

Study of Aromaticity in Phosphorus Analogues of the Cyclopentadienyl Anion

E. J. Padma Malar

Department of Physical Chemistry, University of Madras, Guindy Campus, Madras 600 025, India

Received November 26, 1991

Phosphorus analogues of the cyclopentadienyl anion are examined by complete structural optimization using the all-valence electron SCF MO method SINDO1. Optimized geometries obtained with inclusion of d-orbitals on phosphorus show that the ring bond lengths CC, CP, and PP are in the ranges 1.37-1.42 Å, 1.74-1.77 Å and 2.17-2.20 Å, respectively. These values are between those of the bond lengths of the respective single and double bonds and are in close agreement with the observed values of the ligated rings in complexes. The bond-order definition of aromaticity, based on the ring-current concept, reveals that the phosphorus analogues of cyclopentadienyl anion retain $\geq 86.0\%$ aromaticity relative to the carbocyclic system $C_5H_5^-$. A rather dramatic result is that the pentaphosphorus analogue P_5^- is as aromatic as the carbocyclic cyclopentadienyl anion.

Introduction

Cyclopentadienyl anion (C_p^-) and arenes play a key role as ligands in organometallic chemistry.¹ Recent studies by Baudler et al. reveal that pentaphosphacyclopentadienyl anion P_5^- , which is iso π -electronic with C_p^- , is aromatic and involves bonding with a number of transition metals.^{2,3} The phosphorus analogue of ferrocene, "decaphosphaferrocene FeP_{10} " is characterized, and spectral studies show that the aromatic P_5^- ring is intact in FeP_{10} .² In recent years, various experimental studies²⁻⁵ have characterized the mono- and polyphosphorus analogues of C_p^- , $(C_nH_nP_{5-n})^-$ where $n = 0-4$. These phosphorus heterocycles form stable complexes with iron and other transition metals.^{2,6-10} These findings are of immense interest as they illustrate the potential of phosphorus heterocycles of C_p^- as ligands and can lead to a wealth of interesting transition-metal complexes parallel to their organic counterparts.

Even though the role of heterocycles of C_p^- with mono and poly in-ring phosphorus atoms as ligands is established through the well-documented mono- and polyphosphaferrocenes,^{2,6-11} the analogous aza complexes are as yet unknown except for the monoazaferrocene.¹² Such a

situation is rather intriguing particularly from the long-held viewpoint that compounds containing phosphorus-carbon $3p_\pi-2p_\pi$ bonds would be inherently unstable.¹³ However, the experimental studies indicate that the introduction of phosphorus atoms in the cyclopentadienyl anion ring does not affect the ligating characteristics of the aromatic ring to any significant extent.^{2,6-11} In order to understand the interesting chemistry of these ligand species it is essential to know their electronic properties, molecular geometries, degree of aromaticity etc. The present understanding of these characteristics of the mono- and polyphosphacyclopentadienyl anions is very limited with a few theoretical studies on the phospholyl anion and P_5^- .¹⁴ In view of the increase in the number of complexes with mono- and polyphosphorus analogues of C_p^- ligands, it is of fundamental interest to understand the electronic properties, particularly the degree of aromaticity, in these species. The present work is the first systematic study of aromaticity in the phosphorus analogues of cyclopentadienyl anion aimed at explaining the capability of these species to participate as ligands in the formation of complexes. The degree of aromaticity is examined theoretically at the equilibrium molecular geometries.

Computational Procedure

The phosphorus analogues of C_p^- are studied by the all-valence SCF MO method SINDO1 which was developed by Jug and co-workers.¹⁵ The SINDO1 approach was parametrized to achieve high accuracy in molecular electronic structure calculations.¹⁵ This method makes use of symmetrically orthogonalized AOs, takes into account the core-valence electron interactions through pseudopotentials,^{15a} and includes d-orbitals in the basis set of second-row atoms.^{15b} The importance of including d-orbitals in the basis set of second-row atoms, such as phosphorus atoms in the present study, has been stressed by numerous earlier studies.¹⁶⁻¹⁸ Further, SINDO1 incorporates the diffuse nature of basis

(1) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*; VCH: Verlagsgesellschaft (FRG), 1989.

(2) Baudler, M.; Akpogloglou, S.; Ouzounis, D.; Wasgestian, F.; Meinigke, B.; Budzikiewicz, H.; Münster, H. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 280.

(3) Baudler, M.; Duster, D.; Ouzounis, D. *Z. Anorg. Allg. Chem.* 1987, 544, 87.

(4) Braye, E. H.; Capiere, I.; Saussez, R. *Tetrahedron* 1971, 27, 5523.

(5) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Hildebrand, V.; Westerhausen, M. *Phosphorus Sulfur Relat. Elem.* 1987, 30, 349 and references cited therein.

(6) (a) Mathey, F.; Mitschler, A.; Weiss, R. *J. Am. Chem. Soc.* 1977, 99, 3537; *Ibid.* 1978, 100, 5748. (b) Mathey, F. *J. Organomet. Chem.* 1977, 139, 77.

(7) De Lauzon, G.; Deschamps, B.; Fisher, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* 1980, 102, 994.

(8) (a) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Organomet. Chem.* 1988, 340, C37; (b) *J. Chem. Soc., Chem. Commun.* 1987, 1146. (c) Hu, D.; Schäufele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 900. (d) Driess, M.; Hu, H.; Pritzkow, H.; Regitz, M.; Roßch, W.; Schäufele, H.; Zenneck, V. *J. Organomet. Chem.* 1987, 334, C35.

(9) (a) Scherer, O. J.; Schwab, J.; Wolmershaeuser, G.; Kaim, W.; Gross, R. *Angew. Chem.* 1986, 98, 349. (b) Scherer, O. J.; Brueck, T.; Wolmershaeuser, G. *Chem. Ber.* 1988, 121, 935.

(10) Nixon, J. F. *Chem. Rev.* 1988, 88, 1327 and references cited therein.

(11) Quin, L. D.; Orton, W. L. *J. Chem. Soc., Chem. Commun.* 1979, 401.

(12) King, R. B.; Bisnette, M. B. *Inorg. Chem.* 1964, 3, 796 and references cited therein.

(13) Corbridge, D. E. C. *Phosphorus*; Elsevier Scientific: Amsterdam, 1980.

(14) (a) Kaufmann, G.; Mathey, F. *Phosphorus* 1974, 4, 231. (b) Guimon, C.; Pfister-Guillouzo, G.; Mathey, F. *Nouv. J. Chim.* 1979, 3, 725. (c) Kotic, N. M.; Fenske, F. *Organometallics* 1983, 2, 1008. (d) Baird, N. C. *Can. J. Chem.* 1984, 62, 341. (e) Gimarc, B. M. *Pure Appl. Chem.* 1990, 62, 423. (f) Hamilton, T. P.; Schaefer, H. F. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 485.

(15) (a) Nanda, D. N.; Jug, K. *Theoret. Chim. Acta* 1980, 57, 95. (b) Jug, K.; Iffert, R.; Schulz, J. *Int. J. Quantum Chem.* 1987, 32, 265. (c) Iffert, R.; Jug, K. *Theoret. Chim. Acta* 1987, 72, 373.

(16) (a) Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. R. *J. Am. Chem. Soc.* 1979, 101, 2002. (b) Baird, N. C.; Taylor, K. F. *J. Comput. Chem.* 1981, 22, 225. (c) Mezey, P. G.; Haas, E.-C. *J. Chem. Phys.* 1982, 77, 870. (d) Mayer, I. *THEOCHEM* 1987, 149, 81.

Table I. Geometries and Energies of Model Systems Containing Phosphorus

| species | bond length (Å) | | | energy (au) | | electron affinity (eV) | | |
|-----------------|-----------------|------------------------|--------------------|---------------------|------------------------|------------------------|------------------------|------------------------|
| | SINDO1 | ab initio ^a | exptl | SINDO1 ^b | ab initio ^a | SINDO1 | ab initio ^a | exptl |
| PH ⁻ | 1.385 | 1.433 ^c | 1.407 ^d | -7.0588 | -341.3776 ^e | | | |
| PH | 1.413 | 1.415 ^c | 1.421 ^f | -7.0230 | -341.3644 ^e | 0.97 | 0.36 ^e | 1.03 ^d |
| PF ⁻ | 1.609 | 1.724 ^g | | -30.3992 | -440.4395 ^h | | | |
| PF | 1.577 | 1.620 ^g | 1.590 ⁱ | -30.3459 | -440.4271 ^h | 1.45 | 0.34 ^h | 1.0 ± 0.2 ^a |

SINDO1 (exptl) bond lengths (Å) and bond angles (deg)
 CH₂=PH^j PC 1.651 (1.673); PH 1.431 (1.420); H_{cis} CP 122.0 (124.4); H_{trans} CP 122.1 (118.4); HPC 98.9
 CH₃-PH₂^k PC 1.835 (1.863); PH 1.427 (1.414); H PC 99.3 (97.5); H PH 103.1 (93.4)
 PH=PH PP 2.085; PH 1.425; P PH 95.0
 PH₂-PH₂^k PP 2.303 (2.219); PH 1.425 (1.417); H PH 103.3 (92.0); H PP 94.6 (94.3)

^a Reference 24a. ^b The total energies given by the SINDO1 method are not comparable with the ab initio values due to the semiempirical nature of SINDO1. However, relative energies predicted by SINDO1 have significance and are comparable with experimental as well as ab initio values. For example, the energy difference between the anionic and neutral species correspond to electron affinity. ^c MP2/6-31G**. ^d Reference 24c. ^e MP4SDTQ/6-31+G**. ^f Reference 24b. ^g MP2/6-31G*. ^h MP4SDTQ/6-31+G*. ⁱ Reference 24d. ^j Experimental data in: Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* 1981, 90, 367. ^k Experimental data in: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619.

Table II. Optimized SINDO1 Geometries of the Various Phosphorus Analogues of Cyclopentadienyl Anion^a

| species | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--|-------------------|-------|-------|-------|-------|-------|-------|
| | Bond Lengths (Å) | | | | | | |
| X ₁ X ₂ | 1.405 | 1.375 | 2.197 | 2.195 | 1.417 | 2.184 | 2.191 |
| X ₂ X ₃ | 1.402 | 1.765 | 1.745 | 1.721 | 1.747 | 2.198 | 2.191 |
| X ₃ X ₄ | 1.749 | 1.749 | 1.405 | 1.767 | 2.182 | 1.738 | 2.191 |
| C ₂ H | 1.073 | 1.076 | | | 1.075 | | |
| C ₃ H | 1.078 | | 1.076 | 1.079 | | | |
| C ₄ H | | 1.075 | 1.078 | | | 1.083 | |
| | Bond Angles (deg) | | | | | | |
| X ₁ X ₂ X ₃ | 114.4 | 117.0 | 94.4 | 97.3 | 119.0 | 102.9 | 108.0 |
| X ₂ X ₃ X ₄ | 108.5 | 94.7 | 115.7 | 124.5 | 105.5 | 101.5 | 108.0 |
| X ₃ X ₄ X ₅ | 94.2 | 116.7 | 120.6 | 96.3 | 90.9 | 131.2 | 108.0 |
| X ₁ C ₂ H | 121.5 | 120.0 | | | 121.0 | | |
| X ₂ C ₃ H | 123.5 | | 124.5 | 117.2 | | | |
| X ₃ C ₄ H | | 121.4 | 118.5 | | | 114.5 | |

^a Numbering system given in Figure 1 is used.

functions in anions by employing charge-dependent orbital exponents.^{15c} In the present study, charge-dependent orbital exponents of all atoms having net negative charges are computed using normalized charges at the optimized geometries as described in method B of ref 15c. The diffuse functions in the anions reduce electronic repulsion and lower the total energy.

The molecular anions under study are examined by complete geometry optimization at the SCF level using the Newton-Raphson procedure. The structures were optimized with tolerance limits for convergence at 0.001 Å for bond lengths and 0.2° for bond angles and dihedral angles. At the optimized geometries, energetics, degree of aromaticity, and other characteristics are examined. The numbering system followed in this work is shown in Figure 1.

Earlier studies¹⁹ with SINDO1 show a significant improvement over other semiempirical methods such as MINDO/3,²⁰ MNDO,²¹

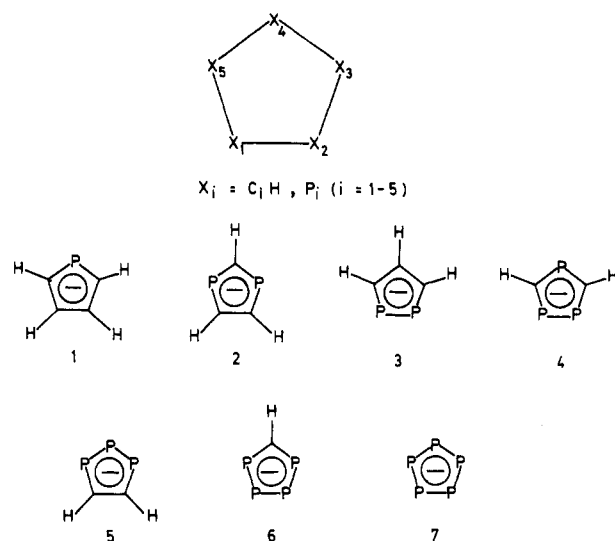


Figure 1. Atomic labeling and numbering used for the phosphorus analogues of cyclopentadienyl anion.

and AM1,²² and the results are closer to experimental observations. Work on a number of sulfur compounds²³ indicates that the

(17) (a) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* 1976, 64, 5142. (b) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1990, 112, 1434 and references cited therein. (c) Pietro, W. J.; Franci, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* 1982, 104, 5039.

(18) (a) Angyan, J. G.; Bonnelle, C.; Daudel, R.; Kucsman, A.; Csizmadia, I. G. *THEOCHEM* 1988, 165, 273. (b) Yadav, A.; Surjan, P. R.; Poirier, R. A. *THEOCHEM* 1988, 165, 297. (c) Smeyers, Y. G.; Randez, J. J.; Randez, F. J.; Haro-ruiz, M. D.; Hernandez-Laguna, A. *THEOCHEM* 1988, 166, 141. (d) Maouche, Y.; Brianso, M. C.; Maouche, B. *THEOCHEM* 1988, 166, 449. (e) Angyan, J. G.; Poirier, R. A.; Kucsman, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* 1987, 109, 2237.

(19) (a) Müller-Remmers, P. L.; Mishra, P. C.; Jug, K. *J. Am. Chem. Soc.* 1984, 104, 2538. (b) Müller-Remmers, P. L.; Jug, K. *J. Am. Chem. Soc.* 1985, 107, 7275. (c) Buas, S.; Jug, K. *J. Am. Chem. Soc.* 1987, 109, 1044. (d) Jug, K.; Iffert, R. *Theoret. Chim. Acta* 1982, 62, 183. (e) Mishra, P. C.; Jug, K. *Theoret. Chim. Acta* 1982, 61, 559. (f) Malar, E. J. P.; Jug, K. *J. Phys. Chem.* 1984, 88, 3508. (g) Malar, E. J. P.; Jug, K. *J. Phys. Chem.* 1985, 89, 5235. (h) Malar, E. J. P.; Jug, K. *Tetrahedron* 1986, 42, 417. (i) Malar, E. J. P.; Chandra, A. K. *J. Phys. Chem.* 1987, 91, 5111. (j) Chandra, A. K.; Malar, E. J. P.; Sengupta, D. *Int. J. Quantum Chem.* 1992, 41, 371.

(20) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, 75, 1285, 1294, 1302, 1307.

(21) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899, 4909. (b) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* 1977, 99, 5231. (c) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* 1978, 100, 58, 777. (d) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* 1975, 97, 1311. (e) Dewar, M. J. S.; Rzepa, H. S.; McKee, M. L. *J. Am. Chem. Soc.* 1981, 100, 3607. (f) Dewar, M. J. S.; McKee, M. L. *J. Comput. Chem.* 1983, 4, 84. (g) Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* 1986, 7, 140.

SINDO1 approach yields results comparable with sophisticated ab initio calculations. However, the reliability of the SINDO1 method for studying molecules containing phosphorus atoms is not established so far. Hence, we have examined model anions PH^- and PF^- and neutral species PH and PF, for which both high-level ab initio data and experimental results are available.²⁴ The doublet ground states of the anions and the triplet ground states of the neutral species are examined by SINDO1 unrestricted Hartree-Fock calculations at the SCF level. The optimized SINDO1 bond lengths and energetics of these systems are compared with ab initio and experimental results in Table I. Geometries of some model compounds containing CP and PP bonds are also compared in Table I. It is seen that the SINDO1 bond lengths agree with the experimental values within an error of 0.03 Å, except for the P-P distance in P_2H_4 which is longer by 0.08 Å. It may be mentioned that the SINDO1 CP and PP lengths are much closer to experimental values than the semiempirical AM1 results²² which show average deviations of 0.125 and 0.223 Å, respectively, for P-C and P-P bonds. The relative energies between the anions and the corresponding neutral species are compared with the experimental electron affinities. The SINDO1 electron affinity of 0.97 eV for PH compares favorably with 1.03 eV obtained from the photoelectron spectrum,^{24c} while the ab initio electron affinity is 0.36 eV.^{24a} This comparative analysis shows that the SINDO1 method is suitable to study the phosphorus analogues of the cyclopentadienyl anion.

Results and Discussion

Molecular Geometries. The optimized geometries of the phosphorus analogues of C_p^- obtained in the present study using the SINDO1 procedure including d-orbitals on phosphorus atoms are shown in Table II. Structural optimization reveals that all the species studied possess planar geometries. Calculations predict that P_5^- exhibits D_{5h} symmetry in agreement with the IR and Raman spectral analyses.² All the remaining anions possess C_{2v} symmetry. It is seen that the CC bonds are in the range 1.37–1.42 Å and are very close to the standard aromatic CC bonds. In the case of phospholyl anion, the SINDO1 calculations with d-orbitals predict that all the CC bond lengths are nearly equal (~ 1.40 Å). This agrees with the observed bond length of 1.41 Å for CC bonds in phosphol-1-yl rings in the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})]$ and $[(\text{CO})_3\text{Mn}[\eta^5\text{-C}_4\text{HMe}_2(\text{COPh})\text{P}]]$.^{6,7} Except for a pair of CP bonds of length 1.721 Å in 1,2,4-triphosphacyclopentadienyl anion, 4, all other CP bond lengths are in the range 1.74–1.77 Å. These SINDO1 values lie between the experimentally observed values of the localized double bond $\text{C}=\text{P}$ (1.66 Å) and the single bond $\text{C}-\text{P}$ (1.83–1.85 Å).¹³ There is a striking agreement between the SINDO1 CP lengths and the crystallographic values of 1.74–1.78 Å observed in $[(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})_2\text{Fe}]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_4\text{H}_2\text{Me}_2\text{P})]$, and $[(\text{CO})_3\text{Mn}[\eta^5\text{-C}_4\text{HMe}_2(\text{COPh})\text{P}]]$.^{6,7} These CP lengths also resemble those found in complexes $[\text{Fe}(\eta^5\text{-C}_2\text{R}_2\text{P}_3)_2]$ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{R}_2\text{P}_3)\text{W}(\text{CO})_5]$ in the range 1.75–1.77 Å.^{8a,b} SINDO1 predicts the phosphorus-phosphorus ring bond lengths to be 2.17–2.20 Å. These lengths also are between the standard P-P single bond of 2.22–2.23 Å¹³ and P=P double bond of 2.00–2.03 Å in $\text{R}-\text{P}=\text{P}-\text{R}$.²⁵ It is interesting to note that the PP distances obtained in the present study agree closely with the average value of 2.170 Å in the spectacular hexaphosphabenzene triple-decker

Table III. Ring Bond Orders in the Various Phosphorus Analogues of Cyclopentadienyl Anion^a

| species | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|------|------|------|------|------|------|------|
| X_1X_2 | 1.66 | 1.55 | 1.86 | 1.69 | 1.51 | 1.84 | 1.77 |
| X_2X_3 | 1.80 | 1.71 | 1.51 | 1.69 | 1.81 | 1.66 | 1.77 |
| X_3X_4 | 1.59 | 1.73 | 1.70 | 1.68 | 1.60 | 1.75 | 1.77 |

^a Numbering system given in Figure 1 is used.

complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}]_2(\mu, \eta^6\text{-P}_6)$, $\text{M} = \text{Mo}, \text{W}$,^{26,27} with P_6 in the middle deck. The SINDO1 PP bond lengths of 2.191 Å in P_5^- are similar to the values of 2.15–2.21 Å found by X-ray structure analysis in the triple-decker complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Cr}]_2(\mu, \eta^6\text{-P}_6)$ with P_5 ring in the middle deck.^{9a}

Although the SINDO1 PP bond distances in the phosphorus analogues of C_p^- are closer to the experimental values in ligated P_5 and P_6 rings positioned symmetrically in the middle deck of the above-mentioned triple decker complexes, shorter PP lengths (~ 2.11 Å) are observed in P_5 rings in pentaphosphaferrocene and -ruthenocene $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{M}(\eta^5\text{-P}_5)]$, $\text{M} = \text{Fe}, \text{Ru}$.^{9b} Since the experimental analyses show significant differences in the PP lengths of ligated P_5 ring in different environments,^{9a,b} it may not be correct to correlate the structure of the isolated ring with that of the ligated ring. Hamilton and Schaefer^{14c} have predicted from ab initio studies that the PP lengths in P_5^- vary from 2.081 to 2.095 Å as the basis set is changed from minimal to extended with polarized and diffuse functions. The ab initio PP lengths are about 0.10 Å shorter than the SINDO1 values.

The internal ring angles $\angle\text{CPC}$ and $\angle\text{PPC}$ centered at phosphorus atoms are found to be around 94° in species 1–5 according to SINDO1 calculations. These bond angles are close to the internal ring angles $\angle\text{CPC}$ of about 90° observed in substituted phospholes, $\text{C}_4\text{H}_4\text{PR}$.²⁸ The mean values of the angles $\angle\text{CPC}$, $\angle\text{PCC}$, and $\angle\text{CCC}$ in phospholyl ring in some iron complexes are 88.2, 113.9, and 111.9° respectively.⁷ The corresponding SINDO1 values in phospholyl anion differ by 6.0, -5.4, and 2.5°, respectively. The angles centered at phosphorus in species 4–7 vary from 90 to 108°.

The optimized MNDO structures obtained by us reveal that the PC and PP bond lengths are in the ranges 1.619–1.671 Å and 1.894–1.952 Å, respectively. It is seen that these lengths are notably shorter than the SINDO1 and experimental values.

Aromaticity. Phosphorus atoms in the anions of five-membered rings $\text{C}_n\text{R}_n\text{P}_{5-n}$ ($n = 1-4$) are dicoordinated, and each contributes one π -electron toward cyclic delocalization, resulting in six π -electron ring systems. In the present study, the degree of aromaticity in the phosphorus analogues of C_p^- is examined using the ring current criterion of aromaticity²⁹ as developed by Jug.³⁰ According to this approach, the weakest ring bond having the lowest ring bond order is used as an index to measure the degree of aromaticity.^{30,31} Bond orders are calculated at the optimized geometries using the maximum bond order principle.³² In calculating bond orders, σ - as well as π -electrons are taken into consideration.

(26) Scherer, O. J.; Schwab, J.; Swarowsky, H.; Wolmershaeuser, G.; Kaim, W.; Gross, R. *Chem. Ber.* 1988, 121, 443.

(27) Scherer, O. J.; Sitzmann, H.; Wolmershaeuser, G. *Angew. Chem.* 1985, 97, 358; *Angew. Chem., Int. Ed. Engl.* 1985, 24, 351.

(28) Mathey, F. *Chem. Rev.* 1988, 88, 429 and references cited therein.

(29) Bergmann, E. D.; Agranat, I. *Aromaticity, Pseudoaromaticity and Antiaromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israel Academy of Sciences and Humanities: Jerusalem, 1971; p 9.

(30) Jug, K. *J. Org. Chem.* 1983, 48, 1344.

(31) Jug, K.; Malar, E. J. P. *THEOCHEM* 1987, 153, 221.

(32) (a) Jug, K. *J. Am. Chem. Soc.* 1978, 100, 6581. (b) Jug, K. *J. Am. Chem. Soc.* 1977, 99, 7800.

(22) Dewar, M. J. S.; Jie, C. *THEOCHEM* 1989, 187, 1.

(23) (a) Jug, K.; Nanda, D. N. *Theoret. Chem. Acta* 1980, 57, 107, 131.

(b) Jug, K.; Iffert, R. *J. Comput. Chem.* 1987, 8, 1004; (c) *THEOCHEM* 1989, 186, 347.

(24) (a) Nguyen, M. T. *Mol. Phys.* 1986, 59, 547 and references cited therein. (b) Ohashi, N.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* 1984, 103, 337. (c) Zittel, P. F.; Lineberger, W. C. *J. Chem. Phys.* 1976, 65, 1236. (d) Douglas, A. E.; Frackowiak, M. *Can. J. Phys.* 1962, 40, 832.

(25) Cowley, A. H. *Acc. Chem. Res.* 1984, 17, 386.

Table IV. Aromatic Character in Phosphorus Analogues of the Cyclopentadienyl Anion (C_p^-)

| species | aromaticity index ^a | % of relative aromaticity |
|---------|--------------------------------|---------------------------|
| C_p^- | 1.72 | 100.0 |
| 1 | 1.56 | 90.7 |
| 2 | 1.52 | 88.4 |
| 3 | 1.48 | 86.0 |
| 4 | 1.65 | 95.9 |
| 5 | 1.48 | 86.0 |
| 6 | 1.63 | 94.8 |
| 7 | 1.73 | 100.6 |

^a Scaled indices.

Table III lists the bond-order values for the ring bonds in the various anions studied. The magnitudes of the bond orders are clearly indicative of the delocalized nature of the π -electrons since these values are neither characteristic of single bonds (bond order ~ 1.25) nor double bonds (bond order ~ 2.15) but are in between in nature. The weakest ring bonds with lowest bond orders are seen to be those involving carbon-phosphorus or phosphorus-phosphorus bondings. The lowest ring bond orders in the anions 1-3 and 5 are in the range 1.50-1.60, and these species are moderately aromatic according to the bond-order definition.^{30,31} The aromaticity indices in the anions 4, 6, and 7 are >1.60 and are highly aromatic species.

In the bond-order definition of aromaticity,³⁰ the carbon-carbon bond order of 1.25 in ethane, as obtained by SINDO1¹⁵ and other semiempirical methods, is taken as the reference value to typify nonaromatic species, and the different limiting values are deduced from analysis of ring systems of first-row atoms. However, in the species that we are concerned with in this work, the weakest bond that determines the extent of the ring current formation is either the carbon-phosphorus or phosphorus-phosphorus bond. From SINDO1 calculations we notice that the bond orders of single bonds C-P in CH_3-PH_2 and P-P in PH_2-PH_2 are 1.266 and 1.272, respectively. These values and the bond orders of some typical double bonds that we have calculated show a slight increase when second-row atoms are present. It is appropriate to get scaled aromaticity indices if we are to compare the degree of aromaticity in the phosphorus heterocycles with the parent cyclopentadienyl anion. We arrive at a scaling factor of 0.98 from the bond orders of ethane and diphosphathane. In Table IV, the scaled aromaticity indices and the percentage of aromaticity relative to cyclopentadienyl anion are presented.

It is dramatic that P_5^- is found to be highly aromatic with the index of 1.73 which is comparable with those of the cyclopentadienyl anion (1.72) and benzene (1.75).³⁰ This prediction is in accordance with the conclusion arrived from UV spectral analysis of P_5^- which exhibits two $\pi-\pi^*$ bands of medium intensity at 260 and 320 nm and a $n-\pi^*$ band at 370 nm.² The present study indicates that there is strong delocalization of π -electrons in the P_5^- ring with uniform distribution over the entire ring and is manifested by equal bond orders for all ring bonds. All phosphorus atoms in P_5^- carry an equal net charge of -0.20. In 1-6, polarization of electrons takes place with phosphorus atoms having more electron density than the carbon atoms, and delocalization of electrons in the ring is not uniform. Hence, the aromatic character in species 1-6 is less than that in C_p^- as seen from Table IV. Phosphoryl anion is moderately aromatic in nature with 90.7% aromatic character relative to C_p^- , though earlier studies have considered it to be highly aromatic.^{14a-c} The diphospha analogues 2 and 3 and 1,2,3-triphosphacyclopentadienyl

Table V. SINDO1 Binding Energies (au) in the Phosphorus Analogues of Cyclopentadienyl Anion

| species | binding energy | species | binding energy |
|---------|----------------|---------|----------------|
| 1 | 1.628 | 5 | 1.114 |
| 2 | 1.442 | 6 | 0.841 |
| 3 | 1.389 | 7 | 0.487 |
| 4 | 1.184 | | |

anion 5 are also moderately aromatic with 86.0-88.4% relative aromaticity. 1,2,4-triphospha and tetraphospha analogues are highly aromatic in nature. Table IV shows that of the two diphospha analogues, the 1,3-isomer has a slightly larger aromaticity index (1.52) than in the 1,2-isomer having two adjacent P atoms (1.48). In the triphospha analogues, the isomer 4 is more aromatic than 5. These observations are in agreement with the earlier finding of Jug,³⁰ in nitrogen heterocycles, which reveals that the ring current decreases the closer the heteroatoms are in the ring.

It is of interest to note that the isomer which is predicted to have larger aromaticity has more binding energy than the isomer which is less aromatic. Incidentally, it is noted that the isomer with larger aromaticity is the one observed to participate in complex formation.^{8,10} Thus, the experimental observations^{8,10} reveal that of the two diphospha isomers 2 and 3, only the 1,3-diphospha analogue 2 forms complexes with transition metals. In the same way, only the 1,2,4-triphospha isomer which is more aromatic than the isomer 5 is reported to form complexes.^{8,10} These observations support the reliability of our computational predictions.

The finding that the phosphorus analogues retain $\geq 86.0\%$ aromaticity relative to the cyclopentadienyl anion accounts for their ability to form complexes.^{2,6-10} Since the ring current concept provides a dynamic view of electron delocalization in terms of nodal properties of the molecular orbitals,³¹ the degree of aromaticity obtained from this concept is related to kinetic stability of the ring system.³³

Binding Energies. The binding energy, which is the difference between the total energy of the system at equilibrium and the sum of energies of the constituent atoms, is given in Table V for the different anions studied. There is a gradual decrease in the binding energies with an increase in the number of in-ring phosphorus atoms. This trend reflects the relative strengths of bonding involved in these species. Thus, for example, the binding energies show that the strength of the π -bonding follows the order $2p_\pi - 2p_\pi > 2p_\pi - 3p_\pi > 3p_\pi - 3p_\pi$. A similar ordering is expected for σ -bonding also. Of the two diphospha analogues, the 1,3-diphospha isomer 2 is 33.3 kcal/mol more stable than the 1,2-isomer 3. This is expected due to the presence of a weak phosphorus-phosphorus bond and lone-pair repulsion between the adjacent phosphorus atoms in the latter.

The aromaticity index also predicts that 2 is more stable than 3. When three phosphorus atoms are present in the ring, the 1,2,4-triphosphacyclopentadienyl anion 4 is 44.2 kcal/mol lower in energy than the 1,2,3-triphospha isomer 5, which is less aromatic.

Conclusion

The ring bond lengths in the phosphorus analogues of cyclopentadienyl anion are found to be between the bond lengths of the respective single and double bonds and are indicative of the aromatic nature of the species. The an-

(33) (a) Fukui, K.; Kato, H.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* 1961, 34, 112. (b) Fukui, K. *Ang. Chem., Int. Ed. Engl.* 1982, 21, 801.

ions studied are found to be moderately or highly aromatic according to the bond-order definition of the ring-current concept. 1,3-Diphosphacyclopentadienyl anion is found to be more aromatic than the 1,2-diphospha isomer. Of the two triphospha analogues, the 1,2,4-triphospha isomer is predicted to be highly aromatic while the 1,2,3-triphospha isomer is moderately aromatic. The isomer predicted to be more aromatic is the one found to participate in complex formation.

Acknowledgment. I thank Prof. Karl Jug, Universität Hannover, Germany, who kindly made available his recent

version of the SINDO1 program. I am grateful to the authorities of the Indian Institute of Technology, Madras, for providing research facilities and the Department of Science and Technology, Government of India, for a research grant vide No. SP/YS/C09/86. The computations were performed on the SIEMENS 7.580-E computer of the Indian Institute of Technology, Madras. Partial support of this work by the University Grants Commission, New Delhi-India, is gratefully acknowledged.

Registry No. 1, 55219-61-9; 2, 133900-30-8; 3, 140929-15-3; 4, 140929-16-4; 5, 131028-95-0; 6, 109660-05-1; 7, 109660-04-0.

A MO Theoretical Study on the Rearrangement of 1-Hydroxy- and 1-(Acyloxy)-1,2,3-triazoles and Their Benzotriazole Analogues: Comparison of ab Initio and Semiempirical Calculations

Ernst Anders*

*Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42,
D-8520 Erlangen, Germany*

Alan R. Katritzky and N. Malhotra

Department of Chemistry, University of Florida, Gainesville, Florida 32611-2046

John Stevens

3M Company, St. Paul, Minnesota 55144

Received December 30, 1991

Energy differences between 1-hydroxy-1,2,3-triazole (**8a**) and its 2*H*- and 3*H*-tautomers **8b** and **8c** were calculated by semiempirical (AM1, PM3) and ab initio (from the 3-21G//3-21G up to the MP4SDTQ/MP2//6-31+G* level) methods and compared. With large basis set size and inclusion of electron correlation effects (ECE), these tautomers are found to be quite close in energy. The 2*H* tautomer **8b** is less stable by 2.57 kcal mol⁻¹ and the 3*H* tautomer **8c** by 1.95 kcal mol⁻¹ compared with the 1*H*-hydroxy form **8a**. A satisfactory treatment of triazoles containing the ⁻O-N(1)⁺ moiety by ab initio methods requires inclusion of ECE (at least second-order Møller-Plesset perturbation theory), while for 1*H*- and 2*H*-triazole (**9a,b**) inclusion of MP2 does not change the energy differences significantly. The differential solvent stabilization of **8c** compared with that of **8a** in the condensed phase was estimated using Tomasi's SCRF theory. The PM3- and AM1-calculated energy differences of isomers **1a/b/c**, **2a/b/c**, and **3a/b/c** (benzotriazole derivatives) and **5a/b/c**, **6a/b/c**, and **7a/b/c** (1,2,3-triazole derivatives) are mutually inconsistent. AM1 predicts the isomers **a**, but PM3 isomers **c** to be the most stable. The errors of both methods were estimated by comparison with ab initio calculations for the related model compounds **9a**, **9b** (1*H*- and 2*H*-1,2,3-triazole), **10a**, **10b** (1*H*- and 2*H*-benzotriazole), and (*Z*)/(*E*)-diazene (**12a**, **12b**). It is concluded that in almost all cases the PM3 method yields results which are more reliable than AM1. Our experimental finding that the rearrangement of **1a** proceeds intermolecularly to **1c**, with the isomer **1b** remaining undetectable, is understandable on the basis of these PM3-calculations. PM3- and AM1-calculated bond lengths are in acceptable agreement with those resulting from the 3-21G basis set but differ significantly from the respective MP2/6-31+G* values.

Introduction

One of our laboratories recently reported that 1-(aroyloxy)benzotriazoles such as **1a** in acetone solution in the presence of catalytic amounts of water and a base (potassium carbonate) rearrange intermolecularly to give exclusively *N*(3)-aroylbenzotriazole 1-oxides **1c**.¹ These, and previous investigations²⁻⁶ on related compounds, reveal that such rearrangements are remarkably solvent-dependent. From our NMR studies¹ we concluded that the

potential intermediate, the *N*(2) isomer **1b**, is unstable and does not have sufficient lifetime to exist in detectable concentration.

To what extent can these results be reproduced by "widely available" quantum mechanical methods? To the best of our knowledge, nothing has been published concerning theoretical investigations of the benzotriazole system **1a/b/c** or even the smaller systems **2a/b/c**, **3a/b/c**, and **4a/b/c**. The same is true for the related 1,2,3-triazole systems **5a/b/c**, **6a/b/c**, and **7a/b/c** (Chart I).

The most closely related theoretically investigated system is that of 1-hydroxy-1,2,3-triazole (**8a**) and its tautomers **8b** and **8c**. As concluded by Fabian⁷ and by Giumon et al.,⁸ semiempirical calculations, especially AM1,⁹

(1) Katritzky, A. R.; Malhotra, N.; Fan, W. Q. *J. Chem. Soc., Perkin Trans. 2* 1991, 1545.

(2) Horiki, K. *Tetrahedron Lett.* 1977, 1901.

(3) Horiki, K. *Tetrahedron Lett.* 1977, 1897.

(4) Huisgen, R.; Weberndörfer, V. *Chem. Ber.* 1967, 100, 71.

(5) Boyle, F. T.; Jones, R. A. Y. *J. Chem. Soc., Perkin Trans. 2* 1973, 160.

(6) Barlos, K.; Papaioannou, D.; Theoropoulos, D. *Int. J. Peptide Protein Res.* 1984, 23, 300.

(7) Fabian, W. M. F. Z. *Naturforsch., A: Phys. Sci.* 1990, 45, 1328.

(8) Giumon, C.; Khayar, S.; Pfister-Guillouzo, G.; Begtrup, M. *Spectrosc. Lett.* 1987, 20(2), 105.