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 (35) For the free state, the lone-pair LMO is the so-called sp^2 lone pair of the NH_2 radical, while in the final NH_3 molecule it is the so-called sp^3 lone pair. However, we found that the contours of the lone-pair LMOs are essentially superimposable at all range of the reaction except for the direction of their axes.

Through-Bond Interaction of Two Mutually Perpendicular π Systems. A Comparison with Spiroconjugation¹

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Abstract: It is postulated that two mutually perpendicular π systems can interact effectively via the σ bonds of a cyclobutane ring. This interaction leads to the opposite splitting as predicted for spiroconjugation. Several model systems are discussed.

If two mutually perpendicular π systems $\pi(A)$ and $\pi(A')$ are linked together as shown in Figure 1a, the associated π orbitals interact through space. This phenomenon has been studied theoretically^{2,3} as well as by experimental techniques^{2,4-6} and is called spiroconjugation. The controlling factors are evident from perturbation arguments.⁷ To result in sizable changes of the electronic structure of such molecules due to spiroconjugation, the following two conditions must therefore be met: (a) The interaction term $\beta_{\text{spiro}}^{\mu\nu} = \langle \pi^\mu(A) | H | \pi^\nu(A') \rangle$ must be large. (b) The interacting orbitals $\pi^\mu(A)$ and $\pi^\nu(A')$ should have degenerate (or nearly degenerate) basis orbital energies. The latter condition leads to the expectation that spiroconjugation is most important for systems in which the formal π fragments $\pi(A)$ and $\pi(A')$ are identical. Such molecules have D_{2d} symmetry if $\pi(A)$ and $\pi(A')$ are mutually perpendicular, planar π systems. Within this symmetry, the total representation of π orbitals factorizes into three sets of A_2 , B_1 , and E symmetry. In other words, π orbitals with an even number of nodal planes split into an A_2 and a B_1 combination, while π orbitals with an odd number of nodal planes remain degenerate, since $\beta_{\text{spiro}}^{\mu\nu}$ is 0 for symmetry reasons. Two points should be noted: (1) π orbitals have one nodal plane to begin with, and (2) the a_2 and b_1 orbitals will remain strictly σ - π orthogonal, while the e levels will mix with appropriate σ orbitals.⁸ Theory^{2,3} supports the expectation that the "in phase" combinations B_1 will be stabilized while the "out of phase" combinations A_2 are destabilized. This is illustrated in Figure 1a.

Apart from these considerations, the effects of spiro conjugation will be determined mainly by the size of the interaction matrix elements $\beta_{\text{spiro}}^{\mu\nu}$. Within the Mulliken approximation⁹ (i.e., $\beta_{\text{spiro}}^{\mu\nu} = kS^{\mu\nu}$), this term will remain small throughout, since the overlap integrals $S^{\mu\nu}$ between the cou-

pling atomic orbitals (i.e., the terminal p orbitals of $\pi(A)$ and $\pi(A')$) are small in magnitude, typically about 0.025.³

The disadvantage of the small overlap integral can be overruled by introducing "relay orbitals". With this we mean orbitals which enforce the interaction. Obviously a cyclobutane ring offers perfect conditions as a through-bond coupling partner: (1) the symmetry of the corresponding molecules is maintained and (2) cyclobutane has high-lying occupied and low-lying unoccupied orbitals of appropriate symmetry.

It should be noted that there is no intrinsic difference between the general case of a through-bond interaction¹⁰ of two π orbitals and the specific case discussed here. The one σ bond in the former is replaced by a four-membered ring in the latter. This way the π bonds are locked into a rigid perpendicular arrangement as in spiro compounds. The four-membered ring as a link is unique insofar as replacing it by any other monocyclic system leads to steric difficulties or a reduction of symmetry (the π bonds are not perpendicular any more). It is known that, if such through-bond interaction¹⁰ is dominant, it results in a reversal of the orbital sequence. This is indicated in Figure 1b.

To discuss the effects of this postulated through-bond spiroconjugation, we will refer to the four typical model systems **1**, **2**, **3**, and **4** shown in Scheme I and compare them with the through-space analogues **1'**, **2'**, **3'**, and **4'**. Furthermore, we wish to illustrate the parallelism and difference to be expected between the two types of systems. The extension to systems where the systems $\pi(A)$ and $\pi(A')$ are no longer equivalent is given later on.

"Relay Orbitals"

As mentioned before, we consider the cyclobutane ring in the tricyclic compounds (Figure 1b) as a relay which enforces

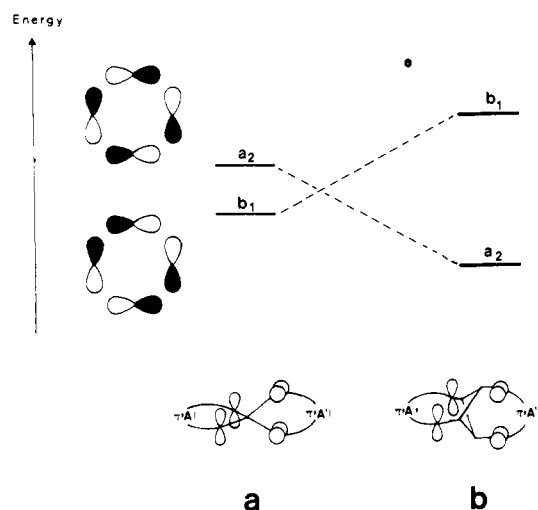
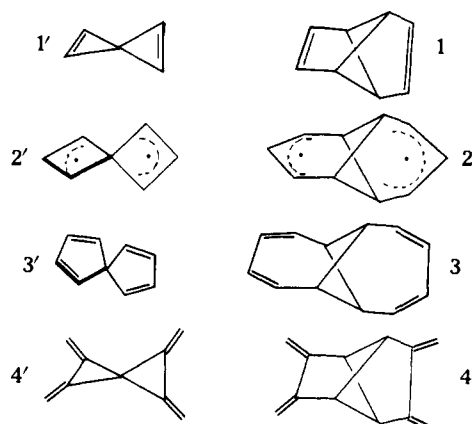


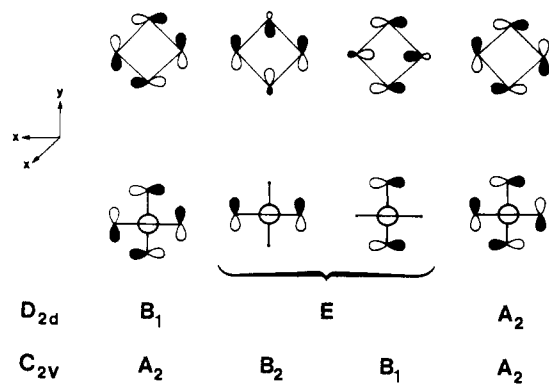
Figure 1. Orbital sequence for b_1 and a_2 in the spiro compounds (a) and the corresponding tricyclic compounds (b).

Scheme I



the interaction between the mutually perpendicular π systems $\pi(A)$ and $\pi(A')$. To understand this "relay effect" we first have to discuss the relevant orbitals in cyclobutane.

Cyclobutane is known to possess D_{2d} symmetry.¹¹ Photoelectron spectroscopy¹² supports theoretical predictions^{13,14} that the three highest occupied molecular orbitals are linear combinations of E and B_1 symmetry with high p character. A convenient representation of the highest occupied (e and b_1) orbitals and unoccupied (a_2) orbital of cyclobutane is given below. These drawings (top row) are compared with the corresponding wave functions of the spiro compounds viewed along the z axis (Newman projection). The symmetry behavior in D_{2d} and C_{2v} symmetry is given below the drawings.



As already indicated, the e orbitals (orbitals corresponding to the irreducible representation E in the point group D_{2d}) will

Table I. Calculated Orbital Energy Differences for 1-4

Compd	Orbitals	EH, eV	MINDO/3, eV
1	$2b_1-1a_2$	1.59	1.06
1'	$1b_1-1a_2$	-0.32	-0.14
2	$2b_1-1a_2$	1.71	6.23
2'	$1b_1-1a_2$	-0.66	-5.33
3	$2b_1-1a_2$	1.00	1.24
3'	$3b_1-2a_2$	0.81	0.23
	$1b_1-1a_2$	-0.55	-0.63
4	$2b_1-2b_2$	-0.60	-0.25
	$2b_1-1a_2$	0.45	0.77
	$3b_1-2a_2$	1.44	0.90
4'	$1b_1-1a_2$	-0.18	-0.08
	$2b_1-2a_2$	-0.31	-0.10

interact with the e combinations of the π systems and will not lead to removal of the degeneracies. The b_1 orbital, however, and to a minor extent the a_2 orbital will affect the corresponding π orbitals and thus lead to a reversal of the orbital sequence as compared to spiroconjugation.

We wish to mention an alternative point of view: Looking at the symmetry properties of the three occupied cyclobutane orbitals shown above the application of a united atom model is suggestive. The two e wave functions transform like the p_x and p_y and the b_1 wave function like the d_{xy} "atomic orbital" of this atom. These orbitals again are the complete subset of an atom including d orbitals that will interact with the two π systems. The most important difference lies in the basis orbital energies relative to those of the adjacent π systems $\pi(A)$ and $\pi(A')$.

Calculation Procedure

To compare the tricyclic molecules of the type defined in Figure 1b with those of the type defined in Figure 1a we have to derive their molecular orbitals. Since the geometries of the molecules are not known we have calculated them by minimizing the total energy of the systems with respect to the geometrical variables using the MINDO/3¹⁵ method. The resulting structures are summarized in Figure 2. Since our qualitative argumentation is based on a simple one-electron model we have preferred to draw our correlation diagram according to the results of extended Hückel (EH)¹⁶ calculations. These were performed, using the geometries derived by the MINDO/3 procedure. In Table I we have listed the calculated energy differences $\Delta = \epsilon(b_1) - \epsilon(a_2)$ for compounds 1-4 and 1'-4'.

Comparison of 1 with 1'

In Figure 3 we have constructed the highest occupied and lowest unoccupied MOs of spiropentadiene (1') from two perpendicular π units (left). As expected from the qualitative arguments outlined above the two occupied π orbitals of the ethylene fragments combine to a degenerate pair of MOs which interact with the σ frame. The unoccupied π^* basis orbitals yield linear combinations of A_2 and B_1 symmetry having different orbital energies.

On the right side of this figure the highest occupied and lowest unoccupied MOs of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (1) have been constructed from the π and π^* MOs of two perpendicular ethylene units and the relevant Walsh orbitals of cyclobutane discussed above.

From Table I and Figure 3 it is evident that the split between $2b_1$ and $1a_2$ of 1 is much larger than the corresponding one ($1b_1$ and $1a_2$) of 1'. This should result in a considerable difference between the electronic spectra of both molecules. So far only 1 has been synthesized. The remarkably low energy of its first transition (300 nm)¹⁷ has been discussed in terms of a similar

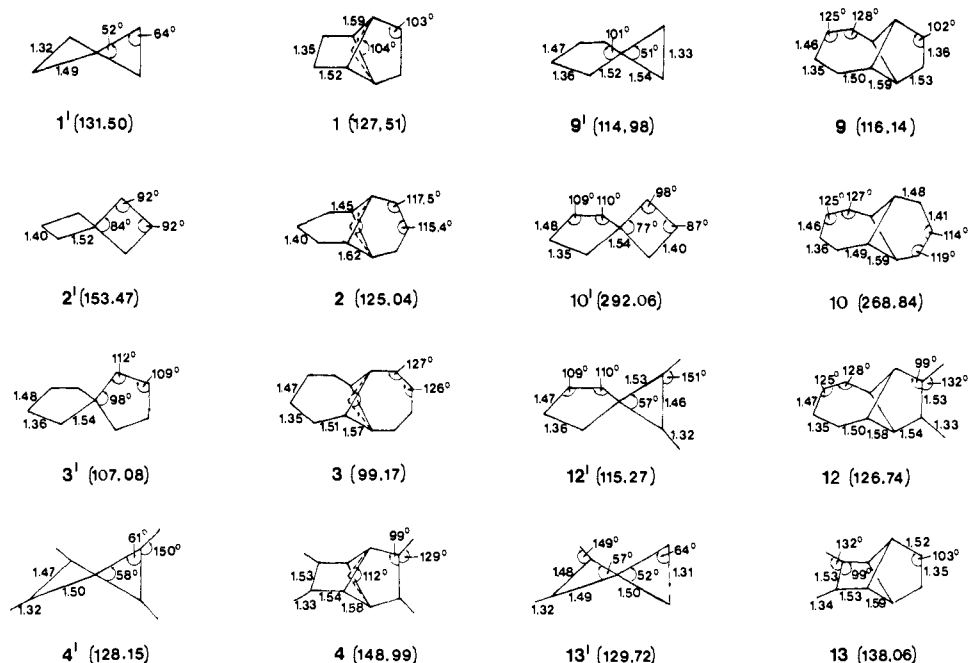


Figure 2. Comparison between the calculated bond lengths and angles for the spiro compounds 1'-4', 9', 10', 12' and 13' with the corresponding tricyclic compounds 1-4, 9, 10, 12, and 13. For compounds 1'-4' and 1-4 D_{2d} symmetry and for the remainder C_{2v} symmetry was assumed. The calculated heats of formation in kcal/mol are given in brackets.

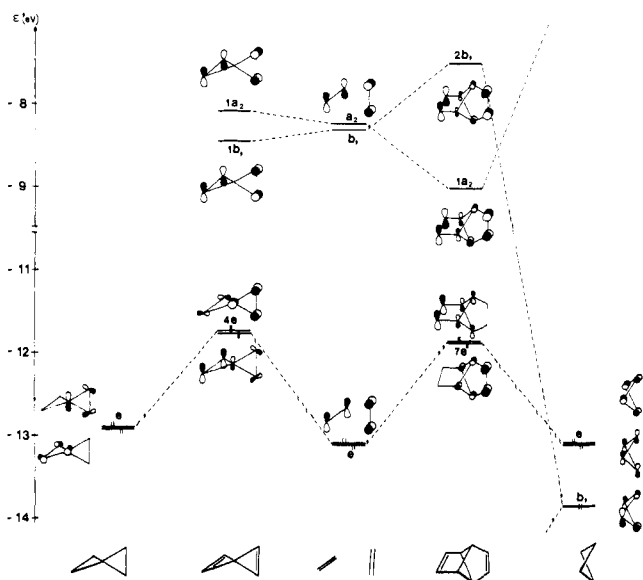


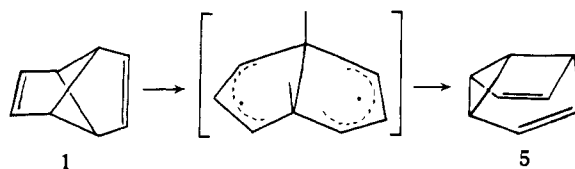
Figure 3. (left) Interaction diagram of two perpendicular ethylene parts in spiro-pentadiene (1). (right) Interaction diagram of two perpendicular ethylene parts with the Walsh orbitals of cyclobutane to yield tricyclo[3.3.0.0^{2,6}]octadiene (1).

interaction diagram shown as in Figure 3^{14,18} but from a different point of view.

The MINDO/3 method predicts a rather long bond length (1.584 Å) in the cyclobutane part of **1** while the C-C bond length in cyclobutane is calculated as 1.535 Å.¹⁹ This might be due to a general shortcoming of the ZDO methods which ignore the repulsion between filled MOs.²² However, it should be noted that for tricyclo[3.3.0.0^{2,6}]octane and tricyclo[3.3.0.0^{2,6}]octene the C-C bond lengths calculated for the cyclobutane part (1.58 and 1.59 Å) by MINDO/3²⁰ were found only slightly longer than the experimental ones (1.56 and 1.58 Å).²¹ This minute discrepancy might be associated with the overestimation of strain by MINDO/3 in such molecules.

The same trends (weakening of the cyclobutane bonds) have been found²² on the basis of population analysis. Experimental evidence¹⁷ supports these results: **1** rearranges to semibullvalene (**5**) at room temperature. From the possible mechanism discussed so far^{23,24} the diradical mechanism (indicated in Scheme II) seems the most likely one.²³

Scheme II



Comparison of **2** with **2'**

As in the case of spiro compounds, the most interesting molecules will be those in which the frontier orbitals are affected by the interaction. Obviously, this situation is given in the diradicals **2** and **2'**.

The corresponding MO schemes shown in Figure 4 are derived as those of Figure 3. MINDO/3 predicts both radicals to have triplet ground states. Hence, the geometries (shown in Figure 2) used for the EHT calculation correspond to the equilibrium structure of the triplet. Again, the predicted split between the a_2 and the b_1 levels (i.e., the HOMO/LUMO separation in this case) is considerably larger for **2** than for **2'**. Accordingly, the calculated triplet/singlet separation for **2** (= 4.9 kcal/mol) is much smaller than for **2'** (= 13.6 kcal/mol). The corresponding singlet energies have been calculated by applying a restricted 3×3 CI treatment.

A π -SCF-CI calculation carried out on **2'**³ predicts that the singlet state (1A_1) is more stable by about 0.6 eV than the triplet state (3B_2). The known tendency of MINDO/3 to exaggerate the stabilities of triplets leads to our conclusion that **2** possesses most likely a singlet ground state.

The rearrangement analogous to that in Scheme II leads for **2** to *cis*-9,10-dihydronaphthalene (**6**) (see Scheme III). Since compound **6** is calculated to be more stable by 50 kcal/mol than **2** and the activation energy of the above reaction is ex-

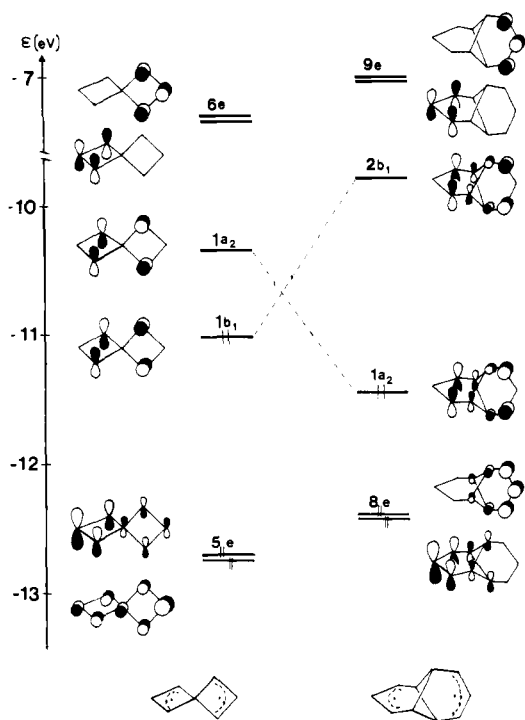
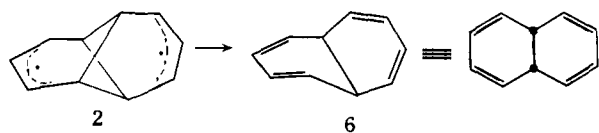


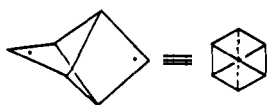
Figure 4. Comparison of the highest occupied and lowest unoccupied π MOs of **2** with **2'**.

Scheme III



pected to be small, compound **2** corresponds at most to a local minimum on the $(\text{CH})_{10}$ hypersurface.²⁵ Even if **2** has a singlet ground state it is unlikely to be isolated. However, it should be mentioned that recent results on the degenerate rearrangements of *cis*-9,10-dihydronaphthalene derivatives²⁷ can be interpreted to occur via a derivative of **2**.²⁸ Analogous to **2'**, the tricyclic compound **2** is just the first member of a series for which stabilization of the singlet state might be possible. In general it is found that a remarkable stabilization occurs only when in the formula given in Figure 1 $\pi(\text{A}) \equiv \pi(\text{A}')$ and each system contains $4q + 3$ ($q = 0, 1, 2$) CH groups.

Among those open-shell structures which are not stabilized we just mention for the sake of curiosity the most simple one, an isomer of benzene:



It represents a three-dimensional drawing of Claus' benzene formula.

Comparison of **3** with **3'**

To conclude the discussion of the highly symmetrical species with endo double bonds, we refer to Figure 5. Again, the MO diagrams of **3** and **3'** are presented as before; the optimized structures are shown in Figure 2.

Spiro[4.4]nonatetraene (**3'**) represents a classical example to study the effects of spiroconjugation. The compound is relatively stable and thus suitable for most experimental techniques.²⁶ Its orbital pattern has, therefore, been discussed on several occasions in the literature within theoretical²⁻⁴ and experimental^{4,6} context. By means of PE and electron spec-

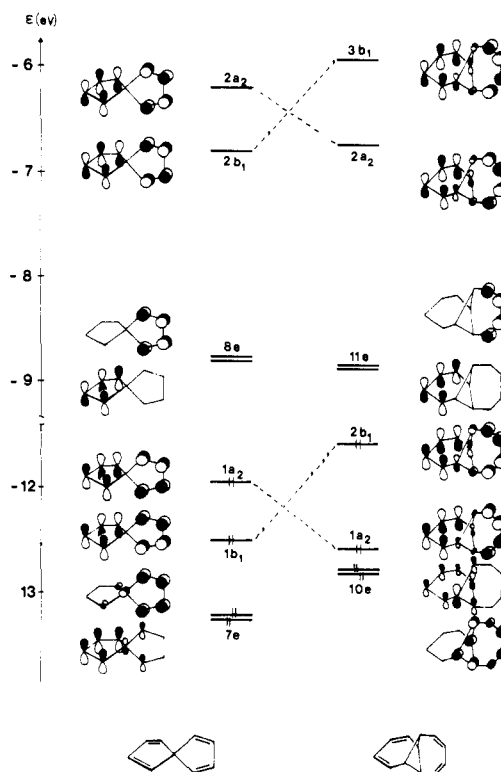
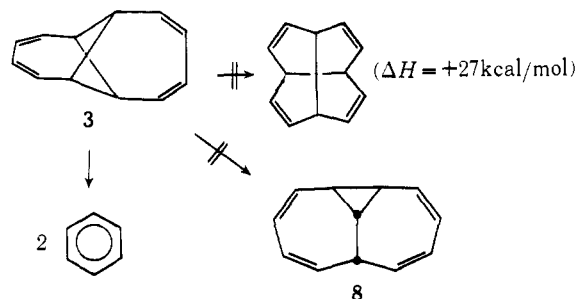


Figure 5. Comparison of the highest occupied and lowest unoccupied π MOs of spiro[4.4]nonatetraene (**3'**) with those of tricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (**3**).

troscopy the gap between $1a_2$ and $1b_2$ has been found to be 1.2 eV. MINDO/3 underestimates the through-space interaction by 33%.²

On the other hand, the through-bond homologue **3** remains a theoretical curiosity so far. It seems to be a possible stable benzene dimer, since the corresponding rearrangement observed with **1** and expected for **2** in this case leads to molecules of even higher energies. While its rearrangement to tricyclo[5.5.0.0^{4,10}]dodeca-2,5,8,11-tetraene (**7**) seems to be energetically unfavorable, Dreiding models of **8** suggest that this molecule is sterically impossible.

Scheme IV



Energetically the most winning rearrangement would be the fragmentation of **3** to yield two benzene molecules. This would be accompanied by a gain of more than 49 kcal/mol. However, such a reaction involves the cleavage of four bonds and is, therefore, most likely associated with a large activation energy. In addition, MINDO/3 is known to overestimate the strain in compact, globular molecules such as **3**. This tends to support the conclusion that **3** is indeed stable.

Comparison of **4** with **4'**

While the systems **1** and **2** are known or predicted to be rather labile toward rearrangement, 3,4,7,8-tetramethylene-

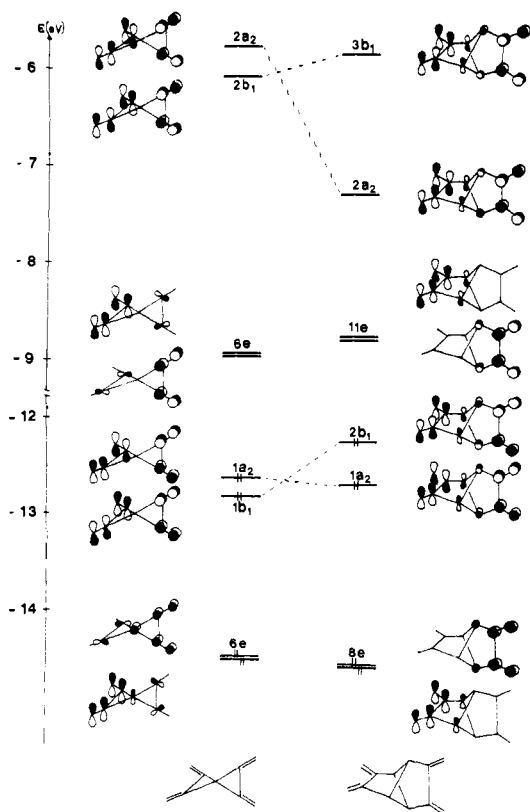
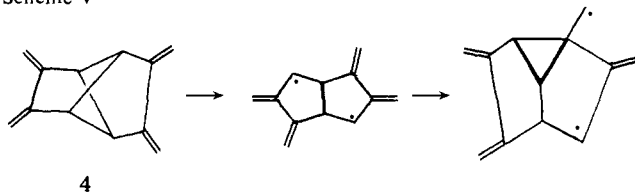


Figure 6. Comparison of the highest occupied and lowest unoccupied π MOs of tetramethylenespiro[2.2]pentane ($4'$) with those of 3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (4).

tricyclo[3.3.0.0^{2,6}]octane (4) should be relatively stable since its 1,2,5,6-tetramethyl derivative is formed by pyrolysis at 380 °C.²⁹ In Figure 6 we have compared the MO diagrams of 4 and $4'$. As anticipated we obtain very similar patterns as shown in Figure 5. The large difference in stability between 1 and 4 can be understood by simply considering a similar path (Scheme V) for a rearrangement of 4 , analogous to that of 1 shown in Scheme II. The proposed rearrangement would lead to a diradical and is obviously not a favorable getaway for 4 . Analogous conclusions were reached by Borden et al.²²

Scheme V



Our calculations corroborate the findings by others²² who explained the observed difference of stability between 1 and 4 in terms of a population analysis and by comparing the energetics of appropriate isodesmic reactions.²² The net π bond order between the unsaturated bridge and the cyclobutane ring is smaller in 1 (0.001) than in 4 (0.034).

A comparison between the calculated net charges on the carbon centers for the molecules with D_{2d} symmetry reveals that the cyclobutane carbon atoms in 1 , 2 , 3 , and 4 possess slightly positive charge as do the central carbons of the spiro systems in $1'$, $2'$, $3'$, and $4'$. The calculated bond lengths (Figure 2) for 1 , 3 , and 4 as well as for their corresponding spiro compounds $1'$, $3'$, and $4'$ are as anticipated; the longest bonds are predicted to occur in the cyclobutane part; the rest show strong alternation.

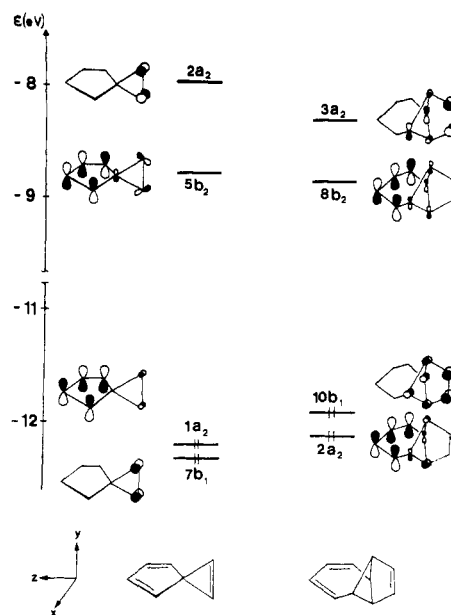


Figure 7. Comparison of the highest occupied and lowest unoccupied π MOs of spiro[4.2]heptatriene ($9'$) with those of tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene (9).

Examples of Lower Symmetry

As outlined in the starting section, spiroconjugation only leads to sizable effects if this interaction is of first order, i.e., if the through-space interaction takes place between degenerate or nearly degenerate π orbitals.

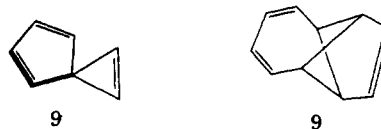
This is quite different in "through-bond spiro" systems. For the indirect coupling via "relay orbitals", the corresponding off-diagonal element

$$H_{\pi\sigma} = \langle \pi | H | \sigma_{B_1} \rangle$$

is larger (numerically about ten times as large as for through-space coupling). This perturbation is second order, but the result is affected by the relative energy of the π orbitals as compared to the coupling Walsh orbitals as well. Hence, even in the case where spiroconjugation has no sizable impact ($A \neq A'$ in Figure 1a), through-bond spiroconjugation might lead to remarkable effects.

There is a large number of possible combinations one can think of between different π systems of moderate size. To proceed, we wish to compare some specific examples with their spiro counterparts. For this class of compounds, the symmetry is no longer D_{2d} but C_{2v} . The symmetry behavior of the "relay orbitals" in this symmetry group has been given above.

As a first example, we shall compare tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene (9) with its spiro counterpart ($9'$). The cor-



responding MO schemes, calculated as outlined above, are compared in Figure 7.

The spiroconjugation in $9'$ should lead to a stabilization of the molecule, since the virtual π^* orbital of the cyclopropene part should interact with the antisymmetric π orbital of the butadiene system in the molecule, which is the HOMO of this molecule. Surprisingly enough, photoelectron spectroscopic evidence³⁰ shows that this effect is negligible and is in fact overruled by small charge drifts in the carbon framework. This explanation was based on a MINDO/3 calculation which satisfactorily parallels the unexpected experimental finding

that the 6,7-diethyl derivative of **9'** has a lower first ionization potential than the corresponding 6,7-dihydrodiethyl derivative.

Calculations on **9** predict that an analogue charge drift is absent, since the responsible orbital ($8b_1(\sigma^*)$ in **9'**) lies much higher in energy and its interaction with occupied orbitals is minute. This manifests itself in a very small calculated dipole moment of **9** (0.05 D) as compared to **9'** (1.39 D). In addition, the MINDO/3 calculation predicts that the mentioned paradox observed in **9'** is absent for the hypothetical molecule **9**. Accordingly, the HOMO of **9** ($\epsilon_{\text{HOMO}} = -8.50$ eV) is slightly stabilized as compared to its dihydro derivative ($\epsilon_{\text{HOMO}} = -8.44$ eV).

Cations

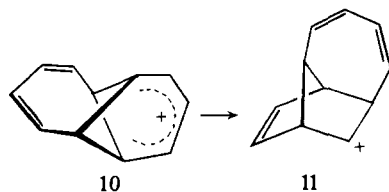
A most interesting class of compounds that should be discussed are closed-shell cations such as the tricyclo[5.4.0.0^{2,8}]-dodeca-3,5,9-trienyl cation (**10**). Cations of this type can be



generated by solvolysis of appropriate systems. A vital question of conjugation in such systems is the distribution of the positive charge in the corresponding cation. This effect essentially determines whether or not the cation can be effectively stabilized by appropriate substitution of the parent molecule. The calculated optimized structures of both molecules are shown in Figure 2.

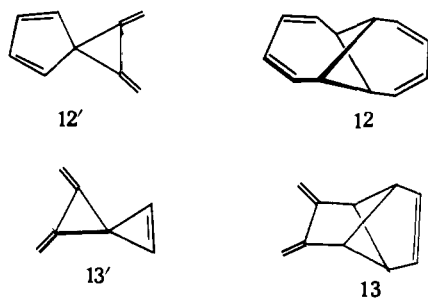
The result is that the interaction between the allylic part and the bicyclo[4.1.1]octa-2,4-diene part is quite effective. While in **10'** the positive charge is essentially localized in the allylic moiety it is delocalized to a larger extent in **10**, especially to the centers 2 and 7.

Strained cations such as **10** might undergo a Wagner-Meerwein rearrangement. In case of **10** such a reaction would lead to the substituted norbornene system **11**.



Exo Methylene

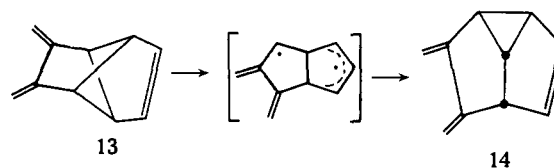
We have already discussed the case of symmetrical 3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**4**). Its stability was thus easily rationalized by the fact that its rearrangement does not lead to a stable product. This argument, however, must not hold for molecules of lower symmetry such as 9,10-dimethylenetricyclo[5.3.0.0^{2,8}]deca-3,5-diene (**12**) or 3,4-dimethylenetricyclo[3.3.0.0^{2,6}]octene (**7**) (**13**). In analogy



to **1** compound **13** is expected to rearrange by the mechanism proposed in Scheme VI.²³ Assuming that this reaction is again the dominant decomposition process of **13** one can estimate the

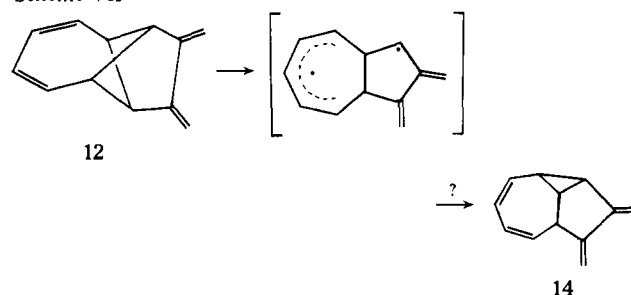
thermal stability²² of this molecule considering the bond length in its cyclobutane moiety. The bond lengths calculated for the cyclobutane bonds in **13** (1.59 Å) are identical with those predicted for **1** (see Figure 2). This should result in approximately the same activation energy for the corresponding rearrangement indicated in Scheme VI.

Scheme VI



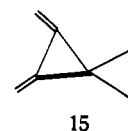
In analogy to the possible rearrangement of **3** to **8** (Scheme IV), for compound **12** a similar rearrangement might also be difficult owing to steric interactions in **14** as indicated in Scheme VII. The calculated bond lengths and angles of **12**, **12'**, **13**, and **13'** are given in Figure 2.

Scheme VII



As anticipated the calculated geometrical parameters and charges as well as the energy differences between the highest occupied and lowest unoccupied π orbitals are about intermediate between **3** and **4** in case of **12** and between **1** and **4** in case of **13**.

The charge distribution in **13'** and the calculated dipole moment (1.26 D) deserve some comments. This parallels very much the results obtained for **9'**.³⁰ A charge transfer in **13'** from the cyclopropane moiety to the 2,3-*exo*-methylenecyclopropane part is predicted. As a result of this the ionization potential which is due to an ionization out of the $1a_2$ orbital of **13'** is predicted to be lower in energy (9.02 eV) than the corresponding one in its dihydro derivative **15'** (9.20 eV).



Concluding Remarks

The main issue of this paper was to demonstrate that two mutually perpendicular π systems can interact with each other quite effectively via the σ bonds of a four-membered ring. The argumentation used is based upon a strong interaction of the Walsh orbitals of the cyclobutane ring and the π orbitals. Such an interaction has been demonstrated by means of electronic absorption spectroscopy¹⁸ and photoelectron spectroscopy.³¹

The MINDO/3 method has been proven extremely reliable in predicting geometries and in reproducing the orbital energies of bicyclic and tricyclic systems^{20,31} of the kind we discussed in this paper. In case of spiro systems, however, the MINDO/3 method seems to underestimate the through-space π interaction by about 33%.²

The most interesting examples are those where the HOMO or LUMO has been influenced by the through-bond interaction. In these cases not only the energy of these frontier orbitals

has been changed but also its symmetry. We expect in these examples interesting consequences for the reactivity.

From the many examples which are possible we only chose a few representative ones to demonstrate our arguments. Including hetero systems there seems to be a large, interesting variety of molecules for which to study through-bond interactions. Synthetic efforts seem worthwhile to investigate the theoretical predictions.

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Oscillations in Chemical Systems. 24.¹ Oscillatory Decomposition of Formic Acid in Sulfuric Acid

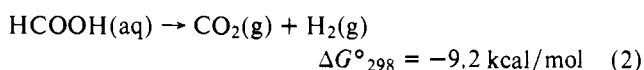
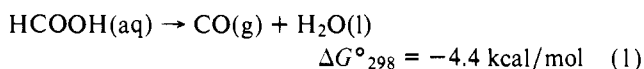
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Abstract: We have confirmed an observation reported by Morgan over 60 years ago that carbon monoxide is evolved in repetitive bursts when formic acid is heated to 55 °C in concentrated sulfuric acid. The principal dehydration-decarbonylation reaction cannot be based on acid catalysis as has been generally believed. Small additions of formaldehyde temporarily inhibit the reaction, and we have developed a mechanism based on hydroxyl radical catalysis of formic acid decomposition. That mechanism also invokes the very large increase in reduction potential of iron(III) salts due to carbonylation of impurities at the parts per million level. This reaction seems more useful than any other presently known to determine how far a system must be displaced from equilibrium before oscillations become possible.

Introduction

Aqueous formic acid is unstable with respect to decomposition to two different sets of products.



Either process could be driven to completion, particularly if the product gases were vented. The various product species equilibrate at a negligible rate at ambient temperatures, and

the products actually obtained from any system will be determined strictly by kinetic rather than by thermodynamic considerations.

Although dilute aqueous formic acid decomposes negligibly slowly, it is destroyed at a conveniently measurable rate in concentrated sulfuric acid, which is a strongly acidic dehydrating medium. The products coincide quantitatively with those of reaction 1. The reaction was studied over 60 years ago by Morgan,² who observed rapid pulses of gas evolution. He claimed that the periodic behavior depended upon the fraction used from his distillation of formic acid and noted an almost explosive reaction of formic acid if nitric acid was added. Morgan² concluded that the periodic behavior was probably