absorbs strongly at 1502 and 1491, 1272 and 1263, 974, and 787 cm^{-1} in the infrared (Nujol) and is evidently comparable to a series of four-coordinate dinitrato complexes reported by Bannister and Cotton.[8]

The dinitrato complex is decomposed rapidly by boiling water with the liberation of nitrate ion; the sulfato complex is considerably more resistant to hydrolysis, but reaction with cyanide ion results in displacement of the coordinated sulfate group and formation of a cyano complex of Pt(II) (infrared band. at 2132 cm^{-1}).

The mechanistic aspects of some of these reactions are currently receiving attention.

Acknowledgment. We thank the National Research Council of Canada and Engelhard Industries (Canada) Ltd. for their support.

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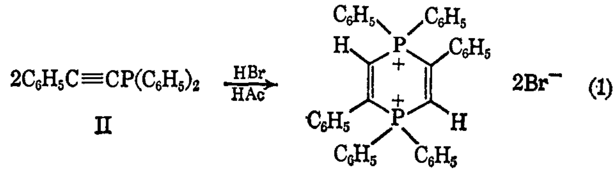
Delocalization of the π-Electron System in 1,4-Dihydrophospha(V)pyrazines

Sir:

The nature of π-electron delocalization in the phosphonitrilic system has been the subject of some controversy.[1,2] The few cyclic phosphorus–carbon six-π-electron systems capable of 3d–2p π delocalization thus far synthesized have been rather unstable.[3,4]

We wish to report the synthesis of a stable 1,4-dihydrophospha(V)pyrazine in which there appears to be delocalization of the four π electrons over the phosphorus atoms.

We have isolated 1,1,2,4,4,5-hexaphenyl-1,4-diphosphoniacyclohexadiene-2,5 dibromide (Ia) in over 60% yield from the 100-hr reaction of phenylethynyldiphenylphosphine[5] (II) with hydrogen bromide in glacial acetic acid at room temperature (eq 1). The orange solid



(1)

II

Ia

Ia melted at 286–290° (from ethyl acetate–methanol). *Anal.* Calcd for $C_{40}H_{32}P_2Br_2 \cdot H_2O$: C, 63.83; H, 4.52; P, 8.24; Br, 21.28. Found: C, 63.85; H, 4.49; P, 8.30; Br, 21.05.

The water solubility, the infrared spectrum, and the fact that it gives an immediate yellow precipitate (Ib) when treated with aqueous sodium picrate show that Ia is a phosphonium salt.

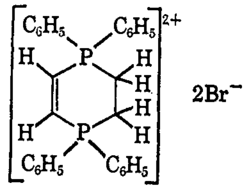
Elemental analysis establishes Ia as a 1:1 adduct of II and HBr, *i.e.*, $[(C_6H_5)_2PC{\equiv}CC_6H_5 \cdot HBr]_n$, while the lack of covalently bound bromine in the adduct is deduced from the analysis of the picrate Ib, mp 245–248° (from acetonitrile). *Anal.* Calcd for $C_{52}H_{36}N_6O_{14}P_2$: C, 60.58; H, 3.50; N, 8.16; Br, 0.00. Found: C, 60.50; H, 3.37; N, 8.14; Br, 0.00.

Table I[a]

Compd	Protons	Multiplicity	J_{P-H}, cps	τ, ppm	Area ratio
Ia	Vinyl	1 Broad complex 1		0.60 1.04 1.5	1
	Phenyl-P	Complex		2.0	10
	Phenyl-C	1		2.38	5
IIIa	CH	Complex		~4.6	1
	Phenyl	Complex		~2.2	15
	CH_2	Complex		~5.6	2
IV	Vinyl	1 Broad complex 1		1.00 1.42 1.84	1
	Phenyl-P	Complex		2.15	10
	CH_2	2 (broad)	8.0	6.11	2

[a] Proton nmr at 60 Mc/sec employing tetramethylsilane as an internal standard and trifluoroacetic acid as solvent.

The proton nmr spectrum of a trifluoroacetic acid solution of Ia at 60 Mc (Table I) shows two sharp peaks at τ 0.6 and 1.5 with a shallow broad complex centered between them. This is similar to the proton nmr spectrum of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide (IV)[6] (Table I). These data



IV

fit a polymeric vinylenebis(diphenylphosphonium) bromide.

$$-\!\!\left[P(C_6H_5)_2CH{=}C(C_6H_5)\right]\!\!-_n^{\,n+} \quad n\mathrm{Br}^-$$

Furthermore, the melting point and complete absence of covalently bound bromine strongly suggest a cyclic structure in which *n* is not very large.

Osmotic pressure depression of methanol solutions of Ia over a range of concentrations (Table II) showed that association occurs at higher concentrations and that the effective molecular weight, obtained by extrapolation, approaches the value of 245 (where $n = 2$).

Table II. Molecular Weight Determination of Ia in Methanol Solution by Osmometric Method

Concentration		
mg/ml	*M*	Mol wt
9.470	0.0320	296
5.995	0.0212	283
3.280	0.0123	267

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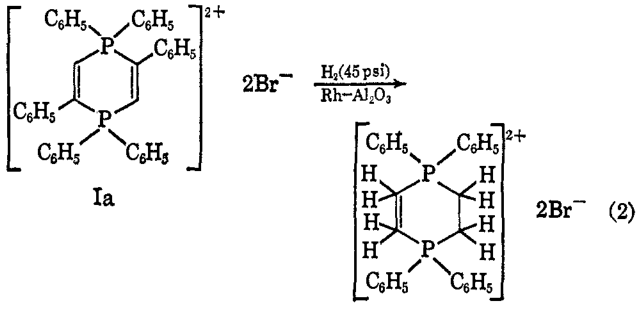
Hydrogenation of Ia employing 5% rhodium on alumina at 45 psi in methanol gave colorless 1,1,2,4,4,5-hexaphenyl-1,4-diphosphoniacyclohexane dibromide (IIIa), mp 269–272° (from acetonitrile–methanol). *Anal.* Calcd for $C_{40}H_{36}Br_2P_2{\cdot}H_2O$: C, 63.49; H, 5.03; Br, 21.16; P, 8.70. Found: C, 63.33; H, 4.89; Br, 20.40; P, 8.77.



Ia

IIIa

(2)

Compound IIIa was also produced by the reaction of *cis*- or *trans*-β-styryldiphenylphosphines[7] (V) with hydrogen bromide in glacial acetic acid (eq 3). As in the case of Ia, the structure of IIIa was established through elemental analysis, solubility, infrared spectrum, formation and analysis of a picrate (IIIb), and proton nmr spectra (Table I).

$$\underset{\text{V}}{2C_6H_5CH{=}CHP(C_6H_5)_2} \xrightarrow[\text{HAc}]{\text{HBr}} \text{IIIa} \qquad (3)$$

Compound IIIb had mp 230–233° (from acetonitrile). *Anal.* Calcd for $C_{52}H_{40}N_6O_{14}P_2$: N, 8.12; Br, 0.00. Found: N, 8.00; Br, 0.00. Absorption in the visible region by Ia is not understandable in terms of the delocalization present in a β-styryldiphenylphosphonium salt since the benzyl bromide salts of *cis*- and *trans*-β-styryldiphenylphosphine (VI) are colorless.

Table III lists the ultraviolet absorbances of Ia and IIIa, along with those of *cis*- and *trans*-VI for comparison. Only a shoulder from the ultraviolet region was found in the visible spectrum of Ia.

Table III. Ultraviolet Absorptions of Methanol Solutions

Compd	λ, mμ	ε
Ia	267 (peak emerging from large shoulder)	18,600
IIIa	269 (shoulder covering the 218 region)	4,600
cis-VI	270	1,100
	218	2,400
trans-VI	278	2,500
	217	3,000

Support for extensive delocalization of the π cloud is obtained from the ^{31}P nmr data listed in Table IV.

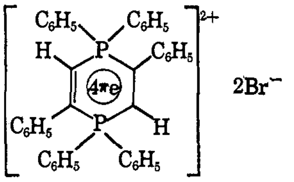
Table IV[a]

Compd	Shift
Ia	+3.5
IIIa	−20.4
IV	−2.8
cis-VI	−13.0

[a] At 40.5 Mc/sec; ^{31}P nmr shifts in parts per million of methanol solutions relative to an external standard of 85% H_3PO_4.

It is seen that the shielding of the phosphorus nucleus is substantially greater in Ia than in any other model compounds. In fact, Ia represents the first report of a phosphonium salt with a positive ^{31}P nmr shift. Most simple phosphonium salts display ^{31}P shifts in the −20- to −30-cps region.[8,9]

The above data are most easily accommodated by assuming delocalization of the π-electronic charge over the phosphorus atoms.



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Heavy-Atom Solvent Effect on the Photodimerization of Acenaphthylene

Sir:

Owing to their ability to enhance spin–orbit coupling, heavy-atom solvents have been used extensively in the study of singlet–triplet absorption and emission spectra.[1] In addition to an effect on the radiative processes, it is known that these solvents often promote nonradiative singlet-to-triplet intersystem crossing.[2] Two recent studies have attempted to make use of this external heavy-atom effect to affect increased intersystem crossing in photochemical reactions. However, no change was observed when heavy-atom solvents were used in a study of the type II photoelimination reactions of aliphatic ketones,[3] nor was an effect observed in the photodimerization of coumarin.[4] Both of these systems contain n–π* excited states. El-Sayed[5] has pointed out that in carbonyl compounds the spin–orbit perturbation due to the carbonyl group is comparable to or larger than an internal heavy-atom perturbation due to halogen substitution on the carbonyl-containing molecule. In addition, the internal heavy-atom perturbation is expected to be much larger than the external perturbation due to a heavy-atom solvent.

In this note we wish first to present evidence to document the heavy-atom solvent effect on the photodimerization of a system not containing n–π* states and second to show that in the two cases easily com-

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