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He(I) Photoelectron Spectrum of Benzocyclobutadiene

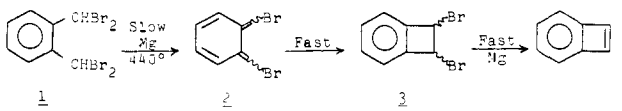
Sir:

Benzocyclobutadiene[1-3] is a member of the class of hydrocarbon which could be expected to be biradicaloid[4] as qualitatively depicted by structure II. In favorable cases, like the

p-quinodimethanes,[5] photoelectron spectra (PES) can give indications of the importance of this biradical character. We presently report a one-step method of generating I from commercially available $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (**1**), our observation of the PES of benzocyclobutadiene, and the results of the structure representation (SR), HAM/3, and HAM/3-CI methods for assignments of the observed bands.

The generation method was pyrolysis of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (**1**) at 440–470 °C over sublimed magnesium

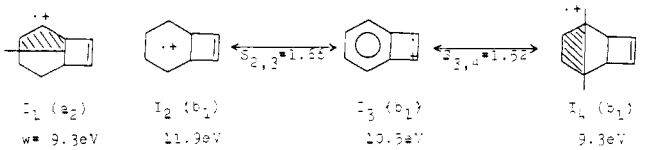
Scheme I



(Scheme I). This route was suggested to us by our inability to observe *o*-xylylene from pyrolysis of the Cava[6] sulfone. All such attempts gave cleanly the spectrum of benzocyclobutene indicating that ring closure of **2** should be fast. The second dehalogenation for the dibromo derivative (**3**), as a fast final step in the overall process, could therefore be expected.

The pyrolysis was first monitored by mass spectrometry. At 470 °C the peaks due to the tetrabromide are negligible and the base peak is *m/e* 102. The only other appreciable peaks (nominal ionizing voltage, 15 eV) are *m/e* 76, the expected fragment of benzocyclobutadiene, and small HBr peaks. The PES from such a pyrolysis stream is shown as Figure 1.

The π part of the PES of benzocyclobutadiene can be simply analyzed by the structure representation (SR) method[7] with the ionic basis structures derived from ground-state structure I (I_1, I_2, I_3, I_4). By inspection, the SR method suggests a $^2A_2$



state at 9.3 eV since symmetry excludes the interaction of this benzenoid ionic species I_1 (a_2) with the olefinic unit (I_3 (b_1)). The second band in the observed spectrum is centered at 9.32 eV.

The interaction constants among the remaining b_1 ionic basis structures (I_2, I_3, I_4) can be derived from the spectra of 1,3-butadiene and 1,4-cyclohexadiene if contributions from

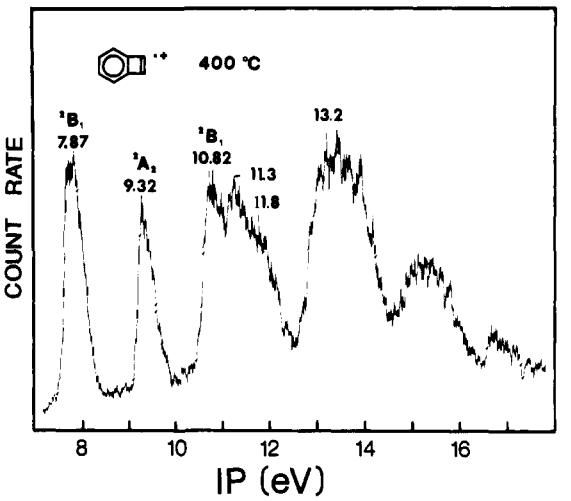


Figure 1. PES of benzocyclobutadiene.

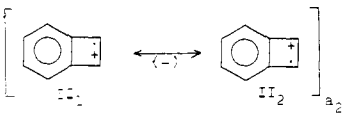
Table I

band	assignment	obsd	SR (π only)	HAM/3[a]	HAM/3-CI
1	$^2B_1$	7.87 ± .02	8.0	8.19	8.26
2	$^2A_2$	9.32 ± .02	9.3	9.74	10.04
3	$^2B_1$	10.82 ± .02	10.5	10.78	10.74
4	$^2A_1$	~11.3		11.96	
5	$^2B_2$	~11.8		12.02	
6	$^2B_1$	~13.2	13.2	12.81	

[a] Notes 8 and 9.

atoms in 1,4 arrangements are neglected throughout. The predictions and assignments of the π-SR scheme are shown in Table I along with those of HAM/3. The first two band assignments seem securely attributable to the formation of the lowest $^2B_1$ and $^2A_2$ ionic states, respectively.

The lowest ionic structure derivable from II would be the negative combination of the two (II_1, II_2) where a localized electron has been lost (II_1–II_2). Appreciable contributions from the diradical structure II would be expected to affect the position and intensity of the second PE band ($^2A_2$) most strongly. The position of the second band is exactly where the SR procedure predicts it[10] and the absence of any other weak band in its vicinity seems to indicate that there is little mixing of I_1 and (II_1–II_2).



In MO language such biradicaloid effects are described by configuration interaction. We have investigated the corrections to the HAM/3 procedure by calculation of (limited) CI corrections to the ground-state wave function from configurations where π electron *pairs* have been promoted from one orbital to another. For the radical cation, CI corrections were calculated from the π configurations with one singly occupied orbital. These calculations showed that, in spite of the small HOMO–LUMO gap (2.45 eV), CI mixing of both the neutral compound and the lowest two radical cation π states is negligible. The calculated character of these $^1A_1$, $^2B_1$, and $^2A_2$ states was 97% in the zero-order configuration. For $^1A_1$ and $^2A_2$ the small mixing was due to the very small CI interaction constants. Both CI results and the SR procedure support the conclusion that little biradical effect is present in benzocyclobutadiene and its electronic structure is most closely related to that depicted by structure I.

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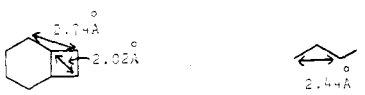
(7) (a) The structure representation procedure has been developed by Simpson[7b] with optical transitions in dyes. The method postulates the existence of many electron functions which can be associated with chemical structures (square root of the structure). These functions, though their mathematical form may be unknown, constitute a basis set. Linear combinations of this basis set are approximations to the many electron wave functions for a selected group of states of the molecule. The method discovers properties of the mathematically unknown basis functions by dediagonalization of symmetry-determined problems. The empirical matrix elements (bond ionization potentials for diagonals and splitting parameters for off diagonals) are postulated to be interchangeable among molecules with interchangeable structural features. The method could be considered as a simplified version of valence bond theory just as the Hückel method is a simplified version of molecular orbital theory. (b) W. T. Simpson and C. W. Looney, *J. Am. Chem. Soc.*, **76**, 6285, 6793 (1954).
(8) The HAM/3 procedure, as it applies to photoelectron spectra, has been described by Lindholm, L. Asbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Lett.*, **52**, 63, 69 (1977). We are grateful to Professor Lindholm for supplying us with a copy of his HAM/3 program.
(9) The geometry used for the HAM/3 calculation was taken from the X-ray structure[3] of the di-*tert*-butyl derivative.
(10) In the SR procedure, a slight decrease in the $S_{2,3}$ value (1.50) and a slight increase in the $S_{3,4}$ value (1.75) gives agreement in the calculated positions of all the π bands with experiment. Such changes in these splitting parameters are in accord with the changes in interatomic distances of the 1,3 type for I compared with butadiene or 1,4-cyclohexadiene.



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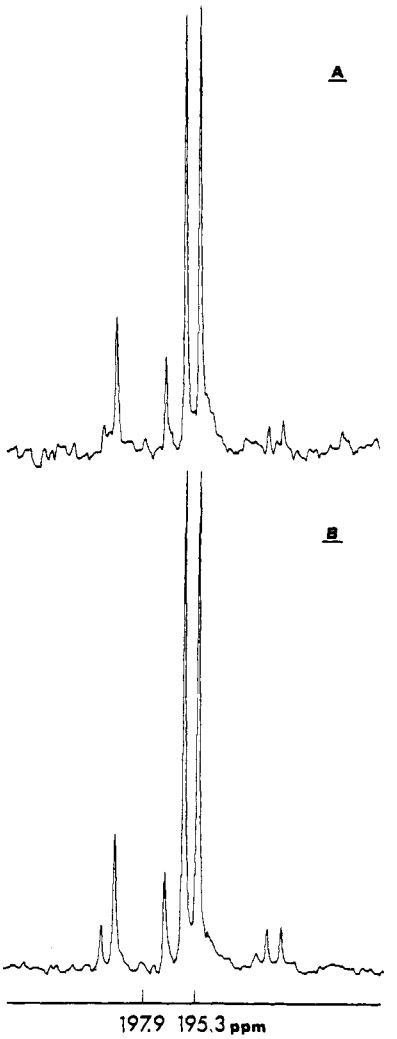
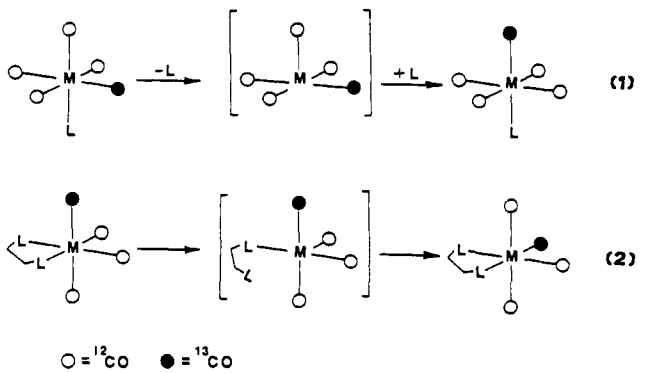


Figure 1. ^{13}C NMR spectra of $W(CO)_5P(OMe)_3$ in $CDCl_3$. (A) Natural abundance spectrum of $W(CO)_5P(OMe)_3$, $\delta(C_{trans})$ 197.9 ppm (J_{P-C} = 37.6 Hz) and $\delta(C_{cis})$ 195.3 ppm (J_{P-C} = 10.7 and J_{W-C} = 125 Hz). Note downfield portion of $\delta(C_{trans})$ overlapped with peak due to $W-C_{cis}$ coupling (this is resolved in the spectrum determined at higher resolution; see Figure 2). (B) Spectrum of $W(CO)_5P(OMe)_3$ prepared from *cis*-$W(CO)_4[P(OMe)_3]NHC_5H_{10}$ and 93% enriched ^{13}CO in octane at 78 °C for 2 days. The ^{13}CO ligand is ~90% randomized.

Intramolecular Rearrangement of Carbonyl Ligands in the Octahedral Complex $W(CO)_5P(OMe)_3$ by a Nondissociative Process: An Example of the Utility of the Oxygen-18 Isotope Shift on the ^{13}C NMR of the Carbonyl Ligand

Sir:

Frequently carbonyl ligand rearrangements in octahedral transition metal complexes have been observed to occur by means of a mechanism involving prior ligand dissociation, e.g., as depicted in eq 1 and 2.[1-8] On the other hand intramolecular



permutation of ligands in complexes of octahedral symmetry by a process which does not involve ligand dissociation is less well documented. Indeed, the barrier to intramolecular rearrangements by a non-bond-breaking process in octahedral transition metal complexes has long been believed to be quite large.[9,10] Several recent studies, however, indicate that the process is the lowest energy mechanism for cis ⇌ trans isomerization reactions involving some of these complexes.[11-14] In this communication stereochemical nonrigidity in $W(CO)_5P(OMe)_3$ occurring by a non-bond-breaking process is unambiguously established.

Upon reacting *cis*-$W(CO)_4[P(OMe)_3]NHC_5H_{10}$ with [^{13}C]carbon monoxide in octane solvent at 78 °C for a prolonged period a nearly statistical mixture of *cis*- and *trans*-$W(CO)_4(^{13}CO)P(OMe)_3$ was obtained (see ^{13}C NMR spectra in Figure 1).[15] If the piperidine substitution reaction is stopped at an earlier stage in the substitutional process the $W(CO)_4(^{13}CO)P(OMe)_3$ product is more highly stereoselectively enriched in the equatorial position, thus indicating that a fluxional process is operative subsequent to the initial ^{13}CO incorporation. The possibility that this stereochemical nonrigidity in the $W(CO)_4(^{13}CO)P(OMe)_3$ species is occurring by a dissociative process is ruled out in that reaction of

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