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MOLECULAR STRUCTURE OF 2-TROPONYLETHOXYCARBONYLMETHYLENETRIPHENYLPHOSPHONIUM BETAINE

Isao Kawamoto, Tadashi Hata, Yukichi Kishida, and Chihiro Tamura
Central Research Laboratories, Sankyo Co., Ltd.
Hiromachi, Shinagawa-ku, Tokyo, Japan

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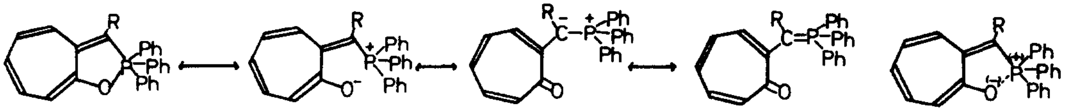
It is known that pentacovalent phosphoranes having positive chemical shifts (+32.1∼ +89 ppm relative to 85% H_3PO_4) in P^{31} nmr spectrum have the trigonal bipyramidal phosphorus.[1, 2a-d] On the course of our chemical and crystallographic investigations,[3] we reported the structure of 2-troponylcyanomethylenetriphenylphosphonium betaine (Ia), which was characterized by a negative chemical shift (-6.8 ppm relative to 85% H_3PO_4), wherein the phosphorus atom was close to the center of a tetrahedral configuration. Our attention was directed to the geometry of the phosphorus atom in connection with the chemical shift in P^{31} nmr spectrum. A very interesting finding is that even 2-troponylethoxycarbonylmethylenetriphenylphosphonium betaine (Ib) which has a positive chemical shift (+66.9 ppm relative to 85% H_3PO_4), does not form the P-O covalent bond and the geometry of the phosphorus atom is close to the trigonal bipyramidal structure.

Investigated Ib (yellow in colour) exhibited: mp 182-3° C; $C_{29}H_{25}O_3P$ (based on mass and analytical data); IR ν(nujol) 1674, 1586, 1502 cm^{-1}; UV λ max (EtOH) 266 (log ε = 4.27), 272 (log ε = 4.27), 403 (log ε = 3.99), 463 (log ε = 3.96) mμ; H^1 nmr ($CDCl_3$) δ ppm, 6.23-7.93 (m, 20H), 3.53 (q, 2H, J = 7.5 Hz), 0.82 (t, 3H, J = 7.5 Hz); P^{31} nmr ($CDCl_3$, vs. 85% H_3PO_4) δ P^{31} = +66.9 ppm.

X-ray diffraction studies of Ib showed it to be orthorhombic, space group $Pna2_1$ with unit cell dimensions a = 16.94, b = 8.79, c = 15.71 Å, V = 2339.26 $Å^3$, Z = 4, Dcalc. = 1.29 gcm^{-3}, Dobs. = 1.27 gcm^{-3}. A total of 1883 three-dimensional intensity data below 2θ = 60° was collected on a Rigaku autodiffractometer by the θ-2θ scan method with Mo-Kα radiation. The structure was solved by the heavy atom technique using the phosphorus atom. The final atomic parameters refined by the least-squares procedures are shown in Table 1. The R factor reached to 0.071.

Figure 1 shows the molecule projected along the a axis. Compound Ib does not form the P-O covalent bond, but evidently there is some strong interaction[4] between the phosphorus and oxygen atoms since the intramolecular P(2)---O(1) distance of 2.14 Å is cosiderably longer than the P-O(apical) covalent bond in oxyphosphoranes (1.76-1.79 Å),[2a-d] and is shorter than that found in Ia (2.36 Å). Furthermore the intramolecular P(2)-O(13) distance, 3.05 Å, lies below the sum of the van der Waals radii (3.30 Å). The bond lengths of C(10)-O(1) and P(2)-C(3) are 1.27 and 1.76 Å, which are significantly longer than those found in Ia, 1.22 and 1.70 Å, respectively. These interesting observations suggest that the resulting P---O distance may be regarded as "bonding betaine (V)[5]" which would be stabilized by a resonance hybrid between the covalent(II) and ionic (I) forms among these structures.[6] In other systems, short S---O intramolecular distances were observed in homologues of thio-thiophthene.[7]



II I a R=CN III IV V
b R=COOEt

The phosphorus atom deviates 0.281 Å from the equatorial plane (C(3), C(16) and C(22)), while that in Ia deviates 0.371 Å. The φee angles in the phosphorus atom are 121.0°, 120.4°, and 111.4°, and the φae angles are 100.5°, 102.8°, and 93.4°. The mean angle of φee is 117.6°, and that of φae is 98.9°. These values indicate that the phosphorus atom is located closer to the center of a trigonal bipyramid than in the case of Ia as shown in Figure 2.

The heptafulvene moiety (C(3)~C(10)) in this compound is planar and the maximum deviation from the least-squares plane is 0.01 Å, and the exocyclic internal rotation angle between C(3) and C(4) atoms is 11.1°.

The structure determination of some other derivatives having positive

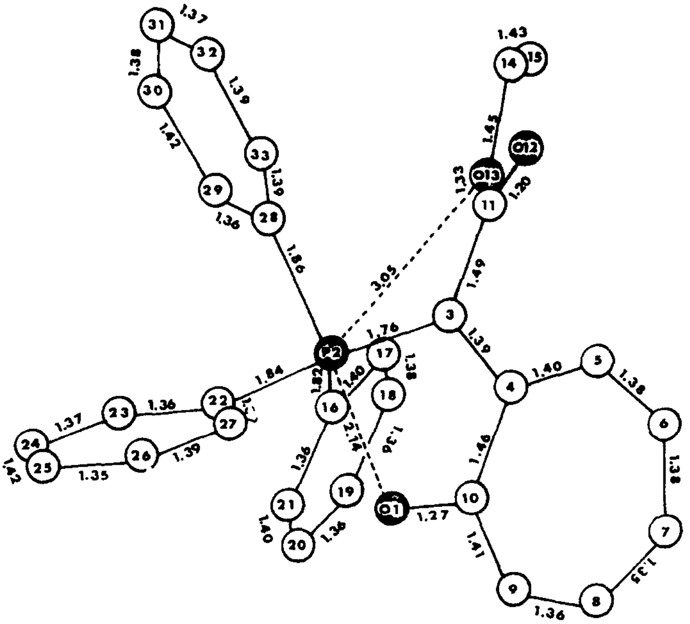


Figure 1. The 2-troponylethoxycarbonylmethylenetriphenylphosphonium betaine molecule projected along the a axis.

Table 1. Atomic fractional coordinates with estimated standard deviations in parentheses.

ATOM	X/a	Y/b	Z/c
O 1	.0541(4)	-.0669(7)	.5532(4)
P 2	.0224(1)	.1468(2)	.4970(2)
C 3	.0697(5)	.2109(8)	.5903(5)
C 4	.1122(5)	.1097(8)	.6409(5)
C 5	.1588(6)	.1567(10)	.7095(6)
C 6	.2027(6)	.0729(13)	.7670(6)
C 7	.2146(6)	-.0821(13)	.7731(7)
C 8	.1844(6)	-.1899(11)	.7217(8)
C 9	.1350(6)	-.1784(11)	.6541(7)
C10	.1007(4)	-.0488(9)	.6160(5)
C11	.0586(5)	.3720(9)	.6164(5)
O12	.1101(4)	.4551(7)	.6417(5)
O13	-.0165(4)	.4148(7)	.6126(4)
C14	-.0347(7)	.5738(12)	.6269(9)
C15	-.1177(8)	.5852(16)	.6412(11)
C16	-.0764(4)	.0667(9)	.5007(6)
C17	-.1370(6)	.1508(12)	.5391(6)
C18	-.2125(6)	.0915(14)	.5460(8)
C19	-.2263(6)	-.0524(14)	.5176(7)
C20	-.1675(6)	-.1349(13)	.4812(7)
C21	-.0913(6)	-.0764(12)	.4720(7)
C22	.0803(5)	.0651(9)	.4092(5)
C23	.0461(5)	.0408(11)	.3322(6)
C24	.0888(8)	-.0127(15)	.2644(7)
C25	.1706(8)	-.0408(14)	.2750(8)
C26	.2038(6)	-.0174(15)	.3521(9)
C27	.1602(6)	.0365(13)	.4208(6)
C28	.0068(5)	.3305(9)	.4408(5)
C29	-.0594(5)	.3676(11)	.3964(6)
C30	-.0646(6)	.5028(14)	.3475(8)
C31	-.0003(7)	.5982(11)	.3435(7)
C32	.0677(6)	.5613(11)	.3854(7)
C33	.0713(5)	.4257(11)	.4308(5)

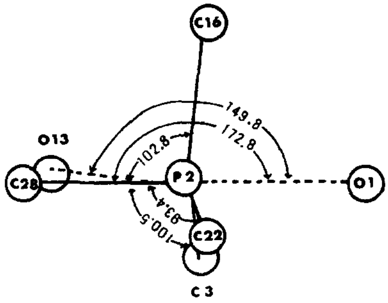


Figure 2. Projection of the atoms (C(3), C(22), C(28), and O(13)) on the plane (O(1)-P(2)-C(16)).

chemical shifts in P^{31} nmr spectrum is also in progress.

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