

the possibility that the isotopic molecules of **1** ( $^{12}\text{C}$  and  $^{13}\text{C}$ ) can be expected to exhibit slightly different extinction coefficients at some wavelengths of the irradiating beam, i.e., the selective excitation of a specific absorption band associated with one isotopic species to the exclusion of the others. An example of this is Hochstrasser's tetrazine photolysis<sup>14</sup> in which laser excitation of a band width of  $0.6\text{ cm}^{-1}$  was used to selectively populate the 0-0 band of the  $n-\pi^*$  state of  $^{12}\text{C}^{14}\text{N}_4\text{H}_2$  in an argon matrix at 4 K, with no coabsorption by undesired species occurring. However, the overall effect on total energy in this case is really exceedingly small; only 0.05-kcal/mol energy difference is noted for [ $^{13}\text{C}$ ]tetrazine compared with the  $^{12}\text{C}$  species, with an energy of the lowest excited state near 50 kcal/mol, so that the total perturbation of the vibronic energy was only 0.1%. Moreover, such an effect would be operating in the opposite direction to the inverse isotope effect observed since the lighter isotope is usually associated with the higher extinction coefficient. For all these reasons, therefore, it can be assumed with confidence that, with the use of wide-band excitation in the photorearrangement under consideration, an isotope absorption effect on the magnitude of the kinetic isotope effect would not be discernible.<sup>15,16</sup>

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## References and Notes

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- (15) A referee has kindly pointed out that we may have observed a magnetic isotope effect resulting from a singlet to triplet crossing.<sup>16</sup> This is unlikely in view of the fact that the triplet state leads to photolytic N-N bond cleavage rather than diazepine.<sup>9</sup> Under the reaction conditions employed in this work only the latter is formed. Moreover, this conclusion is confirmed by the results reported in the previous article.<sup>5</sup> Therein, an inverse secondary deuterium isotope effect ( $k_H/k_D \ll 1.0$ ) was found, contrary to the normal isotope effect ( $k_H/k_D \gg 1.0$ ) to be expected for a mechanism involving crossing to the triplet state; see N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, 1965, p 70.
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tope effect of naturally abundant  $^{15}\text{N}$  (0.37%) would have resulted in a very slightly lower magnitude.

- (18) A correction for a naturally abundant  $^{15}\text{N}$  isotope effect was not made because this is a minimum value for the dissociative transition state. Such a correction would have led to a slightly greater value of  $k_I/k_H$ .
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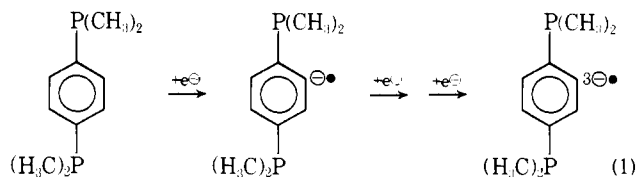
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## Radical Anion and Radical Trianion of 1,4-Bis(dimethylphosphino)benzene<sup>1,2</sup>

Sir:

Surveying nonmetal compounds with low first ionization potentials as promising radical cation precursors,<sup>3</sup> we observed, much to our surprise, that the title compound rather accepts electrons to form not only the radical anion<sup>4-6</sup> but also the ESR spectroscopically detectable radical trianion<sup>7-11</sup> (eq 1).



The compound—synthesized via a more convenient odorless route<sup>12</sup>—exhibits in the low energy region of its photoelectron spectrum four ionizations (Table I). Comparison with those of the  $\pi$  isoelectronic tetramethyl-*p*-phenylenediamine reveals that (i) the first ionization energy of the phosphorus derivative is too high ( $IE_1 > 8\text{ eV}$ ) to obtain the corresponding radical cation<sup>1-3</sup> in solution and (ii) dimethylamino substituents exercise a much larger perturbation of the benzene  $\pi$  system ( $IE_1 = 9.24$ ) than  $(\text{H}_3\text{C})_2\text{P}$  groups, inductively ( $\Delta IE = 9.24 - IE_3$ ) as well as by conjugation ( $\Delta IE = IE_2 - IE_1$  or  $\Delta IE = IE_4 - IE_3$ ).

The relatively poor donor effect of dimethylphosphino substituents in benzene  $\pi$  radical cation states (Table I) led to the expectation that, on the other hand, they might stabilize the  $\pi$  radical anion states—analogously to the phosphorus substituted  $\pi$  systems<sup>4-6</sup> or to numerous other known species with third row elements groups, e.g., like  $\text{R}_3\text{Si}^{13}$  and contrary to  $\text{R}_2\text{N}$  substituents.<sup>14</sup> Electrochemical reduction in a solution of  $\text{R}_4\text{N}^+\text{BF}_4^-$  in RCN mixtures or reaction with Na or K in ethers under addition of dicyclohexyl-18-crown-6 yielded the ESR spectrum of the radical anion (Figure 1, A with simulation B). Prolonged contact with the alkali metal without addition of any complexing reagent finally the radical trianion (Figure 1, C with simulation D). Both ESR spectra exhibit 195 signals due to sets of each 2-, 4-, and 12-equiv nuclei with nuclear spin  $I = 1/2$ , but different (temperature dependent<sup>2</sup>) coupling constants (Table II).

The different spin populations in the radical anion and the radical trianion can be discussed using the squared HMO coefficients of an 8-center  $\pi$  system modified for the phos-

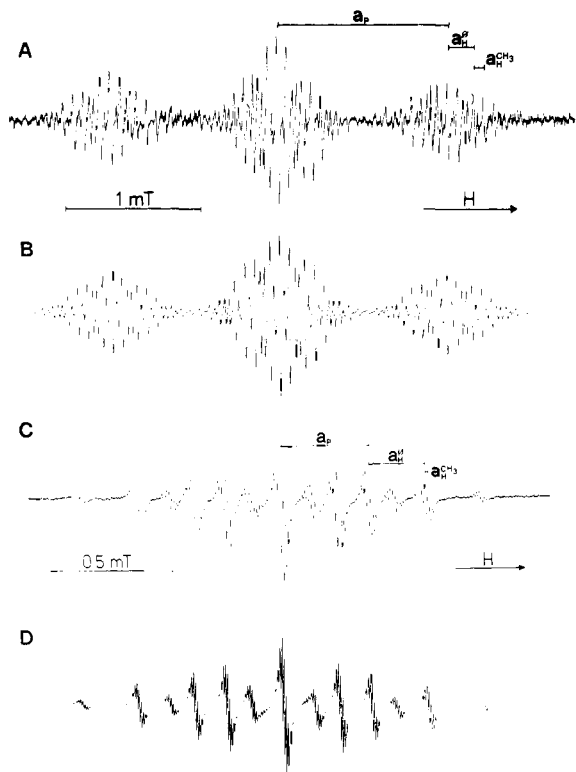


Figure 1. ESR spectra of (A) 1,4-bis(dimethylphosphino)benzene radical anion (generated by cathodic reduction in propionitrile/butyronitrile solution of  $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$  at 243 K) with (B) simulation and of (C) its radical trianion (generated using Na in THF at 215 K) with (D) simulation.

Table I

compd	X	eV			
		IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>
	P(CH <sub>3</sub> ) <sub>2</sub>	8.2	8.50	9.10	9.4
	N(CH <sub>3</sub> ) <sub>2</sub>	6.75	8.35	8.70	10.00
orbital assignment		 n <sub>x</sub> - π <sub>s</sub>	 n <sub>x</sub> +	 π <sub>is</sub>	 π <sub>s</sub> + n <sub>x</sub> -

phorus substitution<sup>15</sup> to approximate the benzene perturbation. The calculated spin populations  $\rho_{\pi}^{\text{HMO}} = (c_{J\mu}^{\text{HMO}})^2$  resemble those obtained by the McConnell relation  $\rho_{\pi}^{\text{exp}} = a_{\pi} \text{C}_6\text{H}_4 / |Q|$

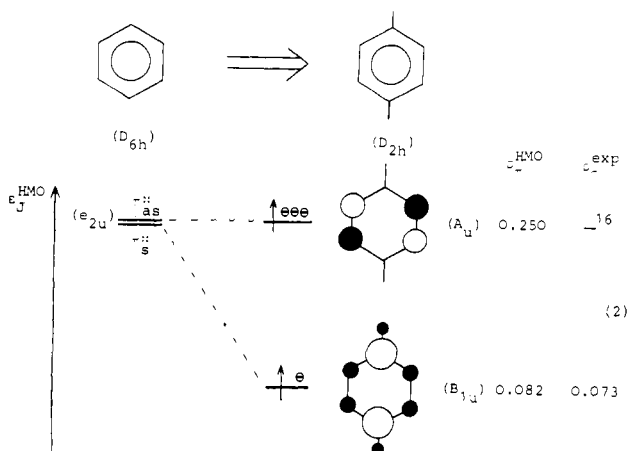


Table II

compd	T = 210 K	mT		
		a <sub>31P</sub>	a <sub>H</sub> <sup>PCH<sub>3</sub></sup>	a <sub>H</sub> <sup>C<sub>6</sub>H<sub>4</sub></sup>
 (H <sub>3</sub> C) <sub>2</sub> P	●●	1.250	0.071	0.176
	●●●●	0.348	0.009	0.222

with the parameter  $|Q| = 2.4 \text{ mT}^{16}$  for the monoanion (eq 2).

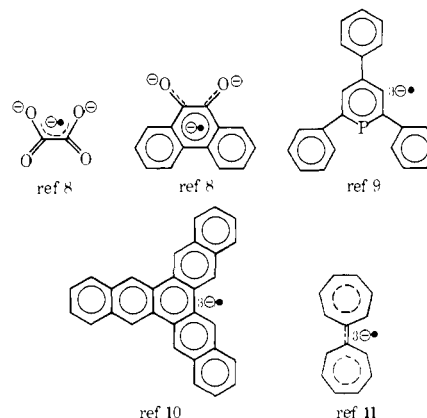
For radical trianions no  $Q$  values are known. According to the orbital diagrams (eq 2), one expects, in the radical anion ground state, some spin population in the (H<sub>3</sub>C)<sub>2</sub>P substituents. In contrast, the radical trianion ground state still resembles some features of a perturbed benzene  $\pi_{as}^*(e_{2u})$  orbital with a tremendous decrease of the spin population in the region of the nodal plane and an increase in the spin population<sup>15</sup> of the unsubstituted  $\pi$  centers. Furthermore, from the conditions to generate the trianion—no cation complexing crown ether—one might tentatively anticipate that the phosphorus lone pairs interact with the counterions<sup>17</sup> and thus the charge is distributed over the whole molecular skeleton.

The multistep reduction process observed ESR spectroscopically displays, as another intriguing facet, that a benzene perturbation MO model allows the description of the spin populations of both the radical anion and trianion.

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References and Notes

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- (13) Cf., e.g., F. Gerson, J. Heinzer, H. Bock, H. Alt, und H. Seidl, *Helv. Chim. Acta*, **51**, 707 (1968), or F. Gerson, U. Krynitz, and H. Bock, *ibid.*, **52**, 2512 (1969).
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- (15) The HMO parameters have been deduced from the photoelectron spectrum:  $\alpha_P = -8.5$ ,  $\alpha_{C(1,4)} = -6.3$ ,  $\alpha_C = -6.15$ ,  $\beta_{PC} = -0.8$ ,  $\beta_{CC} = -3.1$  eV. The ionization potentials calculated with this set—8.16, 8.52, 9.25, and 9.71 eV—agree reasonably well with the experimental values (cf. Table I).
- (16) The parameter  $|Q| = 2.4$  mT (cf. F. Gerson, "High-resolution ESR Spectroscopy", Verlag Chemie, Weinheim/Bertstr., 1970) is probably smaller for radical trianions.
- (17) The hyperfine coupling of the alkali cations is not observed and must be smaller than 0.002 mT.

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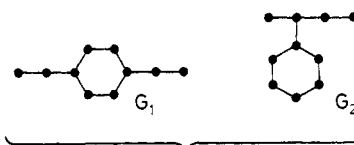
## Spectral Differences between "Isospectral" Molecules<sup>1</sup>

Sir:

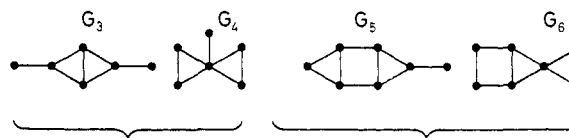
The past few years have witnessed a considerable increase in the number of papers concerning applications of graph theoretical methods<sup>2a</sup> to chemistry.<sup>2b,c</sup> As in other fields, major achievements have been a more transparent description of sequential processes (e.g., configurational<sup>3</sup> and/or conformational<sup>4</sup> changes), efficient methods for computer-assisted storage of structural information,<sup>5</sup> and useful shorthand notations for involved mathematical formulae (e.g., in many-electron treatments<sup>6</sup>). In contrast, the numerous applications of graph theory to simple Hückel-type independent electron models<sup>7</sup> have experienced (in our opinion) only moderate success, inasmuch as they have mainly led to more elegant and mathematically pleasing re-formulations of known results. All of these applications rely in the final analysis on a fundamental observation, due to Günthard and Primas,<sup>8</sup> that such models are purely topological in nature and are thus completely defined by simple, connected graphs  $G$  and their adjacency matrices  $A = A(G)$ . Note that the latter are only defined up to a similarity transformation  $A \sim PAP^T$ , where  $P$  is any permutation matrix. In particular the set  $\{x_j\}$  of the eigenvalues obtained by solving  $\det(A - xI) = 0$ ; i.e., the so-called "spectrum" of the graph  $G^9$  is postulated to yield the orbital energies  $\epsilon_j = \alpha + \beta x_j$  of such models.<sup>10</sup>

One of the few novel concepts to emerge from graph theory, when applied to molecular orbital theory, is the existence of "isospectral" molecules. Whereas  $\{x_j\} \neq \{x'_j\}$  necessarily implies that the underlying graphs  $G$  and  $G'$  are not isomorphic,  $G \neq G'$ , surprisingly, the converse is not true. As late as 1957 Collatz and Sinogowitz<sup>9</sup> discovered that two nonisomorphic graphs  $G \neq G'$  can indeed have the same spectrum  $\{x_j\} \equiv \{x'_j\}$ , notwithstanding the fact that  $A' \neq PAP^T$  for all possible permutation matrices  $P$ . Such graphs are called "isospectral" and a classical example is provided by the pair  $G_1$  and  $G_2$ :  $\{x_j\} \equiv \{\pm 2.214; \pm 1.675; \pm 1.000; \pm 1.000; \pm 0.539\}$ .

Molecular systems which can be associated with such graphs via a Hückel-type model, e.g., 1,4-divinylbenzene (**1**) with  $G_1$ , 2-phenylbutadiene (**2**) with  $G_2$ , are called "isospectral molecules".<sup>7,11</sup> Obviously  $G_1$  and  $G_2$  are meant to refer only to their  $\pi$  system.



Apart from  $G_1$  and  $G_2$  many other pairs of isospectral graphs have been described in the literature,<sup>12</sup> many of which are, however, unconnected and thus hardly relevant for chemistry. Even pairs of connected isospectral graphs, e.g.,  $G_3$ ,  $G_4$  or  $G_5$ ,  $G_6$ , will not have real molecules as counterparts, for which an independent electron model would give rise to adjacency matrices corresponding to such graphs.



The fundamental, admittedly pragmatic question is whether pairs of "isospectral" molecules, e.g., **1** and **2**, possess measurable physicochemical properties which reflect their "isospectricity". Clearly, a direct measurement of their  $\pi$ -ionization energies by photoelectron spectroscopy is the method of choice<sup>12e</sup> to answer such a question, since all other properties depend to a much lesser degree on purely topological features of the molecular system. For this reason we have recorded the photoelectron spectra of mass- and NMR-pure samples of **1**<sup>13</sup> and **2**,<sup>14</sup> which are presented in Figure 1. In Table I are collected the observed ionization energies  $I_j^m$  (= positions of the band maxima) together with the ionization energies calculated by the SPINDO<sup>15</sup> and ab initio STO-3G models,<sup>16</sup> assuming planar  $\pi$  systems and standard geometries.<sup>17</sup>

It is at once obvious that the photoelectron spectra of **1** and **2** differ at least as much as those of any other "nonisospectral" pair having  $\pi$  systems of comparable size, e.g., naphthalene<sup>18</sup> or azulene,<sup>19</sup> except for the more pronounced vibrational fine structure observed in the latter cases resulting from increased rigidity of the molecules.

It is important to realize that the difference between the two spectra shown in Figure 1 is not due to conformational changes. Thus, on the basis of previous experience<sup>20</sup> both the  $C_{2h}$  and  $C_{2v}$  conformations of **1** will lead to identical  $\pi$ -band systems. Furthermore, slight deviations from coplanarity of the order  $\varphi \leq 20^\circ$  (for the vinyl/phenylene twist angle in **2**), suggested by force-field calculations and by the conformational analysis of 1,3-butadiene or stilbene,<sup>21</sup> cause only insignificant shifts of the band positions ( $\sim 0.1$ – $0.2$  eV). Support for the absence of major deviations from planarity can be found in the excellent

Table I. Observed ( $I_j^m$ ) and Calculated Ionization Energies for 1,4-Divinylbenzene (**1**) and 2-Phenylbutadiene (**2**)<sup>a</sup>

$j$	<b>2</b>					<b>1</b>				
	$I_j^m$	$-\epsilon_j^{\text{STO-3G}}$	$I_j^{\text{calcd}b}$	$-\epsilon_j^{\text{SPINDO}}$	orbital	$I_j^m$	$-\epsilon_j^{\text{STO-3G}}$	$I_j^{\text{calcd}b}$	$-\epsilon_j^{\text{SPINDO}}$	orbital
1	8.60	6.34	8.43	8.77	5a'' $\pi$	8.11	6.00	8.21	8.58	3b <sub>g</sub> $\pi$
2	9.28	7.54	9.21	9.34	4a'' $\pi$	9.18	7.61	9.26	9.34	2b <sub>g</sub> $\pi$
3	9.5	8.03	9.54	9.73	3a'' $\pi$	9.80	8.57	9.89	10.14	2a <sub>u</sub> $\pi$
4	11.2	9.26		10.26	20a' $\sigma$	11.0	10.54	11.18	11.14	1b <sub>g</sub> $\pi$
5	11.54	10.83	11.73	11.39	2a'' $\pi$	11.46	11.50		11.57	10a <sub>g</sub> $\sigma$
6		11.63		11.78	19a' $\sigma$	12.19	11.54		11.91	9a <sub>g</sub> $\sigma$
7		12.41		12.30	18a' $\sigma$		12.38		12.00	10b <sub>u</sub> $\sigma$
8		12.89		12.64	1a'' $\sigma$		12.92		12.68	1a <sub>u</sub> $\pi$

<sup>a</sup>All values are in electronvolts. <sup>b</sup> $I_j^{\text{calcd}}$  from linear regression  $-\epsilon_j^{\text{STO-3G}} = 1.53 I_j^m(\pi) - 6.56$  (correlation coefficient  $r = 0.991$ ).