

II
Ha, broad singlet (1 proton) at τ 4.76; Hb, doublet (two protons), centered at τ 4.30 ($J \sim 1.9$ cps); Hc, doublet (two protons), centered at τ 3.03 ($J \sim 1.9$ cps); Hd, multiplet (three protons), centered at τ 3.37; He series of multiplets (eight protons), ranging from τ 6.88 to 8.13.

shifts has been well established.⁸ Allinger, *et al.*,^{8b} predict that [7]paracyclophane should have a long-wavelength absorption band at 288 $m\mu$ and that the 1,4-carbon atoms are bent out of the plane of the other four by about 26°. The question of whether the band at 291 $m\mu$ in the spectrum of II is the predicted absorption is a matter for conjecture.

The long-wavelength charge-transfer band in the visible spectrum of the tetracyanoethylene π salt of II in methylene dichloride occurred at 455 $m\mu$. This transition is of higher energy than that of any of the other paracyclophanes^{9a} and is between that of *m*-xylene (440 $m\mu$) and *p*-xylene (460 $m\mu$).^{9b} This fact implies that II is a weaker π base than either [2.2]-paracyclophane (π salt, λ_{\max} 521 $m\mu$)^{9a} or [2.2]metacyclophane (π salt, λ_{\max} 486 $m\mu$).¹⁰

The structure of hexahydropyrene III was assigned on the basis of its combustion analysis,³ melting point,⁴ the melting point of its orange picrate (150.4–150.6°, lit.⁴ 147–148°), its vpc retention time (close to that of pyrene), the similarity of its ultraviolet spectrum to that of alkylated naphthalenes, and its nmr spectrum in carbon tetrachloride. The five aromatic protons occurred as a multiplet centered at τ 2.82; the five benzylic protons as a multiplet extending from τ 6.75 to 7.5; the six methylene protons as a multiplet extending from τ 7.65 to 8.95.

Two possible driving forces are envisioned for the rearrangement of I to II. Compound I has about 31 kcal/mole strain energy,¹¹ much of which is probably associated with π - π repulsion. In the conversion of I to II, the rings are decentered and π - π repulsions decreased. Although one of the two benzene rings of II (*para*-substituted) is probably more deformed than the two rings of I, the other (*meta*-substituted) is probably less deformed, and the over-all deformation strain of the two systems might be comparable.

The second driving force for rearrangement could derive from the facts that *m*-dialkylbenzenes are

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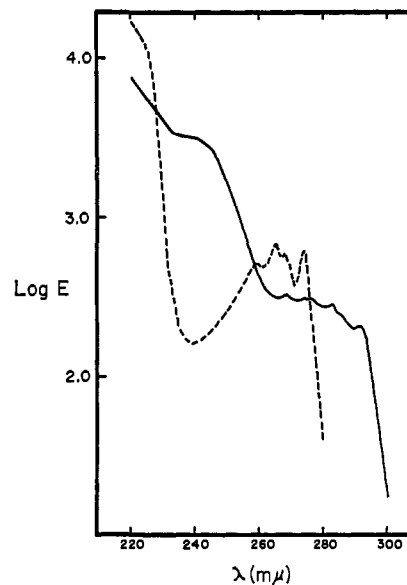
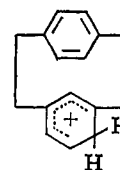


Figure 1. Ultraviolet absorption spectra (Cary Model 14 spectrophotometer) in 95% ethanol: [2.2]metaparacyclophane (II), —; *m,p'*-dimethylbibenzyl (V), ---.

stronger bases toward protons than *p*-dialkylbenzenes,¹² and that the conjugate acid of II is of lower energy than that of I. The highly colored reaction mixtures suggest the presence of these conjugate acids. Production of hexahydropyrene III probably occurs through [2.2]-metacyclophane as an intermediate, which when treated with aluminum chloride is known⁴ to produce III. A trace of [2.2]metacyclophane has been detected in the reaction mixture for rearrangement by vpc and nmr methods, but the substance occurs in too small an amount to be isolated. Acid-catalyzed rearrangements of methylene groups in paracyclophane systems have been observed previously,¹³ particularly in strained systems.

The chemistry of [2.2]metaparacyclophane is under active investigation.



conjugate acid of II

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Toward a Better 2p π -Atomic Orbital for π -Electron Theory¹

Sir:

The concept of a carbon 2p π atomic orbital (AO) plays a key role in the theory of the electronic structure

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Table I. Results of Minimization of Carbon Valence-State Energy for Alternant Hydrocarbon Ground State

Basis type and total energy, au	γ	Basis functions	n Principal quantum no.	ξ orbital exponent	Coefficient for atomic orbitals				
					1s	2s	2p σ	2p π	
I. Integral n , minimal -37.2264492	0.5061 au 13.77 ev	s	1	5.6787	0.99715	-0.24872			
		s	2	1.6649	0.012074	1.02763			
		p σ	2	1.6136			1.00000		
		p π	2	1.2929				1.00000	
II. Nonintegral n , minimal -37.2938082	0.4785 au 13.02 ev	s	0.9859	5.5965	0.99783	-0.23300			
		s	2.2417	1.8540	0.00974	1.02463			
		p σ	1.6609	1.3468			1.00000		
		p π	1.4803	0.9633				1.00000	
III. Nonintegral n , "double ξ " -37.3197624	0.4549 au 12.38 ev	s	0.9918	5.727	0.98132	0.21820			
		s	2.7821	2.519	0.16262	0.94180			
		s	4.8307	2.079	-0.01242	0.23911			
		s	4.4118	3.563	-0.13384	-0.08623			
		p σ	1.8362	1.215			0.74564		
		p σ	1.8803	2.291			0.29711		
		p π	1.7491	0.772				0.69702	
		p π	1.8190	1.915				0.39386	

of π -electron molecules.² This AO is usually imagined to be a hydrogen-like 2p orbital with an effective nuclear charge $Z = 3.18$,^{3,4} although values of Z ranging from 1.85 to 3.25 may be found in the literature.⁵⁻¹² Occasionally this 2p π orbital is represented by an atomic Hartree-Fock orbital.¹³

What is the best carbon 2p π -AO for π -electron theory? Perhaps a large part of the discrepancy between so-called nonempirical theory and experiment, as for example in the Goepfert-Mayer and Sklar (GMS) type calculations^{3,14-17} on benzene, is due to the choice of AO. In this communication we present a candidate for a better 2p π -AO which was obtained by minimizing the energy of a valence state of carbon in an alternant hydrocarbon ground state. We also indicate why a π -electron calculation with this AO should give results closer to experiment than calculations with the AO's used formerly.

Within the π -electron approximation,¹⁸ we imagine that the σ -electron part of the wave function of an alternant hydrocarbon in the ground state (AHC-gs) is described by valence-bond theory¹⁹ and the π -electron part by self-consistent field LCAO-MO theory.²⁰

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Invoking the zero-differential overlap approximation²¹ for both σ and π orbitals, we write the energy expression for the molecule and, in the spirit of the valence state model,^{22,23} keep only those integrals involving a single carbon atom. This procedure yields the following expression for the valence-state energy.

$$E_{CVS-AHC-gs} = E_{C^+} + \alpha + \frac{1}{4}\gamma \quad (1)$$

where

$$E_{C^-} = 2I_{1s} + J_{1s1s} + 3I_{\sigma_1} + 3J_{\sigma_1\sigma_1} - \frac{3}{2}K_{\sigma_1\sigma_1} + 6J_{1s\sigma_1} - 3K_{1s\sigma_1} \quad (2)$$

$$\alpha = I_{2p\pi} + 2J_{1s2p\pi} - K_{1s2p\pi} + 3J_{2p\pi\sigma_1} - \frac{3}{2}K_{2p\pi\sigma_1} \quad (3)$$

$$\gamma = J_{2p\pi 2p\pi} \quad (4)$$

and where $I_\phi = \langle \phi | -\frac{1}{2}\nabla^2 - (6/r) | \phi \rangle$, $J_{\phi_1\phi_2} = \langle \phi_1\phi_2 | (1/r_{12}) | \phi_1\phi_2 \rangle$, $K_{\phi_1\phi_2} = \langle \phi_1\phi_2 | (1/r_{12}) | \phi_2\phi_1 \rangle$, and σ_j are sp²-hybrid σ orbitals. Note especially that the $\frac{1}{4}\gamma$ in eq 1, which does not appear in previous discussions of carbon valence states,²⁴ is brought in by the molecular-orbital description of the π electrons.

The 2p π -AO's obtained by minimizing²⁵ $E_{CVS-AHC-gs}$ using three progressively more flexible bases are summarized in Table I. These theoretical valence-state orbitals²⁶ contrast strikingly with those obtained from consideration of the atomic carbon ground state.^{4,5,13} The effective nuclear charge, $Z = 2.59$ ($Z = 2\xi$) of the basis I 2p π orbital is considerably lower than 3.18. The lowest value of γ ($= 12.38$ ev) obtained with the most flexible basis III is considerably closer to the experimental values²⁷⁻³¹ (~ 11 ev) than are the previous theoretical values of 16.93³² or 15.71 ev.³³

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The closer agreement of γ_{theor} with γ_{exptl} suggests that the nonempirical approach might be more successful using a valence-state AO. Moreover, the AO obtained by minimizing a valence-state energy should³ on theoretical grounds be more appropriate for calculations of molecular properties (not only energy) than are the orbitals obtained by minimizing the ^3P ground-state energy of the carbon atom.

In a future paper³⁴ we shall present a detailed theoretical and computational discussion of the valence state appearing in eq 1, its extension to π -electron excited states (including the associated changes in the σ - and π -AO's), and the effect of inclusion of molecular-orbital character in the σ -electron wave function.

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Intermediates in the Conversion π - to σ -Allylic Complexes of Palladium

Sir:

The temperature dependence of the nmr spectra of π -allylic complexes of palladium provides evidence and clarification of intermediates¹ in the conversion of π - to σ -allylic complexes.

The temperature dependence of the 60-Mc/sec nmr spectrum of crotylpalladium(II) chloride in solution in CDCl_3 , to which has been added 3 moles of $\text{DMSO}-d_6$ /mole of Pd (20% $\text{DMSO}-d_6$ in CDCl_3), is shown in Figure 1, and the parameters for the low-temperature species (-20°) and the high-temperature species (80°) are listed in Table I. The spectrum of the low-temperature species indicates that the complex is in the π -allylic form with the resonances at τ 5.90 and 6.90 corresponding to the *cis* and *trans* protons b and c. Although all of the resonances are slightly affected by an increase in temperature, the *cis* and *trans* protons converge. The spectra clearly rule out the allylic rearrangement possible for symmetrical species² since this would necessitate the averaging of proton d also, and this does not occur over the temperature range

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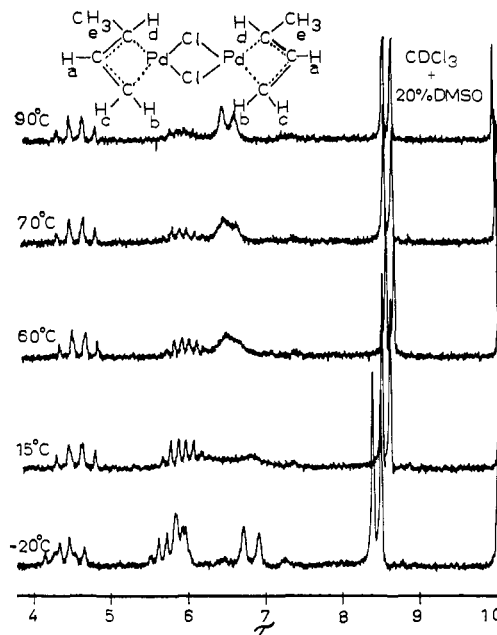
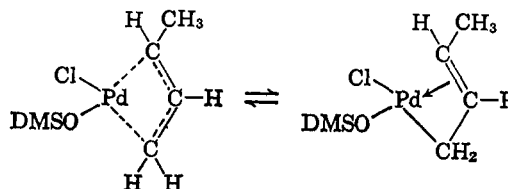


Figure 1. Temperature dependence of the nmr spectrum of crotylpalladium(II) chloride in a 20% $\text{DMSO}-d_6$ - CDCl_3 solution.

covered. The most likely process appears to be a π to σ equilibration



which is similar to the conversion postulated by Shaw and co-workers¹ for methallylpalladium(II) chloride upon addition of triphenylphosphine.

The temperature dependence of the 100-Mc/sec spectrum of this latter complex $[\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\text{Pd}(\text{Ph}_3\text{P})\text{Cl}]$ in CDCl_3 is shown in Figure 2, and the nmr

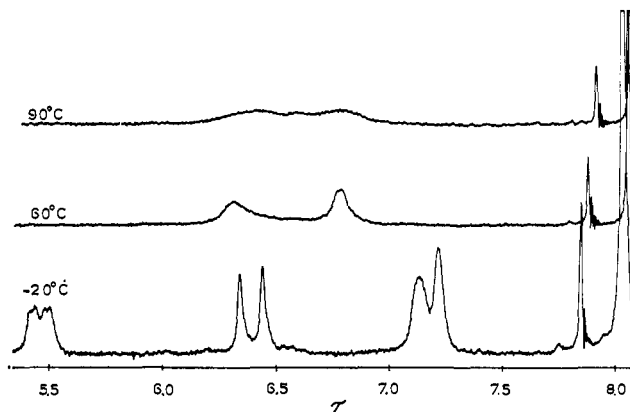


Figure 2. Temperature dependence of the nmr spectrum of the triphenylphosphine adduct of methallylpalladium(II) chloride in solution in CDCl_3 .

parameters for the equilibrating species are listed in Table I. The resonances centered at τ 7.19 were previously interpreted as corresponding to methylene pro-