A Quantitative Treatment of Spiroconjugation. Long-Range "Through-Space" Interactions and Chemical Reactivity of Spirenes

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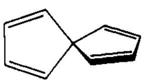
Abstract: A number of spiroconjugated hydrocarbons have been studied theoretically with the valence-electron CNDO/2, MINDO/3, and SPINDO methods. Critical examination of the MO data for spiro[4.4]nonatetraene (**1**) yields disappointing results for all three techniques and reveals that the normally reliable MINDO and SPINDO approaches underestimate the magnitude of the "through-space" π interaction by 33 and 60%, respectively. It is concluded that although each method gives acceptable values for typical bonding interactions, the calculated spiro core resonance integral, which dominates the long-range spiro interactions, decreases too rapidly with distance with the error most severe for SPINDO. A realistic approach to correct the deficiency is presented, and application within the MINDO framework gives a predicted orbital splitting for **1** which is within 5% of experiment. The implications of these findings with regard to the theoretical assessment of "through-space" and "through-bond" molecular interactions are discussed. Both the experimentally observed absence of rate enhancement in the Diels-Alder cycloaddition of **1** with electron-deficient dienophiles and the accelerated self-dimerization of this spiroconjugated molecule relative to less electron-rich cyclopentadiene derivatives can be understood by a consideration of frontier orbital interactions and perturbation theory and are shown to be consequences of spiro effects. The spiro LUMO splitting for (1,1)-spirene (**7**) is predicted to be 0.28 eV.

Introduction

Since the theory of spiroconjugation[1,2] was formulated almost a decade ago, a number of spiroconjugated compounds have been prepared, including the prototype spiro[4.4]nonatetraene,[3] and their spectral data and chemical reactivity have been discussed with considerable success in terms of these long-range π interactions using qualitative perturbational arguments.[1] However, no quantitative molecular orbital studies have appeared except the CNDO/2 calculations by Tajiri and Nakajima,[4] in which they concluded that the minimum energy configuration of spirenes would have the two polyene rings perpendicular to one another. Since meaningful experimental data now exist in this area, we extended our theoretical study to assess the magnitude of "through-space" interactions in a quantitative fashion by using valence-electron MO methods. In this paper we examine the applicability of the following standard semiempirical SCF techniques: (1) CNDO/2,[5] (2) MINDO/3,[6] (3) SPINDO.[7]

Results and Discussion

A. (2,2)-Spirene. 1. Spiro Interaction. It is useful to consider first the (2,2)-spirene, spiro[4.4]nonatetraene (**1**), since for symmetry reasons spiroconjugation in this system can be evaluated purely by π through-space interactions.[8] When two cyclopentadienes (**2**) are juxtaposed as in **1**, the highest occupied molecular orbital (HOMO) is degenerate and pure π. Spiroconjugation theory predicts that this degenerate orbital should be split by "through-space" interactions. The symmetry properties of the spiro-stabilized $1b_1(\pi)$ and spiro-destabilized $1a_2(\pi)$ orbitals are depicted below. The orbital energy splitting calculated for **1** by the valence-electron MO methods varies over a wide range, as shown in Table I, and differs substantially from the experimental value, 1.23 eV, determined by the photoelectron (PE) and electronic spectra of **1**.[8,9] The CNDO/2 value is too large by 82%, whereas MINDO/3 and SPINDO underestimate it by 32 and 63%, respectively. The SPINDO deviation is unusually large despite the fact that this technique has been parameterized to yield optimum agreement for ionization energies and has reproduced PE spectral data for a large number of aliphatic and aromatic hydrocarbons.[11]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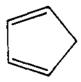
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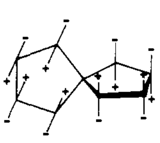
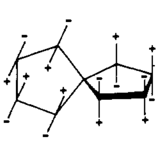

$1b_1(\pi)$


$1a_2(\pi)$

The first-order perturbation eq 1,[1] on the other hand, indicates that the core resonance integral β_{spiro} is the key parameter governing the magnitude of the observed energy splitting $\Delta\epsilon$:

$$\Delta\epsilon = 2(C_1C_{1'} - C_1C_{\omega'} - C_{\omega}C_{1'} + C_{\omega}C_{\omega'})\beta_{\text{spiro}} \quad (1)$$

Schweig and co-workers[12] have obtained a linear correlation between $\Delta\epsilon$ determined by the PE spectra of various (2,2)-spirenes and MINDO/2 coefficients and derived 0.49 ± 0.05 eV for β_{spiro}. The corresponding values calculated by various MO techniques are presented in Table II.

In the CNDO/2 and MINDO/3 methods the core resonance integral β_{xy} between two atoms x and y is assumed to be proportional to overlap S:

$$\beta_{xy} = K_{xy}S_{xy} \quad (2)$$

where K is a constant which depends on the atoms and the type of atomic orbitals (e.g., 2s, 2p). A more complex expression that includes a distance term is assumed in the SPINDO method:

$$\beta_{xy} = \left(K_1{}^{xy} + \frac{K_2{}^{xy}}{R^2}\right) S_{xy} \quad (3)$$

In each method S is determined by orbitals represented by a single Slater-type function (STO), and the exponents for a pair of $2p\pi$ carbon atoms are assumed to be 1.625 (standard Slater exponent), 1.71 ("energy optimized" exponent), and 1.925 for CNDO/2, MINDO/3, and SPINDO, respectively. The actual values of the terms in eq 2 and 3 for the spiro interaction in **1** are included in Table II. The term K_{AB} for CNDO/2 is more

Table I. Predicted Spiro-Orbital Energies for Spiro[4.4]nonatetraene[a]

	Method			
	CNDO/2	MINDO/3	SPINDO[c]	Exptl[d]
$\epsilon[1a_2(\pi)]$[b]	11.56	8.42	8.96	7.99
$\epsilon[1b_1(\pi)]$	13.80	9.26	9.41	9.22
$\Delta\epsilon$	2.24	0.84	0.45	1.23

[a] D_{2d} symmetry was assumed in all calculations with $d_{C_{sp^3}\text{-}C_{radial}} = 1.505$, $d_{C_{radial}\text{-}C_{peripheral}} = 1.35$, $d_{C_{peripheral}}\text{-}d_{C_{peripheral}} = 1.475$, and $d_{C\text{-}H} = 1.10$ Å except for SPINDO where values of 1.509, 1.342, 1.475, and 1.07 Å, respectively were used. [b] All values given in eV. [c] C. Batich, personal communication. [d] Reference 8.

Table II. Resonance Integral Contributions for Spiro Interaction in **1**[a]

	Method		
	CNDO/2	MINDO/3	SPINDO
K_{AB}	−21	−9.69	−9.59
S_{spiro}	0.03493	0.02819	0.01581
β_{spiro} (eV)	−0.7335	−0.2732	−0.1516

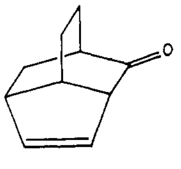
[a] $\beta_{spiro} = K_{AB}S_{spiro}$.

Table III. Calculated π-Resonance Integral for Two Bonded Aromatic Carbon Atoms

Method	β_π, eV
Pariser and Parr (R = 1.397)	−2.39
CNDO/2 (R = 1.40)	−5.13
MINDO/3 (R = 1.40)	−2.10
SPINDO (R = 1.40)	−1.72

than twice that of the other two techniques leading to a much larger β_{spiro} value, whereas the SPINDO β_{spiro} is considerably smaller than its MINDO counterpart because of a substantial decrease in overlap. It should also be noted that the relative magnitude of these integrals parallels the calculated orbital splittings reported in Table I. Application of eq 1 using the β_{spiro}'s in Table II and coefficients obtained from the corresponding MO methods on cyclopentadiene (**2**) yields an orbital splitting which in each case is about 85% of the value given in Table I. π-Orbital reorganization accounts for the additional energy differences. This aspect will be discussed later.

Although the core resonance integrals are optimized for bonding distances in molecules for obvious reasons, the β_π values in the three MO methods for a pair of $2p\pi$ carbon atoms at a bonding distance of 1.40 Å vary considerably as shown in Table III. Only the MINDO/3 value is similar to that suggested by Pariser and Parr[13] for π-electronic spectral calculations. Moreover, it has been recognized that single Slater functions are not entirely satisfactory for evaluating overlaps for atomic separations which are important in long-range interactions such as in spiroconjugation. For example, Cusachs and Corrington[14] noted that the overlaps determined by STO fall off too rapidly as the interatomic distance increases and concluded that STO should have smaller orbital exponents for long-range interactions in order to simulate SCF basis functions which consist of linear combinations of a number of Slater terms of varying exponents. Beveridge and Hinze[15] also noted in an analysis of the PPP π-electron method that π orbitals are actually more diffused than those suggested by standard Slater exponents. In fact, Allinger and co-workers[16,17] used SCF atomic-like basis orbitals[18] represented by a linear combination of four Slater terms of varying exponents[19] and successfully reproduced π-spectral data for homoconjugated molecules such as **3**.



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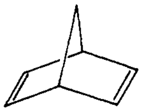
We have thus applied this orbital representation[19] to spiroconjugated molecules. The overlap values calculated by using different basis sets at various distances are presented in Table IV. Although the magnitudes of the overlaps evaluated by the multifunctional atomic basis set are found always to be greater than those involving the molecular $2p\pi$ representations, we may assume the changes in the $2p\pi$ interactions as a function of distance are proportional to those of the atomic basis set. Using the optimized overlaps for a bonding distance of 1.40 Å as normalization values, we find that the MINDO/3 spiro overlap for **1** decreases 43% faster than the value obtained with the atomic basis set. The corresponding CNDO/2 and SPINDO values fall off too rapidly by 30 and 83%, respectively. Employing these overlap data, we adjusted the β_{spiro} values in Table II for **1**. Application of eq 1 using the new MINDO/3 core resonance integral yields an orbital splitting of 1.03 eV. An additional correction of 0.12 eV due to π-orbital reorganization results in a "corrected" MINDO/3 splitting of 1.15 eV[20] which is in excellent agreement with experiment. On the other hand, the SPINDO method with similar overlap corrections still underestimates $\Delta\epsilon$, whereas the CNDO/2 technique predicts an even greater splitting than that reported in Table I.

In order to evaluate the validity of the above approach for assessing "through-space" interactions, we have examined long-range interactions in norbornadiene (**4**). For symmetry reasons, in this and other related systems, "through-bond" interactions actively compete with "through-space" terms, and their individual contributions cannot be experimentally determined. Heilbronner and Schmelzer[21] found that the two terms calculated by CNDO/2, MINDO/2, and SPINDO for **4** essentially cancel each other.[22] In another study,[23] Heilbronner concluded that the magnitude of "through-bond" interactions for this and related hydrocarbons should be similar to the MINDO/2 value[21] of 1.41 eV.[24] Since the "through-space" contribution calculated for **4** by MINDO/2 is 1.55 eV, the orbital splitting is predicted to be 0.14 eV, which is considerably less than the experimental value, 0.85 eV.[25] If we assume, however, that the MINDO "through-space" interaction for **4** is underestimated by a similar 40% found for **1**,[26] the "improved" "through-space" interaction is calculated to be 2.17 eV. This yields a predicted orbital splitting of 0.76 eV which is in good agreement with the experimental value.



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Based on the two analyses presented above, we conclude that the MINDO technique using properly corrected overlaps can yield realistic predictions on the magnitude of "through-space" interactions.

2. Other Molecular Properties. We next discuss other properties of **1** influenced by spiroconjugation and compare

Table IV. Overlap Calculations

	SCF basis[a]	MINDO/3	CNDO/2	SPINDO	Comment
1. C(2pπ)-C′(2pπ) ($R_{C\text{-}C'}$ = 1.40 Å)	0.3392	0.2156	0.2443	0.1552	
2. Two C(2pπ) spiro-oriented of **1** ($R_{C\text{-}C'}$ = 2.499)	0.06328	0.02819	0.03493	0.01581	Normalized SCF result 43% greater than MINDO value
3. Two C(2pπ) spiro-oriented of **7** ($R_{C\text{-}C'}$ = 2.823)	0.01188	0.00393	0.00513	0.00194	Normalized SCF result 92% greater than MINDO value

[a] Carbon wavefunction given in note 19.

Table V. MINDO/3 Results for (2,2)-Spirene[a,b,g]

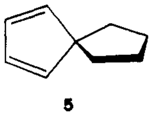
	Orbital energies[c]		π orbital coefficients (C_r^π)		
	Exptl[d]	Calcd	C_1^π	C_2^π	C_3^π
HOMO-1 (π)	7.99	8.42	0	+0.394	+0.306
HOMO-2 (π)	9.22	9.26	0	+0.414	+0.281
HOMO-3 (π/σ)	10.55	10.12			
HOMO-4 (σ)	11.7	9.95			
LUMO-1 (π)		−1.05[f]			
$\epsilon_{\text{HOMO-1}}-\epsilon_{\text{HOMO-2}}$	1.23	0.84			

	Charge densities[e]		π-bond orders	
	q^T	q^π		
C-1	+0.157 [+0.069]		C-1-C-2	0.185
C-2	−0.054 [−0.012]	−0.026 [−0.028]	C-2-C-3	0.932
C-3	0.000 [−0.007]	−0.002 [−0.022]	C-3-C-4	0.312
H-10	+0.016 [+0.007]			
H-11	−0.011 [−0.005]			

[a] Numbering sequence is given in Figure 1. [b] Geometry and bond lengths are given in footnote a in Table I. [c] Negative of calculated orbital energies are recorded. [d] Reference 8. [e] Values in the brackets are obtained by CNDO/2. [f] Doubly degenerate level. [g] ΔH_f = 113.7 kcal/mol

the present results with the previous assessment[1] and experimental observations. Relevant MINDO/3 data are compiled in Tables V and VI. The predictions for cyclopentadiene are in excellent agreement with available experimental results. Although the magnitudes of the three lowest π ionizations of (2,2)-spirene agree with those determined by PE spectroscopy, an unreasonably high-lying σ orbital is calculated, as was found for the MINDO/2 technique.[8] Thus exaggerated σ/π mixing observed for previous MINDO parameterizations[28] appears to remain in the latest version.

Comparison of the charge densities between **1** and **2** reveals that the peripheral carbons are very slightly less positively charged in **1** relative to **2**, 0.000 vs. +0.008. CNDO/2 charges, which are included in Tables V and VI because they tend to be superior to MINDO values,[29] reveal also a slight decrease of electron density on the radial carbons of **1** relative to 2; −0.012 vs. −0.022. These same trends were found in the previous HMO calculations.[1] In contrast to the previous results,[1] electron density on the radial carbons is found to be greater than that of the peripheral carbons in **1**. These results, however, offer no obvious rationalization for the observations[3] that the ^{13}C NMR signals for the unsaturated carbons of **1** are shifted to substantially lower fields (~18 ppm) relative to the corresponding atoms of **2** and that the peripheral carbons of **1** are strongly deshielded compared with spirodiene **5** and spirotriene **6**. The standard theoretical explanation which has been highly successful in reproducing ^{13}C chemical shifts for a vast number of unsaturated aliphatic and aromatic molecules[30] would suggest that the charge densities on the trigonal carbons of **1** have been reduced compared with those of cyclopentadiene, whereas the peripheral carbons of **1** have substantially reduced charges relative to their counterparts in **5** and **6**. As noted the theoretical calculations display none of these trends. Consideration of mobile bond-order terms[31] fails to improve the situation. No obvious explanation can be given at this time, since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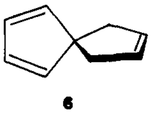
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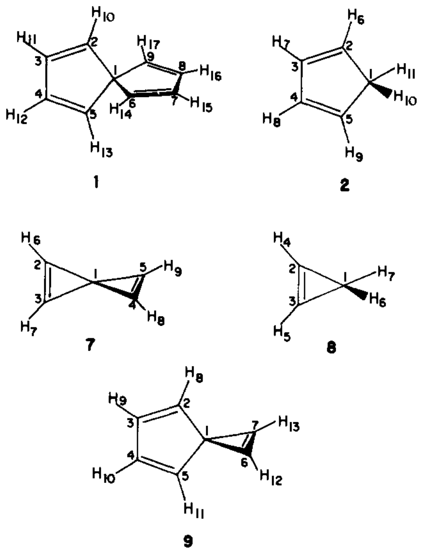

Figure 1. Nuclear arrangements and atom numberings of spirenes and related compounds for which calculations have been performed.

Table VI. MINDO/3 Results for Cyclopentadiene[a]

	Exptl	Calcd[b]
ΔH_f, kcal/mol	39.4	42.5
μ, D	0.45	0.26

	Orbital energies		π orbital coefficients (C_r^π)		
	Exptl[c]	Calcd	C_1^π	C_2^π	C_3^π
HOMO-1 (π)	8.60	8.77	0	−0.571	−0.417
HOMO-2 (π)	10.75	10.72			
HOMO-3 (σ)	11.2	11.06			
LUMO-1 (π)		−1.02	−0.141	−0.511	+0.412

	Charge densities		π-bond orders	
	q^T	q^π		
C-1	+0.111 [+0.011]		C-1-C-2	0.189
C-2	−0.055 [−0.022]	−0.026 [−0.030]	C-2-C-3	0.937
C-3	+0.008 [0.000]	+0.006 [−0.010]	C-3-C-4	0.298
H-6	+0.012 [0.000]			
H-7	−0.003 [−0.008]			
H-10	−0.018 [+0.025]			

[a] See footnotes a, b, c, and e in Table V. [b] Reference 6. [c] Reference 8.

all the factors influencing ^{13}C chemical shifts still remain poorly understood.[32]

One of the consequences of π-orbital reorganization is to make the MO coefficients different between the spiro-stabilized $1b_1(\pi)$ and spiro-destabilized $1a_2(\pi)$ orbitals. The radial carbon atoms have greater coefficients in the $1b_1$ than in the $1a_2$ orbital as shown in Table V. As a result, the $1b_1(\pi)$ level is stabilized more relative to the HOMO level of **2** than the corresponding destabilization of the $1a_2(\pi)$ orbital. These features are common to all MO methods which we have investigated. Thus, spiroconjugation should impart a net stabilization. The predicted asymmetric disposition of the split orbitals of **1** relative to the HOMO of **2** is, however, too small to be detected in the PE spectra; the average of the first and the second IP's of **1** is identical with the first IP of **2** within the experimental accuracy. It is possible that the stabilization is masked by different cationic redistributions in the two molecules which were not considered explicitly by the calculations. The electronic spectral data, on the other hand, may be construed as an indication of this phenomenon: the lowest energy transition of **1**, ΔE_{max}(hexane) = 4.61, 5.85 eV,[8] is closer to the first energy transition of **2**, ΔE_{max}(hexane) = 5.16 eV[33a] and ΔE_{max}(i-octane) = 5.14 eV.[33b]

One of the most intriguing experimental observations on **1** is the enormously accelerated self-dimerization,[3] although the Diels-Alder reaction with the electron-deficient dienophile, dimethyl acetylenedicarboxylate, is not accelerated at all compared with the corresponding cycloadditions of **5** or **6**. For an understanding of cycloaddition processes it is useful to evaluate the total π-stabilization energy (ΔE) in the transition state which is given by the second-order perturbation eq 4:[34]

$$\Delta E = 2\left(\sum_{R}^{occ}\sum_{S}^{unocc} - \sum_{R}^{unocc}\sum_{S}^{occ}\right)\frac{\left(\sum_{ab} c_a c_b \gamma_{ab}\right)^2}{E_R - E_S} \qquad (4)$$

In this equation γ_{ab} is the resonance integral between the two interacting AO's of both diene (R) and dienophile (S). Because the orbital energy terms appear in the denominator, the frontier orbitals play the most significant role. Furthermore, if a dienophile is strongly electron deficient, the second summation term can be neglected.[35] In fact, a good correlation has been obtained[36] between ionization potential of a series of substituted 1,3-dienes and their Diels-Alder reactivity with dienophiles.

On the basis of ionization potential alone, therefore, one should expect the rate of cycloaddition of **1** (IP = 7.99 eV) with dimethyl acetylenedicarboxylate to be greater than that of **5** (IP = 8.10 eV)[8] and **6** (8.25 eV);[8] however, no rate enhancement is observed.[3] The coefficients of the $1a_2$ orbital of **1** at the reacting carbons are reduced compared with those of the HOMO's for **5** and **6**, but the changes are too small to significantly reduce interactions of $1a_2(\pi)$ with the dienophile. However, an inspection of molecular models reveals that when a dienophile approaches symmetrically above the terminal carbons of the diene system[37] of **1**, the dienophile also interacts with the spiroconjugated $p\pi$ orbital which is about 1.2 Å above the reacting diene plane. The nodal property of the $1a_2$ orbital is such, as depicted in Figure 2, that the $p\pi$ orbital of C-6 overlaps unfavorably with the dienophile throughout the course of the reaction. The magnitude of this destabilization is estimated to be comparable with the internal spiro interaction for molecular separations of 2.5–2.8 Å where meaningful application of eq 4 has been demonstrated.[39] Thus, in the cycloadditions of Class II spirenes[3] with electron-deficient dienophiles, spiroconjugation manifests itself not only in rate enhancement by lowering ionization potential, but also in considerable reduction of the effective interaction between LUMO (dienophile) and HOMO (spirene) by unfavorable overlap between dienophile LUMO and spiroconjugated p orbital of the spirenes. The absence of any observed rate enhancement for **1** compared with **5** and **6** can be accounted for by these two opposing effects.

As mentioned previously, Semmelhack and co-workers[3] reported that the dimerization of **1** is strongly accelerated compared with **5** and **6**. Eaton and Hudson[40a] also observed that the spiroconjugated ketals of cyclopentadienone dimerize much more rapidly than does **2**.[40b] In these reactions we must consider both summation terms in eq 4 since the denominator remains identical. The first summation corresponds to interactions of diene HOMO with dienophile LUMO, in which unfavorable interactions discussed above also operate between the dienophile and the spiroconjugated p_π orbital as depicted

Table VII. MINDO/3 Results for (1,1)-Spirene (7) and Cyclopropene (8)[a,b]

	(1,1)-Spirene		Cyclopropene Calcd	Cyclopropene Exptl[c]
ΔH_f, kcal/mol	132.5		60.7	66.2
μ, D			0.62	0.455
Orbital Energies,[d] eV	Calcd		Calcd	Expt[c]
HOMO-1	8.13 (π/σ)		9.28 (π)	9.7
HOMO-2	8.13 (π/σ)			
LUMO-1	−2.06 (π)		−2.04	
LUMO-2	−2.20 (π)			
Charge Densities	q^T	q^π	q^T	q^π
C-1	+0.133		+0.098	
C-2	−0.066	+0.038	−0.050	+0.032
H-4			+0.047	
H-6	+0.032		−0.046	
π-Bond Orders				
C-1-C-2		0.193	0.192	
C-2-C-3		0.962	0.068	

[a] See footnotes a and c in Table V. [b] Assumed geometry in each case was d(C-1-C-2) = 1.505, d(C-2-C-3) = 1.335 and d(C-H) = 1.10 Å, and D_{2d} symmetry for 7. [c] Reference 6. [d] Significant σ/π mixing occurs in some orbitals.

Table VIII. MINDO/3 Results for (1,2)-Spirene[a,b,c]

Orbital energies		π coefficients C-2	C-3	C-4	C-5	C-6	C-7
HOMO-1	8.60 (π)	+0.573	+0.414	−0.414	−0.573	+0.020	−0.020
HOMO-2	8.87 (π/σ)						
HOMO-3	9.25 (π/σ)						
LUMO-1	−0.84 (π/σ)						
LUMO-2	−1.87 (π)	+0.029	−0.074	+0.074	−0.029	+0.703	−0.703

Charge densities	q^T	q^π
C-1	+0.140	
C-2	−0.077	−0.034
C-3	+0.004	−0.003
C-6	−0.058	+0.019
H-8	+0.009	
H-9	−0.006	
H-12	+0.058	

π-bond orders	
C-1-C-2	0.236
C-2-C-3	0.924
G-3-C-4	0.316
C-1-C-6	0.148
C-6-C-7	0.979

[a] See footnotes a and c in Table V. [b] Assumed geometry: d(C-1-C-2) = d(C-1-C-6) = 1.505, d(C-2-C-3) = 1.35, d(C-3-C-4) = 1.475, d(C-6-C-7) = 1.335, and d(C-H) = 1.10 Å. [c] ΔH_f 118.4 kcal/mol; μ 1.11 D.

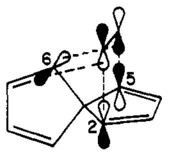

Figure 2. Interaction of dienophile LUMO with HOMO ($1a_2$) of **1**. Only relevant orbitals are depicted.

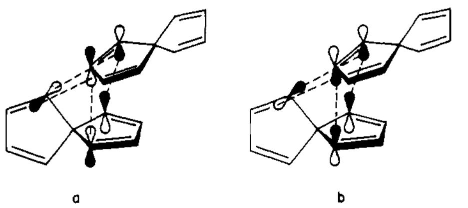

Figure 3. Dimerization modes of **1**: only relevant AO's depicted. (a) HOMO as diene and LUMO as dienophile; (b) HOMO as dienophile and LUMO as diene.

in Figure 3a. However, in the combination of diene LUMO and dienophile HOMO the unfavorable interaction does not exist because of the symmetry of the degenerate LUMO orbital as shown in Figure 3b. For this reason the rates of dimerization of **1** and the ketals should truly reflect the HOMO-LUMO energy gap within the frontier orbital approximations, and strongly accelerated dimerization is expected for Class II spirenes[1] compared with their constituent dienes. An obvious implication of this conclusion is that these spirenes are more

Table IX. Predicted Spiro Bond Orders[a]

Spirene	MINDO/3	CNDO/2	π electron[b]
1	0.031	0.04	0.089
9	0.023	0.04	0.204

[a] Term defined in ref 1. [b] Reference 1.

reactive as an electron-donating dienophile than simple dienes such as **2, 5,** and **6,** whereas the reactivity as a diene is essentially unchanged. Thus, the cycloaddition of these spirenes as a dienophile with cyclopentadiene **2** may proceed as readily as their self-dimerizations, if their LUMO levels are indeed unaffected as first-order spiroconjugation theory predicts. Although experimental assessment of the LUMO levels, e.g., reduction potentials, are not available, the MINDO/3 predicts that **1** and **2** have essentially identical LUMO energies.

Alternatively, the LUMO energy $\epsilon(\psi_{-1})$ may be calculated by its relationship, eq 5, with the singlet HOMO-LUMO excitation energy ($^1E_{1,-1}$) and the first ionization potential which is assumed to correspond to the HOMO energy $\epsilon(\psi_1)$. In this equation:

$$^1E_{1,-1} = -\epsilon(\psi_1) + \epsilon(\psi_{-1}) - J_{1,-1} + 2K_{1,-1} \qquad (5)$$

$J_{1,-1}$ (the Coulomb integral) and $K_{1,-1}$ (the exchange integral) have the usual meanings. If we assume that the term $-J_{1,-1} + 2K_{1,-1}$ is constant for a series of closely related compounds,[41] the LUMO energies are estimated to be essentially identical (±0.04 eV) for **1, 2,** and **6** whereas the LUMO of **5** is calculated to be 0.24 eV higher than that of **2.** Since the IP data show that **5** is less bonding than **2** by 0.50 eV, the cross-dimerization between **2** and **5** is predicted to be more facile than their respective self-dimerizations.

B. (1,1)-Spirene. For the unknown symmetric (1,1)-spirene **7** spiroconjugation theory predicts a splitting of its LUMO levels. MINDO/3 data for **7** and cyclopropene **8** are presented in Table VII. It is well known that semiempirical techniques tend to underestimate[42] the ionization potential of cyclopropene as a result of exaggerated σ/π mixing, thus a very small orbital energy (i.e., easily ionizable) is calculated for the doubly degenerate HOMO level of **7.** Nevertheless some σ/π interaction is to be expected, and it is anticipated that spirene **7** will be easier to ionize than **8.** With regard to spiroconjugation, the pure π LUMO splitting in (1,1)-spirene is predicted by MINDO/3 to be only 0.14 eV. Equation 1 yields an identical value; no π-orbital reorganization is possible for this system. Application of the "improved" "through-space" overlap scheme developed in the previous section increases the predicted $\Delta\epsilon$ by a factor of two (see Table IV), and the "corrected" orbital splitting for (1,1)-spirene is assessed to be 0.28 eV. The substantially reduced spiro splitting predicted for **7** relative to **1** can be attributed to the dramatic decrease in spiro overlap for **7** even with the SCF basis set due to a bending back of the $2p\pi$ orbitals of the three-ring system.

In summary one expects a small splitting of the low-energy electronic transition for **7.** However, because of an IP destabilization in **7** relative to **8** due to σ/π mixing, both of the split bands may be shifted bathochromically from the lowest energy excitation of **8.**

C. (1,2)-Spirene. MINDO/3 data for the asymmetric (1,2)-spirene **9** is given in Table VIII. Spiroconjugation theory[1] suggests that the HOMO level should be stabilized. However the MINDO/3 results display only a minor spiro mixing, and this orbital remains essentially a cyclopentadiene $a_2(\pi)$ orbital. The situation will remain the same using an "improved" value for β_{spiro} because of the negligible orbital interaction between the two rings. This prediction on the lack of spiroconjugated stabilization is in agreement with recent PE data on a diethyl derivative of **9.**[43] Spiro-bond orders determined by various theoretical methods for **1** and **9** are compared in Table IX. The small spiro interaction predicted for (1,2)-spirene by MINDO/3 is consistent with the expected unfavorable overlap imposed by the cyclopropene ring. Earlier π-electron calculations[1] did not consider this decreased overlap explicitly, and thus overestimated spiroconjugation effects onto **9.**

The previous π-electron calculations[1] also predicted unusual charge transfer directed from the cyclopentadiene ring toward the cyclopropene ring of **9.** The MINDO/3 data, however, indicate that substantial σ-electron density redistribution makes the five-member ring negatively charged. Also as noted in Table VIII a sizable dipole of 1.1 D with its moment directed from the smaller ring to the larger is predicted for this molecule. A similar trend was observed with the CNDO/2 method.[4] Interestingly the MINDO/3 π-electron densities of all three unique unsaturated carbon atoms of **9** are greater than those of the corresponding atoms in **1, 2, 7,** and **8.** The mechanism for this π-electron growth is via spiro mixing for the cyclopropene carbon atoms, whereas the radial and peripheral carbons of the cyclopentadiene ring acquire increased density from the central carbon's $2p_z$ orbital. Finally, in spite of the small spiro interactions in **9,** π-bond orders suggest that delocalization in the five-member ring of this asymmetric hydrocarbon is slightly greater than in other compounds investigated containing this group.

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(20) As noted in ref 21, the predicted orbital splittings for unsaturated hydrocarbons can be very sensitive to the assumed geometry. A MINDO/3 calculation with the following bond distances [C_{sp3}–C_{radial} = 1.478, C_{radial}–

$C_{peripheral}$ = 1.335, $C_{peripheral}$–$C_{peripheral}$ = 1.442, C–H = 1.10] gives uncorrected and corrected energy splittings of 0.92 and 1.22 eV, respectively. The total energy for this configuration was ~10 kcal/mol less stable than that obtained with the standard geometry given in Table I.
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Conformational Analysis and Chromic Acid Oxidation. The Rationalization of the Rates of Oxidation of Secondary Alcohols

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Abstract: The strain of 47 secondary alcohols has been evaluated from force-field calculation of the corresponding methyl hydrocarbons. The rates of chromic acid oxidation of these alcohols to ketones are correlated with the strain change in going from the alcohol to the carbonyl product. The correlation which covers a rate range of 15 000 has a slope of −0.3 and a correlation coefficient of 0.91. On the grounds of this correlation it is concluded that the properties of the product are reflected in the transition state of oxidation.

Introduction

The understanding of the rates of oxidation of secondary alcohols to ketones with chromic acid represents a test case for conformational analysis and structure reactivity correlations.[1] Because of the wide synthetic applications of the reaction considerable attention has been directed toward the elucidation of the mechanism[2] which has been analyzed in great detail.[3] The complete reaction scheme is complicated; however, if the very fast equilibrium reactions between alcohol and chromic acid, preceding the rate-determining step, as well as the reactions of the intermediate valence states of chromium are not considered, the oxidation rate expresses simply the conversion of the sp^3-hybridized alcohol to the corresponding sp^2-hybridized ketone. Under the conditions usually employed for reactivity studies (80–90% acetic acid, alcohol in large excess over chromic acid), the kinetically relevant steps of the reaction scheme are:

$$R_2CHOH + HCrO_4^- + H^+ \overset{fast}{\rightleftarrows} R_2CHO\text{-}CrO_3H + H_2O$$

$$R_2CHOCrO_3H \xrightarrow{slow} R_2C{=}O + Cr(4)$$

In general the steady-state approximation may be applied to the intermediate chromate ester, so that the oxidation rates reflect directly the energy difference between alcohol and the respective transition state. Because of this simplicity one might expect that rate constants for the oxidation of alcohols should be easy to interpret. This is, however, not the case. In particular, the nature of the transition state always remained controversial. The observation that axial hydroxyl groups on the cyclohexane ring are more reactive than their equatorial epimers was interpreted with a strain decrease in going from the sp^3-hybridized alcohol to the sp^2-hybridized ketone.[4] This interpretation required a productlike transition state which was expected to lead a correlation between oxidation rates and ketone strain, as measured by the carbonyl stretching frequency.[6] However, no such correlation could be established.[5] Alternatively a rather eductlike transition state was also proposed,[6,7] and the contradiction between these hypotheses could not be resolved.

Structure reactivity correlations require the evaluation of strain in educt and a hypothetical transition state. In the absence of entropy effects the strain difference between transition state and educt should be related to the activation energy. In recent times computer calculations have been used successfully for the determination of strain and have been applied to re-