Found: C, 62.79; H, 6.56.
(12) Numerous others have investigated the reaction of cuprous chloride with oxygen in various solvents; for a more recent study see C. E. Kramer, G. Davies, and R. W. Slaven, *J. Chem. Soc., Chem. Commun.*, 606 (1975).
(13) Davies and his co-workers[12] suggested the presence of a copper(I) peroxide complex in pyridine solution.
(14) As early as in 1937 F. Kubowitz, *Biochem. Z.*, **292**, 221 (1937); **299**, 32 (1939), proposed that in oxidation of catechol to *o*-benzoquinone catalyzed by copper oxidases, the function of oxygen was to regenerate copper(I) -enzyme to copper(II)-enzyme, which was the actual oxidizing reagent. Similar conclusion was reached by Hay, Endres, and their co-workers[6] who felt that in the catalytic oxidative polymerization of phenols the function of oxygen was the same and that in their reaction too the copper(II) was the true oxidizing reagent.
(15) Wacker process for conversion of ethylene and oxygen into acetaldehyde is an example; for details see G. Szonyi, *Adv. Chem. Ser.* **No. 70**, 53 (1968).

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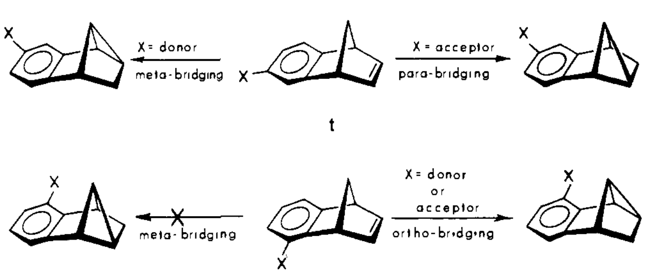
Bridging Regioselectivity in Triplet-Sensitized Di-π-methane Photorearrangements of Ortho-Substituted Benzonorbornadienes. A Case for the Importance of Benzene HOMO and LUMO Polarization

Sir:

We have recently delineated the striking regioselectivity observed in the triplet-sensitized di-π-methane rearrangements of donor and acceptor meta-substituted benzonorbornadienes (**1**)[1] and developed a simple MO model which accounts for the preferential benzo–vinyl bonding, which operates in *opposite directions.*[2] At the level presented, the model would predict no selectivity in rearrangements of ortho-substituted benzonorbornadienes. Yet, as summarized in Figure 1 and Table I, this substitution pattern can exert large directive effects, although they are now in the *same direction.* Double resonance studies and experimental determination of LIS values established the major products to be **3** in several cases. That all such benzonorbornadienes (except X = F) adopt the same triplet bonding preference was confirmed additionally by chemical methods and ^{13}C NMR spectroscopy. All photoproducts showed no inclination for further reaction under the conditions employed.

These results can be accounted for by further elaboration of our model,[2] taking into account the polarization of frontier orbitals caused by donor or acceptor substituents.[3] As indicated in Figure 2,[4] the influence of a donor group (e.g., amino, as an extreme) is to split the degeneracy of the highest occupied molecular orbitals (HOMO's) and lowest unoccupied molecular orbitals (LUMO's) of benzene. The donor orbital (n) conjugatively interacts most with the symmetric (b_1 in C_{2v}) HOMO and to a lesser extent with the symmetric (b_1*) LUMO. In addition to these changes in energy, the substituent causes a mixing of b_1 orbitals. The sign and magnitude of mixing of ψ_1, ψ_4, and ψ_6 into the HOMO can be numerically calculated by perturbation theory as demonstrated by Libit and Hoffmann,[3] but can be qualitatively determined by the following simple rules: (1) the extent of mixing of an orbital (ψ_n) into the HOMO (or any orbital, ψ_i) is inversely dependent on both the difference in energy between the HOMO and ψ_n, and the difference in energy between the HOMO and the perturbing orbital; (2) a low-lying perturbing orbital will cause the HOMO (or any other orbital, ψ_i, lying higher in energy than the perturbing orbital) to mix in all lower lying orbitals in a bonding fashion, and to mix in all higher lying orbitals in an antibonding fashion; (3) a high-lying perturbing orbital will cause the HOMO (or any other orbital, ψ_i, lying lower in energy than the perturbing orbital) to mix in all lower lying orbitals in an antibonding fashion, and to mix in all higher lying orbitals in a bonding fashion. "Bonding" or "antibonding" is determined at the site of substitution.



1

4 **2** **3**

Figure 1. Regiochemistry of triplet-sensitized di-π-methane rearrangements of benzonorbornadienes.

Table I. Product Distribution Data for Triplet-Sensitized Irradiation of **2**[b]

X	**3**, %	**4**, %	X	**3**, %	**4**, %
$-NO_2$	>99		$-OCH_3$	89.3	10.7
$-COCH_3$	>99		$-NH_2$	82.6	17.4
-CN	96	4	$-CH_3$[a]	70	30
			-F	50	50

[a] J. R. Edman, *J. Am. Chem. Soc.*, **91**, 7103 (1969). [b] Dilute C_6H_6 solutions, Pyrex, 3500-Å radiation with acetophenone present.

Returning to the benzene case, the following generalizations may be made on the basis of these rules: For all perturbing donor orbitals whose energies lie below that of ψ_3 (the HOMO), ψ_3 will be polarized by mixing in ψ_1 in a bonding fashion and some of ψ_4 in an antibonding fashion at the site of attachment of D. That is, ψ_3 becomes $\psi_3' = \psi_3 + \psi_1 - \psi_4 - D$ (D having been mixed in first order), where coefficients of mixing have been omitted for clarity. The mixing in of ψ_1 will cause the HOMO ipso and ortho coefficients to be increased, while the meta and para will be decreased; mixing in of ψ_4 decreases the ipso and meta coefficients and increases the ortho and para coefficients. Since ψ_4 has large ipso and para coefficients, the effect on these coefficients is largest. As shown in Figure 2, the strong donor amino group gives HOMO (ψ_3') coefficients in the order para > ipso $\gtrsim$ ortho > meta. As pointed out by Zimmerman, the benzyl anion represents the extreme of donor substitution.[5] In general, as the donor strength increases, the ortho/meta coefficient ratio increases from 1 toward ∞, and the para/ortho ratio decreases from 2 to 1. The SLUMO (ψ_4') of donor-substituted benzene is polarized by a similar mechanism, but to the opposite extent and in the opposite direction.

An acceptor group will generally have not only a low-lying vacant orbital, but will have a weak donor orbital also. The vacant orbitals of acceptor-substituted aromatics will be important in both reaactions with nucleophiles and in photochemical reactions. The influence of vacant acceptor orbitals, whose energies lie above ψ_4 and ψ_5 of benzene, on the LUMO (ψ_4) of benzene is the mirror image of the influence of a donor orbital on the filled orbitals. Thus, ψ_4 is lowered most by strong acceptors, and coefficient magnitudes are para > ipso $\gtrsim$ ortho > meta, as represented in Figure 2 by the nitrobenzene orbitals. For this molecule, the SHOMO (ψ_3') polarization is dominated by the nitro acceptor orbital, but this will vary depending on the energy of the acceptor filled orbital.

Turning to the photochemical phenomena in question, in the meta-substituted cases discussed in our previous communication, the fact that the b_1* orbital contributed more to the

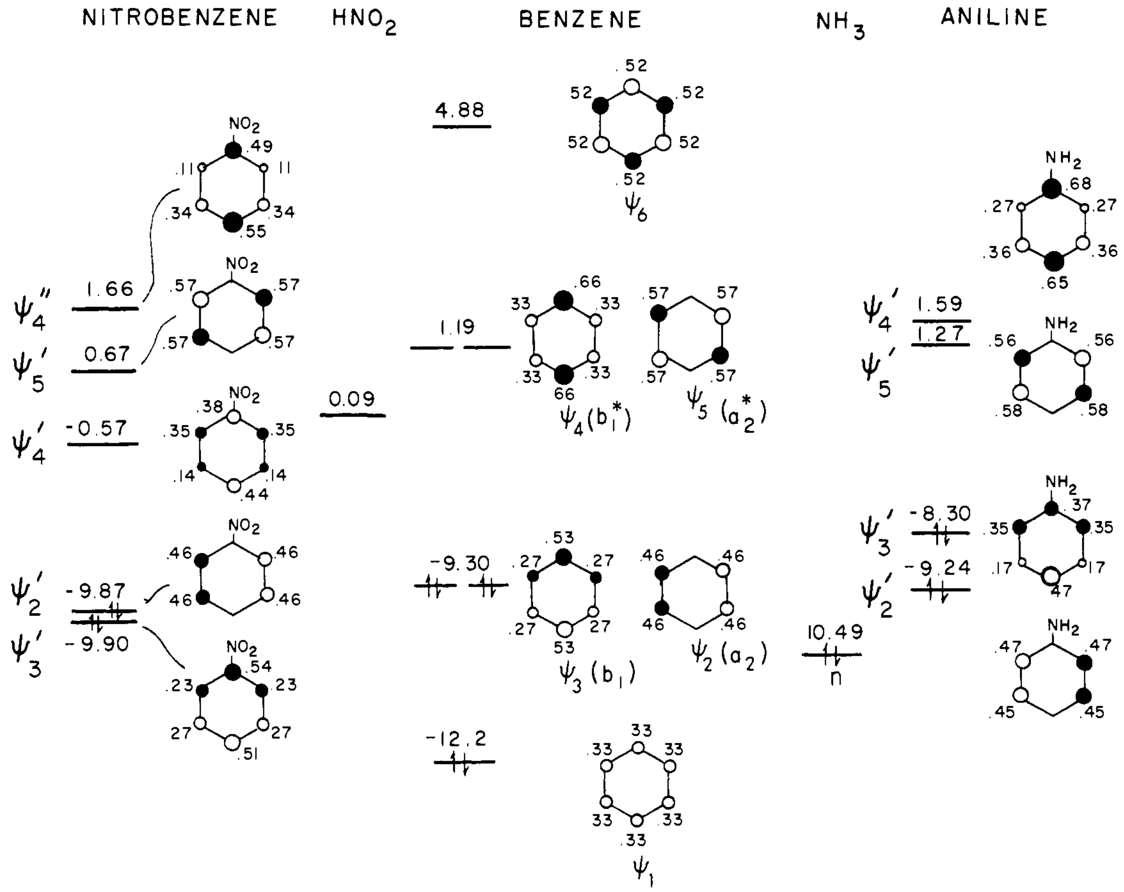


Figure 2. Energy levels and coefficients for benzene and acceptor- or donor-substituted benzenes.

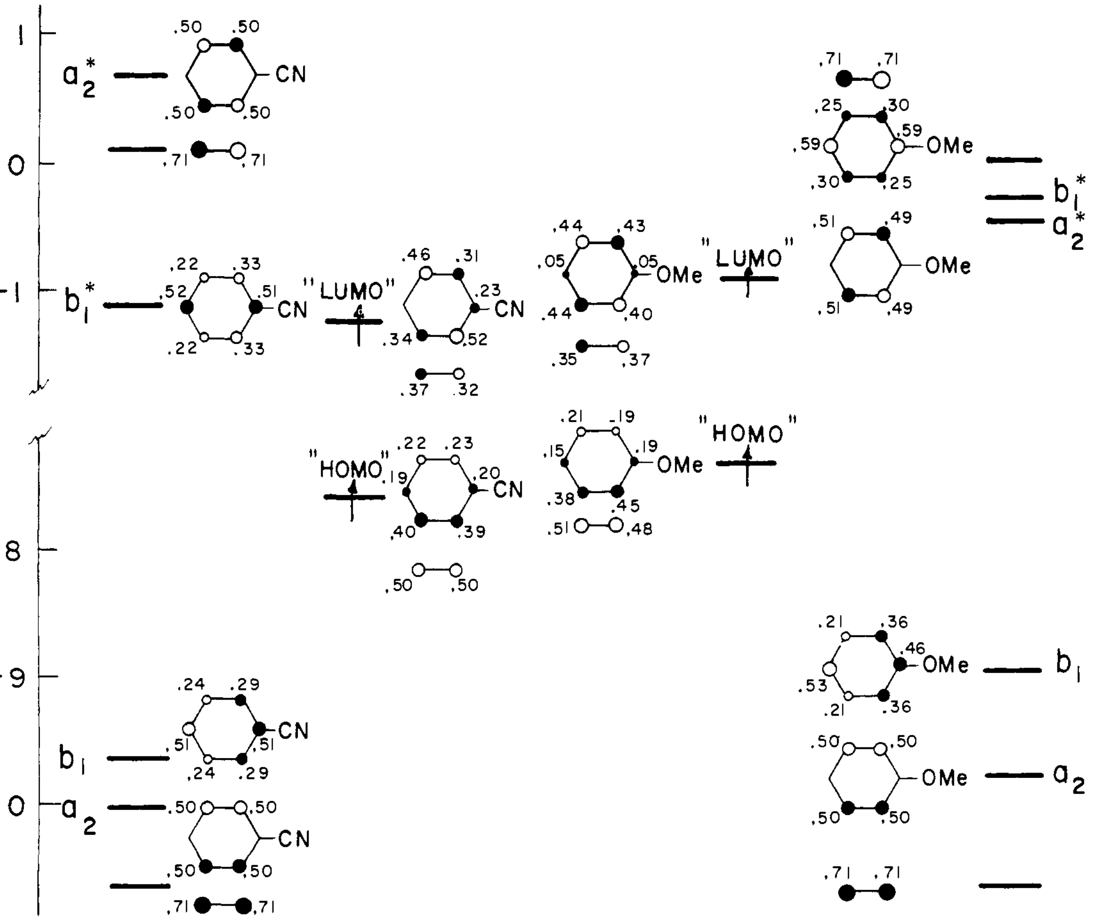


Figure 3. Singly occupied MO's of acceptor- and donor-substituted benzene-ethylene complexes and the isolated benzenes and ethylene.

triplet state than the $a_2{}^*$ for the acceptor-substituted case, and the $a_2{}^*$ more than the $b_1{}^*$ in the donor-substituted case led to a ready rationalization of the experimental results. In the cases reported here, it is the LUMO ($b_1{}^*$) polarization in the acceptor-substituted case and the HOMO (b_1) polarization in the donor-substituted case which promote ortho regioselectivity.

Computations on triplet states of simplified models of **2** by the CNDO/S method,[6] using a complex of substituted benzene and ethylene situated in parallel planes separated by 2.5 Å,[2] verify the importance of the HOMO polarization in the triplet state of donor-substituted **2** and the LUMO polarization in the acceptor-substituted **2.** Figure 3 shows the singly occupied molecular orbitals of these complexes. The CNDO/S calculations, which include configuration interaction between singly excited configurations, suggest that the configuration involving single occupation of the HOMO and LUMO orbitals such as those shown is by far the main contributor to the lowest triplet (~86% for NH_2, MeO, Me, F, CO_2Me, and CN substituents), whereas isolated benzenes have lowest triplets consisting of nearly equal contributions of $a_2 \rightarrow a_2{}^*$ and $b_1 \rightarrow b_1{}^*$ configurations.

Considering first the acceptor-substituted case, as exemplified by the benzonitrile-ethylene complex (Figure 3), the LUMO, which is half-occupied in the triplet state, is the bonding combination of ethylene LUMO and the $a_2{}^*$ orbital of benzonitrile. Most significantly, a small admixture (6%) of the $b_1{}^*$ orbital occurs, since the ortho and meta coefficients are unequal in this orbital. This small admixture, in a net bonding fashion to the ethylene LUMO, leads to significantly different ortho and meta coefficients in the LUMO of the complex, and distortion of the triplet state of the molecule toward an *ortho*-bridged diradical is significantly favored. Since the occupied b_1 orbital of benzonitrile is much less polarized, b_1 mixes to a smaller extent into the complex HOMO.[7]

In the donor-substituted case, exemplified by an anisole-ethylene complex in Figure 3, the HOMO of the complex is significantly more polarized than the LUMO. The ethylene HOMO mixes in mainly the a_2 anisole orbital in an antibonding fashion, but some admixture of the anisole b_1 orbital in a net antibonding fashion results in a larger anisole ortho coefficient. Again, ortho bonding is favored. The donor-substituted molecules are expected to show less regioselectivity than the acceptor-substituted cases, since the HOMO and LUMO of the complex work in opposite directions for the donor case, and polarization appears smaller in the donor case.

Weak donors (e.g., methyl or fluoro) are expected to show very low regioselectivity, since these groups cause only small polarizations of the occupied b_1 orbitals. In general, the ratio of relative rates of ortho and meta bridging should increase as the strength of the donor substituent or of the acceptor substituent increases. The experimental results (Table I) are in good agreement with this prediction of the model.

We note as a general caution that the exact magnitude of the polarization is rather sensitive to the type of calculation, and the numbers in Figure 3 are of qualitative significance at best. Nevertheless, these considerations provide a theoretical framework which reveals the origin of ortho- and para-bridging regioselectivity found in donor-substituted benzonorbornadienes.

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(6) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 563 (1969).

(7) A referee has suggested that a lowest $n\pi^*$ triplet state might be involved in the carbonyl or nitro cases. If such were the case, the π^* orbital alone will determine regioselectivity.

(8) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.

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Reactions of Transition Metal Ions with Alkyl Halides and Alcohols in the Gas Phase: Evidence for Metal Insertion and β-Hydrogen Atom Shift

Sir:

Recently, vaporized transition metal atoms[1-3] and gaseous ionized transition metal complexes[4-10] have been found to have a rich and interesting chemistry. We have examined the gas-phase chemistry of transition metal ions with a number of alkyl halides and alcohols and find it to be instructive and interesting. In particular, we wish to report evidence for two important elementary processes in the reactions of gas-phase metal ions. The first is the insertion of transition metal ions into a C-X bond. Numerous reactions of vaporized transition metal atoms[1] and metal complexes in solution[11] appear to involve such a metal insertion. The second process is the shift of a hydrogen atom in a metal alkyl complex from the β carbon onto the metal. This process is also assumed to be important in a variety of reactions involving transition metals.[11-15] We believe the present results to be the first direct evidence that transition metal ions insert into R-X bonds ad participate in β-hydrogen atom shifts in bimolecular gas-phase reactions. Since theories and models of chemical reactions are frequently constructed in terms of gas-phase bimolecular processes, it is of interest that these processes, which are important in a wide variety of useful reactions, occur in the gas phase.

Metal ions are produced for these studies by electron impact on volatile metal complexes such as metal carbonyls. The reactions of the metal ions with the vapors of alkyl halides and alcohols are examined using standard ion cyclotron resonance techniques.[16] Since the studies are carried out at very low pressure (10^{-6}-10^{-4} Torr), only bimolecular ion-molecule processes are observed. Both the reactant neutral and the reactant ion which give rise to a given product ion may be unambiguously identified using the ion cyclotron double resonance technique.[16] The product ion is observed directly and identified from its mass. Isotopic labeling readily provides considerable mechanistic information.

Methyl iodide reacts with transition metal ions by oxidative addition (eq 1). As noted elsewhere, limits on the metal to carbon bond strength in $MCH_3{}^+$ may be inferred from eq 1.[4]