

## The Crystal Structure of *m*-Tolidine Dihydrochloride

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The crystal structure of *m*-tolidine dihydrochloride has been determined by two-dimensional Fourier methods. The two phenyl rings in each molecule are mutually inclined at an angle ( $70.6^\circ$ ) which brings the two methyl groups into contact. The length of the diphenyl link is  $1.52_5$  Å. The interatomic distances between carbon atoms in the phenyl rings vary considerably; some of them are unusually short. The molecules lie in sheets which are bound together by ionic forces between the  $\text{NH}_3^+$  groups and the  $\text{Cl}^-$  ions. Streaks which occur in photographs of certain specimens are attributed to multiple twinning.

### Introduction

The X-ray examination of a number of substituted diphenyls was begun in this Department in an attempt to determine whether differences in chemical behaviour, observed in industrial use, are due to differences in the spatial configurations of the molecules. An account of a general survey of the physical and optical properties and the space-group symmetries of some of these compounds, and a preliminary description of the structure

tory. The work on *m*-tolidine dihydrochloride, which was suspended during the war, has been resumed, and the atomic parameters have been determined more accurately by an extension in the range of  $F$  values used in the Fourier summations, by the evaluation of the summations at smaller intervals in the projections, and by a more accurate determination of the unit-cell dimensions.

### Physical and X-ray data

The dihydrochloride of *m*-tolidine crystallizes from water in transparent rectangular plates with monoclinic symmetry. The crystals are harder than is usual in aromatic compounds and cleave parallel to the edges [100] and [010] of the plate face (001). Many crystals form contact twins on the plate face with [100] as twin-axis.

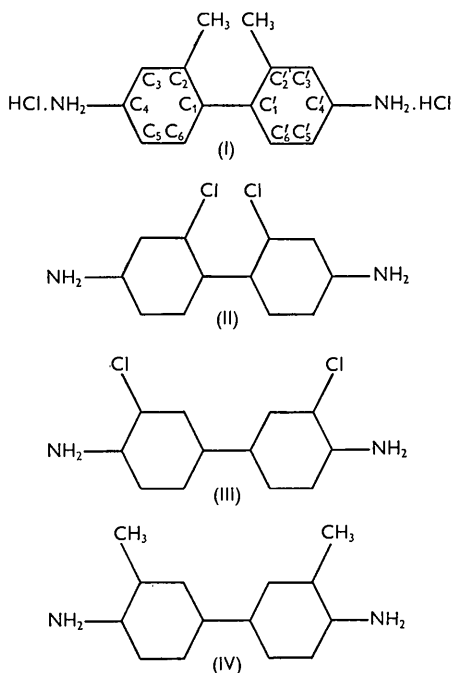
The unit-cell dimensions determined from measurements on oscillation photographs (Farquhar & Lipson, 1946) are:

$$a = 4.9475 \pm 0.0005, \quad b = 6.1796 \pm 0.0005, \\ c = 23.246 \pm 0.002 \text{ \AA.}, \quad \beta = 91^\circ 20' \pm 3'.$$

(The wave-length of  $\text{Cu K}\alpha_1$  radiation has been taken as  $1.5405$  Å.) This unit cell contains two molecules (measured density  $1.32_4$  g.cm. $^{-3}$ , calculated density  $1.331$  g.cm. $^{-3}$ ).

Reflexions  $hkl$  are absent when  $(h+k+l)$  is odd, and since there are no other systematic absences in the reflexions the space group must be  $I2/m$ ,  $Im$  or  $I2$ . It is not possible to determine the crystal class by goniometric examination of the crystals because of the absence of suitable faces, but the centrosymmetrical space group  $I2/m$  is ruled out by a test for pyroelectricity which reveals that the crystals are strongly polar. The choice between the space groups  $Im$  and  $I2$  has to be made indirectly; this is discussed in the next section.

The atomic parameters were finally determined from two-dimensional Fourier projections parallel to the [100] and [010] axes of the crystal. Reflexions  $0kl$  and



of one of them, *m*-tolidine dihydrochloride (I), have been given by Hargreaves (1940) and Hargreaves & Taylor (1941). The structure of 2-2'-dichlorobenzidine (II) has been determined by Smare (1948), and the structure of 3-3'-dichlorobenzidine (III) is under examination by Toussaint (1948), whilst *o*-tolidine (IV) and *m*-tolidine base are being examined in this labora-

$h0l$  were recorded on Weissenberg photographs using  $\text{Cu K}\alpha$  radiation, and, with the exception of a few weak reflexions, the intensities were measured on an integrating photometer similar to that described by Robinson (1933) and Dawton (1937). The weak reflexions were recorded again on small-angle oscillation photographs of long exposure and the intensities measured by visual comparison with calibration spots of known relative exposure. The intensities of the  $h0l$  reflexions were corrected for absorption by the method described by Albrecht (1939), and it was found that the absorption factor varies between the limits 0.66 and 0.74  $\text{cm}^{-1}$  for a specimen of rectangular cross-section ( $0.110 \times 0.80 \text{ mm}^2$ ). Absorption corrections were not applied to the  $0kl$  reflexions since the specimen used is almost square in cross-section ( $0.080 \times 0.085 \text{ mm}^2$ ), and it is evident that the variation in the absorption factor for different reflexions must be considerably less than the variation of about 12% calculated for the  $h0l$  reflexions. When an approximate structure had been determined, the measured  $F$  values were placed on an absolute scale by multiplying them by the factor which gives the closest agreement between measured and calculated  $F$  values. Comparison of the measured and calculated  $F$  values (Tables 1 and 2) indicates that extinction errors are considerable for only a few reflexions from planes of large spacings. Rough calculations showed that the parameters determined from the Fourier summations would not be modified appreciably if the  $F$  values for these reflexions were corrected for extinction, and accordingly no extinction corrections have been made.

In photographs of certain specimens streaks are observed which lie along rows parallel to the axis  $[001]^*$  in reciprocal space. In many specimens the streaks are either absent or barely detectable. A possible explanation of the origin of the streaks is discussed in the last section of this paper.

### Determination of the structure

#### (i) Space group and approximate structure

In the determination of an approximate structure it is reasonable to assume (cf. diphenyl (Dhar, 1932), terphenyl (Pickett, 1933), and quaterphenyl (Pickett, 1936)) that the phenyl groups are plane hexagons of side 1.4 Å., that the centres of the two phenyl rings lie along the line joining  $C_1$  and  $C'_1$ , and that intermolecular distances are of the order of 3.5 Å. or more. Since there are four equivalent general positions in both of the possible space groups  $Im$  and  $I2$  it follows that the two molecules in the unit cell must lie in special positions. In the space group  $Im$  the molecular planes must coincide with, or be perpendicular to, the reflexion planes  $m$  in  $(x, 0, z)$  and  $(x, \frac{1}{2}, z)$ , and this is possible only if the two phenyl rings are coplanar. If the phenyl rings lie in the reflexion planes, the symmetry requirements are satisfied if the molecule has either the *cis* or *trans* configuration; but in neither orientation can the molecule

be accommodated in the unit cell—for example, the spacing  $d_{100}$  is shorter than the shortest width of the molecule in the (010) plane. If the phenyl rings of one molecule lie above and below the reflexion plane, the molecule must be *cis* to satisfy the symmetry requirements; but the length of the molecule (approximately 13 Å.) is now much greater than the length of the  $b$  axis (6.2 Å.) to which it is parallel. It follows that the space group  $Im$  must be rejected.  $I2$  is therefore the correct space group. In the space group  $I2$  the molecules must lie on twofold rotation axes with the diphenyl link  $C_1-C'_1$  perpendicular to the twofold axis. Without loss of generality the mid-points of the diphenyl links may be fixed at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  on the pair of rotation axes  $[0, y, 0]$  and  $[\frac{1}{2}, y, \frac{1}{2}]$ . The symmetry elements place no restriction on the angle  $\omega$  between the planes of the two phenyl rings, or on the orientations of the molecules about the axis  $[010]$  which are determined by the angle  $\phi$  between the diphenyl link and the axis  $[001]$ .

From stereochemical considerations it is possible to determine the approximate positions of all scattering groups (except the chlorine atoms) in the unit cell in terms of the parameters  $\omega$  and  $\phi$ . The possible values of the parameters  $x_{\text{Cl}}$ ,  $y_{\text{Cl}}$  and  $z_{\text{Cl}}$  of the chlorine atoms for any given values of  $\omega$  and  $\phi$  are restricted considerably if they are tentatively placed in large cavities which occur between the nitrogen atoms. Graphical methods led quickly to an approximate structure when the parameters  $\omega$ ,  $\phi$ ,  $x_{\text{Cl}}$ ,  $y_{\text{Cl}}$  and  $z_{\text{Cl}}$  were varied over the ranges permitted by packing considerations until the calculated and observed  $F$  values were in reasonable agreement. The approximate structure was then refined by successive Fourier summations.

#### (ii) Fourier syntheses

The electron density was evaluated at intervals of  $a/30$ ,  $c/120$  and  $b/30$ ,  $c/120$  in the  $[010]$  and  $[100]$  projections respectively. Intervals of  $c/60$  had been used in the earlier work (Hargreaves & Taylor, 1941), and in order to obtain intervals of  $c/120$  from Beever-Lipson strips, which give values of the appropriate trigonometrical function at intervals of  $\frac{1}{60}$ th of the cell edge, the axes of the body-centred cell were changed to those of a face-centred cell. The new  $l$  indices are always even for the reflexions used in both projections and this enables the summations to be carried out at intervals of  $c/120$  by selection of strips with half the true value of the  $l$  indices. The individual features of each projection are discussed briefly below.

$[010]$  projection. The signs of the additional reflexions used in this synthesis were calculated from the coordinates derived in the earlier work. Recalculation of the structure amplitudes using the new set of atomic co-ordinates suggested a change of sign in one of the additional weak reflexions. The contour diagram is reproduced in Fig. 1. Calculated and observed values of  $F_{h0l}$  are given in Table 1.

Table 1. Observed and calculated values of  $F_{hol}$ , arranged in order of increasing  $\sin \theta$

| $hOl$  | $F_{obs.}$ | $F_{calc.}$ | $hOl$  | $F_{obs.}$ | $F_{calc.}$ | $hOl$  | $F_{obs.}$ | $F_{calc.}$ | $hOl$  | $F_{obs.}$ | $F_{calc.}$ |
|--------|------------|-------------|--------|------------|-------------|--------|------------|-------------|--------|------------|-------------|
| 000    | —          | 300         | 305    | 4          | 4           | 1.0.21 | 0          | 1           | 2.0.24 | 3          | 4           |
| 002    | 8          | 13          | 2.0.12 | 24         | 22          | 4.0.10 | 42         | 39          | 0.0.26 | 12         | 10          |
| 004    | 16         | 15          | 2.0.12 | 9          | 12          | 1.0.21 | 7          | 5           | 4.0.18 | 4          | 5           |
| 101    | 34         | 34          | 307    | 5          | 3           | 3.0.17 | 11         | 13          | 5.0.11 | 0          | 1           |
| 101    | 0          | 6           | 1.0.15 | 17         | 14          | 2.0.20 | 7          | 4           | 5.0.13 | 8          | 9           |
| 103    | 69         | 105         | 1.0.15 | 11         | 14          | 4.0.12 | 0          | 1           | 3.0.23 | 9          | 7           |
| 103    | 25         | 16          | 307    | 5          | 7           | 0.0.22 | 3          | 1           | 4.0.20 | 5          | 9           |
| 006    | 33         | 35          | 0.0.16 | 19         | 15          | 2.0.20 | 28         | 27          | 5.0.13 | 3          | 1           |
| 105    | 69         | 92          | 309    | 6          | 5           | 3.0.17 | 26         | 26          | 3.0.23 | 3          | 3           |
| 105    | 27         | 31          | 2.0.14 | 17         | 19          | 4.0.12 | 14         | 14          | 1.0.27 | 4          | 3           |
| 008    | 31         | 28          | 309    | 3          | 1           | 4.0.14 | 4          | 3           | 2.0.26 | 5          | 4           |
| 107    | 46         | 50          | 2.0.14 | 9          | 7           | 3.0.19 | 10         | 11          | 1.0.27 | 5          | 8           |
| 107    | 51         | 48          | 1.0.17 | 25         | 21          | 1.0.23 | 0          | 7           | 4.0.20 | 7          | 8           |
| 200    | 17         | 15          | 3.0.11 | 9          | 5           | 501    | 5          | 5           | 5.0.15 | 0          | 3           |
| 202    | 29         | 23          | 1.0.17 | 9          | 7           | 501    | 13         | 15          | 2.0.26 | 4          | 6           |
| 202    | 29         | 31          | 0.0.18 | 8          | 8           | 503    | 5          | 4           | 0.0.28 | 10         | 10          |
| 0.0.10 | 15         | 14          | 3.0.11 | 11         | 11          | 4.0.14 | 3          | 2           | 600    | 13         | 16          |
| 109    | 28         | 24          | 2.0.16 | 11         | 11          | 1.0.23 | 15         | 13          | 5.0.15 | 11         | 11          |
| 204    | 5          | 8           | 2.0.16 | 16         | 14          | 2.0.22 | 35         | 30          | 602    | 5          | 9           |
| 204    | 34         | 37          | 400    | 0          | 6           | 503    | 8          | 12          | 3.0.25 | 7          | 7           |
| 109    | 74         | 65          | 402    | 33         | 39          | 505    | 6          | 9           | 602    | 10         | 9           |
| 206    | 16         | 17          | 3.0.13 | 20         | 19          | 3.0.19 | 3          | 2           | 604    | 9          | 11          |
| 206    | 26         | 28          | 402    | 8          | 1           | 0.0.24 | 4          | 4           | 4.0.22 | 6          | 8           |
| 1.0.11 | 17         | 18          | 404    | 10         | 10          | 2.0.22 | 14         | 15          | 604    | 3          | 5           |
| 0.0.12 | 65         | 59          | 404    | 9          | 4           | 505    | 18         | 18          | 606    | 5          | 3           |
| 1.0.11 | 14         | 6           | 3.0.13 | 21         | 19          | 507    | 15         | 15          | 5.0.17 | 3          | 2           |
| 208    | 12         | 12          | 1.0.19 | 46         | 43          | 4.0.16 | 7          | 10          | 3.0.25 | 7          | 7           |
| 208    | 2          | 8           | 406    | 10         | 9           | 507    | 29         | 26          | 608    | 0          | 3           |
| 2.0.10 | 58         | 59          | 1.0.19 | 8          | 2           | 4.0.16 | 3          | 4           | 606    | 9          | 3           |
| 1.0.13 | 9          | 7           | 406    | 14         | 14          | 509    | 17         | 16          | 4.0.22 | 13         | 11          |
| 1.0.13 | 11         | 15          | 0.0.20 | 0          | 4           | 3.0.21 | 6          | 8           | 1.0.29 | 2          | 3           |
| 2.0.10 | 11         | 11          | 2.0.18 | 5          | 3           | 1.0.25 | 6          | 9           | 5.0.17 | 8          | 7           |
| 0.0.14 | 37         | 30          | 408    | 16         | 19          | 509    | 12         | 7           | 1.0.29 | 5          | 6           |
| 301    | 5          | 4           | 3.0.15 | 21         | 22          | 2.0.24 | 14         | 15          | 608    | 5          | 8           |
| 301    | 29         | 31          | 2.0.18 | 5          | 3           | 3.0.21 | 5          | 5           | 2.0.28 | 4          | 2           |
| 303    | 19         | 19          | 408    | 5          | 7           | 1.0.25 | 15         | 14          | 6.0.10 | 2          | 2           |
| 303    | 25         | 28          | 3.0.15 | 24         | 23          | 4.0.18 | 8          | 9           |        |            |             |
| 305    | 19         | 19          | 4.0.10 | 0          | 2           | 5.0.11 | 3          | 6           |        |            |             |

Table 2. Observed values of  $F_{okl}$  and calculated values of  $F_{okl}$  and  $\alpha_{okl}$ , arranged in order of increasing  $\sin \theta$

| $OkL$  | $F_{obs.}$ | $F_{calc.}$ | $\alpha_{calc.}$ (°) | $OkL$  | $F_{obs.}$ | $F_{calc.}$ | $\alpha_{calc.}$ (°) | $OkL$  | $F_{obs.}$ | $F_{calc.}$ | $\alpha_{calc.}$ (°) |
|--------|------------|-------------|----------------------|--------|------------|-------------|----------------------|--------|------------|-------------|----------------------|
| 000    | —          | 300         | 0                    | 046    | 12         | 10          | 351                  | 0.5.15 | 16         | 17          | 64                   |
| 002    | 7          | 10          | 180                  | 048    | 0          | 3           | 138                  | 0.0.24 | 4          | 3           | 0                    |
| 011    | 36         | 55          | 340                  | 0.3.13 | 11         | 10          | 188                  | 068    | 5          | 7           | 143                  |
| 004    | 13         | 15          | 0                    | 0.1.17 | 10         | 8           | 256                  | 0.6.10 | 10         | 8           | 35                   |
| 013    | 8          | 11          | 11                   | 0.2.16 | 29         | 28          | 187                  | 0.4.20 | 13         | 11          | 226                  |
| 006    | 27         | 31          | 180                  | 0.0.18 | 6          | 9           | 0                    | 0.2.24 | 14         | 10          | 315                  |
| 015    | 28         | 38          | 165                  | 0.4.10 | 19         | 17          | 10                   | 0.1.25 | 16         | 14          | 354                  |
| 020    | 50         | 69          | 11                   | 0.3.15 | 4          | 6           | 2                    | 0.5.17 | 11         | 9           | 87                   |
| 022    | 47         | 62          | 168                  | 051    | 10         | 7           | 349                  | 0.3.23 | 23         | 22          | 177                  |
| 008    | 25         | 28          | 180                  | 053    | 4          | 6           | 320                  | 0.6.12 | 22         | 20          | 174                  |
| 017    | 39         | 47          | 6                    | 0.1.19 | 26         | 26          | 157                  | 0.0.26 | 13         | 12          | 180                  |
| 024    | 38         | 38          | 6                    | 0.4.12 | 20         | 20          | 176                  | 071    | 12         | 12          | 301                  |
| 026    | 20         | 16          | 324                  | 055    | 19         | 16          | 193                  | 073    | 0          | 4           | 302                  |
| 019    | 29         | 33          | 165                  | 0.2.18 | 15         | 12          | 96                   | 0.4.22 | 5          | 4           | 221                  |
| 0.0.10 | 13         | 13          | 0                    | 0.0.20 | 0          | 2           | 180                  | 0.5.19 | 20         | 19          | 193                  |
| 028    | 18         | 13          | 252                  | 057    | 21         | 21          | 355                  | 0.6.14 | 18         | 16          | 13                   |
| 031    | 12         | 13          | 156                  | 0.3.17 | 4          | 1           | 115                  | 075    | 13         | 12          | 169                  |
| 0.1.11 | 16         | 17          | 25                   | 0.4.14 | 29         | 26          | 18                   | 0.7.26 | 10         | 10          | 213                  |
| 033    | 16         | 16          | 355                  | 059    | 18         | 17          | 191                  | 0.1.27 | 3          | 5           | 175                  |
| 0.0.12 | 53         | 58          | 180                  | 0.1.21 | 28         | 28          | 28                   | 077    | 16         | 15          | 9                    |
| 035    | 12         | 4           | 252                  | 0.2.20 | 18         | 17          | 98                   | 0.3.25 | 7          | 8           | 4                    |
| 0.2.10 | 22         | 22          | 352                  | 0.5.11 | 12         | 11          | 352                  | 0.6.16 | 7          | 7           | 159                  |
| 037    | 35         | 34          | 353                  | 0.0.22 | 2          | 2           | 180                  | 079    | 8          | 8           | 153                  |
| 0.1.13 | 29         | 29          | 197                  | 0.4.16 | 24         | 22          | 162                  | 0.0.28 | 11         | 11          | 0                    |
| 0.0.14 | 32         | 33          | 0                    | 0.3.19 | 18         | 18          | 169                  | 0.5.21 | 10         | 11          | 326                  |
| 0.2.12 | 38         | 38          | 191                  | 060    | 39         | 46          | 345                  | 0.4.24 | 6          | 6           | 57                   |
| 039    | 32         | 35          | 183                  | 062    | 20         | 16          | 224                  | 0.7.11 | 8          | 8           | 47                   |
| 040    | 29         | 27          | 0                    | 064    | 5          | 4           | 349                  | 0.2.28 | 11         | 11          | 350                  |
| 042    | 37         | 40          | 189                  | 0.5.13 | 9          | 9           | 139                  | 0.6.18 | 4          | 4           | 353                  |
| 0.1.15 | 21         | 19          | 277                  | 0.2.22 | 7          | 6           | 79                   | 0.1.29 | 7          | 5           | 4                    |
| 044    | 23         | 24          | 345                  | 0.1.23 | 19         | 18          | 170                  | 0.3.27 | 6          | 7           | 179                  |
| 0.3.11 | 15         | 15          | 5                    | 066    | 7          | 8           | 153                  | 0.7.13 | 8          | 10          | 177                  |
| 0.2.14 | 28         | 27          | 341                  | 0.4.18 | 4          | 5           | 211                  | 0.5.23 | 11         | 14          | 188                  |
| 0.0.16 | 16         | 16          | 180                  | 0.3.21 | 22         | 21          | 13                   | 0.4.26 | 5          | 7           | 151                  |

[100] projection. Three new syntheses were made for this non-centrosymmetrical projection. The calculated and observed values of  $F_{0kl}$ , with phase angles, are given in Table 2, and the contour diagram is reproduced in Fig. 2.

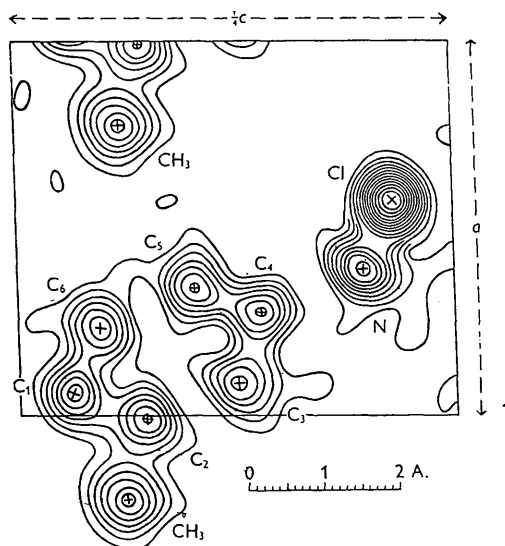


Fig. 1. Electron density in *m*-tolidine dihydrochloride projected on (010). Contour lines are drawn at intervals of 1 e.A.<sup>-2</sup>, except for the chlorine atom, where the intervals are 2 e.A.<sup>-2</sup>; the lowest contour line represents 2 e.A.<sup>-2</sup>.

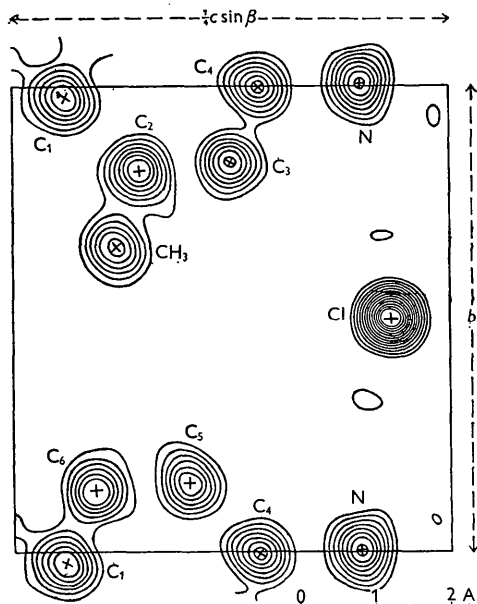


Fig. 2. Electron density in *m*-tolidine dihydrochloride projected along [100]. Contour lines are drawn at intervals of 1 e.A.<sup>-2</sup>, except for the chlorine atom, where the intervals are 2 e.A.<sup>-2</sup>; the lowest contour line represents 2 e.A.<sup>-2</sup>.

The atomic co-ordinates obtained from the [010] and [100] projections are given in Table 3. Since every atom is perfectly resolved in both projections, two measured co-ordinates can be quoted for each projected

atom. The average deviation from the mean  $z$  co-ordinates for the two projections is 0.005 Å. (maximum deviation 0.010 Å.). It is considered, however, that this does not give a reliable measure of the accuracy of the co-ordinates since the  $z$  co-ordinates used in calculating the phase angles for the non-centrosymmetrical [100] projections were taken as the mean values derived from the [010] projection and the preceding [100] projection. The data used in calculating the [100] projection are thus partially dependent on data derived from the [010] projection. The quantity  $\frac{\sum ||F_{\text{obs.}}| - |F_{\text{calc.}}||}{\sum |F_{\text{obs.}}|}$  has the value 0.17 for the [010] projection and 0.13 for the [100] projection. The accuracy of the co-ordinates is discussed further in the next section.

Table 3. Atomic co-ordinates

(All values in Ångström units.)

|                | $x$               | $y$                | $z_1$             | $z_2$             |
|----------------|-------------------|--------------------|-------------------|-------------------|
| C <sub>1</sub> | 0.29 <sub>6</sub> | -0.15 <sub>0</sub> | 0.70 <sub>0</sub> | 0.71 <sub>8</sub> |
| C <sub>2</sub> | 4.91 <sub>0</sub> | -1.11 <sub>2</sub> | 1.67 <sub>0</sub> | 1.67 <sub>2</sub> |
| C <sub>3</sub> | 0.44 <sub>0</sub> | -1.00 <sub>2</sub> | 2.89 <sub>6</sub> | 2.90 <sub>5</sub> |
| C <sub>4</sub> | 1.37 <sub>8</sub> | -0.01 <sub>7</sub> | 3.25 <sub>8</sub> | 3.23 <sub>8</sub> |
| C <sub>5</sub> | 1.68 <sub>8</sub> | 0.90 <sub>8</sub>  | 2.34 <sub>0</sub> | 2.34 <sub>8</sub> |
| C <sub>6</sub> | 1.17 <sub>2</sub> | 0.82 <sub>0</sub>  | 1.09 <sub>0</sub> | 1.09 <sub>0</sub> |
| C <sub>7</sub> | 3.83 <sub>6</sub> | 4.06 <sub>2</sub>  | 1.37 <sub>6</sub> | 1.39 <sub>2</sub> |
| N              | 1.94 <sub>6</sub> | 0.03 <sub>0</sub>  | 4.60 <sub>2</sub> | 4.59 <sub>5</sub> |
| Cl             | 2.85 <sub>0</sub> | 3.09 <sub>8</sub>  | 5.02 <sub>2</sub> | 5.01 <sub>6</sub> |

$z_1$  co-ordinates from the [010] projection,  $z_2$  co-ordinates from the [100] projection.

### Description of the structure

#### (i) Configuration of the molecule

The bond lengths and bond angles calculated from the co-ordinates given in Table 3 (mean  $z$  co-ordinates) are given in Fig. 3. The equation of the best plane through the atoms in the phenyl ring has been calculated by a least-squares method. The mean displacement of the individual atoms from the best plane is found to be 0.017 Å. and the maximum displacement 0.031 Å. These figures indicate that the phenyl ring is approximately planar. They also give some indication of the accuracy of the co-ordinates determined, since if the phenyl rings are truly planar the mean error in the atomic co-ordinates will be of the order of 0.017 Å. If, however, the true positions of the atoms depart appreciably from the best plane through them, then the mean error in the co-ordinates determined may be considerably less than 0.017 Å.

The angle between the mean planes of the two phenyl rings in each molecule is 70.6°, the phenyl rings being rotated in opposite directions about the diphenyl link through 35.3° from the *cis*-planar configuration. The distance between the two methyl groups C<sub>7</sub> and C<sub>7</sub>' in each molecule is 3.54 Å., considerably less than the usual methyl-methyl separation of approximately 4 Å., and repulsion between these groups will oppose any tendency of the phenyl rings to approach more closely towards the *cis*-planar configuration. This fact is discussed further below.

The bond lengths in Fig. 3\* show differences up to 0.06 Å. from those quoted in the less accurate structural determination by Hargreaves & Taylor (1941). The largest changes occur in the bonds C-N and C-CH<sub>3</sub>, which now approach more closely the normal single-bond distances. The molecular configurations of *m*-toluidine dihydrochloride and 2-2'-dichlorobenzidine (Smare, 1948) may be compared in Figs. 3 and 4. The phenyl rings are united by a bond C<sub>1</sub>-C'<sub>1</sub> of length 1.52<sub>5</sub> Å. in *m*-toluidine dihydrochloride and 1.53 Å. in 2-2'-dichlorobenzidine. These lengths, which correspond within experimental error to the length of the standard single bond, may be compared with the length 1.48 Å. observed for the molecules diphenyl (Dhar, 1932), terphenyl (Pickett, 1933) and quaterphenyl

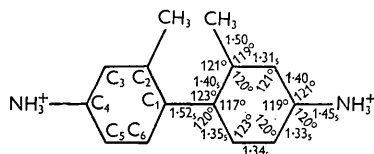


Fig. 3. Bond lengths and bond angles in *m*-toluidine dihydrochloride.

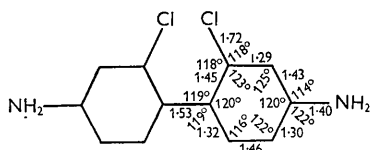


Fig. 4. Bond lengths and bond angles in 2-2'-dichlorobenzidine.

(Pickett, 1936), and with the mean length  $1.52 \pm 0.04$  Å. observed for diphenyl, terphenyl and tetraphenylene by Karle & Brockway (1944). If the bond C<sub>5</sub>-C<sub>6</sub> is excepted, similar C-C distances are observed in the phenyl rings in *m*-toluidine dihydrochloride and 2-2'-dichlorobenzidine. In both molecules the lengths of the bonds C<sub>2</sub>-C<sub>3</sub>, C<sub>4</sub>-C<sub>5</sub> and C<sub>6</sub>-C<sub>1</sub> are much shorter than the bond lengths which are usually found in aromatic rings, and, within the limits of experimental error, are all of the same length as the standard carbon double bond. It is emphasized that in the original trial structures for *m*-toluidine dihydrochloride and 2-2'-dichlorobenzidine it was assumed that the phenyl rings are plane regular hexagons of side 1.40 Å., and that the irregularities which occur in the bond lengths finally quoted, and which are very similar for both structures, have arisen automatically with refinement of the structures by Fourier methods. It is perhaps worthy of mention that Abrahams & Robertson (1948) report distances varying between 1.31 and 1.39 Å. in the aromatic ring in *p*-nitroaniline, although they consider that the shorter distances are doubtful because of poor definition in the projections.

\* The labelling of the carbon atoms C<sub>1</sub>, C<sub>2</sub>, ..., etc., in each phenyl ring differs from the nomenclature adopted by Hargreaves & Taylor (1941) and is now consistent with that adopted by Smare (1948).

It will be interesting to compare the above bond lengths and bond angles with those for *o*-toluidine and 3-3'-dichlorobenzidine when the latter structures have been determined. It now seems possible that substitution of methyl groups or chlorine atoms in the *ortho* positions in the benzidine molecule will produce a different distribution of bond lengths in the phenyl rings and that this may account for the observed differences in chemical behaviour of *ortho*- and *meta*-substituted benzidines.

#### (ii) Packing of the molecules in the crystal

The arrangement of the molecules in the crystal is indicated in Fig. 5. The molecules lie in sheets parallel to (001). All the sheets are identical in structure, but adjacent sheets are laterally displaced by half lattice

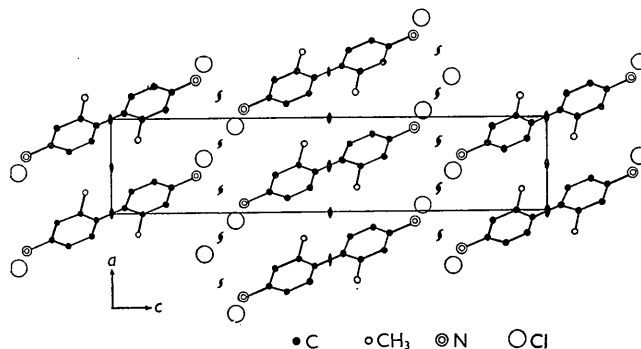


Fig. 5. Structure of *m*-toluidine dihydrochloride projected on (010).

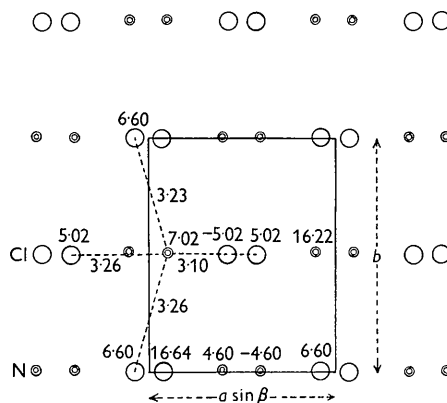


Fig. 6. Arrangement of NH<sub>3</sub><sup>+</sup> groups and Cl<sup>-</sup> ions in *m*-toluidine dihydrochloride when the structure is viewed along [001]. Heights above the plane of the diagram are indicated alongside the ions. Distances between the ions are indicated alongside the broken lines. All heights and distances are in Angstrom units.

translations parallel to [100] and [001] due to the body-centring of the lattice. The packing of the molecules is largely determined by the forces between the nitrogen and chlorine atoms, or, more precisely, between the NH<sub>3</sub><sup>+</sup> groups and the Cl<sup>-</sup> ions. Each NH<sub>3</sub><sup>+</sup> group is in contact with four Cl<sup>-</sup> ions (Fig. 6) at distances 3.10, 3.22, 3.26 and 3.26 Å., and similarly each Cl<sup>-</sup> ion

touches four  $\text{NH}_3^+$  groups at the same distances, all  $\text{NH}_3^+$  groups and  $\text{Cl}^-$  ions lying near planes which are parallel to (001) and pass through  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ ; the corresponding bond angles  $\text{C}_4\text{-N-Cl}$  are 108, 105, 101 and  $148^\circ$ .

The bonds, between the  $\text{NH}_3^+$  groups and the  $\text{Cl}^-$  ions, which link the molecules to one another, are stronger than the weak van der Waals forces which often determine the packing of aromatic molecules. This accounts for the hardness of the crystals and suggests a reason for the abnormally short distance of 3.54 Å. between the methyl groups of the same molecule and for the distance 3.36 Å. between atoms  $\text{C}_6$  and  $\text{C}_6'$  in adjacent molecules, which is the only abnormally short intermolecular distance. For in order to increase the methyl-methyl separation in the same molecule it is necessary to rotate the phenyl rings away from the *cis*-planar configuration, an operation which reduces still further the already

of course, identical with those found in the untwinned structure. The C-N-Cl bond angles at the twin boundary are 88, 91, 104 and  $154^\circ$ , which may be compared with the values 101, 105, 108 and  $148^\circ$  observed in the untwinned structure. The proposed mechanism for twinning does not, then, give rise to abnormal bond distances at the twin boundary, and this may account for the frequency with which twinning occurs. It has been pointed out, furthermore, that it is the forces between nitrogen and chlorine atoms which are largely responsible for binding the molecules together, and since the relative positions of the nitrogen and chlorine atoms at the twin boundary are the same as in the untwinned structure, it is evident that the twin components will be bound by considerable forces.

In the earlier section on physical and X-ray data, it is noted that streaks appear in photographs of certain specimens. If the twinning mechanism suggested above

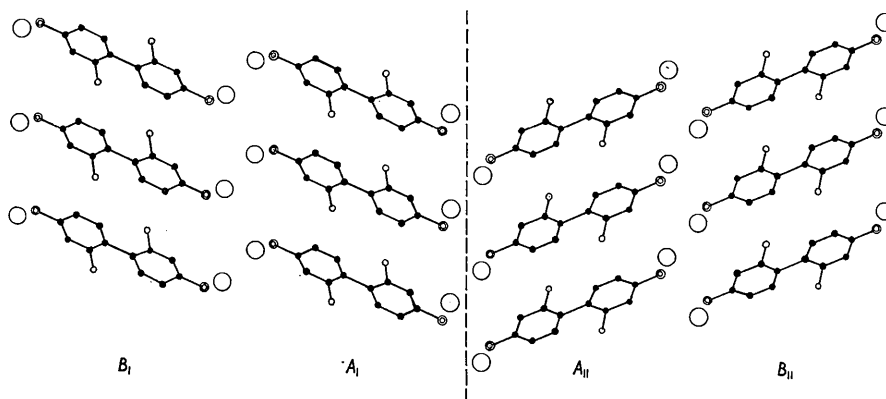


Fig. 7. Twinning in *m*-tolidine dihydrochloride. The structure is projected on (010). The dashed line indicates the boundary between the twin components I and II.

small distance between carbon atoms  $\text{C}_6$  and  $\text{C}_6'$  of adjacent molecules. The bonds which fix the  $\text{NH}_3^+$  groups amongst the  $\text{Cl}^-$  ions are presumably sufficiently strong to prevent the increase in the separation of the molecules, parallel to the *c* axis, which would permit an increase in both the methyl-methyl and  $\text{C}_6\text{-C}_6'$  distances.

### (iii) Twinning

The twinning of the material has been described in a previous section. It is suggested that the relative positions of the twin components I and II are as indicated in Fig. 7. The twin boundary lies between the sheets of molecules  $A_I$  and  $A_{II}$ . In component I the molecules in adjacent sheets are related as  $B_I, A_I$ . The sheets of molecules  $A_{II}, B_{II}, \dots$ , lie, relative to component I, in the orientation of the twin component II, but the nitrogen and chlorine atoms in sheet  $A_{II}$  which are nearest to the twin-boundary remain in the positions they would occupy if sheet  $A_{II}$  were a continuation of component I. With this arrangement the nearest approach between carbon and chlorine atoms at the twin boundary is 3.5 Å., and the N-Cl distances are,

is accepted, it may now be seen that repeated twinning will give rise to streaks similar to those observed. Referring to Fig. 7, it may be seen that if twinning occurs again after a few sheets of molecules  $A_{II}, B_{II}, \dots$  of twin component II are laid down, then the new twin component III will be parallel in orientation to twin component I. It cannot, however, be regarded as a continuation of component I because of a lateral displacement, parallel to the *a* axis, the magnitude of which is dependent on the number of sheets of molecules in component II. It may be noted that throughout components I, II and III the distance between any two adjacent layers is the same, viz. the spacing [001]. Thus when repeated twinning occurs in a specimen the layers of molecules  $A_I, B_I, \dots, A_{III}, B_{III}, \dots, A_V, B_V, \dots$ , etc., are identical in structure, and the molecules in each layer are arranged in a fully ordered two-dimensional lattice. All layers are parallel in orientation, and the distance between any two layers is an integral multiple of the [001] spacing, but there is a random displacement, parallel to the *a* axis, between layers in different components. This type of disorder will give rise to streaks in the X-ray diffraction pattern of the specimen which lie,

in reciprocal space, perpendicular to the planes (001) of the layers (see, for example, Zachariasen (1947)). This is the direction in which the streaks are actually observed. Similar streaks will, of course, be expected to occur in the diffraction pattern of the twin components II, IV, VI, ... The number of specimens which we have examined is comparatively small, but rather surprisingly the strongest streaks have been recorded with a specimen which does not appear to show twinning. Presumably, in this specimen, the twin components I, III, V, ... have grown much larger than the twin components II, IV, VI, ...

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## Vector Sets\*

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This paper is concerned with the relations between a set of points, called the *fundamental set*, and the set of points at the ends of vectors between the points of the fundamental set, called the *vector set*. This is the same relation, in idealized form, that obtains between an electron-density map and the Patterson map of a crystal structure. A simple algebra is first set up to handle the characteristics of interest in these two sets of points. A most useful characteristic of the vector set is that in it are images of the polygons of points in the fundamental set. These polygon images can be systematically examined with the aid of a matrix concerned with the points of the vector set.

A vector set can be synthesized into images of several lines of the fundamental set. These line images can be combined in a very limited number of ways, one of which comprises the points of the fundamental set. Furthermore, any vector set of  $n^2$  points can be synthesized into images of polygons in two different ways, either of which requires only  $(n-1)$  steps. The last stage provides the fundamental set. Thus, any vector set can be solved for its fundamental set. This implies that, practical difficulties aside, a Patterson synthesis can be transformed into an electron-density synthesis.

The relations between the symmetries of the fundamental set and vector set are discussed with the aid of the vector-set matrix. It is shown that every symmetry element present in the fundamental set occurs as its parallel, translation-free residue at the lattice points of the vector set. Only twenty-three space groups occur in vector sets. A table provides a list of the space groups of vector sets corresponding with the space groups of fundamental sets.

Although the translation components of the symmetry elements of the fundamental set are not transferred to the symmetry elements of the vector set, nevertheless these translation components are not lost, and can be distinguished by concentrations of points in the vector set. With the aid of this feature, the space group of the fundamental set can be identified in the vector set, except that space groups of the fundamental set which differ only by a group of inversions, or which are related by an inversion, cannot be separately distinguished. An example of the practical use of this theory in determining the space group of a crystal is provided.

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\* The material of this paper was first presented as part of a series of lectures at the National Faculty of Philosophy, University of Brazil, Rio de Janeiro, in December 1948.