

## Structural Studies of Benzene Derivatives.

I. Refinement of the Crystal Structure of *p*-Phenylenediamine Dihydrochloride

BY ALDO DOMENICANO

*Istituto di Chimica Farmaceutica e Tossicologica, Università di Roma, Città Universitaria, 00185 Roma and Laboratorio di Strutturistica Chimica del CNR 'Giordano Giacomello', 00016 Monterotondo Stazione, Italy*

ELISABETTA FORESTI SERANTONI

*Istituto di Mineralogia e Petrografia, Università di Bologna, Piazza S. Donato 1, 40127 Bologna, Italy*

AND LODOVICO RIVA DI SANSEVERINO

*Istituto di Mineralogia e Petrografia, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy*

(Received 28 July 1976; accepted 8 October 1976)

The crystal structure of *p*-phenylenediamine dihydrochloride, determined by Chandrasekaran [*Acta Cryst.* (1969), B25, 369–374] from photographic data, has been refined by full-matrix least squares to a final *R* of 0.0276, with 1281 independent non-zero reflexions measured on an automated single-crystal diffractometer. Crystals are triclinic, space group  $P\bar{1}$ , with  $a = 8.680$  (3),  $b = 5.835$  (3),  $c = 4.333$  (2) Å,  $\alpha = 99.86$  (9),  $\beta = 96.28$  (4),  $\gamma = 110.19$  (9)°,  $Z = 1$ . The C hexagon has  $D_{2h}$  (*mmm*) symmetry within experimental error. The distortions from  $D_{6h}$  (*6/mmm*) symmetry are highly significant, and testify to the strong  $\sigma$ -electron-withdrawing character of the substituent. The internal angle at the *ipso* carbon,  $\alpha_{NH_2}$ , is 121.9 (1)°.

## Introduction

The geometry of the C hexagon in the mono-substituted derivatives of benzene is known to be sensitive to the electronic properties of the substituent (Domenicano, Vaciago & Coulson, 1975*a,b*, and references therein; Domenicano & Vaciago, 1975; Domenicano, Mazzeo & Vaciago, 1976). The structural data available for these molecules indicate that the deformations induced by substitution are generally limited to the  $a$  bonds and to the  $\alpha$  and  $\beta$  angles (Fig. 1).<sup>\*</sup> Among these parameters,  $\alpha$  appears to be the most suitable for making quantitative assessments about the influence of different functional groups on the ring geometry, since (i) its values span a rather wide range, 114–125°, and (ii) as a bond angle, it is generally affected less than the C–C bond distances by thermal motions in the crystal (Wheatley, 1959).

The structural results from *para* (and *meta*) di-substituted derivatives strongly suggest the following rule: the  $\alpha$  angle associated with a given substituent is not affected by *para* (or *meta*) substitution. Within the limits of validity of this rule<sup>†</sup>  $\alpha$  may be regarded as a

substituent constant. This is, of course, only an approximate conclusion, based upon a body of structural information that, albeit large, is neither exhaustive nor very accurate.

There is, in fact, a surprising lack of precise [ $\sigma(\alpha) \leq 0.2^\circ$ ] structural data on simple benzene derivatives with familiar functional groups. Many of these molecules were studied by X-ray diffraction analysis several years ago, when today's instrumental and computing facilities were not generally available. The present series of structural studies aims to fill the information gap, and to investigate to what extent the presence of a second substituent affects the internal angle at the *ipso* C,  $\alpha_X$ , associated with a given functional group,  $X$ . It is expected that our results will also contribute to a better understanding of the electronic effects of the substituents.

In the present paper we describe the geometry of the *p*-phenylenediaminium dication, as obtained from a

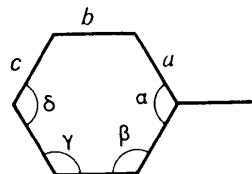


Fig. 1. Lettering of the C–C bonds and C–C–C angles in mono-substituted benzene derivatives.  $C_{2v}$  (*mm*) symmetry has been assumed.

<sup>\*</sup> Very small (usually  $< 1^\circ$ ) deviations of the  $\gamma$  and  $\delta$  angles from  $120^\circ$  occur with some substituents that interact strongly with the  $\pi$  system of the ring (Domenicano & Vaciago, 1976; Di Rienzo, Domenicano, Portalone & Vaciago, 1976).

<sup>†</sup> Exceptions have been observed in some cases, notably when a strong  $\pi$  donor is *para* to a potential  $\pi$  acceptor (Domenicano, Vaciago & Coulson, 1975*a*).

refinement of the crystal structure of *p*-phenylenediamine dihydrochloride, carried out with diffractometer data. The crystal structure of this salt was determined by Chandrasekaran (1969) from photographic data. The limited accuracy of the data set used led, however, to standard deviations on the bond lengths and angles of the benzene ring as high as 0.013 Å and 1.0° respectively. Thus a new structural study was mandatory if the subtle variations in the ring geometry caused by substitution were to be investigated.

### Experimental

A crystal, ca 0.67 × 0.48 × 0.35 mm, was selected from a batch of commercial product (Carlo Erba) and mounted on a Philips PW 1100 automatic single-crystal diffractometer. Accurate values for the cell parameters were derived by a least-squares fit to the measured  $\theta$  values for 25 accurately centred reflexions. The values obtained are in reasonable agreement with those given by Chandrasekaran (1969) (Table 1).

The intensities were measured in the  $\omega$ -2 $\theta$  scan mode, with graphite-monochromatized Mo  $K\alpha$  radiation. The scan width was 2.4°, the scan time 30 s, and the back-scan was measured for 8 s at each end of the scan. The size of the collimator employed was 0.8 mm. 1378 independent reflexions in the  $\theta$  range 2–32° were measured, and 1281 with  $I > 3\sigma(I)$  were considered as observed and used in the refinement. Three standard reflexions were monitored every 200 reflexions; their intensities proved to be constant within  $\pm 2.5\%$ . The intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction [ $\mu(\text{Mo } K\alpha) = 7.35 \text{ cm}^{-1}$ ].

Table 1. *Crystal data*

*p*-Phenylenediamine dihydrochloride, C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>, FW 181.07, triclinic, space group  $P\bar{1}$ ,  $Z = 1$ .

	This work*	Chandrasekaran (1969)
<i>a</i> (Å)	8.680 (3)	8.75
<i>b</i>	5.835 (3)	5.87
<i>c</i>	4.333 (2)	4.34
$\alpha$ (°)	99.86 (9)	99.78
$\beta$	96.28 (4)	95.57
$\gamma$	110.19 (9)	111.17
<i>V</i> (Å <sup>3</sup> )	199.5 (1)	201.4; 201.8†
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.507	1.508; 1.490†
<i>D<sub>o</sub></i>	—	1.51

\* Standard deviations are given in parentheses as units in the last digit. The radiation used was Mo  $K\alpha$  ( $\lambda = 0.71069$  Å).

† The first value is that given in the original paper; the second has been calculated by us from the given cell parameters.

### Refinement

A structure factor calculation based on the positional parameters for the non-H atoms given by Chandrasekaran (1969), and with  $B = 2.02$  Å<sup>2</sup> from a Wilson plot, gave an  $R$  of 0.108. This was reduced to 0.101 by full-matrix isotropic least-squares refinement, and then to 0.045 by anisotropic refinement (unit weights). At this stage a difference synthesis computed from terms with  $\sin \theta/\lambda \leq 0.40$  showed all the H atoms as well defined peaks, in positions reasonably close to those given by Chandrasekaran (1969). Their introduction in a structure factor calculation lowered  $R$  to 0.034.

The final refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, was carried out by full-matrix least squares with three different weighting functions to check how far the choice of the latter may affect the final molecular geometry. The number of observations per refined parameter was  $1281/66 = 19.4$ . The weighting functions used were:  $w = 1$  (refinement 1),  $w = 1/\sigma^2(F_o)$  (refinement 2) and  $w = \sin \theta/\lambda$  (refinement 3). Convergence was achieved in all cases with five cycles, with all the shifts less than  $0.02\sigma$  (non-H atoms) or  $0.2\sigma$  (H atoms). The final  $R$  and  $R_w$  were 0.0283 and 0.0334 for refinement 1, 0.0290 and 0.0438 for refinement 2, and 0.0276 and 0.0332 for refinement 3. The standard deviations on the atomic parameters obtained from the three inverse matrices are strictly comparable.

The atomic parameters from refinement 3 are given in Tables 2 and 3.\* This refinement not only resulted in lower values for  $R$  and  $R_w$ , but also gave a lower dispersion for the mean values of the minimized function,  $\sum w(|F_o| - K|F_c|)^2$ , over ranges of either  $F_o$  or  $\sin \theta/\lambda$ . A weighting scheme based on  $\sin \theta/\lambda$  should also, in principle, yield more accurate positional parameters for non-H atoms. Comparison of the molecular geometries obtained through the three refinements shows, however, that no difference between corresponding bond distances and angles is greater than  $3\sigma$ .†

The scattering factors of Cromer & Mann (1968) were used for Cl<sup>-</sup>, N and C. For H the values used were those of Hanson, Herman, Lea & Skillman (1964).

Preliminary calculations were performed on the CDC 6600 of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale. Refinements and geo-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32295 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† The internal angle at the *ipso* C,  $\alpha$ , is 122.0 (1)° from refinement 1, 122.2 (1)° from refinement 2 and 121.9 (1)° from refinement 3.

Table 2. Final coordinates ( $\times 10^5$ ) and anisotropic thermal parameters ( $\times 10^4$ ) for non-hydrogen atoms

Estimated standard deviations are given in parentheses as units in the last digit. The form of the anisotropic temperature factor is  $T = \exp[-(h^2b_{11} + hb_{12} + hb_{13} + k^2b_{22} + kb_{23} + l^2b_{33})]$ .

	x	y	z	$b_{11}$	$b_{12}$	$b_{13}$	$b_{22}$	$b_{23}$	$b_{33}$
Cl	37150 (4)	17385 (6)	6901 (8)	84.8 (5)	137 (1)	97 (1)	189 (1)	236 (2)	390 (2)
N	32594 (14)	68195 (22)	36052 (30)	60 (1)	73 (3)	79 (5)	183 (3)	189 (7)	387 (6)
C(1)	15761 (14)	58972 (21)	43337 (29)	56 (1)	66 (3)	45 (4)	136 (3)	108 (7)	291 (6)
C(2)	4835 (16)	70596 (23)	35874 (33)	73 (2)	101 (4)	91 (5)	158 (3)	231 (8)	377 (7)
C(3)	11193 (15)	38512 (23)	57266 (32)	69 (2)	113 (4)	75 (5)	168 (4)	222 (8)	369 (7)

Table 3. Final coordinates ( $\times 10^3$ ) and isotropic thermal parameters for hydrogen atoms

Estimated standard deviations are given in parentheses as units in the last digit.

	x	y	z	$B(\text{\AA}^2)$
H(2)	81 (3)	845 (5)	248 (6)	1.6 (4)
H(3)	192 (3)	307 (4)	620 (6)	1.4 (4)
H(1N)	342 (3)	558 (5)	231 (7)	2.5 (5)
H(2N)	340 (3)	805 (5)	252 (6)	1.7 (4)
H(3N)	404 (3)	737 (4)	547 (6)	1.2 (4)

metrical calculations were carried out on the Univac 1110 of the University of Rome with local crystallographic programs (Carruthers & Spagna, 1975).

## Results and discussion

### The *p*-phenylenediaminium dication

Bond lengths and angles in the *p*-phenylenediaminium dication, as calculated from the atomic parameters from refinement 3, are shown in Fig. 2 and Table 4.\* The equation of the least-squares plane through the six C atoms of the ring and the displacements of all the atoms from this plane are given in Table 5. The overall symmetry of the dication is  $C_i(\bar{1})$ , as imposed by space-group symmetry. The C hexagon, however, has  $D_{2h}(mmm)$  symmetry within experimental error.

Of the three crystallographically independent C—C bonds of the benzene ring one, C(2)—C(3'), is only 0.004 Å shorter than the C—C bond of unsubstituted benzene, 1.397 (1) Å (Stoicheff, 1954; Langseth & Stoicheff, 1956), whilst the other two, C(1)—C(2) and C(1)—C(3), are shorter by 0.012–0.013 Å. Although just at the level of significance (4 $\sigma$ ), this small difference is in keeping with the  $\sigma$ -electron-withdrawing character of the  $-\text{NH}_3^+$  substituent (Domenicano, Vacigo & Coulson, 1975a).

\* No corrections have been applied for the effects of thermal motion. These are expected to be small because of the high melting point of the material.

Much more significant (*ca* 30 $\sigma$ ) is the difference between the  $\alpha$  and  $\beta$  bond angles (Fig. 2).  $\alpha$ , 121.9 (1)°, is in the range of values observed with other functional groups having marked  $\sigma$ -electron-withdrawing character, like —Cl, —CN and —NO<sub>2</sub> (Domenicano, Mazzeo & Vacigo, 1976).

Only a few derivatives of benzene with the  $-\text{NH}_3^+$  functional group have been studied with comparable accuracy by X-ray crystallography. The best structural results for *para* and *meta*-substituted anilinium cations, as well as for the unsubstituted cation, are given in Table 6. The values of  $\alpha_{\text{NH}}$ , range from 120.6 (4) to 122.0 (4)°, mean 121.7 (2) [1]°.

Table 4. Bond lengths, bond angles and torsion angles involving the  $-\text{NH}_3^+$  substituent

Estimated standard deviations are given in parentheses as units in the last digit. Signs for the torsion angles have been given according to the convention of Klyne & Prelog (1960).

(a) Bond lengths (Å)			
C(1)—N	1.463 (2)	N—H(2N)	0.91 (3)
N—H(1N)	0.90 (3)	N—H(3N)	0.92 (2)
(b) Bond angles (°)			
C(1)—N—H(1N)	109 (2)	H(1N)—N—H(2N)	106 (3)
C(1)—N—H(2N)	112 (2)	H(1N)—N—H(3N)	110 (3)
C(1)—N—H(3N)	110 (2)	H(2N)—N—H(3N)	111 (2)
(c) Torsion angles (°)			
H(1N)—N—C(1)—C(2)	−122 (2)	H(2N)—N—C(1)—C(3)	174 (2)
H(1N)—N—C(1)—C(3)	58 (2)	H(3N)—N—C(1)—C(2)	118 (2)
H(2N)—N—C(1)—C(2)	−5 (2)	H(3N)—N—C(1)—C(3)	−63 (2)

Table 5. Deviations from planarity

The equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes) is

$$0.1376x + 2.2854y + 3.3868z = 2.8361.$$

Displacements (Å) of atoms from the plane (standard deviations in the atomic positions are given in parentheses as units in the last digit)

C(1)	0.001 (1)	N	−0.012 (1)	H(1N)	−0.73 (3)
C(2)	−0.001 (1)	H(2)	−0.05 (3)	H(2N)	−0.10 (3)
C(3)	−0.001 (1)	H(3)	−0.01 (2)	H(3N)	0.76 (2)

An accurate X-ray diffraction study of *o*-phenylenediamine dihydrochloride has recently been published (Stålhandske, 1974). Comparison of the ring geometries for the two isomeric dications shows that the angular distortions observed in the *para* isomer are absent in the *ortho* isomer, where none of the C—C—C bond angles differ from 120° by more than 0.2°.

The length of the C(1)—N bond in *p*-phenylenediamine dihydrochloride, 1.463 (2) Å, is in good agreement with the other values of Table 6, and also with the length of the corresponding bond in *o*-phenylenediamine dihydrochloride, 1.457 (2) Å (Stålhandske, 1974), and in orthonilic acid, 1.470 (5) Å (Hall & Maslen, 1967). The weighted mean from all the values, 1.462 (2) [1] Å, may be considered as the 'standard' length of the bond connecting an —NH<sub>3</sub><sup>+</sup> group to an aromatic C.

The conformation of the —NH<sub>3</sub><sup>+</sup> group is such that one of the H atoms is almost eclipsed with the ring (Fig. 3 and Table 4). Calculations with the published atomic parameters show that the same conformation occurs in anilinium tetrachlorocuprate(II) (Larsen, 1974) and in

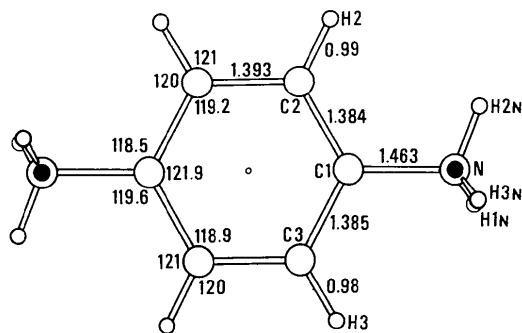


Fig. 2. Bond lengths (Å) and angles (°) of the benzene ring in the *p*-phenylenediaminium dication. Estimated standard deviations are 0.002 Å for C—C and C—N bonds, 0.03 Å for C—H bonds, 0.1° for C—C—C and C—C—N angles, and *ca* 1.5° for C—C—H angles.

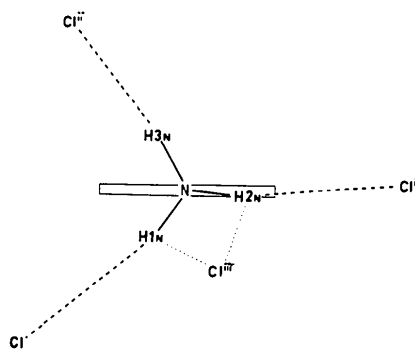


Fig. 3. Projection of the —NH<sub>3</sub><sup>+</sup> group along the N—C(1) bond. The system of intermolecular hydrogen bonds is also shown. The symmetry operations relating Cl<sup>i</sup>, Cl<sup>ii</sup> and Cl<sup>iii</sup> to Cl are: *x*, 1 + *y*, *z*; 1 - *x*, 1 - *y*, 1 - *z*; and 1 - *x*, 1 - *y*, -*z* respectively.

Table 6. C—N bond lengths and α angles in *para* and *meta*-substituted anilinium cations

Bond lengths are in Å, angles in degrees. Estimated standard deviations, σ, are given in parentheses as units in the last digit. Only compounds with α(α) ≤ 0.4° have been included in this table.

No.	Compound	Ref.	C—N	α <sub>NH<sub>3</sub></sub>
1	Anilinium tetrachlorocuprate(II)	(a)	1.468 (3)	121.4 (2)
2	<i>p</i> -Toluidinium hexafluorosilicate dihydrate	(b)	1.477 (7)	122.0 (4)
3	<i>p</i> -Ethoxycarbonylanilinium bis( <i>p</i> -nitrophenyl)phosphate	(c)	1.464 (5)	120.8 (3)
4	<i>p</i> -Phenylenediamine dihydrochloride	(d)	1.463 (2)	121.9 (1)
5	<i>m</i> -Aminobenzoic acid hydrochloride	(e)	1.461 (4)	121.7 (2)
6	<i>m</i> -Aminobenzene-sulphonamide hydrochloride	(f)	1.458 (5)	120.6 (4)
Weighted mean values*			1.464 (2) [1]	121.7 (2) [1]

(a) Larsen (1974). (b) Denne, Mathieson & Mackay (1971). (c) Pletcher, Sax & Yoo (1972). (d) This work. (e) Arora, Sundaralingam, Dancz, Stanford & Marsh (1973). (f) Le Bars, Alleaume & Hauw (1973).

\* Here and throughout this paper mean values and their standard errors have been calculated from the individual values with the formulae:

$$x_m = \frac{\sum_{i=1}^N (x_i/\sigma_i^2)}{\sum_{i=1}^N (1/\sigma_i^2)} ; \sigma_m = \sqrt{\frac{\sum_{i=1}^N [(x_i - x_m)^2/\sigma_i^2]}{i-1}}$$

$$\sigma'_m = \frac{1}{\sqrt{\sum_{i=1}^N (1/\sigma_i^2)}}$$

where  $\sigma_i$  is the estimated standard deviation of the quantity  $x_i$ . Values of  $\sigma_m$  are given in parentheses and values of  $\sigma'_m$  in square brackets. It should be pointed out that whilst  $\sigma_m$  is a measure of the 'external' consistency of the data averaged,  $\sigma'_m$  is a measure of their 'internal' consistency.

Table 7. Geometry of the hydrogen bonds

Estimated standard deviations are given in parentheses as units in the last digit. The symmetry operations relating Cl<sup>i</sup> and Cl<sup>ii</sup> to Cl are given in the caption to Fig. 3.

(a) Distances (Å)

Cl <sup>i</sup> ...N	3.190 (2)	Cl <sup>i</sup> ...H(1N)	2.34 (3)
Cl <sup>ii</sup> ...N	3.249 (2)	Cl <sup>ii</sup> ...H(2N)	2.36 (3)
Cl <sup>iii</sup> ...N	3.171 (2)	Cl <sup>iii</sup> ...H(3N)	2.27 (2)

(b) Angles (°)

Cl <sup>i</sup> ...H(1N)—N	158 (3)	Cl <sup>ii</sup> ...H(3N)—N	166 (2)
Cl <sup>ii</sup> ...H(2N)—N	168 (2)		

*m*-aminobenzoic acid hydrochloride (Arora, Sundaralingam, Dancz, Stanford & Marsh, 1973). This conformation may be responsible for the small in-plane bending of the C(1)–N bond [the N–C(1)–C(2) angle is 1° greater than N–C(1)–C(3)]. Note that the N atom is also slightly out of the ring plane (Table 5).

#### *Intermolecular hydrogen bonding*

As originally shown by Chandrasekaran (1969), each of the three H atoms of the substituent is involved in a hydrogen bond to a chloride ion (Fig. 3 and Table 7). N...Cl separations are in the range 3.17–3.25 Å. A fourth chloride ion, Cl<sup>iv</sup> in Fig. 3, is only 3.34 Å from N, although none of the H atoms point in its direction. The distances of Cl<sup>iv</sup> from H(1N) and H(2N) are 3.01 and 2.97 Å respectively. The next N...Cl contact in the crystal is 3.71 Å.

We wish to thank Professor A. Vaciego for constant encouragement and stimulating discussions, and also for computing time. We gratefully thank the Centro di Cristallografia Strutturale del CNR, Pavia, for the collection of the intensity data. Financial support by CNR, Roma (to EFS and LRS), is also acknowledged.

#### References

- ARORA, S. K., SUNDARALINGAM, M., DANCZ, J. S., STANFORD, R. H. & MARSH, R. E. (1973). *Acta Cryst.* **B29**, 1849–1855.
- CARRUTHERS, J. R. & SPAGNA, R. (1975). Seventh Meeting, Italian Cryst. Assoc., Bologna, Italy. Abstracts, pp. 65–67.
- CHANDRASEKARAN, R. (1969). *Acta Cryst.* **B25**, 369–374.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DENNE, W. A., MATHIESON, A. MCL. & MACKAY, M. F. (1971). *J. Cryst. Mol. Struct.* **1**, 55–62.
- DI RIENZO, F., DOMENICANO, A., PORTALONE, G. & VACIAGO, A. (1976). Second Yugoslav–Italian Cryst. Conf., Dubrovnik, Yugoslavia. Abstracts, pp. A102–A104.
- DOMENICANO, A., MAZZEO, P. & VACIAGO, A. (1976). *Tetrahedron Lett.* pp. 1029–1032.
- DOMENICANO, A. & VACIAGO, A. (1975). *Izv. Jugosl. Cent. Krist. (Zagreb)*, **10**, 37–50.
- DOMENICANO, A. & VACIAGO, A. (1976). Third European Cryst. Meeting, Zürich, Switzerland. Abstracts, pp. 274–276.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975a). *Acta Cryst.* **B31**, 221–234.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975b). *Acta Cryst.* **B31**, 1630–1641.
- HALL, S. R. & MASLEN, E. N. (1967). *Acta Cryst.* **22**, 216–228.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- LANGSETH, A. & STOICHEFF, B. P. (1956). *Canad. J. Phys.* **34**, 350–353.
- LARSEN, K. P. (1974). *Acta Chem. Scand.* **A28**, 194–200.
- LE BARS, M., ALLEAUME, M. & HAUW, C. (1973). *Cryst. Struct. Commun.* **2**, 383–386.
- PLETCHER, J., SAX, M. & YOO, C. S. (1972). *Acta Cryst.* **B28**, 378–387.
- STÅLHANDSKE, C. (1974). *Acta Cryst.* **B30**, 1586–1589.
- STOICHEFF, B. P. (1954). *Canad. J. Phys.* **32**, 339–346.
- WHEATLEY, P. J. (1959). *Struttura delle Molecole*, pp. 203–208. Roma: Accademia Nazionale dei Lincei.