

Photoelectron Spectra of Ortho- and Meta-Substituted Benzenorbornadienes. Relationships to Regioselectivities in Triplet Di- π -methane Rearrangements

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Abstract: The ionization potentials of 16 aromatic-ring substituted benzenorbornadienes have been measured by photoelectron spectroscopy. Ortho substitution causes changes in the first three ionization potentials paralleling closely the changes observed upon substitution of benzene. The shapes of the molecular orbitals of these molecules have been determined by ab initio STO-3G SCF calculations. Meta substituents alter orbital energies and "rotate" the nodal planes of the aromatic MOs. The various models (orbital interaction, configuration interaction, and bond-order methods) of photochemical reactivity and regioselectivity are compared and shown to be equivalent. Qualitative correlations between orbital shapes and energies in the benzenorbornadienes and the regioselectivity of triplet di- π -methane rearrangements are found.

Introduction

The remarkable regioselectivity of the triplet di- π -methane rearrangements of benzenorbornadienes,²⁻⁵ summarized in Scheme I, has been satisfactorily explained by qualitative theoretical treatments.^{3,6} The investigation reported here was undertaken, in part, to provide quantitative information about the orbital energies in these systems and thus to quantitate the theory of regioselectivity in photorearrangements of benzenorbornadienes.

The ionization potentials (IPs) of these systems, as measured by photoelectron spectroscopy, are of interest for several additional reasons. First, there have been some disagreements about the assignments of the various IPs of substituted aromatics.⁷ The HOMO degeneracy in benzene⁸ is lifted by substituents, but in the case of electron-withdrawing substituents, it is difficult to decide which of the two lowest nondegenerate radical cation states is lowest in energy, or, in Koopmans' theorem⁹ language, which of the two highest occupied molecular orbitals is highest in energy. In benzenorbornadiene, the IPs resulting from the two highest occupied aromatic orbitals have been assigned unequivocally,^{10,11} and, thus, the influence of substituents on these orbitals can be clearly discerned.

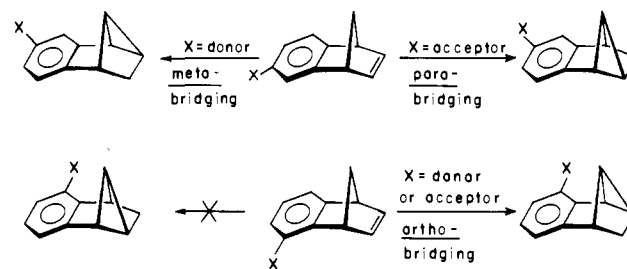
Second, the through-space interactions between the orbitals of the aromatic ring and of the ethylene moiety provide a simple model for the type of interactions which influence the stabilities of "charge-transfer", or molecular, complexes.¹² Third, the benzenorbornene skeleton has been a fruitful template for the investigation of neighboring group participation between substituted aromatic rings and developing carbonium ion centers at the 5 or 7 positions.¹³

Because of current interest in all of these phenomena, we have measured the photoelectron spectra of an extensive series of ortho- and meta-substituted benzenorbornadienes, and analyzed these spectra by correlative analyses assisted by ab initio STO-3G calculations. The phenomena outlined above are also discussed in light of the experimental results obtained here.

Photoelectron Spectra

The spectra reported here were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer at Louisiana State University, using xenon and argon as internal calibration standards. Resolution was 20–25 meV in all cases. Peak positions reported are the average of at least five separate determina-

Scheme I



tions, and are accurate to within ± 0.05 eV. The vertical IPs were taken as the maximum in the vibrational envelope of each band.

Benzenorbornadiene. The photoelectron spectrum of benzenorbornadiene and the orbitals from which the first three ionizations originate are shown in Figure 1. These positions correspond closely to those reported by Haselbach and Rossi,¹⁰ earlier by us,¹¹ and by Morishima et al.¹⁴

The benzenorbornadiene π molecular orbitals are classified here with respect to the plane of symmetry present in the molecule. The benzenoid molecular orbitals are classified as symmetric (S) and antisymmetric (A) with respect to the plane of symmetry, while the alkene π molecular orbital will be referred to here simply as π . The band at 8.34 eV in benzenorbornadiene has been assigned to the IP arising from the antibonding combination of S and π molecular orbitals ($S - \pi$) and the 9.27-eV band to ionization from a $\pi + S$ orbital. The 8.98-eV band is assigned to the ionization originating from the benzenoid A orbital which is of the wrong symmetry to interact with the alkene π orbital.

Ortho-Substituted Benzenorbornadienes. The photoelectron spectra of these molecules are shown in Figures 2 and 3. The ionization energies and orbital assignments of ortho-substituted benzenorbornadienes are shown in Figure 4.

The assignments can be made in a correlative fashion by comparison with the ionization energies of the corresponding substituted benzenes. Although the substituents destroy the C_s symmetry of benzenorbornadiene, the approximate symmetry of the benzenoid orbitals is retained. Thus, the HOMO of benzenorbornadiene has a node at the ortho carbons, and substituents influence this orbital to about the same extent as they influence the a_2 orbital of benzene. The SHOMO (second highest occupied MO) of benzenorbornadiene, like the b_1 orbital of monosubstituted benzenes, has a relatively large

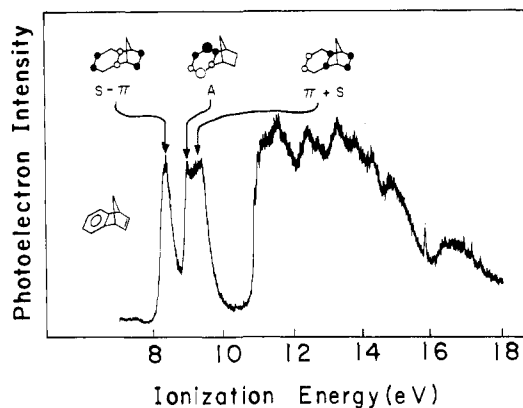


Figure 1. Photoelectron spectra and corresponding orbitals of benzenorbornadiene.

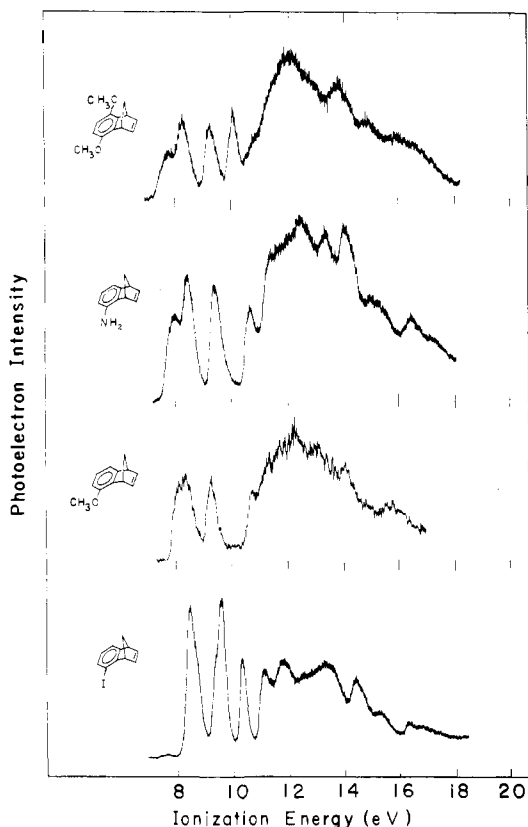


Figure 2. Photoelectron spectra of ortho-donor-substituted benzenorbornadienes.

coefficient at the site of substitution, and is influenced more by substitution than are the HOMO of benzenorbornadiene or the a_2 HOMO of benzene. The third highest occupied MO (THOMO) of benzenorbornadiene is mainly norbornene π in character, but the admixture with the S orbital of the benzo group indicates that the HOMO and THOMO should be influenced in parallel fashion by substituents. The ionization potentials of monosubstituted benzenes are given in Table I and Figure 5. The b_1 ionization potentials decrease upon donor substitution and increase upon acceptor substitution, while the a_2 IPs are essentially unchanged by donor substitution and increased by acceptor substitution. However, since both the a_2 and b_1 orbitals of benzene are influenced to a similar extent by acceptors, there has been some difficulty in making unequivocal assignments.⁷

The assignments for the three most strongly donor-substituted benzenorbornadienes are unequivocal. The first IPs differ from that of the A (SHOMO) orbital IP of benzenorborna-

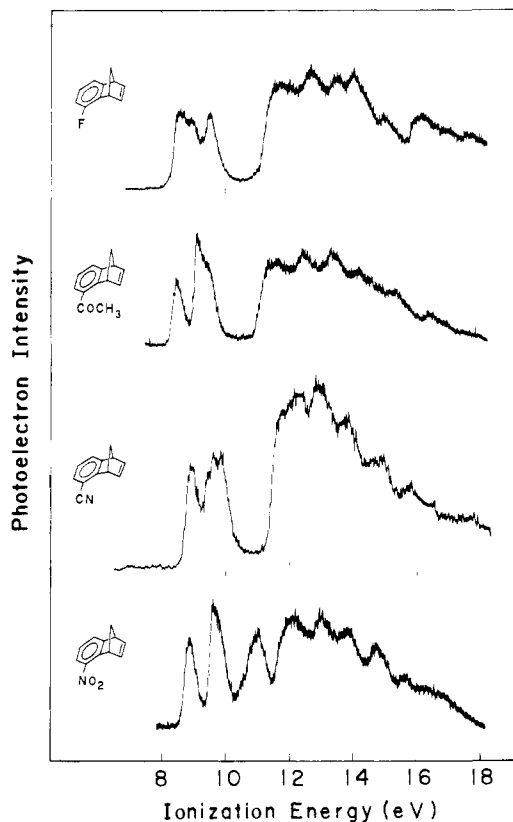


Figure 3. Photoelectron spectra of ortho-acceptor-substituted benzenorbornadienes.

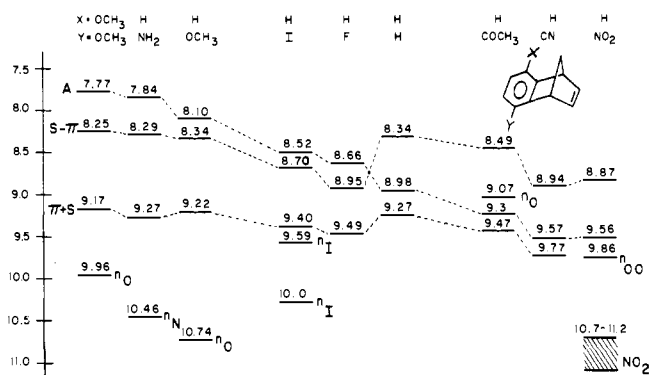


Figure 4. Ionization energies and assignments for ortho-substituted benzenorbornadienes.

diene by essentially the same amount as the first IPs of the corresponding benzenes differ from the first IP of benzene. The second IPs of dimethoxy-, amino-, and methoxybenzenorbornadienes are essentially the same as the first IP of benzenorbornadiene, and the third IPs are only slightly lower than the third IP of benzenorbornadiene. The fluoro and iodo IPs are more difficult to assign. While the third IPs undoubtedly correspond to the third, mainly alkene, IP of benzenorbornadiene, the first two IPs can be only tentatively assigned on the basis of preference for minimum differences between IP changes of benzenorbornadiene and benzene.

Upon acceptor substitution, the same order of IPs for benzenorbornadiene and the substituted derivatives is assured, since acceptors increase both b_1 and a_2 IPs to a similar extent. Furthermore, the greater increase in the energy of the A orbital than the S π orbital suggests that the assignment of acceptor substituted benzenes orbital energies as b_1 above a_2 is correct.

Additional IPs due to orbitals essentially localized on the

Table I. Ionization Energies and Orbital Assignments for Monosubstituted Benzenes

benzene substituent	ionization potentials, eV			ref
	b ₁	a ₂	other	
<i>p</i> -di-MeO	7.90	9.25	10.25 (n ₀)	a
NH ₂	8.05 (7.71)	9.21 (8.94)	10.81 (n _N + π)	b (c)
MeO	8.42 (8.39)	9.23 (9.22)	11.02 (n)	a (b)
I	8.67	9.38	9.64, 10.45 (n ₁)	d
Me	8.85	9.34		b
F	9.11	9.82		c
H	9.24	9.24		e
CO ₂ CH ₃	9.31	9.4–9.5	10.24 (n ₀)	f
CH ₃ CO	9.55	9.77	9.37 (n ₀)	b
CN	9.73	10.15	11.93 (π'CN)	c
NO ₂	9.99	10.35	11–11.6 (NO ₂ n and π)	g

^aH. Bock, G. Wagner, and J. Kroner, *Chem. Ber.*, **105**, 3850 (1972). ^bT. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **47**, 2563 (1974). ^cJ. W. Rabalais, "Principles of Ultraviolet Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1977, Chapter 10; J. W. Rabalais and R. J. Colton, *J. Electron Spectrosc. Relat Phenom.*, **1**, 83 (1972–1973). (d) T. P. Debies and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 355 (1972–1973). (e) L. Åsbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1972). (f) J. Meeks and S. P. McGlynn, unpublished results. (g) J. W. Rabalais, *J. Chem. Phys.*, **57**, 960 (1972).

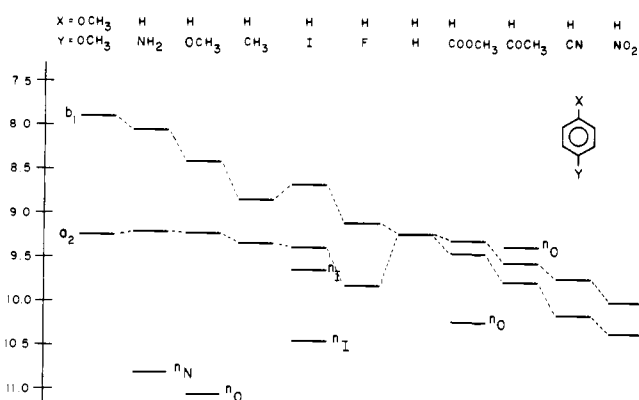


Figure 5. Ionization energies of substituted benzenes.

substituents are also assigned in Figure 4. Assignments are based on analogy to position of the corresponding orbitals of substituted benzenes (Figure 5).

Meta-Substituted Benzonorbornadienes. The photoelectron spectra of these compounds are given in Figures 6 and 7, and the ionization energies and orbital assignments of meta-substituted benzonorbornadienes are given in Figure 8. In these cases, the symmetries of the various orbitals are more seriously influenced by substitution than in the ortho cases. Thus, all three of the first IPs are influenced to a significant extent and in the same direction by a given substituent. However, there is still a qualitative correspondence between the IP changes and the size of the coefficient at the site of substitution in the corresponding orbital. As can be seen in Figure 1, the size of the meta coefficient decreases in the first three orbitals in the order $S - \pi > \pi + S > A$, or $HOMO > THOMO > SHOMO$, and this is, for the most part, the same order of change of IP upon meta substitution. However, there are some deviations from this generalization, and these, as well as the changing shapes of the orbitals upon substitution, can best be understood with the aid of calculations.

Calculations on Benzonorbornadienes. Ab initio SCF calculations,¹⁵ using the STO-3G basis set,¹⁶ were carried out on benzonorbornadienes and various substituted derivatives to assist in interpretations of the photoelectron spectra and to prove the change in orbital shape upon substitution. The molecular orbitals of benzonorbornadiene and several ortho-substituted benzonorbornadienes are given in Figure 9, and those of meta-substituted benzonorbornadienes are shown in Figure 10.

Although the calculations do not quantitatively reproduce the IPs of benzonorbornadiene and its derivatives, there is a

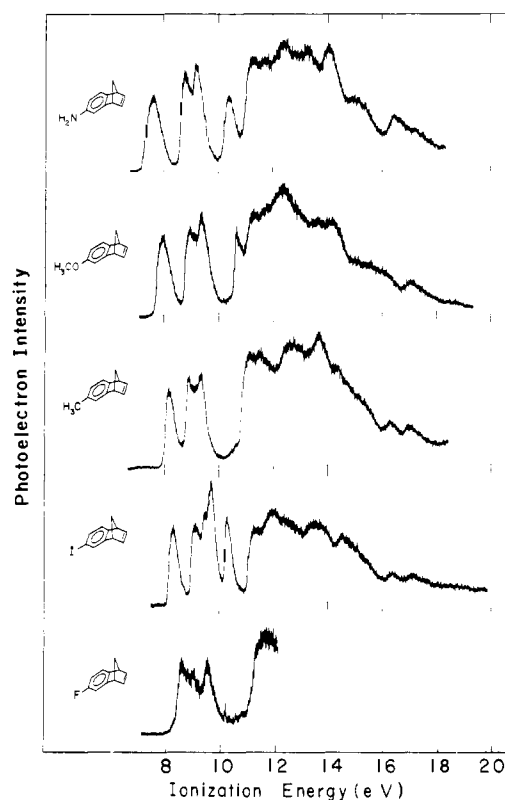


Figure 6. Photoelectron spectra of meta-donor-substituted benzonorbornadienes.

good linear correlation between negatives of calculated orbital energies and the measured IPs for the benzonorbornadienes and substituted benzenes. A least-squares treatment of these values for substituted benzenes (Figure 5) and benzonorbornadienes gives the following correlation (in eV):

$$IP(\text{exptl}) = -0.97\epsilon(\text{STO-3G}) + 1.87$$

which has a correlation coefficient (r) of 0.957. Because of this correlation, we have some confidence that the assignments given in Figures 4 and 8 are correct, as they agree with the orbital energy order obtained from STO-3G calculations.¹⁷

MOs of Ortho-Substituted Benzonorbornadienes. The STO-3G MOs of *o*-amino- and *o*-cyanobenzonorbornadienes are correlated with those of the parent molecule in Figure 9. The two highest occupied MOs and the two lowest vacant, which will be of some importance in the subsequent discussions

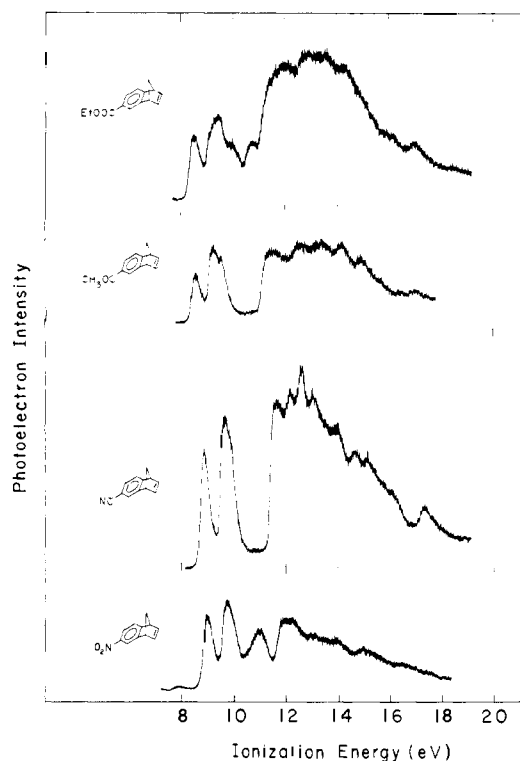


Figure 7. Photoelectron spectra of meta-acceptor-substituted benzenorbornadienes.

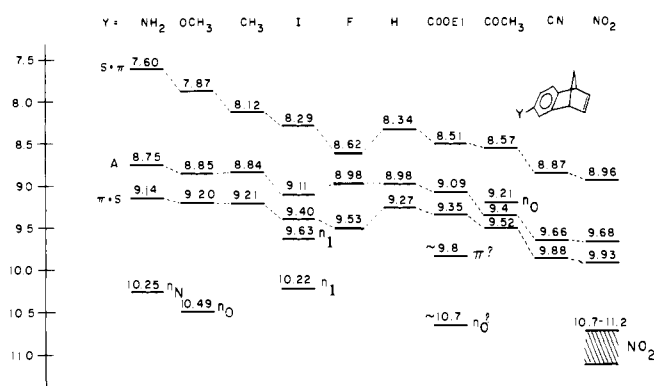


Figure 8. Ionization energies and assignments for meta-substituted benzenorbornadienes.

of the photochemistry of these species, are shown. Although the MOs retain shapes roughly like those of benzenorbornadiene, substituents cause destruction of the precise symmetry of the benzenorbornadiene MOs, and polarization of the type expected on the basis of earlier generalizations.^{3,18} Thus, the HOMO of the amino-substituted compound has a buildup of density at the positions ortho to the amino group at the expense of the meta positions. As noted previously, this arises from the mixing of the A* vacant MO into the SHOMO in a negative (antibonding) fashion at the site of substitution.^{3,18} On the other hand, the LUMO of the cyano compound is most polarized, the result of mixing in of the occupied A into the unoccupied S* orbital in a negative (antibonding) fashion.

MOs of Meta-Substituted Benzenes. Figure 10 shows two extremes of meta substitution, along with the MOs of the corresponding monosubstituted benzenes. As can be seen from a comparison of the aniline MOs to those of *m*-aminobenzenorbornadiene, the amino group dominates the local symmetry of the filled aromatic orbitals. Similarly, the cyano group has a dominant influence on the vacant MOs. The resemblances between the benzenorbornadiene MOs and those of the cor-

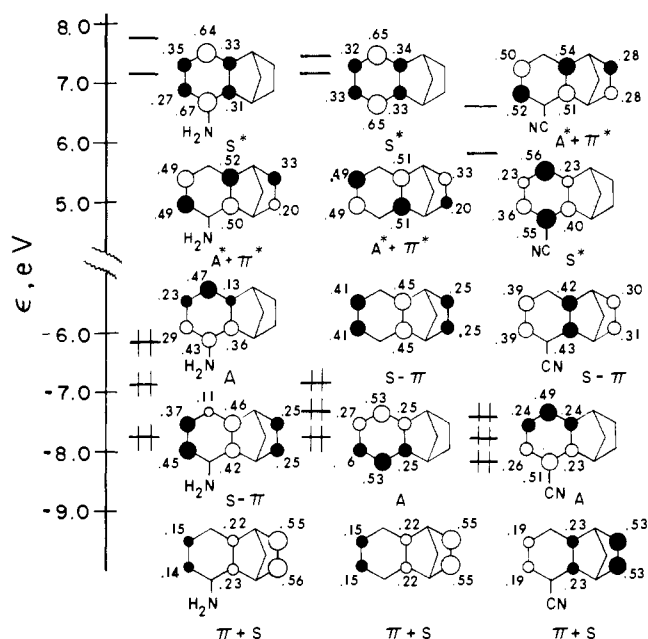


Figure 9. Molecular orbitals (STO-3G) of some ortho-substituted benzenorbornadienes.

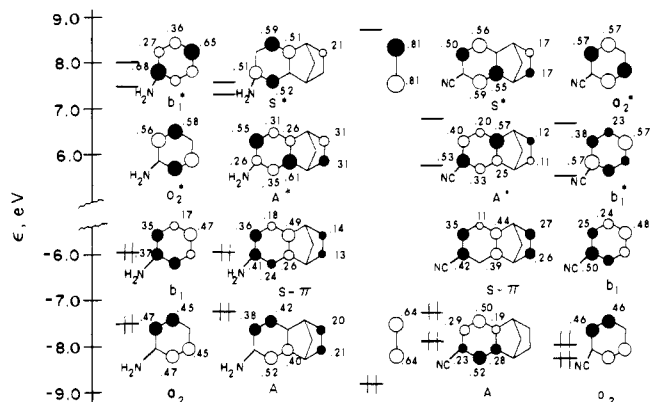


Figure 10. Molecular orbitals (STO-3G) of some meta-substituted benzenorbornadienes and the corresponding monosubstituted benzenes.

responding aromatics will be discussed first, and then the derivation of the meta-substituted benzenorbornadiene MOs from those of benzenorbornadiene will be discussed.

Both the b_1 and a_2 orbitals of aniline can mix with the ethylene π orbital; likewise, both the b_1^* and a_2^* orbitals of aniline can mix with the π^* alkene orbital. The b_1^* and a_2^* orbitals mix more extensively with each other under the influence of π^* because of the smaller energy differences between b_1^* and a_2^* and between these two orbitals and π^* . As a result, the A* and S* orbitals of *m*-aminobenzenorbornadiene, although retaining some symmetry properties of the a_2^* and b_1^* from which they were derived, respectively, are very much polarized by this extensive mixing. The b_1 and a_2 orbitals which are separated from each other and from the perturbing alkene orbital by larger energy differences do not mix much and the benzenoid portion of S - π and A come out essentially identical with the aniline b_1 and a_2 orbitals from which they were derived. Conceptually, these mixings can be thought of as occurring in two steps: (1) mixing of the individual aromatic MOs with the π and π^* MOs of ethylene; (2) mutual mixing of the aromatic MOs under the influence of the ethylene MOs. For example, the HOMO of *m*-aminobenzenorbornadiene arises from the antibonding combination of the aniline HOMO and the ethylene π orbital, polarized to a small extent by admixture of the SHOMO of aniline. This relatively small mixing results

in an increase of the coefficient at C-2, and a decrease of the ortho coefficient. The opposite occurs in the SHOMO.

The appearance of the LUMOs of aniline and *m*-aminobenzonorbornadiene are quite different. The LUMO of the latter results from a bonding admixture of both the SLUMO and LUMO of aniline with the LUMO of ethylene, or, in other words, the ethylene π^* orbital causes the SLUMO to mix into the LUMO in a positive (bonding) fashion at the major site of interaction (C-2). Conversely, π^* causes the aniline LUMO to mix in a negative way into the aniline SLUMO at C-2.

Alternatively, the *m*-aminobenzonorbornadiene MOs may be viewed as perturbed benzenorbornadiene MOs. In first order, mixing of the lone pair of the amino group with benzenorbornadiene MOs will raise all π orbitals, but will have the largest effect on these orbitals which are closest in energy to the amino lone pair and have the largest coefficient at the site of amino attachment. Thus, of the occupied orbitals, the HOMO is destabilized most, followed by the lower lying MOs which have smaller coefficients at the site of amino group attachment. The SHOMO is destabilized least, since in second order, the S - π and A orbitals of benzenorbornadiene are mixed, further raising the HOMO energy, and stabilizing the SHOMO. According to the rules of second-order perturbation theory, the donor amino group causes the S - π orbital to mix into the A orbital in a negative fashion at the site of donor substitution, and the A to mix into the S - π in a positive fashion. The effect of this perturbation is to "rotate" the nodes of the HOMO and SHOMO of benzenorbornadiene. Although computations have not been performed for less potent donors, the evolution of the benzenorbornadiene HOMO from pure S - π character in the parent to an orbital resembling the SHOMO of aniline should be a smooth "rotational" process as the meta-substituent donor ability is increased.

The shapes of the vacant *m*-aminobenzonorbornadiene MOs can be rationalized in a similar fashion. The LUMO is essentially the LUMO of benzenorbornadiene mixed, in a negative fashion at the site of amino substitution, with an equal amount of the benzenorbornadiene SLUMO. The SLUMO of the amino derivative is the corresponding positive combination.

The *m*-cyanobenzonorbornadiene MOs can be understood in a similar way. Starting from the viewpoint of uniting benzonitrile and ethylene, the LUMOs are essentially unchanged in the two molecules, because the a_2^* and b_1^* orbitals of benzenorbornadiene and the perturbing alkene orbital are far apart in energy so that the LUMOs are essentially unchanged in these two molecules. The more nearly degenerate benzonitrile HOMO and SHOMO mix more extensively under the influence of π because of the proximity of these three orbitals. The S - π and A orbitals of *m*-cyanobenzonorbornadiene, although retaining the symmetry properties of the b_1 and a_2 benzonitrile orbitals, are very much polarized by admixture of one into the other.

The orbital shapes and energies for substituted benzenorbornadienes can be summarized as shown in Figure 11. The figure is idealized and oversimplified but embodies the following generalizations: (1) Donors raise occupied orbitals to a large extent, the magnitude of this effect depending on the orbital density at the site of substitution, and barely influence the energies of vacant orbitals. (2) Acceptors lower vacant orbital energies to a large extent, but also significantly lower occupied orbital energies. For acceptors, the extent of vacant orbital lowering depends on the orbital density at the site of substitution, but for occupied orbitals, the density at the site of substitution is relatively unimportant.

The shapes of the orbitals arising from meta substitution can be qualitatively understood through the following mnemonic: (1) donors cause the frontier MO nodes to be "rotated" in a counterclockwise direction (as drawn), while (2) acceptors cause the LUMO and SLUMO nodes to be "rotated" in a

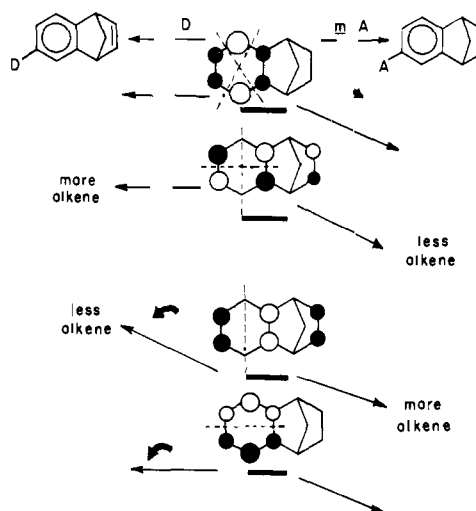


Figure 11. Generalized frontier MOs of substituted benzenorbornadienes (long arrows indicate orbital energy changes; bold arrows indicate direction of node "rotation".)

clockwise direction (as drawn). More generally, since donors cause higher lying orbitals to mix into lower in a negative fashion at the site of substitution, the node rotates toward the substituent in the lower energy orbital of each pair, and away from the substituent in the upper. The influence of the acceptor should be exactly opposite, except that the donor and acceptor nature of substituents such as cyano cancel out, leaving the HOMO and SHOMO essentially unchanged in conjugating-acceptor substituted benzenorbornadienes (cf. Figure 10). The effect discussed here is not energetically significant, involving admixture of filled orbitals with filled, and vacant with vacant. Such interactions merely "rotate" the orbitals to match the "effective symmetry" of the molecule, in the same way that substituents such as methyl cause the degenerate HOMOs of benzene to be "rotated" from arbitrary directions toward the effective b_1 symmetry of toluene.

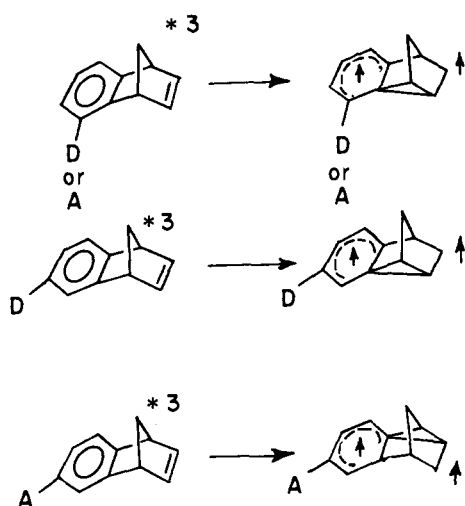
The *m*-aminobenzonorbornadiene orbitals shown in Figure 10 are extremes of "rotation", involving approximately 50:50 mixtures of the benzenorbornadiene HOMO with the SHOMO and of the LUMO with the SLUMO. These "rotations" are extreme, while weaker donors, such as methyl, will cause much smaller "rotations".

It is important in understanding the reactivities of these species to note that donors on the aromatic moiety decrease the extent of alkene contribution to the HOMO, and increase the alkene contribution to the LUMO. Acceptors have exactly the opposite influence on density of alkene π orbitals contributing to the frontier MOs.

Finally, one exception to the generalizations noted here has to do with the fluorine substituent. Calculations on *m*-fluorobenzonorbornadiene indicate that the orbital shapes follow the generalizations made here, but the orbital energies are not changed as expected for a donor, owing to the compensating electronegativity (electron-withdrawing effect) of the fluorine.

Regioselectivities in the Triplet-Sensitized Di- π -methane Rearrangement of Benzenorbornadienes. As noted in Scheme I, ortho-substituted benzenorbornadienes give di- π -methane products resulting from ortho bridging upon triplet-sensitized irradiation, while the direction of bridging with the meta-substituted compounds is different for donors and acceptors. Thus, the excited triplet states of these molecules distort in the fashion shown in Scheme II. Whether or not the diradicals shown are intermediates in these reactions is a subject which has attracted considerable attention.¹⁹ Zimmerman and co-workers have shown that similar triplet diradicals formed from

Scheme II



the sensitized irradiations of azo compounds do indeed form the di- π -methane products, establishing these species as plausible intermediates.²⁰ For ortho-substituted benzonorbornadienes, bridging occurs so as to give the more stable diradical intermediate. Thus, ortho bridging occurs to the following extents: NH₂, 82.6%; MeO, 89.3%; Me, 70%; F, 50%; COMe, >99%; CN, 96%; NO₂, >99%.²⁻⁵ However, the meta-substituted benzonorbornadienes gave mainly meta-bridged products when the substituent is a donor (NH₂, 70%; MeO, 78%; Me, 50%; F, 91%) and only para-bridged products when the substituent is an acceptor (CO₂Et, 100%; COMe, 100%; CN, 100%; NO₂, 100%).²⁻⁵ (Scheme II). While the latter mode of bridging might be rationalized in terms of the formation of the more substituted diradical intermediate, the former may not. Furthermore, the relative stabilities of potential diradical intermediates are probably not the most important factors in determining the shapes of excited state potential surfaces.²¹

Various models have been proposed to treat reactivity and regioselectivity in photochemical reactions. Although these have been applied, for the most part, to intermolecular reactions such as cycloadditions, the benzonorbornadiene di- π -methane rearrangement may be considered formally as the attack of a triplet excited benzene on an ethylene, so that these intermolecular treatments are relevant. The various methods may be roughly classified as (1) orbital interaction methods, (2) configuration interaction methods, and (3) bond-order methods. Before embarking on the discussion of benzonorbornadiene di- π -methane regioselectivity, we wish to show the similarities between, indeed identities of, these various models.

Orbital Interaction Methods. Salem,²² Devaquet and Salem,²³ Herndon and Giles,²⁴ Herndon,²⁵ and Epiotis²⁶ have used perturbation molecular orbital theory to approximate the interactions of the various singly occupied molecular orbitals of an excited molecule with the filled and vacant orbitals of a ground-state molecule. The usual approximate perturbation formulas are used,²⁷⁻²⁹ wherein the extent of interaction between two orbitals depends directly upon the square of their overlap and inversely upon their energetic separation: $\Delta\epsilon \approx S_{ij}^2/(\epsilon_i - \epsilon_j)$, where S_{ij} is the overlap integral and ϵ_i and ϵ_j are orbital energies before interaction.

The essence of such models is conveyed in Figure 12, which could, for example, represent the interaction of an excited ethylene with a ground-state ethylene. As the molecules interact, the π and π^* orbital pairs will interact, leading to a stabilized complex, or "exciplex", which may be observable experimentally. In fact, this type of theory has been used to

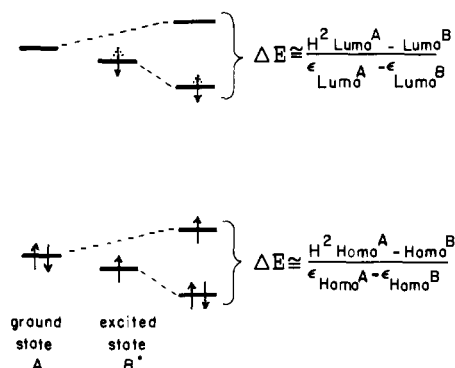


Figure 12. Orbital interaction representation of interaction of a ground state ethylene with a $\pi\pi^*$ excited state ethylene.

describe the stabilization of such species.³⁰ Using IPs and EAs instead of orbital energies, the interaction of the HOMO's (one of which is now half occupied in the excited molecule) leads to stabilization equal to $S_{ij}^2/(IP_A - IP_B)$, and the interaction of the LUMOs gives a stabilization energy of $S_{ij}^2/(EA_A - EA_B)$, where we have lazily used i and j to index the interacting orbitals.

Herndon has used ionization potentials for orbital energies and the difference between the ground- and excited-state energy, that is, the electronic transition energy, to determine vacant orbital energies.³¹ This means that the denominator of the perturbation expression for the interaction of LUMOs will be $(IP_A - \Delta E_A) - (IP_B - \Delta E_B)$, where the ΔE 's are the electronic transition energies. However, since the transition energies, $\Delta E = IP - EA - C$, where C is the electron repulsion between an electron in the HOMO and one in the LUMO of the molecule, the Koopmans' estimate of LUMO energies and Herndon's estimate lead to identical expressions, as long as the C 's for the excited states of molecules A and B are identical. This will be approximately correct if the electronic transitions on A and B are similar in character.³²

In the "orbital interaction" method, the initial orbital interactions are assumed to dictate the geometrical distortion leading to an exciplex, which ultimately falls through a "funnel" to ground-state product.³³⁻³⁵

Configuration Interaction Methods. In 1961, Fukui, Morokuma, and Yonezawa proposed a configuration interaction treatment of photochemical reactions,³⁶ and Fukui and co-workers have since elaborated upon these methods, in which the interactions between two molecules are evaluated by considering the extent of mixing of various excited and charge-transfer configurations with the ground or excited configurations of the isolated molecules.^{29,37} Epiotis generalized the qualitative use of configuration interaction methods for the understanding of photochemical phenomena,³⁸ and has dubbed this method the linear combination of fragment configurations (LCFC) method. Similar approaches have also been applied to ground and excited states of molecular complexes by Mulliken.³⁹

In CI or LCFC methods, an excited configuration, the two lowest energy charge-transfer configurations, and two excited charge-transfer configurations represent a different way of filling the available electrons into the π and π^* orbitals of the two ethylene molecules. The importance of the latter two has been proposed by Inagaki and Hirabayashi.⁴⁰

The interaction between a ground-state molecule and an excited state of a second molecule leads to electronic interactions which can be represented as a linear combination of configurations. If a one-electron operator is used, only configurations differing by the occupation of two orbitals will interact.⁴¹ Thus, the ground-state configuration (A,B) can be stabilized by mixing with charge-transfer configurations

(A⁺,B⁻) (A⁻,B⁺), while the excited configuration (A,B*) can mix with charge-transfer and excited charge-transfer configurations, but not with the ground state. The extent of interaction between configurations can be evaluated, using the fact that the extent of interaction depends only upon interaction of those orbitals which differ in occupation in two configurations.

The mixing of (A⁺,B⁻) with (A,B*) depends on the interaction between the two HOMOs. Numerically, $\Delta E = H_{ij}^2 / (E(A^+,B^-) - E(A,B^*))$, where *i* and *j* are now the HOMOs of A and B, respectively. The denominator is the difference between the energies of the two configurations, or:

$$\begin{aligned} E(A^+,B^-) - E(A,B^*) &= (IP_A - EA_B - C) - (IP_B - EA_B - C') \\ &= (IP_A - IP_B - (C - C')) \end{aligned}$$

Here *C* is a correction due to the electrostatic attraction between the A⁺ and B⁻ at the internuclear distances present in the assumed complex (frequently 4–5 eV),^{32,38,42} while *C'* is the Coulombic attraction between the hole in the HOMO and the electron added to LUMO. The latter quantity is also often 4–5 eV for $\pi\pi^*$ excited states.^{32,38} Thus, the stabilization of (A,B*) by mixing with (A⁺,B⁻) is $H(\text{HOMO}_A - \text{HOMO}_B)^2 / (IP_A - IP_B)$, the same expression obtained earlier for HOMO–HOMO interaction by the orbital interaction method. Similarly, the mixing of (A⁻,B⁺) with (A,B*) can be evaluated as approximately $H(\text{LUMO}_A - \text{LUMO}_B)^2 / (EA_A - EA_B)$, the same expression found by the orbital interaction method.

Inagaki and Hirabayashi have proposed that “excited charge-transfer” configurations (A⁻,B*⁺) and A*⁺,B⁻) also can admix significantly into the excited configuration. Admixture of A⁻,B*⁺ into A,B* is equivalent to the interaction of the HOMO of B with the LUMO of A, while a contribution of A*⁺,B⁻ to A,B* cannot occur under the influence of a one-electron operator. However, admixture of A*⁺,B⁻ into A*,B, a HOMO_A–LUMO_B interaction, can occur. The extent of these interactions depends on the HOMO–LUMO overlaps, and the symmetries between the excited configurations and the excited-charge transfer configurations.

Bond Order Methods. A third method, which has been applied primarily to the consideration of the intramolecular rearrangements, was proposed by Malrieu and others,^{43,44} and recently has been applied extensively by Muszkat.⁴⁵ Zimmerman et al. have recently proposed a similar method.⁴⁶ First, one considers the bonding in the ground-state complex to two alkenes. On a one-electron level, where the presence or absence of electrons in an orbital does not influence how the orbital interacts with a second orbital, the changes in orbital energies are exactly those calculated in Figure 12. To decide whether a reaction is favored in the excited state, one considers changes in bond order upon electronic excitation. For example, we consider here the transition from the HOMO to the LUMO of the complex. In the case under consideration, an electron is removed from an orbital which is antibonding and placed into an orbital which is bonding, leading to increased bond order, or increased bonding, in the excited state.

It is possible to show that this method, like the two discussed earlier, gives numerical results identical with those of the other two methods discussed, when similar approximations are used to evaluate energetic changes. Thus, to determine the intermolecular partial bond orders for the HOMO or LUMO, one first calculates the amount of the HOMO (ψ_i) of A mixed with the HOMO (ψ_j) of B, or of the LUMO (ψ_i^*) of A with the LUMO (ψ_j^*) of B. According to perturbation theory for nondegenerate systems, the coefficient of mixing of ψ_j into ψ_i is¹⁸ $C_{ji} = H_{ji} / (\epsilon_j - \epsilon_i)$. Since the energy associated with a

particular bond order is $p_{ji}H_{ji}$, the net contribution to the energy due to this bond order is $-H_{ji} / (\epsilon_j - \epsilon_i) \times H_{ji}$, or $H_{ji}^2 / (\epsilon_j - \epsilon_i)$. Using Koopmans' theorem, $\Delta E = -H_{ji}^2 / (IP_j - IP_i)$. The change in energy due to the change in bond order is, therefore, numerically identical with that evaluated by the other methods.

Other Methods. For systems which can undergo several different di- π -methane rearrangements, Zimmerman suggested that bridging would occur in a fashion which minimized the excited-state energy.¹⁹ For example, to decide whether a triplet excited benzene would bridge with a second benzene ring or with an ethylene, the triplet energies of biphenyl and styrene were used to estimate which “transition state” would be at lower energy. This method is similar in spirit to the others discussed here, but uses an entirely different method of evaluation.

The result of this brief review of qualitative methods for considering organic photoreactivity is simple: the orbital interaction, configuration interaction (LCFC), and bond-order methods are identical when numerically evaluated using the same approximations. Although the methods differ only semantically, there are certain conceptual advantages of each method in considering certain types of phenomena.

Finally, having shown the relationships between various qualitative models of organic photoreactivity, we turn to consideration of benzonorbornadiene di- π -methane regioselectivity and the relationships to ionization potentials.

Ortho-Substituted Benzonorbornadienes. An understanding of these regioselectivities requires an understanding of the MO nature of the triplet states of substituted benzenes. In benzene itself and monosubstituted benzenes with *C*_{2v} symmetry, the lowest triplet state is composed of equal amounts of a configuration with the b₁ and b₁* orbitals singly occupied, and a configuration with a₂ and a₂* each singly occupied. In benzonorbornadiene, since the (S - π) \rightarrow (A* + π^*) configuration will be considerably lower in energy than the A \rightarrow S* (which correspond to the a₂ \rightarrow a₂* and b₁ \rightarrow b₁* of benzene, respectively), the lowest triplet will be composed of more of the (A)² (S - π)¹ (A* + π^*)¹ (S*)⁰ configuration than of the (A)¹ (S - π)² (A* + π^*)⁰ (S*)¹ configuration. In the substituted benzonorbornadienes, the ratio of contributions of these configurations to the triplet state will depend upon the relative energies of these two configurations.

As can be seen in Figure 9, the S - π \rightarrow A* + π^* and A \rightarrow S* configurations do not differ greatly in energy. The former is somewhat lower in energy, and should contribute more to the lowest triplet state in acceptor-substituted cases and less than the latter in donor-substituted cases. For the ortho-acceptor substituted cases, only the S* orbital is significantly polarized, and it is this orbital which dictates bridging regioselectivity. As the bridging begins to occur through the stabilizing interaction between C-2 (the ortho position) of the S* orbital and C-6 of the alkene π^* orbital, the difference in C-2 (ortho) and C-3 (meta) coefficients is further magnified. That is, the π^* orbital causes the A* + π^* orbital to mix into the S* in a bonding fashion at the site of greatest interaction with the π^* orbital, that is, at C-2.

For the ortho-donor substituted cases, the A HOMO is the only orbital which is substantially polarized. The lowest triplet will be lowered in energy when the partially half-occupied A HOMO interaction with the ethylene π orbital is maximized. Bonding at C-2 (ortho bridging) occurs. Once again, this will become even more important as geometrical distortion begins to occur, because the π orbital will cause the A orbital to mix into the S - π in a bonding fashion at the point of maximum interaction with the π orbital, i.e., at C-2. Ortho bridging is favored once again. Since the polarization of the HOMO or LUMO will increase as the IP of the donor-substituted molecule decreases, or as the EA of the acceptor-substituted mol-

ecule increases (which is qualitatively related to the increase in IP),⁴⁶ the regioselectivity should increase as the first IP is either increased or decreased relative to benzonorbornadiene.

Furthermore, there is a second factor influencing regioselectivity which is difficult to treat quantitatively, but is even more directly related to the IPs of benzonorbornadienes. Since it is the A orbital of ortho-donor-substituted benzonorbornadienes which is polarized and consequently causes ortho-bridging regioselectivity, the more this orbital is involved in the excited triplet state, the greater the regioselectivity should be for donor-substituted molecules. Since donor substituents raise A more than S*, and have essentially no effect on S - π and A* + π^* , the decrease in IP of the A orbital should parallel the increase in ortho-bridging regioselectivity. With ortho-acceptor groups, the lowering of the S* orbital, which occurs faster than the lowering of the A orbital as acceptor strength is increased, should lead to greater contribution of the A \rightarrow S* configuration to the lowest triplet state, and increased regioselectivity. Thus, an increase in the second IP for ortho-acceptor substituted benzonorbornadienes should lead to increased regioselectivity.

Finally, the charge-transfer contribution to the excited state, represented by Epiotis as a result of admixture of A,B with A*,B and A⁺,B⁻ and A⁻,B⁺, or by Inagaki as A**⁺,B⁻ and A⁻,B**⁺ with A*,B and A,B*, also reinforces the ortho bridging. That is, for a donor-substituted molecule, contribution of Ar**⁺,A⁻ (where Ar is the aromatic moiety and A the alkene moiety) will enhance the ortho bond order in the excited state due to the polarization of the Ar HOMO (ortho > meta), while the configuration, Ar**⁻,A⁺, of probable importance for an excited acceptor substituted molecule, will also favor ortho substitution. Once again, these effects will increase as the IP of donor-substituted molecules decreases, or as the EA of acceptor-substituted molecules increases. That this effect is significant is indicated by the *o*-fluoro case, for which STO-3G calculations indicate polarization similar to the *o*-amino case, but the fluorine does not significantly influence orbital energies.

The facts, summarized earlier, are in qualitative accord with these arguments, except that *o*-aminobenzonorbornadiene undergoes reaction somewhat less selectively than might be expected on this basis.

Meta-Substituted Benzonorbornadienes. These cases are considerably more complicated than the ortho-substituted cases because all of the relevant MOs are polarized to some extent. For the acceptor-substituted cases, the lowest energy configuration will be mainly (S - π) \rightarrow (A* + π^*) in character. Both of these orbitals are polarized such as to favor para bridging, although the LUMO is clearly polarized more, and, like the ortho-acceptor case, dominates regioselectivity. An increase in EA, reflected qualitatively by an increase in IP, should be followed by an increase in regioselectivity.

For the meta-donor-substituted case, the (S - π) \rightarrow A* + π (each rotated) configuration is much lower than the opposite configuration. S - π weakly favors para bridging, but the A* orbital more strongly favors meta bridging. Although the net effect is a preference for meta bridging, the conflicting effect of the HOMO and LUMO indicates that these systems should experience the lowest regioselectivity. This is the case. In fact, the interaction of the donor aromatic HOMO with the alkene HOMO favors the para adduct, and it is possible that the decrease in regioselectivity observed with the amino compound signals a significant contribution of this type.

A more definite treatment of the regioselectivities must await both experimental studies of molecules with donors on the aromatic and acceptors on the alkene moiety, and vice versa, as well as more precise descriptions of the excited states of molecules of this complexity.

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References and Notes

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