THEORY OF CYCLOADDITIONS OF EXCITED AROMATICS TO ALKENES

K.N. Houk

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260, USA

Abstract: A qualitative molecular orbital rationalization of the
selectivities in ortho, meta, and para cycloadditions of singlet
excited states of substituted benzenes to alkenes, and of triplet
state di-π-methane rearrangements of substituted benzonorbornadienes
is presented.

As the name suggests, excited states of benzene and substituted benzenes are
prone to aroused reactivity tendencies, rearranging to high energy isomers,
or combining with a variety of reagents toward which they are inert in the
ground states.[1,2] This generalization is particularly clearly manifested in
the photoreactions of aromatic molecules with alkenes.[1-4] In a cycloaddition
between benzene and ethylene, the two ethylene carbons may become united to
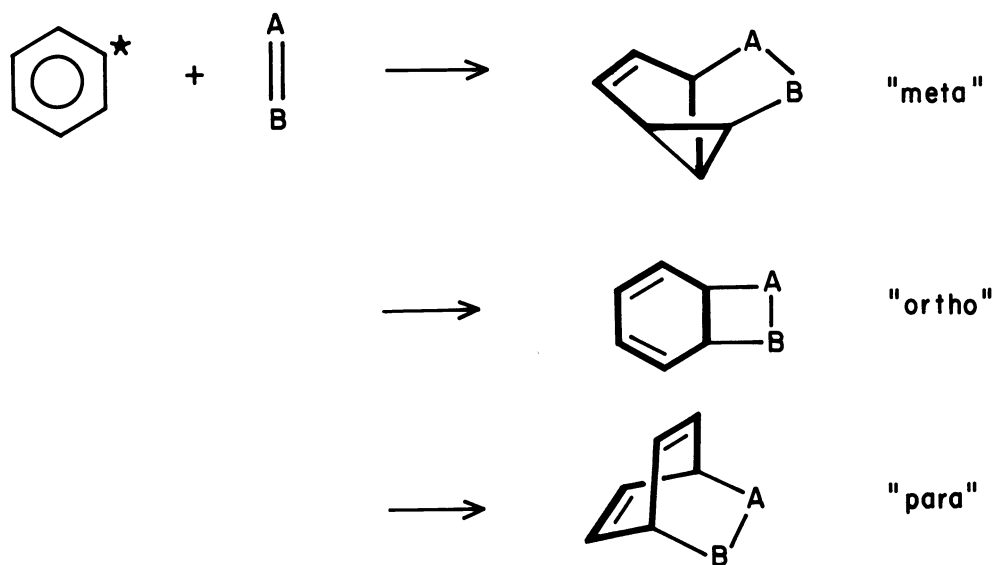two carbons of benzene disposed ortho, meta, or para to each other, as shown
in Fig. 1.

Fig. 1. The possible benzene-ethylene cycloaddition modes.

The ortho cycloaddition was first observed by Angus and Bryce-Smith,[5] and is
the common photoreaction of substituted benzenes with electron-deficient
alkenes such as maleic anhydride or acrylonitrile.[1-4] The para cycloaddition
occurs to a lesser extent with reactants of this type. Although discovered
later,[6] the meta cycloaddition is now known to be the usual outcome of
irradiation of substituted benzenes with alkylethylenes.[1-4] Bryce-Smith and
coworkers have found that the meta cycloaddition is particularly favored

when the difference between the ionization potentials of the arene and alkene is small.[1-4] This reaction is also highly regioselective in cases where substituted benzenes combine with alkenes, so much so that the intramolecular version of this reaction, discovered by Morrison and Ferree,[7] has been used to spectacular advantage by Wender for the synthesis of α-cedrene and isocomene,[8] outlined in Fig. 2.
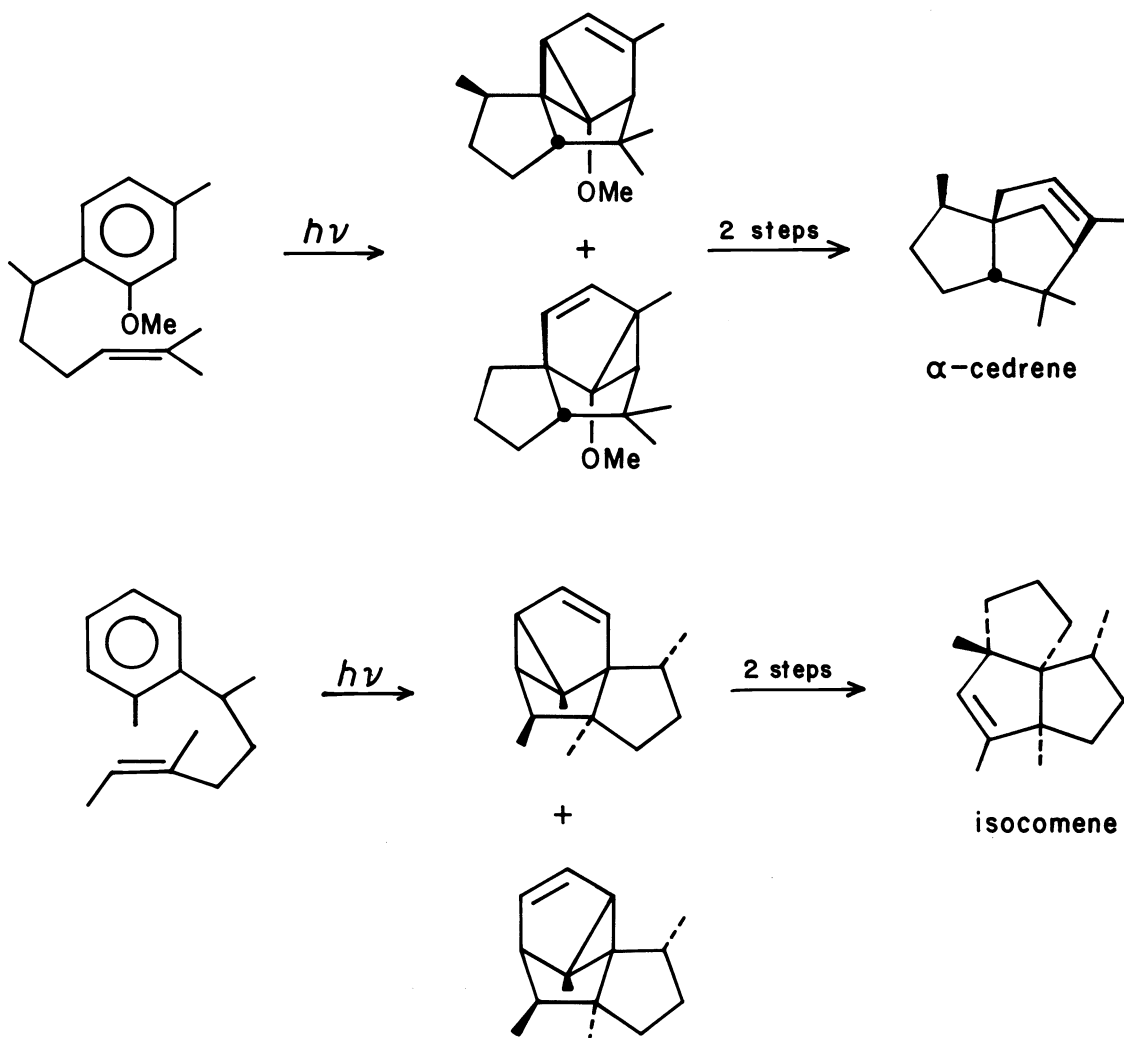

Fig. 2.   The Wender syntheses of α-cedrene and
isocomene using intramolecular arene-alkene cycloadditions.

The examples given in Fig. 2 demonstrate a second phenomenon commonly observed in <u>meta</u>-photocycloadditions, namely that the reaction is regioselective, generally occuring by bonding of the alkene to the two atoms <u>ortho</u> to the most potent donor on the benzene ring.[2-4]

These cycloadditions generally involve the singlet excited states of aromatics.   Triplet states of aromatics are usually quenched by energy transfer to alkenes.   However, when the aromatic and the alkene are held in rigid proximity in a molecule such as benzonorbornadiene, interactions between these moieties can occur and lead to deep-seated rearrangements. For example, Fig. 3 shows the remarkable selectivities observed in triplet-

sensitized rearrangements of substituted benzonorbornadienes. Paquette and coworkers have synthesized a variety of unsymmetrically substituted benzonorbornadienes, and have detected patterns of selectivity summarized in Fig. 3.[9-12]
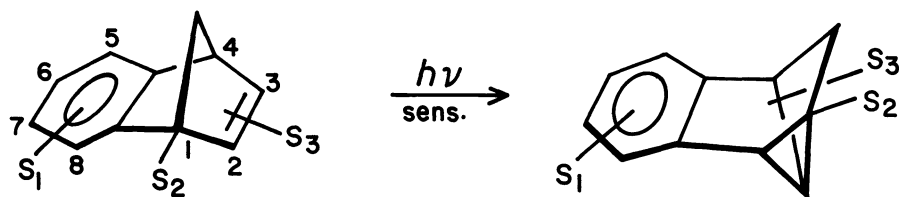

bridging is favored:

    ortho to 8-donor
    ortho to 8-acceptor
    meta to 7-donor
    para to 7-acceptor
    adjacent to 1-substituent (except D)
    β to 2-substituent

Fig. 3. Selectivities observed in triplet
di-π-methane rearrangements.

What are the electronic origins of the selectivities observed in both singlet and triplet excited state reactions of aromatics with alkenes? Bryce-Smith, Longuet-Higgins, and Gilbert have considered the orbital symmetry aspects of singlet photocycloadditions,[1-4,13] and we have described the relationships between excited state orbital electron distributions in triplet aromatics and regioselectivities in di- -methane rearrangements of the benzonorbornadienes studied experimentally by Paquette and coworkers.[10,11,14] Here, I will describe the molecular orbitals and configurations of the excited singlet and triplet states of substituted benzenes, and will attempt to establish a comprehensive, if necessarily qualitative, description of the origin of the various selectivities described earlier. The qualitative ideas described here represent the planning for a computational study of the reactions which we have now begun. We must express a considerable debt to Professors Bryce-Smith and Gilbert for providing an elegant orbital symmetry analysis of the singlet photocycloaddition problem, and for the many experimental investigations which provide grist for the theoretical rationalization mill!

The excited states of benzene cannot be described in terms of a single electronic configuration, due to the degeneracy of the HOMOs and of the LUMOs.[15] These orbitals are represented in Fig. 4 in a form which is suitable for discussion of both benzene and monosubstituted benzenes. The orbitals are labeled according to their symmetries with respect to a plane perpendicular to the benzene ring and passing through the position of attachment of a substituent (the bottom carbon).
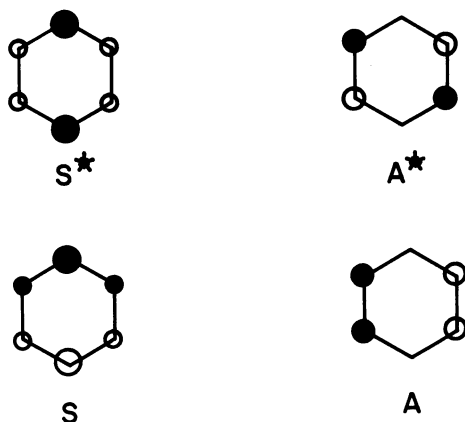
One electron configurations: SS^*, AA^*
                            SA^*, AS^*

States: B_{2u} $(SA^* - AS^*)$ lowest excited singlet state
          B_{1u} $(SS^* + AA^*)$ lowest triplet state
          E_{1u} $(SS^* - AA^*; SA^* + AS^*)$ degenerate states

Fig. 4.   Frontier molecular orbitals, excited configurations,
          and excited states of benzene.

As described in detail by Salem,[15] the four possible degenerate one-electron
transitions couple to form four states, which are represented at the bottom
of Fig. 4.

The lowest excited singlet state of benzene is $^1B_{2u}$, which is observed
experimentally at 4.71eV above the ground state (λ_{max} = 254nm). This state
is lowest in energy because the electron repulsion in this singlet is less
than that in any of the other three singlet states.[15] By contrast, the
lowest triplet state has B_{1u} symmetry, and has an energy 3.59eV above the
ground state. As a simple mnemonic, it is useful to remember that the
lowest singlet state is the negative combination of transitions involving
orbitals of opposite symmetry ($A \rightarrow S^*$ and $S \rightarrow A^*$), while the lowest triplet
involves a positive combination of transitions between orbitals of the same
symmetry ($S \rightarrow S^*$ and $A \rightarrow A^*$).

Monosubstitution of benzene or interaction of benzene with a second molecule
removes the degeneracy of the HOMOs and of the LUMOs, so that the excited
states will no longer consist of an equal mixture of two configurations.
This simplifies the description of the excited states of substituted
benzenes, but before considering the consequences of this simplification, it
is useful to consider first the molecular orbital treatments of excited
state reactions, and the formaolism that will be used here.

Among the various models used for photochemical reactivity, the frontier
molecular orbital method of Fukui is perhaps the moft revealing, and
Herndon[16] and Epiotis[17] have pioneered in the application of these ideas to
the understanding of regioselectivity in photochemical reactions. We have
shown earlier how frontier orbital interaction, configuration interaction,
and bond order models are essentially equivalent treatments of photochemical

reactivity.[10] As described by many authors,[18] photochemical pericyclic reactions involve interactions of an excited state of one molecule with the ground-state of a second. The general approach is shown in Fig. 5 for the [2+2] dimerization of ethylene.
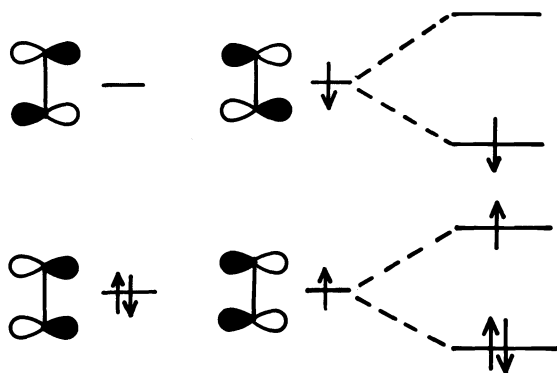

Fig. 5. Interaction scheme for reaction of
excited ethylene with ground-state ethylene.

The interactions of singly occupied orbitals of the excited state molecule with either doubly occupied or vacant orbitals of the ground-state molecule stabilize the complex. In the case of a singlet excited state, this stabilized complex will have a geometry and energy close to that of the transition state for the corresponding thermal reaction, particularly if this is a ground-state orbital symmetry forbidden process. Rapid internal conversion will deposit the "excited complex" on the ground-state surface. This is shown schematically in Fig. 6. Here the arrows indicate how the excited-state, ground-state complex relaxes to an energy minimum due to orbital interactions of the type shown in Fig. 5. The so-called excited state minimum has an extremely short lifetime in such a reaction, rapidly undergoing internal conversion to form the distorted ground-state, which subsequently relaxes to products.[18]
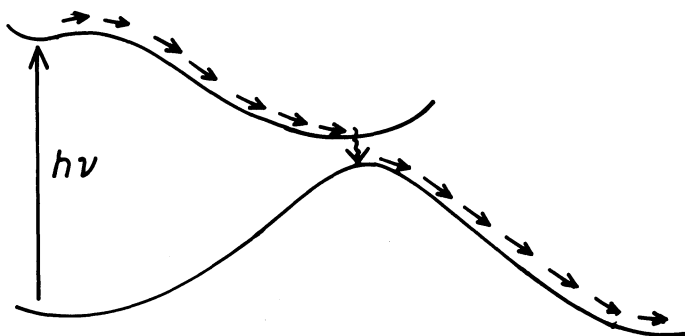

Fig. 6. Schematic representation of a photochemical cycloaddition.

In the case of a triplet state, a similar process will occur, although a "pericyclic" geometry is less likely for the triplet complex, and intersystem crossing seems to occur more generally in biradical geometries. In the frontier orbital method, the initial distortions which lead to the "funnel"[18] in which the formal internal conversion occurs from a singlet excited state, can be predicted by maximizing interactions between singly

occupied excited state orbitals and doubly occupied or vacant orbitals with
similar energies in the ground-state molecule.

The interaction of an excited aromatic with an alkene is somewhat more
complicated, since the aromatic excited state, whether singlet or triplet,
cannot be represented by a single configuration. It is useful first to
consider independently how each of the benzene HOMOs and LUMOs, if singly
occupied, would best interact with the ethylene HOMO and LUMO. Fig. 7 shows
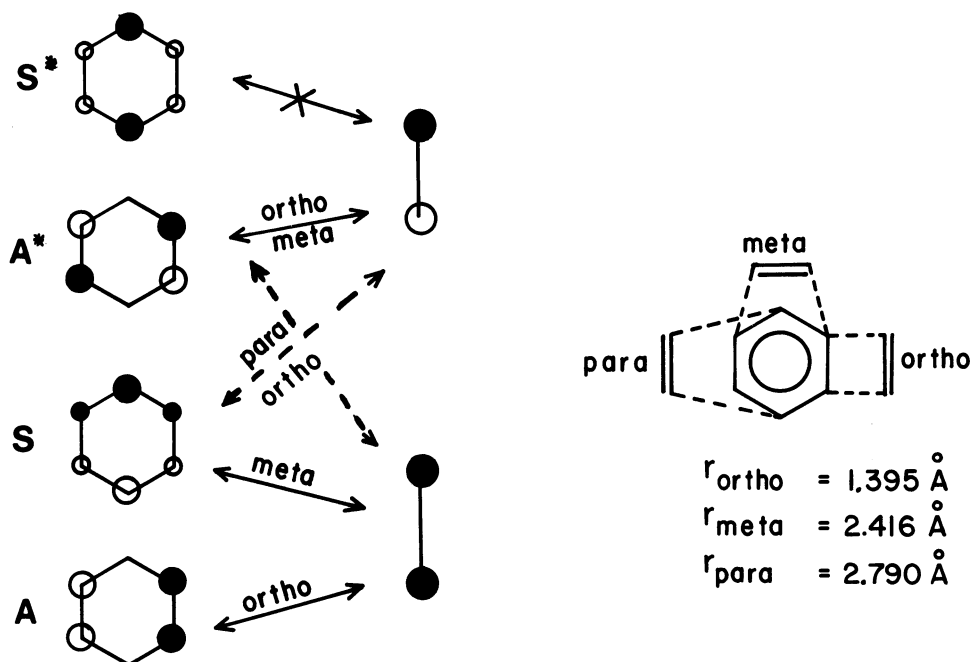this diagramatically.

Fig. 7. The benzene-ethylene orbital interactions
hich lead to excited singlet state stabilization.

In the ortho approach of ethylene to benzene, stabilization may be achieved
either by interaction of the benzene A orbital with the ethylene π HOMO, or
of the benzene A^* orbital with the ethylene π^* LUMO. Although generally of
lesser significance, the ethylene HOMO might interact with S^* and the
ethylene LUMO with S. For meta approach in the sense shown, the ethylene
HOMO interacts with S and the ethylene LUMO interacts with A^*. The other
two possible interactions are much weaker. Finally, in the para approach,
the ethylene HOMO interacts with no filled orbitals, only with S^*, while the
ethylene LUMO can interact only with S. The consequently extremely weak
excited state interaction is directly connected to the fact that such a
reaction is thermally allowed and photochemically forbidden, whereas the
other reactions are of the [6+2] (or[2+2]) variety, and have stabilizing
frontier orbital interactions in the excited state.

For benzene itself, the excited state might be considered to have each of
these four benzene frontier orbitals one-quarter occupied. Both ortho and
meta attacks experience favorable SOMO (singly occupied MO)-HOMO and SOMO-
LUMO interactions. In fact, benzene and ethylene give nearly equal amounts
of ortho and meta photocycloadditions in the singlet state. However, as

first pointed out by Bryce-Smith,[13] the particular combination of configurations that make up the lowest singlet excited state of benzene are such that it is not possible for the four frontier orbitals of benzene to interact randomly with those of ethylene. Instead, we must think of the interaction of the S→A* configuration, which stabilizes the meta complex more than the ortho, and of the A→S* configuration, which stabilizes the ortho complex only, separately. Evidently, for ethylene, the net result of the interaction of these two configurations with ethylene is that both complexes are equally stabilized.

On the right of Fig. 7, the distances between the benzene carbons undergoing cycloadditions in the various modes are shown. Clearly, the ortho cycloaddition is favored by overlap considerations alone, since the alignment of p orbitals on the aromatic carbons will be more nearly ideal with the ethylene p orbitals for the ortho cycloaddition. This is expected to be true even when the benzene ring is somewhat expanded, as it is expected to be in the excited singlet state.

The relevant orbital interactions are considered in more detail in Fig. 8. This diagram shows how the energies of benzene orbitals in the ground-state are influenced by the approach of an ethylene in the ortho, meta, or para fashion.
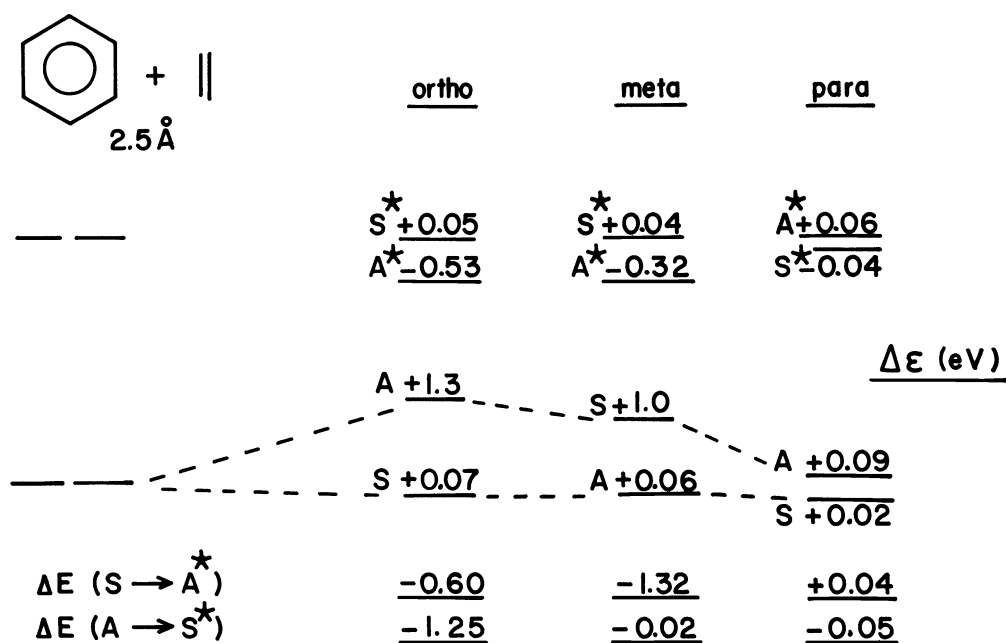

Fig. 8. STO-3G ground-state orbital energy changes
upon complexation of ethylene with ground-state benzene.

The calculations were performed with the STO-3G basis set by fixing ground-state ethylene and benzene in the appropriate parallel planes arrangement at a distance of 2.5Å. The interactions described in Fig. 7 are more clearly revealed here, and the greater changes in the frontier orbitals upon ortho

approach are manifestations of the greater orbital overlap in the _ortho_ approach as compared to the _meta_. At the bottom of Fig. 8, the total change in energies of the two configurations contributing to the excited singlet state of benzene (assuming only one-electron changes) are given. For the _ortho_ approach, the $A \rightarrow S^*$ configuration is highly stabilized due to the strong mixing of A with the lower-lying ethylene HOMO. As the complex forms, the excited state of the complex will shift to become more heavily concentrated in this configuration, and the relative importance of the $S \rightarrow A^*$ configuration will diminish. This is somewhat different from the conclusions of Bryce-Smith[13], who described this reaction as orbital symmetry forbidden. Since we are only looking at the interactions early along the reaction path, the eventual correlation of the benzene S orbital with the product ψ^3 orbital of the butadiene system in the product is overlooked. For the _meta_ approach, the $S \rightarrow A^*$ configuration is highly stabilized, and the complex is expected to consist mainly of this configuration. Even though overlap for a particular pair of orbitals is less than for the _ortho_ approach, the raising of the S orbital and lowering of the A^* orbital causes more net stabilization than for the _ortho_ approach. The raising of S and the simultaneous lowering of A^* in the _meta_ complex is equivalent to Bryce-Smith's observation that the _meta_ cycloaddition is allowed.[13] While we would not necessarily have predicted a 1:1 mixture of adducts on this basis, it is amusing that the predicted stabilization of the _ortho_ and the _meta_ complexes is essentially identical! Clearly both the _ortho_ and _meta_ excited complexes will be highly stabilized, and so the formation of both adducts is nicely rationalized.

Bryce-Smith and Gilbert have made the famous generalization that alkenes with ionization potentials nearly the same (±0.4eV) of that of benzene undergo _meta_ cycloadditions, whereas electron-deficient or electron-rich alkenes give primarily _ortho_, and some _para_, cycloadducts.[1-4] They deduced that _ortho_ and _para_ cycloadditions occur from polar (charge-transfer) complexes.

How does the alteration of the ionization potential of the alkene influence the product ratio? In Fig. 9, the orbital energies, from ground-state ionization potentials[19] and electron affinities[20], are shown for benzene, acrylonitrile, ethylene, _cis_-2-butene, and tetramethylethylene. These four alkenes give all _ortho_, 1:1 _ortho_:_meta_, all _meta_, and 1:8 _ortho_:_meta_ adducts, respectively.

In the case just discussed, that involving benzene and ethylene, the separation between the S or A of benzene and π of ethylene (1.28eV) is about twice as large as the separation between S^* or A^* of benzene and π^* of ethylene (0.63eV). This implies that the interaction of A^* with π^* is the more important interaction leading to stabilization of the _ortho_ and _meta_ complexes with ethylene, as can also be deduced from the diagram in Fig. 8.

+2.22

+2.27

+1.78

+1.15

+0.21

-8.34

-9.24   -9.13
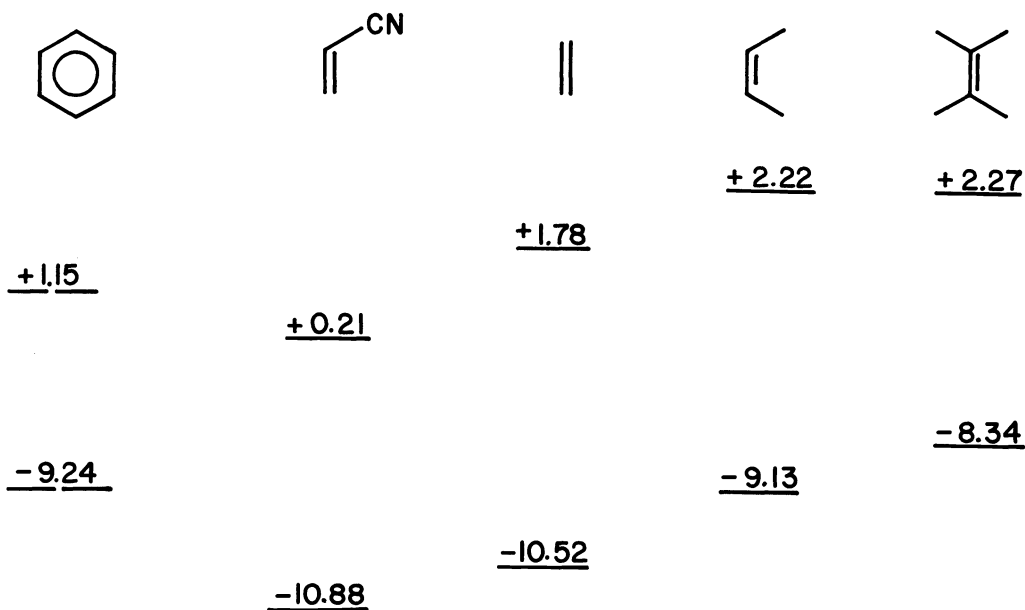
-10.52

-10.88

Fig. 9. The frontier orbital energies of benzene and representative alkenes.

The frontier MO's of an electron-deficient alkene are stabilized with respect to those of ethylene. This diminishes the interaction of S or A with π, but since π^* is now appreciably below S^* and A^* in energy, considerable stabilization of a complex occurs primarily by charge transfer, as shown in Fig. 10.
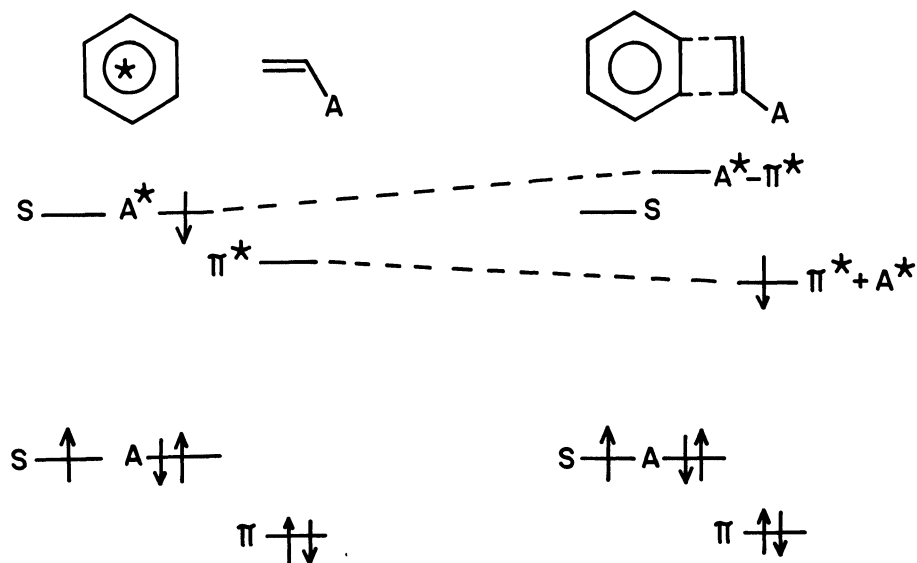

Fig. 10. Orbital energies for excited benzene,
an electron-deficient alkene, and the ortho complex.

On the left are shown a single configuration of the singlet state of benzene, and the ground-state of an electron-deficient alkene (A=acceptor). At the right are shown the orbitals and occupations for the ortho complex. The electron is now in the lower energy orbital which is the bonding combination of π^* and A^* for the ortho or meta complexes. An electron has been partially transferred from A^* to π^* during the mixing process. Exactly

the same diagram could be drawn for the <u>meta</u> complexation, but the preference for <u>ortho</u> cycloaddition can be attributed to the better overlap of π^* with A^* in the <u>ortho</u> complex. Additional stabilization of the <u>ortho</u> complex can occur by interaction of S with π^*.

When the ionization potential of the alkene is decreased by alkyl substitution, a situation analogous to that shown for benzene and ethylene in Fig. 8 occurs. The S or A interaction with π is maximized here due to the near degeneracy of these orbitals. The A^* interaction with π^* is also large. As described earlier, such a situation leads to <u>meta</u> cycloaddition because the $S \rightarrow A^*$ configuration is highly stabilized upon interaction with the alkene in the <u>meta</u> complex. The controlling factor here appears to be the fact that both orbitals belonging to a single configuration can simultaneously interact with the alkene in the <u>meta</u> complex.

For an alkene with IP less than that of benzene, such as tetramethylene, charge-transfer from the alkene to the aromatic will occur in the following way. As shown in Fig. 11, the interaction of one of the aromatic HOMOs with the tetramethylene HOMO will result in great stabilization due to the usual orbital mixing and because one electron is transferred from π to the lower energy $A + \pi$ orbital. The $S^* - \pi$ interaction also adds stabilization. The <u>ortho</u> cycloadduct is favored because the overlap of A with π in the <u>ortho</u> fashion is greater than that of S with π in the <u>meta</u> fashion.
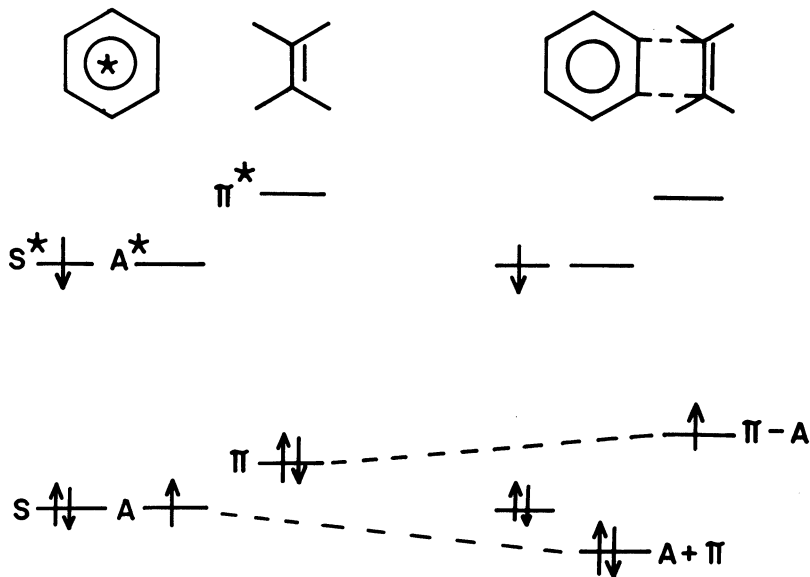

Fig. 11. Benzene singlet orbital interactions with tetramethylethylene.

To summarize, the <u>ortho</u> adduct is favored when the alkene is either a better donor or a better acceptor than benzene. This is of course simply the Bryce-Smith generalization, derived in a slightly different way. This argument can be extended to substituted benzenes, as well. In such cases, a single orbital interaction can be identified as the controlling frontier orbital interaction. For electron-deficient alkenes, the alkene-LUMO, aromatic-LUMO interaction dictates the preferred product, while for electron-rich alkenes, the alkene-HOMO, aromatic-HOMO interaction is controlling. When the SOMO-HOMO and SOMO-LUMO interactions are both important, as for benzene, <u>cis</u>-2-

butene, the favored cycloaddition is that which can benefit from simultaneous interactions of both types, with both benzene SOMO's belonging to a single cofiguration contributing to the benzene singlet excited state.

The relevant orbital interactions which produce the selectivity observed for various types of alkenes are shown in Fig. 12.
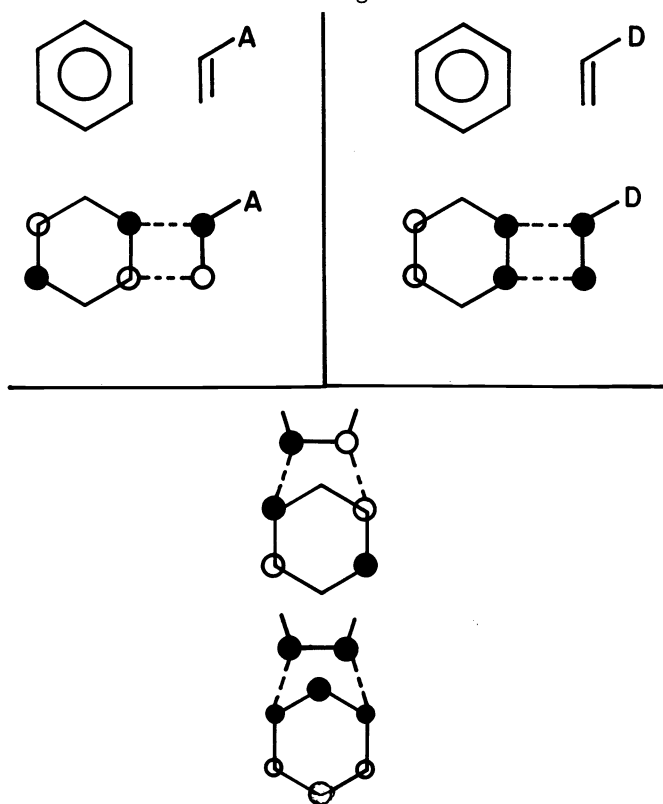
Fig. 12. Orbital interactions which control cycloaddition periselectivity.

This variation in selectivity can also be viewed in terms of the relative energies of excited and charge-transfer states for a series of alkenes.

	$^1B_{2u}$	+ •	− + •	o/m
	0	+6.3	+7.0	1:1
	0	+6.5	+6.2	0:only
	0	+6.8	+4.8	8:1
CN	0	+5.0	+7.4	only:0

The chart shown above indicates the relative energies (in eV) of $^1B_{2u}$ benzene plus ground-state ethylene, and the various electron-transferred

states. The latter energies are for radical ions at infinite separation, whereas the Coulombic attraction would make these electron-transfer complexes $\sim$5eV more stable if they were separated by only 2-3Å. For benzene plus ethylene or cis-2-butene, the electron-transfer states are sufficiently high in energy so that they would be expected to mix with the excited state and provide stabilization, but not be formed exothermically. For acrylonitrile and tetramethylene, the electron-transfer states are low enough in energy to be essentially identical in energy to $^1B_{2u}$ benzene plus the alkene. In these cases, significant electron-transfer is expected to be involved in the complex. In fact, these electron-transfer configurations may become the most important contributor to the electronic structure of the complex.

We can use these conclusions to discuss the regioselectivities and stereoselectivities observed in cycloadditions of substituted benzenes. For meta cycloadditions, one well-known generalization is that donor substituents on the benzene cause the ethylene to bond at the 2 and 6 positions of the benzene ring.[1-4] This is usually attributed to the formation of an exciplex, as shown in Fig. 13.[21]
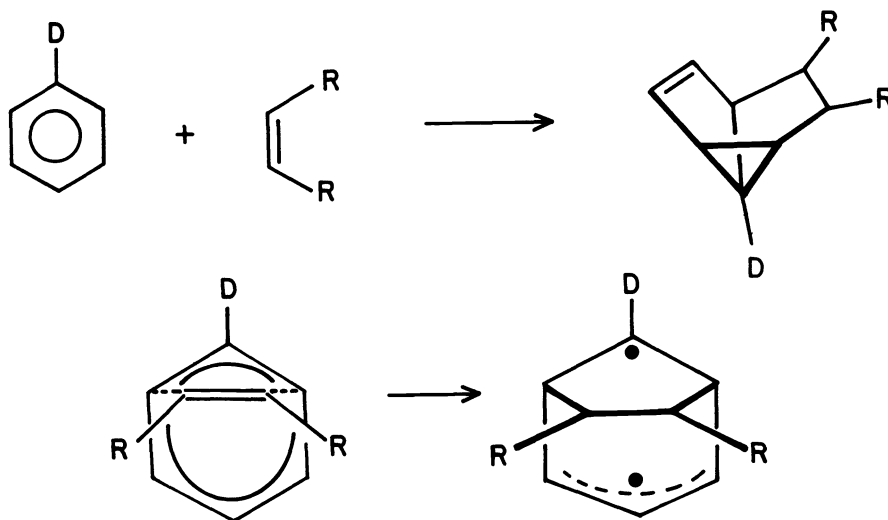

Fig. 13. Regioselectivity of donor-substituted benzene cyloadditions to alkenes.

This is easily rationalized on the basis of the polarization of the benzene orbitals induced by a donor substituent. As we have described before,[14] a donor causes the changes in orbital energies and shapes shown in Fig. 14. The HOMO is derived from S, and is increased in energy. The ortho and para coefficients are increased in magnitude at the expense of the ipso and meta coefficients. The other orbital involved in interaction with the alkene orbital, A*, is essentially unchanged. The regioselectivities can be attributed to the increased size of the ortho coefficients relative to the meta in the S orbital. Thus, the complex leading to 2,6-bonding is more stable than that leading to 3,5-bonding.
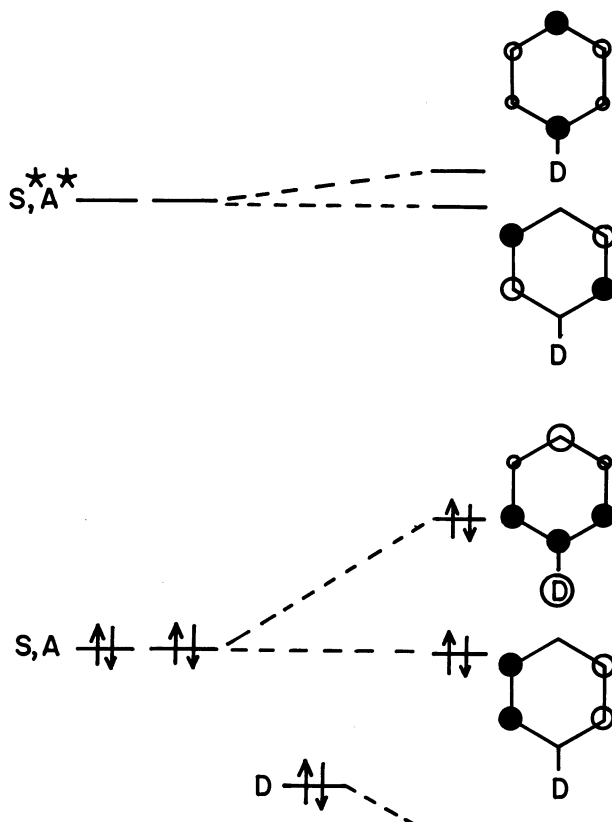
Fig. 14. The orbitals of a donor-substituted benzene.

The <u>endo</u>-stereoselectivity observed in many <u>meta</u> cycloadditions of <u>cis</u>-alkenes[3,4,21,22] can also be rationalized on the basis of the interaction of S and A[*] with π and π^*. Fig. 15 shows the relevant orbitals of benzene and <u>cis</u>-2-butene. Secondary orbital interactions stabilize the <u>endo</u> complex and destabilize the <u>exo</u> complex.
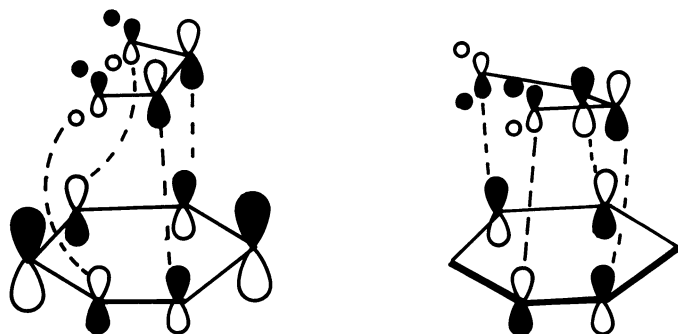

Fig. 15. Secondary orbital interactions which stabilize the <u>endo</u> complexes.

Turning to the <u>ortho</u> cycloadditions, relatively low regioselectivity is observed. For a highly donor-substituted benzene, the donor-substituent, rather than the approaching ethylene, will determine the symmetry of the orbitals. The 1,2- and 3,4-selectivity[3] is apparently dominated by the

interactions of S with the alkene π, since the $A^*-\pi^*$ interaction would result in 2,3-selectivity.

In many cases, the ortho-cycloadditions are accompanied by exo selectivity. This can also be attributed to secondary orbital interactions between the alkene substituents and the secondary positions of the benzene, which are antibonding.

We have provided qualitative rationales of the various selectivities observed in singlet cycloadditions, and a model which we hope will provide general predictive value. I should also reiterate the similarities and differences between this model and an earlier one due to Bryce-Smith[13]. He analyzed these cycloadditions in orbital symmetry terms. To summmarize his conclusions, the ortho and para cycloadditions are forbidden as concerted processes from $^1B_{2u}$ benzene and ground-state ethylene, while the meta cycloaddition is allowed either as a concerted process, or with the "prefulvene" diradical as intermediate. All three of these processes become symmetry allowed if they involve charge-transfer from excited benzene to ethylene, or vice versa. Both substituent and solvents are consistent with the nonpolar nature of the meta cycloaddition and polar, charge-transfer, nature of the ortho and meta cycloadditions. Our model differs from this primarily in our concentration on the strength of various orbital interactions at an early stage in the interaction. These are, of course, directly related to the orbital correlations deduced by Bryce-Smith from symmetry considerations.

Let us turn to the interaction of triplet excited aromatics with alkenes. As mentioned earlier, energy transfer, rather than cycloaddition, is the frequent outcome of intermolecular interaction of a triplet aromatic with an alkene, due to the much lower energy of a relaxed triplet alkene as compared to triplet benzene. For intermolecular reactions, such as the benzonorbornadiene rearrangement described earlier, rearrangement can be considered to be triggered by interaction of the aromatic excited state with the alkene ground-state. The alkene cannot rotate much in a constrained system, so bond formation to form a diradical is necessary for stabilization. The usual diradical mechanism for bridging in the two possible ways is shown in Fig. 16.

There is considerable evidence from the work of Paquette et al.[12] that the system does not pause at the first intermediate, but undergoes a concerted rearrangement at least to the second intermediate shown in the Figure. Nevertheless, we can understand regioselectivity of the reaction if we can understand whether the interaction of the aromatic triplet with the alkene is stronger at C-2 or at C-3.
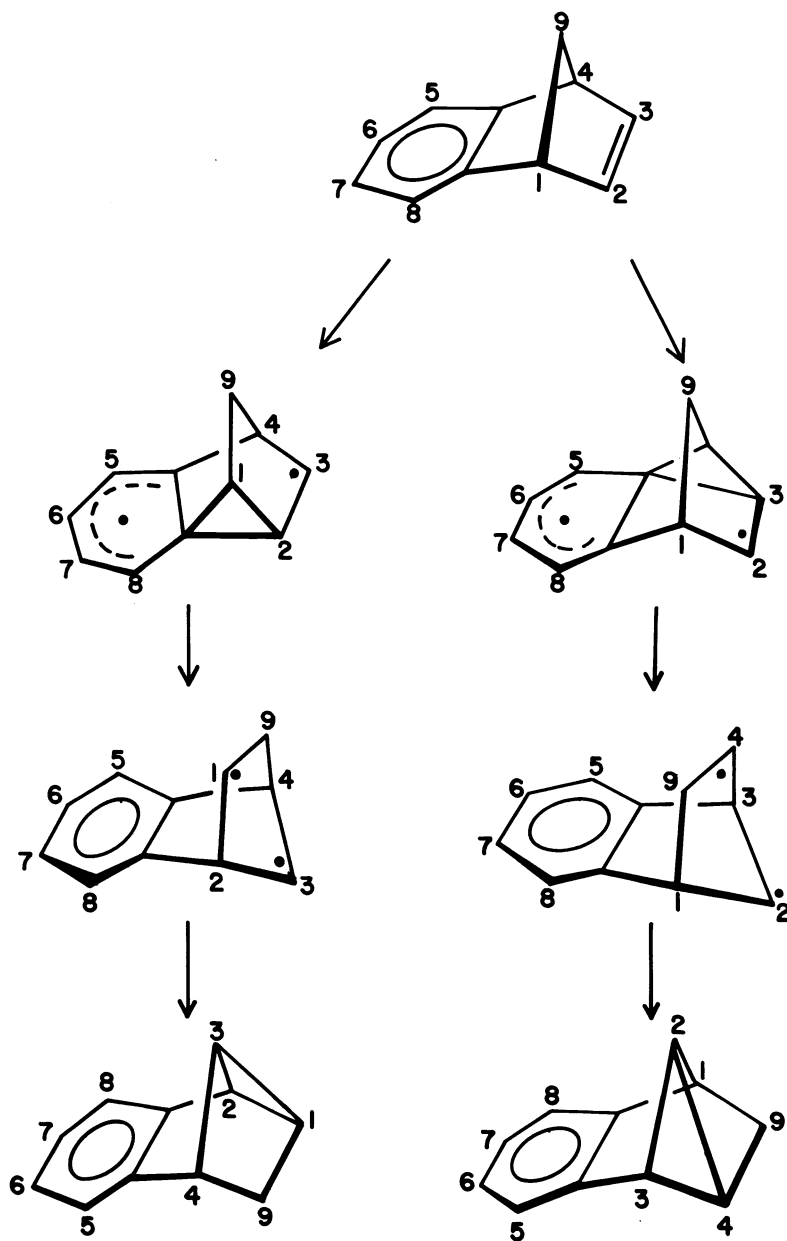
Fig. 16. Diradical mechanism for the triplet di-π-methane rearrangement
of benzonorbornadiene in the two possible bridging modes.

As mentioned earlier, the triplet state of benzene consists of equal
contributions of S → S* and A → A* configurations. As described for the
singlet, substitution can alter the orbital energies and the relative
contributions of these configurations to the lowest triplet. This, and the
coefficient polarization induced by substituents, influence
regioselectivity. We have published a detailed description of the
electronic structure of aryl-substituted benzonorbornadienes,[10] and present
here only a brief summary of our rationalization of selectivity for these
species.

Because of the disubstitution of the benzene ring and the interaction of the phenyl π orbitals with the alkene π orbitals, the degeneracy of the aromatic orbitals is lifted in benzonorbornadiene. The orbital assignments in Fig. 17 come from STO-3G calculations on benzonorbornadiene, while the orbital energies for the occupied orbitals are negative of ionization potentials we have measured by photoelectron spectroscopy,[10] and the electron affinities are estimated from those of related monochromophoric models.[20]
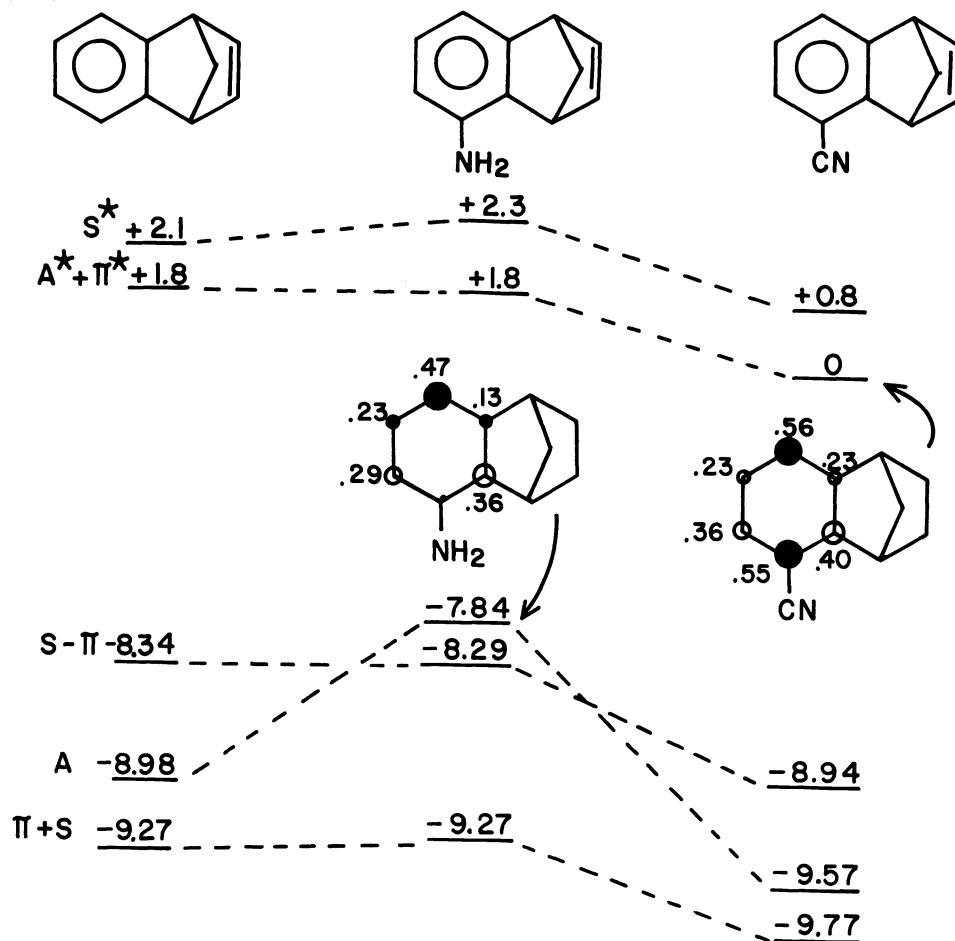

Fig. 17. Orbital energies of benzonorbornadiene
and ortho-substituted derivatives.

S and A are used in the same sense as in previous diagrams, even though the symmetry plane in benzonorbornadiene is at right angles to the one used for previous designations.

The frontier orbitals which are most significantly polarized in the ortho-substituted derivatives are shown in Fig. 17. The numbers are STO-3G p orbital coefficients. Since donors influence filled orbitals much more than vacant, the HOMO of o-aminobenzonorbornadiene is polarized most. The cyano group, a strong electron-withdrawer, lowers the vacant orbitals most and polarizes the LUMO much more than the occupied orbitals. As a result, both ortho donor- and acceptor-substituted species bridge ortho to the substituent.

For the <u>meta</u>-substituted molecules, we attribute the <u>meta</u>-bridging in the donor-substituted, and <u>para</u>-bridging in the acceptor-substituted, to the differing shapes of the LUMOs of these species. The orbital energies are given in Fig. 18, and the idealized shapes of the LUMOs are shown in the drawing. Due to the absence of symmetry in these molecules, the orbital mixing is sufficient to prevent labelling these as S or A, but the LUMO is predominantly A* in the convention used for monosubstituted benzenes, while the LUMO of the acceptor-substituted case is S*.
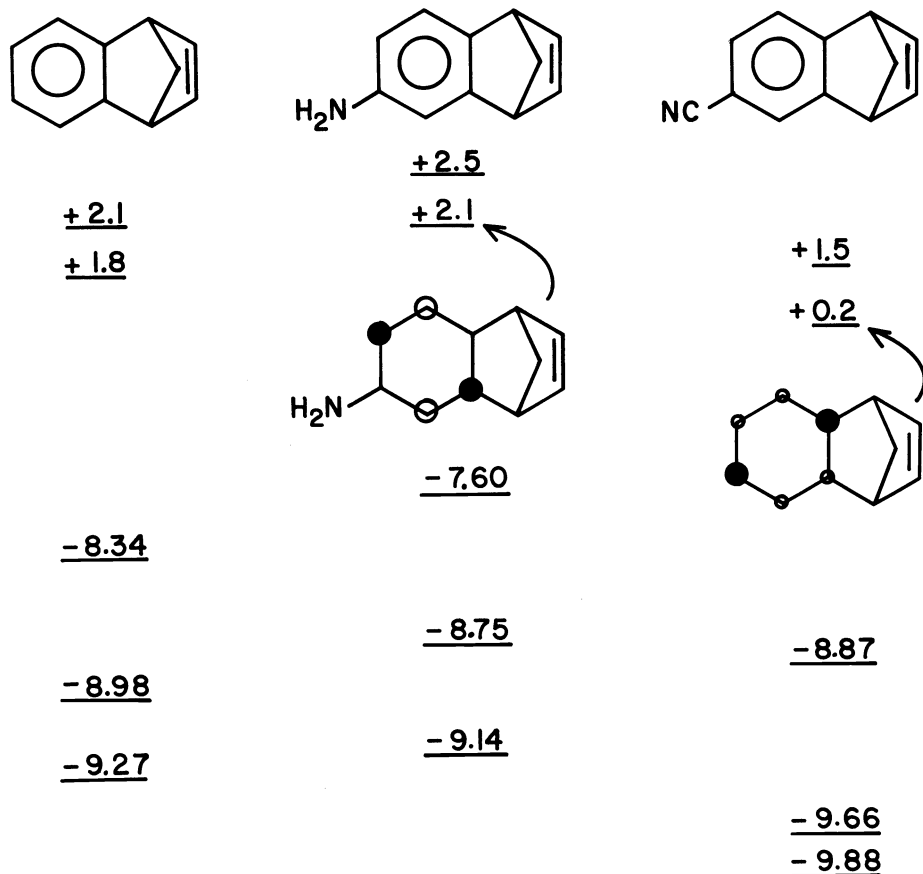

Fig. 18. Orbital energies of benzonorbornadiene
and <u>meta</u>-substituted derivatives.

These qualitative models provide rationales of the bridging selectivity found for cycloadditions of singlet excited benzenes with alkenes, and for the triplet di-π-methane rearrangements initiated by the interaction of triplet benzenes with alkenes. We are currently performing direct computations on excited benzenes in order to provide quantitative support for these models.

REFERENCES

1. D. Bryce-Smith and A. Gilbert, Tetrahedron, 32, 1309 (1976).
2. D. Bryce-Smith and A. Gilbert, Tetrahedron, 33, 2459 (1977).
3. A. Gilbert, Pure and Applied Chem., 52, 2669 (1980); A. Gilbert and P. Yianni, Tetrahedron, 37, 3275 (1981).
4. D. Bryce-Smith, B. Foulger, J. Funester, A. Gilbert, B.H. Orger, and H.M. Tyrrell, J. Chem. Soc., Perkin I, 56 (1980).
5. H.J.F. Angus and D. Bryce-Smith, Proc. Chem. Soc., 326 (1959).
6. K.E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 88, 2066 (1966); D. Bryce-Smith, A. Gilbert, and B.H. Orger, Chem. Comm., 512 (1966).
7. H. Morrison and W. Ferree, Jr., J. Chem. Soc., Chem. Comm., 268 (1969); W. Ferree, Jr., J.B. Grutzner, and H. Morrison, J. Am. Chem. Soc., 93, 5502 (1971).
8. P.A. Wender and J.J. Howbert, J. Am. Chem. Soc., 103, 688 (1981); P.A. Wender and G.B. Dreyer, Tetrahedron, 37, 4445 (1981).
9. L.A. Paquette, D.M. Cottrell, R.A. Snow, K.B. Gifkins, and J. Clardy, J. Am. Chem. Soc., 97, 3275 (1975).
10. C. Santiago, K.N. Houk, R.A. Snow, and L.A. Paquette, J. Am. Chem. Soc., 98, 7443 (1976).
11. A.Y. Ku, L.A. Paquette, M.D. Rozeboom, and K.N. Houk, J. Am. Chem. Soc., 101, 5981 (1979) and references therein.
12. L.A. Paquette and E. Bay, J. Am. Chem. Soc., in press. We thank Professor Paquette for a preprint of this paper.
13. D. Bryce-Smith and H.C. Longuet-Higgins, Chem. Comm., 593 (1966); D. Bryce-Smith, Chem. Comm., 806 (1969).
14. C. Santiago and K.N. Houk, J. Am. Chem. Soc., 98, 3380 (1976).
15. L. Salem, "Molecular Orbital Theory of Conjugated Systems", W.A. Benjamin, New York, 1966.
16. W.C. Herndon, Chem. Rev., 72, 157 (1972); W.C. Herndon, J. Feuer, W.B. Giles, D. Otteson, and E. Silber in G. Klopman, Ed., "Chemical Reactivity and Reaction Paths" Wiley, New York, 1974, Chapter 7.
17. N.D. Epiotis, "Theory of Organic Reactions", Springer-Verlag, Berlin, 1978.
18. J. Michl, Mol. Photochem., 4, 243, 257 (1972); Top. Curr. Chem., 46, 1 (1974); Pure Appl. Chem., 41, 507 (1975); R.C. Dougherty, J. Am. Chem. Soc., 93, 7187 (1971); R.A. Caldwell and D. Creed, Accounts Chem. Research, 13, 45 (1980).
19. P. Masclet, D. Grosjean, G. Mouvier, and J. Dubois, J. Electron Spectrosc. Rel. Phenomena, 2, 225 (1973).
20. K.D. Jordan and P.D. Burrow, Accounts Chem. Res., 11, 341 (1978).
21. J.A. Ors and R. Srinivasan, J. Org. Chem., 42, 1321 (1977).
22. R. Srinivasan, J. Am. Chem. Soc., 93, 3555 (1971).