

energy as compared to **9**,<sup>11</sup> whereas the pericyclic transition state **8** maintains the cyclopropene level of ring strain.

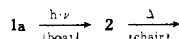
In the preceding paper<sup>2</sup> we have shown that a prismane intermediate is unlikely to occur in photochemically induced bicyclopropenyl  $\rightarrow$  benzene rearrangements. Although we cannot at present exclude an alternative involving initial retrocarbene fission of one cyclopropene ring,<sup>12</sup> it is tempting to consider intermediates of type **10** as common intermediates for both Cope rearrangement (corresponding to fission of one peripheral cyclobutane bond) and aromatization (corresponding to electrocyclic collapse of the inner cyclobutane bonds) to yield ortho x,y-substituted benzene derivatives. If this latter process is a stepwise one then as a further local energy minimum down the bicyclopropenyl  $\rightarrow$  benzene energy cascade "pre-fulvene" intermediates will have to be considered with their possibility of ortho-meta scrambling of x,y-substituents.<sup>13</sup>

We feel that this possibility may well form a basis for understanding the photochemical behavior of **1b** and are presently elaborating on this point. Our further research is aimed at mechanistic details of the photo-Cope process and at the implications of the thermal counterpart for the mechanism of thermal bicyclopropenyl  $\rightarrow$  benzene rearrangements.<sup>14</sup>

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## References and Notes

- Reactions of coupled three-membered rings, part VIII; presented in part at the Chemiedozententagung, Stuttgart, April 1-4, 1974.
- For part VII of this series see: R. Weiss and H. Kölbl, *J. Am. Chem. Soc.*, preceding paper in this issue.
- 1a** was synthesized from **1b** following a procedure described in ref 2 for the synthesis of **1b** from 1,2,1',2'-tetraphenyl-bicyclopropenyl-3,3' (mp 170°; NMR (CDCl<sub>3</sub>)  $\tau$  8.44 (6 H, s)).
- Ir and NMR spectra kindly provided by Professor G. Maier, Marburg.
- R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965). The configuration of **4** could not be determined.
- No other isomeric bicyclopropenyl systems could be detected.
- R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Lett.*, 3955 (1965).
- N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1967, p 186.
- For instance the combination



would not regenerate **1a** but give rise to a structural isomer with one methyl group at a bridgehead position and one at a double bond.

- For a leading reference see M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Am. Chem. Soc.*, **96**, 5242 (1974).
- Assuming that the strain energy of **10** is equal, or nearly so, to anti-tricyclohexane.
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- As is easily verified this could happen via the benzvalenes which can be derived from a prefulvene precursor.
- NOTE ADDED IN PROOF. A further example of a thermal bicyclopropenyl-Cope rearrangement has just been published: W. H. de Wolf, I. J. Lau-dheer, and F. Bickelhaupt, *Tetrahedron Lett.*, 179 (1975).

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## Helium(I) Photoelectron Spectrum of *p*-Quinodimethane

Sir:

We wish to report our observation of the He(I) photoelectron spectrum of *p*-quinodimethane<sup>1</sup> (**2**) formed from the flash vacuum pyrolysis<sup>2</sup> of [2.2]paracyclophane (**1**), and our analysis of the first three ionic states in terms of the structure representation (SR)<sup>3</sup> method. The spectra were obtained using a modified Perkin-Elmer PS-18 photoelec-

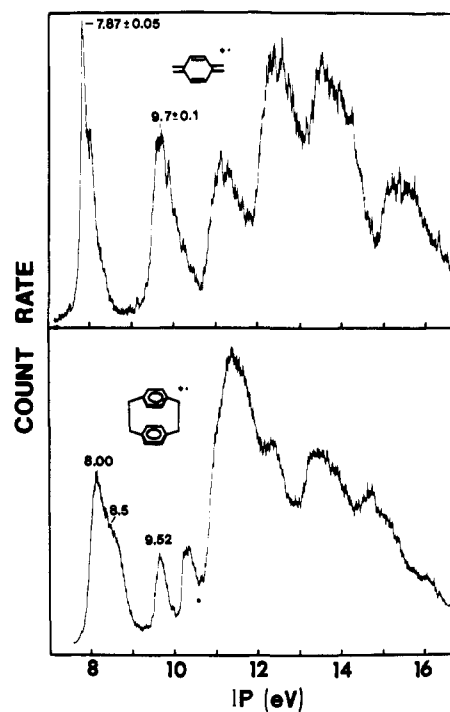
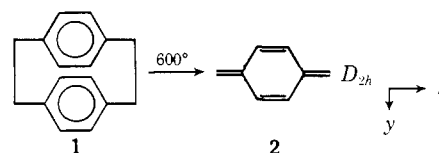


Figure 1.



tron spectrometer. The basic modifications include the insertion of a pyrolysis tube between the He(I) light source and the target chamber as described previously.<sup>4</sup> The sample was introduced from a sublimation chamber, directly attached to the furnace base, which was heated by a separate induction coil. The experimental spectra of the [2.2]paracyclophane (**1**) precursor<sup>5</sup> and the transient (**2**) are shown as Figure 1.

Chemical evidence that the observed transient species is **2** is the fact that a film of its polymer was isolated from the liquid nitrogen trap after warming to room temperature. Previous investigations<sup>6</sup> of the PMR, ir, and uv spectra of **2**, obtained by a similar pyrolysis and collection at low temperature, indicate clean formation of **2** in the pyrolysis. The present PES spectrum (Figure 1) is like the PMR, ir, and uv spectra in that its appearance is entirely consistent with formation of essentially pure **2**.

The position of the second band maximum in the observed spectrum of **2** (9.7 eV) is strikingly close to that observed<sup>7</sup> for the related 1,4-cyclohexadiene, 1,4-dihydropyridine, and *N*-methyl-1,4-dihydropyridine. This result is predicted by the SR analysis, offered for interpretation of the spectra of the latter three compounds, if this band is the antisymmetric combination of the ionic structures derived from the two endocyclic double bonds ( ${}^2B_{1g}$ ,  $1/\sqrt{2}(\Psi_{III} - \Psi_{IV})$ , Figure 2) with inductive effects being ignored. The position of this band is thus entirely determined by the direct interaction across the ring ( $S_{1,4} = 0.74$  eV).<sup>7</sup>

The same method predicts the first band should be assigned to the mixed symmetric combination of the endocyclic and exocyclic ion structures ( ${}^2B_{3u}(-)$ ,  $N_1(\Psi_I + \Psi_{II}) - N_2(\Psi_{III} + \Psi_{IV})$ , Figure 2) and should be observed near 7.98 (obsd 7.87 eV). This band position is mainly determined by the interaction constant between the ionic struc-

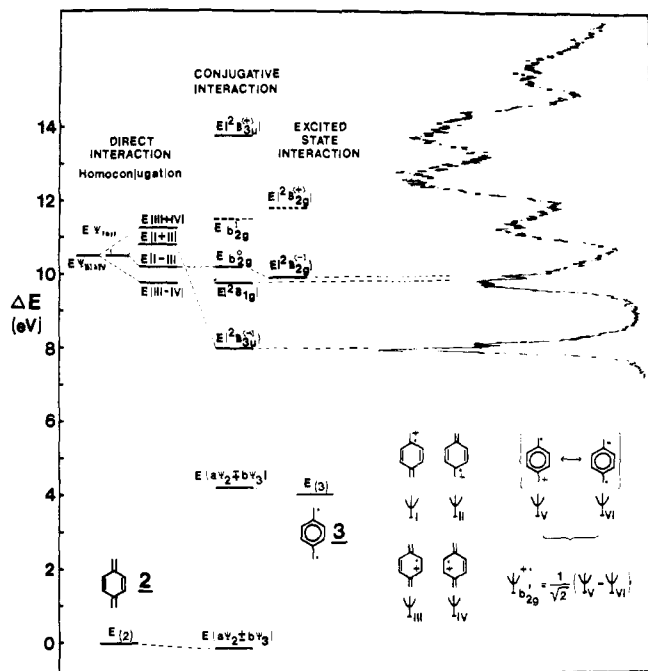


Figure 2.

tures of the conjugated diene units ( $S_{1,3} \approx 1.44$  eV). The observed positions of the first two bands in the spectrum of **2** are therefore in excellent agreement with the predictions of the simple SR method.

The zero-order SR method also predicts the position of the third  $\Pi$  band in the spectrum of **2** ( ${}^2B_{2g}$ ,  $1/\sqrt{2}(\Psi_I - \Psi_{II})$ , Figure 2) at 10.2–10.5 eV. The value depends on the magnitude of the *direct* interaction between the ionic structures derived from the exocyclic ene units, which should be less than 0.3 eV. The observed spectrum shows no clear band maximum in this region although the measured total area under the second peak is greater (1.2:1) than that under the first. This observed second band could thus possibly arise from the unresolved superposition of the zero-order  ${}^2B_{2g}$  and  ${}^2B_{1g}$  stationary states.

We believe that a more likely explanation for both the low energetic position (band maximum less than 10.2 eV) and low apparent intensity of the third  $\Pi$  band is mixing of the zero-order  $b_{2g}$  structure ( $b_{2g}^0$ ,  $1/\sqrt{2}(\Psi_I - \Psi_{II})$ ) with the antisymmetric combination of the two *ionic* structures ( $\Psi_V$ ,  $\Psi_{VI}$ , Figure 2) derived from the singlet diradical (**3**, Figure 2). The latter combination ( $1/\sqrt{2}(\Psi_V - \Psi_{VI})$ ) corresponds to an optically excited (PES "forbidden")<sup>8a</sup> structure of the radical cation which is also of  $b_{2g}$  symmetry ( $b_{2g}^1$ ).<sup>8b</sup> The stationary state giving rise to the lowest  $b_{2g}$  PES band must be a linear combination of the two  $b_{2g}$  ionic structures ( $\Psi_{2B_{2g}}^{+,+} = a^+\Psi_{b_{2g}^0}^{+,+} \pm b^+\Psi_{b_{2g}^1}^{+,+}$ ). The energy of the first  ${}^2B_{2g}$  stationary state will be lowered by this "through structure interaction". The ratio of intensity of transition to the mixed  ${}^2B_{2g}$  state over that to a relatively unmixed state ( ${}^2B_{1g}$  say) can be approximated<sup>9</sup> as

$$\frac{I_{1A_{1g} \rightarrow 2B_{2g}}}{I_{1A_{1g} \rightarrow 2B_{1g}}} = \left[ \frac{\langle \Psi_{1A_{1g}} | \Psi_{2B_{2g}}^{+,+} \rangle}{\langle \Psi_{1A_{1g}} | \Psi_{2B_{1g}}^{+,+} \rangle} \right]^2 \approx [a^+]^2 \quad (1)$$

The intensity contribution of the lowest  ${}^2B_{2g}$   $\Pi$  band should be somewhat low unless  $[a^+]^2 \approx 1$  (no mixing).

These qualitative considerations lead us to suggest that the lowest  ${}^2B_{2g}$  band maximum is fortuitously near that for the  ${}^2B_{1g}$  band (9.7 eV) and that the former contributes only a fractional intensity increment to the superposition. This

assignment requires the  $b_{2g}^1$  diradical ionic basis structure to be fairly close, in energy, to the  $b_{2g}^0$  structure so that mixing is strong *in the ionic states*.<sup>10</sup> The assignments of the first two bands are more straightforward and indicate that the ground state structure of *p*-quinodimethane is that of a polyene as indicated by **2** though diradicals with lifetimes less than  $10^{-5}$  sec (4,4'-dimethylbibenzyl),<sup>11</sup> which intervene between **1** and **2**, would not be detected.

## References and Notes

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- (7) T. Koenig and H. Longmaid, *J. Org. Chem.*, **39**, 560 (1974).
- (8) (a) M. Okuda and N. Jonathan, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 19 (1974); A. Potts and T. Williams, *ibid.*, **3**, 3 (1974). (b) Use of a single  $\rightarrow$  basis structure for ions formed by the loss of an electron from each pair in the neutral ground state deletes a large number of excited states from consideration. The present case is a possible example where this simplification is not adequate.
- (9) As shown in Figure 2, the ground state must also contain a component of the neutral diradical (**3**) ( $\Psi_{1A_{1g}} = a\Psi_{2^0} \pm b\Psi_{3^0}$ ) and a less approximate expression for the intensity ratio is,

$$\frac{I_{1A_{1g} \rightarrow 2B_{2g}}}{I_{1A_{1g} \rightarrow 2B_{1g}}} \approx \left[ \frac{a^+a \pm b^+b}{a} \right]^2$$

The approximation in eq 1 neglects ground state mixing ( $b \approx 0$ ). The mixing of excited structures in the  ${}^2B_{2g}$  and  ${}^2B_{1g}$  stationary states has also been neglected. These interactions as well as that for the ground state ( $2 \leftrightarrow 3$ ) should be small because of the larger energy gap between zero- and first-order basis structures.

- (10) This suggested assignment of the third  $\Pi$  band should be tested through the investigations of substituted analogs in which the accidental degeneracy would be lifted.
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- (12) National Science Foundation Undergraduate Research Participant, 1974. The authors are grateful to the National Science Foundation for additional support of this project in the form of research and instructional grants.

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## Acidities of Carbon Acids. V. Correlation of Acidities in Dimethyl Sulfoxide with Gas-Phase Acidities

Sir:

The degree of dissociation of an acid in solution, relative to the gas phase, is enormous because solvation enthalpies of ions are exothermic to the extent of 50–90 kcal/mol. It is not surprising, then, to find that substituent effects on solution acidities are greatly attenuated compared to those observed in the gas phase. For example, the Hammett  $\rho$  for acidities of meta- and para-substituted benzoic acids is about 2.5 in dimethyl sulfoxide (DMSO)<sup>1</sup> as compared to about 10 in the gas phase.<sup>2</sup> In contrast to these results, we now report two examples where substituent effects on acidities in solution (DMSO) not only parallel those found in the gas phase,<sup>3</sup> but also approach them in magnitude (Table I, Figure 1).

These results suggest that the substituent effects on solution acidities in DMSO for these molecules correspond to a