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The Crystal Structure of 1-*p*-Bromophenyl-4,5-(1,2-*cis*-D-glucofurano)imidazolidine-2-thione

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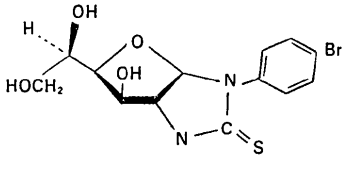
1-*p*-Bromophenyl-4,5-(1,2-*cis*-glucofurano)imidazolidine-2-thione crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a=4{\cdot}691$ (2), $b=9{\cdot}930$ (7), $c=31{\cdot}800$ (15) Å; $Z=4$. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined anisotropically by full-matrix least-squares procedures. The final R value for 1518 independent reflexions is 0·047. The absolute configuration was fixed from the anomalous dispersion correction to the atomic scattering factors of Br and S. The structure consists of two chains of molecules which lie parallel to the b axis. These molecules, related by a twofold screw axis, are linked by hydrogen bonds to form a helicoidal packing arrangement.

Introduction

The crystal structure of 1-*p*-bromophenyl-4,5-(1,2-*cis*-D-glucofurano)imidazolidine-2-thione



has been determined as a part of a systematic structural investigation of compounds obtained by reaction of 2-amino-2-deoxy-D-glucose with alkyl(aryl) isothiocyanates. Previous research, connected with this programme, involved the following X-ray structural determinations: 4-(β-D-erythrofuranosyl)imidazoline-2-thione (Pérez-Garrido, López-Castro & Márquez, 1973); 1-methyl-4,5-(D-glucofurano)imidazolidine-2-thione (Jiménez-Garay, López-Castro & Márquez, 1974); 1-*p*-chlorophenyl-4-(α-D-erythrofuranosyl)-4-imidazoline-2-thione (Pérez-Garrido, Conde & Márquez, 1974). In earlier publications (Fernández-Bolaños, García-González, Gasch & Menéndez, 1963; Morell, 1961; Krüger & Rudy, 1963; Fritz & Wacker, 1968; García-González, Fernández-Bolaños & Pradera, 1976) both furanoid and pyranoid structures were proposed for the sugar moieties of these compounds. It has been demonstrated (Jiménez-Garay *et al.*, 1974) that the sugar ring in 1-methyl-4,5-(D-glucofurano)-imidazolidine-2-thione adopts the furanoid conformation.

The structure determination of the title compound was undertaken to establish the molecular conformation, which could not be assigned by methods other than X-ray analysis.

Experimental

Crystals of the title compound were supplied by Professor Fernández-Bolaños of this University. They are colourless needle-shaped prisms, elongated along the a axis.

Crystal data

$M=375$, $a=4{\cdot}691$ (2), $b=9{\cdot}930$ (7), $c=31{\cdot}800$ (15) Å, $V=1481{\cdot}3$ Å^3, $Z=4$, $D_m=1{\cdot}65$, $D_c=1{\cdot}68$ g cm^{-3}, $F(000)=760$, $\mu=53{\cdot}6$ cm^{-1}, λ(Cu $K\alpha$)$=1{\cdot}5418$ Å. Space group $P2_12_12_1$ (from systematic absences).

Rotation and Weissenberg photographs were used to determine the space group and approximate unit-cell dimensions; more accurate values were calculated by a least-squares treatment of $(\theta,\chi,\varphi)_{hkl}$ angles measured on an automated diffractometer for 25 reflexions.

A crystal of dimensions $0{\cdot}18\times0{\cdot}14\times0{\cdot}12$ mm was chosen to collect intensities up to $\theta\leq65°$ with an automated on-line Siemens AED single-crystal diffractometer and Ni-filtered Cu radiation. The ω–2θ scanning method was used. 1518 independent reflexions were recorded, and of these, 150 having $I<2\sigma(I)$ were considered as unobserved.

The intensity of a standard reflexion was measured periodically and subsequently used for scaling; no significant change was observed in the intensity of this reflexion during data collection. The structure amplitudes were corrected for Lorentz and polarization effects, but no absorption corrections were applied ($\mu R<0{\cdot}1$).

Structure determination and refinement

The structure was determined by the heavy-atom technique. The position of the Br atom was derived from a three-dimensional Patterson map. The sulphur and other non-hydrogen atom positions were obtained by the iterative Fourier synthesis technique with the initial set of phases based on the Br atom position. Isotropic temperature factors $\exp(-B\sin^2\theta/\lambda^2)$ were used to calculate structure factors and the R value was 0·26. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

The structure was refined by full-matrix least-squares

Table 1. *Atomic parameters*

(*a*) Positional and anisotropic thermal parameters for non-hydrogen atoms with their estimated standard deviations ($\times 10^4$). The expression used is $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	6941 (3)	5780 (1)	−686 (0)	997 (9)	200 (1)	5·5 (1)	−78 (3)	14 (1)	6 (0)
S	8274 (5)	2207 (5)	1147 (0)	607 (10)	69 (1)	6·9 (1)	39 (4)	12 (1)	1 (0)
O(1)	3549 (11)	6458 (3)	1481 (1)	485 (29)	67 (3)	4·4 (3)	36 (9)	−10 (3)	0 (1)
O(2)	1789 (12)	5991 (4)	2370 (1)	474 (26)	91 (4)	6·3 (3)	73 (10)	14 (3)	4 (1)
O(3)	7408 (11)	7791 (4)	2389 (1)	540 (33)	76 (3)	4·5 (3)	38 (10)	−11 (3)	−2 (1)
O(4)	7689 (18)	1·0033 (4)	1853 (1)	1291 (57)	71 (4)	5·6 (3)	−57 (12)	4 (4)	−1 (1)
N(1)	4865 (13)	4385 (4)	1146 (1)	501 (33)	66 (4)	3·9 (3)	4 (11)	4 (3)	1 (1)
N(2)	4866 (14)	3280 (4)	1738 (1)	564 (39)	62 (4)	5·5 (4)	17 (11)	19 (4)	2 (1)
C(1)	5322 (15)	4703 (5)	707 (1)	447 (35)	71 (5)	4·5 (4)	11 (12)	6 (4)	1 (1)
C(2)	6804 (18)	5830 (5)	612 (2)	613 (42)	77 (6)	6·1 (5)	−21 (15)	−3 (4)	2 (1)
C(3)	7375 (17)	6170 (6)	191 (2)	586 (50)	101 (6)	6·1 (5)	−32 (14)	−2 (4)	2 (1)
C(4)	6199 (18)	5314 (6)	−118 (2)	592 (52)	102 (6)	5·8 (5)	17 (15)	14 (4)	2 (1)
C(5)	4693 (19)	4195 (7)	−25 (2)	631 (48)	123 (7)	5·5 (5)	−64 (18)	−6 (5)	−4 (2)
C(6)	4195 (19)	3880 (6)	402 (2)	606 (47)	111 (7)	5·9 (5)	−52 (16)	2 (5)	−3 (1)
C(7)	5935 (15)	3289 (5)	1345 (1)	450 (38)	51 (4)	5·4 (4)	−29 (11)	2 (4)	−1 (1)
C(8)	2859 (15)	4351 (5)	1825 (2)	342 (32)	80 (5)	5·8 (4)	4 (13)	3 (4)	2 (1)
C(9)	2794 (16)	5139 (5)	1397 (1)	422 (38)	73 (5)	5·5 (4)	27 (13)	−5 (4)	1 (1)
C(10)	5430 (15)	6429 (5)	1839 (1)	420 (34)	65 (5)	4·2 (4)	20 (12)	−2 (4)	2 (1)
C(11)	4062 (14)	5403 (5)	2134 (1)	366 (32)	66 (5)	4·7 (4)	29 (11)	6 (3)	0 (1)
C(12)	5797 (16)	7856 (5)	2010 (1)	449 (35)	72 (5)	4·0 (4)	30 (13)	−5 (4)	1 (1)
C(13)	7364 (18)	8717 (5)	1682 (1)	621 (50)	65 (5)	5·4 (4)	0 (13)	−2 (4)	1 (1)

Table 1 (*cont.*)

(*b*) Positional parameters for the hydrogen atoms ($\times 10^3$)

	x	y	z
H(C2)	830	650	78
H(C3)	840	710	14
H(C5)	320	361	−21
H(C6)	320	295	43
H(C8)	120	401	197
H(C9)	100	528	123
H(C10)	730	580	175
H(C11)	570	500	232
H(C12)	410	835	205
H1(C13)	620	891	142
H2(C13)	945	830	159
H(N2)	483	258	196
H(O2)	130	568	262
H(O3)	860	720	250
H(O4)	790	1003	158

methods varying all positional parameters and temperature factors. Six cycles, of which the last three were with anisotropic thermal factors, reduced R to 0·067. The program *ORFLS* (Busing, Martin & Levy, 1962) with unit weights was used. The absolute configuration was fixed from the anomalous dispersion correction to the atomic scattering factors of Br and S. The R values for the enantiomorphous structures were 0·067 and 0·055 and so the latter was considered as real.

An examination of the $\langle\omega\Delta^2\rangle$ ($\Delta=F_o-F_c$) values as a function of $|F_o|$ suggested that the best weighting scheme was $w=1/(C|F_o|^2+B|F_o|+A)$ with $C=0{\cdot}0125$, $B=-0{\cdot}67$ and $A=12{\cdot}5$. A full-matrix least-squares cycle gave R 0·052.

At this stage a difference Fourier synthesis, calculated with $\sin\theta$ up to 0·45, revealed the positions of the 15 H atoms. A further cycle of refinement including the H atoms with isotropic temperature factors equal to those of the bonded atoms and varying only the parameters of the non-hydrogen atoms reduced R to 0·047.

The atomic parameters from the final least-squares cycle are given in Table 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31510 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond distances* (Å) *and angles* (°) *with their standard deviations*

Br—C(4)	1·897 (6)	C(4)—C(3)	1·412 (9)
S—C(7)	1·660 (6)	C(5)—C(4)	1·350 (10)
O(1)–C(9)	1·383 (6)	C(3)—C(2)	1·406 (9)
O(1)–C(10)	1·441 (6)	C(2)—C(1)	1·352 (8)
O(2)–C(11)	1·429 (7)	C(1)—C(6)	1·374 (8)
O(3)–C(12)	1·424 (6)	C(6)—C(5)	1·413 (9)
O(4)–C(13)	1·424 (6)	C(9)—C(8)	1·570 (7)
N(1)–C(1)	1·447 (5)	C(8)—C(11)	1·542 (8)
N(1)–C(9)	1·463 (8)	C(11)–C(10)	1·526 (7)
N(1)–C(7)	1·355 (7)	C(10)–C(12)	1·527 (7)
N(2)–C(8)	1·448 (8)	C(12)–C(13)	1·536 (7)
N(2)–C(7)	1·347 (6)		
Br—C(4)–C(3)	116·4 (5)	N(2)—C(8)—C(9)	102·3 (5)
Br—C(4)–C(5)	120·4 (5)	N(2)—C(8)—C(11)	112·4 (5)
C(1)–C(2)–C(3)	120·6 (6)	C(9)—C(8)—C(11)	102·8 (5)
C(2)–C(3)–C(4)	116·3 (6)	N(1)—C(9)—O(1)	114·8 (5)
C(3)–C(4)–C(5)	123·2 (7)	N(1)—C(9)—C(8)	101·9 (4)
C(4)–C(5)–C(6)	118·7 (7)	C(8)—C(9)—O(1)	107·5 (4)
C(5)–C(6)–C(1)	118·9 (6)	C(9)—O(1)—C(10)	106·9 (4)
C(6)–C(1)–C(2)	122·2 (6)	C(8)—C(11)–O(2)	109·8 (4)
N(1)–C(1)–C(2)	118·2 (5)	C(8)—C(11)–C(10)	102·4 (4)
N(1)–C(1)–C(6)	119·6 (5)	O(2)—C(11)–C(10)	111·3 (4)
C(7)–N(1)–C(9)	113·7 (4)	O(1)—C(10)–C(11)	104·0 (4)
C(1)–N(1)–C(7)	124·8 (5)	O(1)—C(10)–C(12)	109·4 (4)
C(1)–N(1)–C(9)	120·9 (4)	C(11)–C(10)–C(12)	116·6 (4)
S—C(7)–N(1)	126·0 (4)	C(10)–C(12)–O(3)	108·6 (4)
S—C(7)–N(2)	126·4 (4)	C(10)–C(12)–C(13)	109·2 (4)
N(1)–C(7)–N(2)	107·5 (5)	O(3)—C(12)–C(13)	110·2 (4)
C(7)–N(2)–C(8)	114·8 (5)	C(12)–C(13)–O(4)	107·6 (5)

Results and discussion

The bond lengths and angles with the estimated standard deviations are given in Table 2. The average bond distances involving H atoms are C–H = 1·04 (7), O–H = 0·88 (4) and N–H = 0·98 (4) Å.

Phenyl ring

The mean aromatic C–C bond length of 1·39 Å shows good agreement with the value of 1·395 Å quoted for this distance. The least-squares plane passing through the six benzene C atoms is given by equation I (Table 3). From this table it is seen that all six atoms are coplanar within the experimental deviation. The two substituent atoms of the phenyl ring, Br and N(1) do not show deviations from the plane. The Br–C(4) bond length of 1·90 Å agrees with the value observed for HJBR-1 by Larsen (1972), Berthou, Jéminet & Laurent (1972) and Coetzer, Jordaan, Lourens & Nolte (1972). The C(1)–N(1) bond of 1·45 Å agrees with the N–C distances given by Ammon & Wheeler (1974) (1·452 Å) and Aupers, Carlisle & Lindley (1974) (1·44 Å). The average phenyl-ring bond angle is 120°. The enlargement of angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5) is similar to that observed by Camerman & Camerman (1974) and Fanfani, Nunzi, Zanazzi & Zanzari (1974).

Glucofurano-imidazolidine ring

The bond lengths and angles in the glucofurano-imidazolidine ring agree well with those of analogous compounds. The S–C(7), C(7)–N(1) and C(7)–N(2) distances indicate the effect of the thiourea resonance system (Dias & Truter, 1974; Valle, Cojazzi, Busetti & Mammi, 1970; Jiménez-Garay, López-Castro & Márquez, 1974). The C(8)–C(9) bond length of 1·57 Å, though rather long, is comparable with the C–C distances observed by Kobayashi, Marumo & Saito (1974) (1·57 Å) and Hoge & Nordman (1974) (1·579 Å). The imidazolidine ring is planar, as expected. The least-squares plane calculated for the five atoms of the ring is given by equation II (Table 3). S and C(1) (not included in the plane calculation) lie almost in the imidazolidine plane, 0·03 and 0·09 Å below the plane respectively.

As found in analogous compounds there is a discrepancy between the C(9)–O(1) and O(1)–C(10) distances: 1·38 and 1·44 Å respectively. This may be due to the anomeric effect (Berman, Chu & Jeffrey, 1967; Conde, Moreno & Márquez, 1975). The C–C and C–O distances in the sugar chain agree with the values reported by Jiménez-Garay *et al.* (1974). The three types of angles in the glucofurano ring, C–C–C, C–C–O and C–O–C, have average values 103, 106 and 107° respectively, and are comparable with those found by Rahman & Wilson (1972) and Jiménez-Garay *et al.* (1974).

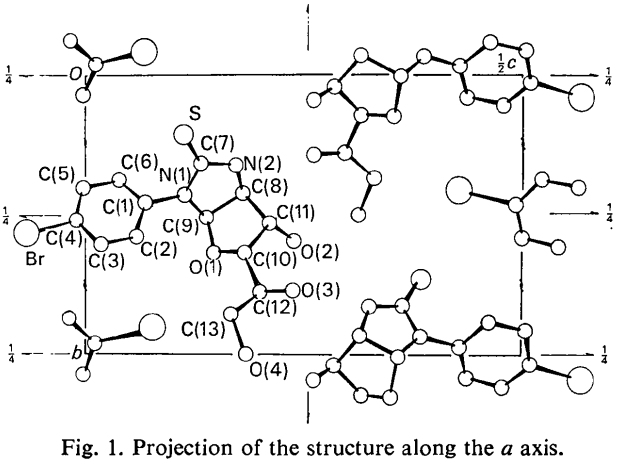


Fig. 1. Projection of the structure along the *a* axis.

Table 3. *Least-squares planes in the molecule*

(*a*) Equations of various planes in the standard orthogonal system in the form $Ax + By + Cz = D$

Plane	*A*	*B*	*C*	*D*
I Phenyl ring	0·8412	−0·5405	0·0136	−0·4043
II Imidazolidine ring	0·7480	0·5774	0·3272	5·3887
III Glucofurano ring	0·8687	−0·4078	−0·2810	−2·2762
IV O(1)–C(8)–C(9)–C(10)	0·8251	−0·3826	−0·4157	−2·8704

(*b*) Deviations in Å from the planes

	I	II	III	IV
Br	0·011*			
S		−0·027*		
O(1)			−0·217	−0·168
O(2)			−1·539*	
N(1)	0·020*	0·025		
N(2)		0·008		
C(1)	0·011	−0·089*		
C(2)	−0·014			
C(3)	0·011			
C(4)	−0·007			
C(5)	0·004			
C(6)	−0·005			
C(7)		−0·021		
C(8)		0·006	0·048	−0·089
C(9)		−0·018	0·092	0·159
C(10)			0·242	0·098
C(11)			−0·164	−0·432*
C(12)			−0·339*	−0·527*

* Atom not included in calculating the plane.

Table 4. *Torsion angles* (°)

N(1)—C(1)—C(2)—C(6)	1·5
C(1)—N(1)—C(9)—C(7)	9·1
S——C(7)—N(1)—N(2)	3·0
O(2)—C(11)–C(8)—C(10)	61·7
C(9)—C(8)—C(11)–C(10)	17·9
C(8)—C(11)–C(10)–O(1)	36·0
C(11)–C(10)–O(1)—C(9)	42·0
C(12)–C(10)–O(1)—C(9)	12·8
C(10)–O(1)—C(9)—C(8)	29·8
O(1)—C(9)—C(8)—C(11)	6·1
C(13)–C(12)–C(10)–O(1)	65·9
O(3)—C(12)–C(10)–C(13)	59·7
O(4)—C(13)–C(12)–C(10)	0·5
C(2)—C(1)—N(1)—C(7)	64·8
N(1)—C(9)—C(8)—O(1)	59·2

The sugar moiety exists in the envelope C(3)-*endo* conformation: C(11) is displaced 0·43 Å from the least-squares plane defined by O(1), C(9), C(8) and C(10) and is situated on the same side of this plane as C(12) (Table 3). The bond lengths and angles in the ring substituents are similar to the usual values.

The most important torsion angles are given in Table 4.

Molecular conformation

The conformation of the molecule is characterized by the valency angles (Table 2) and the torsional angles of the individual bonds, which are given in Table 4. The dihedral angles between the mean planes of the phenylimidazolidine rings and the glucofurano-imidazolidine rings are 72 and 108° respectively. These angles defined by various authors for the sequence of atoms C(2)–C(1)–N(1)–C(7) and N(1)–C(9)–C(8)–O(1) are 65° and 59°.

Molecular packing

Fig. 1 shows the arrangement of the molecules in the unit cell along [100]. The molecular packing is clearly dominated by the formation of hydrogen bonds. Details of molecular interactions are given in Table 5, which contains the intermolecular contacts less than the sum of the van der Waals radii. The structure consists of two chains of molecules which lie parallel to the *b* axis. These molecules, related by a twofold screw axis, are linked by hydrogen bonds to form a helicoidal packing arrangement. Each molecule is involved in a strong O···O contact of 2·66 Å between O(2) and O(4) of the nearest neighbour molecule. There is an O···O contact of 2·72 Å between O(3) and O(2), an N···O of 3·01 Å between N(2) and O(3), and two C···O of 2·95 and 3·09 Å corresponding to C(8)···C(3) and C(3)···C(11) contacts between the two nearest neighbour molecules. In addition there is an intramolecular contact O(4)···O(3) of 2·71 Å, which might also be a hydrogen bond.

Table 5. *Interatomic contacts less than the van der Waals radii (distances in* Å; *standard deviation* 0·006 Å)

Br·····S	$(-\frac{1}{2}+x,\frac{1}{2}-y,z)$	3·728
S·····O(4)	$(x,-1+y,z)$	3·127
O(2)···O(3)	$(-1+x,y,z)$	2·719
O(2)···O(4)	$(1-x,-\frac{1}{2}+y,\frac{1}{2}-z)$	2·658
O(3)···O(4)	(x,y,z)	2·810
O(3)···N(2)	$(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$	3·012
O(3)···C(8)	$(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$	2·946
O(3)···C(11)	$(1-x,\frac{1}{2}+y,\frac{1}{2}-z)$	3·088
S·····C(9)	$(1+x,y,z)$	3·682

The S···Br distance of 3·73 Å is shorter than the sum of the van der Waals radii, 3·80 Å (Pauling, 1960), and may be interpreted as a weak S···Br interaction.

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References

AMMON, H. L. & WHEELER, G. L. (1974). *Acta Cryst.* B**30**, 1146–1154.

AUPERS, J., CARLISLE, C. H. & LINDLEY, P. F. (1974). *Acta Cryst.* B**30**, 1228–1233.

BERMAN, H. M., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.

BERTHOU, J., JÉMINET, G. & LAURENT, A. (1972). *Acta Cryst.* B**28**, 2480–2485.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

CAMERMAN, A. & CAMERMAN, N. (1974). *Acta Cryst.* B**30**, 1832–1840.

COETZER, J., JORDAAN, A., LOURENS, G. J. & NOLTE, M. J. (1972). *Acta Cryst.* B**28**, 3538–3542.

CONDE, A., MORENO, E. & MÁRQUEZ, R. (1975). *Acta Cryst.* B**31**, 648–652.

DIAS, H. W. & TRUTER, M. R. (1974). *Acta Cryst.* B**28**, 937–943.

FANFANI, F., NUNZI, A., ZANAZZI, P. F. & ZANZARI, A. R. (1974). *Acta Cryst.* B**30**, 273–281.

FERNÁNDEZ-BOLAÑOS, J., GARCÍA-GONZÁLEZ, F., GASCH, J. & MENÉNDEZ, M. (1963). *Tetrahedron*, **19**, 1883–1892.

FRITZ, H. C. J. & WACKER, O. (1968). *Helv. Chim. Acta*, **51**, 569–576.

GARCÍA-GONZÁLEZ, F., FERNÁNDEZ-BOLAÑOS, J. & PRADERA, M. A. (1976). *An. Real Soc. Esp. Fís. Quím.* In the press.

HOGE, R. & NORDMAN, C. E. (1974). *Acta Cryst.* B**30**, 1435–1440.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JIMÉNEZ-GARAY, R., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1974). *Acta Cryst.* B**30**, 1801–1805.

KOBAYASHI, A., MARUMO, F. & SAITO, Y. (1974). *Acta Cryst.* B**30**, 1495–1498.

KRÜGER, F. & RUDY, H. (1963). *Liebigs Ann.* **669**, 146–153.

LARSEN, I. K. (1972). *Acta Cryst.* B**28**, 1136–1151.

MOREL, C. J. (1961). *Helv. Chim. Acta*, **44**, 403–412.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd. ed., p. 260. Ithaca: Cornell Univ. Press.

PÉREZ-GARRIDO, S., CONDE, A. & MÁRQUEZ, R. (1974). *Acta Cryst.* B**30**, 2348–2352.

PÉREZ-GARRIDO, S., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1973). *An. Físi.* **69**, 179–188.

RAHMAN, A. & WILSON, H. R. (1972). *Acta Cryst.* B**28**, 2260–2270.

VALLE, G., COJAZZI, G., BUSETTI, V. & MAMMI, M. (1960). *Acta Cryst.* B**26**, 468–477.