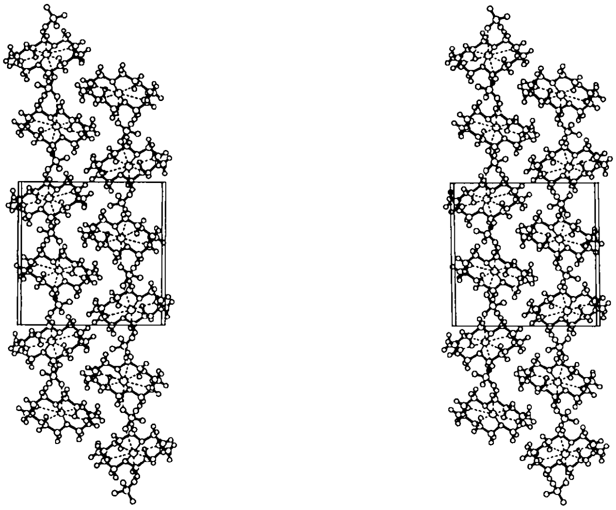

Fig. 2. Packing diagram of the title complex, viewed down the *a* axis (*SCHAKAL* representation, Keller, 1980).

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References

Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* **B35**, 2331–2338.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 1–19.

Barnes, J. C. & Collard, J. (1988). *Acta Cryst.* **C44**, 565–566.

Birchall, T. & Vetrone, J. A. (1988). *J. Chem. Soc. Chem. Commun.* pp. 877–879.

Buschmann, J., Müller, E. & Luger, P. (1986*a*). *Acta Cryst.* **C42**, 873–876.

Buschmann, J., Müller, E. & Luger, P. (1986*b*). *Acta Cryst.* **C42**, 1274.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Dunitz, J. D., Dobler, M., Seiler, P. & Phizackerley, R. P. (1974). *Acta Cryst.* **B30**, 2733–2738.

Dunitz, J. D. & Seiler, P. (1974). *Acta Cryst.* **B30**, 2339–2341.

Eerden, J. van, Harkema, C. & Feil, D. (1990). *Acta Cryst.* **B46**, 222–229.

Fan, Y., Xu, H., Zhou, Zh. & Yu, K. (1988). *J. Struct. Chem.* **7**, 196.

Goldberg, I. (1975). *Acta Cryst.* **B31**, 754–762.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Jeffrey, G. A., Pople, J. A., Binkley, J. S. & Vishweshwara, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Keller, E. (1980). *Chem. Unserer Zeit*, **14**, 56–60.

Luger, P., Denner, L., Cerny, M., Jindrich, J. & Trnka, T. (1991). *Acta Cryst.* **C47**, 66–70.

Maverick, E., Seiler, P., Schweizer, W. B. & Dunitz, J. D. (1980). *Acta Cryst.* **B36**, 615–620.

Patz, M. (1990). Dipolmarbeit, Univ. Hamburg, Germany.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Sheldrick, G. M. (1985). *SHELX*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Sheldrick, G. M. (1986). *SHELX*86. Program for crystal structure determination. Univ. of Göttingen, Germany.

Shoham, G., Lipscomb, W. N. & Olsher, U. (1983). *J. Chem. Soc. Chem. Commun.* pp. 208–209.

Stewart, J. M. & Hall, S. R. (1987). Editors. *The XTAL System of Crystallographic Programs.* Tech. Rep. TR-1364.2. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zobel, D., Dreissig, W. & Luger, P. (1990). *Acta Cryst.* **A46**, C-30.

Zobel, D. & Luger, P. (1990). *J. Appl. Cryst.* **23**, 175–179.

Zobel, D., Luger, P. & Dreissig, W. (1991). *Z. Kristallogr.* **194**, 297.

Acta Cryst. (1992). **B48**, 37–41

Structure of Liquid Benzyl Alcohol at 293 K

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Abstract

The experimental intermolecular function of the electron density distribution was determined by X-ray scattering from a liquid sample and compared with the corresponding theoretical functions calculated for the most probable assumed models of the alcohol structure. The best fitting theoretical curve for the intermolecular distribution function was assumed. The model describes the nearest surroundings of an alcohol molecule and determines the mutual arrangement of the planes of the benzene rings. It only

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allows for the presence of dimer associates of benzyl alcohol with a distance of 2.86 Å between the hydroxyl groups.

Introduction

The molecular structure of benzyl alcohol has been the subject of many studies by different methods, chiefly IR and NMR spectroscopy and electron diffraction. The studies were started by Fox & Martin (1937) and continued by Schleyer, Trifan & Bacskai (1958), Ōki & Iwamura (1959), Abraham & Bakke (1978), Traetteberg, Ostensen & Seip (1980), Ito & Hirota (1981), Visser & Van der Maas (1986), and Schaefer, Sebastian, Peeling, Penner & Koh (1989). Independently of the applied methods, a number of models have been proposed, corresponding to conformers differing in the assumed position of the H atom of the hydroxyl group and the position of the latter relative to the benzene ring. There are conformers with the torsion angle around the C_{ar}—C bond equal to $\varphi = 0°$ (Ito & Hirota, 1981; Visser & Van der Maas, 1986), $\varphi = 42.9°$ (Schaefer *et al.*, 1989), $\varphi = 54°$ (Traetteberg *et al.*, 1980) and $\varphi = 60°$ (Abraham & Bakke, 1978; Visser & Van der Maas, 1986). Furthermore, Abraham & Bakke (1978) recognized the presence of conformers with a free rotation around the C_{ar}—C bond.

This paper reports the results of an X-ray investigation of liquid benzyl alcohol which, in contrast to the previous spectroscopic studies, was used in the form of a pure liquid. Information was obtained from the analysis of the diffraction pattern of the alcohol along with model interpretations.

Experimental

The alcohol under investigation was placed in a flat thermostated cuvette closed by mica windows of thickness 0.025 ± 0.001 mm. The distance between the mica windows was 1.00 ± 0.01 mm and the temperature was maintained at 293.0 ± 0.2 K. The sample was obtained by recrystallization of analytically pure benzyl alcohol. The intensity of the scattered Mo *Kα* X-radiation, $\lambda = 0.7107$ Å, was measured after it had passed through the sample, between $s_o = (4\pi/\lambda)\sin\theta_o = 0.300$ Å^{-1} and $s_m = 11.831$ Å^{-1}. There was a planar crystalline monochromator in the path of the X-rays between the source of the radiation and the sample. The scattered X-radiation was normalized to electron units according to the Norman (1957) method. Before normalization of the intensity curve, corrections for absorption, polarization and Compton scattering were applied. The experimental results were interpreted by the pair-function method (Warren, 1969) which is described in detail in earlier works (Mikusińska-Planner, 1977, 1983*a*).

Experimental results

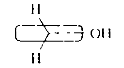
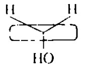
The experimental curve $i(s) = [I_{eu}(s)/N - \sum_{uc} f_j^2]/g^2(s)$ (g is a sharpening factor) marked in Fig. 1 by the solid line, is a structurally sensitive part of the total experimental coherent intensity $I_{eu}(s)/N$ per molecule, and represents the so-called total function of structure because it involves both intra- and intermolecular scattering effects. In order to separate the intermolecular effects from the $i(s)$ curve, the molecular function of structure was calculated from the Debye (1941) formula:

$$i_m(s) = \textstyle\sum_i \sum_{j \neq i} f_i f_j \exp(-l^2 s^2/2) \sin(sR_{ij}) [\sum_i f_i(s)]^{-2},$$

which describes the scattering by a single molecule. Molecular parameters R_{ij} and the coefficients l (l is the root-mean-square variation in the distance R_{ij} between pairs of atoms or appropriate atomic groups) (Table 1) have been fitted by a testing method (Narten, 1979) assuming that $i(s) \simeq i_m(s)$ for high values of s. The procedure of fitting $i_m(s)$ to the experimental curve $i(s)$ for $s \geq 5$ Å^{-1} was carried out for the two most probable models of the benzyl alcohol molecule which differ in the position of the hydroxyl group. In the first model the hydroxyl group lies in the benzene-ring plane while in the second model it comes out of the plane and takes a symmetric position with respect to the benzene ring. As the $i_m(s)$ function calculated for the first model (Table 1; curve 1 in Fig. 1) is a much better approximation of the experimental $i(s)$ curve (for high values of s; curve '*a*' in Fig. 1), curve 2 in Fig. 1, obtained for the second model, is henceforth disregarded. Fig. 1 also includes the so-called distinct structure function $i_d(s) = i(s) - i_m(s)$, the dotted line *b*, which provides the information about intermolecular correlations and is not affected by high-angle scattering. The application of Fourier transforms (Wasser & Schomaker, 1953; Konnert & Karle, 1973) to the experimental curve $i(s)$ and the curve $i_d(s)$ gave the total and intermolecular functions of electron density distribution denoted by crosses in Figs. 2(*a*) and 2(*b*), respectively. The distribution functions were interpreted by the Warren (1969) method by comparing them with their calculated correspondents.

The calculated functions of distribution for the assumed model of the molecule (Table 1, model 1) are presented in Fig. 2(*a*) by the solid and broken lines. The lines correspond to the simplified model of the molecule in which the CH, CH_2 and OH groups are treated as individual scattering units (Narten, 1979) and to the non-simplified model in which the atoms H, C and O are treated as being separate. Both functions calculated for intramolecular interactions are created by the summation of partial functions $P_{ij}(R)$ (Warren, 1969) for the number of interacting pairs of structural units N_{ij} at a distance

Table 1. *Intramolecular distances between atomic groups in benzyl alcohol and coefficients l*

	Model 1 			Model 2 		
Bond	Number of bonds	Bond length (Å)	l (Å)	Number of bonds	Bond length (Å)	l (Å)
CH—C	2	1.39	0.05	2	1.39	0.05
	2	2.40	0.08	2	2.40	0.08
	1	2.78	0.08	1	2.78	0.08
CH—CH	4	1.39	0.05	4	1.39	0.05
	4	2.40	0.08	4	2.40	0.08
	2	2.78	0.08	2	2.78	0.08
CH—CH_2	2	2.50	0.08	2	2.50	0.08
	2	3.77	0.12	2	3.77	0.12
	1	4.28	0.15	1	4.28	0.15
C—CH_2	1	1.50	0.05	1	1.50	0.05
C—OH	1	2.52	0.08	1	2.52	0.08
CH_2—OH	1	1.42	0.05	1	1.42	0.05
CH—OH	1	2.90	0.12	2	3.37	0.12
	1	3.79	0.15	2	4.62	0.15
	1	4.29	0.15	1	5.14	0.15
	1	4.93	0.15			
	1	5.14	0.15			

R_{ij}. As follows from a comparison between the experimental and calculated curves (Fig. 2*a*), the broken curve fits closely to the experimental curve only for the shortest distances in the molecule, *i.e.* for distances $1 < R < 2$ Å. For distances $R \geq 2$ Å we expect to get a better fit for the curves calculated for the simplified model. It is very likely that intermolecular interactions calculated for this model describe intermolecular interactions in the real liquid (Mikusińska-Planner, 1983*b*), since for longer R distances, X-radiation 'sees' the scattering structural units OH, CH and CH_2 better than individual H atoms.

Interpretation of results

The first maximum of the intermolecular distribution function for $2.5 < R < 3$ Å (Fig. 2*b*) was ascribed to the specific bond responsible for associates forming. Using a trial method, the theoretically calculated intermolecular distribution functions were fitted to the experimental curve marked by crosses in Fig. 2(*b*). The function drawn in a bold solid line is the best approximation of the experimental run (crosses). The bold line (Fig. 2*b*) is a sum of partial-pair functions for the interactions listed in Table 2, following from the proposed model presented in Fig. 3. Intermolecular interactions between individual pairs of atoms are represented in Fig. 4 by discrete maxima of pair functions (thin lines).

Fig. 3 shows that the central molecule is a molecule *A* which is linked with molecule *B* through a specific bond of length $R_{OH\cdots O} = 2.86$ Å. According to the accepted molecular model, molecules *A* and *B* are coplanar with molecule *C* and their C(6)—C(7) bonds are parallel to each other. The other molecules which also enter into the nearest neighbourhood of the central molecule *A* take four configurations depicted as *b*, c_1, c_2 and *d* (see Fig. 4). All the planes of the benzene rings of molecules in conformations *b*, c_1, c_2 and *d* are perpendicular to the benzene ring of the central molecule *A*.

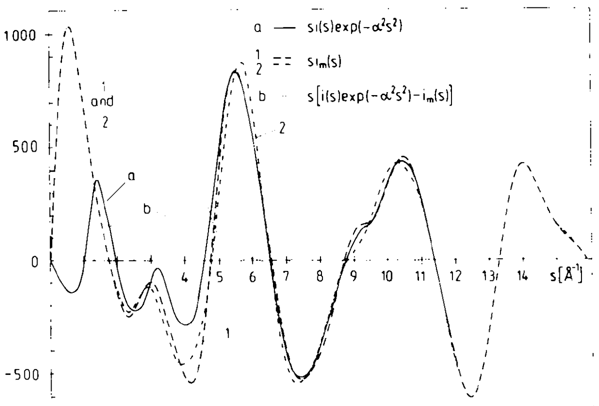


Fig. 1. Curve *a* (continuous line) is the experimental structure function $si(s)\exp(-\alpha^2s^2)$, where $\exp(-\alpha^2s^2)$ is the convergence factor. Curve *b* (dotted line) is the distinct structure function obtained by subtracting curve 1 from curve *a*. 1 and 2 (broken lines) are theoretical molecular functions of the structure calculated for models 1 and 2.

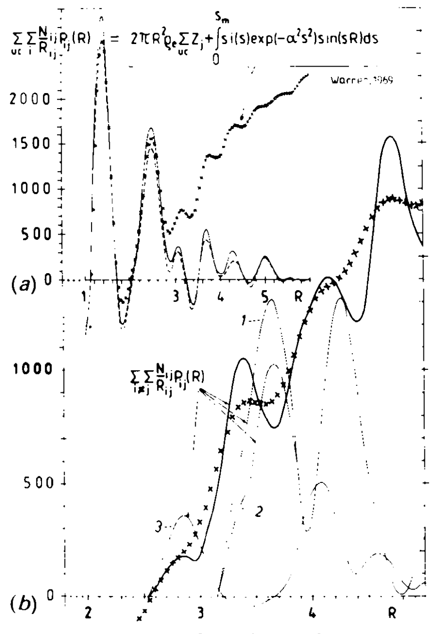


Fig. 2. Experimental curves of (*a*) the total (crosses) and (*b*) the intermolecular (crosses) functions of electron density distribution. Solid and broken lines in (*a*) are the intramolecular distribution functions calculated for simplified and non-simplified intramolecular interactions. The bold solid line in (*b*) is the intermolecular distribution function calculated for the model from Fig. 3. Lines 1, 2 and 3 in (*b*) are calculated curves for the parallel and antiparallel orientations of benzene rings and trimer.

Table 2. *Types of intermolecular interactions and values of* $\sum_{uc}\sum_i N_{ij}/R_{ij}$ *for the proposed model shown in Fig.* 3

Type of interaction with central molecule	$\Sigma\Sigma N_{ij}/R_{ij}$ Configurations				
A (Fig. 3)	*a*	*b*	c_1, c_2^*	*d*	*e*
OH—OH	1/2.86	1/4.20	1/4.80		
OH—CH$_2$	2/3.28	1/3.28	1/4.70*		
		1/4.15	1/5.78*		
		1/4.72			
OH—CH	4/5.62	1/3.50	2/3.44*	2/3.25	
		1/4.70	1/3.98*	2/4.10	
		1/4.75	2/4.60*	1/4.20	
			1/5.70*	1/4.72	
				1/4.78	
				1/5.20	
OH···C	2/4.80	1/3.80	1/3.98*	1/4.72	
		1/5.12			
CH$_2$—CH$_2$	1/4.17	1/3.50	1/5.60*		
		1/4.60	1/5.64*		
CH$_2$—CH		1/4.00	2/4.63*	1/3.90	
		1/4.85	1/4.95*	1/4.20	
		1/5.06	1/5.00*	2/4.32	
		1/5.95	2/5.38*	2/4.82	
				1/5.15	
				1/5.30	
CH$_2$—C	2/5.60	1/4.28	1/5.00*	1/5.30	
	2/5.63	1/4.72	1/5.70*		
		1/5.20			
CH—CH		1/4.88	2/3.93*	1/3.50	1/4.00
		1/5.28	1/4.25*	1/3.70	2/4.20
			2/4.40*	2/3.73	1/4.75
			2/4.48*	2/3.80	2/5.25
			1/4.95*	2/4.28	2/5.30
			2/5.12*	2/4.70	2/5.60
			2/5.50*		
CH—C		1/4.90	1/4.25*	1/3.50	
		1/5.06	1/4.95*	1/3.70	
		1/5.48	1/5.10*	2/4.62	
		1/5.65	2/5.12*	2/4.70	
				1/4.82	
C—C		1/5.22	1/5.10*	1/4.82	
		1/5.95			

In the proposed model, Fig. 3, neither parallel nor antiparallel arrangements of benzene rings in neighbouring molecules or in molecules piled over one another were found. The intermolecular distribution functions calculated for such configurations are characterized by high maxima at about 3.65 Å (Fig. 2*b*, curves 1 and 2). The occurrence of such maxima has not been confirmed by the experimental curve (Fig. 3, crosses). Also, assuming associations of an order higher than two we do not get an agreement with the experimental curve as the maximum at $R_{OH\cdots O} = 2.86$ Å is too high (Fig. 2*b*, curve 3). As follows from Fig. 2(*b*), the character of the intermolecular distribution functions (the bold solid line and crosses) is the same and the positions of their maxima correspond to one another. The maxima of the calculated curve (bold solid line) oscillating about the smoother experimental curve (crosses) are sharper. The character of the theoretical curve is a consequence of the rigid character of the assumed theoretical model. A comparison between the theoretical and experimental curves (Fig. 2*b*) has been carried out for distances up to $R = 5$ Å because for greater distances the course of the curves is quantitatively inconsistent. This is, however, a consequence of the fact that it is impossible to take into account the interactions of the model atoms with the atoms of the external environment. The random error of the radial distribution function has been estimated according to the Konnert & Karle (1973) method and does not exceed 4%.

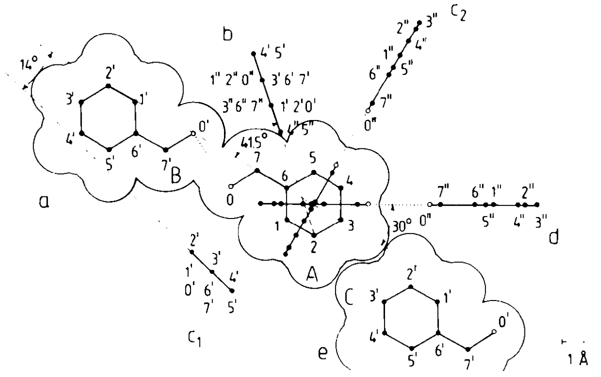


Fig. 3. A model of the intermolecular structure in benzyl alcohol. *a*, *b*, c_1, c_2, *d* and *e* are the particular configurations made by molecules in the nearest neighbourhood of the central molecule *A*. The planes of the molecules of configurations *b*, c_1, c_2 and *d* are perpendicular to the plane of the figure. Dotted lines show specific bonds of the associate.

Discussion

As follows from the results of this paper, liquid benzyl alcohol undergoes dissociation in which the alcohol molecules combine into dimers of an open

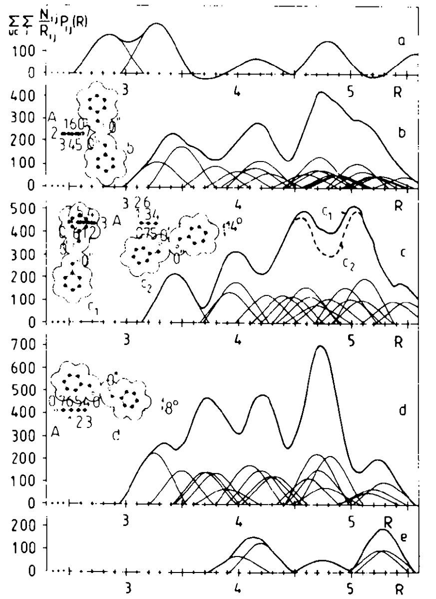


Fig. 4. A set of pair functions calculated for individual configurations of molecules: *a*, *b*, c_1, c_2, *d* and *e* from Fig. 3. Thin solid lines are discrete maxima of the calculated pair functions for the individual intermolecular interactions specified in Table 2.

configuration. The mean shortest intermolecular interaction distance was ascribed to the interaction OH···O and was estimated to be 2.86 Å. According to Fig. 3, the hydroxyl groups and benzene rings of the associated molecules lie in the same plane. The molecules which do not belong to the same associates lie in mutually perpendicular planes. It should be remembered, however, that the assumed arrangement is an averaging as the real structure of the liquid can be described by giving statistical means for the positions about which atoms and molecules oscillate. Molecules and atoms can also locally exchange their positions. Owing to the poor stability of the dimers (Staveley & Taylor, 1956) and the low energy of their bonding (Bellamy & Pace, 1966), the dimers break up in time and recombine. The rearrangement of the molecules is faster, whilst the intermolecular bond is weaker. The molecules forming associates at the moment of combination have the most energetically favourable arrangement (Taylor & Kennard, 1982); they lie symmetrically in the same plane. Formation of temporary chain associates cannot be excluded although the assumed model does not predict the formation of associates of an order higher than dimers. Schaefer *et al.* (1989) suggest the presence of trimers of benzyl alcohol studied as a solution with CS_2 at a concentration of 2.5 mol%. The studies of hydroxyl protons in a dilute solution led the same authors to conclude that associates of an order higher than two are more likely to occur in low concentrations. This does not exclude the fact that in the crystalline state benzyl alcohol can form long-chain associates as in 4-chlorobenzyl alcohol (Hashimoto, Nakamura & Hamada, 1988). As follows from Fig. 3, a molecule of benzyl alcohol has the structure of the so-called planar conformer ($\varphi = 0°$), in contradiction to the earlier studies referred to in the *Introduction*. The privileged position of the hydroxyl group in the plane of the benzene ring has also been reported by Pope, Dubro, Doane & Westerman (1986). The structure of the planar conformer for which the torsion angle around the C_{ar}—C bond is 0° has also been assumed by Ito & Hirota (1981) and Hehre, Radom & Pople (1971), as well as by Visser & Van der Maas (1986). The controversy over the determination of this angle is most probably due to the fact that the conformer structure depends on the actual intermolecular interactions, which may change under the specific experimental conditions required by the method of investigation employed. However, it is resonable to assume that in pure alcohol the intramolecular interactions OH···π of energy 2.0 ± 0.6 kJ mol^{-1} (Lutskii, Granzham, Shuster & Zaitser, 1969) do not occur because of the presence of much stronger OH···O intermolecular interactions. The former may be realized as an intermolecular interaction between the hydroxyl group of one molecule and π electrons of the benzene ring of another molecule. Such an interaction may be favoured by the perpendicular arrangement of the benzene rings of molecules which do not belong to the same associates.

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References

ABRAHAM, R. J. & BAKKE, J. M. (1978). *Tetrahedron*, **34**, 2947–2951.

BELLAMY, L. J. & PACE, R. J. (1966). *Spectrochim. Acta*, **22**, 525–534.

DEBYE, P. (1941). *J. Chem. Phys.* **9**, 55–60.

FOX, J. J. & MARTIN, A. E. (1937). *Proc. R. Soc. London*, **162**, 419–424.

HASHIMOTO, M., NAKAMURA, Y. & HAMADA, K. (1988). *Acta Cryst.* C**44**, 482–484.

HEHRE, W. J., RADOM, L. & POPLE, J. A. (1971). *J. Am. Chem. Soc.* **94**, 1496–1499.

ITO, M. & HIROTA, M. (1981). *Bull. Chem. Soc. Jpn*, **54**, 2093–2098.

KONNERT, J. H. & KARLE, J. (1973). *Acta Cryst.* A**29**, 702–710.

LUTSKII, A. E., GRANZHAM, V. A., SHUSTER, Y. A. & ZAITSER, P. M. (1969). *Zh. Prikl. Spectrosk.* **11**, 913–919.

MIKUSIŃSKA-PLANNER, A. (1977). *Acta Cryst.* A**33**, 433–437.

MIKUSIŃSKA-PLANNER, A. (1983*a*). *Acta Cryst.* B**39**, 394–399.

MIKUSIŃSKA-PLANNER, A. (1983*b*). *Acta Phys. Pol.* A**64**, 461–470.

NARTEN, A. H. (1979). *J. Chem. Phys.* **70**, 299–304.

NORMAN, H. (1957). *Acta Cryst.* **10**, 370–373.

ŌKI, M. & IWAMURA, H. (1959). *Bull. Chem. Soc. Jpn*, **32**, 950–955.

POPE, J. M., DUBRO, D., DOANE, J. W. & WESTERMAN, P. W. (1986). *J. Am. Chem. Soc.* **108**, 5426–5433.

SCHAEFER, T., SEBASTIAN, R., PEELING, J., PENNER, G. H. & KOH, K. (1989). *Can. J. Chem.* **67**, 1015–1021.

SCHLEYER, P. VON R., TRIFAN, D. S. & BACSKAI, R. (1958). *J. Am. Chem. Soc.* **80**, 6691–6692.

STAVELEY, L. A. K. & TAYLOR, P. F. (1956). *J. Chem. Soc.* **1**, 200–209.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

TRAETTEBERG, M., OSTENSEN, H. & SEIP, R. (1980). *Acta Chem. Scand. Ser. A*, **34**, 449–454.

VISSER, T. & VAN DER MAAS, J. H. (1986). *Spectrochim. Acta Part A*, **42**, 599–602.

WARREN, B. E. (1969). *X-ray Diffraction*. Reading, Massachusetts: Addison-Wesley.

WASSER, J. & SCHOMAKER, V. (1953). *Rev. Mod. Phys.* **25**(3), 671–690.