assignment. These two studies, as well as several others[4h-j,p-t] employing sophisticated computational procedures, also find values of Δ_{ST} in good agreement with our experimental one. However, efforts to check for the presence of hot bands, the supposed cause of the misassignment, have failed so far to detect their existence[15] and the origin of this discrepancy remains unresolved.

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Ground States of Molecules. 50.[1] MNDO Study of Hydroboration and Borohydride Reduction. Implications Concerning Cyclic Conjugation and Pericyclic Reactions

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Abstract: MNDO calculations are reported for the reduction of formaldehyde or methyl formate by borohydride ion and for the reactions of borane with acetone and ketene. Borohydride reduction is predicted to be strongly "forbidden" in the gas phase. The ease of hydroboration is explained in terms of a type of cyclic conjugated system (cruciconjugated) previously recognized in the phosphonitrile chlorides. The analogy between conjugation by $p\pi$:$d\pi$ and $p\sigma$:$p\sigma$ interactions is pointed out and used to interpret the abnormal ("anti-Hückel"; "Moebius") systems in pericyclic transition states. The inappropriateness of the term "Moebius" in this connection is emphasized.

Introduction

Hydroboration[2] and the reduction of carbonyl groups by borohydride ion (BH_4^-)[3] have become two of the better known reactions in synthetic organic chemistry. Each formally involves a cycloaddition of a B–H moiety to a double bond, a process which would be classified in Woodward-Hoffman terminology[4] as a $(_\sigma 2_s + _\pi 2_s)$ cycloaddition, i.e.
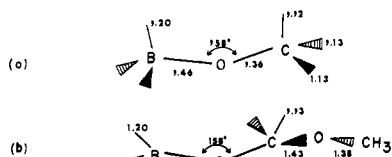
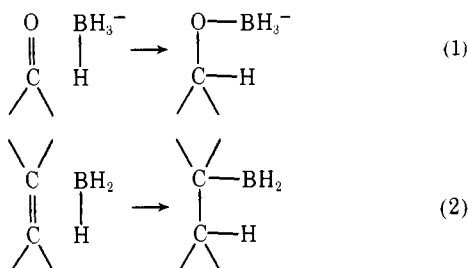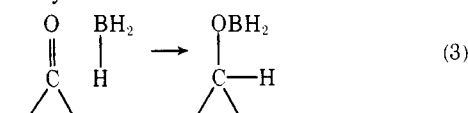**Figure 1.** Geometries calculated for (a) **3** and (b) **4.**

(1)

(2)

This analogy is further indicated by the fact that diborane can also reduce the carbonyl function, by a similar addition of borane to the carbonyl double bond:

(3)

All of these processes are "forbidden" in terms of the Woodward–Hoffmann rules[4] or Evans' principle;[5] yet all three take place readily in solution under mild conditions. This indeed is why they are so useful in organic synthesis. Furthermore, 1,3-dienes react[2] with diborane by 1,2-addition, not 1,4-addition, although the latter process is "allowed" and the former "forbidden". Clearly this anomaly needs to be resolved if current ideas[4,5] concerning pericyclic reactions are to retain their universality.

Recent work in these laboratories has led to the development of a new semiempirical SCF MO method (MNDO[6]) which has proved superior to the earlier MINDO/3[7] treatment. In particular, we have been able to parametrize it successfully for boron,[8] and extensive tests have shown that the resulting procedure gives satisfactory results for a wide variety of boron compounds, including boron hydrides[8,9] and carboranes.[8,10] Using MNDO, we have studied reactions 1–3 in detail. The results for (1) (hydroboration) have already been reported.[11] Here we give those for the other reactions, together with a general analysis of their implications concerning the theory of pericyclic processes.

Procedure

The calculations were carried out by the standard MNDO method,[6] using the recommended[6,8] parameters. All geometries were optimized by the standard[6,7] Davidon–Fletcher–Powell (DFP) procedure, no assumptions of any kind being made. Transition states were located approximately from plots of energy vs. a suitable reaction coordinate and refined by minimizing the scalar gradient, following McIver and Komornicki.[12] All stationary points were characterized by calculating and diagonalizing the Hessian (second derivative, force constant) matrix.[12] In the case of a local minimum on the potential surface, all of the eigenvalues must be positive, while a saddle point (transition state) has one, and only one, negative eigenvalue.

The kinetic isotope effect (k_H/k_D) for reactions of BH_4^-/BD_4^- with CH_2O was calculated[13] to be 1.282.
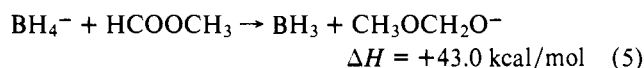
Results

We first studied the reactions of BH_4^- with formaldehyde (**1**) and methyl formate (**2**) to form **3** and **4**, respectively, these

Figure 2. Calculated MERPs for the reactions of BH_4^- with (a) CH_2O (**1**) and (b) $HCOOCH_3$ (**2**).

being the simplest examples of the reduction of an aldehyde (or ketone) and of an ester. As we had expected, both reactions were predicted to be quite strongly exothermic, the calculated heats of reaction being -28 and -21 kcal/mol, respectively. Calculated heats of formation (kcal/mol) are shown under the formulas, and the calculated geometries of **3** and **4** are shown in Figure 1.

Next we studied the course of each of the two reactions in detail, using the distance between one hydrogen atom of the borohydride ion and the carbon atom as the reaction coordinate. Figure 2 shows the resulting reaction profiles. It will be seen that both reactions are predicted to involve a very endothermic transfer of hydride ion to give borane and an alkoxide ion, i.e.

$$BH_4^- + CH_2O \rightarrow BH_3 + HCH_2O^-$$
$$\Delta H = +40.8 \text{ kcal/mol} \quad (4)$$

$$BH_4^- + HCOOCH_3 \rightarrow BH_3 + CH_3OCH_2O^-$$
$$\Delta H = +43.0 \text{ kcal/mol} \quad (5)$$

With this geometry of approach, each reaction profile showed a steady rise throughout, the reverse processes requiring no activation and the products ($BH_3 + RO^-$) showing no tendency to revert to **3** or **4**.

In order to study the possibility of a concerted path for these reactions, we next carried out a two-dimensional grid search for that of formaldehyde (**1**), using the lengths of the forming C–H and B–O bonds as the reaction coordinates. The results are shown in Figure 3. It will be seen that there is *no* concerted path for the reaction. The products can be formed only via a complete initial transfer of hydride (eq 4). The activation energy for the overall reduction (**1 → 3**) is therefore the same as the heat of reaction for the first step, i.e., 40.8 kcal/mol. Presumably, the same situation holds for the reduction of methyl formate (**2**). We did not study this in detail since it seemed unlikely that the results could justify the cost of the necessary calculations.

Our conclusions are clearly consistent with the reactions being "forbidden" processes. In the gas phase, they apparently take place by nonconcerted mechanisms involving an initial hydride transfer to form borane and an alkoxide ion. The fact that the reactions apparently[3,14-16] take place very rapidly in protic solvents or in the presence of metal cations is presumably due to stabilization of the intermediate alkoxide ion, either by
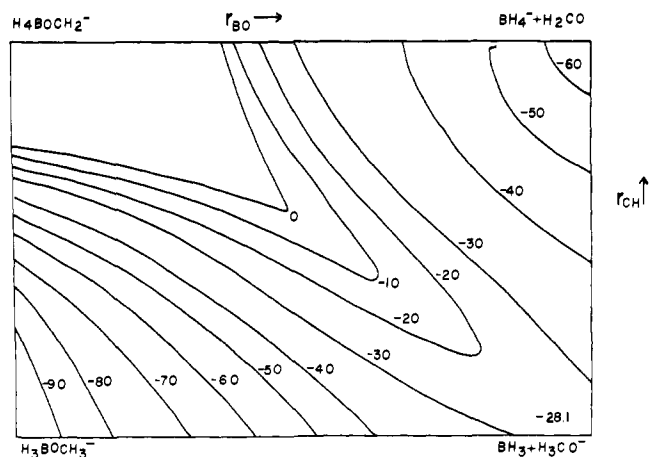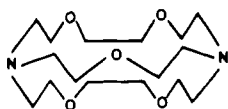
Figure 3. Two-dimensional projection of the potential surface for the reaction $H_4B^- + CH_2O \rightarrow 3$, using as coordinates the lengths of the forming C–H and B–O bonds.

hydrogen bonding to the solvent or by coordination to the cation. Indeed, Pierre and Handel[17] have recently reported that the reduction of cyclohexanone by sodium borohydride in diglyme can be suppressed by addition of enough of an appropriate crown ether (**5**) to complex the sodium ions and so destroy their ability to coordinate to the carbonyl oxygen. Addition of uncomplexed sodium ions, in the form of otherwise inert salts, led to resumption of the reduction. The reactions in hydroxylic solvents may also be facilitated by stabilization of the borane by coordination to the solvent, as suggested by the kinetic studies of Wigfield and Gowland[18] and Adams, Gold, and Rueben.[19] Wigfield et al.[20] have also obtained further evidence for the "forbidden" nature of the overall addition by showing that the reactions in diglyme are accelerated by uv light.

Next, we examined the reactions of borane with acetone (**6**) and ketene (**7**).

Figure 4(a) shows the minimum energy reaction path (MERP) calculated for addition of borane to **6** to form first the complex **8** and then isopropoxyborane (**9**). The first step
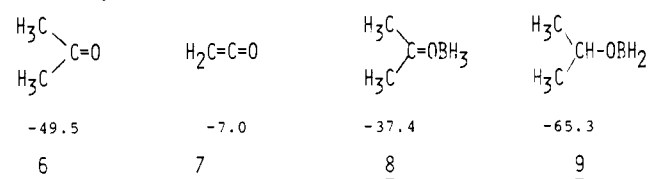
is predicted to be almost thermoneutral, with a low (12.3 kcal/mol) activation energy while the second is strongly exothermic with a much higher activation energy (21 kcal/mol). These results imply that **6** should react with borane in the gas phase to form a loosely bound complex whose further conversion to **9** should occur only at higher temperatures. The geometries of the various species are shown in Figure 5.
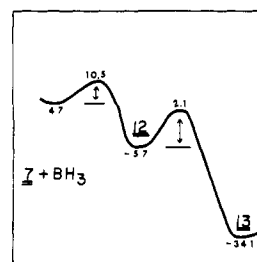
These conclusions are in complete agreement with those reached by Fehlner[22] from studies of the reaction in a fast-flow reactor, the borane being derived from its complex with phosphorus trifluoride. He concluded that the reaction led only to a complex of borane with **6** in which boron is coordinated to oxygen, no addition taking place to the double bond.
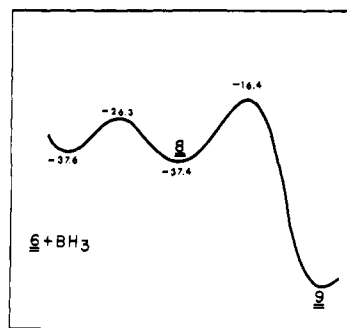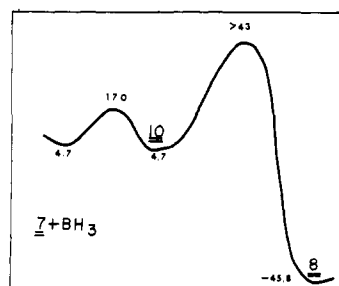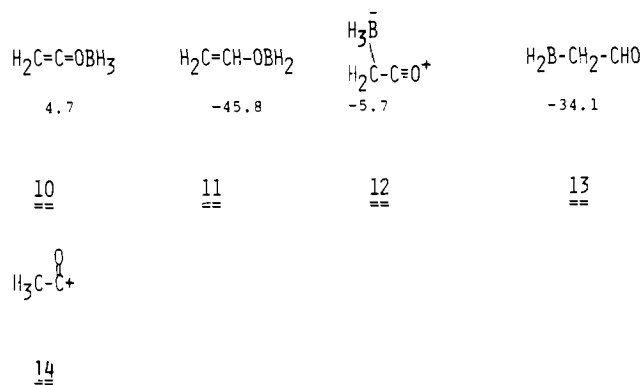

(c)

Figure 4. Calculated MERPs for the reactions of BH_3 (a) with acetone, (b) with ketene (addition to C=O); and (c) with ketene (addition to C=C). Heats of formation (kcal/mol) are given.

Figure 4(b) shows the corresponding MERP for addition of borane to the carbonyl group of ketene (**7**). Its general form is similar to that for the acetone reaction, corresponding to the thermoneutral formation of adduct **10** which rearranges exothermically to vinyloxyborane (**11**). However, the barriers to the formation of **10**, and to its conversion to **11**, are much higher than in the corresponding reactions of **6**. The second transition state (**10** → **11**) was not located precisely, but we established that the corresponding activation energy was greater than 38 kcal/mol. The geometries calculated for **10** and **11** are shown in Figure 5.
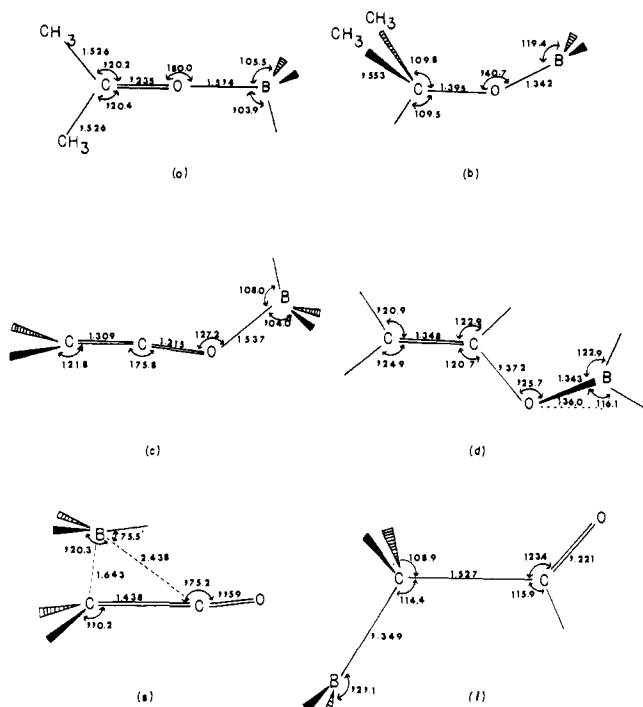
Figure 5. Geometries calculated for (a) **8**, (b) **9**, (c) **10**, (d) **11**, (e) **12**, and (f) **13**.

Figure 6. Orbital overlap in a $p\pi{:}d\pi$ bond, viewed (a) from one side and (b) from above. (c) Orbital overlap in a $s\sigma{:}p\sigma$ bond.

Since **7** contains both C=C and C=O double bonds, it can undergo hydroboration as well as addition of borane to the carbonyl group. Figure 4(c) shows the MERP calculated for the former reaction. This time a zwitterionic intermediate **12** is formed in an exothermic reaction with a low activation energy (5.8 kcal/mol), conversion of **12** to the product **13** requiring somewhat more activation (7.8 kcal/mol). Under conditions where the heat of reaction liberated in the first step can be rapidly dissipated, **12** should then be detectable as a stable intermediate. Fehlner[22] concluded from a study of the reaction in a fast-flow reactor that the product was a π complex with borane attached to the π electrons of the C=C double bond. Since **12** can be regarded as a classical isomer of such a π complex, our calculations are consistent with his observations.

The addition of borane to **7** to form **12** has analogies in other reactions involving electrophilic attack on ketene. One of the unshared pairs of electrons on the oxygen atom of ketene can conjugate with the π electrons of the C=C bond, leading to a vinyl-ether-like system and so facilitating electrophilic attack at the methylene carbon. Thus the reactions of ketene with alcohols are strongly acid-catalyzed, protonation of ketene leading to the acetyl cation **14** which reacts rapidly with the alcohol.

Discussion

The results reported here imply that addition of BH to a double bond is not in itself a facile process. On the contrary, addition of BH_4^- to carbonyl functions is so strongly "forbidden" that the reaction takes place in two distinct steps, by an initial complete transfer of hydride to form a borane and an alkoxide ion. A similar situation seems[21] to occur in the hydrolysis of BH_4^- in alkaline solution, no assistance being apparently provided by nucleophilic attack by hydroxide ion on boron. Here, however, an inverse deuterium kinetic isotope effect was observed, due to the high zero point energy of H_2.

It is therefore evident that the ease of hydroboration must be due to the presence of an empty (2p) AO in borane. This
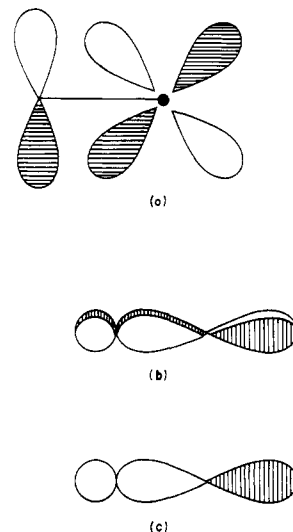
could lead to the formation of an intermediate π complex[22] with the olefin, and rearrangement of the π complex to the product might not be "forbidden".[23] However, the transition state for this rearrangement is in fact similar to that for a direct concerted cycloaddition. Formation of such an intermediate would not therefore in itself account for the ease of hydroboration.

The mode of action of the empty boron AO can in fact be understood very simply from the PMO treatment used by Dewar, Lucken, and Whitehead[24] in 1960 to explain the properties of the phosphonitrile chlorides. In constructing MOs (ψ_μ) from a set of AOs (ϕ_i), we are free to replace the ϕ_i by any arbitrary set of independent linear combinations (χ_m). It may be possible to do this in such a way that the χ_m fall into groups χ_m^ρ, such that each member of a given group but not with any member of any other group. We can then use these χ_m^ρ to construct *localized* MOs ψ_μ^ρ, each ψ_μ^ρ being a function only of the group functions χ_m^ρ. It is easily shown that a description of the molecule in terms of such localized MOs will give results very similar to those from the "correct" description in terms of the nonlocalized MOs ψ_μ. The conventional description of nonconjugated molecules in terms of localized two-center bonds is based on this *localized-bond principle*,[24] the χ_m^ρ being hybrid AOs that overlap in pairs. Localization of this type may be called *overlap localization*. It arises from the directional properties of σ bonds formed by p AOs and on the further directionality confined on them by hybridization.

In the case of a $p\pi{:}p\pi$ conjugated molecule, the π MOs cannot be subdivided by overlap localization because the π bonds formed by a given p AO are nondirectional. In forming π bonds, a p AO behaves in the same way as an s AO does in forming σ bonds. It is true that classical conjugated systems do exhibit localization,[25] but this is due to another effect. In the case of a classical conjugated system, i.e., one for which only a single classical structure can be written, the nodes of the π MOs are concentrated between "singly bonded" pairs of atoms. The π bonds between such pairs of atoms are consequently much weaker than those between pairs of atoms which are doubly bound. This type of localization may be termed *nodal* localization to distinguish it from localization due to overlap.

In the case of $p\pi{:}d\pi$ conjugation, however, overlap localization again becomes possible because π bonds formed by d AOs show directional properties similar to those of σ bonds formed by p AOs (Figure 6). A localized-bond representation can be derived in which each phosphorus atom is $p\pi{:}d\pi$ bonded
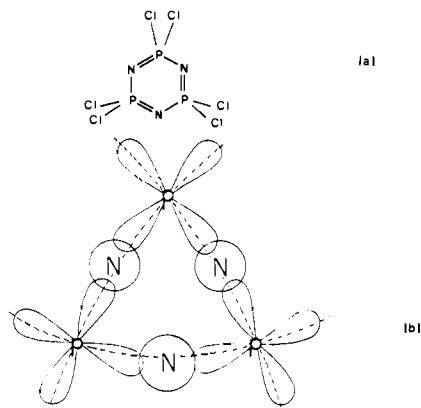
Figure 7. (a) The $PNCl_2$ trimer. (b) Localized $d\pi:p\pi:d\pi$ three-center bonds in the trimer.

Figure 8. Overlap of p AOs in a symmetrical Diels–Alder transition state.

Figure 9. Orbital overlap (a) in the transition state for hydroboration of ethylene, (b) in the transition state for synchronous addition of BH_4^- to CH_2O, (c) in cyclobutadiene, and (d) in the pentadienyl ion. The AOs in (a) and (d) and in (b) and (c) are numbered to indicate the parallel topology of overlap.

to the two neighboring nitrogen atoms via different d AOs of phosphorus. The π system then consists of weakly interacting three-orbital ($d\pi:p\pi:d\pi$) units (Figure 7), each isoconjugate with the allyl cation. All of the PN bonds are thus equivalent, suggesting at first a delocalized π system analogous to that in an aromatic ring. In fact, however, these molecules behave as though the π electrons occupied localized three-center segments, those of their properties that depend on the π electrons being independent of molecular size or topology.

As Evans first realized,[27] the transition state for a synchronous pericyclic reaction is isoconjugate with a π-conjugated system of similar size and connectivity.[5] The difference lies only in the fact that one or more pairs of AOs overlap in σ fashion instead of π fashion. One can classify such interactions as being of $p\sigma:p\sigma$ type. Thus Evans' original example, the transition state for a synchronous Diels–Alder reaction between ethylene and butadiene (Figure 8), contains two $p\sigma:p\sigma$ interactions and four $p\pi:p\pi$ ones.

In the case of conjugated systems where atoms from the third or higher periods participate, the π MOs may become divided into localized segments as a result of such atoms using different d AOs to form π bonds to their neighbors; cf. Figure 7. A similar effect is possible in the case of conjugated systems containing only second-period elements if $p\sigma$-type interactions are present. A second-period atom can use different p AOs to form $p\sigma:p\sigma$ bonds to its neighbors. For this to be possible, it is of course necessary that the atom in question should have two free p AOs to form such bonds. Such a situation can therefore arise only in the case of atoms with isolated p AOs, either empty (as in the case of boron) or filled (nitrogen or oxygen).

The transition state for hydroboration clearly fulfills these conditions (Figure 9(a)). The boron atom can use a sp^3 AO (e) to form the bond to hydrogen (H*) that breaks during the reaction and a second (2p) AO (a) to interact with a 2p AO (b) of the carbon atom to which the boron is eventually linked. Because of the geometry of the system, AO (e) is almost orthogonal to b, while a is almost orthogonal to the 1s AO (d) of H*. The conjugated system is therefore *not* analogous to that in the transition state of a "normal" ($_\sigma 2_s + _\pi 2_s$) cycloaddition. The latter (Figure 9(b)) contains a cyclic arrangement of four interacting AOs, isoconjugate with cyclobutadiene (Figure 9(c)), whereas the transition state for hydroboration contains a linear arrangement of *five* interacting AOs, isoconjugate with the linear pentadienate system (Figure 9(d)). The transition state is therefore *not* antiaromatic. On the contrary, it is isoconjugate with the nonaromatic (but highly resonance-stabilized) pentadienate cation. It is therefore easy to see why hydroboration occurs so readily, in contrast to borohydride reductions. In the borohydride ion, boron has no
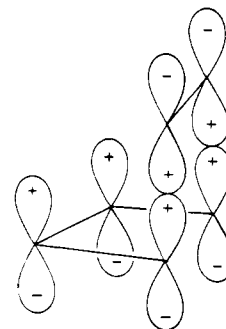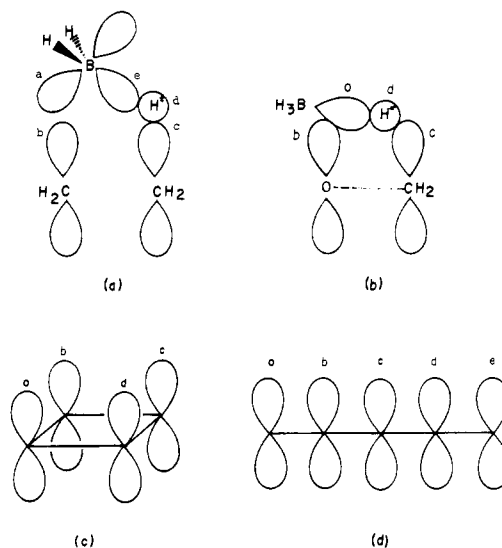
free AO available, so in the transition state it has to use the same AO to form the breaking (B–H) and forming (B–O) bonds.

In the phosphonitrile chlorides and related compounds, two π systems cross one another without interacting, by using different AOs of the atom located at the crossing point. In the transition state for hydroboration, a single σ-conjugated system crosses itself. An analogous crossing in a single π-conjugated system probably occurs in thiabenzenes and related compounds. Clearly some term is needed to describe conjugation of this kind. Since the term cross-conjugation is already bespoken in another sense, *cruciconjugation* seems appropriate.

Lemal et al.[28] first pointed out that the presence of the empty boron AO leads to a break in the cyclic overlap of AOs. They apparently assumed that this in itself was sufficient to explain the ease of the reaction, orbital correlation effects operating only in cyclic systems. The same effects can, however, equally well operate in the case of acyclic ones. Thus the combination of singlet carbene with carbon monoxide by a linear path, to form ketene, is "forbidden" for the same reason that the "least motion" addition of CH_2 to H_2 is "forbidden". Lemal et al. also assumed that effects of this kind can only occur in *pseudopericyclic* processes, these being defined as ones in which a nonbonding AO and a bonding AO interchange roles. This definition, however, not only includes reactions of quite different type but also excludes ones that are cruciconjugated.
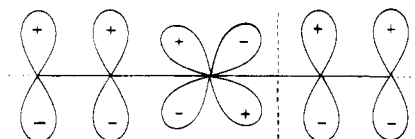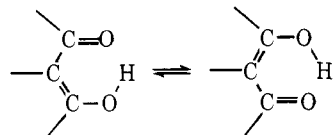
Figure 10. Phase dislocation in a cyclic conjugated system through inclusion of a d AO (after Craig[29]).

Thus they cite the interconversion of isomeric dienols:

Here the conjugated systems in the reactant, product, and transition state are qualitatively similar, the bond alternation being due to a difference in electronegativity between the oxygen atom cores. This is an isoconjugate reaction, not a cruciconjugated one.

Conversely, the following process would be cruciconjugated although no nonbonded AO is involved:
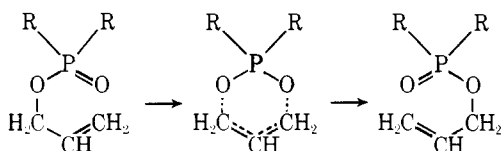

The phosphorus atom is π bonded throughout to both adjacent oxygen atoms, using different d AOs of phosphorus (cf. Figure 7). The transition state contains a seven-AO cruciconjugated system similar to that in thiabenzene and related compounds.

This discussion also has a bearing on the structures of the transition states of genuine pericyclic reactions which, in Evans' theory,[27] have cyclic conjugated structures which may be aromatic or antiaromatic.

In normal planar cyclic pπ-conjugated systems, the phases of the p AOs can be chosen so as to make all overlap between adjacent AOs positive. Craig[29] showed in 1958 that this may no longer be the case if the ring contains d AOs as well as p AOs, the relationship between stability and ring size being different for a ring containing alternating p and d AOs from that for normal Hückel cyclic polyenes. He used this model to interpret the behavior of the phosphonitrile chlorides but subsequent work,[26] referred to above, showed this to be incorrect.

As Craig pointed out, replacement of a p AO in a cyclic polyene by a d AO leads to a phase dislocation, due to the change in phase on passing from one side of a d AO to the other (Figure 10). If the number of d AOs in a ring is odd, it is impossible to cancel out the phase dislocations by altering the phases of the AOs. One *essential* phase dislocation remains. It is immediately evident from the PMO theory of aromaticity, proposed by Dewar[30] in 1952, that the rules for aromaticity in this alternative type of cyclic conjugated system are exactly the opposite of those for normal Hückel systems.[31] The distinction arises from the different nodal properties of the π MOs in the two systems. The topology of the π MOs is the same in both; i.e., each π MO is split into two mirror-image rings by a nodal plane.

In 1964 Heilbronner[32] examined species derived from linear polyenes by twisting them through 180° and then joining the ends to form conjugated rings. Assuming the twist to be evenly shared between the methine groups and using simple HMO theory, he showed that the rules for aromaticity in such systems are exactly the reverse of those in normal Hückel cyclic polymethines. Here again an essential phase dislocation is present,
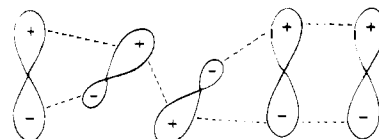
(a)
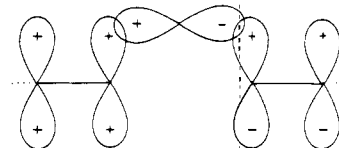
(b)

Figure 11. (a) Transition state for a conrotatory electrocyclic reaction. (b) Topologically equivalent structure in terms of pσ conjugation.

so such compounds also belong to the anti-Hückel class indicated above.[31] Here, however, the topology of the π MOs is different, each π MO forming a single continuous ring with the topology of a Moebius strip. Similar systems can be envisaged in which the angle of twist is a multiple at 180°. Systems where the multiple is even are of Hückel type and those where it is odd of anti-Hückel type. The former resemble normal Hückel systems in that each π MO essentially forms two distinct rings, effectively separated by a nodal plane, while the latter resemble the simple Moebius systems in that each π MO forms a single continuous ring.

Three distinct types of cyclic π-conjugated systems have thus been recognized: normal Hückel pπ-conjugated systems; anti-Hückel pπ:dπ-conjugated systems; and anti-Hückel Moebius-type systems.

The idea that pericyclic transition states might be of anti-Hückel type was first proposed in print by Zimmerman,[33] who restated Evans' theory of pericyclic reactions without acknowledgment. Since Zimmerman was also apparently unaware of Criag's[29] work and since Heilbronner did not refer to it in his paper,[32] Zimmerman described anti-Hückel transition states as being of Moebius type, presumably in the belief that this was the only kind of π system that could exhibit essential phase dislocations. This term has been widely adopted although in fact *no* pericyclic transition state has yet been reported which has Moebius-type topology. As our discussion of hydroboration has shown, replacement of a pπ AO in a conjugated ring by a pσ AO has the same effect as replacing it by a d AO. Anti-Hückel transition states arise in this way, as can be shown most clearly by a specific example, i.e., the transition state for a synchronous conrotatory electrocyclic reaction. The overlap here (Figure 11(a)) is topologically equivalent to that in an otherwise pπ-conjugated ring where one pπ AO has been replaced by a pσ one (Figure 11(b)). This in turn plays the role of half a d AO (cf Figure 11(b) with Figure 10).

Since systems with genuine Moebius topology may be discovered in the future, it seems inappropriate to use the term in a more general sense, to describe any cyclic conjugated system containing an essential phase dislocation. We would urge use of the neutral term anti-Hückel for the general case.

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ENDOR of Organic Triplet- and Quartet-State Molecules in Liquid Solutions and in Rigid Media

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Abstract: ESR, ENDOR, electron-nuclear-triple resonance (TRIPLE), and ENDOR-induced ESR measurements have been performed on a variety of phenoxyl-type biradicals and triradicals in isotropic fluid solutions and in rigid media. The free nuclear frequency absorption lines, previously predicted for triplet-state molecules, could readily be detected in the rigid-matrix ENDOR spectra of the biradicals. For the first time the fluid-solution and rigid-media ENDOR spectra of triradicals in the quartet spin state could be obtained. The unambiguous assignment of the resonance lines to the respective spin states was achieved by using TRIPLE and ENDOR-induced ESR techniques. The signs of the zero-field splitting parameters D could be determined relative to those of the hyperfine couplings thus providing some structural conclusions for the radicals under study. A qualitative outline of the dependence of the spin relaxation processes on the electron–electron dipolar interaction of the multispin systems is given.

Introduction

In recent years there has been considerable interest in studying organic multispin systems by means of electron spin resonance (ESR).[2] Unfortunately, most of the isotropic solution ESR spectra are only poorly resolved due to the anisotropic electron–electron dipolar interaction (zfs) which often exceeds 100 MHz and is then no longer averaged out by the Brownian motion. Moreover, the exchange interaction, also present in all multispin systems, reduces the hyperfine splittings as compared to those of the corresponding monoradicals. It therefore appeared promising to apply the electron nuclear double resonance (ENDOR) technique with its larger resolving power.

Recently[3] we reported the first successful ENDOR experiments on some galvinoxyl biradicals in liquid solution. Apart from being able to resolve hyperfine splittings not yet observed by ESR, the most remarkable result was the absence of the line at the free proton frequency ν_p expected for biradicals such as

Yang's biradical (**1c**) in which the exchange integral J is much larger than the hyperfine coupling. This "ν_p line" was expected to arise from NMR transitions within the $M_S = 0$ electron spin manifold. Actually it was the absence of this line which in some cases prevented the unambiguous assignment of the ENDOR spectrum to a biradical. The failure to observe the ν_p line could be explained by considering that, in liquid solution, the ESR transitions $|-1,M_I\rangle \leftrightarrow |0,M_I\rangle$ and $|0,M_I\rangle \leftrightarrow |1,M_I\rangle$ are degenerate within the ESR line width. Therefore both transitions are pumped equally strongly thus leaving the thermal nuclear spin polarization in the $M_S = 0$ manifold undisturbed.

Alternatively, one would expect the ν_p line to show up in a *rigid-matrix* ENDOR spectrum since the degeneracy of the ESR transitions is now lifted by the electron–electron dipolar interaction. The present communication contains a detailed report and discussion of our biradical studies in rigid matrices. We have reported on ENDOR measurements on some carbon-13-labeled galvinoxyl biradicals in rigid media.[4]

For a quartet-state molecule with $S = 3/2$ and $|J| \gg |a|$ one expects a distinctly different behavior of the transitions $|3/2, M_I\rangle \leftrightarrow |1/2,M_I\rangle$ and $|-3/2,M_I\rangle \leftrightarrow |-1/2,M_I\rangle$ on the one hand

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