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°).

(24) R. E. Buckles and E. A. Hausman, *J. Am. Chem. Soc.*, **70**, 415 (1948).

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).

(25) We are grateful to Dr. D. W. Wiley for this experiment.
(26) C. U. Kim and T. Fukunaga, to be published.
(27) W. Wislicenus and A. Kötzle, *Ann.*, **252**, 80 (1889).

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
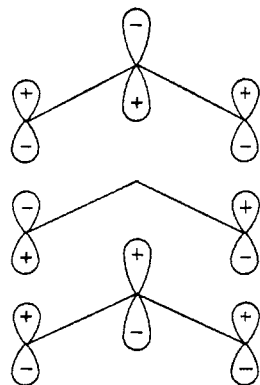
Figure 1. The three molecular orbitals of the allyl system.
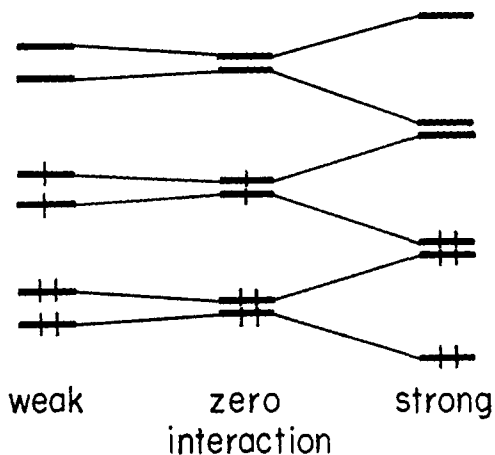
weak   zero   strong

interaction

Figure 2. Two allyl systems (center) may interact weakly (left), with a triplet ground state resulting, or strongly (right), leading to a stabilized singlet.
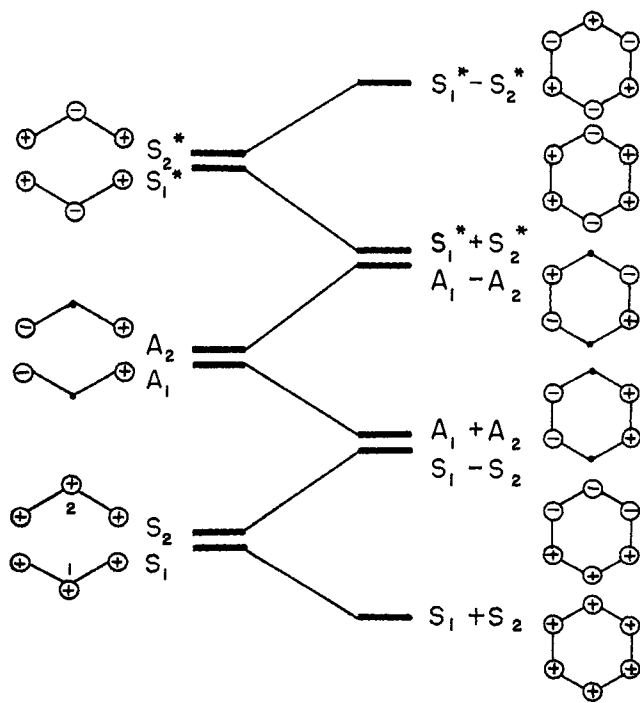
$S_1^* - S_2^*$

$S_1^* + S_2^*$

$A_1 - A_2$

$A_1 + A_2$

$S_1 - S_2$

$S_1 + S_2$

S_1^*

S_2^*

A_2

A_1

S_2

S_1

Figure 3. An illustration of how the benzene levels may be derived from those of two allyl systems.

D_{2d} geometry) but the antisymmetric nonbonding orbitals are both of symmetry AA and so may interact. The magnitude of the actual interaction is of great im-

σ^*

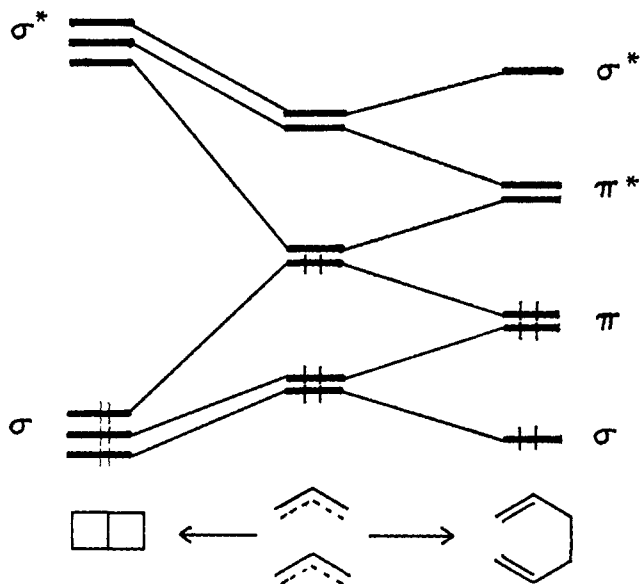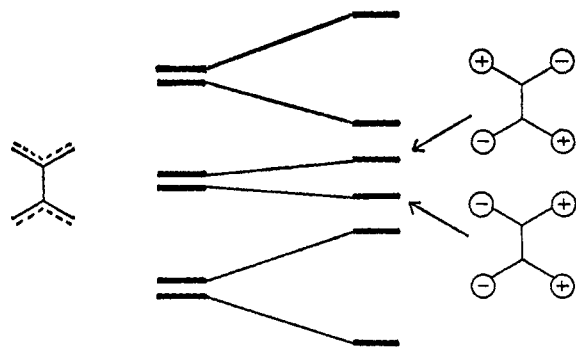σ^*

π^*

π

σ

σ

Figure 4. Two ways in which allyl radicals interact strongly, to give 1,5-hexadiene or bicyclo[2.2.0]hexane. This is *not* a correlation diagram for some specific geometry of approach.

Figure 5. An inefficient way to couple two allyl radicals. The nonbonding orbitals interact very weakly.

portance and will be discussed below. For now we would like to focus merely on the restrictions symmetry places on the presence or absence of the all-important

I

II

III

IV
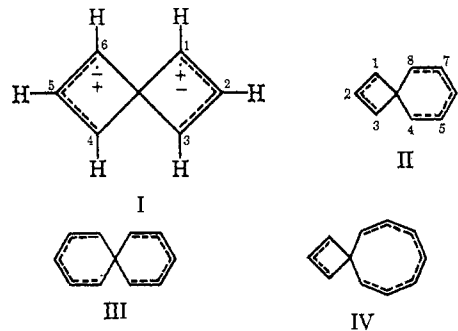
interaction between nonbonding orbitals. Interaction diagrams are shown below in Figure 8 for the [3.5]-, [5.5]-, and [3.7]spirarenes. Assume throughout that the first component lies in plane 1, the second in plane 2. The significant interaction is noted in [3.7]- and is absent in [3.5]- and [5.5]spirarenes. The generalization to an arbitrary case [m.n] is simple. An interaction leading to a stabilizing interaction can only occur when
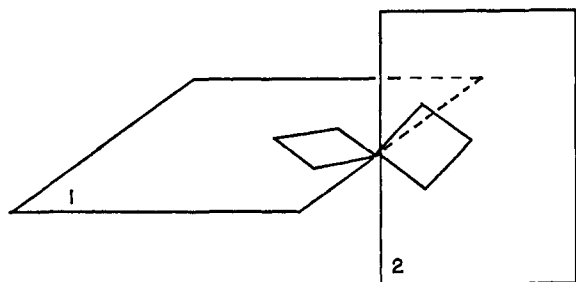
$(m) \bowtie (n)$ *vs.* $(m \quad n)$
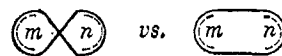
Figure 6. A drawing of the [3.3]spirarene.
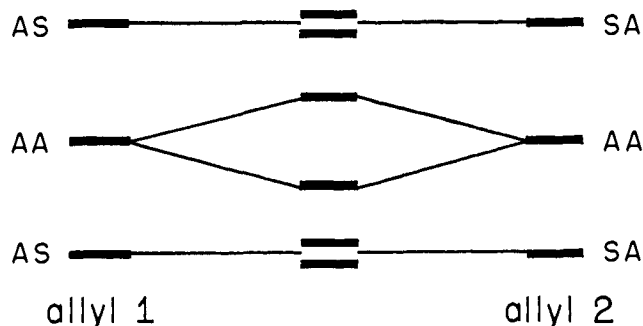
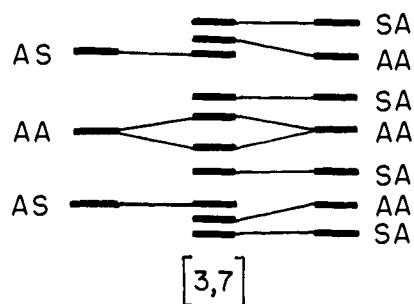Figure 7. The energy levels of two allyl systems interacting in [3.3]-spirarene.

Figure 8. Interaction of allylic systems in some higher spiro systems. Only AA levels may interact.

the nonbonding orbital of both systems has AA symmetry which occurs for the cases $m.n = 3, 7, 11$, etc., i.e., both m and n must be $4q + 3$ where $q = 0, 1, 2 \ldots$ This stabilization rule for a spiro system is thus in amusing contrast to Hückel's rule for a lateral interaction of two allylic fragments, which states that stabilization will occur whenever $m + n = 4q + 2$.

Figure 9 shows the appearance of the middle levels of the [3.3]spirarene after interaction. The view is end on, down the S_4 axis of the molecule. AA is characterized by four sideways interactions of p orbitals of an allyl in one ring with an allyl in the other. The splitting between AA and AA* is given by an extended Hückel calculation[1] as 1.0 ev for a CC distance of 1.45 in each perfect four-membered ring, 0.75 ev for a CC distance of 1.54. The overlap which gives rise to each interaction would appear to be quite inefficient; in fact at a ring CC distance of 1.45 A the two carbons are separated by 2.51 A and the overlap is 0.025. One can make a rough estimate of the stabilization to be expected by comparing with benzene imagined as arising from the interaction of two allyl systems. In benzene the two allyl fragments are coupled by $\pi-\pi$ overlaps at a distance of 1.40 A, each having the value of approximately 0.25. Thus it would seem that the overlap in benzene is ten times as efficient as in [3.3]spirarene. However benzene has two such overlaps but AA contains four such, and so in fact one would anticipate that the spiro interaction is worth about one-fifth of the benzene stabilization. This correlates with the magnitude of the splitting observed in the extended Hückel calculations.

When the splitting of two levels is small and two electrons are to be placed in these levels, it is critical to determine if the ground state of the system is expected

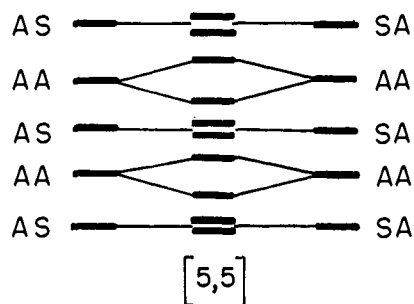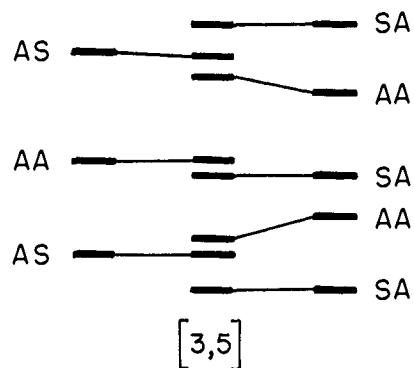(1) R. Hoffmann, J. Chem. Phys., 39, 1397 (1963), and subsequent papers. Here we use a H 1s Slater exponent of 1.3.
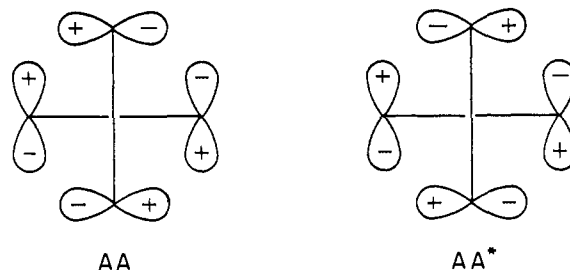

Figure 9. The two nonbonding allylic levels after interaction in the [3.3]spirarenes. In D_{2d} symmetry AA is b_1 and AA* is a_2.

to be a singlet or a triplet. The extended Hückel calculations are useless for this purpose and we have attacked the question with the aid of the Pariser–Parr–Pople method.

We limit ourselves to the basis set consisting of six 2p orbitals, the π-electron systems of the two allyls.

In the π-electron SCF scheme[2-4] the secular eq 1 is to be solved.

$$|F_{rs} - \epsilon S_{rs}| = 0 \qquad (1)$$

S_{rs} is the overlap integral and F_{rs} is the matrix element of the Fock operator, given by

$$F_{rs} = I_{rs} + \sum_t \sum_u P_{tu}\{(rs|tu) - \tfrac{1}{2}(rt|su)\} \qquad (2)$$

where I_{rs} and $(rs|tu)$ are the core and electron repulsion integrals, respectively

$$I_{rs} = \int \chi_r(1)\left(-\frac{\hbar}{2m}\Delta_1 + V(1)\right)\chi_s(1)\,d\tau_1 \qquad (3)$$

$$(rs|tu) = \int \chi_r(1)\chi_s(1)\frac{e^2}{r_{12}}\chi_t(2)\chi_u(2)d\tau_1 d\tau_2$$

P_{tu} is the element of the density matrix

$$P_{tu} = \sum_i c_{it}c_{tu} \qquad (4)$$

where c_{tt} is the coefficient of the tth AO in the ith MO, and the summation extends over all occupied molecular orbitals.

The usual simplifying assumptions of the π-electron SCF method are then made: neglect of overlap in eq 1, neglect of differential overlap in the evaluation of electron repulsion integrals, neglect of penetration integrals. The core coulomb integrals are given as

$$I_{rr} = -W_r - \sum_{s \ne r} (rr|ss) \qquad (5)$$

where W_r is the valence-state ionization potential of atom r. The core resonance integrals are estimated as

$$I_{rs} = 0.5S_{rs}(W_r + W_s) \qquad (6)$$

With the above assumptions the matrix elements of the Fock operator have the following form

$$F_{rr} = -W_r - \tfrac{1}{2}P_{rr}(rr|rr) + \sum_{s \ne r}(P_{ss} - 1)(rr|ss) \qquad (7)$$

$$F_{rs} = 0.5S_{rs}(W_r + W_s) - \tfrac{1}{2}P_{rs}(rr|ss) \qquad (8)$$

The valence-state ionization potentials are taken from the compilation of Hinze and Jaffé.[5] For the electron repulsion integrals we find that we cannot apply the usual method of evaluation since our basis orbitals do not lie all in the same plane. This problem has been faced in other calculations.[6] The general two-center integral may be represented as follows.

$$(rr|ss) = C_1(\sigma_r\sigma_r|\sigma_s\sigma_s) + C_2(\pi_r\pi_r|\pi_s\pi_s) +$$

$$C_3(\sigma_r\sigma_r|\pi_s\pi_s) + C_4(\pi_r\pi_r|\sigma_s\sigma_s) + C_5(\pi_r\pi_r|\bar\pi_s\bar\pi_s) +$$

$$C_6(\sigma_r\pi_r|\sigma_s\pi_s) + C_7(\pi_r\bar\pi_r|\pi_s\bar\pi_s) \qquad (9)$$

where $c_1, c_2, \ldots c_7$ are determined by the relative orientation of the two atomic orbitals, i.e., are pure trigonometric factors. The basic integrals are estimated semiempirically. The one-center integral $(\pi_r\pi_r|\pi_r\pi_r)$ is obtained by the Pariser–Parr approximation[2] using

the tables of Hinze and Jaffé. There are two other types of one-center integrals $(\pi_r\pi_r|\bar\pi_r\bar\pi_r)$ and $(\pi_r\sigma_r|\pi_r\sigma_r)$. These are calculated assuming a proportionality between theoretical and semiempirical values. Thus

$$(\pi_r\pi_r|\bar\pi_r\bar\pi_r)_{\text{semiemp}} = \frac{(\pi_r\pi_r|\pi_r\pi_r)_{\text{semiemp}}}{(\pi_r\pi_r|\pi_r\pi_r)_{\text{theor}}}(\pi_r\pi_r|\bar\pi_r\bar\pi_r)_{\text{theor}} \qquad (10)$$

$$(\pi_r\sigma_r|\pi_r\sigma_r)_{\text{semiemp}} = \frac{(\pi_r\pi_r|\pi_r\pi_r)_{\text{semiemp}}}{(\pi_r\pi_r|\pi_r\pi_r)_{\text{theor}}}\cdot(\pi_r\sigma_r|\pi_r\sigma_r)_{\text{theor}}$$

The theoretical values are calculated with the formulas given by Roothaan,[7] using Slater orbitals. The following relations give us all the one-center integrals.

$$(\pi_r\pi_r|\pi_r\pi_r) = (\sigma_r\sigma_r|\sigma_r\sigma_r)$$

$$(\pi_r\pi_r|\pi_r\bar\pi_r) = (\pi_r\sigma_r|\pi_r\sigma_r) \qquad (11)$$

$$(\pi_r\pi_r|\bar\pi_r\bar\pi_r) = (\sigma_r\sigma_r|\pi_r\pi_r)$$

These estimates of the one-center integrals are quite close to the values obtained semiempirically,[8] so that the approximation of proportionality, eq 10, appears to be valid.

The next problem is to estimate the two-center integrals. Many approximations have been presented for these, among them those of Pariser and Parr,[2] Mataga and Nishimoto,[9] and Ohno.[10] In the present paper, the two-center integrals at atomic distances greater than 2.8 A were calculated theoretically with the formulas given by Roothaan.[7] In the case of interatomic distances less than 2.8 A, the following expressions are obtained using interpolation formulas in a manner similar to that of Pariser and Parr.[2,6]

$$(\pi\pi|\pi\pi) = 0.2595r^2 - 2.938r + 11.13$$

$$(\sigma\sigma|\sigma\sigma) = 0.1210r^2 - 2.337r + 11.13$$

$$(\pi\pi|\bar\pi\bar\pi) = 0.1568r^2 - 2.231r + 9.93$$

$$(\sigma\sigma|\pi\pi) = 0.0977r^2 - 1.972r + 9.93 \qquad (12)$$

$$(\pi\bar\pi|\pi\bar\pi) = 0.0514r^2 - 0.354r + 0.60$$

$$(\sigma\pi|\sigma\pi) = 0.0587r^2 - 0.384r + 0.60$$

The resulting values for the ionization potential and the one-center electron repulsion integrals are as follows (ev): ionization potential (-11.16), $(\pi_r\pi_r|\pi_r\pi_r)$ (11.13), $(\pi_r\pi_r|\bar\pi_r\bar\pi_r)$ (9.93), $(\pi_r\pi_r|\bar\pi_r\bar\pi_r)$ (0.60).

By using these expressions we can estimate all the integrals needed for an SCF calculation. The computations were initially carried out on the [3.3]spirarene with C–C bond distances of 1.40 A, CCC angles of 90° within each ring. The carbon 2p Slater exponent was 3.25.

The SCF calculation put the triplet of the $(AA)^1$-$(AA^*)^1$ configuration 0.30 ev below the singlet of the $(AA)^2$ configuration. It seemed obvious that as a result of the small splitting of the AA and AA* levels the configuration interaction (CI) of the $(AA)^2$ and $(AA^*)^2$ configurations would be particularly strong. We proceeded to carry out a CI calculation, including all singly and doubly excited configurations. The results are shown in Table I.

(2) R. Pariser and R. G. Parr, J. Chem. Phys., 21, 466, 767 (1953).
(3) J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
(4) An excellent general reference for π-electron calculations is L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., N. Y., 1966.
(5) J. Hinze and H. Jaffé, J. Am. Chem. Soc., 84, 540 (1962).
(6) Y. Gondo, J. Chem. Phys., 41, 3928 (1964).

(7) C. C. J. Roothaan, ibid., 19, 1445 (1951).
(8) T. Anno, ibid., 29, 1161 (1958).
(9) N. Mataga and K. Nishimoto, Z. Phys. Chem., 13, 140 (1957).
(10) K. Ohno, Theor. Chim. Acta, 2, 219 (1964).

Table I. Energies of the Lowest States of [3.3]Spirarene from SCF + CI Calculations[a]

Configuration	State[b]	SCF	SCF + CI
····(AA)²	¹A₁	0.0	−1.340
····(AA)¹(AA*)¹	³B₂	−0.297	−0.700
····(AA)¹(AA*)¹	¹B₂	2.891	2.554

[a] The energy zero is that of the lowest singlet before CI. [b] Here we use the proper D_{2d} symmetry designations.

As anticipated, CI stabilizes the $(AA)^2$ configuration (predominantly as a result of heavy mixing with $(AA^*)^2$) by much more than the lowest triplet. It is thus predicted that the ground state of [3.3]spirarene will be a stabilized singlet. The lowest triplet is here calculated to lie only 0.64 ev above the ground state. The calculated energy for the first allowed transition $^1B_2 \leftarrow {}^1A_1$ is 3.89 ev.

We have also repeated the SCF − CI calculation for a molecule with all C–C distances 1.54 A to provide a check on the stability of our results to the (unknown) distances in the spiro ring. The calculation led to a ground state $^1A_1$, with $^3B_2$ 0.481 ev, and $^1B_2$ 3.963 ev above it. Thus the level ordering is not very sensitive to the distances.

Table II below lists the electron densities and bond orders in the three lowest states. The charge distribution is fairly uniform. Most noteworthy is the spiro (1–4) bond order which has a large value in the lowest singlet and as might have been expected is negligible in the B_2 states.

Table II. Electron Densities and Bond Orders from SCF − CI Calculation at C–C 1.54 A

State	Electron density 1	2	Bond order 1–2	1–3	1–4
¹A₁	1.033	0.933	0.669	0.034	0.225
³B₂	1.034	0.932	0.680	0.034	0.004
¹B₂	1.032	0.936	0.689	0.043	0.005

Our calculations of the [3.5]spirarene also yielded some surprises. Figure 8 would make it appear that the SA orbital of the pentadienyl fragment and the AA orbital of allyl are nearly degenerate. In reality the AA orbital is somewhat destabilized by its interaction with AA orbitals of pentadienyl. The lower configurations that we have to consider in an SCF calculation are shown below.

I $(SA_5)^2(AS_3)^2(AA_5)^2(SA_5)^2 \longrightarrow {}^1SS$

II $(SA_5)^2(AS_3)^2(AA_5)^2(SA_5)^1(AA_3)^1 \longrightarrow {}^1AS, {}^3AS$

III $(SA_5)^2(AS_3)^2(AA_5)^2(AA_3)^2 \longrightarrow {}^1SS$

The subscript indicates the origin (allyl or pentadienyl) of the orbital. Strong CI mixing of I and III is expected. The SCF calculation without CI was interesting. Though the SCF orbitals were derived for configuration I both ¹AS (−0.939 ev) and ³AS (−1.028 ev) came out at lower energy than ¹SS. Though our closed shell calculation was forcing the occupation I, the molecule clearly preferred configuration II. In the CI treatment we included all singly and doubly excited configurations which could give rise to singlets or trip-

lets, and nearly half of the doubly excited configurations with four electrons in four different orbitals. The total was 67 configurations. The final level ordering and some bond orders are shown in Table III.

Table III

State	Energy	Bond order 1–3	1–4	1–5	4–8
¹SS	1.370	0.273	0.231	0.164	0.261
³AS	0.053	−0.068	0.169	0.021	0.023
¹AS	[0.0]	−0.056	0.177	0.031	0.014

The unusual result here again is the stabilization of ¹AS and ³AS. Probably an open-shell calculation is necessary to clarify the nature of the ground state. There are considerable spiro (1–4) bond orders in all states. ¹SS also has a sizable (1–5) bond order which can be traced to interaction of AA_3 with the two AA_5 levels which do have density at 5. We also found most interesting the large (1–3) and (4–8) bond orders in the ¹SS state. This is a charge-transfer state corresponding to $(allyl)^+(pentadienyl)^-$ and the large end–end bond orders make one think of a contributing structure.


In postulating the chemical stability of a radical species one must always worry about possible reactions by which the radical could rearrange to a stabler species. Fortunately the [3.3]spirarene is an extremely hydrogen-deficient species, C_7H_6, so that abstraction reactions appear very unlikely. The classical collapse of the spirarene leads to the interesting molecule V, a bicyclopentene twice over. V could by a single (thermally
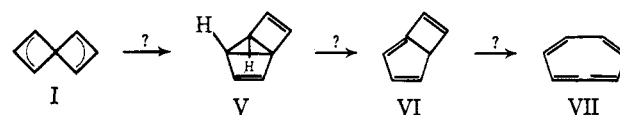
forbidden) electrocyclic reaction open to VI, which may be the stable point for these isomerizations, since the further electrocyclic opening would give rise to the impossibly strained VII. Of course there exist C_7H_6 isomers (e.g., hepta-1,3-diyn-5-ene) but they all seem very far removed in geometry from I. Still another possible reaction, the dimerization of the spirarene, seems to be possible.

Though we have not carried out any calculations, it appears to us that similar stabilization should obtain when an allyl radical is replaced by a benzyl radical, as in the model molecule VIII.

VIII
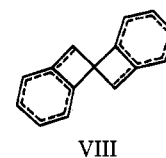
Conjugation in a spiro arrangement is of course not limited to interacting allylic systems. The same phenomenon for spiro-linked polyenes, e.g., the molecules IX, X, and XI, may be analyzed in precisely the

same manner. In fact derivatives of X and XI,[11] as well as the interesting molecule XII,[12] have recently been synthesized.

IX   X   XI   XII

However, we feel that there is a basic difference between spiroconjugation of polyenes and that of polyenyl radicals which makes analysis of the latter phenomenon more interesting. In the polyene case once again only AA levels interact (e.g., π^* of ethylene, ψ_2 and ψ_4 of butadiene, etc.). However, the interaction is primarily among bonding or antibonding levels. As a result of this interaction some levels are pushed up, some pushed down. The net result as for the stabilization of the ground state of the system is highly ambiguous: the results of spiral conjugation are more directly felt in transition energies and ion stabilities. But for two interacting "radicals" in a spiro system it is clear that interaction, the removal of the degeneracy of the nonbonding orbitals, is a matter of crucial importance in determining the very multiplicity and stability of the ground state.

The analysis of interaction among polyenes in a spiro geometry and in mixed polyene–polyenyl molecules does present some problems of interest and so we will illustrate the results with some simple cases.

Below are drawn interaction diagrams for models IX and XI. As should be apparent by now only AA levels

IX

XI
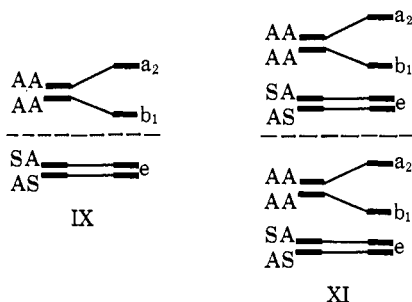
interact, giving rise to combinations with the general appearance of AA and AA*, and transforming in D_{2d} as b_1 and a_2, respectively. In XI the filled levels are split by the interaction, and in IX the lowest unfilled.

(11) E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, **31**, 4260 (1966).

(12) G. Farges and A. S. Dreiding, *Helv. Chim. Acta* **49**, 552 (1966).

The consequence on the spectrum should be identical: a splitting of the $\pi \rightarrow \pi^*$ band into two allowed components, and a red shift of the highest wavelength band. The anions of IX and the cations of XI should be stabilized.

The mixed system X has a different interaction pattern. Plane 1 is the plane of the ethylene, plane 2 that
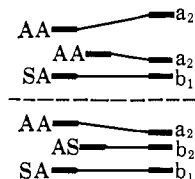
of the diene. The levels are classified in C_{2v} symmetry, and as a result of interaction with levels of like symmetry, the highest occupied MO is stabilized, whereas the lowest unoccupied remains approximately at constant energy. The net result should be a blue shift in the spectrum.

Next consider the mixed systems XIII and XIV.

XIII   XIV

The interaction diagram for these is shown below.

XIII   XIV

One can conclude that in the spiro arrangement the anion of XIII will be stabilized, but not the cation. In XIV both the cation and anion should be stabilized. The arguments we use should be clear by now. They can be applied to a large number of molecules, and further developments must await the synthesis of some representative species.