parable with the energy increase associated with moving a hydroxyl group from an equatorial to an axial orientation in a cyclohexane ring. On the basis of IR data Masschelein[22] calculated 0.38 kcal/mol, while Neelakantan[23] obtained 0.65 kcal/mol from Raman spectroscopy.

^{13}C NMR affords a method of examining the conformation of **1** in solution. The vicinal ^{13}C-C-C-^{31}P coupling, to C(3) and C(6) from P, was found to be 10.9 Hz. Employing model compounds[3,4] and the torsion angles we observed in the twist-chair, the expected coupling is $\sim$6.5 Hz, if 12.6 Hz is used for $\omega \simeq 170°$ and 0.5 Hz for $\omega = 90°$. The observed coupling of 10.9 Hz suggests that in solution there is an enhanced population of chair relative to twist-chair compared with the solid phase. Using 12.5–13.0 Hz as a value for $\omega \simeq 170°$, it can be calculated that $\sim$65% of the solution conformation of **1** is in the chair form. It is difficult to rationalize the apparent preference for the chair form in solution. It should be noted, however, that the energy difference between chair and twist-chair is small and subtle features of solvation may bias the conformational equilibrium.

Acknowledgment. G.W.B. acknowledges financial support of this work from the National Research Council of Canada.

Supplementary Material Available: Listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Electrochemical and Electron Paramagnetic Resonance Studies of a Series of 1,4-Diphosphoniacyclohexa-2,5-diene Salts. Electrochemical Generation of the Radical Cations of a Series of Diphosphabenzene Compounds

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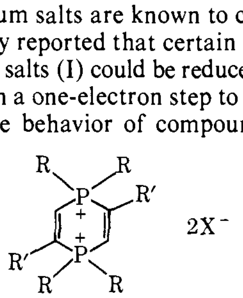
Contribution from the Departments of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, North Dakota State University, Fargo, North Dakota 58102, Tulane University, New Orleans, Louisiana 70118, and Rhode Island College, Providence, Rhode Island 02908. *Received March 30, 1977*

Abstract: Electrochemical studies were conducted on a series of 1,4-diphosphoniacyclohexa-2,5-diene salts (I), and these salts were found to give stable one-electron-reduction products. These stable radical cations were studied by electron paramagnetic resonance. Evidence for significant conjugative interaction by the tetravalent phosphorus atoms in these radical cations is presented.

Most phosphonium salts are known to cleave upon reduction.[2-7] We recently reported that certain 1,4-diphosphoniacyclohexa-2,5-diene salts (I) could be reduced at low potentials (−0.4 to −1.0 V) in a one-electron step to stable radical cations.[8,9] This unique behavior of compounds of structure I suggests stabilization of the radical cation by conjugative interaction from the phosphonium moiety since the reduction products of neither ethylene nor R_4P^+ are stable. The concept of dπ–pπ bonding involving phosphorus has been a subject of controversy for a number of years.[10,11] From the electrochemistry of I and related compounds and the electron paramagnetic resonance (EPR) of the radical cations from reduction of I, the significance of conjugative interaction in $I^{+\cdot}$ is evaluated in this paper.



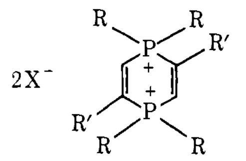
I

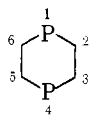
Previous electrochemical reduction of compounds I led to saturation of the double bonds.[15]

Results

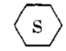
Electrochemical data for the first reduction wave (Figure 1) of compounds II–XVI are presented in Table I. The stability of the reduction products is indicated by the values of i_{pa}/i_{pc} being near unity. The reversibility of the electron transfer is indicated by $E_{3/4} - E_{1/4}$ and $E_{pa} - E_{pc}$ being near the one-

Table I. Electrochemical Behavior of Salts of Structure I in Dimethylformamide[a] (First Wave)





Number system used in text.

Compd	R	R'	X⁻	$-E_{1/2}$[b]	i_{pa}/i_{pc}[c]	$E_{3/4} - E_{1/4}$,[b] mV	$E_{pa} - E_{pc}$,[c] mV	I_d
II	Ph	Ph	Br	0.515	0.98	50	60	0.95
III	Ph	Ph	Cl	0.488	0.92	60	60	0.98
IV	Ph	$C(CH_3)_3$	Br	0.723	0.99	58	60	1.01
V	Ph	$C(CH_3)_3$	Cl	0.705	1.01	56	65	0.96
VI	Ph		Cl	0.73[d]	0.92[d]	42	57[d]	1.01
VII	Ph	CH_2CH_3	Br	0.969[f]	1.07	59	60	1.04
VIII	Ph	CH_3	Br	0.81[h]	1.04	67	60	0.99
IX	Bz	CH_3	Cl	0.845[h]	g	h		0.88[e]
X	*p*-FPh	Ph	Cl	0.457	1.07	59	60	0.75
XI	*p*-MeOPh	Ph	Br	0.622	1.11	58	58	0.78
XII	*p*-MePh	Ph	Cl	0.526	0.96	53	61	1.05
XIII	*o*-MePh	Ph	Cl	0.488	1.06	54	58	1.11
XIV	*o*-MeOPh	Ph	Cl	0.826	1.05	60	59	1.04
XV	CH_2CH_3	Ph	Cl	0.774	1.12	55	60	1.15
XVI	Ph	H	Br	0.56	g	h		1.27[e]

[a] Saturated calomel electrode (SCE) reference. [b] From polarography data at a dropping mercury electrode (±10 mV). [c] From cyclic voltammetry at a hanging mercury drop electrode, sweep rate 50 mV/s. [d] Platinium bead electrode. [e] Maxima cause uncertainty in the error of these data. [f] Prewave observed. [g] Reduction product unstable. [h] Poorly shaped wave.

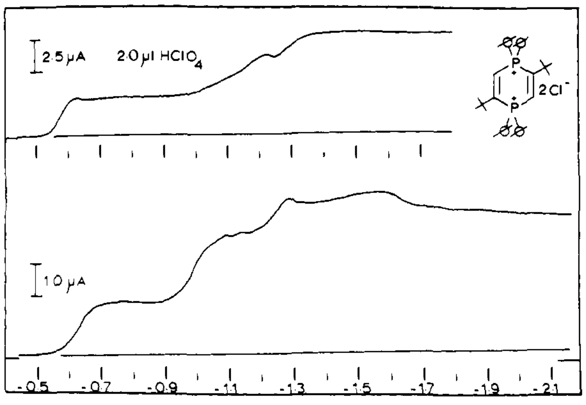


Figure 1. DC polarogram of V. The solution contained 1.0 mM V and 0.12 *m* TEAP in DMF with a dropping mercury electrode. For top polarogram, solution contained 2.0 μL of $HClO_4$.

electron reversible values (56 mV). Further evidence for the single electron nature of the first wave is the observation of EPR signals when these compounds are electrolyzed at the first wave. The fact that I_d, the diffusion current constants, are near unity also suggests a one-electron process.[12] In general, the limiting currents are proportional to the square root of the corrected height of the mercury column and $i_{pc}/c^0n^{1/2}$ is constant.

Additional electrochemical studies on III showed that the half-wave reduction potential ($E_{1/2}$) of the first wave was independent of concentration. The second wave ($E_{1/2} = -1.15$ V, Figure 1) is complicated by a small maximum. The diffusion current at −2.0 V is twice that of the first wave, suggesting that the second reduction is also a one-electron process.

Cyclic voltammetry (CV) including the second reduction wave (Figures 2 and 3) shows no anodic current for the second wave until sweep rates near 40 V/s are used. The peak potential (E_{pc}) shifts cathodically about 30 mV for each tenfold increase in sweep rate.

The polarogram and CV of V in 90% dimethylformamide (DMF)/10% water (H_2O) is shown in Figure 4. The $E_{1/2}$ of the first wave is −0.750 V; its $E_{3/4} - E_{1/4}$ value is 56 mV. The current ratio (CV) (i_{pa}/i_{pc}) is unity at 0.05 V/s sweep rate and $E_{pa} - E_{pc}$ is 60 mV. Thus, the addition of water shifts the reduction potential slightly, but otherwise the first reduction wave is unaffected. The second reduction wave occurs at $E_{1/2} = -1.34$ V.

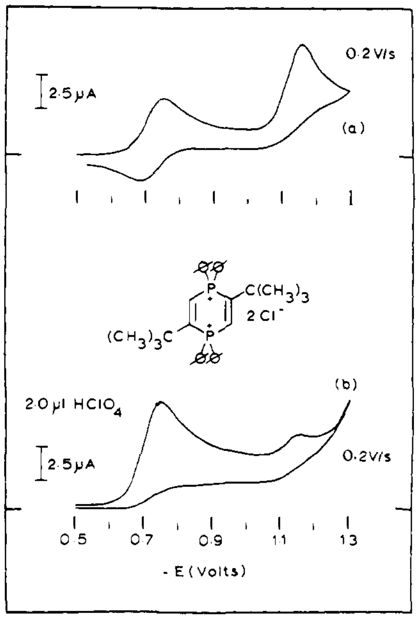


Figure 2. Cyclic voltammogram of V. The solution contained 1.0 mM V and 0.12 M TEAP in DMF with a hanging mercury drop electrode. In bottom cyclic voltammogram solution contained 2.0 μL of $HClO_4$.

The effects of the addition of 2 μL of 70% perchloric acid (1.5 mM) on the electrochemistry of V is illustrated in Figures 1–3. Polarographically (Figure 1) the first wave reduces at $E_{1/2} = -0.675$ V with $E_{3/4} - E_{1/4} = 45$ mV. The diffusion current was twice the value under nonacidic conditions. $E_{1/2}$ for the second wave = −1.3 V.

CV at slow sweep rates (Figure 2) shows the first wave to be increased in height while the second is greatly decreased. Also, there is no anodic current for the first wave. Increasing

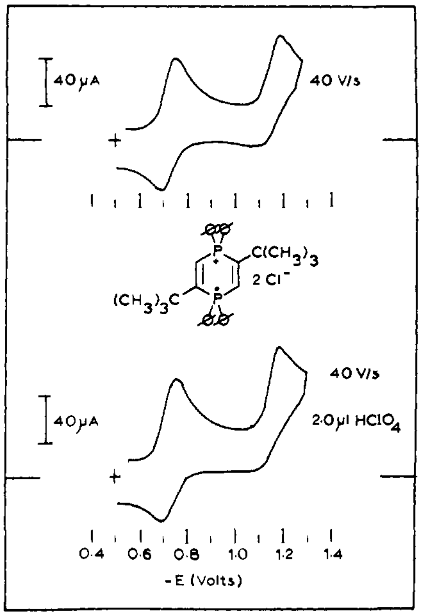


Figure 3. Cyclic voltammogram of V. The solution contained 1.0 mM V and 0.12 M TEAP in DMF with a hanging mercury drop electrode. Solution for bottom cyclic voltammogram contained 2.0 μL of HClO$_4$.

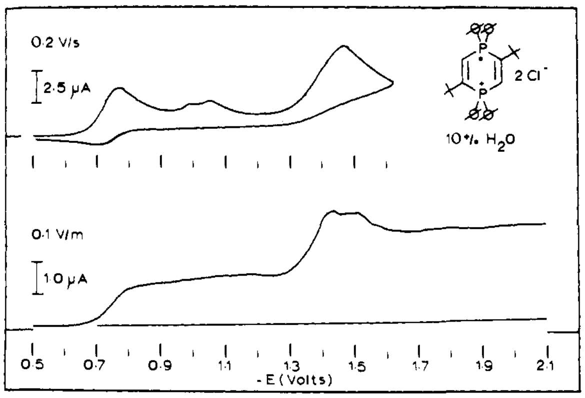


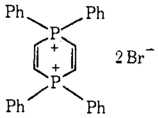
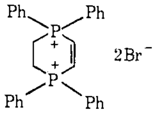
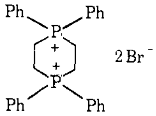
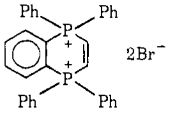
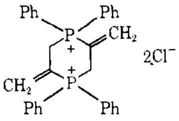
Figure 4. Upper: Cyclic voltammogram of V. The solution contained 1.0 mM V and 0.12 M TEAP in 90% DMF-10% H$_2$O. The electrode was a hanging mercury drop. Lower: DC polarogram of 1.0 M solution of V with 0.12 M TEAP with a dropping mercury electrode in 90% DMF-10% H$_2$O.

Table II. Reduction Potential of the "Second"[a] Wave of Compounds of Structure I

Compd	$-E_{1/2}$	Compd	$-E_{1/2}$
II	0.84	X	0.70
III	0.78	XI	0.87
IV	1.08	XIV	1.04
VII	1.42	XV	1.13
VIII	1.36		

[a] The wave judged to be the second faradic process; see text.

Table III. Reduction Potentials of Various Diphosphonium Salts

	$-E_{1/2}$ (Hg)	I_d	$-E_{1/2}$ (Pt)
 XVI	0.56	1.27	0.61
 XVII	0.75	1.37	0.79
 XVIII	1.84	2.43	1.70
 XIX	0.70	1.30	0.74
 XX	1.10	2.15	1.22

the sweep rate (Figure 3) causes an increase in both the anodic current for the first wave and the cathodic current for the second wave with a concurrent decrease in the cathodic current of the first wave. At 40 V/s sweep rate, i_{pa}/i_{pc} is unity and $E_{pa} - E_{pc}$ is 60 mV for the first wave.

In Figures 1 and 4 maxima are apparent at potentials negative to the first wave. This behavior is characteristic of the electrochemistry of compounds of structure I. Thus, the number and size of the waves past the first are unique for each compound. However, by comparing polarographic data and CV data on mercury and platinum, the wave corresponding to faradic processes can be distinguished. The reduction potentials of the second faradic wave of compounds of structure I are given in Table II.

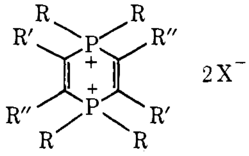
In order to investigate the anodic behavior of salts I, acetonitrile solutions of IV with nitrate or perchlorate as anions were prepared by adding the respective silver salt to a solution of IV and filtering the silver bromide. Tetraethylammonium perchlorate was the supporting electrolyte. No oxidation waves for these solutions at potentials less positive than +2.1 V were observed, indicating that the cationic moiety of IV is very difficult to oxidize.

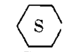
The radical cations of structure I in which R′ = H are not stable. Electrochemical data for these and related compounds are given in Table III. Polarographically, the first reduction wave of XVI is complicated by a postwave. There is no detectable anodic current up to 40 V/s by CV. Compound XVII gives $E_{3/4} - E_{1/4} = 44$ mV (polarography) and from cyclic voltammetry at rates faster than 2 V/s anodic current can be observed for the first wave. The polarogram of compound XVIII is complicated by a large maximum at the foot of the wave. An $E_{1/2}$ value of -1.84 V can be estimated from the wave visible after subsidence of the maximum. Cyclic voltammetry on mercury gives a spike followed by a wave at $E_{pc} = -1.93$ V with no anodic current detected. The spike is eliminated by use of a platinum bead electrode with the remaining wave at $E_{pc} = -1.73$ V. Compound XIX is reduced polarographically at $E_{1/2} = -0.70$ V with $E_{3/4} - E_{1/4} = 58$ mV. CV at 2 V/s (platinum) gives i_{pa}/i_{pc} about unity and $E_{pa} - E_{pc}$ equals 0.1 V. Polarographically compound XX gives a broad wave ($E_{3/4} - E_{1/4} = 105$ mV) at $E_{1/2} = -1.10$ V followed by a maximum at -1.62 V and a wave of high slope at -1.7 V. This wave is about half the height of the first wave. There is also a wave (10% larger than the first) at -2.5 V.

On CV, there is no anodic current below 0.5 V/s for the first reduction wave. The electrochemical behavior of XX is significantly different from that of its isomer, VIII.

Electron Paramagnetic Resonance. The general appearance of the EPR spectra of the radical cations produced by reduction at the first wave of compounds of structure I is a triplet of

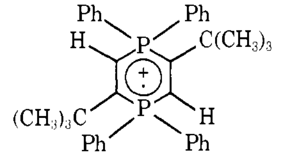
Table IV. Hyperfine Splitting Constants[b]



Compd	Temp, °C	R	R'	R''	X^-	Line width	g value[d]	a_H[e]	a_p[e]	a_{me}[e]
II	−40	Ph	Ph	H	Br	0.200[c]	2.0042	0.38	1.60	
II[a]	−40	Ph	Ph	D	Br	0.32[e]			1.60	
IV	−40	Ph	*t*-Bu	H	Br	0.125[c]	2.0043	0.28	1.60	
VI[a]	−40	Ph		H	Cl	0.4[f]			1.6	
VIII	−40	Ph	CH_3	H	Br	0.100[c]	2.0039	0.25	1.58	0.48
X	−40	*p*-FPh	Ph	H	Cl	0.195[c]	2.0042	0.37	1.63	
XI	−40	*p*-MeOPh	Ph	H	Cl	0.200[c]	2.0043	0.38	1.64	
XII	−40	*p*-MePh	Ph	H	Cl	0.200[c]		0.35	1.59	
XIII	−40	*o*-MePh	Ph	H	Cl	0.250[c]		0.37	1.73	
XIII	−24					0.240[c]		0.36	1.71	
XIII	5					0.175[c]		0.35	1.66	
XIV[a]	−40	*o*-MeOPh	Ph	H	Cl	0.20[e]		0.37	1.60	
XV	−40	Et	Ph	H	Cl	0.310[c]		0.48	1.42	

[a] Acetonitrile/0.1 M tetraethylammonium perchlorate solvent. [b] In millitesla (1 mT = 10 G). [c] ±0.005 mT. [d] ±0.00002. [e] ±0.01 mT. [f] ±0.1 mT.

Table V



DMF			AN	
a_H, mT	a_P, mT	Temp, °C	a_P, mT	a_H, mT
0.29	1.61	−50		
0.28	1.61	−40	1.64	0.28
0.28	1.59	−30	1.62	0.27
0.28	1.58	−20	1.62	0.28
		−10	1.61	0.28
0.28	1.55	0	1.59	0.28
0.28	1.54	+20	1.57	0.28

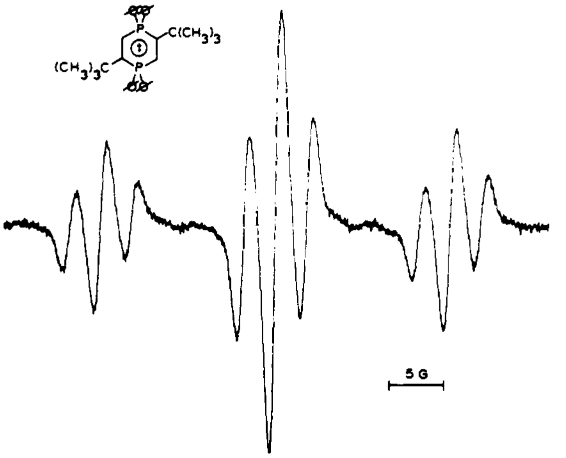


Figure 5. ESR spectrum of the radical cation of V in DMF at −40 °C.

triplets (Figure 5). The larger triplet with the hyperfine splitting constant (hfsc) of about 1.6 mT has been assigned[9] to the phosphorus atoms while the smaller hfsc of about 0.35 mT was assigned to the ring protons.[9] This assignment is confirmed by the spectrum of IIa$^{+\cdot}$ which can be successfully simulated using $a_D = 0.057$ mT ($a_D = 2/13(a_H)$). The fact that substitution of deuterium for the ring protons removes the triplet of smaller hfsc and does not affect the triplet of larger hfsc is unequivocal proof that the larger hfsc is due to the phosphorus atoms.

The spectrum of VIII$^{+\cdot}$ includes splittings by the methyl group as well as the two phosphorus atoms and the ring protons. For VI$^{+\cdot}$ the large line width of the spectrum apparently obscures all splittings except for those of the phosphorus atoms.

There is a large temperature dependence of the spectra of I$^{+\cdot}$ (Tables IV and V). As the temperature is lowered, the phosphorus hfsc increases in both DMF and acetonitrile (AN) while the proton hfsc changes relatively little if at all. Similar effects were also observed by Gerson et al.[14]

Discussion

The electrochemical behavior of salts of structure I, as exemplified by V, consists of two one-electron reductions. The first electron transfer is reversible and produces a stable radical cation. This radical cation is unusually stable in the presence of water but decomposes rapidly in the presence of strong acid (Figure 2). In strong acid, the limiting current for the first wave is about twice that in neutral DMF, suggesting an ECE[12] mechanism in which protonation is the chemical step. This hypothesis is supported by the fact that at 40 V/s (Figure 3), the electrode process appears to be a one-electron transfer and the radical cation is stable on this time scale. The high sweep rate has apparently suppressed the effects of the chemical step.

Protonation is an unusual mechanism for the decomposition of a radical cation. Also, the generation of a radical cation by a reduction process is unusual. Examination of Figure 6 will help clarify the structure of the electrode products and explain the ability of these species to be protonated. Structures A and B (Figure 6) illustrate the ylide nature of radical cation V$^{+\cdot}$, with structure B emphasizing the well-known carbanionic nature of ylide carbon atoms. We note that electrolysis of salts of structure I in aqueous ethanol has led to isolation of fully saturated 1,4-diphosphoniacyclohexane (cf. XVIII) products without cleavage of the ring.[15] Thus, it seems reasonable to postulate protonation of the radical cations at the ring carbon atoms by strong acid. The negative charge in the radical cations is spread over all the ring atoms (vide infra) and they are thus fairly weak bases.

Addition of the second electron to V$^{+\cdot}$ would strongly enhance the ylide character of the carbon atoms (Figure 6, C and

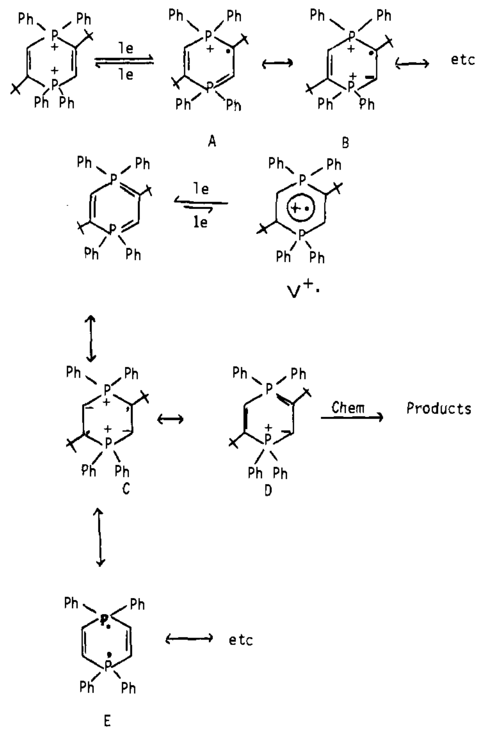


Figure 6.

D), leading to a stronger base. Indeed, doubly reduced V is very unstable, possibly reacting with residual water in the solvent system. Another possible reason for the instability of the neutral diphosphabenzene is the resemblance to reduced monophosphonium salts (Figure 6E) which are known to fragment rapidly.[2-7,16] Thus, it appears that reduction of the radical cation $V^{+\cdot}$ leads to the heretofore unknown diphosphabenzene.

The instability of $XVI^{+\cdot}$ is puzzling in light of the stability of $I^{+\cdot}$ ($R' \neq H$). The fact that $I^{+\cdot}$ is stable whether R′ is electron withdrawing or donating suggests that its stabilizing effect may be a steric effect. The steric effect may be to prevent dimerization of $I^{+\cdot}$.

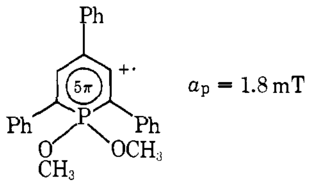
For compound IX there is no anodic current in the cyclic voltammogram below 10 V/s. Benzyl substituents are among those most easily cleaved from phosphonium salts by electrochemical reduction.[3] Apparently $IX^{+\cdot}$ owes its instability to the labile benzyl substituents.

Examination of Table I reveals that changes in $E_{1/2}$ with substituents generally follow known inductive and mesomeric effects.[17] Compound X with *p*-fluorophenyl groups on the two phosphorus atoms is the most easily reduced compound followed by the unsubstituted phenyl ring (II), the *p*-tolyl compound (XII), the anisole compounds XI and XIV, and the ethyl-substituted compound (XV). The *o*-tolyl salt (XIII) is more easily reduced than expected on the basis of normal substituent effects. Salt II with phenyl substituents in the 2 and 5 positions reduces more easily than those salts (IV, VI, VII, VIII) with alkyl groups in the 2 and 5 positions. The reduction potential of these latter salts does not follow the normal patterns of substituent effects by alkyl groups. The effect of having either chloride or bromide as counterion is small.

The difference in electrochemical behavior between the 1,4-diphosphoniacyclohexadiene salts of this study and the type of phosphonium salt previously studied is well illustrated in Table III. Salt XVIII reduces in a two-electron process (from Id) while salts XVI, XVII, and XIX reduce in a one-electron process. Phosphonium salts previously studied have shown reduction currents of at least one electron per phosphonium moiety.[2-7,18] There also appears to be a significant difference in the reduction potentials of the diene salt XVI and the partially saturated salts XVII and XIX. This difference should be viewed with caution, however, owing to the nonideal electrochemical behavior of XVI and XVII.

Salt XX can be formed by the acid-catalyzed isomerization of VIII.[19] XX is reduced to a two-electron process (from Id) at a relatively negative potential to yield an unstable product. The great difference in electrochemical behavior of XX and VIII demonstrates that VIII is not isomerizing to XX under the conditions of the electrochemical experiment.

The EPR of the radical cations generated by reduction of I generally have phosphorus hfsc near 1.6 mT, similar to 1,1-bismethoxy-2,4,6-triphenyl-λ^5-phosphorin radical cation (XXI).[20] The ring proton and methyl hfsc of compound $VIII^{+\cdot}$



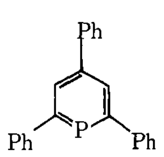
XXI

are particularly important since they are indications of the spin density on the carbon atoms of $VIII^{+\cdot}$. Thus, using McConnel's[29] relation

$$a^{H} = Q\rho \qquad (1)$$

and Q values derived from extensive data on aromatic hydrocarbons ($Q_H = -2.37$ mT;[21] $Q_{CH_3} = -2.72$ mT[21]) the odd electron density at carbon atom 3 is 0.105 while that at carbon atom 2 is 0.177. The sum of electron density at the carbon atoms is thus approximately 0.6. The remaining electron density must reside primarily on the phosphorus atoms (electron density on the aryl substituents of phosphorus is very small; see the discussion below of contributions to line widths), suggesting that in $VIII^{+\cdot}$ the odd electron density on each phosphorus atom is approximately 0.20. This large amount of spin density on the phosphorus suggests a significant amount of conjugation by phosphorus in a π-bonding manner. The hfsc of the other cation radicals in Table IV are similar to that of $VIII^{+\cdot}$, suggesting similar spin distribution. Thus, the proton and methyl hfsc of Table IV provide strong evidence for delocalization of the odd electron in $I^{+\cdot}$ onto the phosphorus atoms.

The g values (Table IV) found for $I^{+\cdot}$ were 2.0040 ± 0.0003. The deviation from the free electron value of 2.0023[22] suggests magnetic interactions involving spin-orbit coupling, implicating interaction of phosphorus unfilled orbitals with the odd electron. Phosphorin XXI has a g value of 2.002158[20] while phosphabenzene XXII has been reported to have a g value of 2.002182[20] for the radical cation and 2.0045[14] for the radical anion.



XXII

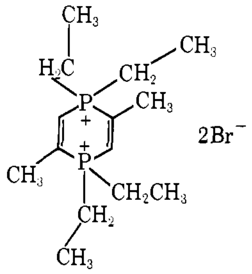
A possible model for the bonding in $I^{+\cdot}$ is that the phosphorus atom acts in only an inductive manner with no conjugative interaction. By this model, $II^{+\cdot}$ and $XV^{+\cdot}$ should have approximately the same ring proton coupling constants since the hydrocarbon moiety is the same in these two molecules. The fact that the 3-hydrogen hfsc are significantly different in $II^{+\cdot}$ and $XV^{+\cdot}$ (0.38 and 0.48 mT, respectively) indicates that this model is inadequate.

The spectra of the radical cations of Table IV have large line widths even though dilute solutions of cation radicals were used. This phenomenon could in part be due to small unresolved couplings by the substituents in the 2 and 5 positions and on phosphorus. The lack of observed splitting by the fluorine atoms in $X^{+\cdot}$ is evidence against significant delocalization of the unpaired electron into the substituents on phosphorus.[13] The fact that the line width of $IV^{+\cdot}$ is 0.125 mT and that of $II^{+\cdot}$ is 0.200 mT suggests that unresolved splitting from substituents in the 2 and 5 positions may be contributing to the large line widths. In a study of phosphabenzene radical anions, Gerson, Plattner, Ashe, and Maerkl[14] observed large line widths (~0.1 mT) for the solution spectra. They attributed these large line widths to high π-spin populations at the phosphorus center which result in large anisotropic parts of the pertinent ^{31}P hfsc.[14] We feel that the same effect could be present in the radical cations of structure I. We note, however, that there is no significant difference in the high and low field components of the spectra of $I^{+\cdot}$ while this difference is an important feature of the spectra of XXII.

Gerson et al.[14] state: "It is highly improbable that this atom [phosphorus] can bear substantial π-spin population unless the ESR spectra exhibit an essentially enlarged line width." The EPR spectra of $I^{+\cdot}$ do indeed have a large line width.

From consideration of phosphazenes, two general models of $d\pi$–$p\pi$ bonding involving phosphorus have emerged. The first postulates through phosphorus delocalization of electrons[23,24] and would correspond to cyclic delocalization of π electrons as indicated by structure $V^{+\cdot}$ in Figure 6. The second pictures[25] phosphorus as an "insulator" atom which, while forming an effective π bond to neighboring atoms, does not enjoy significant through phosphorus bonding. In $I^{+\cdot}$ this latter model would picture the bonding as consisting of two degenerate molecular orbitals ("islands" of delocalization) each consisting of the moiety P–C–C–P. Compounds XVII and XIX (Table III) contains this moiety as the electrophore. The island model would predict that XVI, XVII, and XIX would have nearly the same reduction potential since the electrophores are the same. But the through-phosphorus delocalization model would predict that XVI would be easier to reduce than XVII or XIX as is observed (Table III). However, these data must be considered cautiously since the reduction products of XVI and XVII are not stable which leads to uncertainty in the meaning of their $E_{1/2}$.[12] In addition, the difference in inductive effect of sp^3 carbons in XVII and XIX and the sp^2 carbons of XVI is difficult to evaluate.

Compounds II and XXIII have been examined by x-ray crystallography.[26,27] II was found to have a ring carbon–carbon bond distance of 1.330 Å and a phosphorus–carbon bond distance of 1.795 ± 0.005 Å for all eight distances. The analogous distances in XXIII were 1.340 and 1.790 ± 0.004 Å. The similarity of the ethylenic bond distance in these molecules to the bond distance in an isolated double bond (1.34 Å[28]) is strong evidence for the lack of significant conjugative interaction in unreduced I. Thus, it appears that while there is significant conjugative interaction by phosphorus in $I^{+\cdot}$, this is not the case in I. This is not unreasonable because the interaction or mixing of two orbitals is going to be strongly dependent on the orbital energies in question. Thus, qualitatively we can picture the very low energy electrons of the two double bonds in I as being highly localized on the carbon atoms. However, upon reduction the higher energy electron in the carbon–carbon double bond antibonding orbital is now closer in energy to the d orbitals on phosphorus. They can mix more effectively now, leading to a delocalized orbital with the unpaired electron appearing on all six atoms in the ring.



XXIII

Conclusion

A new class of stable radical cations ($I^{+\cdot}$) has been reported. Electron paramagnetic resonance data on these radical cations indicate significant conjugative interaction by the phosphorus atoms. Finally, a diphosphabenzene was generated electrochemically as an unstable intermediate.

Experimental Section

General. Melting points were taken with a Thomas-Hoover oil bath melting point apparatus and were corrected. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer. A Hewlett-Packard Model S750-B gas chromatograph was used. NMR spectra were recorded on a JEOL C-60HL spectrometer. EPR spectra were determined on a JEOL JES-ME instrument. Temperatures were determined with a copper–constantan thermocouple. Computer simulations of theoretical EPR spectra were done using a Fortran IV program for mixtures employing Lorentzian line shapes written by R. G. Griffin.[30] The program used for the Hückel MO calculations was written by Munch and Rieke[31] and modified by T. H. Ridgeway for simplified input. Elemental analyses were obtained from Galbraith Laboratories.[32] UV spectra were taken on the Unicam SP 800B spectrophotometer. Most of the electrochemical studies were performed on the UNC Electrochemistry unit designed and built by Fox.[33] A Data Technology Model 351 digital voltmeter was used to accurately determine initial potential settings. The sampled dc, pulse, and differential pulse polarograms were performed using a PAR 174.

Data were recorded on a Hewlett-Packard Model 7004-B X-Y recorder, a Tektronix type R564B oscilloscope with two type 2A63 modules, and a Tektronix C-12 Polaroid camera unit or a Houston Omnigraphic X-Y recorder. All salts were dried in vacuo at 100 °C before use.

Electrochemistry. Two methods were used for the preparation of dry acetonitrile. CH_3CN (Fisher commercial) was rapidly distilled from $KMnO_4/Na_2CO_3$ and stored over dry (24 h at 200 °C in vacuo) 4A molecular sieves (MCB). Alternatively, spectrograde acetonitrile (MCB) was treated with dry molecular sieves (MCB). The water content from either of these procedures was 1 mM or less.

Dimethylformamide was prepared by allowing spectrograde DMF (MCB) to stand over dried 4A molecular sieves overnight followed by vacuum distillation (≤ 1 mmHg) with ice water circulated through the condenser. The DMF was stored under N_2 at room temperature.

Tetraethylammonium perchlorate (TEAP) was prepared by dissolving tetraethylammonium bromide in boiling water and adding perchloric acid. The TEAP was filtered and recrystallized twice from distilled water and dried at 60 °C in vacuo. It was again dried immediately before each use.

Water analyses were done using the method of Hogan et al.[42] Analyses were done using a 6-ft column of Porpak Q, 80–100 mesh (Waters Associates). Injection volumes were 50 μL.

Water content of the solution in the cell was determined by withdrawal of a 50-μL sample directly from the cell and injecting in the GC. The water content was determined by comparison of the area of the peak to that of a known concentration of methanol. Water concentration in the cell was found to be 5–10 mM and determinations were considered accurate to ±1mM.

Bethlehem Instrument Grade mercury was used in the precision hanging mercury drop electrode (Metrohm); triple distilled mercury was used for polarography.

The PBE was cleaned with aqua regia before each use.

The DME used in the majority of this study was characterized by $m^{2/3}t^{1/6} = 1.40$ and $m = 1.04$ mg/s at 40 cmHg; at 50 cmHg, $m^{2/3}t^{1/6} = 1.57$ and $m = 1.28$ mg/s; at 60 cmHg, $m^{2/3}t^{1/6} = 1.64$ and

m = 1.41 mg/s. The DME used for the reduction of XIII was characterized by $m^{2/3}t^{1/6}$ = 1.54 and m = 1.22 mg/s at 45 cmHg; at 55 cmHg, $m^{2/3}t^{1/6}$ = 1.82 and m = 1.71 mg/s; at 65 cmHg, $m^{2/3}t^{1/6}$ = 2.05 and m = 2.19 mg/s.

The electrochemical and EPR cells and their operation have been described previously.[10,41]

Compounds. The syntheses of the following phosphonium salts used in this study have been previously published: II,[34] III,[36] IV,[44] V,[44] VI,[35] VII,[35] VIII,[35] IX,[36] X,[43] XI,[43] XII,[43] XIII,[43] XIV,[43] XV,[36] XVI,[37] XVII,[38] XVIII,[39] XIX,[40] and XX.[35]

1,1,2,4,4,5-Hexaphenyl-1,4-dideuterio-1,4-diphosphoniacyclohexa-2,5-diene (IIa). Phenylethynyldiphenylphosphine[35] (1 g) was dissolved in 12 mL of acetic acid-d_1 in a sealable tube. Dry hydrogen bromide was slowly bubbled through the solution for 30 min and the tube sealed. After 100 h the tube was opened and the acetic acid removed in vacuo. Several recrystallizations from ethyl acetate–methanol and petroleum ether–methylene chloride gave IIa, mp 284–287 °C (lit.[34] 286–290 °C for the hydrogen derivative). The vinyl protons[34] of IIa were unobservable by ^{1}H NMR. It was also found that the EPR spectra of IIa$^{+\cdot}$ could not be simulated if a significant amount of proton hfsc was included in the computer simulated spectra. Thus, the percent of undeuterated IIa was small.

Acknowledgment. Financial support of this investigation by the National Science Foundation (MPS7506421) is gratefully acknowledged.

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