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## Photoelectron and Charge-Transfer Spectra of Benzobicycloalkenes. Relationships between Through-Space Interactions and Reactivity

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**Abstract:** Photoelectron and charge-transfer spectra of a variety of bicyclic and tricyclic alkenes fused to phenyl rings have been measured. The molecules studied are the benzo derivatives of norbornene, bicyclo[3.2.1]oct-6-ene, bicyclo[4.2.1]non-7-ene, norbornadiene, 2,6-bicyclo[3.2.1]octadiene, 2,7- and 3,7-bicyclo[4.2.1]nonadiene, 2,4,5-bicyclo[4.2.1]nonatriene, *exo*- and *endo*-tricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene, tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene, and *exo*- and *endo*-tricyclo[4.2.1.0<sup>2,5</sup>]nona-3,7-diene. As the through-space interactions between the benzene ring and the alkene moieties increase, the photochemical di- $\pi$ -methane and electrophilic reactivities increase.

### Introduction

The interactions between nonconjugated alkene moieties in polycyclic hydrocarbons have been thoroughly explored by photoelectron spectroscopy,<sup>2</sup> but little attention has been paid to the through-space interactions between phenyl and alkene moieties. Because of our interests in the photochemistry and electrophilic reactivity of these systems, we have studied the photoelectron, ultraviolet absorption, and charge-transfer spectra of benzonorbornadiene and related compounds, 1-13, containing phenyl groups and alkene, diene, or cyclopropyl moieties not conjugated with the benzene ring. The extent of interaction between these nonconjugated moieties has been estimated, and the relationships between these interactions and the reactivities of these compounds have been explored.

### Experimental Section

Preparations of the compounds studied here have been reported elsewhere.<sup>3</sup> Photoelectron spectra were recorded on a Perkin-Elmer

PS-18 photoelectron spectrometer operating with a resolution of 25-35 meV. Four to five spectra of each sample were recorded using xenon and argon as internal calibrants. Ultraviolet absorption spectra were recorded in 95% ethanol or hexane. Charge-transfer spectra were recorded on a Cary 118 UV-vis spectrophotometer, using dichloromethane as reference. Solutions were prepared by dissolving 50-100 mg of each hydrocarbon in 3 mL of a  $3.90 \times 10^{-3}$  M solution of tetracyanoethylene (resublimed) in dichloromethane.

### Molecular Orbitals of Benzobicycloalkenes

The degenerate highest occupied orbitals of benzene, which give rise to ionization potentials (IPs) of 9.24 eV, are split by ortho dialkylation. The influence of dialkylation is larger on the "Ph<sub>S</sub>" orbital than the "Ph<sub>A</sub>", because the hyperconjugative interaction of the alkyl group is larger with the orbital with larger coefficients at the site of substitution. For example, *o*-xylene has IPs of 8.57 (the Ph<sub>S</sub>, or b<sub>1</sub> IP) and 9.10 eV (the Ph<sub>A</sub>, or a<sub>2</sub> IP), shifted by 0.67 and 0.14 eV, respectively,<sup>4</sup> from the IP of benzene.

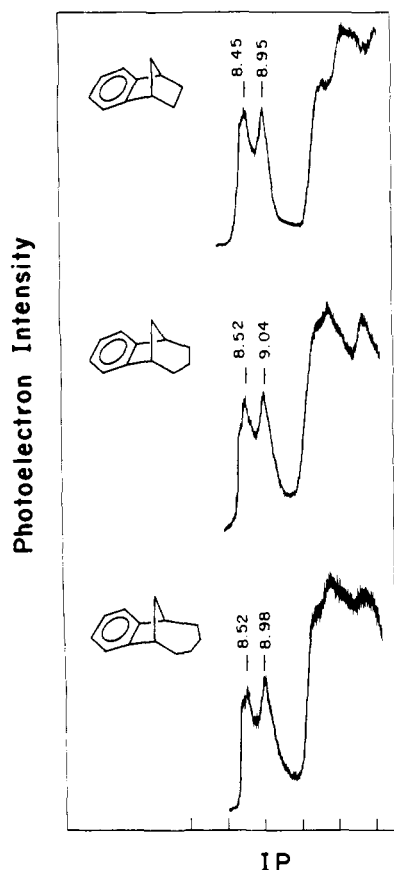
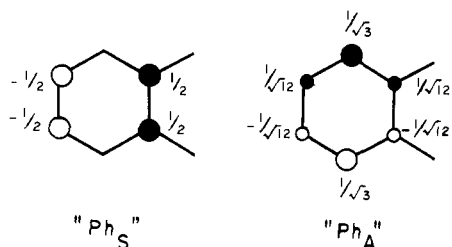


Figure 1. Photoelectron spectra of benzo derivatives of norbornene (1), bicyclo[3.2.1]octene (2), and bicyclo[4.2.1]nonene (3).



Cycloalkyl fusion has a similar effect. Thus, benzocyclohexene has IPs of 8.44 and 8.96 eV, 0.80 and 0.28 eV lower than those of benzene.<sup>4</sup> The ratio of IP changes in this case, 3:1, is the same as the ratio of the squares of the coefficients in the two orbitals at the site of substitution, implying a dominant role of hyperconjugative interactions between the alkyl group and the aromatic  $\pi$  orbitals.

For substitution onto the benzene ring of an alkyl group containing an unsaturated part, the two aromatic orbitals are expected to be influenced not only by the hyperconjugative influence of the alkyl substituent, but by through-space interactions of the  $\pi$  orbital(s) of the substituent with the  $\text{Ph}_S$  and  $\text{Ph}_A$  orbitals. These through-space interactions will be strongly symmetry dependent; the hyperconjugative effects are also symmetry dependent, but in a reasonably large alkyl group, there are ordinarily sufficient orbitals of both S and A symmetry to interact with both  $\text{Ph}_S$  and  $\text{Ph}_A$ , and to destabilize them to a similar extent. In this paper, the photoelectron spectra of the benzo compounds 1-13 are reported and analyzed in terms of these simple ideas.

#### Photoelectron Spectra of Benzobicycloalkenes, 1-3

The spectra of the benzo derivatives of the bicyclic monoalkenes, 1-3, are given in Figure 1. Vertical ionization

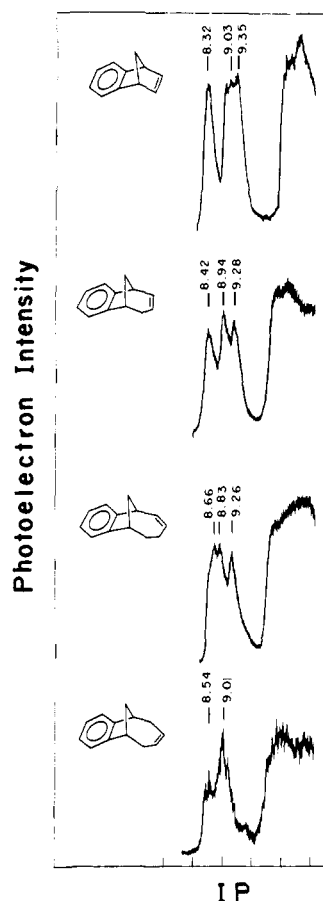
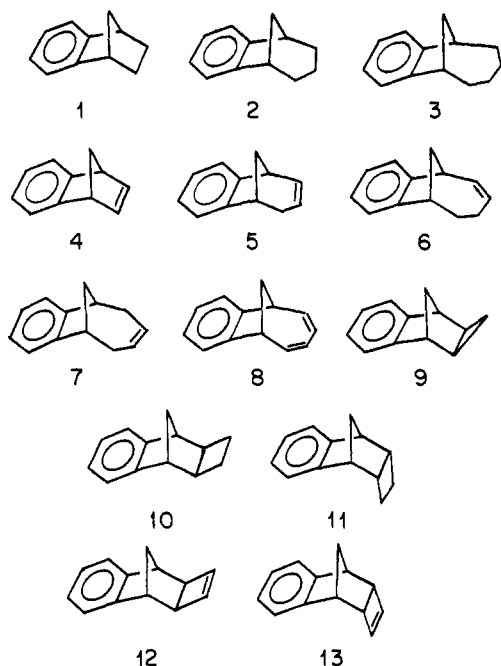


Figure 2. Photoelectron spectra of benzo derivatives of norbornadiene (4), bicyclo[3.2.1]octa-2,5-diene (5), bicyclo[4.2.1]nona-2,7-diene (6), and bicyclo[4.2.1]nona-3,7-diene (7).

potentials of the low energy bands are shown in this and succeeding figures. The spectra are all extremely similar to each other, and to those of benzocycloalkenes reported by Heilbronner and co-workers.<sup>4</sup> Thus, 1-3 have two bands at low IP, with a shoulder (the adiabatic or 0-0 transition) on the first band separated about 0.12 eV ( $\sim 1000 \text{ cm}^{-1}$ ) from the maximum of the band. This spacing is similar to that found in the first band of various alkylbenzenes.<sup>5</sup> 1-3 have lowest vertical IPs of 8.45-8.52 eV and second IPs of 8.95-9.04 eV. Because of the broadness of these bands, there is no significant experimental difference between the IPs of these three compounds. There are significant differences in the higher IPs, arising from the  $\sigma$  orbitals of these molecules. 1-3 have IPs similar to those of indan, tetralin, and benzocycloheptene ( $\text{IP}_1 = 8.45 \pm 0.01 \text{ eV}$ ;  $\text{IP}_2 = 9.00 \pm 0.01 \text{ eV}$ ).<sup>4</sup> The conclusion that  $\text{Ph}_S$  lies above (has a lower IP than)  $\text{Ph}_A$  is clear.

#### Photoelectron Spectra of Benzobicycloalkadienes and -triene, 4-8

These spectra are given in Figures 2 and 3. The photoelectron spectrum of benzonorbornadiene (4) has been reported several times before,<sup>6,7</sup> and Haselbach and Rossi have thoroughly analyzed the spectrum.<sup>7</sup> Our values are within experimental error of those reported by these workers. The interpretation of the spectrum can be made without recourse to calculations. That is, the first IP is lowered with respect to the  $\text{Ph}_S$  IPs of 1-3, while the second is unchanged. The third IP of 4 at 9.35 eV is significantly higher than that of norbornene (8.97 eV).<sup>8</sup> The symmetric  $\text{Ph}_S$  and norbornene  $\pi$  orbitals should mix, raising  $\text{Ph}_S$  (lowering its IP) and lowering the norbornene  $\pi$  (raising its IP). Thus, the IPs of 8.32, 9.03, and 9.35 eV are assigned to IPs arising from  $\text{Ph}_S$ - $\pi$ ,  $\text{Ph}_A$ , and  $\pi$  +



$\text{Ph}_S$  orbitals, respectively, where  $\text{Ph}_S-\pi$  indicates the  $\text{Ph}_S$  orbital mixed in an antibonding fashion with some of the norbornene  $\pi$  orbital and  $\pi + \text{Ph}_S$  indicates the  $\pi$  orbital mixed in a bonding fashion with  $\text{Ph}_S$ . This is represented schematically in Figure 4.

In order to assess the amount of through-space interaction, it is necessary to estimate the energies of the  $\text{Ph}_S$  and  $\pi$  orbitals after "inductive", but before conjugative, interactions. That is, the introduction of the  $\pi$  orbital into the benzonorbornene skeleton will cause alterations of the  $\sigma$  skeleton which change the hyperconjugative interactions of the bicycloalkene group with the benzene ring. The choice of models in such a calculation is, of course, crucial. For example, the  $\text{Ph}_S-\pi$  orbital of benzonorbornadiene (**4**) is 0.13 eV higher in energy than the  $\text{Ph}_S$  orbital of benzonorbornene (**1**). This can be considered to result from an "inductive" energy lowering of  $\text{Ph}_S$ ,  $\delta A(\text{Ph}_S)$ , caused by incorporation of the  $\pi$  orbital into the carbon skeleton, and the through-space interaction between the  $\text{Ph}_S$  and  $\pi$  orbitals, resulting in an energy change,  $C(\text{Ph}_S, \pi)$ . Similarly, the 0.38-eV lowering of the  $\pi$  orbital from its energy in norbornene results from an inductive lowering,  $\delta A(\pi)$ , and the conjugative interaction. Thus, the orbital energies are<sup>7b</sup>

$$\begin{aligned} \epsilon(\text{Ph}_S-\pi) &= \epsilon(\text{Ph}_S) + \delta A(\text{Ph}_S) - C(\text{Ph}_S, \pi), \text{ or} \\ -8.32 &= -8.45 + \delta A(\text{Ph}_S) - C(\text{Ph}_S, \pi) \end{aligned}$$

which gives

$$\delta A(\text{Ph}_S) - C(\text{Ph}_S, \pi) = 0.13 \text{ eV}$$

and

$$\begin{aligned} \epsilon(\pi + \text{Ph}_S) &= \epsilon(\pi) + \delta A(\pi) + C(\text{Ph}_S, \pi), \text{ or} \\ -9.35 &= -8.97 + \delta A(\pi) + C(\text{Ph}_S, \pi) \end{aligned}$$

which gives

$$\delta A(\pi) + C(\text{Ph}_S, \pi) = -0.38 \text{ eV}$$

thus

$$\delta A(\text{Ph}_S) + \delta A(\pi) = -0.25 \text{ eV}$$

where a  $\delta A < 0$  implies a lowering of orbital energies, or a raising of IPs. That is, according to this simple model, the total mutual inductive effect between an olefinic  $\pi$  orbital and an aromatic  $\pi$  orbital is twice the difference between the average

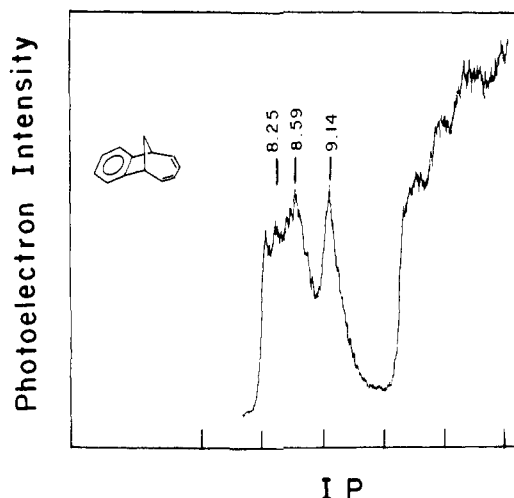


Figure 3. Photoelectron spectrum of 7,8-benzobicyclo[4.2.1]nona-2,4,7-triene (**8**).

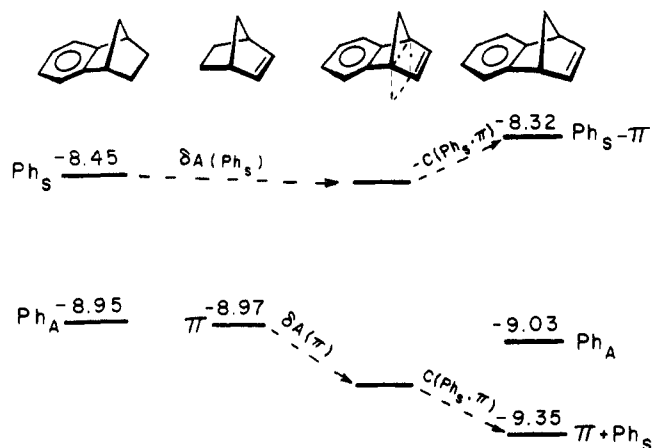


Figure 4. Schematic representation of the "Koopmans' orbital energies" of benzonorbornadiene and its analogues. The model in the center of the figure represents a benzonorbornadiene with the through-space interaction of the phenyl and vinyl moieties deleted. The inductive ( $\delta A$ ) and through-space conjugative ( $C$ ) parameters are defined in the text.

of the orbital energies in the full molecule and the average of the orbital energies in the noninteracting models. Even making these gross assumptions, the value of  $C(\text{Ph}_S, \pi)$  can vary over a wide range, depending on the assumptions made in estimating the  $\delta A$  value. It is reasonable to assume that both  $\delta A$ 's are negative, since our models involve changing saturated ( $\text{sp}^3$ ) carbons to unsaturated ( $\text{sp}^2$ ) carbons. With this assumption,  $C$  may range from  $-0.13$  ( $\delta A(\text{Ph}_S) = 0$ ) to  $-0.26$  eV ( $\delta A(\text{Ph}_S) = \delta A(\pi) = -0.125$  eV). In the case of benzonorbornadiene, the through-space interaction estimated by Haselbach and Rossi is  $-0.17$  eV.<sup>7</sup> We will adopt this value, since we are primarily interested in the change in interaction along the series. Using our values of IPs and  $-0.17$  eV as the value of  $C(\text{Ph}_S, \pi)$  leads to  $\delta A(\text{Ph}_S) = -0.04$  eV and  $\delta A(\pi) = -0.21$  eV.

The value of 0.17 eV for orbital energy changes caused by through-space interaction should be compared to the value of  $C(\pi, \pi)$  of 0.42 eV found in norbornadiene.<sup>2a</sup> The smaller interaction in the benzonorbornadiene case results both from the smaller  $\pi$  coefficients at the fused carbons in  $\text{Ph}_S$  and the difference in energy between  $\text{Ph}_S$  and  $\pi$ .

In the unsymmetrical molecules, **5** and **6**, the symmetry restriction preventing interaction of  $\text{Ph}_A$  with the alkene is removed, and both  $\text{Ph}_S$  and  $\text{Ph}_A$  may interact with the  $\pi$  orbital. The effect of placing a double bond in the benzobicy-

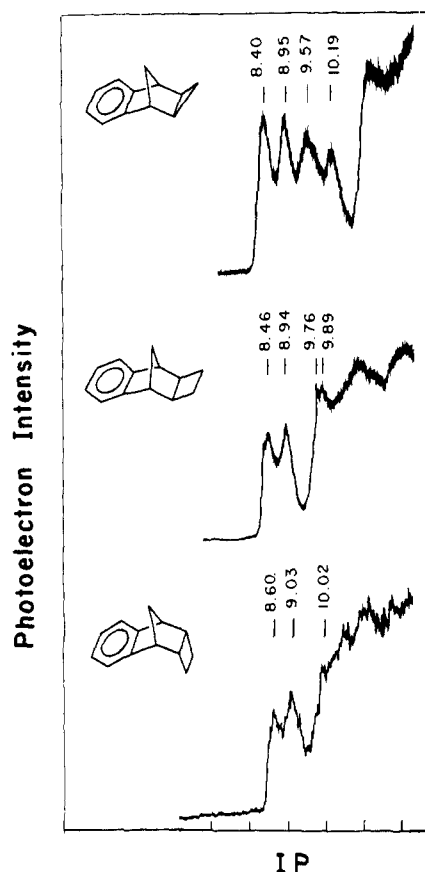


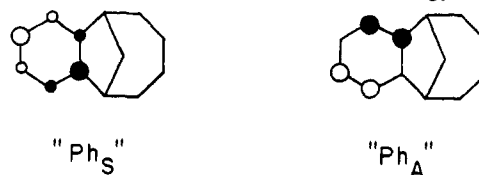
Figure 5. Photoelectron spectra of benzo derivatives of *exo*-tricyclo[3.2.1.0<sup>2,4</sup>]octene (**9**), *exo*-tricyclo[4.2.1.0<sup>2,5</sup>]nonene (**10**), and *endo*-tricyclo[4.2.1.0<sup>2,5</sup>]nonene (**11**).

clo[3.2.1]octadiene skeleton should be to "inductively" lower  $\text{Ph}_S$  about half as much as is calculated for **4**, since effectively only one terminus of the alkene is close enough to the benzo group to cause a significant inductive effect. The effect on  $\text{Ph}_A$  is expected to be about one-third the effect of  $\text{Ph}_S$ , owing to the relative magnitudes of the coefficients at the fused carbons. Thus,  $\delta A(\text{Ph}_S)$  and  $\delta A(\text{Ph}_A)$  are estimated as  $-0.02$  and less than  $-0.01$  eV, respectively. The adiabatic IP of bicyclo[3.2.1]oct-2-ene (8.76 eV) has been measured by Demeo and El-Sayed.<sup>9</sup> We crudely estimate that the Ph inductive effect will lower this  $\pi$  orbital energy ( $-8.92$  eV) by half that in **4**, or  $-0.10$  eV. Thus, the orbital energies before through-space interaction are estimated as  $\text{Ph}_S = -8.54$  eV,  $\text{Ph}_A = -9.05$  eV;  $\pi = -9.02$  eV. In the PE spectrum of **5**, the  $\text{Ph}_S$ - $\pi$  and  $\text{Ph}_A$ - $\pi$  ionizations are lowered by 0.12 and 0.09 eV, with respect to the values estimated for the  $\text{Ph}_S$  and  $\text{Ph}_A$  ionizations before interaction. This should lower the  $\pi$  energy by 0.21 eV, whereas the observed value is 0.26 eV. Considering that the experimental peak positions are uncertain by  $\pm 0.05$  eV, the experimental result is in fair agreement with that estimated from the model.

Compound **6** displays a shoulder on the first band attributed to the vibrational structure in the  $\text{Ph}_S$  band. In this molecule, the inductive effects on  $\text{Ph}_S$ ,  $\text{Ph}_A$ , and  $\pi$  (estimated IP of bicyclo[4.2.1]non-2-ene = 8.83 eV) are assumed to be the same as those in **5**, leading to orbital energies of  $-8.54$ ,  $-8.99$ , and  $-8.93$  eV, respectively, before conjugation. The PE spectrum of **6** is substantially different from that of **5**. The first two bands in **6** are separated by only 0.17 eV, whereas this separation is 0.52 eV in **5**. The separation between the first and third bands of **6** is 0.60 eV, suggesting that the first and third bands of **6** are due to aromatic orbitals; the corresponding separation in the parent compound, **3**, is 0.46 eV. The third orbital is lowered

by 0.27 eV relative to the value estimated for  $\text{Ph}_A$  after inductive effects. This should raise the  $\pi$  orbital energy by 0.27 eV while interaction with the higher energy  $\text{Ph}_S$  orbital will lower the  $\pi$  orbital energy. Thus, the observed 0.10-eV increase in the energy of the  $\pi$  orbital should be reflected by a 0.17-eV increase in the energy of  $\text{Ph}_S$ . Exactly the opposite is observed: the  $\text{Ph}_S$  orbital is lowered in energy by 0.08 eV, relative to the noninteracting orbital estimate of  $-8.54$  eV. We can only conclude that the model used is woefully oversimplified, and that a specific conformation exists for this molecule which substantially changes the nature of the orbitals.

The NMR spectrum of **6** indicates that the molecule is quite rigid. The olefinic protons differ by 0.6 ppm and the lower field proton has both strong coupling to the bridgehead ( $J = 9$  Hz) and to one of the allylic protons ( $J \sim 3$  Hz). This is compatible with a rigid conformation in which this proton is deshielded by the phenyl group, and suggests that C2 is relatively close to, and interacts strongly with, the phenyl ring. If the vinyl  $\pi$  orbital interacts strongly at only one carbon of the benzene ring and this interaction dominates, then the local symmetries of the aromatic orbitals can be substantially changed, resembling those shown below. These may be closer in energy than those



of other ortho dialkyl compounds, such as **1-5**, because the inductive lowering and through-space homoconjugative raising both influence the " $\text{Ph}_S$ " orbital much more than the " $\text{Ph}_A$ ", leading to  $\text{Ph}_S$ - $\pi$  and  $\text{Ph}_A$  orbitals of similar energy.

In **7**, the  $C_s$  symmetry of the molecule is restored. The inductive and conjugative interactions between the aromatic ring and the vinyl group should be quite small. Thus, the "noninteracting" orbital energies in **7** should be  $\text{Ph}_S = -8.52$ ,  $\text{Ph}_A = -8.98$  (values in **3**),  $\pi = -8.98$  eV.<sup>11</sup> The spectrum of **7** shows a lowest IP ( $\text{Ph}_S$ ) of 8.54 eV, and overlapping bands at 9.01 eV. We conclude that there are essentially no interactions between the  $\text{Ph}_S$  and  $\pi$  orbitals in **7**.

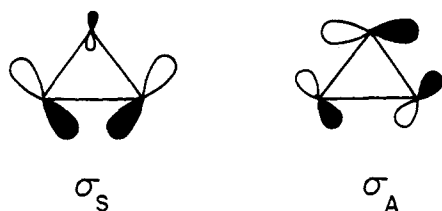
In **8**, four orbitals are expected to give rise to low-energy IPs. Starting from the model compound, **3**, the  $\text{Ph}_S$  and  $\text{Ph}_A$  orbitals are estimated to be influenced inductively similarly to those in **4**. The diene  $\pi_A$ (HOMO) and  $\pi_S$ (SHOMO) orbitals, which give IPs of 8.23 and 10.46 eV, respectively, in bicyclo[4.2.1]nona-2,4-diene,<sup>12b</sup> should be inductively lowered, upon conversion to **8**, to an extent similar to that of the  $\pi$  orbital in **4**. However, the  $\pi_S$  orbital should be lowered less than the  $\pi_A$ , because of the larger coefficients at the diene termini in the latter. We estimate that  $\pi_S$  is lowered by 0.35 eV relative to that of the ethylene moiety in **4**, and  $\pi_A$  by 0.65 eV relative to that of the ethylene moiety. Thus, the inductively altered energy estimates are  $\text{Ph}_S$ ,  $-8.56$ ;  $\text{Ph}_A$ ,  $-8.99$ ;  $\pi_A$ ,  $-8.37$ ;  $\pi_S$ ,  $-10.53$  eV. The spectrum of **8** shows prominent maxima at 8.25, 8.59, and 9.14 eV, and a  $\sigma$  onset of 10.19 eV. The  $\text{Ph}_S$  orbital is assigned to the IP at 8.59 eV, essentially unchanged owing to the great difference in energy between  $\text{Ph}_S$  and  $\pi_S$ . The  $\pi_A$  and  $\text{Ph}_A$  orbitals are relatively close in energy and interact strongly.  $\pi_A$ - $\text{Ph}_A$  is assigned to the first IP at 8.25 eV, and  $\text{Ph}_A$  +  $\pi_A$  to the IP at 9.14 eV. The lower energy combination is stabilized by 0.15 eV, and the upper is destabilized by 0.12 eV.

The nonbenzo analogue of **8**, bicyclo[4.2.1]nona-2,4,7-triene, has been investigated by photoelectron spectroscopy.<sup>12</sup> The corresponding diene, bicyclo[4.2.1]nona-2,4-diene, has IPs of 8.23 and 10.46 eV, which are shifted to 8.36 and 10.55 eV in the triene by inductive and conjugative interactions with the additional double bond. If 8.36 eV had been used as the

estimate for the energy of the  $\pi_A$  orbital in **8** before homoconjugative interaction, the final position of the  $\pi_A$ -Ph<sub>A</sub> IP in **8** (8.25 eV) would imply a *C* of 0.1 eV. The nonconjugated 7,8  $\pi$  orbital of bicyclo[4.2.1]nona-2,4,7-triene has an IP of 9.02 eV, essentially unchanged from its expected position in bicyclo[4.2.1]nona-6-ene. Thus, only small through-space interactions occur between this orbital and the  $\pi_S$  diene orbital in the triene, as we have found in the benzo analogue. Heilbronner and co-workers conclude that there is no exceptional homoaromaticity manifested in the PES of the triene,<sup>12a</sup> and this conclusion can be extended to **8**.

### Photoelectron Spectra of Benzotricycloalkenes, 9–13

The photoelectron spectra of **9–13** are shown in Figure 5. Tricyclo[3.2.1.0<sup>2,4</sup>]octane has IPs of 9.40 and 10.00 eV, which have been assigned to the Walsh orbitals,  $\sigma_S$  and  $\sigma_A$ , respectively.<sup>13</sup> These orbital energies are probably inductively lowered by benzo fusion, perhaps by the 0.12 eV by which the alkene  $\pi$  orbital of norbornene is lowered by benzo fusion. By contrast, the orbital energies of the Ph<sub>S</sub> and Ph<sub>A</sub> orbitals of **1**,



observed at  $-8.45$  and  $-8.95$  eV, are expected to experience little inductive change upon cyclopropyl fusion. Thus, for the Ph<sub>S</sub>, Ph<sub>A</sub>,  $\sigma_S$ , and  $\sigma_A$  orbitals in **9**, energies of  $-8.45$ ,  $-8.95$ ,  $-9.61$ , and  $-10.21$  eV are expected before through-space interaction. Four well-resolved IPs of 8.40, 8.95, 9.57, and 10.19 eV are observed in the spectrum of **9**. Essentially no through-space interaction between the aryl and cyclopropyl moieties is revealed in the spectra, in contrast to the 0.70–0.20  $\pi$ - $\sigma_S$  interactions found in the nonbenzo analogue.<sup>13</sup> The smaller interaction in the case of the benzocyclopropyl case is expected, because the aromatic coefficients are smaller than the ethylene coefficients at the sites of interaction, and the aromatic and cyclopropyl orbital energies differ more than those in the nonbenzo analogue.

Since the Walsh orbitals of cyclobutane are slightly lower in energy and less concentrated at each carbon than those of cyclopropane, phenyl-cyclobutyl interactions in **10** and **11** are expected to be negligible. In the exo compound, **10**, IPs of 8.46 and 8.94 eV are observed, within experimental error of the corresponding IPs in the exo cyclopropyl compound, **9**, and very close to the values of the IPs of the simple benzobicycloalkenes, **1–3**. The endo cyclobutyl compound, **11**, has slightly higher IPs of 8.57 and 9.03 eV. It is likely that the slightly lower IPs of the exo compound arise from better through-bond (hyperconjugative) mixing of the cyclobutyl  $\pi_{CH_2}$  orbitals and the phenyl orbitals (via the 1,2 and 5,6 bonds) in the exo compound than in the endo compound.

The spectra of the corresponding dienes, **12** and **13**, shown in Figure 6, are dramatically different. The endo compound, **13**, has one resolved IP at 8.42 eV, and two overlapping bands with a maximum at 9.04 eV, whereas the exo compound, **12**, has three well-separated bands at 8.35, 8.90, and 9.51 eV. In both of these compounds, the phenyl orbitals would be expected to experience only minor inductive effects from the cyclobutene double bond. Thus, Ph<sub>S</sub> and Ph<sub>A</sub> IPs of 8.45–8.52 and 8.95–9.04 eV (those of **1–3**), respectively, are expected before interaction. The cyclobutene double bond should not be inductively altered much from its position in bicyclo[4.2.1.0<sup>2,5</sup>]non-3-ene (9.00 eV).<sup>14</sup> Therefore, we conclude that **13** experiences essentially no through-space or through-bond inter-

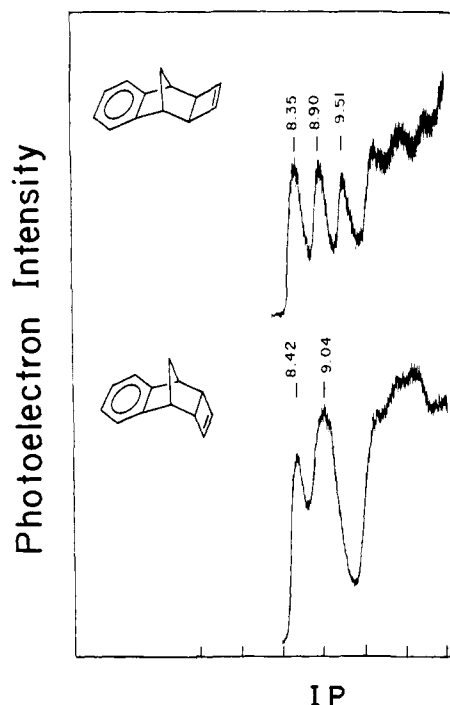


Figure 6. Photoelectron spectra of benzo derivatives of *exo*- and *endo*-tricyclo[4.2.1.0<sup>2,5</sup>]nona-3,7-diene (**12** and **13**).

actions, and assign the IPs as Ph<sub>S</sub> (8.42 eV), Ph<sub>A</sub> (9.0 eV), and  $\pi$  (9.0 eV).

The IPs of the endo molecule are essentially exactly those expected for a molecule in which the Ph and  $\pi$  orbitals do not interact at all. However, in the exo compound, **12**, the first IP has been lowered by 0.07 eV with respect to that of **13**, the second is essentially unchanged, or perhaps slightly lowered with respect to that of **13**, and the third is raised by about 0.47 eV. Since the Ph<sub>A</sub> orbital should be affected little by the change in geometry, we assign the 8.35 and 9.51 eV IPs to the through-bond interacting combinations of Ph<sub>S</sub> and cyclobutene  $\pi$  orbitals. The separation of these orbitals is 0.5–0.6 eV greater in the exo compound than in the endo, implying far greater through-bond coupling of the Ph<sub>S</sub> and  $\pi$  orbitals in the exo compound than in the endo.

This result has an interesting bearing on the question of through-bond vs. through-space interactions in molecules such as the syn and anti dimers of cyclobutadiene, which has been the subject of some debate.<sup>15,16</sup> Our results indicate that through-bond interactions are essentially absent in the endo compound, **13**, and large in the exo compound, **12**, whereas previous results on similar systems implied that only the through-space interactions differed in such isomers.

### Ultraviolet and Charge-Transfer Spectra

The UV spectra are summarized in Table I. Only the diene has a spectrum significantly altered from that of the models. This seems, at first sight, surprising; for example, **5** has an 0.1 eV lower IP than **3**, but the UV spectrum of the former has absorptions shifted by only 0.03 eV or less to lower energy. The lowest energy singlet (<sup>1</sup>L<sub>B</sub> or <sup>1</sup>B<sub>2u</sub>) of benzene consists of equal contributions from a configuration with "Ph<sub>S</sub>" and "Ph<sub>S</sub>\*" singly occupied ("Ph<sub>S</sub>\*" is the LUMO of benzene with the same C<sub>s</sub> symmetry as "Ph<sub>S</sub>") and a configuration with "Ph<sub>A</sub>" and "Ph<sub>A</sub>\*" each singly occupied. As the energy of these four orbitals is varied, the extent of mixing of these two configurations into the lowest singlet state varies. Thus, as Ph<sub>S</sub> is raised in energy and Ph<sub>S</sub>\* is lowered, the Ph<sub>S</sub> → Ph<sub>S</sub>\* configuration becomes lower in energy than the Ph<sub>A</sub> → Ph<sub>A</sub>\* configuration. However, because of the difference in energy between the two

Table I. Ultraviolet Spectra of Benzocycloalkenes

Compd	$\lambda_{\max}$ ( $\epsilon$ )	Solvent <sup>a</sup>
1 <sup>b</sup>	258.5 (662), 264.5 (989), 271.3 (1120)	
2		
3	260 (770), 265.9 (1230), 272.8 (1470)	E
4		
5	255 sh (180), 263.0 (300), 267.5 (463), 274.5 (515)	H
6	253.6, 259.5, 266, 273	H
7	252.5, 259.2, 265.5, 272.2	H
8	252.7 (3220), 261.0 (4480), 270.4 (5070), 281.9 (3260)	
9		
10		
11		
12 (exo)	252.4 sh, 259.2, 265.2, 272.3	H
13 (endo)	252.6 sh, 259.6, 265.5, 272.5	H
Bicyclo[4.2.1]nona-2,4-diene <sup>c</sup>	250 sh (2120), 259 (5250), 268 (2150), 280 sh (930)	
Bicyclo[4.2.1]nona-2,4,7-triene <sup>d</sup>	258 (4200), 268 (4000), 279 (2200)	

<sup>a</sup> H = hexane; E = 95% ethanol. <sup>b</sup> H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965). <sup>c</sup> C. W. Jefford, U. Burger, and R. Delay, *Helv. Chim. Acta.*, **56**, 1083 (1973). <sup>d</sup> W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

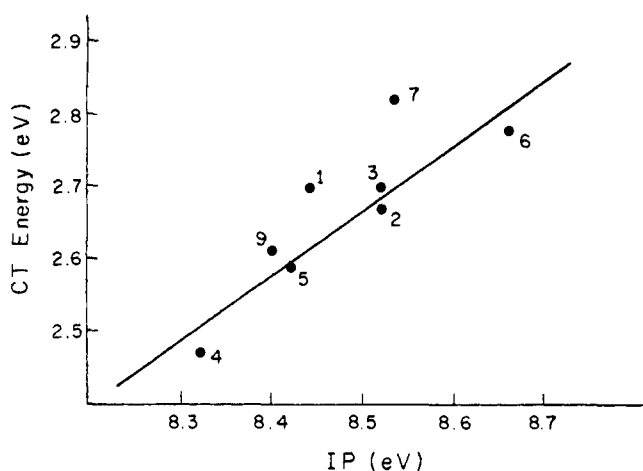


Figure 7. Plot of charge-transfer transition energy (complex with TCNE) vs. the first vertical IP of the aromatic.

configurations, there is less mutual mixing, and the singlet state does not change much in energy, but becomes more Ph<sub>S</sub> → Ph<sub>S</sub>\* in character.

In compound **8**, the absorption energies are about the same as in the model diene, bicyclo[4.2.1]nona-2,4-diene, but the extinction coefficients in **8** are greater than in the model diene in the two longest wavelength bands. The effect here may be trivial; that is, the aromatic <sup>1</sup>B<sub>2u</sub> absorption overlaps with the diene HOMO → LUMO absorption in this region. However, it may be a result of increased allowedness caused by strong mixing of the π<sub>A</sub> and Ph<sub>A</sub> orbitals, or, in alternative language, by the mixing of diene HOMO → LUMO and aryl <sup>1</sup>B<sub>2u</sub> singlet configurations.

Charge-transfer complexes of the compounds studied here with tetracyanoethylene (TCNE) gave broad overlapping absorption bands which were resolved by the method of Voigt and Reed, using a band half-width of 147 nm. A plot of the CT transition energies vs. the IPs measured here is given in Figure 7. Least-squares fitting gave the correlation equation

$$h\nu_{CT} = 0.89 \text{ IP}_{\text{donor}} - 4.90 \text{ eV}$$

This compares well with a similar correlation for a variety of substituted benzenes:<sup>17</sup>

$$h\nu_{CT} = 0.83 \text{ IP}_{\text{donor}} - 4.42 \text{ eV}$$

The main deviation from this line is due to compound **7**, which has a significantly higher CT transition energy than expected.

Table II. Electrophilic Nitration Reactivities, β/α Product Ratios, and Aromatic IPs of Some Benzocycloalkenes

Compd	$k_{\text{rel}}^a$	β/α <sup>a</sup>	IP(Ph <sub>S</sub> )	IP(Ph <sub>A</sub> )
Tetralin	1.00	1.8	8.44	8.96
Indan	1.01	2.8	8.46	9.04
Benzonorbornene ( <b>1</b> )	3.92	33	8.45	8.95
<b>9</b>	6.47	510	8.40	8.95
Benzonorbornadiene ( <b>4</b> )	6.28	990	8.32	9.03

<sup>a</sup> Reference 3c.

However, for this compound, and for others involving donors with relatively high IPs, there are difficulties arising from overlap of the lowest energy transition with one at shorter wavelengths.<sup>18</sup>

#### Comparisons of Spectral Data and Reactivity

Although no single reactivity index is available to compare with the PE, UV, and CT data, there are interesting parallels between interactions, measured by PE spectra, and photochemical reactivity on the one hand, and between rates of electrophilic nitration and aromatic IPs on the other.

Benzonorbornadiene (**4**) undergoes an efficient ( $\Phi = 0.5$ ) sensitized di-π-methane photorearrangement<sup>19</sup> and does not fluoresce,<sup>20</sup> while **5**, which has a smaller interaction, rearranges less efficiently ( $\Phi_{\text{direct}} = 0.06$ ;  $\Phi_{\text{sens}} = 0.04$ ) and fluoresces nearly as efficiently ( $\Phi_f = 0.15$ ) as the saturated analogue, **2**.<sup>20</sup> No di-π-methane rearrangements are observed with **6** or **7**.<sup>21</sup> Irradiation in solution gives dimers inefficiently. Thus, as the extent of interaction decreases, aromatic fluorescence properties like those of isolated systems are observed, while the strongly interacting systems give efficient di-π-methane rearrangements, and no emission, both presumably due to the strong phenyl-π bonding in the excited state.

Compound **8**, for which we have deduced substantial π<sub>A</sub>-Ph<sub>A</sub> interactions, is very reactive upon direct or sensitized irradiation.<sup>21</sup> Direct irradiation gives exo and endo cyclobutenes (**12** and **13**) with quantum yields of 0.07 and 0.094, respectively, and the di-π-methane product with  $\Phi = 0.24$ . The last product is also formed on sensitized irradiation, along with dimer. The di-π-methane rearrangement products arise from initial diene-phenyl bonding, and the efficiency of this process compares favorably with the large Ph-diene interaction observed in the PE spectrum.

The saturated tricyclics, in which we detect no interaction, are photochemically unreactive. The cyclobutenes, **12** and **13**, undergo photoreduction of the cyclobutene double bond, apparently involving the cyclobutene triplet.<sup>22</sup> The PE results indicate through-bond interaction in the exo case, but little or no interaction in the endo case. However, both compounds probably give a cyclobutene triplet after formation of, and intersystem crossing by, the aromatic singlet.

Finally, nitration data are available for several of the compounds studied here.<sup>3c</sup> As can be seen in Table II, there is a rough pattern in the four compounds with saturated moieties fused to the phenyl. As the rate of reaction increases, the preference for  $\beta$  substitution increases, as measured by the ratio of  $\beta$  to  $\alpha$  substitution. In the first four compounds, the difference between IPs is due mainly to different hyperconjugative effects of the alkyl moiety, so that orbital coefficients will not be substantially different in the orbitals of different molecules. As the IP of the aromatic decreases, the reactivity of the aromatic toward electrophiles should increase, a result of enhanced aromatic HOMO-electrophile LUMO interaction in the transition state. Furthermore, as the difference between the  $\text{Ph}_S$  and  $\text{Ph}_A$  orbital energies increases, the reactivity of the  $\beta$  position should increase relative to the  $\alpha$ . The interaction of the  $\text{Ph}_S$  orbital with the electrophile stabilizes only attack at the  $\beta$  or ipso positions, since these are the positions with large coefficients. The  $\text{Ph}_A$  orbital will primarily stabilize transition states leading to  $\alpha$ -attack, since the  $\alpha$  coefficients are much larger than the  $\beta$  in this orbital. Thus, raising the  $\text{Ph}_S$  orbital increases reactivity, but also shifts substitution to the  $\beta$  position. The IPs change very little in the four compounds, but the general trend agrees with the model proposed here. We attribute discrepancies to the much greater sensitivity of nitration data than PE data to small changes in IP.

Benzonorbornadiene (**4**) appears anomalous, since the reactivity of this molecule is slightly less than that of **9**, yet the  $\beta/\alpha$  ratio is larger and the IP is smaller for **4** than for **9**. This apparent anomaly can be explained in terms of the model given above. Upon interaction of the  $\text{Ph}_S$  and  $\pi$  orbitals, the  $\text{Ph}_S$  orbital is raised, but the coefficients on the aromatic ring are decreased. This has the effect of tempering the reactivity which would otherwise have increased. The partial rate factor for nitration of **4** is slightly smaller (9.9) than that of **9** (10.2), but the partial rate factor for  $\alpha$  substitution is decreased, no doubt owing to the decrease in energy of the  $\text{Ph}_A$  orbital.

Finally, the positional selectivity observed in the electrophilic nitration of compound **5** fits in with the "orbital reorientation" we discussed earlier for the unsymmetrical compounds, **5** and **6**. Since the HOMO (the perturbed " $\text{Ph}_S$ " orbital) has the largest coefficient para to the aromatic terminus which over-

laps with the alkene  $\pi$  orbital, electrophiles are expected to attack at the para position more readily than the meta, even though both of these are formally  $\beta$  positions. Experimentally, para attack is favored over meta by 4:1.<sup>23</sup>

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