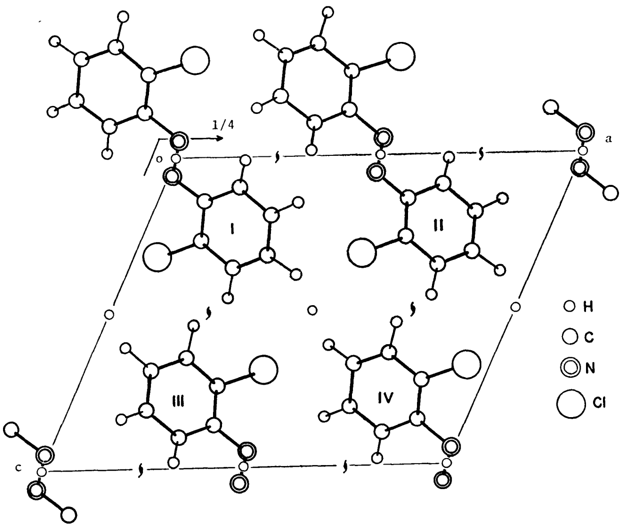

Fig. 2. The projection of the crystal structure along the b-axis.
Key for molecules I: *x*, *y*, *z*; II: 1/2+*x*, 1/2−*y*, *z*; III: 1/2−*x*, 1/2+*y*, 1−*z*, IV: 1−*x*, −*y*, 1−*z*.

and N–C–C (*cis* and *trans* relative to the central double bond) bond angles are well consistent with the corresponding values of the related compounds.

The intramolecular distance between Cl and N atoms (2.98 Å) is considerably shorter than the sum of the van der Waals radii of Cl and N atoms (3.3 Å). Hence the steric repulsion between these two atoms must exist. As mentioned above, however, the bond lengths and angles are hardly affected by the introduction of Cl atom into *ortho* position with respect to azo group.

As shown in Table 3, the benzene ring including N and Cl atoms is planar within 0.02 Å. This plane (plane 1) makes a dihedral angle of 12.8° with the N=N–C plane (plane 2). From the inspection of Table 3, it can be concluded that the dihedral angle between these two planes is the twisting angle of the benzene ring around the N–C bond. As mentioned in the section of structure determination, this compound has the center of symmetry. The two benzene rings must be symmetrically twisted around the azo group. This is in accord with the previous suggestion that the molecule is twisted in the same manner. The cause of the twist has already been discussed in some detail.1)

The mode of packing of the molecules in the crystal can be seen in Fig. 2. The short intermolecular contacts are summarized in Table 4. They show the normal van der Waals interaction.

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