

## Structural Studies of Benzene Derivatives. X.\* Refinement of the Structure of *p*-Chlorobenzoic Acid

BY MARCELLO COLAPIETRO AND ALDO DOMENICANO

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

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### Abstract

The crystal structure of *p*-chlorobenzoic acid,  $C_7H_5ClO_2$ ,  $M_r = 156.57$ , previously determined by Miller, Paul & Curtin [*J. Am. Chem. Soc.* (1974), **96**, 6334–6339], has been refined to  $R = 0.0361$  on 1431 counter intensities. The crystals (m.p. 512–514 K) are triclinic, space group  $P\bar{1}$ , with  $a = 14.376(4)$ ,  $b = 6.213(2)$ ,  $c = 3.854(2)$  Å,  $\alpha = 88.66(4)$ ,  $\beta = 100.23(2)$ ,  $\gamma = 93.23(2)^\circ$ ,  $Z = 2$ . The benzene ring has  $C_{2v}$  (*mm*) symmetry within experimental error. The deviations of the internal angles of the ring from  $120^\circ$  are highly significant and are due primarily to the Cl substituent. The angle *ipso* to the Cl atom,  $\alpha_{Cl} = 122.0(2)^\circ$ , agrees with the values obtained by different techniques for chlorobenzene and a number of its *meta*- and *para*-substituted derivatives. The value of  $\alpha_{Cl}$  obtained for chlorobenzene by microwave spectroscopy,  $120.16^\circ$ , appears to be in error. It is shown that microwave spectroscopy may not be the method of choice for determining the geometry of the *ipso* region in monosubstituted benzene rings.

### Introduction

As a part of our programme of accurate determination of the molecular structures of *para*-substituted benzoic acids (Colapietro, Domenicano & Portalone, 1980, and references therein) we report here the structure of *p*-chlorobenzoic acid, as obtained from a new X-ray diffraction study.

An analysis of the crystal structure of this compound was reported earlier (Miller, Paul & Curtin, 1974). The least-squares refinement, based on 924 counter intensities, led to a final  $R$  value of 0.071, and to e.s.d.'s of the bond lengths and angles of the C skeleton equal to 0.007 Å and 0.3–0.5°, respectively. Differences as

large as 0.028 Å and  $1.1^\circ$  occurred, however, between parameters expected to be chemically equivalent in a *para*-disubstituted benzene derivative. We deemed the accuracy of the analysis to be inadequate for determining the structural effects of substitution, and have carried out a new refinement with a more accurate set of intensity data.

### Experimental

Colourless tablets were grown from a benzene/acetone solution of the commercial product (Fluka, *puriss.*). A crystal,  $ca\ 0.86 \times 0.35 \times 0.20$  mm, was mounted on a Syntex  $P2_1$  diffractometer. The cell parameters were determined by least-squares techniques from the measured  $\theta$  angles of 17 reflexions, well distributed in reciprocal space (Mo  $K\alpha$  radiation,  $\theta$  range 18–22°). The values obtained are compared in Table 1 with those given by other authors.

Table 1. *Crystal data*

	This work <sup>i,ii</sup>	Pollock & Woodward (1954) <sup>iii</sup>	Miller, Paul & Curtin (1974) <sup>iv,ii</sup>
$a$ (Å)	14.376 (4)	14.355	14.392 (2)
$b$ (Å)	6.213 (2)	6.213	6.227 (1)
$c$ (Å)	3.854 (2)	3.852	3.861 (1)
$\alpha$ (°)	88.66 (4)	88.75	88.68 (3)
$\beta$ (°)	100.23 (2)	100.18	100.12 (4)
$\gamma$ (°)	93.23 (2)	93.24	93.31 (2)
$V$ (Å <sup>3</sup> )	338.2 (2)	337.6 <sup>v</sup>	340.1
$D_c$ (Mg m <sup>-3</sup> )	1.537	1.540 <sup>v</sup>	1.529 <sup>v</sup>
$D_m$ (Mg m <sup>-3</sup> )	1.535 <sup>vi</sup>	–	1.54

Notes: (i) Measured at 293 K with Mo  $K\alpha$  ( $\lambda = 0.71069$  Å). (ii) E.s.d.'s are given in parentheses as units in the last digit. (iii) Measured at 291 K with Cu  $K\alpha$  radiation. We have transformed the original cell parameters through the matrix 101/010/001. (iv) Measured with Cu  $K\alpha$  radiation. (v) Calculated from the given cell parameters. (vi) Measured at 293 K by flotation in a mixture of chloroform and bromoform.

\* Part IX: Colapietro, Domenicano, Marciante & Portalone (1981).

Intensities were measured at room temperature in the  $\theta$ - $2\theta$  scan mode with graphite-monochromatized Mo  $K\alpha$  radiation, using a collimator of appropriate size. The scanning interval was from  $2\theta(K\alpha_1) - 1.1^\circ$  to  $2\theta(K\alpha_2) + 1.3^\circ$ . The scanning speed was varied according to the intensity, from a minimum of  $0.027^\circ \text{ s}^{-1}$  to a maximum of  $0.49^\circ \text{ s}^{-1}$ . The background was measured for one quarter of the scanning time at each end of the scan. Three standard reflexions were monitored every 100 reflexions: their intensities indicated no counter or crystal instability. A recentring routine was run every 500 reflexions. 2600 reflexions in the  $\theta$  range  $1.5$ – $32^\circ$  were scanned; 1631 of these, having  $I \geq 4\sigma(I)$ , were considered as non-zero. 199 reflexions were scanned twice; these included the reflexions of the  $h = 0$  layer, which were measured as  $0kl$  and  $0k\bar{l}$ . After averaging and merging [internal  $R(F_o) = 0.028$ ] a set of 1432 independent observations was obtained.\* The intensities were corrected for Lorentz and polarization effects, but not for absorption ( $\mu$  for Mo  $K\alpha$  is  $0.492 \text{ mm}^{-1}$ ). A secondary-extinction correction was applied during the final stages of refinement.

### Refinement

The positional parameters of the non-H atoms given by Miller, Paul & Curtin (1974) were used as a starting set ( $R = 0.242$ ). Full-matrix isotropic and then anisotropic least-squares refinement, followed by the introduction of the four H atoms of the benzene ring as given by a difference synthesis, lowered  $R$  to 0.055. Further refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, converged to  $R = 0.043$  (one intense reflexion omitted). At this point the carboxylic H atom was located on a difference Fourier map as a well-defined peak. Further refinement of all the atomic parameters led to  $R = 0.037$  (seven intense reflexions omitted). Inspection of the structure factor list revealed that  $|F_o|$  for the most intense reflexions was systematically lower than  $|F_c|$ . A plot of  $\log(I_c/I_o)$  vs  $I_c$  was essentially linear for all but the most intense reflexion in the data set,  $20\bar{1}$ , which was thus definitely excluded. The value of the secondary-extinction coefficient (Stout & Jensen, 1968) was  $g = 3.16 \times 10^{-5}$ . The  $I_o$  values were corrected accordingly.

The final refinement was by full-matrix least squares, minimizing  $\sum w(|F_o| - k|F_c|)^2$ ; the number of observations per refined parameter was  $1431/111 = 12.9$ . Weights were given as  $w = 1/(a + b|F_o| + c|F_o|^2)$ , with  $a = 2.00$ ,  $b = 1.00$  and  $c = 0.075$ . The final  $R$  and  $R_w$  were 0.0361 and 0.0521, respectively, with all final

\* The reflexions  $0\bar{1}1$  and  $2\bar{1}0$  were too intense to be measured accurately and were excluded from the data set.

Table 2. Final coordinates ( $x \times 10^5$ ;  $y$ ,  $z \times 10^4$ ) and equivalent values of the anisotropic temperature factors for non-hydrogen atoms

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	$x$	$y$	$z$	$B_{eq} (\text{\AA}^2)^*$
Cl	42630 (4)	7861.9 (9)	8298.1 (15)	4.68
O(1)	11944 (9)	194 (2)	602 (4)	3.85
O(2)	2067 (9)	2414 (2)	2307 (4)	4.22
C(1)	18405 (10)	3343 (2)	3671 (4)	2.86
C(2)	27675 (11)	2772 (3)	3766 (4)	3.30
C(3)	35170 (12)	4153 (3)	5212 (5)	3.62
C(4)	33263 (12)	6109 (3)	6516 (4)	3.39
C(5)	24111 (13)	6706 (3)	6453 (5)	3.48
C(6)	16656 (12)	5309 (3)	5028 (5)	3.29
C(7)	10413 (11)	1868 (3)	2086 (4)	3.11

\* Defined as  $(B_1 B_2 B_3)^{1/3}$ , where  $B_i = 8\pi^2 U_i^2$  ( $i = 1, 2, 3$ ). The  $U_i^2$  are the mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid.

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

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	$x$	$y$	$z$	$B (\text{\AA}^2)$
H(2)	290 (2)	139 (4)	278 (6)	2.5 (4)
H(3)	418 (2)	381 (4)	529 (6)	2.7 (5)
H(5)	232 (2)	798 (4)	744 (6)	2.0 (4)
H(6)	102 (2)	573 (4)	484 (6)	2.6 (5)
H(O)	-32 (3)	131 (7)	93 (11)	9.2 (12)

shifts less than  $0.01\sigma$ ; the resulting atomic parameters are given in Tables 2 and 3.\* As in previous cases (Di Rienzo, Domenicano & Riva di Sanseverino, 1980, and references therein), other weighting schemes gave higher dispersions for the mean values of the minimized function over ranges of either  $|F_o|$  or  $\sin \theta/\lambda$ , and afforded a less symmetrical C hexagon.

Calculations were carried out on the Univac 1100/22 computer of the University of Rome and on the HP 21MX minicomputer of the CNR Research Area. The computer programs and atomic form factors were the same as those in part V (Colapietro, Domenicano & Pela Ceccarini, 1979).

### Results and discussion

Bond lengths and angles are given in Fig. 1; they have not been corrected for the effects of thermal motion.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36723 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

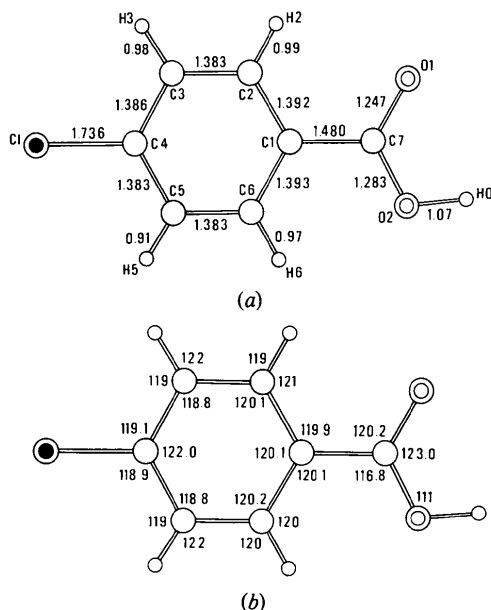


Fig. 1. Molecular geometry of *p*-chlorobenzoic acid: (a) bond lengths (Å), (b) bond angles (°). E.s.d.'s (calculated from the standard deviations in the atomic parameters given in Tables 2 and 3) are 0.002–0.003 Å for C–C, C–O and C–Cl bonds, 0.03 Å for C–H bonds, 0.04 Å for the O–H bond, 0.13–0.18° for angles not involving H atoms, 1.4–2.5° for angles involving H atoms.

Table 4. Deviations from planarity

Equation of the least-squares plane through the six C atoms of the benzene ring (referred to the crystallographic axes):  $-1.9281x - 2.5463y + 3.4775z = 0.0723$ . The e.s.d.'s in the atomic positions are 0.0005 Å for Cl, 0.0013–0.0018 Å for the O and C atoms, 0.04 Å for H(O), 0.02 Å for the other H atoms.

Displacements (Å) of atoms from the plane

C(1)*	0.002	O(1)	0.143
C(2)*	0.002	O(2)	-0.075
C(3)*	-0.005	H(2)	0.02
C(4)*	0.003	H(3)	0.01
C(5)*	0.001	H(5)	-0.04
C(6)*	-0.003	H(6)	0.04
C(7)	0.023	H(O)	0.02
Cl	0.0105		

\* Atoms defining the plane.

The equation of the least-squares plane through the C atoms of the benzene ring and the displacements of all atoms from this plane are given in Table 4. Torsion angles are reported in Table 5.

#### The benzene ring

The symmetry of the benzene ring is  $C_{2v}(mm)$  within experimental error (Fig. 1 and Table 4), as in *p*-fluorobenzoic acid (Colapietro, Domenicano & Pela

Table 5. Torsion angles (°)

Signs have been given according to the convention of Klyne & Prelog (1960). The e.s.d.'s are 0.2°.

O(1)–C(7)–C(1)–C(2)	-5.4
O(1)–C(7)–C(1)–C(6)	173.9
O(2)–C(7)–C(1)–C(6)	-5.6
O(2)–C(7)–C(1)–C(2)	175.1

Ceccarini, 1979) and *p*-nitrobenzoic acid (Colapietro & Domenicano, 1977). The asymmetries of the ring geometry obtained in the previous study (Miller, Paul & Curtin, 1974) have now disappeared.

The deviations of the ring geometry from  $D_{6h}$  ( $6/mmm$ ) symmetry are highly significant and involve bond distances as well as angles. They consist of: (i) a lengthening (by 0.009–0.010 Å,  $5\sigma$ ) of the C(1)–C(2) and C(1)–C(6) bonds with respect to the central C–C bonds of the ring; (ii) an increase from 120° (by 2.0°,  $12\sigma$ ) of the C(3)–C(4)–C(5) angle,  $\alpha_{C1}$ ; and (iii) a decrease from 120° (by 1.2°,  $7\sigma$ ) of the C(2)–C(3)–C(4) and C(4)–C(5)–C(6) angles,  $\beta_{C1}$ .

Since the COOH group is known to cause only minor changes of the ring angles (Domenicano & Murray-Rust, 1979; Bruno & Randaccio, 1980), the angular distortions occurring in *p*-chlorobenzoic acid should be attributed primarily to the Cl substituent. Indeed the value of  $\alpha_{C1}$ , 122.0(2)°, is close to the values obtained for the corresponding parameter in a variety of *para*- and *meta*-substituted derivatives of chlorobenzene,  $X-C_6H_4-Cl$ , where the angular changes caused by the *X* substituent in the *para* or *meta* positions of the ring are known (or expected, on the basis of the nature and electronic properties of *X*) to be at most a few tenths of a degree (Table 6).

Of course the most intriguing comparison is that with chlorobenzene itself. The geometry of this molecule has been determined by three different techniques, namely microwave spectroscopy (Michel, Nery, Nosberger & Roussy, 1976), gas-phase electron diffraction (Penionzhkevich, Sadova & Vilkov, 1979) and NMR spectroscopy in a nematic solvent (Diehl & Jokisaari, 1979). The values of  $\alpha_{C1}$  obtained by electron diffraction and NMR spectroscopy are 121.7(6)° and 121.8°,\* respectively, both close to the present experimental result for *p*-chlorobenzoic acid and to the value of 121.9° predicted for chlorobenzene from the empirical angular parameters of Domenicano & Murray-Rust (1979). (These parameters have been derived for a number of substituents from the ring bond angles observed in many mono and *para*-disubstituted benzene derivatives, among which were several *para*-

\* Calculated from the published geometrical parameters (values corrected for harmonic vibrations).

Table 6. Values of the endocyclic angle  $\alpha_{\text{Cl}}$  ( $^{\circ}$ ) in *para*- and *meta*-substituted chlorobenzenes

Only compounds with  $\sigma(\alpha_{\text{Cl}}) \leq 0.4^{\circ}$  and where the *para* or *meta* substituent has a marginal effect on  $\alpha_{\text{Cl}}$  have been included.

Compound	Reference	Technique*	$\alpha_{\text{Cl}}^{\dagger}$
<i>p</i> -Chlorocinnamide	<i>a</i>	XC	121.8 (3)
<i>trans-p,p'</i> -Dichloroazobenzene	<i>b</i>	XC	121.7 (3)
Ethylene glycol bis( <i>p</i> -chlorobenzoate)	<i>c</i>	XC	121.6 (2)
<i>p,p'</i> -Dichlorodiphenyl disulphide	<i>d</i>	XC	121.6 (3)
Bis( <i>m</i> -chlorophenyl)-acetylene	<i>e</i>	XC	121.5 (3)
<i>p</i> -Dichlorobenzene ( $\alpha$ phase)	<i>f</i>	LXC	122.0 (3)
<i>p</i> -Dichlorobenzene ( $\beta$ phase)	<i>f</i>	LXC	121.6 (4)
<i>p</i> -Dichlorobenzene ( $\gamma$ phase)	<i>f, g</i>	LXC	122.1 (3)
<i>p</i> -Dichlorobenzene	<i>h</i>	ED	121.6 $\pm$ 0.2
<i>N</i> -(1-Pyridinio)chlorobenzene- <i>p</i> -sulphonamidate	<i>i</i>	XC	121.7 (2)
<i>m</i> -Chlorobenzoic acid	<i>j</i>	XC	121.8 (4)
<i>p</i> -Chlorobenzoic acid	<i>k</i>	XC	122.0 (2)

References: (*a*) Rabinovich (1969). (*b*) Hope & Victor (1969). (*c*) Pérez & Brisse (1975). (*d*) Spirlet, van den Bossche, Dideberg & Dupont (1979). (*e*) Espiritu & White (1977). (*f*) Wheeler & Colson (1976). (*g*) Wheeler & Colson (1975). (*h*) Schultz, Hargittai & Domenicano (1980). (*i*) Cameron & Duncanson (1976). (*j*) Gougoutas & Lessinger (1975). (*k*) This work.

\* XC, room-temperature X-ray crystallography; LXC, low-temperature X-ray crystallography; ED, gas-phase electron diffraction.

$\dagger$  E.s.d.'s are given in parentheses as units in the last digit; total errors are given as error limits.

substituted derivatives of chlorobenzene but not chlorobenzene itself.)

The value of  $\alpha_{\text{Cl}}$  obtained in the microwave study of chlorobenzene is surprisingly low,  $120.16^{\circ}$  (Michel *et al.*, 1976). The study was based on 20 isotopic species and led to a complete 'substitution' structure, which should – in principle – be extremely accurate. In the present case, however, the coordinate of the *ortho* C atoms along the *a* principal axis of the molecule is too small ( $\sim 0.26 \text{ \AA}$ ) to be determined accurately by the 'substitution' method; also rather small is the *a* coordinate of the *ipso* C atom ( $\sim -0.44 \text{ \AA}$ ). Thus the published 'substitution' structure of chlorobenzene should be considered as rather inaccurate, as far as the *ipso* region of the ring is concerned, and a revised structure has recently been proposed (Schultz, Hargittai & Domenicano, 1980).

A similar problem is posed by the microwave structure of nitrobenzene (Høg, 1971), which appears to be unrealistically distorted in the *ipso* region (Di Rienzo, Domenicano & Riva di Sanseverino, 1980).

The experimental results discussed in the present paper reinforce the view that X-ray crystallography can provide accurate values for bond angles (Domenicano & Vaciago, 1979). They also show that microwave spectroscopy – although generally a very accurate technique of structural analysis – may not be the method of choice for determining the geometry of the *ipso* region in monosubstituted benzene derivatives, where the centre of gravity of the molecule is often near the *ipso* C atom.

#### The Cl substituent

The Cl atom is slightly bent out of the plane of the ring, on the same side as C(7) (Table 4). The length of the C(4)–Cl bond obtained here,  $1.736 (2) \text{ \AA}$ , is probably shortened to some extent by the effects of thermal motion. The vibration of the Cl atom is in fact anisotropic,\* with the minor axis of the thermal ellipsoid almost exactly collinear with the C(4)–Cl bond. The present C–Cl bond length is in the range of values obtained by crystal structure analysis for 18 *para*-substituted derivatives of chlorobenzene [ $1.728$ – $1.750 \text{ \AA}$ , mean  $1.7404 (11) \text{ \AA}$  (Domenicano, Vaciago & Coulson, 1975)]. It also compares well with the values obtained by gas-phase electron diffraction for chlorobenzene,  $r_g = 1.737 (5) \text{ \AA}$  (Penionzhkevich, Sadova & Vilkov, 1979), and *p*-dichlorobenzene,  $r_g = 1.730 \pm 0.004 \text{ \AA}$  (Schultz, Hargittai & Domenicano, 1980).

#### The COOH substituent

The dimensions of the carboxyl group are similar to those observed in *p*-fluorobenzoic acid (Colapietro, Domenicano & Pela Ceccarini, 1979) and *p*-methoxybenzoic acid (Colapietro & Domenicano, 1978). As in those cases, the moderate differences occurring in the lengths of the two C–O bonds and in the values of the two C–C–O angles (Fig. 1), as well as the rather high *B* value for H(O) ( $9.2 \text{ \AA}^2$ ), suggest some rotational disorder of the substituent.

The observation that the carboxyl group is not perfectly coplanar with the benzene ring (Miller, Paul & Curtin, 1974) is confirmed by the present study. The plane through C(7), O(1) and O(2) makes an angle of  $5.7^{\circ}$  with the least-squares plane of the ring, mainly a twist about the C(1)–C(7) bond (Table 5).

#### The hydrogen bonding

As in the isostructural *p*-fluoro and *p*-bromo analogues (Colapietro, Domenicano & Pela Ceccarini, 1979; Ohkura, Kashino & Haisa, 1972) the molecules

\* The principal axes of the thermal ellipsoid are  $B_1 = 2.52$ ,  $B_2 = 5.91$ ,  $B_3 = 6.89 \text{ \AA}^2$ .

of *p*-chlorobenzoic acid are hydrogen-bonded in pairs across centres of symmetry, and the pairs are arranged in stacks. A detailed analysis of the crystal packing and of its relationship to the anisotropy of the solid-state reaction with gaseous ammonia has been given (Miller, Paul & Curtin, 1974).

The geometrical parameters obtained here for the O(2)—H(O)···O(1')\* hydrogen bond are: distances O(2)···O(1') = 2.618 (2); O(2)—H(O) = 1.07 (4); H(O)···O(1') = 1.56 (4) Å; angle O(2)—H(O)···O(1') = 170 (4)°. Note that the O(2)···O(1') distance is the same as in *p*-fluorobenzoic acid (Colapietro, Domenicano & Pela Ceccarini, 1979).

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\* The symmetry operation relating O(1') to O(1) is  $-x, -y, -z$ .

### References

- BRUNO, G. & RANDACCIO, L. (1980). *Acta Cryst.* **B36**, 1711–1712.
- CAMERON, A. F. & DUNCANSON, F. D. (1976). *Acta Cryst.* **B32**, 1991–1994.
- COLAPIETRO, M. & DOMENICANO, A. (1977). *Acta Cryst.* **B33**, 2240–2243.
- COLAPIETRO, M. & DOMENICANO, A. (1978). *Acta Cryst.* **B34**, 3277–3280.
- COLAPIETRO, M., DOMENICANO, A., MARCIANTE, C. & PORTALONE, G. (1981). *Acta Cryst.* **B37**, 387–396.
- COLAPIETRO, M., DOMENICANO, A. & PELA CECCARINI, G. (1979). *Acta Cryst.* **B35**, 890–894.
- COLAPIETRO, M., DOMENICANO, A. & PORTALONE, G. (1980). *Acta Cryst.* **B36**, 354–358.
- DIEHL, P. & JOKISAARI, J. (1979). *J. Mol. Struct.* **53**, 55–60.
- DI RIENZO, F., DOMENICANO, A. & RIVA DI SANSEVERINO, L. (1980). *Acta Cryst.* **B36**, 586–591.
- DOMENICANO, A. & MURRAY-RUST, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.
- DOMENICANO, A. & VACIAGO, A. (1979). *Acta Cryst.* **B35**, 1382–1388.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 1630–1641.
- ESPIRITU, A. A. & WHITE, J. G. (1977). *Acta Cryst.* **B33**, 3899–3901.
- GOUGOUTAS, J. Z. & LESSINGER, L. (1975). *J. Solid State Chem.* **12**, 51–62.
- HØG, J. H. (1971). Thesis, Univ. of Copenhagen.
- HOPE, H. & VICTOR, D. (1969). *Acta Cryst.* **B25**, 1849–1853.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- MICHEL, F., NERY, H., NOSBERGER, P. & ROUSSY, G. (1976). *J. Mol. Struct.* **30**, 409–415.
- MILLER, R. S., PAUL, I. C. & CURTIN, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6334–6339.
- OHKURA, K., KASHINO, S. & HAISA, M. (1972). *Bull. Chem. Soc. Jpn*, **45**, 2651–2652.
- PENIONZHKEVICH, N. P., SADOVA, N. I. & VILKOV, L. V. (1979). *Zh. Strukt. Khim.* **20**, 527–529.
- PÉREZ, S. & BRISSE, F. (1975). *Can. J. Chem.* **53**, 3551–3556.
- POLLOCK, J. MCC. & WOODWARD, I. (1954). *Acta Cryst.* **7**, 605.
- RABINOVICH, D. (1969). *J. Chem. Soc. (A)*, pp. 2361–2366.
- SCHULTZ, GY., HARGITTAI, I. & DOMENICANO, A. (1980). *J. Mol. Struct.* **68**, 281–292.
- SPIRLET, M. R., VAN DEN BOSSCHE, G., DIDEBERG, O. & DUPONT, L. (1979). *Acta Cryst.* **B35**, 203–205.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 411. London: Macmillan.
- WHEELER, G. L. & COLSON, S. D. (1975). *Acta Cryst.* **B31**, 911–913.
- WHEELER, G. L. & COLSON, S. D. (1976). *J. Chem. Phys.* **65**, 1227–1235.

*Acta Cryst.* (1982). **B38**, 1957–1962

## Structures of (*RR*) and (*RS*)-Bis[1-(2,4,6-trimethylphenyl)ethyl] Ether: A Relative-Configuration Problem

BY C. FOCES-FOCES, F. H. CANO AND S. GARCÍA-BLANCO

*Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain*

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### Abstract

$C_{22}H_{30}O$ ,  $M_r = 310.481$ ; *RR* compound (*A*): monoclinic,  $P2_1/c$ ,  $a = 8.0827$  (2),  $b = 31.6784$  (26),  $c = 7.7624$  (2) Å,  $\beta = 103.092$  (2)°,  $V = 1935.9$  (2) Å<sup>3</sup>,  $D_x = 1.065$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Cu } K\alpha) = 0.4471$

mm<sup>-1</sup>, final  $R = 0.053$  for 2217 observed reflexions; *RS* compound (*B*): orthorhombic,  $Pc2_1n$ ,  $a = 11.8337$  (6),  $b = 10.3267$  (4),  $c = 15.5781$  (10) Å,  $V = 1903.7$  (1) Å<sup>3</sup>,  $D_x = 1.083$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Cu } K\alpha) = 0.4546$  mm<sup>-1</sup>, final  $R = 0.067$  for 1193 observed reflexions. A description of the relative configuration of