X-Ray Structural Evidence for Dipolar Character in the Arsonium Ylide Triphenylarsonium 2-Acetyl-3,4,5-triphenylcyclopentadienylide

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Summary Molecular dimensions found in a crystal structure analysis of triphenylarsonium 2-Acetyl-3,4,5-triphenylcyclopentadienylide establish that a dipolar form with an $As^+ \cdots O^-$ intramolecular interaction makes a significant contribution to the ground-state structure.

ARSONIUM YLIDES are well known[1] and can be represented generally by such canonical forms as (I) and (II).

$$R_3As = C< \qquad R_3\overset{+}{A}s - \overset{-}{C}<$$
$$\text{(I)} \qquad\qquad \text{(II)}$$

Thus, in the case of triphenylarsonium 2-acetyl-3,4,5-triphenylcyclopentadienylide[2] canonical forms (III) and (IV) must be considered. Neither of these forms is however consistent with the low value (1565 cm^{-1}) of the carbonyl

(III)   (IV)   (V)
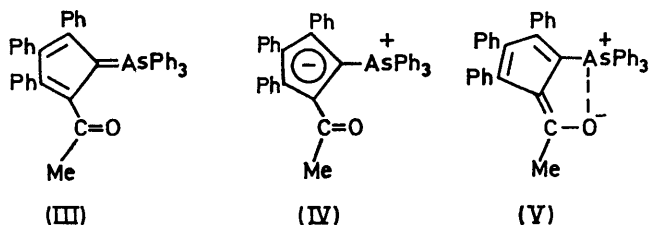
stretching frequency in the i.r. spectrum, but the inclusion of a further canonical form wherein the negative charge is sited on the oxygen atom rather than on the five-membered ring would account for this value.[3] For such a canonical form there is the possibility of intramolecular association between oxygen and arsenic, as implied in formula (V). With the availability of good 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.
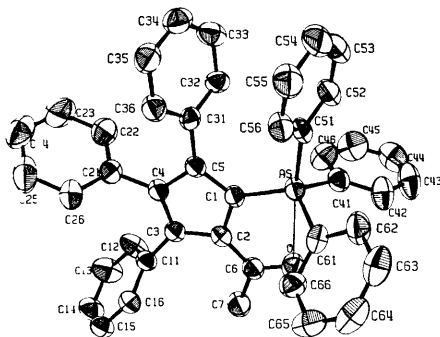

FIGURE 1. *Molecular conformation and numbering scheme for triphenylarsonium 2-acetyl-3,4,5-triphenylcyclopentadienylide.*

Figure 1 shows the molecular conformation which, with its intramolecular $As \cdots O$ association, clearly supports the inclusion of (V) as a valid canonical form. The principal distances and angles and their e.s.d.'s are shown in Figure 2 where it may be seen that the bond lengths within
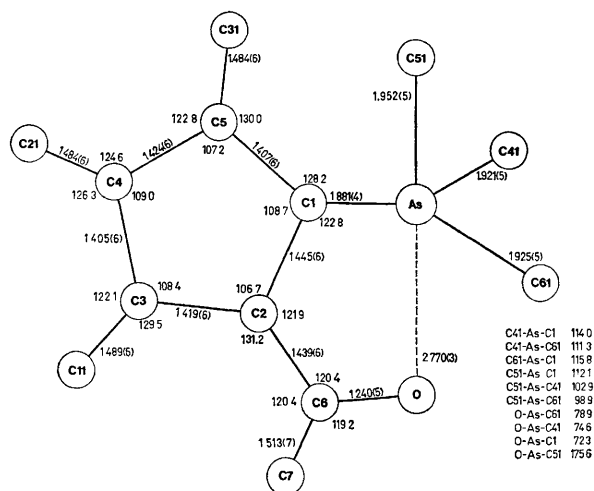

FIGURE 2. *Principal distances with (e.s.d.'s) and angles.*

the five-membered ring fall into three categories: C(1)–C(5) and C(3)–C(4), average 1·406 Å; C(2)–C(3) and C(4)–C(5), average 1·422 Å; and C(1)–C(2), 1·445 Å. Qualitatively it may thus be deduced that the ground-state population of (V) exceeds that of (III), because the C(1)–C(5) and C(3)–C(4) bonds [double bonds in (V)] are shorter than the C(2)–C(3) and C(4)–C(5) bonds [double bonds in (III)]; identical (III) and (V) populations would have resulted in all four bonds being equal. The C(1)–C(2) distance (1·445 Å) is significantly less than C–C single bonds in cyclo-octatetraene 1·462(1) Å,[4] arguing for the inclusion of (IV), while the C(1)–As bond length, 1·881 Å, being shorter than a normal phenyl–arsonium distance, 1·897 Å,[5] is consistent with the participation of (III). The C(2)–C(6) distance (1·439 Å) is in very good agreement with the value [1·436(6) Å] reported recently for a bond in a similar situation in 2-formyl-6-dimethylaminopentafulvene for which dipolar character is also claimed.[6] Reference to tables of standard bond lengths[7] allows one to speculate that population densities of the order of 30—35% (III), 20—30% (IV), and 40—45% (V) would satisfactorily account for the bond-length distribution in and around the five-membered ring.

The oxygen atom has interacted appreciably with the arsenic to distort the tetrahedral-type geometry implied in (III) and (IV) towards a trigonal bipyramidal configuration with C(51) and O at the vertices [angle C(51)–As–O is 175·6(1)°] and C(1), C(41), C(61) at the equator. The As $\cdots$ O distance, 2·770 Å, is considerably less than the sum of the appropriate van der Waals radii (3·40 Å) but is much greater than typical covalent As^+–O distances (1·70 Å).[8] As a result of this interaction the three As–C-(phenyl) distances are longer than normal, the bond [As–C(51)] directly opposite the oxygen atom appreciably so, and bond angles C(1)–As–C(41), C(1)–As–C(61), and C(41)–As–C(61) are splayed out (Figure 2).

Triphenylarsonium 2-acetyl-3,4,5-triphenylcyclopentadienylide $C_{43}H_{33}OAs$, F.W. = 640·7, orthorhombic, a = 15·353(2), b = 24·377(3), c=17·361(2) Å. Space group $Pbca$. Intensity data were collected on a Hilger and Watts Y290 computer controlled 4-circle diffractometer. 4053 independent reflexions were measured, of which 2977 were considered observed and subsequently used in structure solution and refinement. The structure was solved by the heavy-atom method and refined by least-squares methods with weights derived from the counting statistics. The thirty-three hydrogen atoms were located from a difference synthesis and included in all structure factor calculations with an overall isotropic thermal parameter but not refined; all other atoms were refined anisotropically. At the conclusion of the refinement R is 0·042.

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