at 60° with a solution of methylenetriphenylphosphorane prepared by treatment of 50 ml of anhydrous dimethyl sulfoxide with 7.48 g (1.56 moles) of 54% sodium hydride dispersion in mineral oil at 60° for 2 hr followed by cooling to 0°, addition of 63.8 g of methyltriphenylphosphonium bromide in 100 ml of anhydrous dimethyl sulfoxide, and stirring at 25° for 30 min. Isolation by addition to water and extraction with pentane gave, on distillation at 90–91° (85 mm), 13.0 g (67% yield) of a colorless liquid, λ_{max} 6.10 and 11.26 μ; nmr spectrum: τ 5.35 (d, 2, CH_2-1) (*Anal.* Calcd for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.9; H, 14.1).

B. **Irradiation.** A solution containing 3.00 g of **26** and 3 ml of xylene in 147 ml of methanol was irradiated in the usual fashion for 6 hr. Gas chromatographic analysis indicated a 95% recovery of olefin which, on collection, was identical in all respects with starting material.

Characterization of Dimeric Products from 1-Methylcyclohexene (3b). For the preparation of a larger quantity of the mixture of dimeric products, a 150-ml solution containing 50 g of 1-methylcyclohexene (**3b**) in xylene was irradiated as described above for 45 hr. Continued irradiation effected no substantial increase in the amount of accumulated dimer. Removal of the solvent by distillation followed by final purification by preparative gas chromatography over SE-30 afforded a colorless liquid which exhibited six poorly resolved peaks on gas chromatography over Carbowax 20M; λ_{max} 6.08 and 11.26 μ; nmr spectrum: τ 5.40 (m) and 6.04 (m); *m/e*: 192, 187, 177, 163, 150, and 149.

Acknowledgments. The authors are deeply grateful to Professor James A. Marshall and Dr. Ronnie D. Carroll for extensive discussion of their work prior to publication, to Dr. J. H. Collins for determination of the isotopic compositions, and to Mr. T. R. Walker for able technical assistance in a portion of the investigation.

Spiroconjugation

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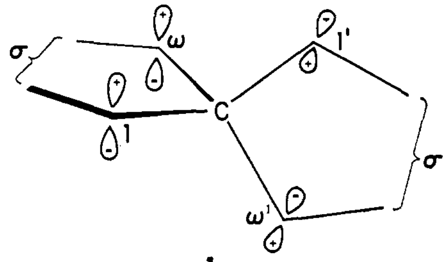
Abstract: When two perpendicular π systems are joined by a common tetrahedral atom, it is postulated that electronic delocalization will produce important and characteristic effects in the electronic spectrum and in chemical reactivity; this special case of homoconjugation has been called spiroconjugation. It will occur whenever four p centers are located by D_{2d} symmetry on atoms bonded to the tetrahedral center. The theory is developed and discussed; in this manner, *e.g.*, the properties of the spirenes, $(CH{=}CH)_mC(CH{=}CH)_n$, and the polyene ketals, $(CH{=}CH)_qC(OR)_2$, can be classified and predicted.

Homoconjugation has been a useful general concept to describe the interaction of systems of p orbitals which are separated by insulating atoms, and its effects seem most important in high-energy species (ions, transition states, and excited states). This paper discusses an extension of the idea of homoconjugation and draws attention to a class of structures in which this concept is expected to be particularly important.

Theory. When two π systems are held in perpendicular planes by a common atom of tetrahedral geometry (*e.g.*, the spiro configuration), the overlap between p orbitals on atoms bound directly to the insulating atom is considerable, and consequently exchange interactions may become significant. In a system of carbon atoms **1**, in which four p orbitals (χ_s) are perpendicular in pairs (s = 1,ω and 1$'$,ω') to the intersecting planes, σ and σ' (local D_{2d} symmetry), the overlap integral of two orbitals in different planes has about 20% of the value for adjacent p orbitals in planar π-electron molecules.[1] Exchange interactions can now remove the energy degeneracy, and symmetry requires the splitting to be $4\beta'$, where β' is the exchange integral between orbitals in different planes (Figure 1). We call such interaction about a tetrahedral center "spiroconjugation."[2,3]



1

Application of these considerations to molecules which contain perpendicular π systems joined by an insulating atom which is approximately tetrahedral predicts interesting consequences for which support is experimentally available. These consequences are solely determined by symmetry and geometry considerations, the former dictating what interactions are allowed and the latter measuring their magnitude. Since chemical and electronic spectral behavior is often reflected by the properties of the frontier molecular orbitals, it is instructive to develop the idea of spiroconjugation by determining its effect on the highest occupied (HOMO) and lowest vacant molecular orbitals (LVMO) of the constituent π systems.[4]

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(1) For a tetrahedral carbon center and bonded (C–C) distances of 1.50 A, the overlap integral is S_{spiro} = 0.042, which amounts to 16% of $S_{\pi\pi}$ = 0.271 (at 1.34 A) and 20% of $S_{\pi\pi}$ = 0.214 (at 1.48 A) in planar systems.

(2) The p orbitals in **1** can be lone pairs or terminals of π systems. We have reserved the term spiroconjugation for the four-orbital case (**1**); however, it should be pointed out that the degeneracy of the two- (1,1$'$) and three-orbital (1,ω,1$'$) cases is removed with smaller splittings of $2\beta'$ and $2\sqrt{2\beta'}$, respectively.

(3) In all calculations in this paper, a value β'/β_0 = $^1/_4$ was uniformly adopted as a matter of convenience, since the results do not depend on this choice in a significant way. In all orbital diagrams, the systems before and after allowance for spiroconjugation are shown in the left and right columns, respectively.

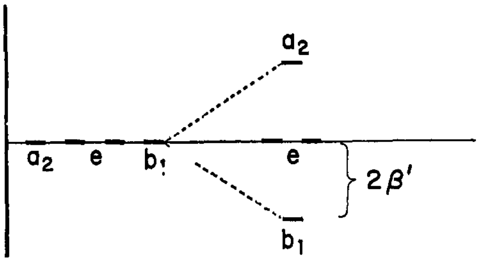
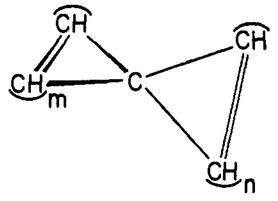


Figure 1. Orbital interaction diagram for four p orbitals arranged tetrahedrally with D_{2d} symmetry (**1**).[3]

The spirene hydrocarbons **2**, two of which were recently synthesized,[5,6] are composed of linear polyenes constrained in perpendicular rings by a saturated carbon atom. To emphasize symmetry considerations, we assume that even the larger rings are planar and that all spiro exchange integrals are equal, so that the symmetry is D_{2d} ($m = n$) or C_{2v} ($m = n$). It is convenient to distinguish the (m,n)-spirenes further according to whether m,n are both odd, both even, or one odd and one even numbers of double bonds, so that the total numbers of π electrons are $4N$, $4N$, and $4N + 2$, respectively, where N is a whole number. The terminal polyene atoms in **2** are $1,\omega$ and $1',\omega'$ according to the convention in **1**. It will be shown that the properties of the spirenes are critically dependent on m and n and fall into a small number of distinct classes.



2

The MO's of the constituent polyenes in **2** can be distinguished according to their behavior under the symmetry operations of rotation about the unique twofold axis (z) and reflections in two perpendicular planes containing this axis (xz and yz) (see Figure 2). The perturbation that mixes the polyene MO's is given by the spirooperator

$$\mathbf{H}_{\text{spiro}} = \mathbf{H}_{1,1'} - \mathbf{H}_{1,\omega'} - \mathbf{H}_{\omega,1'} + \mathbf{H}_{\omega,\omega'}$$

where the matrix elements of the one-electron operators $\mathbf{H}_{st}$ over AO's are simply $\langle \chi_s | \mathbf{H}_{st} | \chi_t \rangle \equiv \beta'$ when $s = 1$ or ω and $t = 1'$ or ω', and are zero otherwise. The spirooperator is symmetric (S) under rotation about z (**C**) and antisymmetric (A) under reflections in the xz and yz planes (σ).

$$\mathbf{C}\mathbf{H}_{\text{spiro}} = +\mathbf{H}_{\text{spiro}}$$

$$\sigma\mathbf{H}_{\text{spiro}} = -\mathbf{H}_{\text{spiro}}$$

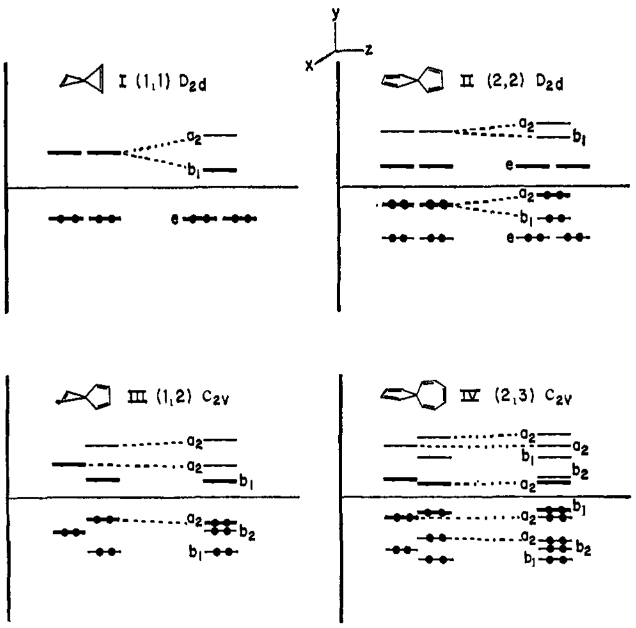


Figure 2. Orbital interaction diagram for the first members of the four classes of spirenes.[3] Only MO's which interact are correlated by dotted lines, and frontier MO's are shown by heavy lines.

Since all π MO's are A to at least one of the σ, they can be classed for our purpose by considering only their behavior under **C**. It can be shown that matrix elements of $\mathbf{H}_{\text{spiro}}$ are nonvanishing between MO's (in particular, frontier MO's) only if they are S under **C**. The frontier MO's of a spirene before considering spiroconjugation are simply the frontier MO's of the longest polyene; after allowing for spiroconjugation all polyene S-MO's can interact, but we need only consider the mixing of the polyene frontier MO's to determine the final frontier orbitals of a spirene. When m or n is odd(even), HOMO and LVMO of the constituent polyenes are A(S) and S(A), respectively, with respect to **C**. It is then easy to show that only four kinds of characteristic behavior of the frontier orbitals result when a spirene is compared with its constituent polyenes.

The four classes of spirenes are shown in Table I, which is interpreted as follows. For example, when m and n are odd numbers of double bonds such that the system contains $4N$ π electrons, spiroconjugation has no effect (0) on HOMO but lowers (↓) the energy of LVMO, the effect on the long-wave length absorption in the electronic spectrum (Δ_s) is a red shift (R), there is no first-order change (0) in π donor or nucleophilic character (Δ^N) in properties where frontier orbital considerations are approximately valid, and there is an increase (+) in π acceptor or electrophilic character (Δ^E); such molecules are called class I. Two classes can be distinguished when one polyene contains an even and the other an odd number of double bonds; *e.g.*, class III occurs when m is odd and n is even ($m \leqq n$), say (3,4), but not (2,3), which is class IV.

In Figure 2 the full orbital interaction diagrams are given for the first member of each class.[3] The role of orbital symmetry in determining the classes is further clarified by the following example. Before interaction, HOMO of the (2,2)-spirene (class II) is a degenerate pair of a_2 and b_1 orbitals, whose wavefunctions are $\psi = \psi_{\text{HOMO}}(\text{diene 1}) \pm \psi_{\text{HOMO}}(\text{diene 2})$. It is readily

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(4) The role of the frontier orbital has been developed by Fukui (see K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Lowdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964.

(5) The ($m = n = 2$) case has been the subject of attempted syntheses by D. J. Cram and B. L. Van Duuren, *J. Am. Chem. Soc.*, 77, 3576 (1955).

(6) Examples of the cases ($m = 1$, $n = 2$) and ($m = n = 2$) have been described by E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, 31, 4260 (1966).

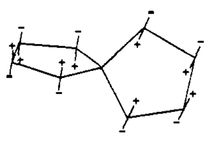
Table I. Classes of the Spirenes

Class	m	$\leqq$	n	Total no. of π electrons	Symmetry of polyene frontier MO under rotation (**C**) $(\text{HOMO})_m$	$(\text{HOMO})_n$	$(\text{LVMO})_m$	$(\text{LVMO})_n$	Behavior of spirenes HOMO	LVMO	Δ_s	Δ^N	Δ^E
I	Odd		Odd	$4N$	A	A	S	S	0	↓	R	0	+
II	Even		Even	$4N$	S	S	A	A	↑	0	R	+	0
III	Odd		Even	$4N+2$	A	S	S	A	↓	0	B	−	0
IV	Even		Odd	$4N+2$	S	A	A	S	0	↑	B	0	−

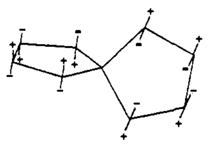
Table II. Charge Densities and Bond Orders of Leading Members of the Classes of Spirenes[3]

	Spirene		Charge density, $q_s^{m,n}$					Bond order,	
			m		n				
Class	m	n	$s = 1$	$s = 2$	$s = 1'$	$s = 2'$	$s = 3'$	p_{spiro}	ΔDE, β^{-1}
I	1	1	1.000	...	1.000	...	...	0	0
II	2	2	0.987	1.013	0.987	1.013	...	0.089	0.089
III	1	2	1.059	...	0.981	0.960	...	0.204	0.213
IV	2	3	0.962	0.964	1.018	1.030	1.025	0.198	0.208

seen that spiroconjugation in the (+)-combination (b_1) allows all spiro exchange integrals to enter the energy with positive signs, so that strong stabilization occurs; on the other hand, the (−)-combination gives all negative exchanges, so that a_2 is strongly destabilized.



b_1



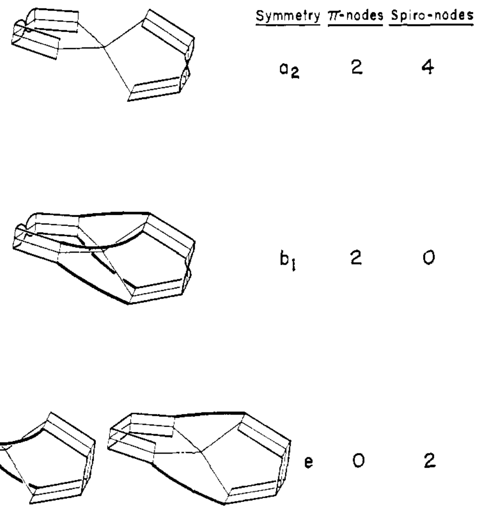
a_2

Planar aromatic hydrocarbons, such as benzene, have cyclic molecular orbitals whose densities are equal above and below the xy plane, and they have a most stable MO which contains no nodes other than this plane. The π nodes of the spirenes can be locally assessed with respect to each of the perpendicular planes, and the spiro nodes can be specified according to whether the overlap between the centers is positive (no node) or negative (one node). Symmetry thus demands that any MO will have either 0, 2, or 4 spiro nodes; spiroconjugation therefore contributes $+2\beta'$ (maximum value), 0, and $-2\beta'$ (maximum value), respectively, to the energy of the MO. The most bonding MO in all spirenes contains no π nodes but two spiro nodes and is therefore not influenced by spiroconjugation; in terms of symmetry, this is because it is antisymmetric with respect to rotation about the twofold axis. The bonding MO's of the (2,2)-spirene can be depicted as shown in Chart I.

Although spirene MO's are not Möbius molecular orbitals,[7] there exists a similarity in certain cases that can best be seen in the e-MO's of the (2,2)-spirene by visualizing the full "streamer" which contains a 360° twist but intersects itself.

In all classes, spiroconjugation causes the total binding energy to decrease (resonance stabilization); however, the stabilization is necessarily larger in the $4N + 2$ classes III and IV. Taken in conjunction with the cyclic nature of the spiro-MO's discussed above, we might regard class III and IV spirenes as weakly aromatic.

Chart I



Illustrative calculations[3] for the spirenes in Figure 2 give the results shown in Table II. The charge densities are given along with the "spiro bond orders," and ΔDE is the gain in delocalization energy above that of the constituent polyenes. The $4N$ classes I and II are characterized by having small ΔDE's which increase monotonically as the series are ascended, whereas in the $4N + 2$ classes III and IV the smallest members have the largest ΔDE values, and these tend to decrease in an oscillatory fashion as the series are ascended. This is a direct consequence of the relative ordering of Hückel molecular orbitals, since in classes I and II the interacting frontier orbitals of the polyenes are either both bonding or both antibonding, so that the net stabilization due to spiroconjugation is zero (or small); it is only in classes III and IV that one interacting frontier orbital is bonding and the other antibonding, so that large net stabilization can occur. When β' is small, the behavior of the classes is determined rather well by consideration of only the polyene frontier MO's. The splitting of the frontier orbitals of the constituent polyenes is given by first-order perturbation theory, when the perturbation is $\mathbf{H}_{\text{spiro}}$, as

$$\Delta E_F \simeq 2(C_1C_1' - C_1C_\omega' - C_\omega C_1' + C_\omega C_\omega')\beta'$$

where the C's are coefficients in the eigenvectors of the

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[7] E. Heilbronner, *Tetrahedron Letters*, 1923 (1964).

appropriate frontier MO's in the smaller (unprimed) and larger (primed) polyene, respectively. The approximation

$$\Delta DE \simeq 4p_{\text{spiro}}\beta'$$

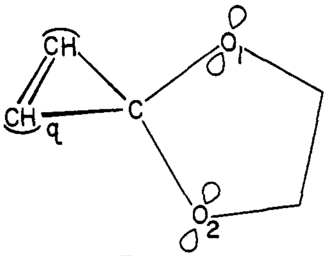
is thus good for all classes.

Furthermore, it can be shown that since the spiro exchange integral is small, net charge transfer between rings must occur so that all C_{2v} spirenes will be polar molecules. The direction of net charge transfer is *from* the longer *to* the shorter polyene in classes I and III and *from* the shorter *to* the longer polyene in classes II and IV. It similarly follows that the charge distributions of D_{2d} spirenes are nonuniform (except $m = n = 1$), although, of course, no net charge transfer occurs.

It is likely that the above considerations will be particularly applicable in predicting effects on the electronic spectrum, ionization potential, and properties related to them. Frontier MO considerations are generally not applicable to problems of chemical reactivity except in certain well-defined cases,[8] and the chemical properties of the spirenes can be projected with less confidence. Such considerations have been successful, however, in discussing the Diels–Alder and related reactions[4,9] of polyenes and can be extended cautiously to the spirenes. Localization energies suggest that the shorter polyene will be the favored site for dienophile additions, but this prediction may be modified because of the inherent polarity of the spirenes. The preferred polarity of the constituent rings can be summarized as follows in the chart. Since the diene component acts as a donor, Diels–Alder additions will be especially favored in the smaller ring in class I and III spirenes but perhaps in the larger ring in class II and IV spirenes. When the symmetrical spirenes, all of which are class I or II, act as diene components, class II structures will show especially enhanced reactivity.

Class	Smaller ring	Larger ring
I	Donor	Acceptor
II	Acceptor	Donor
III	Donor	Acceptor
IV	Acceptor	Donor

Spiroconjugation is also expected to be important in molecules other than hydrocarbons whenever four orbitals of p character are on atoms separated by an insulating tetrahedral atom such that approximate spiro geometry is observed. When less than four p orbitals surround the center,[2] homoconjugation of a similar character should exist but generally should be of lesser importance. Ketals of cyclic polyenones, for example, have lone-pair oxygen orbitals of largely p character that can interact with the polyene MO's, particularly when the oxygen atoms are constrained in a ring, *e.g.*, the ethylene ketals **3**, where the orbitals shown are meant to represent pure p components. Although the oxygen lone pairs, O_1 and O_2, do not interact significantly, it is convenient to consider the MO's, $(1/\sqrt{2})\cdot(O_1 \pm O_2)$. The (+)-combination is of b_1 symmetry under C_{2v} and so cannot interact with any polyene orbitals, which are a_2 and b_2. The (−)-combination is of a_2 symmetry and thus can spiroconjugate with a_2 polyene orbitals. It is immediately clear that when q is odd, LVMO will be perturbed, and when q is even, HOMO will be perturbed. The nature of this interaction is such that when q is odd, the molecule belongs to class IV, and when q is even, it belongs to class II. When $q = 1, 2, 3$, the molecules are the ethylene ketals of cyclopropenone, cyclopentadienone, and tropone, respectively. The perturbation of the diene orbitals of cyclopentadienone ketal by the oxygen lone pairs was first commented upon by Garbisch and Sprecher.[10]



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The application of the spiroconjugation perturbation concept to electronic spectra has some interesting consequences but will not be discussed in detail here. In the spirenes **2**, if M_0 is the wave function for the ground state of the shorter polyene and N_0 that of the longer, then M_0N_0 is the ground-state wave function for the spirene which must be taken into account in first-order perturbation theory. Excited states arise from locally excited configurations, M_0N_j, M_iN_0, and M_iN_j, where M_i and N_j are, *e.g.*, singly excited configuration wave functions, and from charge-transfer configurations, M^+N^- and M^-N^+, where an electron is transferred from one polyene to the other.

When the perturbation is neglected and letting $\psi_{00} = M_0N_0$, etc., the splitting of the lowest energy excited configuration depends on the integral

$$\langle\psi_{0j}|e^2/r_{12}|\psi_{i0}\rangle$$

where i and j here refer to the lowest energy excited configurations in M and N, respectively.[11] This integral reduces to

$$\int\rho_{0j}{}^{\text{M}}\rho_{0i}{}^{\text{N}}(e^2/r_{12})\mathrm{d}\tau_1\mathrm{d}\tau_2$$

where the transition densities ρ are

$$\rho_{0i}{}^{\text{M}} = \int M_0{}^*M_i\mathrm{d}\tau$$

and

$$\rho_{0j}{}^{\text{N}} = \int N_0{}^*N_j\mathrm{d}\tau$$

In all spirenes, the transition densities $\rho_{0i}{}^{\text{M}}$ and $\rho_{0j}{}^{\text{N}}$ lie in perpendicular planes and the vectors are furthermore perpendicular. The latter is so since, in all *cis* conformations, the lowest energy configuration corresponds to a state to which transition from the ground state is allowed and is polarized in a direction parallel to a line joining the terminal atoms. Therefore, it is concluded that exciton delocalization cannot influence the spectra of spirenes (neglecting vibronic effects), and the only significant mechanism for interaction in these molecules is electronic delocalization. Furthermore, the interaction between charge-transfer states,

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[8] (a) M. J. S. Dewar, *Advan. Chem. Phys.*, 8 110 (1965); (b) H. H. Greenwood and R. McWeeny, *Advan. Phys. Org. Chem.*, 4, 112 (1966).

[9] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965), and subsequent papers.

[10] E. W. Garbisch, Jr., and R. F. Sprecher, *ibid.*, 88, 3433, 3434 (1966).

[11] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 136.

such as $\langle M_a{}^+N_b{}^-|\mathbf{H}|M_c{}^-N_d{}^+\rangle$, vanishes under the zero-differential-overlap approximation, and only interactions between locally excited and charge-transfer states, such as $\langle M_a{}^+N_b{}^-|\mathbf{H}|M_iN_j\rangle$, contribute to the spirene excited states; **H** is here the full π-electron operator. It is only in the latter type of matrix elements that the spiro exchange integral occurs. The spectral predictions are summarized in Table III. The effect of spiroconjugation on the oscillator strengths is not easy to assess without direct calculation, for they depend intimately on the geometry of the spirene and on the quality of the molecular orbitals employed. Using Hückel orbitals[3] it can be shown that, *e.g.*, the long-wavelength transition of the (1,2)-spirene (class III) will be enhanced in intensity, whereas that of the (2,2)-spirene (class II) will be decreased.

Table III

Spirene	Class	Lowest energy configuration	Symmetry	(V ← N) transition	Polarization
D_{2d}	I	$(\cdot\cdot e^3b_1\cdot\cdot)$	E	$E \leftarrow A_1$	(x,y)
	II	$(\cdot\cdot a_2e\cdot\cdot)$	E	$E \leftarrow A_1$	(x,y)
C_{2v}	III	$(\cdot\cdot a_2b_1\cdot\cdot)$	B_2	$B_2 \leftarrow A_1$	y
	IV	$(\cdot\cdot b_1a_2\cdot\cdot)$	B_2	$B_2 \leftarrow A_1$	y

Similar considerations apply for the polyene ketals **3**. In these molecules, however, there arises the possibility that perturbation of the polyene spectrum could occur by mixing of the locally excited polyene states with the oxygen (2p → 3p) transition, since the transition moment of this excitation lies parallel to the moment of the long-wavelength transition of the polyene. This would predict that all spirene ketal spectra are red shifted with respect to the constituent polyene, in contrast to the alternating effect predicted by spiroconjugation (electron delocalization). It is shown below that experimentally the alternating effect is realized. All of the polyene ketals **3** are predicted to show decreased intensity of the long-wavelength band.

Finally, it must be kept in mind that conclusions drawn from one-dimensional wave functions when used to approximate three-dimensional systems cannot be rigorously justified when no coordinate system exists that will allow separability of the three-dimensional wave function. To this extent, the conclusions drawn here may require modification.

Evidence for Spiroconjugation. The low-energy transitions of the various ketals of cyclopentadienone appear at 270–280 mμ, as shown in Table IV(A). The values can be compared with other appropriately substituted cyclopentadienes, *e.g.*, **2** *vs.* **6** and **7** and **3** *vs.* **9** and **10**. The observed bathochromic shifts of 20 and 23 mμ correspond to energy differences of 8 and 10 kcal/mole, respectively. The fact that the red shift is most pronounced for the ethylene ketals **9** and **10** compared to the noncyclic ketals **6** and **7** and the nonrigid cyclic ketal **8** is in accord with predictions, since the most favorable conformation for spiroconjugation between the oxygen lone pairs and the diene π systems is achieved in **9** and **10**. It is further seen that the intensity of the low-energy transition is decreased in accord with theory.

A similar bathochromic shift is observed for the chlorides of tetrachlorocyclopentadiene and the ketals of tetrachlorocyclopentadienone, as shown in Table IV(B). If one takes 1,2-dialkyl-4,5,6,7-tetrachlorospiro[2.4]hepta-4,6-dienes (**12**) as reference compounds, the bathochromic shifts for **14** and **17** are calculated to be about 26 and 35 mμ or 8.5 and 11 kcal/mole, respectively, similar to those found for the nonchlorinated series. That chlorine causes slightly larger shifts than oxygen may be due to the more diffuse chlorine 3p orbitals which overlap more effectively. It is also possible that the vacant 3d orbitals of chlorine contribute to such spectral shifts. Further support for the spiroconjugation explanation is the decrease in intensity of the diene absorption.

As discussed above, the red shifts observed for the class II ketals are to be attributed largely to destabilization of HOMO due to spiroconjugation which should also result in an increase in π-donor character. In accord with this prediction, it has been reported[10,12,13] that the reactivity toward dimerization and Diels–Alder reactions of the ketals and chlorides increases with increasing λ_{max}. Similarly, spiroconjugation is believed to be responsible for the high reactivity of thiophene 1,1-dioxide toward dimerization as well as the extraordinarily long wavelength absorption (λ_{max} 289 mμ).[10,14] This is further supported by a recent observation[15] that thiepin 1,1-dioxide (class IV, *vida infra*) has its absorption maximum [λ_{max}^{EtOH} 262 mμ (ϵ 4610)] nearly identical with or slightly hypsochromically shifted from that of tropilidene [see Table IV(C)].

In contrast to the class II compounds, the ketals of cyclopropenone and tropone (class IV), prepared in this study, were found to show hypsochromic shifts (Table IV, C and D) in agreement with prediction. The absorption maxima of the ethylene and trimethylene ketals of tropone **39** and **40** occur at 11 and 16 mμ shorter wavelengths, respectively, than those of 2,7,7- and 3,7,7,-trimethyltropilidene. The shifts correspond to an energy difference of 5–7 kcal/mole and are smaller than those found for the class II compounds. In this case, spiroconjugation causes a small enhancement of intensity of the triene band, whereas first-order theory predicts a small decrease. These considerations are complicated, however, since the tropilidenes are not planar.

It is interesting to note that the absorption maxima of these ketals are essentially identical with those of compounds **30–33**, which have only one p-orbital-bearing substituent at the 7 position. This may also be a consequence of the tropilidene ring puckering, which enables only one oxygen atom to participate strongly in spiroconjugation.

The long-wavelength band of diphenylcyclopropene derivatives consists usually of three vibrational peaks, as shown in Table IV(D). If one compares the Frank–Condon peaks of the compounds **41**, **42**, and **45–47**, it is found that a blue shift of about 10 mμ is associated with introduction of each p-orbital-bearing substituent. Thus, the blue shifts on going from **41** and **42** to **45** and

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[12] P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, 87, 2769 (1965).

[13] W. H. Chang, *Chem. Ind.* (London), 709 (1964); *J. Chem. Soc.*, 2305 (1965).

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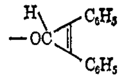
Table IV. Ultraviolet Spectral Data[a]

	R_1	R_2	λ_{max} mμ	$\epsilon \times 10^{-3}$	Solvent	Ref
			A. 5,5-R_1,R_2-Cyclopentadienes			
			Reference Compounds			
1	H	H	241	3.16	i-C_8H_{18}	*e*
2	CH_3	CH_3	250	2.88	C_2H_5OH	*f*
3	$-CH_2CH_2-$		257	2.69	C_2H_5OH	*f*
4[b]	$-CHRCR_2-$		257–262	2.5–3.9	n-C_5H_{12}	*g*
5	$-CH_2CH_2CH_2CH_2-$		254	2.75	C_2H_5OH	*f*
			Class II Ketals			
6[c]	OR	OR	270	...	n-C_5H_{12}	12
7[d]	OCH_3	OCH_3	270	1.23	i-C_8H_{18}	10
8	$-OCH_2CH_2CH_2O-$		272	...	n-C_5H_{12}	12
9	$-OCH_2CH_2O-$		280	...	n-C_5H_{12}	12
10[d]	$-OCH_2CH_2O-$		280	1.11	i-C_8H_{12}	10
			B. 5,5-R_1,R_2-1,2,3,4-Tetrachlorocyclopentadienes			
			Reference Compounds			
11	H	H	276	4.8	C_2H_5OH	*h*
12[b]	-CHRCHR-		287 ± 2	3.0–5.0	C_2H_5OH	*i*
			Class II Ketals			
13	OCH_3	OCH_3	308	2.34	i-C_3H_7OH	13
14	$-OCH_2CH_2O-$		313	2.39	i-C_3H_7OH	13
15[b]	-OCHRCHRO-		312–313	1.33–1.88	i-C_3H_7OH	13
			Class II Chlorides			
16	H	Cl	307	1.7	C_2H_5OH	*h*
17	Cl	Cl	322	1.5	C_2H_5OH	*h*
			Class II Spirenes			
18	$-[C(CH_3)]_4-$		320	0.56	C_2H_5OH	6
19	$-[C(C_2H_5)]_4-$		325	0.50	C_2H_5OH	6
			Class III Spirenes			
20	$-[C(C_2H_5)]_2-$		284	3.40	C_2H_5OH	6
21	$-[C(C_6H_5)]_2-$		See part D **43**			
			C. Tropilidenes			
			Reference Compounds			
22	Unsubstituted		261	3.47	i-C_8H_{18}	*j*
23	1-CH_3		269	3.40	C_2H_5OH	*k*
24	2-CH_3		258	2.63	C_2H_5OH	*k*
25	3-CH_3		260	3.80	C_2H_5OH	*k*
26	7-CH_3		257			*l*
27	1,7,7-$(CH_3)_3$		278	4.37	C_2H_5OH	*m*
28	2,7,7-$(CH_3)_3$		270	3.63	C_2H_5OH	*m*
29	3,7,7-$(CH_3)_3$		268	4.07	C_2H_5OH	*m*
			Class IV			
30	7-CN		255	3.72	i-C_8H_{18}	*j*
31	Ditropyl		255	7.08	i-C_8H_{18}	*j*
32	Ditropyl ether		256–260	10.5	i-C_8H_{18}	*j*
33	Ditropyl sulfide		254–258	6.46	i-C_8H_{18}	*j*
39	Tropone ethylene ketal		258	4.90	i-C_8H_{18}	*n*
40	Tropone trimethylene ketal		253	4.74	i-C_8H_{18}	*n*

D. 1,2-Diphenyl-3,3,R_1,R_2-cyclopropenes

	R_1	R_2	λ_{max} mμ	$\epsilon \times 10^{-3}$	λ_{max} mμ	$\epsilon \times 10^{-3}$	λ_{max} mμ	$\epsilon \times 10^{-3}$	Solvent	Ref
				Reference Compounds						
41	H	CH_2OH	332	17.4	316	23.4	...	...		*o*
42	H	CH_2OTs	328	22.9	312	31.6	298	21.9	Hexane	*o*
				Class III						
43	—CCl=CClCCl=CCl—		318	30.6	301	38.6	287 (sh)	29.2	C_2H_5OH	6
44	—OCOCPh=CPH—		313	28.6	297	39.3	284 (sh)	35.2	C_2H_5OH	*p*
				Class IV						
45	H		318	44.0	302	59.0	288 (sh)	46.0	CH_3CN	*q*
46	H	CN	318	29.4	303	38.4	295	28.7	C_2H_5OH	*q*
47	$-OCH_2CH_2O-$		305	17.2	290	23.6	278	22.3	i-C_8H_{18}	*n*

[a] Only the lowest energy transitions are shown. [b] R = H or alkyl. [c] R = CH_3 or C_2H_5. [d] 3-*t*-Butylcyclopentadienone ketal. [e] S. L. Friess and V. Boekelheide, *J. Am. Chem. Soc.*, **71**, 4145 (1949). [f] C. F. Wilcox, Jr., and R. A. Craig, *ibid.*, **83**, 4258 (1961). [g] R. A. Moss, *J. Org. Chem.*, **31**, 3296 (1966). [h] J. D. Idol, Jr., C. W. Roberts, and E. T. McBee, *ibid.*, **20**, 1743 (1955). [i] E. T. McBee, J. A. Basoms, and C. J. Morton, *ibid.*, **31**, 768 (1966). [j] W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957). [k] N. H. Nelson, J. H. Fassnacht, J. V. Piper, *ibid.*, **83**, 206 (1961); **81**, 5009 (1959). [l] K. Conrow, M. E. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963). [m] J. A. Berson and M. R. Willcott, III, *ibid.*, **88**, 2494 (1966). [n] Present work. [o] R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962). [p] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965). [q] R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

46 and from the latter to **47** amount to an energy difference of 5 kcal/mole.

The recent synthesis of spirenes by McBee and coworkers[6] further verifies the predictions of spiroconjugation. The long-wavelength absorptions of the spiro[4.4]nonatetraenes **18** and **19**, which belong to class II and are expected to show red shifts, are found at 320 and 325 mμ, respectively, and are thus shifted more than 30 mμ or 10 kcal/mole to longer wavelength compared to the reference compound **12**. On the other hand, the spiro[2.4]heptatriene **20**, which belongs to class III and is thus expected to show a blue shift, has this absorption at 284 mμ which is essentially identical with the reference absorption of **12**. The spectrum of 1,2-diphenyl-4,5,6,7-tetrachlorospiro[2.4]heptatriene (**43**) should be compared, however, with those of the diphenylcyclopropenes, since it is the diphenylcyclopropene moiety that dictates the frontier orbitals of **43**. It is seen that the Frank-Condon peak (λ_{max} 301 mμ) of the long-wavelength band is blue shifted about 10 mμ or about 5 kcal/mole with respect to **41** and **42**.

In summary, the absorption spectra show that in the class II compounds the low-energy transitions are bathochromically shifted by 10 kcal/mole and they are apparently associated with a hypsochromic effect. In the class III and IV compounds, the observed hypsochromic shifts range from none to about 7 kcal/mole, and the absorption intensities fall in the range of those of the reference compounds.

In contrast to the ample spectral data, there is little experimental evidence for spiroconjugation effects on chemical reactivity (but see the class II ketals). It is, however, anticipated that spiroconjugation is a general phenomenon that modifies the classically expected properties of many molecules when the criteria of symmetry and geometry can be met. In this connection, we draw attention to such observations as the tendency of polycarbonyl compounds to hydrate at an internal carbonyl (*e.g.*, 1,2,3-indantrione[16] and rhodizonic and croconic acids[17]) and special stabilization of some spiroheterocycles.[18a,b] Spiroconjugation may be important in interpreting the rate enhancement of the hydrolysis of cyclic sulfates and phosphates[18c] and delocalization of the odd electron in diphenyl sulfone anion radical.[18d]

Finally, it is noted that spiroconjugation can account for the observation that the monoanion radical of 9,9′-spirobifluorene[19] has an esr spectrum which is consistent with delocalization of the odd electron over the perpendicular biphenyl systems and that the dianion is a triplet.[22] Similar experiments with 9,9′-spirobifluorene containing a C^{13} spiroatom substantiated that the delocalization does not occur through the σ framework or higher energy orbitals on the spiro atom.[23]

Experimental Section

Boiling points and melting points are not corrected. Ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer in ethanol and isooctane. Nmr spectra were obtained with a Varian A-60 or HA-100 spectrometer in deuteriochloroform, unless otherwise noted, and are reported as δ in ppm from internal tetramethylsilane.

Tropone Ethylene Ketal (39). A solution of 6.72 g of ethoxytropylium fluoroborate in 40 ml of freshly distilled ethylene glycol was allowed to stand for 3 days under nitrogen atmosphere and then poured into a stirred mixture of 10 g of sodium carbonate and 100 ml of hexane. After the mixture was stirred for 10 min, 50 ml of water was added, and the hexane layer was separated. The aqueous layer was extracted twice with hexane, and the combined hexane solutions were washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. The solvent was evaporated and the oily residue was distilled to give 3.78 g (83%) of a colorless liquid, bp 62–65° (0.7 mm). An analytical sample was obtained by redistillation and had bp 62° (0.7 mm).

Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71; mol wt, 150. Found: C, 72.09, 71.89; H, 6.73, 6.66; mol wt, 150 (cryoscopic in benzene).

The infrared (neat) showed ν_{max} 1620, 1525, 1150, and 1000 cm^{-1}. The 100-Mc nmr showed a spike at 3.92, a doublet (J = 10 cps) with further minor splittings centered at 5.77, and two overlapping multiplets between 6.25 and 6.70 of relative areas 4, 2, and 4, respectively.

Hydrolysis of 150 mg of **39** in 5 ml of water in the presence of one drop of 10% H_2SO_4 for 3 hr at room temperature followed by three extractions with ether gave 93.5 mg of an almost colorless oil, the infrared of which was identical with that of tropone.

Tropone Trimethylene Ketal (40). To a solution of 10.0 g of triethyloxonium floroborate in 10 ml of methylene chloride was added 5.3 g of tropone under nitrogen atmosphere. The resulting pale yellow solution was cooled intermittently until the moderately exothermic reaction subsided and was allowed to stand at room temperature for 8 hr. After 30 ml of trimethylene glycol was added, the mixture was kept at room temperature for 3 days and worked up in the same manner to give 5.75 g (70%) of **40** as a colorless oil, bp 64–68° (0.5 mm). An analytical sample was obtained by passing a hexane solution of the oil through a short column of neutral alumina followed by distillation; bp 81.5° (1.4 mm).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.05, 73.06; H, 7.43, 7.20.

The nmr (60 Mc, neat) showed a quintuplet (J = 5.5 cps) at 1.53 (2 H), a triplet (J = 5.5 cps) at 3.74 (4 H), a doublet (J = 10 cps) with further minor splittings at 5.75 (4 H), and two mutiplets between 6.10 and 6.70 (6 H). The infrared (neat) showed ν_{max} 1640, 1540, 1140, 1110, 1055, and 1020 cm^{-1}.

Diphenylcyclopropenone Ethylene Ketal (47). A solution of 12.4 g of diphenylcyclopropenone in 15 ml of methylene chloride was added to a solution of 12 g of triethyloxonium fluoroborate in 20 ml of methylene chloride. Immediately after the addition a voluminous amount of colorless, feathery crystals precipitated. The mixture was transferred under nitrogen atmosphere with the aid of *ca.* 150 ml of methylene chloride into a stirred solution of the sodium salt of ethylene glycol, prepared from 0.3 g of sodium and 75 ml of ethylene glycol. The mixture was stirred at 10–20° for 1 hr and poured into ice-water. The organic layer was separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic solutions were washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. Evaporation of the solvent gave 17.0 g of slightly colored crystals. Two recrystallizations from cyclohexane gave three crops of colorless crystals weighing 7.3, 2.5, and 1.7 g, respectively, which contained varying amounts of 2-hydroxyethyl *cis*-1,2-diphenylacrylate. A cyclohexane solution of the first

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(16) It was found in this work that 1,2,3-indantrione readily forms the corresponding ethylene ketal (see Experimental Section). The low-energy $\pi \rightarrow \pi^*$ transition of this class IV ketal in ethanol appears at 283 mμ which is blue shifted by 8 mμ as compared to that of 2,2-dimethyl-1,3-indandione.

(17) See, for example, K. Yamada and Y. Hirata, *Bull. Chem. Soc. Japan*, 31, 543 (1958).

(18) (a) R. Huisgen and V. Wekerndorfer, *Experientia*, **17**, 566 (1961); (b) R. Kikumoto and T. Kobayashi, *Tetrahedron*, 22, 3337 (1966); (c) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *J. Am. Chem. Soc.*, **87**, 3781 (1965); (d) E. T. Kaiser, M. M. Urberg, and D. H. Eargle, *ibid.*, **88**, 1037 (1966).

(19) J. H. Weisburger, E. K. Weisburger, and F. E. Ray, *ibid.*, **72**, 4253 (1950), reported that the low-energy transition occurs in 95% EtOH at 308 mμ (ϵ 13,180); in this case, the theory predicts a weak bathochromic shift (class II). 9,9-Dimethylfluorene[20] and fluorene[21] have this absorption at 302 and 300 mμ, respectively.

(20) P. M. Everitt and E. E. Turner, *J. Chem. Soc.*, 3478 (1957).

(21) E. J. Greenhow, D. McNeil, and E. N. White, *ibid.*, 986 (1952).

(22) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

(23) G. Urry, private communication.

crop was passed through a short column of neutral alumina and the eluate was evaporated. The colorless crystalline residue was recrystallized twice from hexane to give an analytical sample, mp 84.8–85.2°.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.63. Found: C, 81.81, 81.92; H, 5.71, 5.93.

The ultraviolet spectrum had the following maxima: λ_{max} (isooctane) 305 (17,200), 290 (23,600), 278 (22,300), 225 (20,000), and 218 mμ (ϵ 21,000). The nmr (60 Mc) showed a spike at 4.15 (4 H) and an unsymmetric aromatic multiplet between 7.25 and 7.85 (10 H). The infrared (Nujol) showed ν_{max} 1770, 1040, 760, and 690 cm^{-1}.

Elution of the chromatogram with methylene chloride afforded colorless crystals which were recrystallized from cyclohexane to give an analytical sample of the **2-hydroxyethyl** ***cis*****-1,2-diphenylacrylate,** mp 98–99°.

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.15, 76.29; H, 6.17, 5.99.

The infrared (Nujol) showed ν_{max} 3045, 1700, 1675, 1255, 1240, and 715 cm^{-1}. The nmr (60 Mc) had a spike at 7.88 (1 H), two aromatic peaks at 7.30 and 7.12 (10 H), a broad peak at 2.34, and an additional set of peaks (A_2B_2 pattern), the high-field portion of which was split further and appeared as a broad peak at 4.30 and 3.80 (4 H). Addition of D_2O eliminated the broad peak at 2.34 and simplified the high-field portion of the A_2B_2 giving rise to a symmetric pattern.

Saponification of the ester in alcoholic sodium hydroxide gave *cis*-α-phenylcinnamic acid, mp 172–174° (lit.[24] mp 172°).

Spiro[1,3-dioxolane-2,2′-indan-1′,3′-dione].[25] To a solution of 16 g of indantrione and 15 g of 2-bromoethanol in 50 ml of tetrahydrofuran was added 16.6 g of potassium carbonate and 50 ml of dimethyl sulfoxide. After being stirred overnight at 35°, the dark blue mixture was poured into 600 ml of water. The precipitate was collected and washed with water to give 15.2 g. (74%) of crude ketal, mp 133–135°. Recrystallization from ethanol-water (1:4) followed by sublimation afforded a bright yellow solid, mp 137–138°.

Anal. Calcd for $C_{11}H_8O_4$: C, 64.71; H, 3.95; mol wt, 204. Found: C, 64.78; H, 3.98; mol wt 204 (mass spectrometric).

The nmr spectrum [$(CD_3)_2CO$] contained two sharp singlets at 4.38 and 8.10 ppm with relative intensities of 2:1, respectively. The infrared ($CHCl_3$) had bands at 1755 and 1725 cm^{-1}.

The ultraviolet spectrum showed the following maxima: λ_{max} (isooctane) 378 (46), 288 (775), 280 (754), 272 (569), 249 (12,100), 228 (51,200), and 222 mμ sh (ϵ 38,600); λ_{max} (EtOH) 371 (51), 290 (867), 283 (904), 251 (11,400), and 230 mμ (ϵ 45,900).

2,2-Dimethyl-1,3-indandione. This compound was prepared by a modification[26] of the procedure reported by Wislicenus and Kötzle.[27] An analytical sample had mp 107–108° (from EtOH).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.78. Found: C, 75.78; H, 5.87.

The ultraviolet spectrum showed the following maxima: λ_{max} (isooctane) 365 (sh) (24), 335 (41), 320 (35), 298 (524), 290 (475), 285 (529), 275 (463), 244 (1120), and 222 mμ (ϵ 60,600); λ_{max} (EtOH) 360 (sh) (26), 328 (45), 300 (626), 291 (693), 247 (1020), and 223 mμ (ϵ 51,200).

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The Spirarenes

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Abstract: Allylic radicals held in a spiro system may under certain conditions interact so that a stabilized singlet could become the ground state. The conditions for the existence of such an interaction are that the number of orbitals in each allylic system should equal $4q + 3$.

The well-known molecular orbitals of an allyl system are shown in Figure 1. If two allyl radicals are brought together in such a way as to produce little interaction among the energy levels then the ground state of the system of the two radicals will surely be a triplet. If the radicals are brought together so that the levels interact appreciably then in fact it is possible that the nonbonding levels interact strongly enough so that the ground state of the six-electron system is a stabilized singlet (Figure 2). Perhaps the most efficient way to couple two allyl radicals is found in the benzene molecule. Since this is not a very popular way of looking at benzene, Figure 3 shows in detail the relation of the familiar π orbitals of benzene to those of two allyl radicals. Two further efficient ways to couple two allyl radicals are found in 1,5-hexadiene and bicyclo[2.2.0]butane (Figure 4).

It should be stressed that these illustrations indicate only relative positioning of levels and are *not* correlation diagrams for some specific geometry of approach.

It is possible to join two allyl radicals in a most inefficient way, for instance by coupling them at the central carbon, to produce a diradical which will be called diallyl (Figure 5). Since the two radicals are coupled at a position where the nonbonding orbitals have nodes, the splitting of the nonbonding orbitals is due only to 1,4 interactions and is very small. The molecule is of considerable interest, however, in view of the many possible isomers to which it could collapse, and these features will be discussed elsewhere.

In this work we would like to discuss still another, moderately efficient way to couple two allyl radicals, and that is to put them in a spiro system. The simplest species of this type, to be called a [3.3]spirarene, is I; [3.5]-, [5.5]-, and [3.7]spirarenes are illustrated in II, III, IV. I is redrawn in Figure 6 to emphasize the perpendicularity of the spiro arrangement. The molecular orbitals of I are classified with respect to the symmetry planes 1 and 2 of Figure 6 in Figure 7. The symmetric allyl orbitals do not interact (in fact they form a degenerate orbital of e symmetry in the assumed