Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Mingos, D. M. P. (1977). *J. Chem. Soc. Dalton Trans.* **6**, 602–610.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Willemse, J., Cras, J. A., Steggerda, J. J. & Keijzers, C. P. (1976). *Struct. Bonding*, **28**, 83–126.
Wing, R. M. (1967). *J. Am. Chem. Soc.* **89**, 5599–5604.
Wing, R. M. (1968). *J. Am. Chem. Soc.* **90**, 4828–4834.
Zalkin, A., Hopkins, T. E. & Templeton, O. H. (1966). *Inorg. Chem.* **5**, 7, 1189–1193.

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Refinement of Aluminium Orthoborate

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Abstract. $AlBO_3$, high-pressure phase, calcite-like structure, trigonal, $R\bar{3}c$, $a = 4{\cdot}4638\ (3)$, $c = 13{\cdot}745\ (1)$ Å, $Z = 6$, $D_x = 3{\cdot}60$ g cm^{-3}, $\mu_{\text{Mo}} = 8{\cdot}66$ cm^{-1}. The B–O bond length is 1·3796 (4) Å. The six crystallographically equivalent Al–O distances are 1·9230 (4) Å. The oxygen arrangement is closer to hexagonal close packing than in the isostructural $NaNO_3$ and $CaCO_3$.

Introduction. The growth of $AlBO_3$ single crystals was achieved under hydrothermal conditions at high pressure. Details of this synthesis have been published by Capponi (1973), whom we thank for providing the crystals. The crystal selected was a rhombohedron whose edge measured about 0·2 mm. Intensities for 1504 reflections were measured within a hemisphere, up to $\theta = 50°$ with monochromated Mo $K\alpha$ radiation. The moduli of 288 averaged independent reflections were used in the refinement. Of these, 278 were significant and 10 were considered as unobserved by the criterion $I \le 3\sigma(I)$.

The scattering factors were from *International Tables for X-ray Crystallography* (1974) for Al, Al^{3+}, O, O^- and B. Most of the calculations were made with the XRAY system (Stewart, Kundell & Baldwin, 1970).

Least-squares refinement on F was started from the parameters reported by Abrahams, Bernstein & Keve (1971) for $LuBO_3$. The structure was refined assuming two models: the first with neutral atoms and the second

Table 1. *Final R values and atomic parameters with their standard deviations*

The U_{ij} ($\times 10^5$) conform to the expression $[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$. The symmetry requirements are: for B and Al, $U_{11} = U_{22} = 2U_{12}$, $U_{13} = U_{23} = 0$; for O, $U_{11} = U_{12} = 2U_{12}$, $U_{13} = \frac{1}{2}U_{23}$. Al and B occupy the special positions (0,0,0) and (0,0,$\frac{1}{4}$) respectively. O is located at (x,0,$\frac{1}{4}$).

	0–50° B, Al, O	0–50° B, Al^{3+}, O^-	0–30° B, Al, O	0–30° B, Al^{3+}, O^-	30–50° B, Al, O	30–50° B, Al^{3+}, O^-
R (%)	1·5	1·6	1·6	1·7	1·2	1·2
R_w (%)	1·6	1·8	1·6	1·6	1·2	1·2
x(O)	0·69093 (6)	0·69095 (6)	0·69096 (13)	0·69064 (13)	0·69098 (5)	0·69099 (5)
U_{33} (O)	420 (9)	427 (10)	352 (20)	404 (25)	449 (9)	458 (9)
U_{12} (O)	148 (3)	150 (4)	136 (8)	145 (9)	156 (4)	160 (4)
U_{13} (O)	−33 (2)	−33 (3)	−36 (7)	−39 (8)	−30 (2)	−30 (2)
U_{33} (Al)	318 (8)	313 (9)	262 (21)	266 (26)	332 (9)	333 (9)
U_{12} (Al)	145 (3)	143 (4)	135 (7)	148 (8)	153 (4)	154 (4)
U_{33} (B)	428 (17)	436 (18)	355 (60)	301 (63)	455 (16)	465 (16)
U_{12} (B)	163 (6)	165 (6)	167 (17)	216 (19)	168 (6)	173 (5)

with atoms B, Al^{3+}, O^{-}. These two models were tried in three refinements in the ranges $0° \leq \theta \leq 50°$, $0° \leq \theta \leq 30°$ and $30° \leq \theta \leq 50°$.

A final refinement was made in space group $R3c$ but no significant differences were observed in either the atomic parameters or the calculated interatomic distances and angles. The final R values were similar for both space groups. $R\bar{3}c$ was chosen on the basis that it gave a more even distribution in the ΔF synthesis.

The O positional coordinates and thermal parameters obtained in each refinement as well as the final R values are listed in Table 1. The weighting was applied by the program *PESOS* (Martínez-Ripoll & Cano, 1975), the weights being of the type $w = K/f^2(s)$ where $f(s)$ was selected so as to give no trends in $\langle w\Delta^2 \rangle$ when analysed against either F_o or $\sin \theta/\lambda$ (s) in the least-squares refinement.*

Discussion. The present investigation was undertaken to obtain an accurate value for the B–O bond length in a compound in which the aluminium allows one to obtain good precision in the determination of the x coordinate of the O atom.

An attempt was made to see if any differences arose in the thermal parameters when refinement was made in the range $30° \leq \theta \leq 50°$ in comparison with refinement at low angles (from 0 to 30°). As shown in Table 1, no significant difference was obtained. Corrections for absorption and TDS seem to be necessary to obtain more reliable thermal parameters. At low angles, very small values of U_{ij} were obtained when unit weights were applied to the reflections, but the values increased significantly when the *PESOS* program was applied. A similar increase in the thermal parameters was also observed when five reflections seriously affected by secondary extinction were corrected by the method of Stout & Jensen (1968).

The value calculated for the B–O bond length is 1·3796 (4) Å, which is in accordance with the value of 1·379 (3) Å obtained in $FeBO_3$ (Diehl, 1975) and with the predicted value of 1·38 Å (Shannon & Prewitt, 1969), but is significantly greater than the value 1·370 (3) Å obtained by Abrahams, Bernstein & Keve (1971) for $LuBO_3$. The six-oxygen octahedron surrounding the Al atom is distorted along the triad axis, giving rise to six crystallographically equivalent Al–O distances of 1·9230 (4) Å, the O–Al–O angle being 91·84 (3)°.

Table 2. *The ω tilt angle in some calcite-like compounds*

The ω angle is defined by the expression $\sin \omega = 3(X - \frac{1}{3})\cos \pi/6$, where X is the free oxygen parameter. For $LuBO_3$ and $AlBO_3$ a value of $X = 1 - X_0$ should be taken. X_0 is the reported value.

	X	ω (°)
$NaNO_3$	0·2402	−14·00
$CaCO_3$	0·2593	−11·09
$LuBO_3$	0·2789	−8·13
$FeBO_3$	0·2981	−5·25
$AlBO_3$	0·3090	−3·62
$NbLiO_3$	0·3802	6·99

Comparison with other calcite-like compounds such as $NaNO_3$ (Cherin, Hamilton & Post, 1967), $CaCO_3$ (Chessin, Hamilton & Post, 1965), $FeBO_3$ (Diehl, 1975), $LuBO_3$ (Abrahams, Bernstein & Keve, 1971) and the high-temperature $LiNbO_3$ (Megaw, 1968) shows that the ω tilt angle (Table 2), defined by Megaw (1970), comes closer to zero for borates than for $NaNO_3$ and $CaCO_3$, the smallest value of ω, −3·62°, corresponding to $AlBO_3$. So the arrangement of the O atoms, in $AlBO_3$, is very close to h.c.p. (in which $\omega = 0$). Of course, the nature of the anionic central atom (B in this work) is not the only cause of the low ω value, as can be seen from the differences in ω for the three borates.

As has been pointed out by Megaw (1970), the size of the XO_3 triangle is controlled by the need to provide the correct X–O distance. In this sense, one could think that there exists a decrease in the stability of the XO_3^{n-} anion in the order NO_3^{-}, CO_3^{2} , BO_3^{3} and LiO_3^{5} . In the case of borates, the orthoborate anion must support a negative formal charge of −3, becoming less stable than the nitrate and carbonate anions. This relative instability could be a reason for the marked tendency of borates to form infinite chains or three-dimensional anionic networks, where the formal charge is decreased and delocalized.

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References

Abrahams, S. C., Bernstein, J. L. & Keve, E. T. (1971). *J. Appl. Cryst.* **4**, 284–290.

Capponi, J. J. (1973). Thèse. Univ. de Grenoble. No. CNRS AO 9139.

Cherin, P., Hamilton, W. C. & Post, B. (1967). *Acta Cryst.* **23**, 455–460.

Chessin, H., Hamilton, W. C. & Post, B. (1965). *Acta Cryst.* **18**, 689–693.

Diehl, R. (1975). *Solid State Commun.* **17**, 743–745.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32866 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto Rocasolano, CSIC, Serrano 119, Madrid-6, Spain.

MEGAW, H. D. (1968). *Acta Cryst.* A**24**, 583–588.

MEGAW, H. D. (1970). *Acta Cryst.* A**26**, 235–244.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY system of crystallographic programs. Univ. of Maryland, College Park, Maryland.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.

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N,N'-(p-Phenylene)dibenzamide (PPDB)*

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Abstract. $C_{20}N_2O_2H_{16}$, monoclinic, $P2_1/c$, a = 18·065 (1), b = 5·247 (1), c = 8·027 (1) Å, β = 93·99 (1)°, Z = 2. The crystal structure has been refined by least-squares techniques. R_w = 7·3%. The structure contains planar phenyl rings which are rotated with respect to the plane of the amide group owing to steric hindrance. The molecules are connected in one dimension by means of hydrogen bonds.

Introduction. Aromatic and mixed aliphatic–aromatic polyamides form a class of polymers having thermal and mechanical properties which are quite different from those of aliphatic polyamides. These exceptional properties are thought to be due to the fact that aromatic polyamides have a very high degree of crystallinity (Northolt & Van Aartsen, 1973). In order to obtain more insight into the structures of the crystalline phase of the polyamides a number of model compounds have been synthesized (Gaymans & Harkema, 1977). The melting behaviour of these compounds has been reported. To obtain detailed

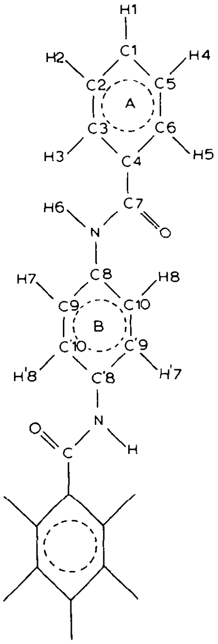

Fig. 1. Atomic arrangement of PPDB.

Table 1. *Atomic positional parameters*

	x	y	z		x	y	z
C(1)	0·5791 (2)	−0·0447 (7)	0·1849 (4)	O	0·8176 (1)	0·3738 (4)	0·0694 (4)
C(2)	0·6358 (2)	−0·2050 (6)	0·2442 (4)	N	0·8506 (1)	−0·0444 (5)	0·0728 (3)
C(3)	0·7093 (2)	−0·1457 (6)	0·2121 (4)	H(1)	0·5255 (22)	−0·1042 (69)	0·2067 (48)
C(4)	0·7244 (1)	0·0689 (5)	0·1225 (4)	H(2)	0·6256 (19)	−0·3618 (68)	0·3084 (45)
C(5)	0·5941 (2)	0·1684 (7)	0·0955 (5)	H(3)	0·7480 (16)	−0·2647 (65)	0·2581 (40)
C(6)	0·6670 (2)	0·2299 (6)	0·0653 (4)	H(4)	0·5551 (14)	0·2817 (70)	0·0488 (44)
C(7)	0·8020 (2)	0·1494 (5)	0·0876 (4)	H(5)	0·6793 (17)	0·3900 (66)	0·0025 (42)
C(8)	0·9265 (1)	−0·0145 (5)	0·0360 (3)	H(6)	0·8322 (19)	−0·1988 (75)	0·0645 (45)
C(9)	0·9566 (2)	−0·2011 (5)	−0·0608 (4)	H(7)	0·9263 (16)	−0·3420 (54)	−0·1097 (36)
C(10)	0·9690 (2)	0·1854 (6)	0·0976 (4)	H(8)	0·9510 (16)	0·3191 (59)	0·1690 (38)

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* The Crystal and Molecular Structure of Model Compounds of Aromatic and Aromatic–Aliphatic Polyamides. I.