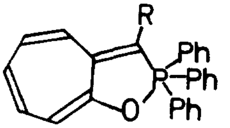
Tetrahedron Letters No. 26, pp. 2417-2420, 1971. Pergamon Press. Printed in Great Britain.

MOLECULAR STRUCTURE OF
2-TROPONYLCYANOMETHYLENETRIPHENYLPHOSPHONIUM BETAINE

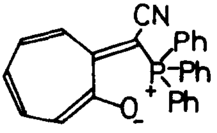
Isao Kawamoto, Tadashi Hata, Yukichi Kishida, and Chihiro Tamura
Central Research Laboratories, Sankyo Co., Ltd.
Hiromachi, Shinagawa-ku, Tokyo, Japan

(Received in Japan 19 May 1971; accepted in UK for publication 25 May 1971)

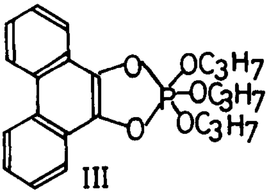
Reactions of 2-chlorotropone with phosphonium ylides gave either 1,2-cycloheptoxaphospholes (I), which were characterized by positive chemical shifts in the P^{31} n.m.r. spectrum (between +34.6 and +66.9 p.p.m. relative to 85% H_3PO_4), or 2-troponylcyanomethylenetriphenylphosphonium betaine (II), which was characterized by a negative chemical shift(-6.8 p.p.m. relative to 85% H_3PO_4).[1]



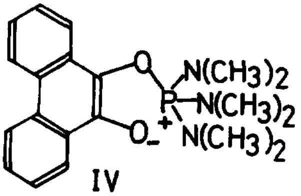
I R=H. CH_3.COOEt



II



III



IV

The structure determination by X-ray analysis of a pentaoxyphosphorane (III) having a positive chemical shift in the P^{31} n.m.r. spectrum has been previously reported.[2a-c] However, X-ray analysis of a dipolar ion (IV) having a negative chemical shift has not yet been performed.[2d] The geometry of the phosphorus atom in compounds I and II, corresponding to III and IV, is of interest in connection with the chemical shift in the P^{31} n.m.r. spectrum. We wish to report the crystal and molecular structure of the phosphonium betaine determined by X-ray analysis.

Investigated 2-troponylcyanomethylenetriphenylphophonium betaine II (orange-red in colour) was: mp 221°C; $C_{27}H_{20}ONP \cdot CH_3OH$; IR ν(nujol) 3410, 2150, 1590, 1506 cm^{-1}; UV λ max (EtOH) 267(shoulder log ε=4.41), 273 (log ε=4.43), 390 (log ε=4.10), 467 (log ε=4.21) mμ; n.m.r. ($CDCl_3$) δ p.p.m., 6.43-7.83 (m), 3.41 (s, OCH_3), 1.29 (s, OH).

X-ray diffraction studies of II showed it to be triclinic, space group $P\bar{1}$ with unit cell dimensions a=9.68, b=16.14, c=9.95Å, α=52°37', β=108°9', γ=116°47', V =1101.0$Å^3$, Z=2. A total of 3609 independent structure amplitudes were derived from visually estimated intensities recorded by equiinclination Weissenberg photography hk0-9 layers. The structure was solved by the direct interpretation of three dimensional Patterson function in the space group of $P\bar{1}$ and simultaneous use of the heavy atom (phosphorus) method. Atomic parameters refined by least-squares procedures are shown in Table 1. The present conventional R is reached to 0.148.

Table 1. Atomic fractional coordinates

ATOM	X/a	Y/b	Z/c	ATOM	X/a	Y/b	Z/c
O 1	.1864	.3604	-.0827	C18	.2355	.1548	.0101
P 2	.0025	.1802	.0631	C19	-.1436	.0419	.1795
C 3	-.0015	.2449	.1463	C20	-.2989	.0291	.1428
C 4	.0974	.3521	.1038	C21	-.4111	-.0717	.2292
C 5	.0868	.3947	.1826	C22	-.3697	-.1619	.3539
C 6	.1738	.4949	.1654	C23	-.2168	-.1520	.3910
C 7	.2935	.5801	.0714	C24	-.1018	-.0515	.3060
C 8	.3617	.5900	-.0375	C25	-.0752	.2223	-.1473
C 9	.3202	.5171	-.0808	C26	-.1165	.1499	-.1936
C10	.2043	.4110	-.0210	C27	-.1791	.1774	-.3554
C11	-.1056	.1814	.2688	C28	-.2080	.2736	-.4703
N12	-.1871	.1336	.3705	C29	-.1680	.3432	-.4206
C13	.1781	.1551	.1176	C30	-.1069	.3163	-.2586
C14	.2586	.1358	.2710				
C15	.3929	.1131	.3217	MeOH			
C16	.4472	.1135	.2140	C31	.3015	.4097	-.4066
C17	.3668	.1329	.0605	O32	.3525	.4579	-.3519

Figure 1 shows the molecule projected along the a axis. The intramolecular P------O distance, 2.36Å, is significantly longer than that found in III (1.76Å), and lies below the sum of the van der Waals radii (3.30Å).[3] Evidently this compound II does not form the P-O bond, but there is an appreciable interaction between the phosphorus and the oxygen atoms in this compound. In spite of disappearance of the $\nu_{c=o}$ absorption in the IR spectrum, the C-O bond length (1.22Å) does not differ significantly from that found in 2-chlorotropone (1.23Å).[4] Further experimentation is necessary to explain fully this interesting observation.

The maximum deviation of the atoms from the least-squares plane through O(1)-N(12) is 0.09Å. The heptafulvene moiety in this compound is approximately planar, as may be expected from the chemical formula.[5]

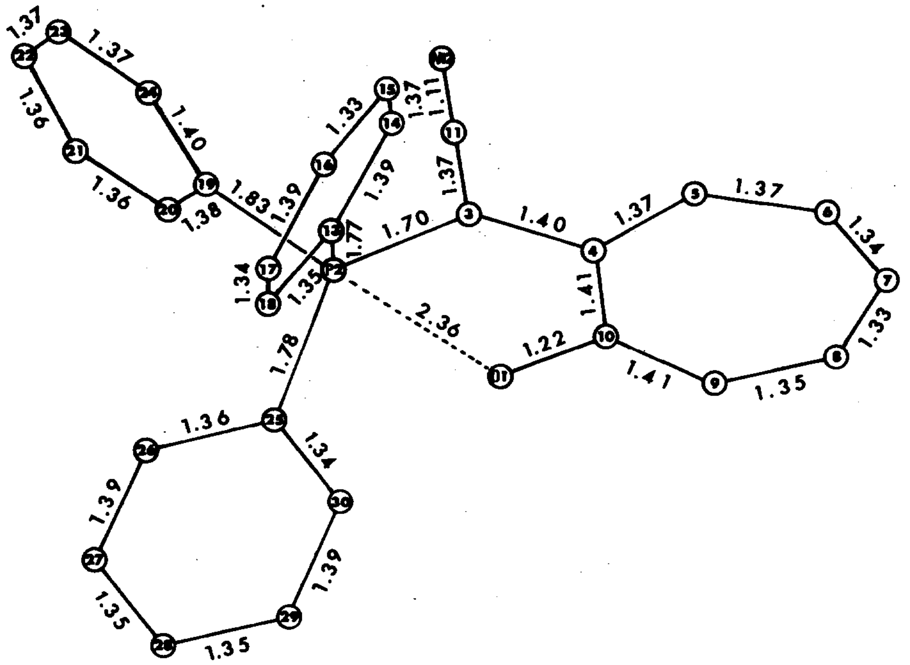


Figure 1. The 2-troponylcyanomethylenetriphenylphosphonium betaine molecule projected along the a axis.

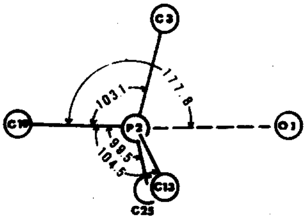


Figure 2. Projection of the atoms (C(13), C(25)) on the plane(O(1)-P(2)-C(3)-C(19)).

Figure 2 shows that the phosphorus atom lies between the center of a trigonal bipyramidal configuration(C(19) and O(1) in apical positions, C(3), C(13) and C(25) in equatorial positions) and the center of a tetrahedral configuration, and is somewhat close to the center of a tetrahedral configuration. The C(equatorial)-P-C(equatorial), ϕ_{ee}, angles are 112°, 116° and 119°, and the C(apical)-P-C-(equatorial), ϕ_{ae}, angles are 100°, 105° and 103°. The mean angle of ϕ_{ee} is 115.7°, and ϕ_{ae} is 102.6° (trigonal bipyramid 120°, 90°; tetrahedral $109^{\circ}28'$, $109^{\circ}28'$; respectively). The apical P(2)-C(19) bond, 1.83Å, is slightly longer than the two equatorial bonds (P(2)-C(13), 1.77Å, and P(2)-C(25), 1.78Å, respectively). On the other hand, the bond length of P(2) - C(3), 1.70Å, is shorter than those in the other two equatorial positions, and is analogous to that found in phosphonium ylides.[6]

The geometry of phosphorus atom seems to be related to the chemical shift in the P^{31} n.m.r. spectrum. A detailed account of this work will be presented in the near future.

We are thankful to Nichiden Varian Co., Ltd. for measurement of the P^{31} n.m.r. spectra. We are also indebted the laboratory technicians for measurement of mass, IR, UV and n.m.r. spectra.

References

1. I. Kawamoto, Y. Sugimura, and N. Soma, Bull. Chem. Soc. Japan, in preparation.
2. (a) W.C. Hamilton, S.J. LaPlaca, and F. Ramirez, J. Am. Chem. Soc., **87**, 127 (1965); (b) W.C. Hamilton, S.J. LaPlaca, F. Ramirez, and C.P. Smith, ibid., **89**, 2268 (1967); (c) R.D. Spratley, W.C. Hamilton, and J. Landell, ibid., **89**, 2272 (1967); (d) F. Ramirez, A.V. Patwardhan, H.J. Kugler, and C.P. Smith, ibid., **89**, 6276 (1967).
3. L. Pauling, "The nature of the chemical bond", 3rd ed. Ithaca, New York: Cornell University Press.
4. E.J. Forbes, M.J. Gregory, T.A. Hamor, and D.J. Watkin, Chem. Comm., **1966** 114.
5. H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, Bull. Chem. Soc. Japan, **39**, 2322 (1966).
6. A.J. Speziale and K. W. Ratts, J. Am. Chem. Soc., **87**, 5603 (1965).