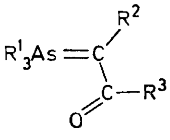
Stereochemistry of Some Organic Derivatives of Group VB Elements. Part XI.[1] Crystal and Molecular Structure of Triphenylarsonium 3,4-dibenzoylcyclopentadienylide

By **George Ferguson** * and **David F. Rendle**, Chemistry Department, The University, Guelph, Ontario, Canada N1G 2W1

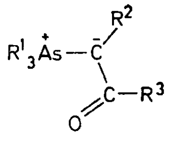
The crystal and molecular structure of the title compound has been determined by three-dimensional *X*-ray analysis. Crystals are monoclinic, space group *C*2/*c*, with a = 25.584(2), b = 13.863(2), c = 18.055(2) Å, β = 113.17(1)°, Z = 8. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to R 0.049 for 2 484 observed reflexions measured by diffractometer.

The crystal structure consists of discrete molecules separated by van der Waals distances; one of the benzoyl groups is disordered over two sites with occupancy factors $\frac{2}{3}:\frac{1}{3}$. Bond lengths lie in the expected ranges [C–C(cyclopentadienyl) 1.383(8)—1.439(9), As–C(Ph) 1.910—1.917(7), As–C(cyclopentadiene) 1.868(5) Å] and those associated with the cyclopentadienyl ring are used to assess the contributions of canonical forms to the ground-state structure.

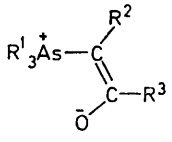
ACYL arsonium ylides (I) are shown by their i.r. spectra [2-4] to have a considerable contribution from the dipolar form (Ic) wherein the negative charge resides on the oxygen atom. In the case of triphenylarsonium (diacylcyclopentadienylide) (II),[5,6] the carbonyl stretching frequency in the i.r. spectrum (1 610 cm^{-1}) indicates that the negative charge resides to some extent on the oxygen atoms (IIc). One might, however, expect a greater contribution from ylide form (IIb) in cyclopentadienylides because the formal negative charge is delocalised over the 'aromatic' ring system. To investigate the relative importance of canonical forms such as (IIa—c), we undertook a crystal structure analysis of (II).



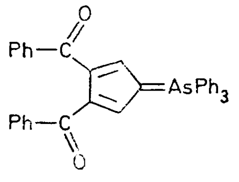
(Ia)



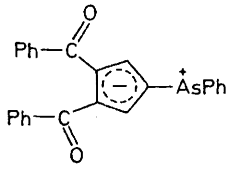
(Ib)



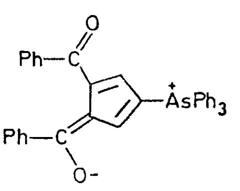
(Ic)



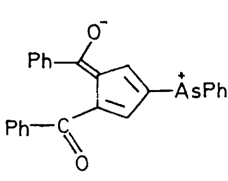
(IIa)



(IIb)



(IIc)



(IId)

EXPERIMENTAL

Crystals of (II) were pale yellow laths, elongated along *b*.

Crystal Data.—$C_{37}H_{27}AsO_2$, M = 578.5, Monoclinic, a = 25.584(2), b = 13.863(2), c = 18.055(2) Å, β = 113.17(1)°, U = 5 887 Å^3, D_m = 1.30, Z = 8, D_c = 1.305, $F(000)$ = 2 384. Space group *C*2/*c* (C_{2h}^6, No. 15) or *Cc* (C_s^4) from systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$, and $0k0$ when $k = 2n + 1$; the former confirmed by subsequent successful refinement. Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 19.6 cm^{-1}.

Crystallographic Measurements.—Oscillation, Weissenberg, and precession photographs, taken with Cu-K_α radiation and a crystal of dimensions 0.16 × 0.38 × 0.08 mm mounted along *b*, established preliminary unit-cell data. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflexions measured on a Hilger and Watts Y 290 computer-controlled diffractometer. Three-dimensional intensity data were collected to a maximum Bragg angle of 57° by the θ—2θ scan technique with Ni-filtered Cu-radiation and a symmetric scan of 70 steps of 0.01° with a 1s count at each step; stationary-crystal–stationary-counter background counts

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of 17.5s were measured at each end of the integrated scan. The intensities of 3 standard reflexions monitored at *ca.* 4 h intervals had maximum variation of <4%. Data were corrected for Lorentz and polarization factors. Of 3 570 measured reflexions, 2 484 having $I > 3\sigma(I)$ were considered observed and used in the structure solution and refinement.

TABLE 1

E Statistics

	Found	Theoretical	
		Centro-symmetric	Non-centro-symmetric
Mean $\|E\|$	0.831	0.798	0.886
Mean $\|E\|^2$	1.000	1.000	1.000
Mean $\|E^2 - 1\|$	0.888	0.968	0.736
$E > 3.0$ (%)	0.06	0.27	0.01
$E > 2.0$ (%)	2.99	4.55	1.83
$E > 1.0$ (%)	36.17	31.73	36.79

TABLE 2

Final positional parameters (As × 10^5, all others × 10^4), with estimated standard deviations in parentheses *

Atom	*X/a*	*Y/b*	*Z/c*
As	23 875(3)	7 561(5)	24 962(4)
O(2)	1 493(2)	4 246(3)	624(2)
C(1)	1 786(2)	1 466(5)	1 761(3)
C(2)	1 217(2)	1 334(5)	1 645(3)
C(3)	901(2)	2 086(4)	1 152(3)
C(4)	1 288(2)	2 695(5)	965(3)
C(5)	1 831(2)	2 326(5)	1 350(3)
C(7)	1 162(2)	3 559(5)	452(4)
C(21)	639(2)	3 591(5)	−312(4)
C(22)	434(3)	2 762(5)	−763(4)
C(23)	−39(3)	2 824(6)	−1 494(4)
C(24)	−297(3)	3 710(6)	−1 760(4)
C(25)	−100(3)	4 524(5)	−1 309(4)
C(26)	378(3)	4 473(5)	−583(4)
C(31)	2 893(2)	226(5)	2 053(3)
C(32)	2 891(3)	591(5)	1 326(4)
C(33)	3 267(3)	213(6)	1 025(4)
C(34)	3 636(3)	−528(6)	1 435(4)
C(35)	3 635(3)	−889(5)	2 148(4)
C(36)	3 255(3)	−519(5)	2 448(4)
C(41)	2 082(2)	−296(5)	2 889(4)
C(42)	2 200(3)	−380(5)	3 706(4)
C(43)	1 967(3)	−1 137(6)	3 964(5)
C(44)	1 630(3)	−1 805(6)	3 426(5)
C(45)	1 517(3)	−1 729(6)	2 616(6)
C(46)	1 746(3)	−975(5)	2 340(4)
C(51)	2 813(3)	1 559(5)	3 391(3)
C(52)	3 389(3)	1 442(5)	3 814(4)
C(53)	3 683(3)	2 061(6)	4 456(4)
C(54)	3 386(4)	2 765(6)	4 653(4)
C(55)	2 800(3)	2 882(6)	4 229(4)
C(56)	2 511(3)	2 287(5)	3 590(4)
O(1a)	139(3)	3 191(5)	846(4)
C(6a)	313(4)	2 376(7)	1 069(5)
C(11a)	−46(4)	1 687(6)	1 212(5)
C(12a)	−414(4)	2 074(7)	1 556(6)
C(13a)	−771(5)	1 445(9)	1 750(7)
C(14a)	−756(6)	546(10)	1 632(8)
C(15a)	−434(6)	59(11)	1 304(9)
C(16a)	−36(5)	716(10)	1 067(7)
O(1b)	136(6)	3 089(10)	935(8)
C(6b)	339(6)	2 210(12)	962(9)
C(11b)	−75(7)	1 362(12)	986(9)
C(12b)	−419(6)	1 480(11)	1 420(8)
C(13b)	−786(9)	712(17)	1 387(13)
C(14b)	−790(13)	−50(23)	986(18)
C(15b)	−412(11)	−198(20)	596(16)
C(16b)	−38(8)	598(15)	593(12)

* One of the benzoyl groups [atoms O(1), C(6), C(11)—(16)] is disordered over two sites with occupancy factors $\frac{2}{3}:\frac{1}{3}$. Letters a and b in atom labels indicate major and minor components respectively.

Solution and Refinement.—The *E* statistics (Table 1) for the intensity data do not clearly differentiate between the centro- and noncentro-symmetric space groups. Inspection of the three-dimensional Patterson synthesis yielded co-ordinates for the arsenic atom and the vector sets were consistent with the choice of *C*2/*c*. The positions of all non-hydrogen atoms were then obtained by the heavy-atom method and block-diagonal least-squares refinement with individual isotropic thermal parameters reduced *R* to 0.128. Molecular geometry calculations revealed that one of the benzoyl groups had chemically unreasonable bond lengths and angles, and also unreasonably high thermal parameters. A difference synthesis was then computed (with the offending benzoyl group atoms omitted from the F_c

TABLE 3

Positional parameters (× 10^4) for hydrogen atoms, numbered according to the carbon atoms to which they are bonded

Atom	*X/a*	*Y/b*	*Z/c*
H(2)	1 049	753	1 887
H(5)	2 218	2 634	1 336
H(22)	641	2 069	−547
H(23)	−210	2 171	−1 864
H(24)	−660	3 770	−2 339
H(25)	−313	5 217	−1 513
H(26)	542	5 125	−225
H(32)	2 602	1 188	1 018
H(33)	3 285	500	475
H(34)	3 925	−842	1 180
H(35)	3 932	−1 466	2 478
H(36)	3 233	−810	2 998
H(42)	2 478	153	4 131
H(43)	2 042	−1 225	4 603
H(44)	1 451	−2 395	3 638
H(45)	1 250	−2 274	2 207
H(46)	1 666	−912	1 703
H(52)	3 617	855	3 645
H(53)	4 147	1 993	4 788
H(54)	3 608	3 243	5 159
H(55)	2 567	3 453	4 409
H(56)	2 053	2 362	3 326

TABLE 4

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

As–C(1)	1.868(5)	C(15a)–C(16a)	1.549(22)
As–C(31)	1.914(7)	C(6b)–O(1b)	1.318(22)
As–C(41)	1.917(7)	C(6b)–C(11b)	1.594(25)
As–C(51)	1.910(6)	C(11b)–C(12b)	1.399(27)
C(1)–C(2)	1.397(9)	C(11b)–C(16b)	1.299(27)
C(1)–C(5)	1.432(9)	C(12b)–C(13b)	1.406(29)
C(2)–C(3)	1.402(8)	C(13b)–C(14b)	1.279(41)
C(3)–C(4)	1.439(9)	C(14b)–C(15b)	1.416(52)
C(3)–C(6a)	1.507(11)	C(15b)–C(16b)	1.461(36)
C(3)–C(6b)	1.351(17)	C(31)–C(32)	1.406(10)
C(4)–C(5)	1.383(8)	C(31)–C(36)	1.383(9)
C(4)–C(7)	1.471(9)	C(32)–C(33)	1.379(13)
C(7)–O(2)	1.230(8)	C(33)–C(34)	1.393(10)
C(7)–C(21)	1.496(7)	C(34)–C(35)	1.383(11)
C(21)–C(22)	1.386(9)	C(35)–C(36)	1.384(11)
C(21)–C(26)	1.386(9)	C(41)–C(42)	1.388(10)
C(22)–C(23)	1.399(8)	C(41)–C(46)	1.392(9)
C(23)–C(24)	1.388(11)	C(42)–C(43)	1.376(12)
C(24)–C(25)	1.366(11)	C(43)–C(44)	1.373(10)
C(25)–C(26)	1.400(8)	C(44)–C(45)	1.379(14)
C(6a)–O(1a)	1.223(11)	C(45)–C(46)	1.383(12)
C(6a)–C(11a)	1.416(14)	C(51)–C(52)	1.376(8)
C(11a)–C(12a)	1.421(16)	C(51)–C(56)	1.401(10)
C(11a)–C(16a)	1.373(16)	C(52)–C(53)	1.400(10)
C(12a)–C(13a)	1.404(18)	C(53)–C(54)	1.368(13)
C(13a)–C(14a)	1.267(19)	C(54)–C(55)	1.398(11)
C(14a)–C(15a)	1.367(23)	C(55)–C(56)	1.373(10)

calculation) and disorder of the benzoyl group of the type shown in Figure 1 was discernible.

At this point, the possibility that the true space group was *Cc*, with two molecules per asymmetric unit very nearly related by a centre of symmetry (destroyed by misalignment of a benzoyl group), could not be overlooked. This was discounted after detailed examination of the difference synthesis indicated an occupancy ratio between the two sites of *ca.* 2 : 1 (space group *Cc* would have required a 1 : 1 ratio for ordered molecules).

Refinement was then continued in *C*2/*c* with the non-disordered atoms allowed anisotropic motion and the disordered atoms restricted to isotropic motion. After 4 cycles, when R was 0.074 a difference synthesis revealed positions for the 22 hydrogens of the ordered portion of the molecule. These hydrogen atoms were allowed for in all subsequent structure-factor calculations (with U_{iso} 0.063 Å^2) but were not refined. In additional refinement cycles the occupancy factors deduced from the difference synthesis did not change significantly and convergence was achieved with R 0.049, R' [$= \Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2$] 0.060 and an average shift-to-error ratio of 0.08. Absolute weights derived from counting statistics were used in the refinement and gave a satisfactory weighting-scheme analysis. Scattering factors were obtained from ref. 7 and corrections for anomalous dispersion by the arsenic atom were included. Programs used are listed in ref. 8.

TABLE 5

Valency angles (°); mean estimated standard deviation 0.6° except for angles involving the disordered atoms (1.8°)

C(1)–As–C(31)	114.1	As–C(41)–C(42)	120.5
C(1)–As–C(41)	108.8	As–C(41)–C(46)	118.6
C(1)–As–C(51)	109.2	C(42)–C(41)–C(46)	120.9
C(31)–As–C(41)	107.6	C(41)–C(42)–C(43)	118.9
C(31)–As–C(51)	108.9	C(42)–C(43)–C(44)	120.7
C(41)–As–C(51)	108.1	C(43)–C(44)–C(45)	120.6
As–C(1)–C(2)	123.8	C(44)–C(45)–C(46)	119.9
As–C(1)–C(5)	126.5	C(45)–C(46)–C(41)	119.1
C(2)–C(1)–C(5)	108.8	As–C(51)–C(52)	122.0
C(1)–C(2)–C(3)	107.7	As–C(51)–C(56)	116.7
C(2)–C(3)–C(4)	107.9	C(52)–C(51)–C(56)	121.3
C(2)–C(3)–C(6a)	124.4	C(51)–C(52)–C(53)	119.3
C(2)–C(3)–C(6b)	123.1	C(52)–C(53)–C(54)	118.7
C(4)–C(3)–C(6a)	125.0	C(53)–C(54)–C(55)	121.8
C(4)–C(3)–C(6b)	128.8	C(54)–C(55)–C(56)	119.8
C(3)–C(4)–C(5)	108.2	C(55)–C(56)–C(51)	118.7
C(3)–C(4)–C(7)	128.7	C(3)–C(6a)–O(1a)	119.8
C(5)–C(4)–C(7)	123.1	C(11a)–C(6a)–O(1a)	120.4
C(4)–C(5)–C(1)	107.4	C(11a)–C(6a)–C(3)	119.7
C(4)–C(7)–O(2)	120.8	C(6a)–C(11a)–C(16a)	124.3
C(4)–C(7)–C(21)	119.9	C(6a)–C(11a)–C(12a)	114.4
O(2)–C(7)–C(21)	119.2	C(12a)–C(11a)–C(16a)	121.3
C(7)–C(21)–C(22)	120.7	C(11a)–C(12a)–C(13a)	118.8
C(7)–C(21)–C(26)	118.8	C(12a)–C(13a)–C(14a)	120.3
C(22)–C(21)–C(26)	120.4	C(13a)–C(14a)–C(15a)	128.4
C(21)–C(22)–C(23)	119.4	C(14a)–C(15a)–C(16a)	113.9
C(22)–C(23)–C(24)	119.8	C(15a)–C(16a)–C(11a)	117.3
C(23)–C(24)–C(25)	120.8	C(3)–C(6b)–O(1b)	119.5
C(24)–C(25)–C(26)	119.8	C(11b)–C(6b)–O(1b)	115.2
C(25)–C(26)–C(21)	119.9	C(11b)–C(6b)–C(3)	123.4
As–C(31)–C(32)	119.9	C(6b)–C(11b)–C(16b)	113.3
As–C(31)–C(36)	119.8	C(6b)–C(11b)–C(12b)	120.0
C(32)–C(31)–C(36)	120.3	C(12b)–C(11b)–C(16b)	126.7
C(31)–C(32)–C(33)	119.0	C(11b)–C(12b)–C(13b)	116.5
C(32)–C(33)–C(34)	120.2	C(12b)–C(13b)–C(14b)	120.3
C(33)–C(34)–C(35)	120.8	C(13b)–C(14b)–C(15b)	123.1
C(34)–C(35)–C(36)	119.3	C(14b)–C(15b)–C(16b)	118.0
C(35)–C(36)–C(31)	120.4	C(15b)–C(16b)–C(11b)	115.2

Final atomic positional parameters are listed in Tables 2 and 3, bond distances and angles in Tables 4 and 5, and selected intra- and inter-molecular contacts in Table 6.

TABLE 6

Selected non-bonded distances <3.5 Å

(*a*) Intramolecular			
As · · · C(56)	2.83	C(22) · · · C(62)	3.31
As · · · C(46)	2.86	C(22) · · · O(11)	3.33
As · · · C(36)	2.87	C(22) · · · C(61)	3.48
As · · · C(42)	2.88	C(26) · · · O(11)	3.38
As · · · C(32)	2.89	C(31) · · · C(41)	3.09
As · · · C(52)	2.89	C(31) · · · C(51)	3.11
C(21) · · · O(1a)	2.90	C(31) · · · ·C(52)	3.38
C(21) · · · O)1b)	3.08	C(36) · · · C(41)	3.41
C(21) · · · C(6b)	3.31	C(41) · · · C(51)	3.10
C(21) · · · C(6a)	3.38	C(42) · · · C(51)	3.27
(*b*) Intermolecular			
C(26) · · · O(1a$^{\text{I}}$)	3.46	O(1a) · · · C(25$^{\text{I}}$)	3.39
C(33) · · · O(2$^{\text{II}}$)	3.35	C(16b) · · · C(16b$^{\text{V}}$)	2.77
C(36) · · · O)2$^{\text{III}}$)	3.30	C(16b) · · · C(15b$^{\text{V}}$)	2.86
C(42) · · · O(2$^{\text{III}}$)	3.12	C(13a) · · · C(11a$^{\text{IV}}$)	3.46
C(43) · · · C(14b$^{\text{IV}}$)	3.40	C(13a) · · · C(12a$^{\text{IV}}$)	3.47
C(52) · · · O(2$^{\text{III}}$)	3.19	C(12a) · · · C(12a$^{\text{IV}}$)	3.23
O(1a) · · · C(25$^{\text{I}}$)	3.29		

Roman numerals as superscripts refer to the following equivalent positions:

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

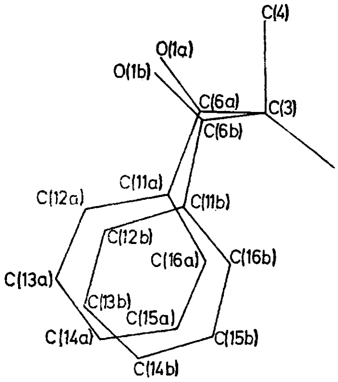

FIGURE 1 Relative position of the atoms of the disordered benzoyl group. Letters a and b in atom labels indicate major and minor components respectively

Final thermal parameters, observed and calculated structure factors, and details of mean plane calculations through various groups of atoms in the molecule, are given in Supplementary Publication SUP 21498 (11 pp, 1 microfiche).* Figure 2 is a stereoview of one molecule; the molecular packing is shown in Figure 3.

DISCUSSION

The principal distances in the five-membered ring fall into three categories: C(4)–C(5) 1.383(8), C(1)–C(5) and C(3)–C(4) (mean) 1.436(9), and C(1)–C(2) and C(2)–C(3)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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

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

(mean) 1.400(9) Å. Qualitatively it may be then deduced that the ground-state populations of (IIa) and (IIc) must be approximately equal, because of the similarity of the C(1)–C(2) and C(2)–C(3) distances. The contribution of (IIb) to the ground-state structure can be gauged by comparison of the bond lengths expected for equal contributions of (IIa) and (IIc) and for a delocalised cyclopentadiene system (IIb) with those observed. Because of the spread of C–C(cyclopentadienyl) bond lengths reported in the literature [9,10] only approximate estimates of the contributions can be made, but population densities of the order of 0.6 (IIb) and 0.2 (IIa) and (IIc) would account satisfactorily for the bond-length distribution within the five-membered ring. The disorder of one of the benzoyl groups precludes any discussion of the relative importance of (IIc) and (IId) from a comparison of the exocyclic C–C distances, but it would appear from the foregoing argument that (IId) must make little contribution or the bond-length pattern in the five-membered ring would be different from that observed. The planes of the two components of the disordered carbonyl groups C(3), C(6a), O(1a), C(11a) and C(3), C(6b), O(1b), C(11b) are inclined at angles of 19.8 and 29.6° respectively to the cyclopentadienyl ring plane, whereas that of the ordered carbonyl group C(4), C(7), O(2), C(21) is inclined at 38.3° to the cyclopentadienyl ring. This latter angle may account for the negligible contribution of (IId) to the ground-state structure compared with that of (IIc), since delocalization of charge from the five-membered ring into the benzoyl groups would be hindered by such out-of-plane rotation.

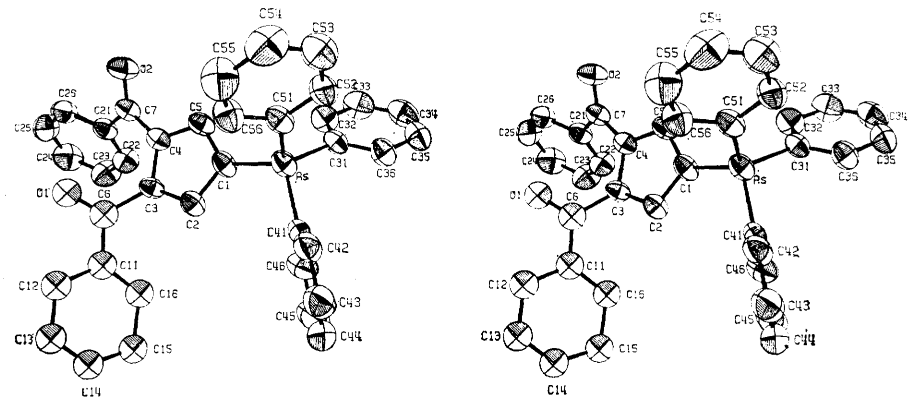

FIGURE 2 Stereoview of one molecule; thermal ellipsoids are at the 50% level

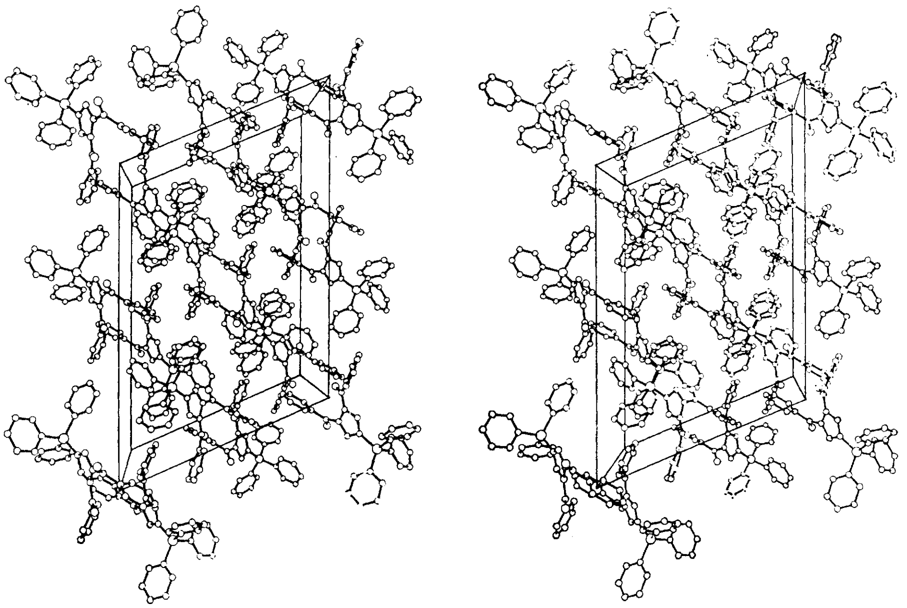

FIGURE 3 Stereopacking diagram viewed in the b direction

The As–C(1) distance [1.868(5) Å] is shorter than normal C(sp)^2–arsonium distances [*e.g.* 1.897 Å in tetra-

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[9] L. E. Sutton, *Chem. Soc. Special Publ.*, No. 18, 1965.

[10] I. D. Brown, ' Bidics,' 1973, Institute for Materials Research, McMaster University, Hamilton, Canada.

phenylarsonium 1,1,4,5,5-pentacyano-3-fluoro-2-azapentadienide[11]] consistent with the participation of (IIa) in the ground-state formulation. The present As–C(1) distance is also shorter than that found in triphenylarsonium 2-acetyl-3,4,5-triphenylcyclopentadienylide[12] (1.881 Å) but comparison cannot be made fairly because the latter has a distorted trigonal bipyramidal configuration at the arsenic atom, which in the present case has near regular tetrahedral geometry. The As–C(Ph) distances do not differ significantly from each other [mean 1.914(7) Å] or from other $\overset{+}{\mathrm{As}}$–C(Ph) distances.[11] The bond lengths in the ordered benzoyl group are within the range expected. The three rings bonded to the arsenic atom are in a regular propeller arrangement (Figure 2) and make the following angles with each other: rings (3)—(4) 82.7, rings (3)—(5) 70.0, and rings (4)—(5) 87.1°.

Intra- and inter-molecular contact distances <3.5 Å are listed in Table 6; none are abnormally short. Atom O(2), of the ordered benzoyl group, has four non-bonded contacts <3.5 Å with neighbouring molecules, something which could possibly prevent high thermal motion or disorder. In the stereodiagram of the molecular packing (Figure 3), only the major component of the disordered ring is shown and its position is such that small movements of the benzoyl group can be accommodated without any undue effect on the neighbouring molecules.

We thank Dr. D. Lloyd for crystals of (II) and stimulating discussions, and the National Research Council of Canada for Operating and Computing grants (to G. F.) and for the award of a post-graduate scholarship (to D. F. R.). Diagrams were prepared using Johnson's ORTEP program.[13]

[5/487 *Received, 12th March,* 1975]

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[11] G. J. Palenik, *Acta Cryst.*, 1966, **20**, 471.

[12] G. Ferguson and D. F. Rendle, *J.C.S. Dalton*, 1975, 1284.

[13] C. K. Johnson, Program ORTEP, Report ORNL 3794, 1965, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.