Crystal Structure of Di-μ-phenyl-bis(diphenylaluminium) (Triphenylaluminium Dimer)

By **J. F. Malone** and **W. S. McDonald**, Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

Crystals of the title compound are triclinic, space group $P\bar{1}$, with one centrosymmetric dimer in the reduced cell of dimensions $a = 9{\cdot}565$, $b = 10{\cdot}813$, $c = 8{\cdot}328$ Å, $\alpha = 106{\cdot}2$, $\beta = 111{\cdot}8$, $\gamma = 102{\cdot}3°$. The structure was determined by Patterson methods from 1636 observed data, visually estimated from Weissenberg photographs, and refined by least-squares methods to R 9·1%. The Al · · · Al vector (2·702 Å) is almost normal (84·4°) to the planes of the bridging phenyl groups; Al–C distances are 2·182 (bridge) and 1·958 Å (terminal), and the Al–C–Al bridge angle is 76·5°.

THE dimeric structure of trimethylaluminium has recently been accurately redetermined both by low-temperature X-ray diffraction on the crystal[1] and by electron diffraction in the vapour phase.[2] The two-electron three-centre bond of the methyl group bridging two metal atoms occurs also in Me_8MgAl_2,[3] in Ph_2N,Me_5Al_2,[4] and in $LiBMe_4$.[5] The ethyl group forms a similar bridge in Et_2Mg (ref. 6) and in $LiAlEt_4$,[7] whilst bridging cyclopropyl groups have recently been demonstrated in (cyclo-$C_3H_5)_6Al_2$.[8] The present work, already reported in a preliminary note,[9] was undertaken to discover if the phenyl group also forms a three-centre bridge bond.

EXPERIMENTAL

Crystal Data.—$C_{36}H_{30}Al_2$, $M = 516{\cdot}6$, Triclinic, $a = 9{\cdot}565 \pm 0{\cdot}05$, $b = 10{\cdot}813 \pm 0{\cdot}05$, $c = 8{\cdot}328 \pm 0{\cdot}04$ Å, $\alpha = 106{\cdot}2 \pm 0{\cdot}3$, $\beta = 111{\cdot}8 \pm 0{\cdot}3$, $\gamma = 102{\cdot}3 \pm 0{\cdot}3°$, $U = 717{\cdot}9$ Å^3, $Z = 1$, $D_c = 1{\cdot}19$, $F(000) = 272$. Space group $P\bar{1}$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 11 cm^{-1}.

Structure Determination.—Cell dimensions were measured from zero-level precession and Weissenberg photographs (Cu-K_α), and the dimensions given describe the reduced cell according to the convention adopted in Crystal Data.[10] The crystals, which react with oxygen and moisture, were transferred under nitrogen and sealed in soft glass capillaries. Intensities were recorded on equi-inclination Weissenberg photographs of reciprocal lattice layers *hk*0–6, yielding 1636 visually estimated data: no absorption corrections were applied.

The structure was solved from a sharpened Patterson synthesis in which the Al · · · Al vector and the 36 Al · · · C vectors were all recognisable, giving a structure conforming to space group $P\bar{1}$. Least-squares refinement of co-ordinates, isotropic temperature factors, and seven layer scales gave R 14·7%. Allowance for anisotropic vibrations reduced R to 10·4%. As a result of attempting to refine anisotropic temperature factors and layer scales of data taken about a single axis the full matrix would have been singular since only the relative values of the U_{33} can be determined in this way.[11] In the block-diagonal approximation used here, with 9 × 9 blocks for each atom and an 8 × 8 block for the scale factors and dummy overall vibration parameter, satisfactory convergence was obtained, with U_{33} of Al remaining very close to its isotropic value. A difference-Fourier map computed at this stage showed peaks close to the positions expected for 14 of the 15 hydrogen atoms. The hydrogen atoms were included at calculated positions and refined with isotropic temperature factors. They refined satisfactorily, but the one which did not appear in the difference-Fourier map did not refine satisfactorily when included in its calculated position, and was taken out again. The final R was 9·1% with the weighting scheme $w = 1/(2{\cdot}5 + F_o + 0{\cdot}08F_o^2 + 0{\cdot}0016F_o^3)$. Scattering factors for aluminium and carbon were taken

---

[1] J. C. Huffman and W. E. Streib, *Chem. Comm.*, 1971, 911.

[2] A. Almenningen, S. Halvorsen, and A. Haaland, *Acta Chem. Scand.*, 1971, **25**, 1937.

[3] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, 1969, **91**, 2538.

[4] V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, 1969, **91**, 2544.

[5] D. Groves, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1971, **93**, 1553.

[6] E. Weiss, *J. Organometallic Chem.*, 1965, **4**, 101.

[7] R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, 1964, **3**, 872.

[8] J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1971, **93**, 1035.

[9] J. F. Malone and W. S. McDonald, *Chem. Comm.*, 1967, 444.

[10] 'Crystal Data Determinative Tables,' 2nd edn., eds. J. D. H. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, Amer. Cryst. Assoc., Washington, 1963.

[11] E. C. Lingafelter and J. Donohue, *Acta Cryst.*, 1966, **20**, 321.

TABLE 1

Final atomic parameters with estimated standard deviations in parentheses

(*a*) Fractional co-ordinates of the heavy atoms

Atom	*x*	*y*	*z*
Al	−0·0112(2)	0·1257(1)	0·0572(2)
C(1)	0·1588(6)	0·0672(5)	−0·0370(6)
C(2)	0·3220(6)	0·1099(5)	0·0981(7)
C(3)	0·4508(7)	0·1625(7)	0·0643(9)
C(4)	0·4263(8)	0·1758(7)	−0·1028(10)
C(5)	0·2674(8)	0·1377(6)	−0·2392(8)
C(6)	0·1399(6)	0·0839(6)	−0·2062(7)
C(7)	−0·1454(5)	0·1887(4)	−0·1214(6)
C(8)	−0·1435(6)	0·3233(5)	−0·0551(7)
C(9)	−0·2290(7)	0·3775(6)	−0·1742(9)
C(10)	−0·3227(7)	0·2955(7)	−0·3616(9)
C(11)	−0·3279(6)	0·1623(6)	−0·4306(7)
C(12)	−0·2436(6)	0·1103(5)	−0·3132(6)
C(13)	0·0986(6)	0·2551(5)	0·3208(6)
C(14)	0·0101(6)	0·2709(6)	0·4233(7)
C(15)	0·0776(8)	0·3682(6)	0·6024(9)
C(16)	0·2391(7)	0·4536(6)	0·6902(8)
C(17)	0·3290(7)	0·4394(6)	0·5947(8)
C(18)	0·2606(6)	0·3424(6)	0·4131(7)

(*b*) Anisotropic temperature factors (Å² × 10³) of the heavy atoms in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Al	39(1)	40(1)	24(1)	22(1)	14(1)	35(1)
C(1)	59(3)	47(2)	23(3)	27(4)	17(4)	51(5)
C(2)	40(3)	52(3)	55(3)	42(5)	20(4)	23(5)
C(3)	57(3)	75(4)	64(4)	54(5)	28(5)	36(6)
C(4)	60(4)	71(4)	88(5)	59(7)	77(7)	21(6)
C(5)	76(4)	70(4)	49(4)	54(6)	65(6)	50(6)
C(6)	58(3)	59(3)	44(3)	35(5)	46(5)	52(5)
C(7)	36(2)	44(2)	32(3)	33(4)	22(3)	27(4)
C(8)	47(3)	46(3)	52(3)	34(4)	38(4)	42(4)
C(9)	63(4)	55(3)	82(4)	73(6)	66(6)	66(6)
C(10)	57(3)	82(4)	74(4)	107(7)	48(6)	69(6)
C(11)	46(3)	75(4)	44(3)	56(5)	11(4)	34(5)
C(12)	49(3)	49(3)	33(3)	28(4)	13(4)	30(4)
C(13)	44(3)	45(2)	33(3)	23(4)	26(4)	35(4)
C(14)	50(3)	65(3)	44(3)	9(5)	41(5)	30(5)
C(15)	68(4)	75(4)	53(4)	11(6)	65(6)	26(6)
C(16)	67(4)	58(3)	41(3)	−2(5)	35(5)	18(6)
C(17)	54(3)	50(3)	58(4)	13(5)	40(5)	4(5)
C(18)	49(3)	56(3)	46(3)	20(4)	40(5)	16(5)

(*c*) Fractional co-ordinates and isotropic temperature factors Å²) in the form $\exp[-8\pi^2U_{\text{iso}}\sin^2\theta/\lambda^2]$ for the hydrogen atoms

Atom	*x*	*y*	*z*	U_{iso}
H(2)	0·355(8)	0·126(7)	0·251(9)	0·10(2)
H(3)	0·583(10)	0·213(8)	0·207(11)	0·13(3)
H(4)	0·526(10)	0·210(8)	−0·138(11)	0·13(3)
H(5)	0·247(10)	0·134(8)	−0·371(11)	0·12(2)
H(6)	0·004(9)	0·064(8)	−0·304(11)	0·13(3)
H(8)	−0·079(7)	0·391(6)	0·091(8)	0·07(2)
H(9)	−0·232(8)	0·470(6)	−0·116(9)	0·08(2)
H(10)	−0·380(12)	0·349(9)	−0·476(12)	0·15(3)
H(11)	−0·395(8)	0·106(7)	−0·571(9)	0·10(2)
H(12)	−0·239(8)	0·020(7)	−0·349(9)	0·09(2)
H(14)	−0·115 †	0·205 †	0·361 †	
H(15)	0·011(8)	0·365(6)	0·691(9)	0·09(2)
H(16)	0·299(14)	0·527(11)	0·846(16)	0·19(3)
H(17)	0·454(10)	0·498(9)	0·665(11)	0·14(3)
H(18)	0·329(8)	0·332(6)	0·345(9)	0·08(2)

† Calc. position.

from ref. 12, and for hydrogen the bonded hydrogen values of ref. 13 were used. The final co-ordinates and vibration parameters with their estimated standard deviations are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20532 (10 pp., 1 microfiche).*

DISCUSSION

The bond lengths and angles with their estimated standard deviations are given in Table 2. The molecular structure and atom numbering are given in Figure 1, and the molecular packing is indicated in Figure 2. The molecules are dimeric, with symmetrically bridging

TABLE 2

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Al–Al′	2·702(2)	C(1)–C(1′)	3·427(9)
Al–C(1)	2·184(5)	Al–C(1′)	2·180(5)
Al–C(7)	1·960(4)	Al–C(13)	1·956(5)
C(1)–C(2)	1·419(6)		
C(2)–C(3)	1·404(8)	C(2)–H(2)	1·14(6)
C(3)–C(4)	1·377(9)	C(3)–H(3)	1·24(7)
C(4)–C(5)	1·400(9)	C(4)–H(4)	1·12(8)
C(5)–C(6)	1·392(8)	C(5)–H(5)	1·03(6)
C(6)–C(1)	1·420(7)	C(6)–H(6)	1·18(8)
C(7)–C(8)	1·399(6)		
C(8)–C(9)	1·387(7)	C(8)–H(8)	1·07(5)
C(9)–C(10)	1·369(8)	C(9)–H(9)	1·00(5)
C(10)–C(11)	1·376(8)	C(10)–H(10)	1·26(9)
C(11)–C(12)	1·356(7)	C(11)–H(11)	1·01(6)
C(12)–C(7)	1·394(6)	C(12)–H(12)	0·95(6)
C(13)–C(14)	1·411(7)		
C(14)–C(15)	1·367(8)	C(14)–H(14)	———
C(15)–C(16)	1·397(8)	C(15)–H(15)	1·14(6)
C(16)–C(17)	1·375(8)	C(16)–H(16)	1·15(9)
C(17)–C(18)	1·379(7)	C(17)–H(17)	1·06(7)
C(18)–C(13)	1·404(7)	C(18)–H(18)	1·01(5)

(*b*) Angles

C(1)–Al–C(1′)	103·5(0·2)	Al–C(1)–Al′	76·5(0·2)
C(1)–Al–C(7)	108·4(0·2)	C(6)–C(1)–C(2)	113·7(0·4)
C(1)–Al–C(13)	111·5(0·2)	C(1)–C(2)–C(3)	122·3(0·5)
C(1′)–Al–C(7)	109·3(0·2)	C(2)–C(3)–C(4)	121·9(0·5)
C(1′)–Al–C(13)	108·1(0·2)	C(3)–C(4)–C(5)	118·0(0·6)
C(7)–Al–C(13)	115·4(0·2)	C(4)–C(5)–C(6)	120·0(0·5)
		C(5)–C(6)–C(1)	124·1(0·5)
C(12)–C(7)–C(8)	116·0(0·4)	C(18)–C(13)–C(14)	116·7(0·4)
C(7)–C(8)–C(9)	122·1(0·4)	C(13)–C(14)–C(15)	121·8(0·5)
C(8)–C(9)–C(10)	119·1(0·5)	C(14)–C(15)–C(16)	120·0(0·5)
C(9)–C(10)–C(11)	120·1(0·5)	C(15)–C(16)–C(17)	119·5(0·5)
C(10)–C(11)–C(12)	120·4(0·5)	C(16)–C(17)–C(18)	120·5(0·5)
C(11)–C(12)–C(7)	122·3(0·4)	C(17)–C(18)–C(13)	121·4(0·5)

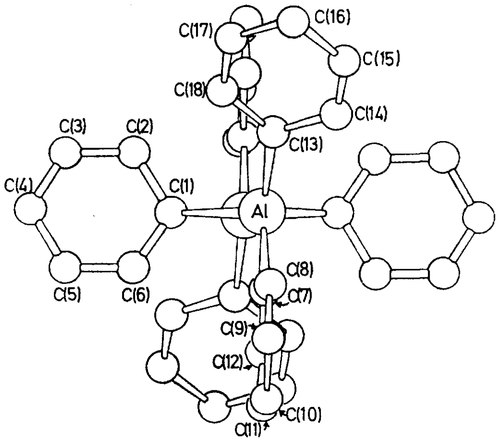

FIGURE 1 Molecular structure and atom numbering

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[12] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[13] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

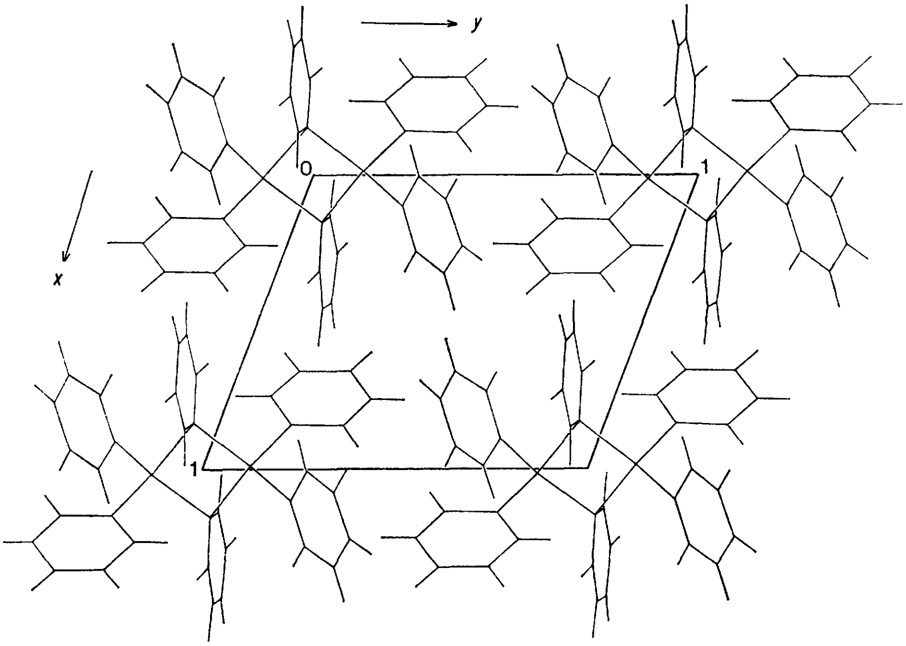

FIGURE 2 A projection of the unit cell down the c axis

phenyl groups, and (Figure 1) approximate to $2/m$ (C_{2h}) symmetry, with the two-fold axis passing through C(4), C(1), C(1′), and C(4′); the site-symmetry is $\bar{1}$ (C_i). The crystallographic symmetry requires the Al_2C_2 ring to be planar, and the mean planes of the bridging phenyl groups make an angle of 84·4° with that plane. On each aluminium atom one of the terminal phenyl groups [C(7)—(12)] is perpendicular to the central Al_2C_2 ring (dihedral angle 89·6°), whilst the other terminal ring is rotated almost 90° from that orientation. The dihedral angle between the two terminal rings is 81·8°, and would be 90° for precise $2/m$ molecular symmetry. The dihedral angles, equations of mean planes and displacements from the planes are listed in Table 3.

TABLE 3

(a) Equations of least-squares best planes referred to orthogonal axes X, Y, and Z, where X is parallel to a^* and Z is parallel to c. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (1):
Al(1), Al(1′), C(1), C(1′) $0{\cdot}6346X - 0{\cdot}0349Y + 0{\cdot}7720Z = 0$
[Al(1) 0, Al(1′) 0, C(1) 0, C(1′) 0]

Plane (2):
C(1)—(6) $0{\cdot}0069X + 0{\cdot}9863Y + 0{\cdot}1649Z = 0{\cdot}0295$
[C(1) −0·003, C(2) 0·005, C(3) 0·002, C(4) −0·009, C(5) 0·010, C(6) −0·004]

Plane (3):
C(7)—(12) $0{\cdot}7770X + 0{\cdot}0397Y - 0{\cdot}6282Z = -0{\cdot}1836$
[C(7) −0·010, C(8) 0·010, C(9) −0·007, C(10) 0·004, C(11) −0·005, C(12) 0·008]

Plane (4):
C(13)—(18) $0{\cdot}2698X + 0{\cdot}8166Y - 0{\cdot}5103Z = 0{\cdot}8913$
[C(13) 0·005, C(14) −0·007, C(15) 0·004, C(16) 0·002, C(17) −0·004, C(18) 0·001]

(b) Angles (°) between planes

(1)–(2)	84·4	(2)–(3)	93·4
(1)–(3)	89·6	(2)–(4)	44·0
(1)–(4)	126·4	(3)–(4)	81·8

The central ring has dimensions similar to those of hexamethyldialuminium. The greatest difference is an increase in the Al–Al distance from 2·606(2) in the methyl compound to 2·702(2) Å in Al_2Ph_6. The Al–C distances are also slightly increased, from 2·124(2) to 2·182(5) Å, although the sp^2 covalent radius is *ca.* 0·02 Å less than the sp^3 value. The bridge angle at carbon is also slightly increased. The bridging phenyl groups are considerably distorted from regular hexagons, the atom C(1) attached to aluminium being mainly involved. The angle C(6)–C(1)–C(2) is only 113·7 (0·4)°, whilst the two C–C(1) distances are 1·419(6) and 1·420(7) compared with the mean for the ring of 1·402 Å. In our preliminary communication [9] we attributed these distortions to the electron-deficient bonding. Although this factor may be partly responsible we have since found [14] similar distortions in other phenyl–metal compounds which do not have three-centre bridges. In the present compound the terminal phenyl groups show similar but smaller departures from regularity.

[2/1486 *Received, 26th June,* 1972]

---

[14] J. F. Malone and W. S. McDonald, *J. Chem. Soc.* (*A*), 1970, 3362.