Orbital Symmetry Relationships for Thermal and Photochemical Concerted Cycloadditions to the Benzene Ring

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Summary Orbital symmetry analysis of various modes of concerted cycloaddition to the benzene ring, including dimerisation, indicates that the Woodward–Hoffmann rules apply, when appropriately viewed, to the thermal reactions, but not to the photochemical ones: the derived relationships accord well with existing experimental observations, and permit various predictions.

THE rules of Woodward and Hoffmann for concerted cycloadditions are based on the orbital and state electronic symmetry properties of nonaromatic carbon frameworks.[1] The problem of photochemical transformations of the benzene ring was first treated by Longuet-Higgins and the present writer.[2] This Communication extends that treatment to a range of known and unknown thermal and photochemical concerted cycloadditions to benzene, including dimerisation, where the transition states should have appropriate planes or axes of symmetry.

In correlation with excited states of benzene, the criterion has been adopted that at least one of the two components of a transition involving degenerate orbitals must have a symmetry which permits correlation with the relevant occupied adduct orbitals *via* a chemically reasonable transition state. Non-Hückel levels for the orbitals have generally to be adopted in realistic accordance with the known energies of excited singlet states. For example, the π_1 level of unsubstituted ethylene is placed below ψ_2 and ψ_3 of benzene. The effects of substituents on the energy levels can alter the relative positions and lead thereby, through operation of the 'no-crossing' rule, to different orbital correlations. Account has been taken of such effects in determining whether a particular concerted process can occur from the lowest excited singlet state in the system; that is from S_1 benzene ($^1B_{2u}$), S_1 addend, or the two possible charge-transfer states.† Any concerted process from T_1 benzene ($^3B_{1u}$) would follow the relationships given for S_2 benzene: such additions would need to be concerted with spin-inversion.

In the Table, either one or both of the reactants is in the electronic ground state, and *A* and *F* denote symmetry-allowed and -forbidden processes, respectively. The listed photochemical relationships apply to systems in which the excited state specified (other than $^1B_{1u}$) is the lowest excited singlet state. Photochemical *A* correlations are with low-lying excited states of products or, in cases 3 and 7, with the ground states of diradicals.

Three general conclusions follow from the relationships listed in the Table. Firstly, the Woodward–Hoffmann rules for concerted *thermal* terminal cycloaddition reactions of π-electron systems can be applied to the additions to benzene (although to do so it is necessary to view the *para*-additions of ethylene and butadiene as 2 + 4 and 4 + 4 processes, respectively).

Secondly, the Woodward–Hoffmann rules are not generally applicable to the photoaddition processes. Perhaps the most marked difference from the rules is in the frequent lack of distinction between *cis–cis-* and *cis–trans*-processes. In these cases, the absence of stereospecificity will not necessarily imply a non-concerted process: compare cases 1, 2 and 4, 5.

Thirdly, the rules for concerted photoadditions to benzene depend on the nature of the excited species (*cf.*

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† Dewar-benzene (bicyclohexadiene) is formed by irradiation of liquid benzene at *ca.* 2000 Å (H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, 1968, **90**, 1055, 5353) but not at 2537 Å (D. Bryce-Smith, A. Gilbert, and D. A. Robinson, unpublished results). Orbital symmetry considerations suggest that it could arise directly from an upper excited singlet state of benzene, probably the $^1B_{1u}$ state, [2a,c] but not from the $^1B_{2u}$ state which is populated by absorption at 2537 Å.

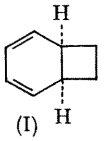
Salem[3]), and the feasibility of charge-transfer excitation. Reactions 1—10 are symmetry-allowed from S_1 addend and all the reactions from charge-transfer states.

More specific implications of some of these findings are now considered.

Thermal reactions. No 1,4-thermal additions of ethylenes to benzenes have yet been reported, but the known 1,4-addition of acetylenes and its retrogression[4] could occur by a concerted mechanism. The allowed *cis-ortho/cis*-1,4-addition of *cis*-1,3-dienes is as yet unknown (case 6), but might be observable in suitable cases (*e.g.* with strongly electrophilic dienes) since no great enthalpy change or ring distortion is involved. The 1,4-additions of *o*-benzynes to 1,3-dienes[5] and benzene[6] can be viewed as concerted processes analogous to cases 6 and 13, respectively, and the lack of stereospecificity in 1,2-addition of *o*-benzyne to ethylenes[7] is likewise in accord with case 1 where there is no allowed concerted thermal *cis*-pathway available.[8] Ozone resembles the allyl anion[9a] and *cis*-butadiene in the symmetry of its occupied π-orbitals: accordingly ozonization of benzene could in principle be a concerted process analogous to case 6.

Of the benzene dimers (XI)—(XIV), dimer (XIII) should have the lowest stability towards thermal dissociation. This low stability (ΔH *ca.* -30 kcal./mole) is reminiscent of some properties attributed to the benzene excimer; but all four dimers would need to be formed in any concerted processes from B_{1u} benzene (T_1 or S_2) rather than B_{2u} benzene (S_1). None of these dimers has yet been found following irradiation of benzene in the $S_0 \rightarrow S_1$ band, for reasons which are now apparent, although dimer (XI) has recently been prepared by an indirect route.[9b]

Photochemical reactions. The relationships in case 1 can explain why *ortho*-photoaddition of ethylenes to benzenes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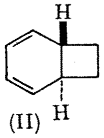
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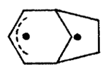
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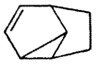
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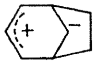
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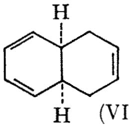
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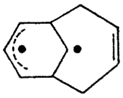
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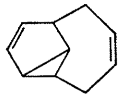
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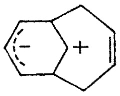
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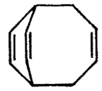
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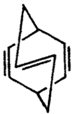
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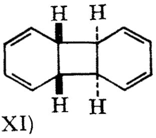
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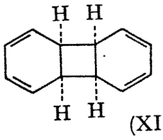
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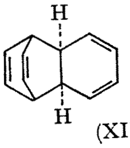
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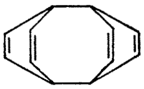

(XIV)


(XV)

Concerted cycloadditions of ethylene and cis- *and* trans-*butadiene to benzene: dimerisation of benzene*

			Excited species			Charge-transfer excitation		
			Addend	Benzene				
Addend	Addition mode	Product	(S_1, T_1)*	B_{2u} (S_1)	B_{1u} (S_2, T_1)	Donor Addend	Donor Benzene	Thermal Reaction
1 Ethylene	*cis-ortho/cis*-1,2-	(I)	*A*	*F*	A^{a}	*A*	*A*	*F*
2 Ethylene	*trans-ortho/cis*-1,2-	(II)	*A*	*F*	*A*	*A*	*A*	*A*
3 Ethylene	*meta/cis*-1,2-	(III)[→ (IIIa)]	*A*	*A*	F^{b}	*A*	*A*	F^{c}
4 Ethylene	*para/cis*-1,2-	(V)	*A*	*F*	A^{d}	*A*	*A*	*A*
5 Ethylene	*para/trans*-1,2-	(V)	*A*	*A*	*A*	*A*	*A*	*F*
6 *cis*-Butadiene	*cis-ortho/cis*-1,4-	(VI)	*A*	F^{e}	*A*	*A*	*A*	*A*
7 *cis*-Butadiene	*meta/cis*-1,4-	(VII)[→ (VIIa)]	*A*	*A*	F^{b}	*A*	*A*	F^{f}
8 *cis*-Butadiene	*para/cis*-1,4-	(IX)	*A*	*F*	A^{a}	*A*	*A*	*F*
9 *cis*-Butadiene	*para/trans*-1,4-	(IX)[g]	*A*	*A*	*A*	*A*	*A*	*A*
10 *trans*-Butadiene	*para/cis*-1,4-	(X)	*A*	*A*	*A*	*A*	*A*	*F*
11 Benzene	*exo-cis*-1,2-*cis*-1′,2′-	(XI)	—	*F*	*A*	*A*		*F*
12 Benzene	*endo-cis*-1,2-*cis*-1′,2′-	(XII)	—	*F*	*A*	*A*		*F*
13 Benzene	*cis*-1,2-1′,4′-	(XIII)	—	F^{e}	*A*	*A*		*A*
14 Benzene	*cis*-1,4-1′,4′-	(XIV)	—	*F*	*A*	*A*		*F*

* Strictly, the relations apply to a T_1 addend only when this is reacting in an effectively planar conformation. T_2 Benzene may be of state $^3E_{1u}$ (S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, 1965, **43**, 2661). Mixing will occur between states similar in geometry (*e.g.* S_1 ethylene and S_2 benzene) if the energies are close.

[a] Correlation noted also by Hoffmann and Woodward (ref. 1). Professor Hoffmann (personal communication) has reached similar conclusions about the relationships in case 1 from a somewhat different type of analysis;

[b] Correlation with first excited state of diradical product;

[c] Correlation with zwitterion (IV);

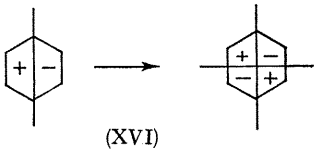
[d] The B_{1u} component (XVI) which apparently permits concerted *para*-additions of ethylene corresponds to a transition between orbitals ψ_3, ψ_5 which each have zero amplitude at the reaction centres. Nevertheless, the addition should still be possible in principle because the ψ_2 ψ_4 and ψ_3 ψ_5 components are equally part of the B_{1u} state;

[e] Allowed correlation with S_2 adduct, which might be accessible in practice;

[f] Correlation with zwitterion (VIII).

[g] It is possible to envisage the production of adduct (X) by this mode of addition; but Professor R. Hoffmann (personal communication) has suggested convincingly that adduct (IX) should be a preferred product.

has only been observed in systems where the ethylene is the lowest excited singlet species (as with maleimides[2c,10]), or where either the ethylene or the aromatic component has marked acceptor properties (as with acrylonitrile + benzene,[11] and benzonitrile + a mono-olefin[12‡]). Irradiation of simple mono-olefins with benzene normally provides B_{2u} benzene as the lowest excited singlet species and leads to 1,3- rather than 1,2-cycloaddition; but the latter process might in principle be able to occur under conditions where a B_{1u} state of benzene is populated.



(XVI)

1,3-Cycloaddition of olefins to benzene has previously been explained through an initial symmetry-allowed transformation of $^1B_{2u}$ benzene into the singlet diradical (XV), termed prefulvene.§[2a–c,13] Another possible route to 1,3-adducts from B_{2u} benzene is considered in case 3, and this may be involved in liquid-phase reactions; but the inability of mono-olefins effectively to quench the fluorescence of benzene in the gas phase[14] favours the prefulvene mechanism, at least for gas-phase additions. The symmetry properties of diradicals (III) and (VII) suggest that their ring-closure to (IIIa) and (VIIa) respectively could be concerted with their formation.

Comparison of cases 8, 9, and 10 shows that butadiene and $^1B_{2u}$ benzene should more readily give the strained *trans*-adduct (X) than the relatively unstrained *cis*-adduct (IX), as found experimentally.[15] A small proportion of the *cis*-adduct (IX) appears to be formed as a primary photochemical product,[16] and might provide an example of case **9**. Comparison of cases 1, 4, and 10 suggests an explanation of the fact that butadiene is much more efficient than ethylene in quenching of benzene fluorescence: the usual singlet energy transfer process would be markedly endothermic in each case.[14] It further follows that cisoid 1,3-dienes (*e.g.* cyclohexa-1,3-diene) should be less efficient than butadiene in this quenching. The extent of chemical quenching will not necessarily be reflected in quantum yields for adduct formation if adducts are reactive or thermally unstable and formed at high vibrational levels, or only incompletely formed as exciplexes: *cf.* refs. 15—17.

It is well recognised that the availability of a closely concerted pathway for a reaction should normally provide a kinetic advantage, but does not exclude the operation of less-concerted mechanisms. The direction and velocity in particular cases will, as usual, be governed by kinetic, thermodynamic, and steric factors. Thus, where concerted 1,2- and 1,4-additions to planar benzene are equally allowed, the former process might be favoured since its transition state should involve less distortion of the benzene ring.

The present relationships do not necessarily apply to naphthalene and higher condensed aromatic hydrocarbons. Strictly, they should not be applied to substituted benzenes and addends of different molecular symmetry; but in practice they should retain some force for systems in which the substituents do not strongly perturb the symmetry of the carbon π-orbitals.

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‡ These two systems show negligible direct charge-transfer absorption (ref. 11; and M. A. Hems, Ph.D. Thesis, University of Reading, 1967), but charge-transfer could well follow excitation. Molecules in electronic excited states will, in general, be better donors and acceptors than in their electronic ground state, since they can donate from an antibonding orbital and accept into a bonding one.

§ The direct concerted transformation of B_{2u} benzene into the ground or a low excited state of benzvalene would be symmetry-forbidden.[2d]

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[2] (a) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593; (b) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *ibid.*, 1967, 240; (c) D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47; (d) I. Haller, *J. Chem. Phys.*, 1967, **47**, 1117, has elaborated the treatment outlined in ref. 2a.

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[17] L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 1968, **16**, 125.