

Photoelectron and Ultraviolet Spectra of Small-Ring Fused Aromatic Molecules as Probes of Aromatic Ring Distortions

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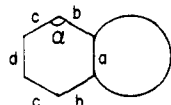
Abstract: The photoelectron and ultraviolet absorption spectra of the symmetrical and unsymmetrical bicycloalkenobenzenes incorporating all combinations of four- and five-membered rings have been measured, along with those of naphtho[*a*]cyclobutene and naphtho[*b*]cyclobutene. The changes in orbital energies, and in ultraviolet absorption energies and intensities, are interpreted to result mainly from changes in the hyperconjugative abilities of the fused rings, but the distortion of a benzene ring by strained ring fusion also has a significant influence on ionization potentials. This distortion is manifested more by changes in internal angle than by changes in bond lengths. The increases in absorption intensities as strain increases are interpreted, with the aid of CNDO/S calculations, to result from changing the configurational composition of the lowest excited single state.

Introduction

Organic chemists have long been fascinated by the possibility of limiting the aromaticity in benzenoid molecules by appropriate substitution. The ~ 98 kcal/mol energy of a carbon-carbon single bond can be reduced to zero by suitable substitution.² Thus it would seem that appropriate substituents might cause an equilateral, hexagonal benzene ring to be more strained than a cyclohexatriene structure with alternating single and double bonds. Suitable substituents might cause a sacrifice of the ~ 36 kcal/mol resonance energy of benzene and induce double bond localization.

Mills and Nixon first proposed bond alternation to explain some anomalous electrophilic substitution results observed for indan.³ Various explanations of the "Mills-Nixon" effect and related phenomena have been proposed, the most compelling of which would be that of Streitwieser and co-workers. These workers suggested that since the carbon-carbon bonds in the small ring of a benzocycloalkene were composed of unusually high *p* character, the σ bonds to the ortho carbons in the benzene ring would therefore possess unusually high *s* character.⁴ Thus, the fused ring serves to increase the effective electronegativity of the bridgehead carbons, but need not induce substantial localization of the double bonds in the aromatic ring.

Theoretical studies by Longuet-Higgins and Coulson indicated that the fusion of a small ring to benzene should shorten bond *a*, lengthen bond *c*, and contract the angle α ,⁵ while



CNDO/2 calculations by Manatt et al. indicated that bonds *a* and *c* should lengthen, *b* should shorten, *d* should remain essentially unchanged, and α should contract.⁶ MINDO/2 and MINDO/3 calculations that we have performed indicate distortions similar to those predicted by Manatt.⁷

Structural data on compounds of this type are as yet sparse. A substituted benzocyclopropene, **1**, shows the shortening of *b* and lengthening of *c*, but *a* is contracted, rather than lengthened.⁸ The substituents may exert a considerable influence in this case. Benzo[1,2:4,5]dicyclobutene (**2**) has short bonds in the small ring and a contracted angle α ⁹ in apparent contradiction to semiempirical results. Biphenylene (**3**) clearly

distorts in the direction of lengthened bonds *a* and *c*, and shortened bonds *b* and *d*; but this is probably due more to the desire of the central ring to avoid cyclobutadiene antiaromaticity than to the strain of the system.¹⁰ Some recent studies on small-ring tris-annelated benzenes show very little distortion of the central aromatic ring.¹¹

Whether or not small distortions from the regular hexagonal nature of benzene result from strain or simply from normal electron donation by substituent alkyl groups will be difficult to decide, since substituents are known to cause appreciable distortion of benzene rings.¹² Thus, toluene has an internal angle of 118° at the site of methyl substitution, and the 1-2, 2-3, and 3-4 bond lengths of a benzene ring substituted by a powerful donor such as tetraphenyl borate are contracted by 0.004, 0.009, and 0.026 Å, respectively.¹² Naphthalene has even greater distortions of bond lengths from the benzene value of 1.397 Å, a phenomenon which can be explained by a simple consideration of the resonance contributors involved (Figure 1).

Synthetic chemists have recently succeeded in constructing systems containing more than one small ring fused to an aromatic nucleus,^{12,13} and it will now be possible for definitive structural work to determine the extent and direction of aromatic bond distortion caused by the fusion of these small rings.^{9,14} In the meantime, we have attempted to probe the influence of strained rings on the electronic structure of an aromatic nucleus by investigating the electronic spectra of some bis-annelated benzenes.

Utilizing photoelectron and ultraviolet absorption spectroscopy, a very crude estimate of the ionization potentials expected for cyclohexatriene, as opposed to benzene, can be made as follows. If benzene had alternating single and double bonds, such as those in butadiene ($r_{12} = 1.337$ Å, $r_{23} = 1.483$ Å), then the resonance integral involving adjacent π bonds should be essentially the same as that in butadiene. Butadiene has π IPs of 9.03 and 11.46 eV,¹⁵ and in a simple LCBMO model in which these are considered to arise from antibonding and bonding combinations of ethylene π orbitals, the resonance integral, *B*, deduced for interaction is $\frac{1}{2}(11.46 - 9.03) = 1.22$ eV. The average of the butadiene IPs (10.25 eV) is somewhat lower than the IP of ethylene (10.51 eV), owing to the different substitution of one terminus.¹⁵ If the occupied orbitals of benzene were considered to arise from the interaction of these stretched ethylenes, each with an IP of *A*, the degenerate first IP would have an energy, *A* - *B*, and a higher energy IP at *A*

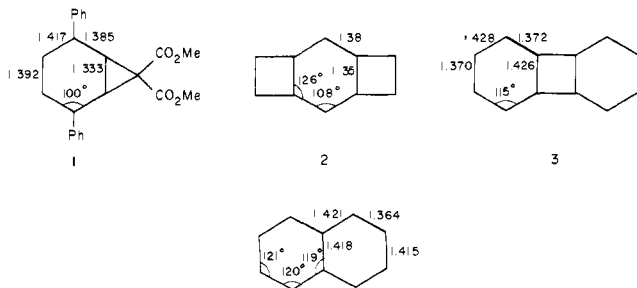


Figure 1. Experimental geometries of aromatics

+ 2*B*. The value of *A* deduced from the benzene IPs of 9.25 and 12.3 eV is 10.27 eV, almost identical with that in butadiene. If three π orbitals interacted across a distance of 1.48 Å, with the resonance integral, B_{23} , of butadiene, the IPs of this distorted benzene can be estimated to be 9.05 (degenerate) and 12.7 eV. Thus, for a "Kekule benzene", or 1,3,5-cyclohexatriene, the first degenerate π IP is expected to be 0.2 eV lower than that of benzene, and the second π IP is expected to be 0.4 eV greater than that of benzene. Even for this drastic molecular distortion, relatively small changes in π IPs are expected. These changes in IPs would be readily detectable, but the substitution to produce this change will cause major intrinsic perturbation of the orbital energies even in the absence of geometrical distortion, so that the effect of molecular distortion may well be obscured. Nevertheless, in spite of formidable obstacles against detecting molecular distortions by these techniques, we have embarked on a study of the photoelectron and ultraviolet spectral properties of such systems. Meier et al. have estimated the ionization potentials from charge-transfer transition energies of a number of bis- and tricycloalkenobenzenes, containing five-through eight-membered rings, and have measured appearance potentials by mass spectrometry.¹⁶ However, the photoelectron spectroscopic data are not only more precise but also give several π ionization potentials, knowledge of which may be of value in detecting electron localization or other effects of small ring fusion.

Photoelectron Spectra

Photoelectron spectra were measured with a Perkin-Elmer PS-18 photoelectron spectrometer. The spectra were recorded in the presence of xenon and argon as calibrants. Resolution at 6.5 eV photoelectron energy was 20–25 meV. The peak positions reported are the average of five or more determinations.

Indan. The vibrational structure of the various bands of an annelated benzene is exemplified by the spectrum of indan, shown in Figure 2. The first band has a distinct 0–0 transition at 8.50 eV and two resolved vibrational progressions. The higher energy vibration which is excited in the radical cation gives rise to a 0–1 transition at 8.71 eV. The 0–0, 0–1 spacing of about 210 meV is the same as that of a progression observed in the 9.241 eV IP of benzene.¹⁷ The lower energy vibration leads to a progression for which the first four members (0–0 through 0–3) can be discerned, with a spacing of approximately 70 meV, again analogous to that in the first band of benzene (85 meV).¹⁷

Because the vibrational band intensities are, in principle, diagnostic of radical cation structure, we digress briefly on the natures of the vibrations excited in ionizations of substituted benzenes. Åsbrink and co-workers have carefully analyzed the vibrational structure observed in the 9.241-eV band in the photoelectron spectrum of benzene.¹⁷ The benzene radical cation formed by loss of an electron from the degenerate (e_{1g}) highest occupied molecular orbitals (HOMOs), has reduced symmetry (D_{2h}) from that of benzene (D_{6h}), and different vibrations are excited upon loss of electrons from b_{1g} or b_{2g}

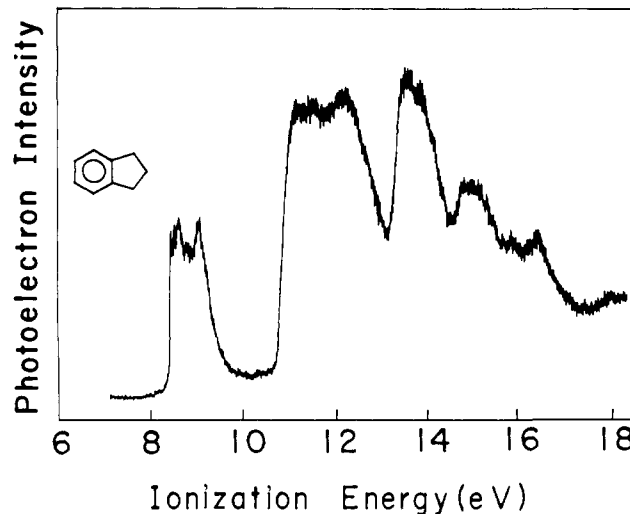


Figure 2. Photoelectron spectrum of indan.

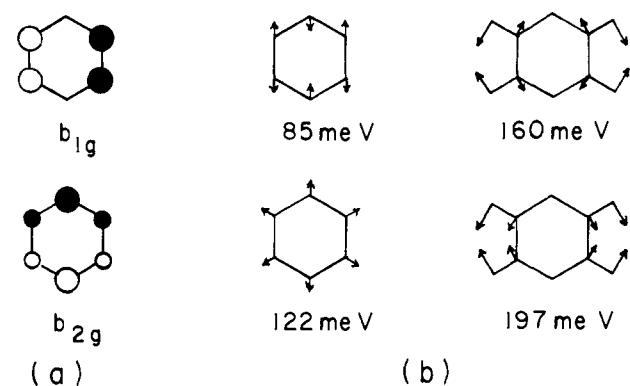


Figure 3. Vibrations excited in the radical cation states of benzene and substituted benzenes.

orbitals (in D_{2h}), as shown in Figure 3, which is adapted from Åsbrink et al.¹⁷ An electron lost from the b_{1g} orbital gives vibrational progressions of 85 and 160 meV, due to the vibrations shown schematically in Figure 3, while loss of an electron from b_{2g} gives vibrational structure of 122 and 197 meV. In the indan spectrum shown in Figure 2, the first band gives vibrational structure similar to that arising from b_{1g} ionization in benzene, while the second band of indan does not have resolved structure. Similar resolution of the vibrational structure in the first bands of monosubstituted benzenes (but with vibrational spacing of ~ 200 and ~ 70 meV) and lesser resolution of the vibrational structure in the second bands in these compounds has been reported.¹⁸

Because the 0–0 and 0–1 bands at 8.51 and 8.67 eV for indan show very similar intensities depending on spectrometer conditions, it is difficult to assign one or the other as the vertical transition. For the purpose of comparing the first and second IPs of annelated benzenes to those of benzene itself, we will therefore consider the 0–1 band as the vertical IP.

Since the second band does not have any well-resolved 0–0 band, but does have a clear maximum at 9.11 eV, this will be taken as the vertical IP. By comparison, Heilbronner and co-workers report vertical IPs of 8.46 and 9.04 eV for indan.¹⁹ Assuming that Heilbronner assigned the 0–0 transition of the first band as the vertical IP, then our first and second IPs are 0.05–0.07 eV higher than those of Heilbronner, just on the fringe of experimental error.

Symmetrical Biscycloalkenobenzenes. The photoelectron spectra of the "symmetrical", or para-fused, benzenes, benzo[1,2:4,5]dicyclopentene (**S-5,5**), 4,5-cyclopentenoben-

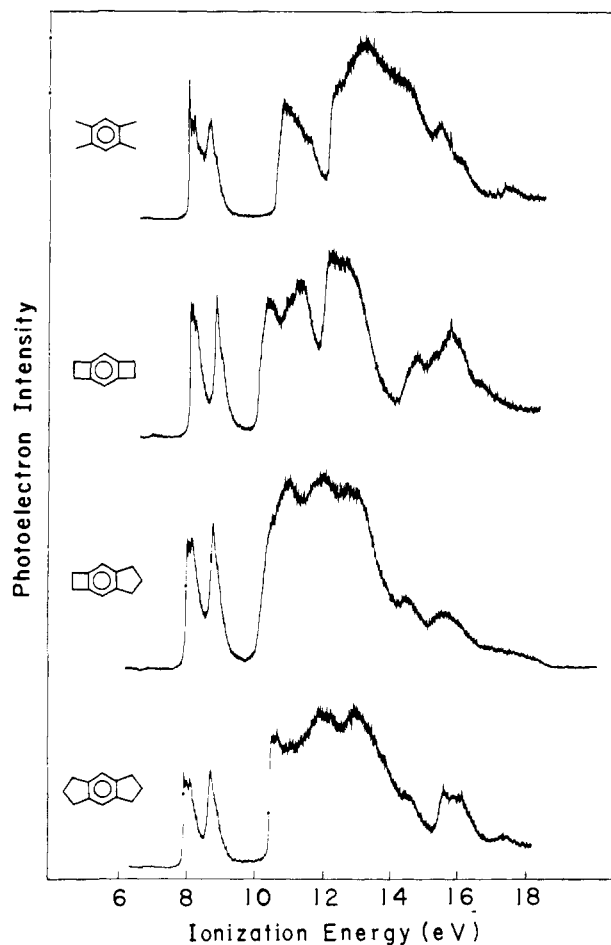


Figure 4. Photoelectron spectra of symmetrical benzodicycloalkenes and durene.

zocyclobutene (S-4,5), and benzo[1,2:4,5]dicyclobutene (S-4,4), are shown in Figure 4, along with that of the tetraalkyl model compound, 1,2,4,5-tetramethylbenzene (durene). The adiabatic (0-0) and vertical (taken here as the most intense band) ionization potentials and vibrational structure observed in each band are listed in Table I. The photoelectron spectrum of durene, like that of indan, has considerable vibrational structure in the first band. The 0-0 transition at 8.07 eV is considerably stronger than the 0-1 transition at 8.24 eV ($\Delta\nu = 170$ meV), and the lower energy progression ($\Delta\nu = 80$ meV) is also apparent. The second band is relatively featureless with a maximum at 8.68 eV. The spectra of the para bis-annelated benzenes are similar to that of durene, except that the 0-0 and 0-1 maxima are of very similar intensity, whereas the 0-0 is clearly the most intense peak in durene. The same vibrational progressions are present in the first bands of indan and of these compounds, consistent with ionization from the orbitals (b_1 in C_{2v}) analogous to b_{1g} shown in Figure 3.

In each spectrum the second band is relatively featureless, like that arising from the asymmetric orbital of indan. The trends in IPs, vibrational spacing, and peak intensities will be discussed later.

Unsymmetrical Bicycloalkenobenzenes. The photoelectron spectra of 1,2,3,4-tetramethylbenzene (prehnitene) and the meta-fused benzenes benzo[1,2:3,4]-dicyclopentene (U-5,5), 3,4-cyclopentenobenzocyclobutene (U-4,5), and benzo[1,2:3,4]dicyclobutene (U-4,4) are shown in Figure 5 and the IPs and vibrational structures are listed in Table I. In these compounds the order of orbital energies is expected to be opposite to that of the symmetrical species. The first band in each compound shows vibrational structure of about 60 and 180

Table I. Ionization Potentials and Vibrational Structure Observed in the Photoelectron Spectra of Bis-Annelated Benzenes and Model Compounds (A = Adiabatic, V = Vertical)

Compd	Band	IP (± 0.03 eV)	Vibrational spacing (± 20 meV)
Indan	1	8.50 (A) 8.71 (V)	210, 70
	2	9.11 (V)	
Durene (1,2,4,5-tetramethylbenzene)	1	8.07 (A,V)	170, 80
	2	8.57 (A) 8.68 (V)	
S-4,4	1	8.17 (A) 8.22 (V)	180, 50
	2	8.80 (A) 8.91 (V)	
S-4,5	1	8.05 (A) 8.19 (V)	140, 50
	2	8.63 (A) 8.77 (V)	
S-5,5	1	7.94 (A) 8.13 (V)	185, 80
	2	8.68 (A) 8.70 (V)	
Prehnitene	1	8.18 (A) 8.29 (V)	110
	2	8.57 (V)	
U-4,4	1	8.18 (A) 8.35 (V)	170, 60
	2	8.69 (V)	
U-4,5	1	8.19 (A) 8.38 (V)	180, 60
	2	8.71 (V)	
U-5,5	1	8.09 (A) ^a 8.24 (V)	150
	2	8.77 (V)	

^a A value of 8.66 eV was determined earlier by mass spectrometry.¹⁶

meV, while the second is featureless, but with a relatively well-defined vertical IP. The first band should arise from ionization from the a_2 orbital (which corresponds to the b_{2g} in D_{2h} symmetry), while the second band should arise from the b_1 (corresponding to b_{1g}). In contrast to the symmetrical series, the 0-1 band is the most intense for all of these compounds. This band, which is separated from the 0-0 transition by about 170 meV in all of these compounds, is taken as the vertical transition.

Naphthocyclobutenes. The photoelectron spectra of the two isomeric naphthocyclobutenes are shown in Figure 6 and the vertical IPs are reported in Table II. In both compounds, the first bands show dramatic vibrational progressions like those observed for naphthalene itself.^{20,21} The vibrational spacing in the first band of these compounds (180 meV) is about the same as that reported by Palmer and Kennedy for naphthalene and corresponds to a ground-state skeletal vibrational frequency of 183 meV.²¹ The second and third bands are similar in shape to those of naphthalene,²⁰ while the fourth band in all of these compounds is partially obscured by the σ envelope.

Because of the similarity of the first four band shapes and positions in the two naphthocyclobutenes and in naphthalene, the ionizations must arise from similar orbitals as discussed in more detail in the following section.

Discussion of the Photoelectron Spectra

A diagram showing correlations between the vertical IPs of the compounds studied as well as those of corresponding alkenes and benzocycloalkenes is given in Figure 7. While *cis*-2-butene has an appreciably lower IP than ethylene owing to

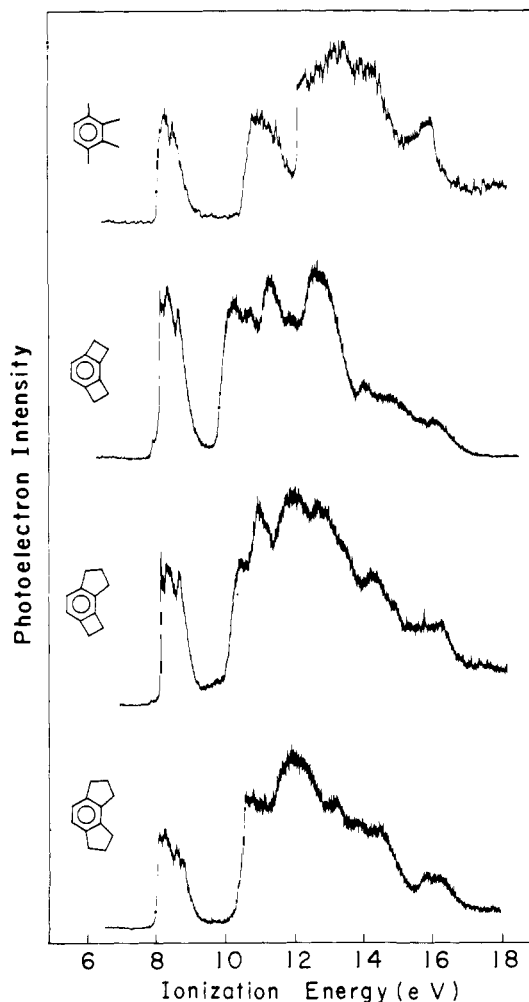


Figure 5. Photoelectron spectra of unsymmetrical benzodicycloalkenes and prehnitene.

Table II. Ionization Potentials in eV (± 0.03) (Vibrational Structure, in meV (± 20)) from Photoelectron Spectra of Naphthalenes

Compd	IP ₁	IP ₂	IP ₃	Ref
Naphthalene	8.15	8.90	10.02	20
	8.15	8.88	10.00	27
	8.16	8.94	10.14	<i>a</i>
Naphtho[<i>a</i>]cyclobutene	7.84 (180)	8.65	9.69 (60)	
Naphtho[<i>b</i>]cyclobutene	7.92 (180)	8.54	9.83 (40)	

^a E. Lindholm, C. Fridh, and L. Åsbrink, *Discuss. Faraday Soc.*, **59**, 127 (1972).

the hyperconjugative donor influence of the methyl groups, cyclization to cyclobutene causes an appreciable increase (0.31 eV) in the IP. This can be rationalized in the following way. Both π_{CH_3} orbitals of the two methyl groups, shown in Figure 8, can hyperconjugate with the π orbital of ethylene. Cyclization of *cis*-2-butene, however, causes appreciable overlap of these two orbitals. The resulting bonding combination, which is the only alkyl orbital of proper symmetry to hyperconjugate with the alkene π orbital, is now of much lower energy, and thus mixes with, and destabilizes, the b_1 (π) orbital to a smaller extent. The energies of the corresponding hyperconjugating orbitals can be estimated from the IPs of the corresponding alkanes.²² For example, whereas the degenerate

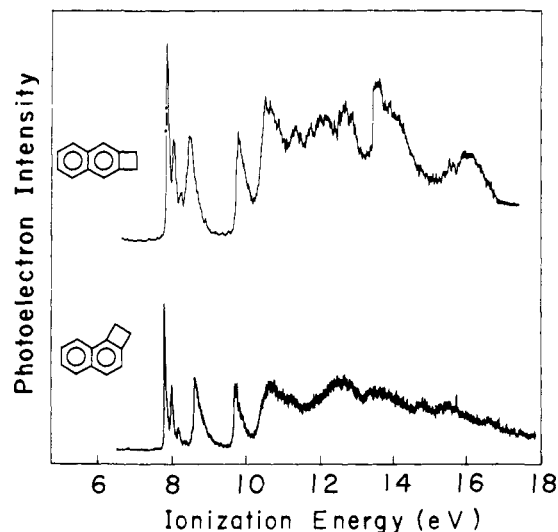


Figure 6. Photoelectron spectra of naphthocyclobutenes.

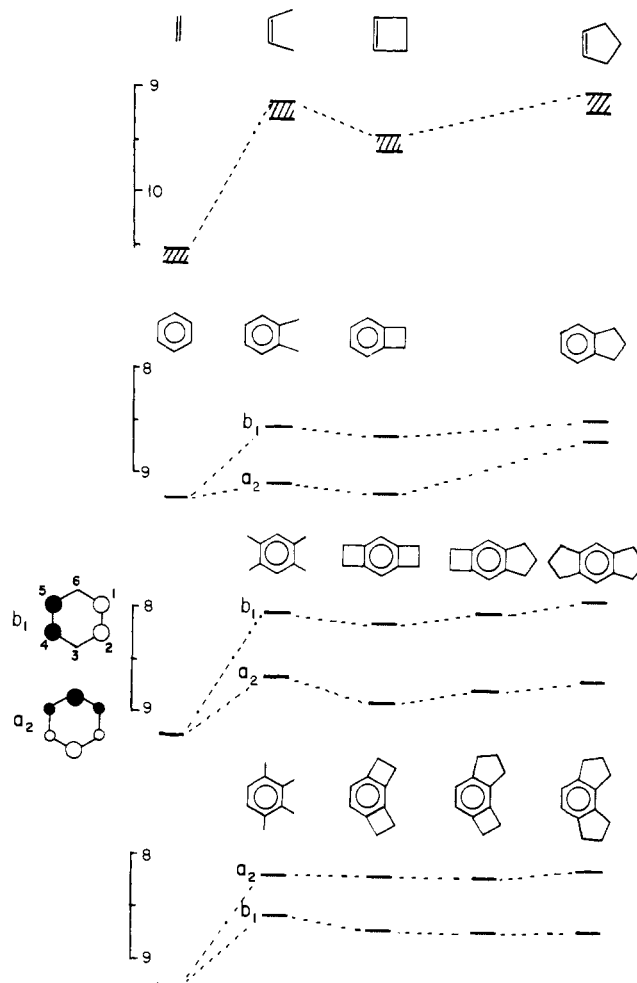


Figure 7. Correlations between first two IPs of the compounds studied and those of simpler analogues.

" π_{CH_3} " orbitals of methane ionize at 14.2 eV, the bonding combination of two of these, present in ethane, results in an IP of 15.4 eV. An alternative explanation, that the change in IP upon cyclization results from bond lengthening (1.339 to 1.342 Å), does not readily explain the *increase* in IP upon cyclization. That is, such lengthening should slightly decrease the p-p π resonance integral, and *decrease* the IP.

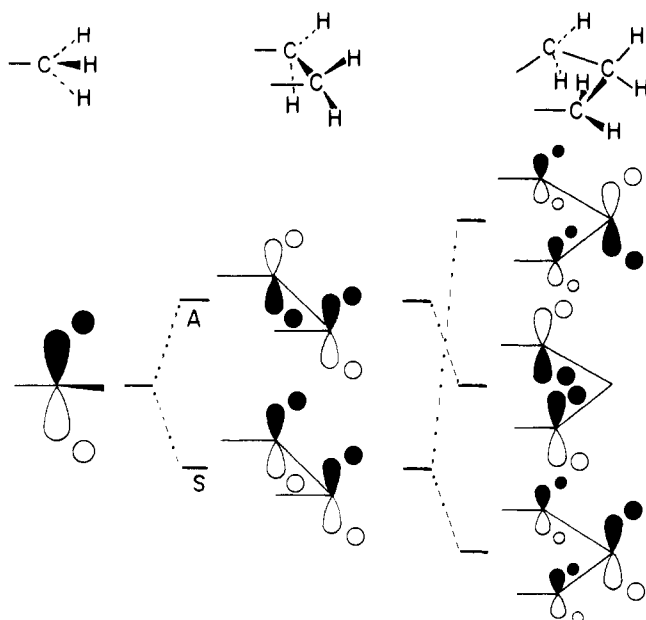


Figure 8. Hyperconjugating orbitals in *cis*-2-butene, cyclobutene, and cyclopentene.

Conversion of a cyclobutene ring to a cyclopentene ring causes a lowering of the IP because the introduction of an additional methylene leads to a higher energy hyperconjugating orbital of the correct symmetry to overlap with the π orbital. Thus the symmetric π -like orbital of propane has an IP of 11.5 eV.²² This could, of course, also be a simple inductive effect resulting from the increase in size of the alkyl group.

Whereas benzene has degenerate HOMOs, and the Jahn-Teller forces in the radical cation are sufficiently small so that removal of an electron from either orbital gives rise to the same IP (9.241 eV), *o*-xylene has a large split in the degeneracy of the two lowest energy radical cation states. The lowest state (2B_1) arises from removal of an electron from the b_1 HOMO, which has relatively large coefficients at the sites of substitution, while the second state (2A_2) is closer to that of benzene, since the a_2 orbital has smaller coefficients at the substitution site. The b_1 and a_2 orbitals are shown at the left of Figure 7. For simplicity, we have used the C_{2v} designation for these orbitals throughout. According to a simple perturbation scheme for substituent effects upon IPs, the influence of a substituent upon an IP should be approximately proportional to the square of the coefficient at the site of substitution. Neglecting overlap, the coefficients at the sites of substitution are $1/\sqrt{2}$, $1/2$, and $1/\sqrt{12}$ for ethylene, the b_1 orbital of benzene, and the a_2 orbital of benzene, respectively, so that methylation should cause changes in the ratio, 1.0:0.5:0.17. The experimental decreases in these IPs are 1.40, 0.67, and 0.14. The first two are in exactly the expected ratio, while the last is too small, perhaps owing to a shift in the vertical IP from 0-0 in benzene to 0-1 in *o*-xylene.

Similarly, cyclization of *o*-xylene to benzocyclobutene should cause half the IP increase for the b_1 orbital that is observed upon cyclization of *cis*-2-butene to cyclobutene. The observed value is $0.09/0.31 = 0.29$, or about one-half the expected value. The a_2 IP also deviates from expectation. That is, cyclization of two methyls to form an ethano bridge should cause destabilization of the alkyl a_2 orbital, and this orbital would now be expected to hyperconjugate with an aromatic a_2 orbital better than two methyls. On the basis of this reasoning, the IP of benzocyclobutene should be somewhat lower than that of *o*-xylene, whereas experimentally the benzocyclobutene a_2 IP is raised by 0.10 eV. The deviation of b_1 and a_2 IPs from expectation upon converting *o*-xylene to benzo-

cyclobutene may be a result of aromatic ring distortions accompanying the increase in strain. The observed IPs indicate that the b_1 orbital has less bonding (lower IP) and the a_2 orbital has more bonding (higher IP) than expected if cyclization were unaccompanied by molecular distortions. Inspection of the b_1 and a_2 orbitals indicates that antibonding in the b_1 orbital and bonding in the a_2 would be increased upon either of two geometric changes: if the C1-C2 (and the C4-C5) bond were stretched or if C1 were brought closer to C5 (and C2 closer to C4). Thus, we attribute the small lowering of the b_1 orbital energy, and the lowering, rather than raising, of the a_2 orbital energy, upon formation of benzocyclobutene from *o*-xylene to such molecular distortions.

Upon formal conversion of benzocyclobutene to indan, the a_2 orbital is destabilized to large extent, and the b_1 to a smaller extent. In indan, the gap between the b_1 and a_2 orbitals is smaller than found in *o*-xylene. The relatively large destabilization of the a_2 orbital relative to that in benzocyclobutene could arise from both increased hyperconjugative interaction between a slightly nonplanar cyclopentene ring and the a_2 orbital, and from destabilization due to the return of the geometry of the phenyl ring to one like that of benzene or *o*-xylene.

Turning to the dicycloalkenobenzenes, the conversion of durene to benzo[1,2:4,5]dicyclobutene causes a stabilization of the b_1 orbital nearly the same as that arising from formation of benzocyclobutene from *o*-xylene. This result can be explained by the larger compression of the angle α (shortening the C-1, C-5 distance) and/or lengthening the C1-C2 bond. Otherwise, one would expect a hyperconjugative change roughly twice that for conversion of *o*-xylene to benzocyclobutene. The a_2 orbital is stabilized to a large extent (+0.23 eV) and this can also result from the distortion of the ring, since the hyperconjugative change should lower this IP as discussed earlier.

Calculations that we have performed on this system also indicate that the IP deviations from hyperconjugative expectation will arise from the types of distortions deduced above. For example, CNDO/S calculations on benzo[1,2:4,5]dicyclobutene with aromatic bond lengths fixed at 1.40 Å and a regular hexagonal ring geometry predict IPs of 8.84 and 9.36 eV, while distortion of the molecule to the experimental geometry results in predicted IPs of 8.87 and 9.54 eV. Thus, the predicted increase in the a_2 IP arising from distortion is verified by calculation.

As with the benzocycloalkene series, conversion of one, and then two, cyclobutene rings to cyclopentenones causes a similar destabilization of both the b_1 and a_2 orbitals. The changes here for each ring are nearly identical with the change observed for one ring in the benzocycloalkenes.

The order of radical cation states (or of orbital energies) in the unsymmetrically substituted benzodicycloalkenes should be opposite to that in the symmetrical cases. The coefficient sizes in the a_2 and b_1 orbitals indicate that tetramethylation should influence these in the ratio of 1.67. Experimentally, a_2 and b_1 IPs of prehnitine are 1.04 and 0.67 eV lower than those of benzene; that is, the ratio is 1.55. Assuming an experimental uncertainty of ± 0.04 eV, the ratio is well within expectation.

Conversion of prehnitine to the corresponding dicyclobutene has an interesting effect: there is no change in the a_2 orbital energy within experimental error, while the b_1 orbital is lowered in energy by 0.12 eV. Because of the symmetries of the orbitals involved, the S orbitals of the ethano bridges can interact with the a_2 orbital more than the A orbital. Thus, the small change in the a_2 orbital can be attributed to the lowered hyperconjugative ability of the S orbital due to the cyclization effect, and to the small interaction of the A orbitals with the a_2 orbital. The b_1 orbital can interact with both the S and A

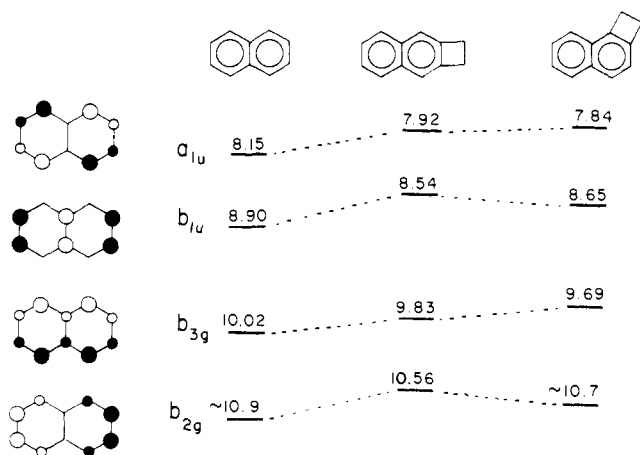


Figure 9. Correlations between ionization potentials of naphthalene and naphthocyclobutenes.

ethano bridge orbitals, so no major difference in prehnitene and the dicyclobutene would be expected in the absence of geometry change. The substantial lowering of this orbital energy may be attributed to a shortening of the 1–2 bond (numbered according to Figure 7) or a distortion which causes atoms 1 and 5 (and atoms 2 and 4) to be moved apart. Conversion of the cyclobutene rings to cyclopentene causes essentially no change in the IPs, or perhaps a slight lowering of the a_2 IP. This observation would seem to indicate that the difference between the IPs of cycloalkenes and of the symmetrical dicycloalkenes is a symmetry-influenced phenomenon, and the actual donor effect of cyclobutene and cyclopentene rings is quite similar in the absence of symmetry restrictions.

In summary, the photoelectron spectra of the benzodicycloalkenes can be interpreted readily only in terms of both differing hyperconjugative effects for various ring sizes and minor geometrical distortions.

Photoelectron Spectra of Naphthocyclobutenes. Figure 9 is a correlation diagram showing the correspondence between the first four IPs of naphthalene and the naphthocyclobutenes. The changes in the first four IPs of naphthalene upon cyclobutene fusion can be understood in terms of the shapes of the naphthalene π MOs shown schematically at the left of Figure 9. For example, the first IP is influenced more by $[a]$ fusion than by $[b]$ fusion, since the coefficients at the site of substitution are larger for $[a]$ fusion. The second IP is influenced more by $[b]$ fusion than by $[a]$, the third more by $[a]$ than by $[b]$, and the fourth more by $[b]$ than by $[a]$. In monosubstituted derivatives, substituents on C- α have a larger influence on the first and third IPs than substituents of C- β , while C- β substituents have a larger effect on the second IP,²⁰ unless an α -electron-donating substituent is unable to achieve the conformation required for maximum donation.²⁷

Ultraviolet Spectra of Dicycloalkenobenzenes. The ultraviolet spectra of the benzodicycloalkenes under investigation have been reported earlier and are tabulated in Table III.^{13c} Three general trends may be noted: (1) for each series, starting from the *o*-xylene through the corresponding cyclopentene to the cyclobutene, there is a regular increase in the intensities of the absorptions, but only minor changes in energies and vibrational structures of the transitions (a similar trend was noted for larger rings in the work of Meier et al.¹⁶); (2) the absorptions of the unsymmetrical compounds are about one-half as intense as those of the symmetrical ones; (3) the symmetrical benzodicycloalkenes have absorptions which are red shifted by 170 meV with respect to the unsymmetrical analogues but both durene and prehnitene have nearly identical transition energies.

In an attempt to understand each of these trends, we turn

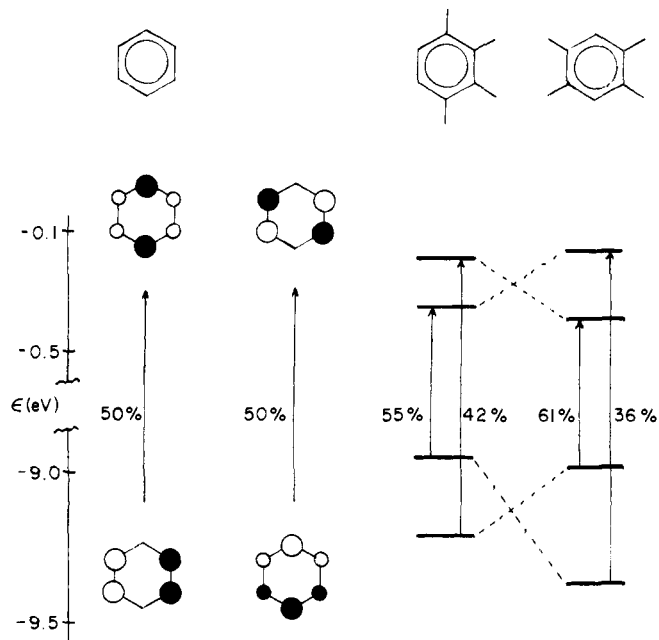


Figure 10. Compositions of first excited singlet of aromatics. On the left are shown the configurations which contribute equally to the lowest singlet. On the right are shown the HOMO and LUMO splittings and configurational composition of the lowest singlet according to CNDO/S calculations.

Table III. Ultraviolet Absorption Spectra (95% EtOH)

	λ_{\max} , nm (ϵ)		
<i>o</i> -Xylene		262 (254)	269.5 (211) ^a
Benzocyclobutené	259 (1380)	265 (2110)	271 (2070)
Indan	259 (889)	266 (1224)	273 (1357)
Durene	268 (712)	273 (654)	278 (727)
S-4,4	276 (4570)	280 (5125)	286 (3890)
S-4,5	276 (4070)	280 (4380)	286 (3752)
S-5,5	277 (3665)	281 (3785)	287 (3797)
Prehnitene	267 (301)	272 (244)	276 (235)
U-4,4	266 (1360)	269 (1370)	275 (1540)
U-4,5	267 (972)	271 (879)	276 (1037)
U-5,5	268 (1008)	272 (870)	277 (1066)

^a In MeOH.

first to a consideration of the nature of the lowest singlet state in benzene and substituted benzenes. For this discussion we use CNDO/S calculations,²⁸ which are semiempirical all-valence-electron SCF calculations which incorporate configuration interaction—an absolute necessity for excited states of aromatic systems. The general features of the lowest singlet excited states of the symmetrically and unsymmetrically fused benzene derivatives can be found in Figure 10. The lowest singlet state of benzene consists of equal amounts of configurations corresponding to transitions from the b_1 HOMO to the b_1 LUMO, and the a_2 HOMO to the a_2 LUMO, where we use the C_{2v} symmetry designations for the substituted molecules which, it should be noted, are different from the C_{2v} designations for monosubstituted benzenes. The ${}^1A_1 \rightarrow {}^1A_1$ (1L_b or ${}^1B_{2u}$) transition is forbidden because of the manner in which the two configurations combine. That is, the two transitions, which mix equally to form the lowest excited singlet, have equal and opposite transition dipoles. The equal mixture of these gives a lowest singlet, and the transition to this state is electronically forbidden. The CNDO/S frontier orbital energies of prehnitene are shown in the center of Figure 10. The contributions of the two configurations to the transition are no longer equal so that the transition dipole becomes nonzero. The HOMO \rightarrow LUMO configuration contribution to the lowest

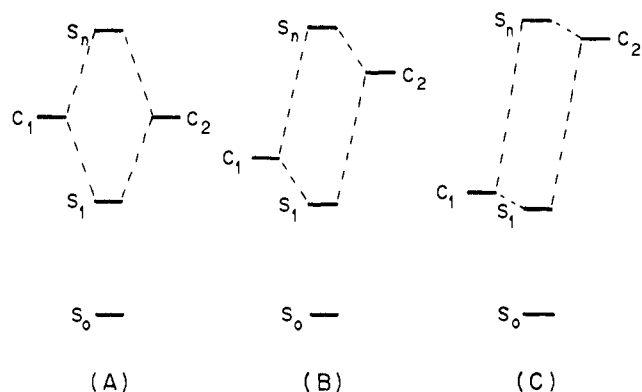


Figure 11. Schematic representation of configuration interaction: (A) degenerate configurations: C₁ and C₂ mix strongly to give lowest excited singlet, S₁, and an upper singlet, S_n; (B) C₁ and C₂ are no longer degenerate, and less mixing occurs to give S₁ and S_n; (C) large split in degeneracy gives S₁ which is nearly "pure C₁" in character.

excited singlet is about 13% greater than the SHOMO → SLUMO configuration (our calculations included CI among the 30 lowest configurations only). In durene, the lowest singlet is even more HOMO → LUMO in character, but the principal configuration in durene (b₁ → b₁) is opposite to that in prehnitene (a₂ → a₂). Although the transition energies are slightly underestimated in the CNDO/S calculations (4.17, 4.39, and 4.37 eV, respectively, for benzene, prehnitene, and durene) as compared to the experimental energies of the 0-0 transitions (4.86, 4.49, and 4.46 eV for the same three molecules), the trends are excellent. Similarly, the CNDO/S calculations predict 0.000, 2.2 × 10⁻³, and 9.2 × 10⁻³ for the oscillator strengths (*f*) of the three molecules. Using the approximate relationship log $\epsilon = 5 + \log f$,²⁹ the calculated *f*'s translate into ϵ 's of 0, 220, and 920 for benzene, prehnitene, and durene, respectively, in reasonable agreement with trends in experimental extinction coefficients of the 0-0 bands, which are 160, 235, and 727, respectively.

Having established that CNDO/S calculations parallel experimental data, we turn to the analysis of the spectral trends mentioned earlier for the benzodicycloalkenes. Both the decrease in transition energy and the increase in intensity along the series benzene, prehnitene, and durene can be directly attributed to the changing nature of the composition of the lowest excited singlet. In prehnitene, the degeneracies of both the HOMOs and LUMOs of benzene are split so that the lowest excited singlet becomes more heavily a₂ → a₂ in character. Since the two configurations do not mix equally in the lowest singlet, the transition dipoles do not exactly cancel and the transition becomes weakly allowed. In durene this trend is followed further, since the split in degeneracy of both the HOMOs and LUMOs is increased. In effect, the calculations indicate that the substituents decrease the symmetry of the system, breaking the HOMO and LUMO degeneracies.

However, the fact that one of the configurations is lowered considerably in energy by substitution does not drastically lower the transition energy. This arises from the fact that configurations, like orbitals, mix most when they are close in energy. Figure 11 shows this schematically. Maximum configuration mixing occurs between degenerate configurations, C₁ and C₂, and as the degeneracy between C₁ and C₂ is split, the two configurations mix less. As the splitting becomes large, the lowest singlet, S₁, becomes more nearly pure C₁ in character and more allowed, but is not necessarily at lower energy than S₁ as in case (A) of Figure 11.

The increased intensity and longer wavelength absorption observed for the symmetrical benzodicycloalkenes as compared with the unsymmetrical ones can be explained in the same way as the differences between durene and prehnitene were ex-

Table IV. Summary of CNDO/S Calculations^a

Compd	S ₁ composition		λ_{\max} (calcd)	<i>f</i>
	% (a ₂ → a ₂)	% (b ₁ → b ₁)		
<i>o</i> -Xylene	42	56	273	2.8 × 10 ⁻³
Benzocyclopentene	41	59	274	4.2 × 10 ⁻³
Benzocyclobutene				
(Std)	41	59	272	5.5 × 10 ⁻³
(Mod) ^b	36	64	279	9.5 × 10 ⁻³
Durene	36	61	284	9.2 × 10 ⁻³
S-5,5	33	66	286	14 × 10 ⁻³
S-4,4				
(Std)	36	64	281	13 × 10 ⁻³
(X ray) ^c	26	74	281	27 × 10 ⁻³
Prehnitene	55	42	282	2.2 × 10 ⁻³
U-5,5	58	42	284	3.3 × 10 ⁻³
U-4,4	57	43	281	3.7 × 10 ⁻³

^a Standard geometries with regular hexagonal benzene rings were used except in the 4,4 compounds, for which calculations were carried out on other geometries, as noted. ^b A modified geometry with $r_{12} = 1.35 \text{ \AA}$, $r_{23} = r_{61} = 1.43 \text{ \AA}$, $r_{34} = r_{45} = r_{56} = 1.41 \text{ \AA}$, $\alpha = 112^\circ$ was used. ^c The x-ray geometry (ref 9) was used.

plained above. That is, there is a greater HOMO-SHOMO split in the symmetrical cases, and the lowest singlet will consist of a less equal mixture of configurations than for the unsymmetrical cases. This explanation was confirmed by CNDO/S calculations which were performed on each of these molecules and which are summarized in Table IV. As the contribution of the two configurations become less equal, *f* increases.

There is a general increase in the intensity of absorption as the site of ring fusion is changed from dimethyl to cyclopentenyl to cyclobutenyl, even though the energy of the transition is unchanged. The explanation for this trend is basically like that given above; that is, as one configuration contributes more to the lowest singlet than the other, the transition to the lowest singlet becomes more allowed, even though the lowest excited singlet energy drops very little.

CNDO/S calculations for the methylated and ring-fused compounds in all three series show that the greater intensities of the transitions in the fused systems arise from the increasing bias of the lowest excited singlet toward one-configuration character. The results are simply explained on the basis of the increasing difference in energy between the occupied b₁ and a₂ orbitals found in the calculations and experimentally by PES. The vacant orbitals show a similar trend according to the CNDO/S calculations. The lowest singlet state energy is determined by mixing of the two configurations and by the energy of each configuration, which is calculated as $\Delta E = -\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}} - J_{\text{HOMO-LUMO}} + 2K_{\text{HOMO-LUMO}}$. The CNDO/S calculations indicate that $J_{\text{HOMO-LUMO}} - 2K_{\text{HOMO-LUMO}}$ remains nearly constant (3.4 eV) in all of these transitions.

However, calculations on benzocyclobutene and benzo[1,2:4,5]dicyclobutene (**2**) do not show the experimentally observed increase in oscillator strength when standard geometries are employed. For example, Table IV shows that benzocyclobutene and indan have nearly the same oscillator strength when both are calculated in standard geometries, as do **S-5,5** and **S-4,4**. However, calculations on the x-ray geometry of **S-4,4** and on a modified geometry of benzocyclobutene where α is decreased to 112° and r_{12} is contracted to 1.35 Å correct the trend, showing greater intensities for the four-membered than for the five-membered fused compounds. Most likely the same would be observed for **U-4,4**, but in the absence of experimental guides as to the direction of distortion, we have not attempted calculations on modified geometries of **U-4,4**.

The predicted intensification in the modified geometries of the four-membered compounds is a direct result of the in-

creased importance of the b₁ → b₁ configuration over the a₂ → a₂, as can be seen in Table IV. This increasing importance of the b₁ → b₁ configuration arises both from orbital energy changes, such as those discussed in connection with the PES interpretation, and from a decrease in K_{HOMO-LUMO} upon distortion, since the exchange integral, K, diminishes as the two sides of the benzene ring are brought together.

Conclusion

Photoelectron and absorption spectra reveal some evidence for the distortion of the benzene rings in fused compounds as a result of ring strain. The changes in orbital energies detected by photoelectron spectroscopy are relatively sensitive probes of distortion, while energies of transitions to the lowest singlet state are poor indicators of such effects. However, intensities, which indirectly reflect orbital energy changes, are, like ionization potentials, relatively sensitive probes of distortion as long as corrections can be made for the inductive effects of ring substituents.

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Acid-Base Properties of 1-Methyl-1,4-dihydroborabenzene, CH₃BC₅H₆

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Abstract: Ion cyclotron resonance techniques are employed to determine the gas-phase Brønsted and Lewis acidities as well as the Brønsted basicity of 1-methyl-1,4-dihydroborabenzene, CH₃BC₅H₆. The ring proton is found to be highly acidic with PA(CH₃BC₅H₅⁻) = 337 ± 3 kcal/mol. This acidity results from the formation of a 6π electron aromatic anion CH₃BC₅H₅⁻, which is isoelectronic with toluene. Both the Lewis acidity toward F⁻ as a reference base and the proton basicity of the parent molecule suggest that there is little interaction between the diene π system and the electron-deficient boron. This is further confirmed by the similarity of both negative and positive ion chemistry of the borabenzene to that of aliphatic boranes.

Introduction

Ionic 6π electron aromatic compounds isoelectronic with benzene can be generated and studied in the gas phase where their intrinsic properties and reactivities can be probed without interference from solvent effects. For example, on protonation

of pyridine to form C₅H₅NH⁺ (Scheme I), the cation retains the aromatic properties of neutral pyridine. The low solution basicity of pyridine compared to aliphatic amines has been interpreted as the result of increased s character in the nitrogen lone pair. This hybridization change is the result of the involvement of nitrogen in the planar π system. Ion cyclotron