Stereochemistry of Some Organic Derivatives of Group Vb Elements. Part IV.† Crystal and Molecular Structure of 1-Acetyl-2,3,4-triphenyl-5-(triphenylarsonio)cyclopentadienide

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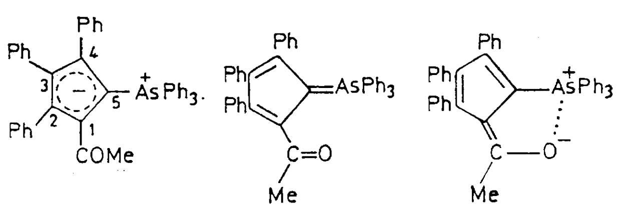
The crystal structure of the title compound has been determined from three-dimensional *X*-ray data. Crystals are orthorhombic, space group *Pbca*, with *Z* = 8 in a unit cell of dimensions: *a* = 15·353(2), *b* = 24·377(3), *c* = 17·361(2) Å. The structure has been refined by block-diagonal least-squares methods to *R* 0·042 for 2977 observed reflexions. Molecular dimensions establish that a dipolar form [$\overset{+}{As}\cdots\overset{-}{O}$ 2·770(3) Å] makes a significant contribution to the ground-state structure and results in distorted trigonal bipyramidal geometry about arsenic. Principal mean dimensions are: As–C(eq Ph) 1·923(5), As–C(ax Ph) 1·925(5), and As–C(C_5H_5) 1·881(4) Å. The contributions of three canonical forms to the ground-state structure are assessed.

ARSONIUM ylides [1] can be represented generally by such canonical forms as (I) $R_3As{:}C$, and (II) $R_3\overset{+}{As}\cdot\overset{-}{C}$. Thus in the case of 1-acetyl-2,3,4-triphenyl-5-(triphenylarsonio)cyclopentadienide [2] canonical forms (III) (which shows the systematic numbering) and (IV) must be considered. Neither of these forms is however consistent with the low value (1565 cm^{-1}) of the carbonyl stretching frequency in the i.r. spectrum, but the inclusion of a further canonical form, wherein the negative charge is sited on the oxygen atom rather than on the five-membered ring, would account for this value.[3] For such a canonical form there is the possibility of intramolecular association between oxygen and arsenic, as implied in formula (V). With the availability of good



(III) (IV) (V)

single crystals of the ylide we undertook a crystal-structure analysis which has now established that canonical form (V) does indeed make a significant contribution to the ground-state structure. A preliminary report of this work has appeared.[4]

EXPERIMENTAL

Crystal Data.—$C_{43}H_{33}AsO$, $M = 640·7$, Orthorhombic, $a = 15·353(2)$, $b = 24·377(3)$, $c = 17·361(2)$ Å, $U = 6498$ Å^3, $D_m = 1·30 \pm 1$, (by flotation), $Z = 8$, $D_c = 1·310$ Space group *Pbca* (D_{2h}^{15}, No. 61) from systematic absences: $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, $hk0$ when $h = 2n + 1$. Cu-K_α *X*-ray radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 18·0 cm^{-1}.

Crystals were golden-yellow octahedra, elongated along *a*. Space group and unit-cell parameters were determined from preliminary oscillation, Weissenberg, and precession photographs. Accurate unit-cell dimensions were obtained from a least-squares refinement of the setting angles of 12 reflexions measured on a Hilger and Watts Y 290 computer-controlled four-circle diffractometer. The crystal chosen for data collection was *ca.* 0·46 × 0·26 × 0·16 mm and intensity data were collected to $\theta_{max.}$ 57° on the diffractometer. The θ—2θ scan technique was used with a symmetric scan of 0·7° and a scan rate of 0·6° min^{-1}. Stationary-crystal–stationary–counter background counts of 17·5 s were measured at each end of the integrated scan. The intensities of the 3 standard reflexions, measured periodically, did not vary by >5%.

Intensity data were corrected for background and the estimated standard deviation for each intensity, $\sigma(I)$, was given by $\sigma(I) = [S + 4(b_1 + b_2) + (pI)^2]^{1/2}$ where S, b_1, and b_2 are the scan and background counts, and p is a factor introduced to avoid overweighting of the intense reflexions.[5] A value of 0·05 was chosen for p and subsequently proved adequate. Of 4053 independent reflexions measured, 2977 having $I > 3\sigma(I)$ were considered observed. Data were corrected for Lorentz and polarization factors, but not for absorption or extinction.

Structure Solution and Refinement.—The co-ordinates of the arsenic atom were determined by inspection of a three-dimensional Patterson synthesis. A Fourier synthesis phased on the arsenic-atom contributions alone revealed twenty-nine of the forty-five non-hydrogen atom positions and *R* at this stage was 0·456. A further Fourier synthesis phased with the contributions from the located atoms revealed the remaining non-hydrogen atoms; in the subsequent structure-factor calculation *R* fell to 0·22. Four cycles of refinement on *F* [with $\sigma(F) = 0·5\ \sigma(F^2)/F$] using the block-diagonal approximation to the full-matrix with individual isotropic thermal parameters then reduced *R* to 0·100. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, and the weights were derived from counting statistics. Corrections for the real and imaginary parts of anomalous dispersion due to the arsenic atom were incorporated during refinement which was then continued with individual anisotropic thermal parameters; four cycles reduced *R* to 0·059. A difference-Fourier synthesis was computed and the thirty-three hydrogen atoms were located, in positions agreeing well with those calculated assuming ideal geometry. Three cycles of block-diagonal least-

† Part III, G. Ferguson and E. W. Macaulay, *J. Chem. Soc.* (*A*), 1969, 1.

[1] A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, pp. 288—290; L. Horner and H. Oediger, *Chem. Ber.*, 1958, **91**, 437; *Annalen*, 1959, **627**, 142.

[2] G. S. Harris, D. Lloyd, N. W. Preston, and M. I. C. Singer, *Chem. and Ind.*, 1968, 1483; D. Lloyd and M. I. C. Singer, *J. Chem. Soc.* (*C*), 1971, 2941.

[3] D. Lloyd and M. I. C. Singer, *Tetrahedron*, 1972, **28**, 353.

[4] G. Ferguson, D. F. Rendle, D. Lloyd, and M. I. C. Singer, *Chem. Comm.*, 1971, 1647.

[5] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

squares refinement with the calculated positional and assigned thermal parameters (U_{iso} 0·063 Å^2) of the hydrogen atoms held constant reduced R to 0·044. Five low-order reflexions were excluded from the refinement as they were considered to suffer from secondary extinction. A final cycle of refinement reduced R to 0·042 at convergence and the largest shift in any parameter was $<0{\cdot}3\sigma$. The weighted residual R' [$= \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$] was 0·054.

In all structure-factor calculations atomic scattering factors were taken from ref. 6. Final observed and calculated structure factors, thermal parameters, and details of least-squares planes are listed in Supplementary Publication No. SUP 21304 (10 pp., 1 microfiche).* Final atomic coordinates with their estimated standard deviations are in Table 1.

TABLE 1

Final positional (fractional) parameters (As $\times$ 10^5, others $\times$ 10^4) with estimated standard deviations in parentheses; hydrogen atoms are numbered according to the carbon atom to which they are bonded

	x/a	y/b	z/c
As	54197(3)	18581(2)	34625(3)
O	4687(2)	1952(1)	4915(2)
C(1)	4712(3)	1239(2)	3624(2)
C(2)	4322(3)	1113(2)	4361(2)
C(3)	3932(3)	588(2)	4289(2)
C(4)	4073(3)	398(2)	3535(3)
C(5)	4545(3)	802(2)	3115(2)
C(6)	4306(3)	1505(2)	4981(3)
C(7)	3832(4)	1376(2)	5723(3)
C(11)	3433(3)	264(2)	4866(2)
C(12)	2540(3)	190(2)	4779(3)
C(13)	2083(3)	−147(3)	5281(3)
C(14)	2503(3)	−404(2)	5879(3)
C(15)	3385(3)	−325(2)	5984(3)
C(16)	3848(3)	0(2)	5474(3)
C(21)	3785(3)	−137(2)	3216(3)
C(22)	3234(4)	−154(2)	2592(3)
C(23)	3016(5)	−656(3)	2256(4)
C(24)	3341(5)	−1135(2)	2523(4)
C(25)	3870(5)	−1123(2)	3163(4)
C(26)	4088(4)	−627(2)	3510(3)
C(31)	4795(3)	732(2)	2295(2)
C(32)	4516(3)	1103(2)	1736(2)
C(33)	4754(3)	1027(2)	965(3)
C(34)	5252(3)	585(2)	752(3)
C(35)	5512(3)	208(2)	1298(3)
C(36)	5286(3)	279(2)	2068(3)
C(41)	4793(3)	2540(2)	3451(3)
C(42)	5169(4)	3025(2)	3678(4)
C(43)	4722(4)	3514(2)	3571(4)
C(44)	3902(4)	3516(2)	3240(4)
C(45)	3517(4)	3031(3)	3041(4)
C(46)	3959(4)	2533(2)	3141(3)
C(51)	5978(3)	1846(2)	2453(3)
C(52)	5734(4)	2225(2)	1890(3)
C(53)	6178(4)	2223(2)	1191(3)
C(54)	6844(4)	1862(2)	1063(3)
C(55)	7086(4)	1484(2)	1620(3)
C(56)	6648(3)	1476(2)	2319(3)
C(61)	6446(3)	1905(2)	4097(3)
C(62)	7131(3)	2230(2)	3840(3)
C(63)	7905(4)	2250(2)	4257(4)
C(64)	7994(4)	1949(2)	4926(4)
C(65)	7319(4)	1619(2)	5170(3)
C(66)	6544(3)	1594(2)	4762(3)
H(12)	2197	409	4319
H(13)	1389	−219	5189
H(14)	2137	−662	6282
H(15)	3725	−526	6458
H(16)	4546	60	5559
H(22)	2951	232	2364
H(23)	2560	−663	1761
H(24)	3190	−1522	2238
H(25)	4129	−1511	3402
H(26)	4515	−622	4023
H(32)	4106	1459	1899
H(33)	4545	1315	521
H(34)	5443	532	151
H(35)	5898	−145	1121
H(36)	5499	−18	2499
H(42)	5816	3026	3950
H(43)	5010	3905	3753
H(44)	3563	3898	3136
H(45)	2866	3035	2803
H(46)	3643	2145	2978
H(52)	5214	2516	2007
H(53)	5980	2514	741
H(54)	7196	1874	516
H(55)	7613	1188	1509
H(56)	6826	1186	2767
H(62)	7063	2471	3307
H(63)	8451	2498	4051
H(64)	8594	1983	5262
H(65)	7408	1364	5691
H(66)	6001	1333	4956
H(71)	3627	953	5738
H(72)	3275	1641	5794
H(73)	4274	1446	6214

DISCUSSION

Figure 1 shows the molecule with its As · · · O association, clearly supporting the inclusion of (V) as a valid canonical form. Bond distances and angles and their estimated standard deviations are listed in Tables 2 and 3. The bond lengths within the five-membered ring fall into three categories: C(1)–C(5) and C(3)–C(4), mean 1·406; C(2)–C(3) and C(4)–C(5), mean 1·422; and C(1)–C(2), 1·445 Å. Qualitatively it may thus be deduced that the ground-state population of (V) exceeds that of (IV), because C(1)–C(5) and C(3)–C(4) [double bonds in (V)] are shorter than C(2)–C(3) and C(4)–C(5) [double bonds in (IV)]; identical (IV) and (V) populations would have resulted in all four bonds being equal. C(1)–C(2) Is significantly less than C–C single bonds in cyclo-octatetraene [1·462(1) Å],[7] arguing for the inclusion of (III), while the C(1)–As bond length 1·881 Å, being shorter than a normal C(sp^2)–arsonium distance, *e.g.* as in tetraphenylarsonium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide (1·897 Å),[8] is consistent with the participation of (IV).

The C(2)–C(6) distance [1·439(6) Å] is in good agreement with that [1·436(6) Å] reported recently for a comparable bond in 2-formyl-6-(dimethylamino)pentafulvene for which dipolar character is also claimed.[9] Reference to tables of standard bond lengths [10] allows speculation that population densities of the order of 20—30% (III), 30—35% (IV), and 40—45% (V) would satisfactorily account for the bond-length distribution in and around the five-membered ring.

The three C(ring)–C(Ph) bonds agree well with one another and are as expected for a C(sp^2)–C(sp^2) single

* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

6 'International Tables for *X*-Ray Crystallography,' vol. III, 1965, Kynoch Press, Birmingham.

7 O. Bastianson, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311.

8 G. J. Palenik, *Acta Cryst.*, 1966, **20**, 471.

9 H. L. Ammon and L. A. Plastas, *Chem. Comm.*, 1971, 356.

10 L. E. Sutton, *Chem. Soc. Special Publ.*, No. 18, 1965.

bond. C(2)–C(6) (1·439 Å) Is however much shorter, and this, coupled with the fact that the carbonyl distance [1·250(5) Å] is longer than that [1·216(6) Å] reported for 2-formyl-6-(dimethylamino)pentafulvene, is further evidence for the inclusion of (V) as a valid canonical form. The arsenic atom sits 0·49 Å above the plane through C(1), C(41), and C(61). The As • • • O distance [2·770(3) Å] is considerably less than the sum of the appropriate van der Waals radii (3·40 Å) [11] but is much greater than typical covalent As–O distances (1·70 Å).[12] As a result

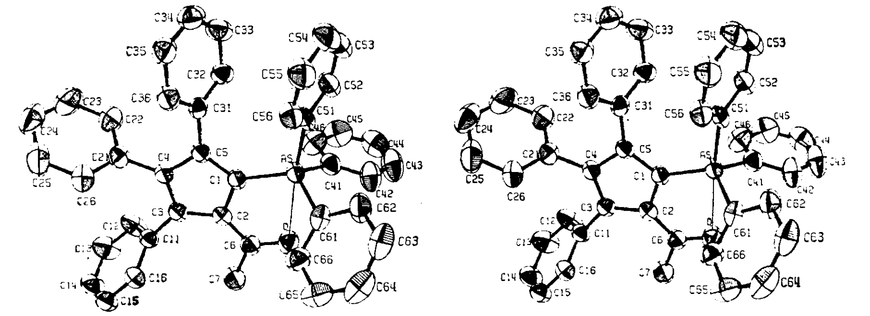


FIGURE 1 Diagram of the molecule, showing the arbitrary atom numbering system used in the crystallographic analysis; thermal ellipsoids are drawn at 50% probability level

The C(6)–C(7) bond length [1·513(7) Å] is in good agreement with that [1·516(5) Å] quoted [10] for C(sp^3)–C(sp^2).

The five-membered ring is rigorously planar, as are all the phenyl rings. The mean C–C distance within the phenyl rings [1·385(8) Å] is not significantly different from the usual value (1·397 Å), especially in view of the

TABLE 2

Bond distances (Å), with estimated standard deviations in parentheses

As–C(1)	1·881(4)	C(25)–C(26)	1·391(8)
As–C(41)	1·921(5)	C(31)–C(32)	1·395(6)
As–C(61)	1·925(5)	C(31)–C(36)	1·393(6)
As–C(51)	1·952(5)	C(32)–C(33)	1·401(6)
O–C(6)	1·240(5)	C(33)–C(34)	1·371(8)
C(1)–C(2)	1·445(6)	C(34)–C(35)	1·380(7)
C(1)–C(5)	1·407(6)	C(35)–C(36)	1·391(7)
C(2)–C(3)	1·419(6)	C(41)–C(42)	1·372(7)
C(3)–C(4)	1·405(6)	C(41)–C(46)	1·390(7)
C(4)–C(5)	1·424(6)	C(42)–C(43)	1·389(8)
C(2)–C(6)	1·439(6)	C(43)–C(44)	1·384(9)
C(3)–C(11)	1·489(6)	C(44)–C(45)	1·366(9)
C(4)–C(21)	1·484(6)	C(45)–C(46)	1·402(8)
C(5)–C(31)	1·484(6)	C(51)–C(52)	1·396(7)
C(6)–C(7)	1·513(7)	C(51)–C(56)	1·388(7)
C(11)–C(12)	1·391(6)	C(52)–C(53)	1·391(8)
C(11)–C(16)	1·391(6)	C(53)–C(54)	1·368(9)
C(12)–C(13)	1·389(8)	C(54)–C(55)	1·385(8)
C(13)–C(14)	1·373(8)	C(55)–C(56)	1·389(7)
C(14)–C(15)	1·380(8)	C(61)–C(62)	1·390(7)
C(15)–C(16)	1·384(6)	C(61)–C(66)	1·391(7)
C(21)–C(22)	1·375(7)	C(62)–C(63)	1·391(8)
C(21)–C(26)	1·380(7)	C(63)–C(64)	1·381(9)
C(22)–C(23)	1·394(9)	C(64)–C(65)	1·379(8)
C(23)–C(24)	1·353(9)	C(65)–C(66)	1·387(7)
C(24)–C(25)	1·378(10)		

fact that no corrections for rigid-body motion were made and thus the true atomic centres may not coincide with the apparent centres of electron density.

The oxygen atom has interacted appreciably with the arsenic atom to distort the tetrahedral type geometry implied in (III) and (IV) towards a trigonal bipyramidal configuration with C(51) and O at the vertices [C(51)–As • • • O 175·6°] and C(1), C(41), and C(61) at the equator.

[11] L. Pauling, 'The Nature of the Chemical Bond,' 1960, Cornell University Press, Ithaca, New York, p. 260.
[12] G. Ferguson and E. W. Macaulay, *Chem. Comm.*, 1968, 1288.

of this interaction the three As–C(Ph) distances are longer than the value of 1·897 Å quoted earlier, the bond As–C(51) directly opposite the oxygen atom

TABLE 3

Valency angles (°); mean σ 0·4°

C(1)–As–C(61)	115·8	C(22)–C(21)–C(26)	118·2
C(1)–As–C(41)	114·0	C(21)–C(22)–C(23)	120·2
C(1)–As–C(51)	112·1	C(22)–C(23)–C(24)	121·7
C(1)–As–O	72·3	C(23)–C(24)–C(25)	118·4
O–As–C(61)	78·9	C(24)–C(25)–C(26)	120·6
O–As–C(51)	175·6	C(25)–C(26)–C(21)	120·8
O–As–C(41)	74·6	C(5)–C(31)–C(32)	120·9
C(41)–As–C(51)	102·9	C(5)–C(31)–C(36)	120·2
C(41)–As–C(61)	111·3	C(32)–C(31)–C(36)	118·8
C(51)–As–C(61)	98·9	C(31)–C(32)–C(33)	120·0
As–C(1)–C(2)	122·8	C(32)–C(33)–C(34)	120·5
C(2)–C(1)–C(5)	108·7	C(33)–C(34)–C(35)	119·9
As–C(1)–C(5)	128·2	C(34)–C(35)–C(36)	120·3
C(1)–C(2)–C(3)	106·7	C(35)–C(36)–C(31)	120·4
C(1)–C(2)–C(6)	121·9	As–C(51)–C(56)	119·0
C(3)–C(2)–C(6)	131·2	C(52)–C(51)–C(56)	120·8
C(2)–C(3)–C(4)	108·4	C(51)–C(52)–C(53)	118·4
C(2)–C(3)–C(11)	129·5	C(52)–C(53)–C(54)	120·7
C(4)–C(3)–C(11)	122·1	C(53)–C(54)–C(55)	121·0
C(3)–C(4)–C(5)	109·0	C(54)–C(55)–C(56)	119·3
C(3)–C(4)–C(21)	126·3	C(55)–C(56)–C(51)	119·8
C(5)–C(4)–C(21)	124·6	As–C(41)–C(42)	122·1
C(1)–C(5)–C(4)	107·2	As–C(41)–C(46)	117·1
C(4)–C(5)–C(31)	122·8	C(42)–C(41)–C(46)	120·6
C(1)–C(5)–C(31)	130·0	C(41)–C(42)–C(43)	119·5
C(2)–C(6)–C(7)	120·4	C(42)–C(43)–C(44)	120·5
C(2)–C(6)–O	120·4	C(43)–C(44)–C(45)	119·7
C(7)–C(6)–O	119·2	C(44)–C(45)–C(46)	120·6
C(6)–O–As	101·7	C(45)–C(46)–C(41)	118·9
C(3)–C(11)–C(12)	120·1	As–C(51)–C(52)	120·1
C(3)–C(11)–C(16)	121·4	As–C(61)–C(62)	118·1
C(12)–C(11)–C(16)	118·3	As–C(61)–C(66)	122·1
C(11)–C(12)–C(13)	120·4	C(62)–C(61)–C(66)	119·7
C(12)–C(13)–C(14)	120·5	C(61)–C(62)–C(63)	120·0
C(13)–C(14)–C(15)	119·8	C(62)–C(63)–C(64)	120·2
C(14)–C(15)–C(16)	120·0	C(63)–C(64)–C(65)	119·7
C(15)–C(16)–C(11)	121·0	C(64)–C(65)–C(66)	120·9
C(4)–C(21)–C(22)	120·3	C(65)–C(66)–C(61)	119·6
C(4)–C(21)–C(26)	121·5		

appreciably so, and bond angles C(1)–As–C(41), C(1)–As–C(61), and C(41)–As–C(61) are splayed out. The attraction between the arsenic and oxygen atoms is also reflected in the non-equivalence of angles C(1)–C(2)–C(6)

(121·9°) and C(3)–C(2)–C(6) (131·2°), which, with the other exocyclic angles associated with atoms C(1) and C(3)—(5), should be *ca.* 126°. The two exocyclic angles associated with atoms C(1) and C(3)—(5) are significantly different from one another (Table 3). This may be explained by reference to the list of intramolecular contacts in Table 4. Atoms C(31) and C(51) are 3·28 Å apart, which explains the increase in C(31)–C(5)–C(1), C(5)–C(1)–As, and C(1)–As–C(51) (130·0, 128·2, and 112·1°) and the decrease in C(31)–C(5)–C(4), C(2)–C(1)–As, C(51)–As–C(61), and C(51)–As–C(41) (122·8, 122·8, 98·9, and 102·9°). Similarly, that angles C(11)–C(3)–C(2) (129·5°) and C(3)–C(2)–C(6) (131·2°) are greater than expected is due to the repulsive effect between atoms C(7) and C(11) which are separated by 3·15 Å. The angles around atom C(4) seem to be the least affected by steric effects since C(21)–C(4)–C(5) and C(21)–C(4)–C(3) are 124·6 and 126·3°. Presumably the repulsive forces experienced by phenyl ring (2) from phenyl rings (3) and (1) must be almost exactly balanced.

TABLE 4

Selected intramolecular non-bonded distances <3·5 Å

O · · · As	2·77	C(31) · · · C(56)	3·38
O · · · C(41)	2·92	C(32) · · · C(51)	3·14
O · · · C(66)	2·99	C(32) · · · C(52)	3·32
O · · · C(61)	3·05	C(41) · · · C(51)	3·03
O · · · C(42)	3·46	C(41) · · · C(52)	3·17
C(11) · · · C(26)	3·36	C(41) · · · C(61)	3·18
C(11) · · · C(21)	3·08	C(42) · · · C(61)	3·44
C(12) · · · C(21)	3·41	C(51) · · · C(61)	2·95
C(21) · · · C(31)	3·07	C(51) · · · C(62)	3·13
C(21) · · · C(36)	3·45	C(56) · · · C(62)	3·30
C(31) · · · C(51)	3·28	C(7) · · · C(11)	3·15

Delocalization of electron density appears to be restricted to the five-membered ring, the arsenic atom, and the acetyl group. The best plane through atoms C(2), C(6), C(7), and O makes an angle of 5·3° with the five-membered ring. Phenyl rings (1)—(3) would have to be approximately coplanar with the five-membered ring to participate in delocalization, but obviously the steric requirements needed to meet this arrangement would be prohibitive. Figure 1 shows that a ' propeller ' type arrangement of phenyl rings (1)—(3) is favoured, minimizing intramolecular contacts. These rings are inclined at 71·1, 61·7, and 58·2° to the plane of the five-membered ring.

The orientation of the arsonium phenyl rings (4)—(6) is such that ring (5) is inclined at 67·4° to the cyclopentadienyl ring, merging with the ' propeller ' arrangement of phenyl rings (1)—(3), whilst rings (4) and (6) appear to be arranged so as to interfere minimally with the As · · · O interaction. Ring (6) makes an angle of 44·6° with the plane through atoms C(61), As, and O whilst ring (4) makes an angle of 94·3° with the plane through atoms C(41), As, O.

A stereodiagram of the contents of one unit cell is shown in Figure 2. No unusually short intermolecular contacts are present and this is borne out by the small number of intermolecular contacts <3·5 Å (Table 5).

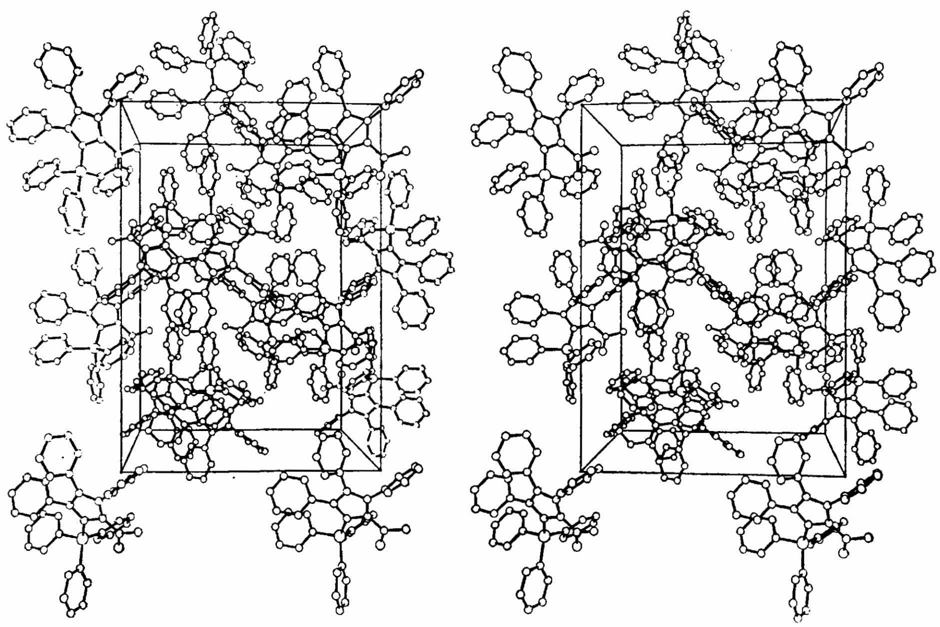


FIGURE 2 Stereodiagram of the arrangement of the molecules in a unit cell. The origin of the cell is in the top right-hand corner, nearer the viewer, with *a* into the page, *b* down, and *c* along

TABLE 5

Intermolecular distances <3·5 Å

C(14) · · · C(22^{I})	3·46	C(14) · · · C(66^{II})	3·43
C(14) · · · C(65^{II})	3·49	C(15) · · · C(66^{II})	3·36

Roman numerals refer to the following equivalent positions:

I $-\frac{1}{2} - x, -y, -\frac{1}{2} + z$ II $-x, -y, -z$

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[13] J. M. Stewart, ' *X*-Ray '72,' Technical Report TR 192, 1972, University of Maryland, Computer Science Center, College Park, Maryland.

[14] C. K. Johnson, ORTEP, Report ORNL 3794, 1965, Oak Ridge National Laboratory, Oak Ridge, Tennessee.