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The structure of 3:3′-dichlorobenzidine.

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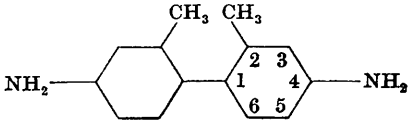
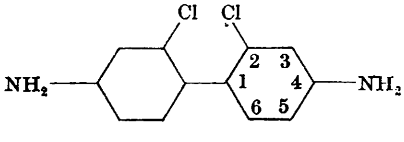
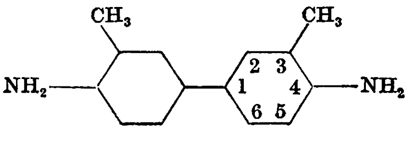
Analysis of the structures of *m*-tolidine dihydrochloride (Hargreaves & Taylor, 1941) and of 2:2′-dichlorobenzidine (Smare, 1942) has shown that in each of these molecules (I, II) the phenyl rings are rotated from the *cis*-planar configuration through approximately 36° in opposite directions around the central diphenyl link, so that the angle between the planes of the phenyl rings is approximately 72°. The non-planar configuration arises from the need to allow clearance between the rather large methyl groups or chlorine atoms attached to the rings at positions 2,2′. It would obviously be of interest to compare the configurations of these molecules with those of *o*-tolidine (III) and 3:3′-dichlorobenzidine (IV), for which a completely planar configuration would seem to be likely, whether the molecule is *cis* or *trans*.



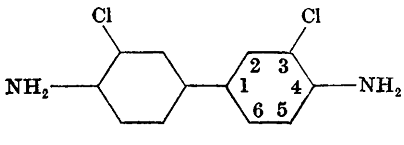
(I)



(II)



(III)



(IV)

The unpublished data of A. Hargreaves and H. F. Kay show that the unit cell of 3:3′-dichlorobenzidine is monoclinic with *a* 12·5 A., *b* 3·85 A., *c* 23·7 A., and β 108°. The cell contains four molecules, the space group is $P2_1/a$, and a special feature of the diffraction patterns is that reflexions $(h0l)$ are absent or very weak when h is odd, indicating that the structure has a pseudo-periodicity $\frac{1}{2}a$ in projection on (010). I am indebted to Dr Hargreaves and Mr Kay for permission to use their experimental data, which include the intensities of all $(h0l)$ reflexions estimated by eye in the usual way.

The present paper describes the results obtained from these data, in an attempt to complete the analysis of the structure.

From the Patterson projection along the b axis it is possible to determine approximate x and z co-ordinates for both chlorine atoms of the molecule; but from these co-ordinates it appears that the chlorine atoms contribute nothing to reflexions $(h0l)$ when h is odd, so that in a first Fourier synthesis the positions of these atoms can be used to determine the signs of reflexions $(h0l)$ only when h is even. The usual method of successive approximations, using only terms $(h0l)$ with h even, leads to the projection in Fig. 1.

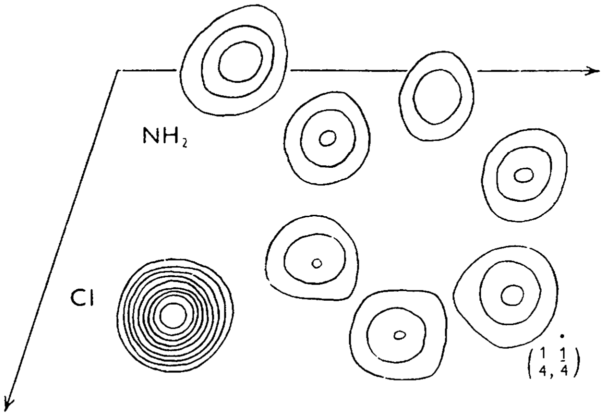


Fig. 1. 3:3′-dichlorobenzidine. Electron density projected on (010)

Since terms $(h0l)$ with h odd have been left out of consideration in the calculation of this projection, it represents an 'average' structure having spurious symmetry additional to the true symmetry of the actual structure. The 'molecule' is an 'average' molecule, with a spurious centre of symmetry at $x=\frac{1}{4}a$, $z=\frac{1}{4}c$ (the point marked $\frac{1}{4}$, $\frac{1}{4}$ in

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Fig. 1). Nevertheless, the weakness of the terms ($h0l$) with h odd indicates that the true molecule, as seen in projection, must be very nearly identical in configuration and orientation with the average molecule. The projection suggests that the molecule is probably planar, or very nearly so, and shows that the chlorine atoms are in the *trans* positions; the plane of the molecule may be inclined to the (010) plane at an angle not exceeding 25°.

Further work is now in progress, using all (hkl) reflexions, from which it is hoped to determine accurately the configuration and orientation of the molecules.

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The crystal structure of the molecular complex of 4:4′-dinitrodiphenyl with diphenyl.

By J. N. van Niekerk and D. H. Saunder. *University of Cape Town, South Africa*

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The structure of this complex seems to be almost identical with the structure of the complex of 4:4′-dinitrodiphenyl with 4-hydroxydiphenyl previously described by one of us (Saunder, 1946). This is confirmed by the very close agreement between the observed F values after allowance has been made for the extra OH group.

The crystals, which grow as pale yellow needles, develop mainly the prism faces {110}, though occasionally the (100) and (001) faces may develop as well. The unit cell dimensions are

$$a=19{\cdot}9\text{ A.},\quad b=9{\cdot}50\text{ A.},\quad c=11{\cdot}0\text{ A.},\quad \beta=99^\circ\ 30',$$

and this cell contains two of the complex groups

$$(C_6H_5C_6H_5).(O_2NC_6H_4C_6H_4NO_2)_3.$$

This may be compared with the dimensions

$$a=20{\cdot}0\text{ A.},\quad b=9{\cdot}46\text{ A.},\quad c=11{\cdot}1\text{ A.},\quad \beta=99^\circ\ 39',$$

for the similar complex with hydroxydiphenyl

$$(C_6H_5C_6H_4OH).(O_2NH_6H_4C_6H_4NO_2)_3.$$

Reflexions of type hkl occur only with $h+k$ even, $h00$ only with h even, and $0k0$ only with k even. The space group may therefore be $C2$, Cm or $C2/m$, and all these space groups are spatially possible. In the case of the complex with hydroxydiphenyl the space group was fixed from spatial considerations as Cm.

Comparative photographs for the two complexes are almost identical, and the thermal vibrations in each produce diffuse reflexions accompanying corresponding spectra.

The $h0l$ spectra were recorded on a Weissenberg photograph taken with a crystal mounted about the b axis. The intensities of these spectra were measured on a microphotometer calibrated against a standard wedge. The values of $F(h0l)$ are compared with the corresponding values of $F(h0l)$ observed for the complex with hydroxydiphenyl (after subtracting the calculated contribution of the OH group) in Table 1. The agreement is excellent.

Assuming the space group $C2/m$, a Fourier projection of the unit cell along b on to the ac plane was made, and the contour diagram thus obtained was found to be closely similar to the corresponding contour diagram for the complex with hydroxydiphenyl, the only significant difference being that there was no peak corresponding to the position of the OH group.

If the space group is either Cm or $C2/m$, it should be noted that, since there are only two 'complex groups' in the unit cell, it is then necessary for the diphenyl molecules to lie completely in the mirror planes, and for the dinitrodiphenyl molecules to lie across the mirror planes, as was found to be the case for the hydroxydiphenyl complex. It should be possible to distinguish between the possible space groups by observing the pyro-electric effect, but we have been unable to obtain single crystals large enough to make satisfactory measurements.

Table 1

$h0l$	D	H
200	80	72
400	120	109
600	82	93
800	41	46
10.0.0	14	27
14.0.0	17	26
001	25	28
002	27	35
003	270	219
004	20	22
005	29	49
006	23	32
007	20	28
201	60	56
202	74	76
204	23	24
205	21	35
$20\bar{1}$	37	29
$20\bar{2}$	53	40
$20\bar{3}$	240	177
$20\bar{4}$	36	41
$20\bar{5}$	71	59
$20\bar{6}$	155	114
402	43	32
403	70	80
404	20	19
405	20	28
$40\bar{1}$	110	88
$40\bar{2}$	36	35
$40\bar{3}$	14	14
$40\bar{4}$	44	42
$40\bar{5}$	16	21
602	120	110
603	56	62
604	22	25
605	15	—
606	17	—
$60\bar{1}$	176	120
$60\bar{2}$	80	68
$60\bar{3}$	23	24
$60\bar{6}$	21	32
$60\bar{8}$	25	28
801	60	69
802	160	146
803	31	59
804	15	24
805	47	71
806	21	25
807	23	26
$80\bar{1}$	27	41
$80\bar{2}$	26	43
$80\bar{3}$	79	81
$80\bar{4}$	58	59
$80\bar{5}$	14	
$80\bar{8}$	22	31
8.0.10	24	34
10.0.1	22	35
10.0.2	44	52
10.0.5	22	21
10.0.6	23	23
$10.0.\bar{1}$	220	197
$10.0.\bar{3}$	19	
$10.0.\bar{4}$	106	84
$12.0.\bar{1}$	39	55
$12.0.\bar{2}$	19	20
$12.0.\bar{7}$	33	38
$14.0.\bar{1}$	37	37
14.0.2	36	42
$14.0.\bar{1}$	82	81
$14.0.\bar{2}$	27	35
16.0.1	33	27
$16.0.\bar{1}$	13	16
$16.0.\bar{2}$	27	44
$16.0.\bar{7}$	37	54

$D=F(h0l)$ observed for the diphenyl complex.

$H=F(h0l)$ observed for hydroxydiphenyl complex, and after subtraction of the contribution of the OH group.

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