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# The Crystal Structure of 2-2′-dichlorobenzidine $(Cl.C_6H_3.NH_2)_2$

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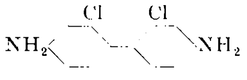
Standard single crystal methods show that the unit cell of 2-2′-dichlorobenzidine is orthorhombic, with *a*, *b*, *c* translations 7·51, 15·20, 10·40 A. respectively; the cell contains four molecules and has space group *Pnca*. The atomic co-ordinates are deduced from two-dimensional Fourier syntheses of electron density projected on (100) and (001). The structure is racemic, the molecules showing a tendency to adopt the *cis*-configuration; steric hindrance, however, necessitates an angle of 72° between the planes of the two rings. The diphenyl link is 1·53 A. and the C–C bonds are alternately long and short with mean values 1·45 and 1·30 A. respectively.

The work described is a contribution to a survey of a number of substituted diphenyls; a preliminary account of the survey has been given by Hargreaves & Taylor (1941).

## Investigation of the structure

2-2′-dichlorobenzidine



crystallizes readily from aqueous alcohol in elongated hexagonal plates of a mauve-brown colour. The crystals are moderately hard and, under a needle, fracture crisply with an imperfect cleavage perpendicular to the longer edges.

Oscillation and rotation photographs obtained with Cu $K\alpha$ (filtered) radiation show that the lattice is orthorhombic. The lattice translations are

*a* (parallel to the longer edge of the plate) = 7·51 A.,
*b* (normal to the plate) = 15·20 A.,
*c* = 10·40 A.,

with a possible error of 0·3 % in each case.

The molecular weight of the compound is 253; with four molecules in the unit cell, the calculated density is $1{\cdot}41_2$ g.cm.$^{-3}$ (measured $1{\cdot}41_6$ g.cm.$^{-3}$).

Absent spectra determine the space group to be (uniquely) $Pnca-D_{2h}^{14}$; the four molecules in the unit cell must therefore occupy special positions, since the general positions for *Pnca* require eightfold repetition. The centre of a molecule may be placed either at a symmetry centre or on a digonal axis. Simple tests of the packing of permitted arrangements and comparison of visually estimated intensities with the calculated values indicate clearly that the probable structure is one in which molecules having an approximately *cis*-configuration lie on digonal axes. A true *cis*-configuration cannot be attained on account of the steric hindrance of the two chlorine atoms; calculation assuming normal van der Waals distances shows that each ring must be rotated approximately 36° away from the *cis*-planar position.

The trial structure suggested that good resolution would be obtained in projections parallel to [100] and [001] respectively. Reflexions of type $0kl$ were recorded on three Weissenberg photographs with different exposure times (Cu $K\alpha$ radiation); a corresponding set recorded reflexions of type $hk0$. The intensities of these reflexions were measured with an integrating photometer, similar to that described by Robinson (1933), with the exception of certain very weak reflexions the intensities of which were estimated visually. The linear absorption coefficient is 46·7 cm.$^{-1}$; absorption corrections for all reflexions were determined by the method described by Albrecht (1939).

The initial calculation of structure amplitudes was made with atomic co-ordinates from the trial structure and atomic scattering factors as follows: for carbon and nitrogen suitably weighted 'average hydrocarbon' data as given by Robertson (1935) and for chlorine scattering data found to be suitable in an investigation of a related compound, *m*-tolidine hydrochloride (Hargreaves & Taylor, 1941).

## Fourier syntheses

For the refining of the structure Fourier syntheses of electron density projected parallel to [100] and [001] respectively were evaluated. The values of $|F_{\text{obs.}}|$, on an arbitrary scale, were multiplied by the mean ratio $|F_{\text{calc.}}|/|F_{\text{obs.}}|$; these modified values were used with the phases (0 or $\pi$) from the calculated structure amplitudes. The electron density was evaluated at intervals of $b/60$, $c/60$; $a/60$, $b/60$, respectively, the summation being carried out with the aid of Beevers and Lipson strips.

The individual features of each projection are discussed briefly below.

(*a*) *Projection parallel to* [100]. The small changes in atomic co-ordinates suggested by the first synthesis produced changes of phase of six terms; the second synthesis incorporated these changes. Such changes in co-ordinates as were made on the basis of the second synthesis caused no further changes of phase.

It is probable that the Fourier series is limited by the wave-length employed in this case, as with Cu $K\alpha$ radiation reflexions are observed up to large values of $\sin\theta$. A third synthesis has therefore been constructed with structure amplitudes modified by an artificial temperature factor which reduces terms with $\sin\theta \sim 1$ to negligible proportions.

The co-ordinates (Table 1 (*a*)) deduced from this third synthesis differ slightly from those deduced from the second synthesis, but no further changes of phase are produced on recalculating the structure amplitudes. The contour diagram of the third synthesis is reproduced in Fig. 1. The following points may be noted:

(i) Atoms $C_1$, $C_2$, $C_3$, $C_4$ and N are perfectly resolved.

(ii) Although atoms $C_5$, $C_6$ and Cl are not perfectly resolved, the lack of resolution is due in each case to the presence of the respective mirror images of these atoms and analysis of the compound peak can be made.

(iii) The contours defining atoms $C_4$ and N are elongated in a direction parallel to [001].

Improved agreement between observed and calculated values of $F_{0kl}$ was obtained by adjusting the atomic scattering factors in the following way. The Robertson scattering data were modified so as to correspond to a lower temperature and each scattering factor thus obtained is multiplied by $e^{-Bl^2}$, where $B$ is a constant having one value for atoms $C_1$, $C_2$, $C_6$ and Cl and a larger value for atoms $C_3$, $C_4$, $C_5$ and N. Physically these adjustments may be interpreted in terms of preferential atomic vibrations parallel (in projection) to [001], the amplitudes of vibration being larger for the second group of atoms.

Table 1. *Atomic co-ordinates in Ångström units*

| | (*a*) | | (*b*) | | (*c*) | | |
|---|---|---|---|---|---|---|---|
| | *y* | *z* | *x* | *y* | *x* | *y* | *z* |
| $C_1$ | 0·76 | 3·80 | 1·77 | 0·76 | 1·77 | 0·76 | 3·80 |
| $C_2$ | 1·39 | 2·83 | 0·90 | 1·39 | 0·90 | 1·39 | 2·83 |
| $C_3$ | 2·64 | 2·80 | 0·63* | — | 0·63* | 2·64 | 2·80 |
| $C_4$ | 3·42 | 3·88 | 1·15 | — | 1·15 | 3·42 | 3·88 |
| $C_5$ | 2·92 | 4·70 | 2·02 | 3·00 | 2·02 | 2·92 | 4·70 |
| $C_6$ | 1·48 | 4·78 | 2·29 | 1·48 | 2·29 | 1·48 | 4·78 |
| N | 2·80 | 1·46 | 0·94* | — | 0·94* | 4·80 | 3·74 |
| Cl | 0·42 | 1·56 | 0·25 | 0·42 | 0·25 | 0·42 | 1·56 |

(*a*) Co-ordinates from the [100] projection.
(*b*) Co-ordinates from the [001] projection.
(*c*) Self-consistent set of co-ordinates.
* Not deduced from the contour diagram.

Calculated and observed values of $F_{0kl}$ are given in Table 2.

(*b*) *Projection parallel to* [001]. In this projection atom $C_3$ of one molecule and atom N from an adjacent molecule are almost superimposed, and it is not practicable to deduce the atomic co-ordinates uniquely from the contour diagram. The co-ordinates for recalculating $F_{hk0}$ values are derived partly from the first synthesis and partly from the final [100] synthesis; the $x$ co-ordinates of atoms $C_3$ and N are adjusted to give the best agreement between observed and calculated $F_{hk0}$ values. The second and third syntheses each incorporate one change of phase; no further changes occur on recalculating $F_{hk0}$ values with co-ordinates deduced from the third synthesis. It has not been considered necessary to modify the structure amplitudes by an artificial temperature factor in this projection as there appears to be a natural termination; reflexions with $\sin\theta > 0{\cdot}93$ have not been observed. The atomic co-ordinates deduced are given in Table 1 (*b*) and the contour diagram is reproduced in Fig. 2. The following points may be noted:

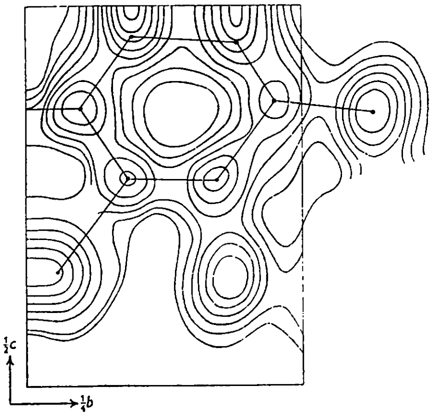


Fig. 1. Projection of electron density on (100).

(i) Atoms $C_1$, $C_2$, $C_5$, $C_6$ and Cl are perfectly resolved.

(ii) Atom $C_4$ is not perfectly resolved, but the $x$ co-ordinate can be deduced.

(iii) The contours defining the chlorine atom are elongated in a direction parallel (in projection) to [100].

For the final calculation of structure amplitudes the scattering factors for C and N are those given by Robertson; the scattering factor for chlorine is multiplied by $e^{-Bh^2}$, an adjustment which can be interpreted in terms of an increased amplitude of oscillation parallel to [100].

Table 2. *Observed and calculated* $F_{0kl}$

| sin $\theta$ | $0kl$ | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | sin $\theta$ | $0kl$ | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | sin $\theta$ | $0kl$ | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·000 | 000 | — | 520 | 0·541 | 066 | 16 | 20 | 0·791 | 0.15.3 | (16) | 16 |
| 0·090 | 011 | (4) | 1 | 0·560 | 0.11.1 | < 4 | $\bar{5}$ | 0·800 | 0.6.10 | < 4 | $\overline{10}$ |
| 0·101 | 020 | 41 | 49 | 0·579 | 057 | 19 | 26 | 0·805 | 0.16.0 | (23) | $\overline{26}$ |
| 0·148 | 002 | 52 | $\overline{58}$ | 0·585 | 095 | < 4 | 4 | 0·807 | 099 | < 4 | 2 |
| 0·170 | 031 | 62 | 68 | 0·585 | 0.10.4 | 38 | 25 | 0·812 | 0.1.11 | < 4 | 4 |
| 0·175 | 022 | 37 | $\overline{34}$ | 0·592 | 008 | 35 | 30 | 0·820 | 0.16.2 | < 4 | 11 |
| 0·202 | 040 | 60 | 60 | 0·598 | 0.11.3 | 20 | $\overline{21}$ | 0·825 | 0.3.11 | 12 | $\bar{9}$ |
| 0·230 | 013 | 87 | $\overline{84}$ | 0·600 | 086 | < 4 | 4 | 0·835 | 0.14.6 | (7) | $\overline{12}$ |
| 0·250 | 042 | 22 | $\overline{14}$ | 0·600 | 028 | 15 | 6 | 0·840 | 0.13.7 | (12) | $\overline{19}$ |
| 0·265 | 051 | 48 | 44 | 0·606 | 0.12.0 | < 4 | $\bar{9}$ | 0·843 | 0.8.10 | < 4 | 6 |
| 0·270 | 033 | 24 | $\overline{34}$ | 0·625 | 0.12.2 | (9) | $\bar{8}$ | 0·845 | 0.15.5 | < 4 | 5 |
| 0·296 | 004 | 64 | $\overline{76}$ | 0·625 | 077 | (7) | 11 | 0·849 | 0.12.8 | < 4 | $\bar{4}$ |
| 0·303 | 060 | 42 | 40 | 0·627 | 048 | (7) | 13 | 0·850 | 0.5.11 | < 4 | $\overline{12}$ |
| 0·315 | 024 | 55 | $\overline{42}$ | 0·660 | 0.13.1 | (8) | $\overline{14}$ | 0·860 | 0.16.4 | (6) | 5 |
| 0·335 | 062 | 23 | $\overline{22}$ | 0·665 | 0.11.5 | 22 | $\overline{17}$ | 0·860 | 0.17.1 | (10) | $\overline{10}$ |
| 0·340 | 053 | 53 | $\overline{56}$ | 0·666 | 019 | (18) | $\overline{18}$ | 0·868 | 0.11.9 | < 4 | 4 |
| 0·360 | 044 | 89 | $\overline{83}$ | 0·668 | 068 | < 4 | 4 | 0·885 | 0.17.3 | (20) | 23 |
| 0·360 | 071 | 59 | 51 | 0·673 | 0.10.6 | 24 | $\overline{10}$ | 0·885 | 0.7.11 | < 4 | $\overline{12}$ |
| 0·375 | 015 | 22 | $\overline{12}$ | 0·676 | 0.12.4 | 36 | 29 | 0·888 | 0.0.12 | < 4 | $\bar{9}$ |
| 0·400 | 035 | 27 | 18 | 0·685 | 039 | < 4 | $\overline{12}$ | 0·890 | 0.2.12 | < 4 | 3 |
| 0·404 | 080 | 60 | $\overline{57}$ | 0·690 | 097 | < 4 | $\bar{2}$ | 0·895 | 0.10.10 | < 4 | $\bar{4}$ |
| 0·420 | 073 | 32 | $\overline{30}$ | 0·693 | 0.13.3 | 32 | 38 | 0·905 | 0.18.0 | (18) | $\overline{18}$ |
| 0·425 | 064 | 27 | $\overline{31}$ | 0·705 | 0.14.0 | 52 | $\overline{55}$ | 0·908 | 0.4.12 | < 4 | 3 |
| 0·430 | 082 | < 4 | 7 | 0·715 | 059 | < 4 | $\bar{8}$ | 0·917 | 0.15.7 | (5) | $\overline{16}$ |
| 0·444 | 006 | 35 | 35 | 0·716 | 088 | < 4 | $\bar{5}$ | 0·920 | 0.18.2 | < 4 | 0 |
| 0·450 | 055 | < 4 | 10 | 0·722 | 0.14.2 | < 4 | $\overline{12}$ | 0·921 | 0.16.6 | < 4 | $\bar{7}$ |
| 0·455 | 026 | 42 | 39 | 0·740 | 0.0.10 | 42 | $\overline{37}$ | 0·925 | 0.14.8 | (5) | $\bar{6}$ |
| 0·460 | 091 | 22 | $\overline{17}$ | 0·746 | 0.2.10 | 21 | $\overline{17}$ | 0·929 | 0.9.11 | < 4 | 2 |
| 0·490 | 046 | 45 | 39 | 0·750 | 0.12.6 | (11) | $\overline{20}$ | 0·934 | 0.6.12 | < 4 | 6 |
| 0·500 | 084 | < 4 | 4 | 0·755 | 079 | < 4 | $\bar{2}$ | 0·935 | 0.17.5 | < 4 | 4 |
| 0·505 | 0.10.0 | 19 | 27 | 0·755 | 0.13.5 | < 4 | 3 | 0·938 | 0.13.9 | (4) | 1 |
| 0·505 | 093 | < 4 | $\bar{1}$ | 0·760 | 0.11.7 | (16) | 22 | 0·957 | 0.12.10 | < 4 | 5 |
| 0·510 | 075 | < 4 | $\bar{4}$ | 0·761 | 0.15.1 | < 4 | $\overline{11}$ | 0·958 | 0.18.4 | < 4 | 4 |
| 0·520 | 0.1.7 | 45 | 47 | 0·765 | 0.14.4 | (18) | 8 | 0·961 | 0.19.1 | (14) | 21 |
| 0·525 | 0.10.2 | (7) | 13 | 0·765 | 0.4.10 | (10) | $\overline{12}$ | 0·971 | 0.8.12 | < 4 | 4 |
| 0·540 | 037 | < 4 | 6 | 0·779 | 0.10.8 | < 4 | $\bar{8}$ | 0·982 | 0.11.11 | < 4 | 5 |

Bracketed values of $F_{\text{obs.}}$ are obtained from visually estimated intensities.

Table 3. *Observed and calculated* $F_{hk0}$

| sin $\theta$ | $hk0$ | $F_{\text{obs.}}$ | $F_{\text{calc}}$ | sin $\theta$ | $hk0$ | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ | sin $\theta$ | $hk0$ | $F_{\text{obs.}}$ | $F_{\text{calc.}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·000 | 000 | — | 520 | 0·590 | 2.11.0 | < 5 | $\overline{13}$ | 0·821 | 810 | < 5 | $\bar{6}$ |
| 0·101 | 020 | 41 | 49 | 0·606 | 0.12.0 | < 5 | $\bar{9}$ | 0·823 | 820 | < 5 | $\bar{2}$ |
| 0·202 | 040 | 52 | 60 | 0·608 | 4.9.0 | < 5 | $\overline{13}$ | 0·825 | 6.11.0 | < 5 | $\bar{9}$ |
| 0·205 | 200 | 15 | 20 | 0·615 | 600 | < 5 | $\bar{2}$ | 0·830 | 830 | < 5 | 0 |
| 0·210 | 210 | 86 | $\overline{85}$ | 0·616 | 610 | 26 | 21 | 0·832 | 2.16.0 | 18 | 22 |
| 0·229 | 220 | 72 | 75 | 0·619 | 620 | < 5 | 6 | 0·841 | 840 | < 5 | 2 |
| 0·255 | 230 | 7 | 0 | 0·630 | 630 | 7 | $\overline{12}$ | 0·854 | 850 | < 5 | $\overline{12}$ |
| 0·287 | 240 | 51 | 51 | 0·637 | 2.12.0 | < 5 | $\bar{9}$ | 0·856 | 4.15.0 | < 5 | $\bar{5}$ |
| 0·303 | 060 | 37 | 40 | 0·644 | 640 | 13 | 10 | 0·859 | 6.12.0 | < 5 | $\bar{3}$ |
| 0·323 | 250 | 14 | $\overline{21}$ | 0·649 | 4.10.0 | 18 | $\overline{15}$ | 0·870 | 860 | < 5 | 1 |
| 0·365 | 260 | 58 | 50 | 0·660 | 650 | 18 | $\overline{24}$ | 0·880 | 2.17.0 | < 5 | $\bar{2}$ |
| 0·404 | 080 | 60 | $\overline{57}$ | 0·680 | 660 | 14 | $\bar{8}$ | 0·885 | 870 | < 5 | $\bar{6}$ |
| 0·406 | 270 | 52 | $\overline{49}$ | 0·686 | 2.13.0 | 28 | $\overline{20}$ | 0·896 | 6.13.0 | 5 | 0 |
| 0·410 | 400 | 18 | 11 | 0·688 | 4.11.0 | 21 | $\overline{18}$ | 0·901 | 4.16.0 | 8 | $\bar{7}$ |
| 0·412 | 410 | 21 | $\overline{24}$ | 0·705 | 0.14.0 | 51 | $\overline{55}$ | 0·905 | 0.18.0 | 19 | $\overline{18}$ |
| 0·420 | 420 | 54 | 53 | 0·705 | 670 | 18 | 23 | 0·909 | 880 | < 5 | $\overline{10}$ |
| 0·435 | 430 | 31 | $\overline{35}$ | 0·728 | 4.12.0 | 32 | 22 | 0·928 | 2.18.0 | 14 | $\overline{16}$ |
| 0·450 | 280 | 28 | 24 | 0·731 | 680 | 23 | 16 | 0·932 | 890 | < 5 | $\bar{8}$ |
| 0·455 | 440 | 40 | 34 | 0·735 | 2.14.0 | 18 | $\overline{19}$ | 0·933 | 6.14.0 | < 5 | 3 |
| 0·479 | 450 | 8 | $\overline{17}$ | 0·760 | 690 | 27 | $\overline{39}$ | 0·947 | 4.17.0 | < 5 | $\bar{3}$ |
| 0·495 | 290 | < 5 | $\bar{3}$ | 0·771 | 4.13.0 | 19 | $\overline{29}$ | 0·960 | 8.10.0 | < 5 | 2 |
| 0·505 | 0.10.0 | 19 | 27 | 0·783 | 2.14.0 | < 5 | 2 | 0·970 | 6.15.0 | < 5 | $\bar{6}$ |
| 0·506 | 4.6.0 | 18 | 14 | 0·792 | 6.10.0 | < 5 | 2 | 0·975 | 2.19.0 | < 5 | 3 |
| 0·539 | 470 | 23 | $\overline{32}$ | 0·805 | 0.16.0 | 25 | $\overline{26}$ | 0·986 | 8.11.0 | < 5 | $\overline{13}$ |
| 0·544 | 2.10.0 | < 5 | $\overline{13}$ | 0·815 | 4.14.0 | < 5 | $\bar{9}$ | 0·992 | 4.18.0 | < 5 | $\overline{10}$ |
| 0·571 | 480 | < 5 | 5 | 0·820 | 800 | < 5 | 10 | | | | |

The calculated and observed values of $F_{hk0}$ are given in Table 3.

(*c*) *Comparison of the two projections.* For each projection the structure amplitudes have been measured on arbitrary scales and adjusted to 'absolute' values by multiplying by a factor 1·62 (for the [100] projection) or by a factor 2·61 (for the [001] projection). Comparison of the values of $F_{0k0}$ therefore gives an indication of the order of accuracy obtained:

| | 020 | 040 | 060 | 080 | 0.10.0 |
|---|---|---|---|---|---|
| From [100] projection | 41 | 59 | 42 | 59 | 19 |
| From [001] projection | 33 | 52 | 37 | 59 | 18 |

| | 0.12.0 | 0.14.0 | 0.16.0 | 0.18.0 |
|---|---|---|---|---|
| From [100] projection | 0 | 52 | 23 | 18 |
| From [001] projection | 0 | 51 | 25 | 17 |

The *y* co-ordinates have been deduced from each projection for atoms $C_1$, $C_2$, $C_5$, $C_6$ and Cl (Table 1). In the case of atom $C_5$ the value from the [100] projection has been adopted owing to the existence of the combined $C_3$–N peak in the [001] projection.

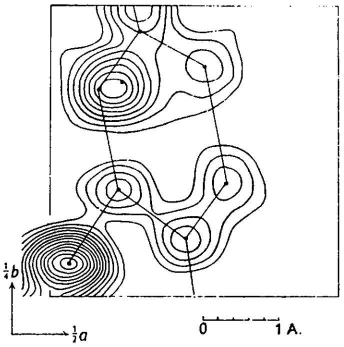


Fig. 2. Projection of electron density on (001).

The self-consistent set of co-ordinates is given in Table 1 (*c*). The intensities of thirty reflexions of type *h0l* and forty-six reflexions of type *hkl* have been calculated and are in good agreement with the observed values (visually estimated).

### Reliability factor

The value of quantity

$$R=\Sigma\,||F_{\text{obs.}}|-|F_{\text{calc.}}||\div\Sigma\,|F_{\text{obs.}}|$$

has been suggested as an index of the reliability of a structure, but the value obtained appears to depend very much on the number of reflexions considered and on the treatment given to reflexions too weak to be observed. If the latter are excluded from the summation, the values obtained for the present structure are 0·17, 0·15 for the (100), (001) projections respectively. When all calculated values are included and $|F_{\text{obs.}}|$ is assumed zero for all reflexions too weak to be recorded, the respective values are 0·33 and 0·32. When each unrecorded reflexion is assigned an $|F_{\text{obs.}}|$ value of one-half of the smallest $|F_{\text{obs.}}|$, the values obtained for $R$ are 0·25 and 0·23 respectively.

### Description of the structure

*Molecular configuration.* The bond lengths and bond angles are represented in Fig. 3. Each ring with its attached atoms is approximately planar and the atoms $NC_4C_1C_{1'}C_{4'}N'$ are approximately collinear. The two rings are rotated, in mutually opposite directions, through an angle of 36° (mean) from the *cis*-planar position, the angular displacements of the individual atoms being: $C_2$, 36°; $C_3$, 36½°; $C_5$, 37½°; $C_6$, 34½°; Cl, 35½°. The diphenyl link $C_1$–$C_{1'}$ with length 1·53 A. is, within experimental error, the standard single bond. The configuration is markedly similar to that of *m*-tolidine hydrochloride (Hargreaves & Taylor, 1941). The same mean C–C distance is obtained (1·38 A.) and the same alternation of long and short bonds is observed; in the present structure the mean long bond is 1·45 A. and the mean short bond 1·30 A., compared with 1·42 and 1·34 A., respectively, in the *m*-tolidine molecule. The C–N distances in the respective structures are 1·40 and 1·39 A. (*m*-tolidine). These distances are appreciably shorter than the C–N single bond of 1·47 A. It may be noted that, quite apart from any double-bond character which may exist, comparable distances have been observed in glycine (Albrecht & Corey, 1939), diketopiperazine (Corey, 1938) and *dl*-alanine (Levy & Corey, 1941).

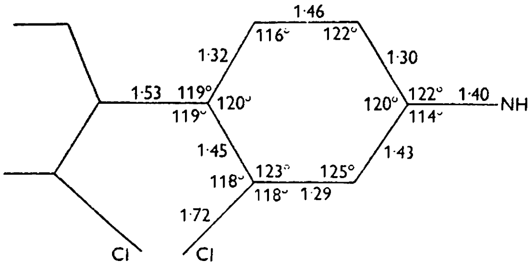


Fig. 3. Bond lengths and bond angles.

The bond C–Cl (1·72 A.) is not significantly different from the value 1·76 A. from Pauling's (1939, p. 154) list of covalent radii, whereas in *m*-tolidine hydrochloride the corresponding bond ($C$–$CH_3$) is reduced to 1·44 A.

Assessment of the accuracy of the bond lengths given is difficult, but some measure of the accuracy of the atomic co-ordinates can be got by comparing the *y* co-ordinates which are obtained independently from two projections. The bond lengths most accurately established are as follows. Bond $C_1$–$C_{1'}$ is determined almost entirely by the *y* co-ordinate. As the same co-ordinate is obtained for both projections this bond may well be accurate to within ±0·02 A. It is estimated that the bonds $C_1$–$C_2$, $C_5$–$C_6$ and $C_4$–N have errors little more than this. Bonds $C_4$–$C_5$ and $C_1$–$C_5$ are somewhat less favourably determined, and a reasonable error would be ± 0·04 A. The probable error in bonds $C_2$–$C_3$ and $C_3$–$C_4$ is somewhat larger still, say ± 0·05 A.

*Arrangement of the molecules in the crystal.* The centres of the molecules lie on digonal axes which are parallel to [001], the mean plane of the molecule being inclined at an angle of 11° to (100). The structure is racemic, the unit cell containing two right-handed and two left-handed molecules (Fig. 4).

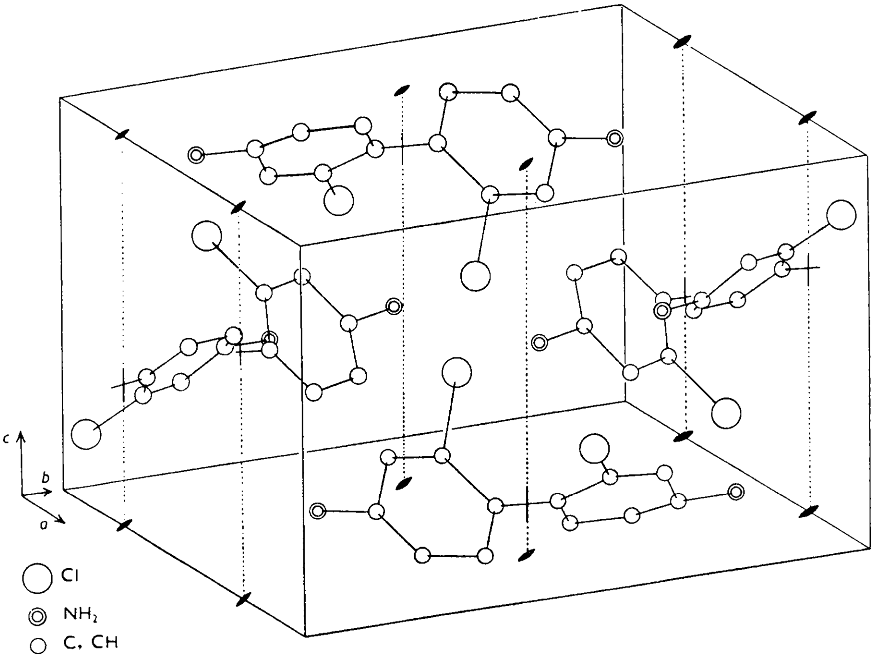


Fig. 4. Isometric projection of the unit cell.

Intermolecular distances are, with few exceptions, of normal magnitudes. In only one instance is the hydrocarbon (C–CH) separation smaller than 3·6 A.; the separation between $C_4$ of one molecule and $C_5$ of an adjacent molecule is 3·45 A. The smallest distance $NH_2$–Cl is 3·55 A., appearing to indicate that only van der Waals forces are exerted between these atoms.

An abnormally small interatomic distance is that between two Cl atoms in adjacent molecules (3·27 A.). This distance is considerably smaller than the van der Waals separation of 3·6 A. and is even slightly smaller than the separation 3·36 A. between two Cl atoms in the same molecule.

I wish to thank I.C.I. Ltd. (Dyestuffs) for the supply of crystals for the investigation and for permission to publish this account. I am glad also to acknowledge my indebtedness to Dr W. H. Taylor for his valued advice and interest throughout the whole course of the investigation.

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