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THE 2-H-ISOPHOSPHINDOLINE-1,3-DIONE ION:
THE PHOSPHORUS ANALOGUE OF THE PHTHALIMIDE ANION.

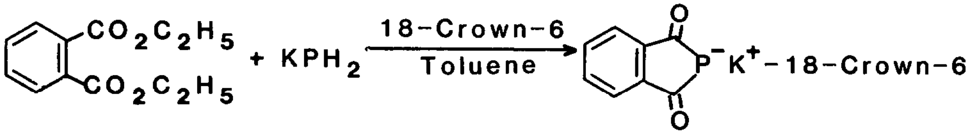
Charles L. Liotta*, Mark L. McLaughlin, Donald G. Van Derveer and Brian A. O'Brien

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Abstract: Reaction of potassium dihydrogenphosphide with diethyl phthalate produces the potassium 18-crown-6 complex salt of the 2H-isophosphindoline-1,3-dione ion (1). The structure of 1 is discussed.

Whereas it is well-known that an electron pair associated with a nitrogen atom is appreciably delocalized when attached directly to a carbonyl function, very little information is known regarding the phosphorus counterpart. We have previously reported the synthesis and chemical properties of benzoylphosphine and benzoylmethylphosphine.[1] Variable temperature ^1H NMR analysis of these molecules suggested no significant barrier to rotation about the carbonyl carbon-phosphorus bond and implied that delocalization of the electron pair onto the carbonyl is small. This lack of significant delocalization was also reflected in the ease with which bimolecular decompostion of these systems takes place to form dibenzoylphosphine derivatives.[1] In an attempt to more fully understand the bonding in these systems, we have now synthesized the potassium 18-crown-6 complex salt of 2H-isophosphindoline-1,3-dione ion (1)- the phosphorus analogue of the phthalimide anion. The structure of 1 has been determined by means of spectroscopic measurements and single crystal X-ray analysis. In addition, semi-empirical molecular orbital calculations (MINDO/3 and Extended Huckel) have been carried out in an attempt to understand the electronic properties of 1.

Compound 1 is readily prepared by reaction of KPH_2 with diethyl phthalate in the presence of a molar equivalent of 18-crown-6. (Reaction 1).



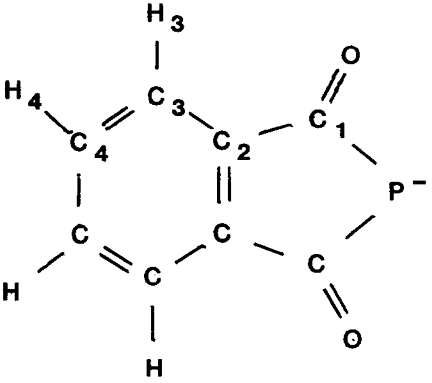
(1)

1

To a well-stirred mixture containing toluene (200 ml), 18-crown-6 (12.01 g, 0.04542 mol) and KPH_2 (3.22 g, 0.0447 mol), under an atmosphere of dry, oxygen-free N_2, is added diethyl phthalate (12.48 g, 0.05616 mol) at room temperature. Within minutes, the reaction mixture undergoes a series of color changes- red to burgundy to dark raspberry. After stirring for 26 hours, isooctane (100 ml) is added and the mixture suction filtered and washed with hexane. A 75.1 % yield (15.67 g, 0.03359 mol) of microcrystalline 1 is obtained. Analytically pure samples may be obtained by recrystallizing from acetonitrile-ethyl ether.[2,3] Pertinent ^{13}C, ^{31}P and ^1H NMR data for the anionic portion of 1 are summarized in Table 1. The assigned chemical shifts are consistent with the reported structure. It is interesting to note that, although the phosphorus atom couples with the adjacent carbonyl carbons and the C_3 positions of the benzene ring, there is no observed coupling with the C_2 and C_4 positions.

Table 1: NMR Data for the Anionic Portion of 1

	Chemical Shifts, ppm	Coupling Constants, Hz
^{13}C NMR		
C_1	189.20(d)	$J_{C(1)P} = 59.5$
C_2	103.50(s)	
C_3	75.20(dd)	$J_{C(3)H(3)} = 100$; $J_{C(3)P} = 4.6$
C_4	89.73(d)	$J_{C(4)H(4)} = 96$
^{31}P NMR	43.43(s)	
^{1}H NMR		
H_3, H_4	7.28(s)	



Compound 1 is a crystalline, maroon solid which is stable to air oxidation, but is slightly hygroscopic readily forming a monohydrate. It is soluble in acetonitrile and dimethylsulfoxide, producing a dark raspberry colored solution. Surprisingly, 1 dissolves in protic solvents, such as ethanol and water, without reaction. This behavior is in sharp contrast to that seen for most other phosphorus(III) anions, which are readily protonated by such solvents.[4] The decreased reactivity at phosphorus is attributed to the electron withdrawing sigma inductive effect of the two carbonyl moieties. That delocalization is not important is supported by the structural parameters derived from a single crystal X-ray analysis performed on the monohydrate. The results are summarized in Figure 1.

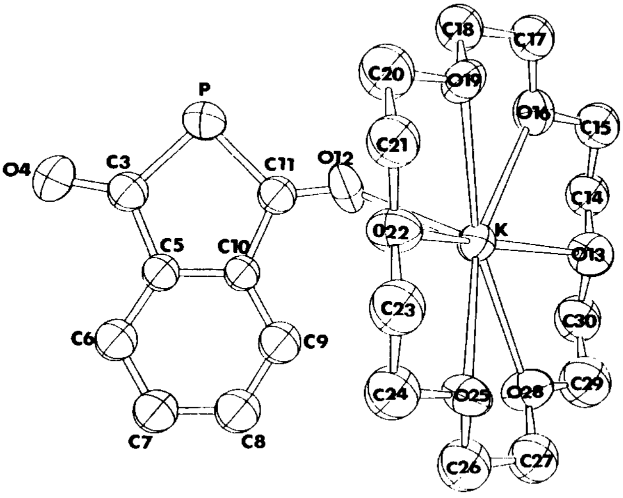
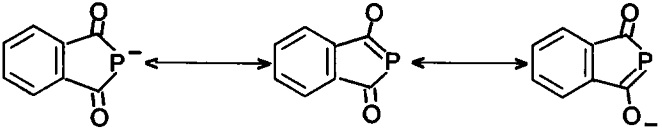


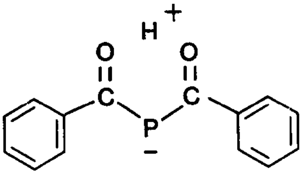
Figure 1. An ORTEP view of 1 with 50% probability ellipsoids.[5] Selected bond lengths (Å): $K-O_{12}=2.723(8)$, $K-O_{crown}=2.846(av)$, $C_{11}-O_{12}=1.22(1)$, $P-C_3=1.80(1)$, $P-C_{11}=1.79$. Selected angles (°): $C_3-P-C_{11}=90.3(5)$, $P-C_3-C_5=112.3(7)$, $C_5-C_{10}-C_{11}=113.2(8)$.

The C-P-C bond angle is approximately 90°. The P-C bond lengths of 1.80 Å and the C-O bond lengths of 1.21 Å are essentially the same as those of the "normal" bond lengths for a P-C single bond (1.83 Å)[6] and a C-O double bond (1.21 Å), respectively. If lone pair delocalization was important, it would be anticipated that the C-P bond length would be substantially shorter and the C-O bond length longer than those of the corresponding "normal" bond lengths. This is not the case. Thus, resonance structures of the type illustrated in 1a and 1b appear to make little contribution to the bonding in 1.



1a 1b

A striking feature of the X-ray structure is that the potassium-crown complex is not proximate to the phosphorus but to the carbonyl oxygen atoms of two molecules of 1. This particular structural feature is analogous to those reported for dibenzoylphosphine[1], diacetylphosphine[7], and dipivaloylphosphine[7] in that the "acidic" proton was found to be located between the carbonyl oxygens and not at the phosphorus (2).



2

MINDO/3 calculations were performed using the atomic coordinates derived from the X-ray structure (Figure 1). The energies of the two highest occupied molecular orbitals are -3.97 and -4.18 ev. Since most of the orbital density for each of these molecular orbitals is located at phosphorus, these correspond to the two "lone pairs" at this atomic center.[8] The energies for the two lowest unoccupied molecular orbitals are +4.08 and +4.52 ev. Thus, according to these semi-empirical calculations, the lowest energy transitions (symmetry forbidden and allowed) range from 8.0 to 8.5 ev. Experimentally, the lowest energy transition corresponds to approximately 2.5 ev (506 nm).[2] It should be emphasized that MINDO/3 calculations do not incorporate d functions in the basis set. Since these functions would be expected to contribute significantly to the electronic description of molecules containing second row elements, the results are not surprising. Qualitative perturbation arguments suggest that the incorporation of d orbitals (of proper symmetry) on the phosphorus would lower the energies of the virtual orbitals to a greater extent than those of the occupied molecular orbitals, thus narrowing the energy gap. Indeed, employing Extended Huckel calculations incorporating d-functions in the basis set narrows the energy differences between the high-lying filled molecular orbitals and the low lying virtual molecular orbitals to 2.05 - 3.39 ev in amazing agreement with experiment. At this juncture, therefore, it would appear that the origin of the maroon color of 1 may lie in an electronic transition between one of the occupied molecular orbitals associated with the phosphorus "lone pairs" and a virtual pi orbital containing a substantial d coefficient at phosphorus.

In conclusion, it has been found (1) that potassium dihydrogen phosphide in the presence of one equivalent of 18-crown-6 readily reacts with diethyl phthalate to produce the crown complex salt of the 2-H-isophosphindoline-1,3-dione ion(1)- the phosphorus analogue of the phthalimide anion, (2) that delocalization of a phosphorus lone pair onto the adjacent carbonyl groups is small as inferred from the C-P bond lengths derived from the single crystal X-ray analysis of 1, and (3) that the origin of the maroon color of 1 may lie in an electronic transition involving a virtual orbital containing substantial d character at phosphorus.

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References

1. C. L. Liotta, M. L. McLaughlin and B. A. O'Brien, Tetrahedron Letters, 0000, 1984.

2. Melting point (sealed capillary under N_2): 159 - 161° C. Elemental analysis: Calculated for $C_{20}H_{28}KO_8P$: C, 51.48 %; H, 6.06 %; Found: C, 51.59 %; H, 6.10 %. IR(KBr pellet; cm^{-1}): 3115-2990 (w), 2940 (m, shoulder), 2897 (s), 2865 (m, shoulder), 2820 (m), 2787 (w), 2740 (w), 2705 (w), 2680 (vw), 1968 (w), 1830 (w), 1665 (w), 1595 (m), 1540 (s, shoulder), 1525 (vs), 1510 (s, shoulder), 1468 (m), 1450 (m), 1430 (m), 1395 (w), 1350 (s), 1325 (m), 1281 (m), 1246 (m), 1235 (w, shoulder), 1190 (w), 1180 (m), 1157 (w), 1130 (m, shoulder), 1100 (vs), 955 (vs), 881 (w), 861 (m), 830 (m), 775 (m), 727 (w). UV-Vis (H_2O; nm, extinction coefficient): 193 (17,000, broad), 224 (18,600, broad), 273 (11,700, broad), 283 (15,200), 290 (12,900, shoulder), 335 (2240), 350 (4010, shoulder), 506 (1180, broad).

3. Potassium 2-carboethoxybenzoate was also produced in small quantities: Melting point (sealed capillary under N_2): 144.5 - 145.3°C; Elemental Analysis: Calculated for $C_{22}H_{33}O_{10}K$: C, 53.20%; H, 6.71%; Found: C, 52.96%, H, 6.78%. Since water was carefully excluded from this reaction, it is believed that this product arose from displacement on ethyl of 2-carboethoxybenzoate via an S_N2 process.

4. Exposure of aqueous solutions of 1 to air causes the loss of the maroon color within one hour. In the absence of air, aqueous solution of 1 are stable for periods up to one month.

5. The compound crystallized in the monoclinic space group C_c with a=13.804(5)Å, b=11.892(3)Å, c=15.558(4)Å, β=111.42(2)°, and Z=4. Data were collected on a Syntex $P2_1$ diffractometer using θ-2θ scans. Full-matrix least-squares refinement using SHELX-76 gave a final R=0.078.

6. J. Emsley and D. Hall, The Chemistry of Phosphorus, Harper and Row, London, 1976; p. 34.

7. V. G. Becker, M. Rossler and W. Uhl, Z. Anorg. Allg. Chem., 473, 7, (1981); V. G Becker, M. Rossler and W. Uhl, ibid., 495, 73 (1982); V. G. Becker and H. P. Beck, ibid., 430, 77 (1977).

8. The molecular orbital at -3.97 ev is associated with the out-of-plane ($p\pi$-type) lone pair, while the molecular orbital at -4.18 ev is associated with the in-plane (sp-σ-type) lone pair.

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