

π, π -Biradicaloid Hydrocarbons: *o*-Xylylene. Photochemical Preparation from 1,4-Dihydrophthalazine in Rigid Glass, Electronic Spectroscopy, and Calculations¹

Charles R. Flynn and Josef Michl*²

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received December 3, 1973

Abstract: *o*-Xylylene has been prepared by irradiation of 1,4-dihydrophthalazine and five other precursors in glassy solutions at -196° . 1,4-Dihydrophthalazine is thermally unstable ($\Delta H^\ddagger = 15.4 \pm 1$ kcal, $\Delta S^\ddagger = -7 \pm 2.5$ eu). *o*-Xylylene appears to be a ground state singlet. It is stable indefinitely in rigid media but dimerizes fast as soon as the medium is softened. Irradiation converts it to benzocyclobutene. It shows characteristic absorption and fluorescence. The emitting state as well as the ground state are most likely planar. The triplet has not been detected. The spectral data are well accounted for by semiempirical π -electron calculations, which also predict the existence of a low-lying partly doubly excited state. CI wave functions of the low-lying states of the three isomeric xylylenes are analyzed in terms of both delocalized and localized frontier orbitals as well as natural orbital occupation numbers to bring out the characteristic features of a biradicaloid species, and approximate relations to classical resonance formulas are established.

Biradicals are an important class of reaction intermediates. First, they are suspected to play a central role in numerous thermal reactions, particularly cycloadditions and isomerizations.³ Second, in photochemical reactions, the geometry possessed by the reacting species at the time of return from the excited to the ground state undoubtedly is of importance in determining the nature of final products. Such geometries are likely to correspond to minima in the excited state potential energy hypersurface and to crossings, or avoided crossings, between it and the ground state surface, and many of them probably are of "biradicaloid" nature.^{4a} We use the adjective biradicaloid for those molecular geometries at which a simple MO picture of the species shows two approximately^{4b} nonbonding molecular orbitals containing a total of two electrons in the ground state, irrespectively of the nature of their distribution in the ground state.⁵ Examples are square-planar geometry of cyclobutadiene and open-chain geometry of tetramethylene, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, both most likely corresponding to minima in the lowest triplet state but quite possibly not in the lowest singlet state. Most commonly, only tetramethylene would be considered a biradical, but our usage of the term biradicaloid geometry is meant to encompass both cases.

Clearly, experimental data on the nature of the elec-

tronic states of molecules at biradicaloid geometries of all kinds would be very helpful for improved understanding of thermal and photochemical reactions. Theoretical considerations indicate that electronic states of various biradicaloid species should share common basic features so that study of suitably chosen model systems should go a long way toward this goal.^{4a,6} The relatively better accessibility of molecules at π, π -biradicaloid geometries (both nonbonding orbitals of π character) makes them a particularly attractive target. A recent study of hydrocarbons of the pleiadene family,⁵ such as **1**, led us to consideration of the *o*-xylylene structural subunit.

o-Xylylene (**2**) and its various derivatives have aroused much theoretical⁷ and experimental⁸⁻¹⁹ in-

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(2) Alfred P. Sloan Fellow, 1971-1973.

(3) R. G. Bergman in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, p 191.

(4) (a) J. Michl, *Mol. Photochem.*, **4**, 257 (1972); see also J. Michl, *Top. Current Chem.*, **46**, 1 (1974). (b) Note that the definition of biradicaloid geometry is purposely vague in that only "approximate" degeneracy of the "nonbonding" orbitals is required and it is not specified exactly just how small the HOMO-LUMO gap needs to be. There are undoubtedly intermediate cases with HOMO-LUMO gaps, and expected properties, somewhere between those of "ordinary" and "biradicaloid" geometries. An example of a gradual transition is conjugated polyenes, where the smallest members do not, but the large members do, qualify as "biradicaloid." In the simplest (HMO) approximation, 1,3,5,7,9-decapentaene has a HOMO-LUMO gap equal to 0.57 β , almost identical with that of *o*-xylylene (0.59 β) which is the subject of the present study (cf. butadiene, 1.24 β). It will be seen in the following that *o*-xylylene appears to be a "borderline" case, and we suspect that decapentaene is one as well.

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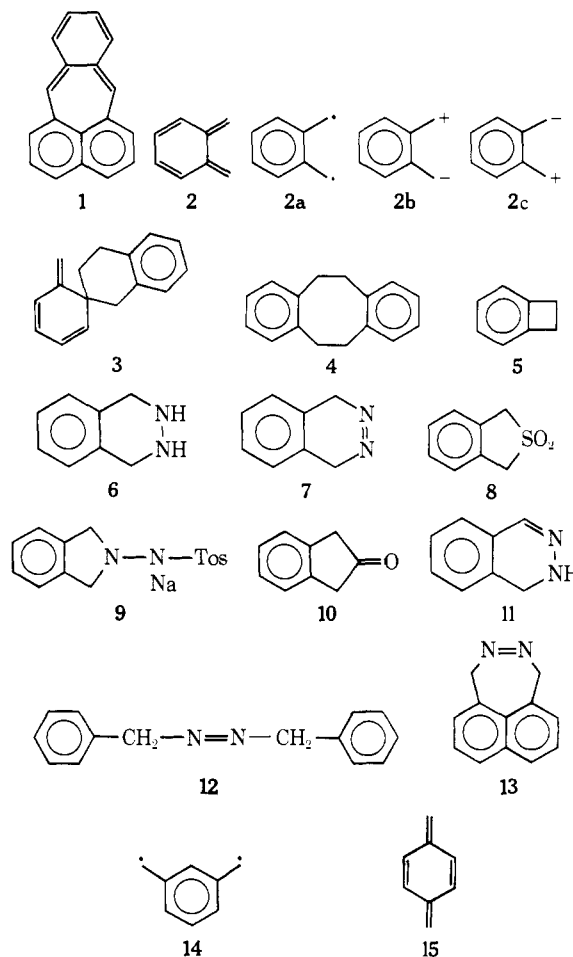
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terest. Commonly asked questions about its electronic structure involve the relative importance of contributions from structures such as **2a–2c** in various electronic states, spacing and even ordering of these states on the energy scale, in particular of the lowest and first excited singlet, S_0 and S_1 , and triplet T_1 , preferred geometry and reaction modes of each state, etc. Questions of particular interest to us have to do with possible presence of a low-lying doubly excited singlet state^{4a,6} and with possible differences in the preferred geometry in the S_1 as opposed to T_1 states. It has been proposed^{4a} that easily understood differences in the location of minima in the S_1 and T_1 hypersurfaces are responsible for a large part of the difference in the products of singlet and triplet photochemical reactions. Simple theoretical arguments indicate that in S_1 tight biradicaloid geometries should usually be advantageous (the two nonbonding orbitals in the same general region of space), while in T_1 loose biradicaloid geometries should commonly be preferred (the two orbitals in separate regions of space). Although the simplicity of the arguments makes them appealing and although they have been shown to account for general trends in known differences in singlet and triplet photochemical reactivity, there is little experimental evidence which would support the contention by direct observation on a suitable biradicaloid species (potential curves for various states of H_2 provide perhaps the best case^{4a}). It seemed to us that **2** might be of sufficiently biradicaloid nature to serve as an example; if the simple arguments are valid, T_1 would be expected to prefer loose geometry (one CH_2 group twisted out of the plane of the ring), as has been predicted by numerical computations,^{7b} while S_1 would be expected to be planar (tight geometry). If absorptions and/or emissions involving S_1 and T_1 were observable, conclusions about molecular shapes of these species might be possible. Thus, it appears desirable to prepare **2** under conditions suitable for spectroscopic study.

In a preliminary communication²⁰ we have reported the first unambiguous direct observation of **2** itself. Previously, various substituted *o*-xylenes of differing stabilities have been observed or even isolated,^{10,19} including a stable metal complex¹¹ of **2**, but evidence for **2** itself had been indirect, based on studies of trapping and self-trapping reactions. The latter yield the Diels–Alder dimer **3**, 1,2:5,6-dibenzocyclooctadiene (**4**), and benzocyclobutene (**5**). Some of the reactions which are believed to involve **2** as a reaction intermediate are the oxidation of 1,2,3,4-tetrahydrophthalazine¹⁵ (**6**) at 0°, presumably proceeding *via* 1,4-dihydrophthalazine (**7**) and spontaneous elimination of N_2 at this temperature, and the thermal decompositions of 1,3-dihydroisothionaphthene 2,2-dioxide^{13,14,16} (**8**) and of the sodium salt of 1,3-dihydro-2-toluene-*p*-sulfonamidoisindole¹⁷ (**9**), as well as uv irradiation of 2-indanone^{18a} (**10**). It had been also suggested²¹ that some of the emissions observed upon prolonged photolysis of alkylbenzenes containing two ortho methyl groups in rigid glass at -196° are due to **2** and its

alkyl derivatives. Our results prove that this assignment was correct and in fact represented the first direct observation of **2**.

We now wish to report the details of our photochemical synthesis of **2** in rigid glass from the previously unknown highly unstable **7** and from five other precursors, some of its spectroscopic properties, and results of calculations. The evidence suggests that the S_1 state is planar, but additional effort will be required before conclusions about the shape of the T_1 state can be drawn.



Results

1,4-Dihydrophthalazine (7). The preparation of **7** was carried out by oxidation of 1,2,3,4-tetrahydrophthalazine (**6**) with *tert*-butyl hypochlorite at -90° . The base **6** was prepared from its readily available¹⁵ hydrochloride under nitrogen atmosphere. Attempts to effect the oxidation of **6** to **7** with other oxidizing agents such as MnO_2 , HgO , $Tl(OCOCF_3)_4$, O_2 , $CuCl_2$, Ag_2O , and Cl_2 at various temperatures resulted in either no reaction or product decomposition or rearrangement, or reaction mixtures too complex to encourage further investigation. The low-temperature uv spectrum of the reaction mixture obtained by the oxidation of **6** with *tert*-butyl hypochlorite contains absorption peaks at 310–330 nm and at *ca.* 360 nm. The 310–330-nm absorption was later shown to be due to 1,2-dihydrophthalazine (**11**), while the 360-nm band is due to **7**.

Removal of methanol solvent (10–15 ml) from the above reaction mixture was carried out by low-tempera-

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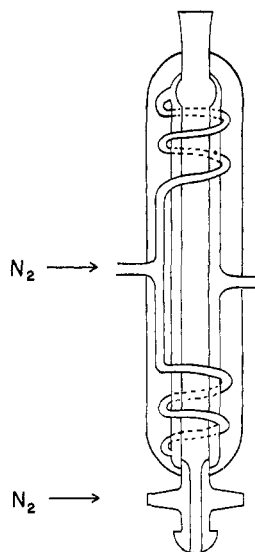


Figure 1. Column for low-temperature chromatography.

ture distillation at -78° and required 3–5 days at 5×10^{-6} Torr. Separation of **7** was achieved at -80° using the chromatographic column²² shown in Figure 1, Florisil or silica gel adsorbents (alumina caused rearrangement to **11**), and propane and dimethyl ether (DME) as solvents. **7** was obtained as a white powder which melted at -9 to -7° (sealed tube) with decomposition and evolution of gas. Uv spectrum (-100°) showed the presence of azo and benzene chromophores. The nmr spectrum in acetone- d_6 at -70° consisted of two singlets of equal integrated intensity (τ 2.59 and 4.96). The value of benzyl proton chemical shift compares well with those of model compounds **12**²³ and **13**¹⁵ which are reported to be τ 5.15 and 4.2, respectively.

Warming of a solution of **7** to temperatures above -40° resulted in rapid disappearance of the characteristic uv and nmr spectra which were replaced by the spectra of the spiro dimer of *o*-xylylene **3**. Presence of small amounts of **4** in the product cannot be excluded. A kinetic study of the decomposition was performed in diethyl ether solutions between -60 and -40° . The reaction was monitored spectrally by following the uv absorption at 365 nm. It was first order, $\Delta H^{\ddagger} = 15.4 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -7 \pm 2.5$ eu (at -50°). Following the rate by monitoring the ^1H nmr signal of **7** at τ 4.96 in acetone- d_6 was much less accurate; the rate constant obtained at $-42.5 \pm 1^{\circ}$ was 2.3×10^{-4} sec $^{-1}$, in reasonable agreement with the uv value at $-42.40 \pm 0.5^{\circ}$ in diethyl ether, 3.2×10^{-4} sec $^{-1}$.

Further elution of the chromatographic column with DME yielded known^{24,25} 1,2-dihydrophthalazine (**11**), identified by comparison with an authentic sample prepared according to Alper.²⁵ This compound is also easily formed from **7** by action of alumina, acids, and bases, even at low temperatures.

***o*-Xylylene (2).** A rigid glassy solution of **7** in EPA was irradiated at -196° with either a low-pressure

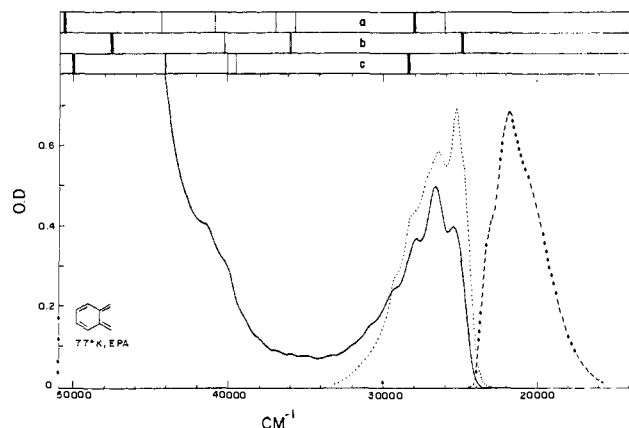


Figure 2. Absorption spectrum of *o*-xylylene (**2**) (—). Optical density 1.0 corresponds approximately to ϵ 6000. Excitation (···) and emission (---) spectra are not corrected for instrument response (arbitrary scale), EPA, 77°K . Calculated transition energies and oscillator strengths are shown on top (thin lines, f below 0.05, thick lines, 0.20 or more). Calculation a, 126-term CI-SCF and b, SCI-SCF, both with all bond lengths equal; c, SCI-SCF with bond lengths obtained from bond orders by iteration. For details see text.

mercury lamp (254 nm) or a high-pressure mercury lamp equipped with a 345 nm cut-off filter (light absorbed only by the azo chromophore). The characteristic uv absorption spectrum of **7** was completely destroyed in a matter of minutes and replaced by that shown in Figure 2 (λ_{max} 373 nm).

The photoproduct shows strong visible emission (λ_{max} 456 nm). Its spectral shape is independent of excitation wavelength. The excitation spectrum is independent of monitoring wavelength and follows the shape of the absorption band. The onsets of absorption and emission almost coincide, but the 0–0 bands are hardly discernible as weak shoulders (Figure 2). These results indicate that all of the absorption curve, at least below about 35000 cm^{-1} , belongs to only one photoproduct and that the emission is its fluorescence. No emission was observed through a phosphoroscope. The Franck-Condon forbidden shape of the absorption band and the vibrational spacing are strongly reminiscent of spectra of substituted *o*-xylylenes^{18b,19} and related *o*-quinomethides.²⁶ At least one substituted *o*-xylylene exhibits fluorescence similar to that of our photoproduct.¹⁹ No half-field epr signal could be detected after completed irradiation under conditions which easily permitted observation of the triplet signals of ground state triphenylene dianion and of phosphorescing irradiated triphenylene, indicating that the new species probably is not a ground state triplet.

Continued strong irradiation of the photoproduct ($\lambda > 345$ nm, collimated 200-W Hg arc) resulted in slow disappearance of the structured band at 373 nm and in appearance of the uv absorption spectrum of **5**. Conversion was virtually complete after 24 hr. Warm-up followed by glc analysis on two different columns confirmed the presence of **5** by comparison with an authentic sample.²⁷

Melting of the glassy solution containing the photo-

(22) The low-temperature column is a modified version of that described by K. Hojo, R. T. Seidner, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 6641 (1970).

(23) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

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(26) V. Dvořák, J. Kolc, and J. Michl, *Tetrahedron Lett.*, 3443 (1972); L. Edwards, J. Kolc, and R. S. Becker, *Photochem. Photobiol.*, **13**, 423 (1971).

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product from **7** resulted in rapid disappearance of the 373-nm absorption band and in the formation of the spectrum of the spiro dimer **3**. Traces of **4** may also be formed. Assuming complete conversion of the photoproduct to **3** and using the known⁸ molar extinction coefficient of **3**, that of the photoproduct is estimated to be *ca.* 3000, very close to that of the disubstituted *o*-xylylene, naphthocarborane.¹⁹ Estimated oscillator strength of the first transition in the photoproduct then is about 0.06.

The above data suggest that the photoproduct is **2**. Confirming evidence was obtained by preparation of the same compound from additional precursors. Irradiation of the glassy solutions of **5**, **8**, **9**, **10**, or *o*-xylylene in EPA at -196° with a low-pressure mercury arc produced a common species having a uv absorption spectrum which appeared identical with that shown in Figure 2, except that additional absorption bands were also present, apparently due to the presence of other photoproducts. In each case, fluorescence emission and excitation spectra were identical with those observed with the photoproduct from **7**, demonstrating convincingly that it is **2**.

The emission and excitation spectra obtained from photolyzed *o*-xylylene agree completely with those reported by Migirdicyan²¹ and assigned by her tentatively to **2**. In the region free of interference by other absorbing species present, the absorption spectrum of this product agrees with that of **2** obtained from other precursors. Migirdicyan's assignment can now be considered fully confirmed.

Discussion

1,4-Dihydrophthalazine (7). This is one of the least stable cyclic azo compounds ever isolated. Its sensitivity to acids and bases is not unexpected (*cf.* the behavior¹⁵ of **13**), and the ease with which it loses nitrogen was also anticipated on basis of previous work. Indeed, the value $\Delta H^\ddagger = 15.4 \pm 1$ kcal/mol is one of the lowest measured so far for decomposition of a cyclic azo compound and, to our knowledge, the first obtained for a compound with 3,6-dihydropyridazine structure, ideally set up for a retro-Diels-Alder reaction.

The stereochemistry of 3,6-dihydropyridazine fragmentations has been investigated previously²⁸ and the reaction is believed to proceed in a concerted fashion. Our value $\Delta S^\ddagger = -7 \pm 2.5$ eu is in line with this reasoning.

***o*-Xylylene (2)**. The smooth photochemical fragmentation of **7** to give nitrogen and **2** has ample precedent.²⁹ Also the other photochemical reactions leading to **2** are of well-known types and require little comment, perhaps with the exception of the formation of **2** from *o*-xylylene.²¹ Strong irradiation of methyl-substituted benzenes in rigid glasses is well known³⁰ to produce benzyl radicals by scission of the benzylic C-H bond in a two-photon process proceeding *via* the T_1 state, and the spectrum of the major reaction product indeed corresponds to that expected for *o*-methylbenzyl radical. The small amount of **2** formed prob-

ably results from its further transformation. Additional experimental work will be required before this interesting reaction can be elucidated in detail. The photochemical formation of **2** from **5**, **8**, and **10**, although much smoother, is still relatively inefficient and it appears likely that at least one of the side products again is a radical formed by scission of one of the benzylic C-H bonds. It had been reported previously^{18b} that **5** is inert to irradiation in a glassy matrix at -196° . The difference is probably due to our use of an intense source and longer irradiation times.

In the case of **9** the reaction proceeds faster. Here, the main undesirable absorbing species undoubtedly is sodium toluene-*p*-sulfonate. Formation of a diazene intermediate was not apparent in the spectra.

The photolysis of **7** was by far the fastest and cleanest and no by-products were detected irrespectively of the wavelength of the light used for the reaction.

Electronic States of the Xylylenes. General. Previous theoretical work⁷ on the xylylenes (**2**, **14**, and **15**) provides a glimpse of the nature of the low-lying electronic states of a biradicaloid species. It is obvious that the least bonding MO and least antibonding MO are in general not really degenerate, only fairly close in energy. In this respect, the so far unknown *m*-xylylene (**14**) at its equilibrium geometry should be the most typically biradicaloid molecule of the three. However, as should often be the case for molecules in which the two frontier orbitals are nearly degenerate, its ground state should be a triplet.^{7a,b} Even after it is prepared, it will be difficult to obtain experimental information about its singlet states. The price one pays for the ability to easily obtain spectroscopic data on singlet states for **2** and *p*-xylylene (**15**) is that they are less typically biradicaloid (*cf.* ref 4b).

We have extended the existing calculations by increasing the extent of configuration interaction, by calculating additional observables, and by expressing the results in terms of various choices of starting orbitals. Details of the method of calculation are described in the Experimental Section.

For a nonpolar biradicaloid species, simple arguments lead one to expect four relatively low-lying states, three singlets, and one triplet.^{4a,6} In terms of delocalized (canonical) molecular orbitals (ϕ_a , ϕ_b), the triplet should be relatively well described by a single configuration with one unpaired electron in each of the frontier (approximately nonbonding) orbitals, while each of the singlets should be well represented as a mixture of three configurations. The first of these ("ground configuration," G) has both nonbonding electrons in the slightly more bonding of the two frontier orbitals (ϕ_b), the second ("doubly excited configuration," D) has both electrons in the other orbital (ϕ_a), and the third ("singly excited configuration," S) has one electron in each of the two orbitals. The lowest of the three singlets, S_0 , and the highest of them, S_2 , correspond approximately to an out-of-phase ($G - D$) and in-phase ($G + D$) combination of the first two configurations, respectively, while the middle singlet, S_1 , is described reasonably well by the third configuration (S). In general, a change in nuclear geometry which pushes the energies of the two approximately nonbonding orbitals apart, such as a distortion leading to bond formation between two reactive centers, causes

(28) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969), reported that 3,6-dimethyl-3,6-dihydropyridazine is too unstable to observe at -50° .

(29) P. S. Engel and C. Steel, *Accounts Chem. Res.*, **6**, 275 (1973).

(30) For leading references, see ref 21 and P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **48**, 851 (1968).

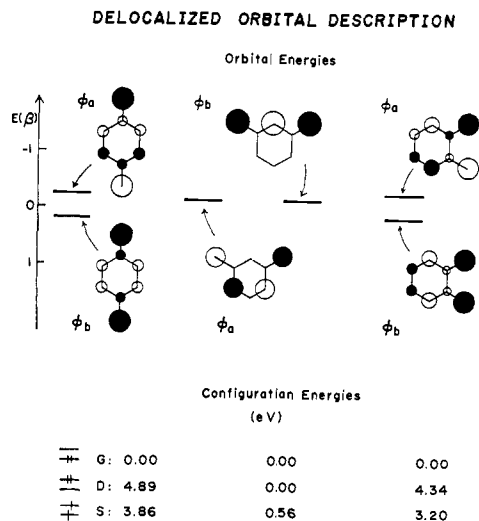


Figure 3. Delocalized MO description of the xylylenes. Only the (Hückel) frontier orbitals ϕ_a and ϕ_b are shown. Size of the MO expansion coefficients is proportional to the circle diameter and the sign is indicated by shading. For configuration energies see text.

the energy of S_0 to decrease (G then prevails over D in its wave function), the energy of S_1 to increase somewhat (S remains a good description), and the energy of S_2 to increase considerably (D prevails over G in its wave function). The species becomes less "biradicaloid" and more like a "normal" molecule, in whose S_0 state G is much more important than D. In the case of the xylylenes, the delocalized approximately nonbonding orbitals have the forms shown in Figure 3. Their energy in the Hückel approximation is also indicated. In the Hückel as well as Pariser-Parr-Pople (PPP) approximations, there is zero net charge on each π center in G, D, and S in **2** and **15** (but not **14**), and in the final states T_1 , S_0 , S_1 , and S_2 in all three xylylenes.

This simplified description can be equally well cast in the language of partly localized nonbonding orbitals. If the plus and minus combinations of the two approximately nonbonding delocalized orbitals are constructed, they are predominantly localized in different regions of space (Figure 4). Their energy (diagonal element of the Hamiltonian) is zero in the Hückel approximation. In terms of these "localized" orbitals, the triplet should still be described by a single configuration with one unpaired electron in each orbital and zero net charge on each π center (symbolically written as formula IIa with identical spins on the two dots), and each of the singlets should again be well represented as a linear combination of the three possible singlet configurations. Now, however, those two in which both electrons are put in one of the two localized orbitals clearly have excess negative charge in the region of space where that orbital is localized, and shortage of negative charge in the region of the other orbital (Figure 4), and are called "ionic" configurations, or structures, I_1 and I_2 . They can be symbolized by formulas **2b** and **2c** where it is understood that the charges are delocalized similarly as they would be in a benzyl cation and benzyl anion. The only singlet configuration with balanced charge is the covalent (correlated) one, C, in which one electron is placed in each of the localized orbitals (symbolized by formula **2a** with opposite spins on the two dots, again assuming that delocalization as in benzyl radical

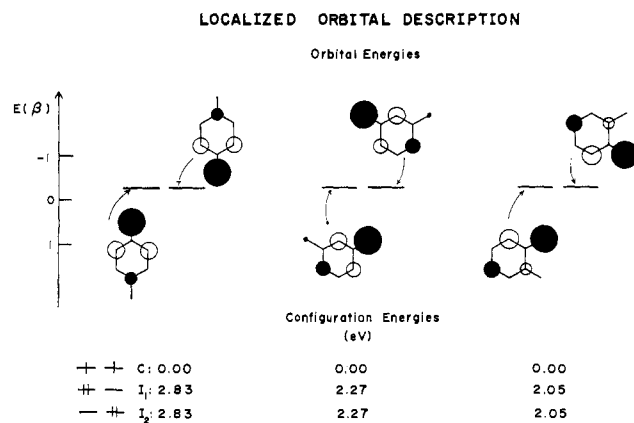


Figure 4. Localized MO description of the xylylenes. Only the (Hückel) frontier orbitals $\phi_a + \phi_b$ and $\phi_a - \phi_b$ are shown (see caption to Figure 3).

is understood). Not surprisingly, in this description, the S_0 state can be expected to be well approximated by C (with growing contribution from I_1 and I_2 if the molecule becomes less "biradicaloid" as the energies of the frontier orbitals move apart), while the higher energy states S_1 and S_2 are described predominantly by $I_1 - I_2$ and $I_1 + I_2$, respectively. Although the distribution of charge densities in I_1 and I_2 is unbalanced, in the final states, T_1 , S_0 , S_1 , and S_2 , the charge distribution will be again uniform since I_1 and I_2 should enter with equal weights. The description becomes slightly more complicated if the two optimally localized orbitals differ in electronegativity, *i.e.*, if the biradicaloid species is polar. However, this does not concern us in the case of the xylylenes.

An important complicating factor which has not been discussed explicitly in previous qualitative discussions^{4a,6} is interaction with other configurations. This may be important in all of the T_1 , S_0 , S_1 , and S_2 states but particularly in S_1 and S_2 . The zeroth-order states simply described above will in general be mixed with additional configurations and as a result their order may be changed and new low-lying states may be introduced. Knowledge of the relative energies of states corresponding to those defined above as S_1 and S_2 at biradicaloid geometries reached in photochemical reactions may well turn out to be crucial for an understanding of pericyclic photochemical processes. S_2 undergoes an avoided crossing with S_0 as the molecule passes through the biradicaloid ("antiaromatic") geometry along the "ground state forbidden" path. If S_2 governs the nuclear motions at that point, as is most likely if it is the lowest excited state, return to S_0 at the biradicaloid geometry is particularly easy (for details and references see ref 4a).

Results of actual PPP calculations on singlet states of the xylylenes using 126-spin-projected configurations and standard parameter values are presented in Table I and show that the reversal of the order of S_1 and S_2 states in a biradicaloid species can indeed occur, at least in theory. We find even in other instances that " S_2 " often lies below " S_1 " as a result of strong configuration interaction and decreased "ionic" character. The physical basis for this difference is now well understood and will be discussed elsewhere.

The results are analyzed in terms of localized and

Table I. Low-Lying Excited Singlets of the Xylylenes

Composition of Wave Functions					
<i>o</i> -Xylylene (C_{2v})		<i>m</i> -Xylylene (C_{2v})		<i>p</i> -Xylylene (D_{2h})	
E , eV	Other config, %	E , eV	Other config, %	E , eV	Other config, %
S_0 0.00 A_1	{ 82% G, 0% S, 9% D, } { 73% C, 9% I ₁ , 9% I ₂ }	9 S_0 0.00 A_1	{ 41% G, 0% S, 41% D, } { 82% C, 0% I ₁ , 0% I ₂ }	18 S_0 0.00 A_{1g}	{ 77% G, 0% S, 13% D, } { 77% C, 6.5% I ₁ , 6.5% I ₂ }
S_2 3.22 A_1	{ 10% G, 0% S, 46% } { D, 6% C, 25% I ₁ , } { 25% I ₂ }	44 S_1 1.04 B_2	{ 0% G, 70% S, 0% D, } { 0% C, 35% I ₁ , 35% I ₂ }	30 S_2 3.18 A_{1g}	{ 14% G, 0% S, 38% D, } { 4% C, 24% I ₁ , 24% I ₂ }
S_1 3.47 B_2	{ 0% G, 90% S, 0% D, } { 0% C, 45% I ₁ , 45% I ₂ }	10 S_2 2.65 A_1	{ 40.5% G, 0% S, 40.5% } { D, 0% C, 40.5% I ₁ , } { 40.5% I ₂ }	19 S_1 4.12 B_{1u}	{ 0% G, 88% S, 0% D, } { 0% C, 44% I ₁ , 44% I ₂ }
Natural Orbital Occupancies in S_0					
1.994; 1.961; 1.961; 1.743; 0.257; 0.039; 0.039; 0.006		1.998; 1.969; 1.967; 1.000; 1.000; 0.033; 0.031; 0.002		1.995; 1.963; 1.962; 1.685; 0.315; 0.038; 0.037; 0.005	

delocalized orbitals. The calculated order of nearly degenerate states, such as S_1 and S_2 in *o*-xylylene, is sensitive to the choice of parameters and nuclear geometry and to the extent of configuration interaction and cannot be considered reliable. The regular hexagonal geometry for which data in Table I were obtained overemphasizes the biradicaloid nature of the three species. However, the PPP model is generally accepted to correctly describe the main features of π -electron behavior, and the general features are independent of the details of the calculation and quite likely to be correct. This belief is strengthened by the agreement of calculated and experimental spectral properties as discussed in the next section.

In the following discussion, we have kept the labels S_1 and S_2 in conformity with the above first-order analysis although in two cases S_2 then actually lies below S_1 . The species which agrees best with the above outlined simple picture of a biradicaloid is the so far unknown *m*-xylylene (**14**). The only difference introduced in this case by the consideration of extensive CI is the admixture of up to 30% of other configurations into the three low-lying singlet states. Of course, in **14** the two nonbonding orbitals are strictly degenerate in the PPP model so that one deals with a "true" biradicaloid system and it is reasonable that the simple picture should be valid. This is also reflected in the calculated occupation numbers of natural orbitals in the ground state. Three natural orbitals are essentially doubly occupied, two are singly occupied, and three are essentially empty. This contrasts strongly with occupation numbers for natural orbitals of "ordinary" molecules, which are all either essentially doubly occupied or essentially empty. The natural orbitals were obtained by diagonalization of the density matrix obtained from the 126-term CI wave function and not from exact complete CI solutions of the PPP model. We believe, however, that they reflect the important features of the exact solution of the PPP model.

Both **2** and **15** deviate from the image of a "perfect" biradicaloid molecule, approximately to the same extent. Such a deviation is expected since one of the two "approximately nonbonding" delocalized orbitals is slightly bonding, the other slightly antibonding, and it would be even more pronounced if the calculation allowed for bond length alternation in the molecule which is expected to exist in its ground state but to lesser extent in the excited states (see below). As a

result, G predominates over D in the S_0 state. In the equivalent localized orbital description, the ionic configurations I_1 and I_2 make a noticeable contribution to S_0 . In standard symbolism, formula **2** then is a fair representation of the ground state S_0 , although the contribution of structure **2a** (spins antiparallel) is higher than usual, and the situation is similar for **15**. Still another expression of the same effect is found in the calculated occupation numbers of the natural orbitals of the S_0 state. Although both in *o*- and *p*-xylylene the occupation number of the least occupied among the "occupied" orbitals is much lower than the value typical of nonbiradicaloid molecules, it also is far from the value 1.0 found for the "true" biradical (**14**).

The S_2 state contains very large contributions of other configurations and as a result is rather low in energy, particularly in **15**. This also destroys to some extent the applicability of the simplified discussion given above, and the representation of this state as a hybrid of the structures **2b** and **2c** is only approximate. Low-lying states with 30–40% doubly excited character may be common in polyolefins, even those not considered "biradicaloid," such as butadiene.³¹ Of course, the transition from normal to biradicaloid species is continuous and long polyenes have relatively small HOMO–LUMO gaps.^{4b} In fact, the first report of an experimental low-lying π – π^* state assigned as partly doubly excited was for 1,8-diphenyloctatetraene.³² The subsequent report³³ of a predominantly doubly excited low-lying π – π^* state was for pleiadene (**1**), which has more clearly biradicaloid nature.

Whether the low-lying partly doubly excited states of *o*- and *p*-xylylenes are viewed as an expression of the biradicaloid nature of the molecules or simply as consequence of their polyolefinic character, their observation would be of considerable interest. It will be difficult in **2** where the $S_0 \rightarrow S_2$ transition should be buried under the much more intense $S_0 \rightarrow S_1$ band. We do not find any spectral evidence for the S_2 state. On the other hand, in **15** the $S_0 \rightarrow S_2$ transition should correspond to the symmetry-forbidden first absorption

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Table II. Calculated Electronic Spectra of the Xylylenes^a

<i>o</i> -Xylylene (C_{2v})				<i>m</i> -Xylylene (C_{2v})				<i>p</i> -Xylylene (D_{2h})			
Energy	Sym	f_r	f_p	Energy	Sym	f_r	f_p	Energy	Sym	f_r	f_p
26.0 (S_2)	A_1	0	0	8.4 (S_1)	B_2	0	0	25.6 (S_2)	A_{1g}	0	0
28.0 (S_1)	B_2	0.21	0.19	21.4 (S_2)	A_1	0.09	0.06	32.6	B_{3g}	0	0
35.7	B_2	0	0	22.3	B_2	0	0	33.2 (S_1)	B_{1u}	0.76	0.72
36.9	A_1	0	0	24.8	A_1	0	0	35.5	B_{3g}	0	0
40.8	B_2	0.01	0.01	36.1	A_1	0.01	0.01	43.0	B_{2u}	0	0
44.2	A_1	0	0	39.9	A_1	0	0	45.1	A_{1g}	0	0
50.5	A_1	1.04	0.87	45.0	B_2	0.74	0.64	48.5	B_{1u}	0	0
				45.9	B_2	0	0	51.3	B_{1u}	0.46	0.42
				47.8	A_1	0.002	0.001				
				49.4	B_2	0	0				

^a Excitation energies in units of 1000 cm^{-1} , oscillator strengths from dipole length (f_r) and dipole velocity (f_p) formulas, and bond orders from 126-term CI wave functions (calculation a).

band, and vibronic interactions should make it even more easily observable than the reported³² case of 1,8-diphenyloctatetraene.

The wave function of the S_1 state in both **2** and **15** corresponds very nicely to the simple considerations introduced in the beginning since admixture of other configurations is minimal. Symbolically, this state is very well described as a hybrid of the two ionic structures such as **2b** and **2c** for the ortho isomer.

Spectral Properties of the Xylylenes. Singlets. As already mentioned, the numerical values of the calculated spectral properties and in particular the order of S_1 and S_2 in **2** depend somewhat on the particular approximations made, but the over-all character remains unchanged and is probably quite reliable. Table II and line a in Figure 2 summarize the results obtained using the same approximation as in Table I, in which standard parameter values are used and resonance integrals of all bonds are assumed equal (this probably results in underestimating the excitation energy of the $S_0 \rightarrow S_2$ transition). Results b and c shown on top of

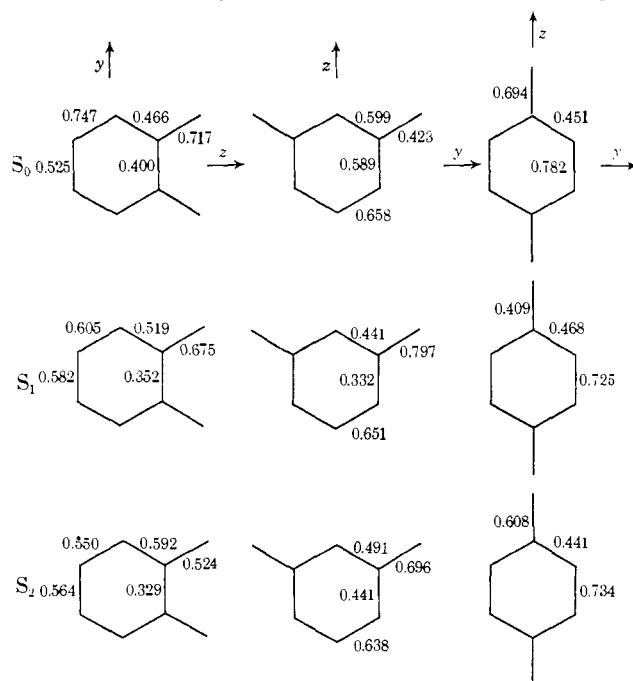


Figure 2 were obtained using only singly excited configurations and two different standard approximations (see Experimental Section). It should be noted that the zero values of oscillator strength for many symmetry-allowed transitions in Table II are an artifact of the

PPP method due to perfect pairing in alternant hydrocarbons and resulting forbiddenness of plus-plus and minus-minus transitions. In reality, one can expect these transitions to be very weakly allowed. Of course, these transitions, as well as the symmetry-forbidden $A_{1g} \rightarrow A_{1g}$ and $A_{1g} \rightarrow B_{3g}$ transitions in **15**, will in general also appear in the spectrum due to vibronic interactions. The differences in the plus and minus characteristics of the states in **2** and **15** on the one hand and **14** on the other, surprising at first sight, are due to the circumstance that the two "almost non-bonding" canonical orbitals of **2** and **15** are paired with each other, whereas the nonbonding canonical orbitals of **14** are each paired with itself.

Agreement with available experimental transition energies and intensities is good for **2** (Figure 2), since S_2 ought to be hidden below S_1 , and probably even for **15** (experimental band at $33,000\text{ cm}^{-1}$), since the first two transitions, calculated to be symmetry forbidden, may have been easily overlooked in the experimental work.³⁴ The large change in bond orders upon excitation is in accordance with the observed Franck-Condon forbidden shape of the absorption and fluorescence bands of both compounds. The degree of Franck-Condon forbiddenness should be even much higher in the $S_0 \rightarrow S_2$ transitions. It seems likely that the ground and fluorescing states of **2** are planar, since the band shape is quite similar to those observed in at least one related compound in which twisting of the exocyclic bond can hardly occur.¹⁹ A much more pronounced Franck-Condon forbidden shape would be expected if S_1 were twisted. Also, the twisted form would be expected to preferentially undergo radiationless decay rather than fluoresce. The relatively strong fluorescence probably also accounts for the inefficiency of the photochemical ring closure to **5**. Planarity of the S_1 state is in nice accord with intuitive expectations based on the picture of this state as hybrid of structures **2b** and **2c**, since it permits the positive and negative charge to be delocalized relatively close to each other, thus minimizing electrostatic energy.^{4a}

Further spectroscopic work on the xylylenes needs to concentrate on the detection of the unusual "doubly excited" S_2 states.

Spectral Properties of the Xylylenes. Triplets. All of the xylylenes should have lowest triplets fairly well symbolized by formulas such as **2a** with parallel spins on the two dots. No experimental information is avail-

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able at present. The triplet of the unknown **14** should be its ground state. It has been predicted to be planar while triplet **2** is expected to prefer slightly a geometry in which one CH₂ group has been twisted out of planarity, and triplet **15** should have essentially free rotation of one CH₂ group.^{7b} Our calculations have been limited to planar geometries for which the PPP model is best suited. Of course, the difference in the energies of the singlet and triplet species is very hard to calculate reliably. Insofar as a parameter selection tested on ordinary aromatic hydrocarbons³⁵ can be trusted, the triplet state of **2** should be 8000 cm⁻¹ above the ground state (S₀), at the geometry in which bond lengths alternate between single and double, and 5000 cm⁻¹ above S₀, at the hexagonal geometry in which all bond lengths are equal to 1.40. Experimentally, there seems little doubt that the ground state is S₀. Not only do we fail to observe a detectable epr signal under conditions where low concentrations of known phosphorescent or ground state triplets give quite strong signals, but the calculated T₁ → T_x absorption spectrum of a planar species disagrees with the observed spectrum and with location of the emission. No calculations were performed for the twisted forms of the xylylenes, but the expected T₁ → T_x spectrum of a twisted species should resemble somewhat the spectrum of the benzyl radical³⁶ while no such similarity is apparent.

At the moment, we have no experimental information about either the S₀ – T₁ energy gap in **2**, or the equilibrium shape of T₁. The results of calculations make it quite likely that phosphorescence will be exceedingly hard to observe even if the equilibrium shape of T₁ is planar and the Franck–Condon factor relatively favorable (low-quantum yield, wavelength in the infrared). However, at twisted geometry triplet **2** probably lies below the lowest singlet and might conceivably be stable at very low temperatures.

***o*-Xylylene. Summary.** The presently reported preparation of and spectral measurements on authentic **2** permit several conclusions. The experimental data make it very likely that (i) the ground state is a singlet, S₀, and (ii) S₀ and S₁ are planar. Since π-electron calculations are in good agreement with the observed spectrum, we also take seriously their additional so far unverified predictions, (iii) S₂, a partially doubly excited state, is approximately degenerate with S₁, (iv) T₁ is less than 10,000 cm⁻¹ above S₀ at the equilibrium geometry of S₀, and (v) the nature of the wave functions is that expected for a biradicaloid species on the basis of simple arguments,^{4a,6} except that the “doubly” excited nature of S₂ is diluted by admixture of additional configurations.

If one were further willing to accept the results calculated for the T₁ state,^{7b} one would reach the conclusion that the equilibrium geometries of the S₁ and T₁ state differ although the nature of orbital occupancy is the same in both, as expected from simple electrostatic arguments. Additional work is clearly required before such a conclusion can be accepted as firm.

Experimental Section

Instrumental Methods. Infrared spectra were obtained using a

Beckman IR-5A spectrophotometer. Proton nuclear magnetic resonance spectra were obtained using Varian XL-100-12 and Varian A-60 instruments. Electronic absorption spectra were recorded with a Cary 17 spectrophotometer.

Low-temperature electronic spectra were mostly taken in 3-methylpentane (3-MP), 2-methyltetrahydrofuran (2-MTHF), and EPA (ethyl ether/isopentane/ethanol, 5:5:2). 3-MP (Phillips 66, pure grade) and 2-MTHF (Matheson Coleman and Bell, chromatography reagent) were purified by refluxing with and distillation from sodium–potassium alloy. EPA mixed solvent (American Instrument Co.) was used without further purification. Suprasil quartz cells of 2–3-mm path length immersed in a quartz dewar with Suprasil windows containing liquid nitrogen were used for photochemistry, emission, and absorption spectroscopy at –196°. Spectroscopy above –196° was accomplished using the same dewar with approximately 1 in. of liquid N₂ in the bottom. The evaporating gas cooled samples, which were held above the surface of the liquid N₂, to about –100°. Emission spectra were measured using a 1-kW Xe arc, two Schoeffel GM-250 monochromators, an S-20 response photomultiplier, and a PAR 124 lock-in amplifier. Front surface excitation was used; the angle between the axes of exciting and collecting optics was 30°. Photochemical conversions were achieved using a 200-W high-pressure mercury arc with *f* = 1.5 quartz optics (PEK, Inc.) equipped with a water heat filter (10-cm path length) and glass cut-off filters (Corning Glass Co.) or with a four-coil low-pressure mercury lamp (Ultra-violet Products, Inc.), as indicated in the text.

Glc analyses were performed using a Hewlett-Packard 700 instrument; the following columns were used: A, 1/8 in. × 6 ft 3% QF-1 on Gas-Chrom Q 100–120 mesh; B, 1/8 in. × 10 ft 20% SE-30 on Chromosorb W 50–80 mesh.

Low-Temperature Column Chromatography. Separations were performed using the column²² shown in Figure 1. Cooling was accomplished by passing gaseous nitrogen through copper coils submerged in liquid nitrogen and then through the column. The temperature was controlled by adjusting the nitrogen flow rate. The eluting solvents were propane containing increasing percentages of dimethyl ether (DME). Commercial propane and DME (Linde Division of Union Carbide) were condensed at atmospheric pressure using a Dry Ice–acetone condenser. Elution of the column was monitored by taking 25–50-ml fractions and determining the uv spectrum of each fraction at about –100°. Care was taken to perform those operations which required exposure to the atmosphere quickly in order to minimize the collection of moisture.

Removal of the eluting solvent from appropriate fractions was accomplished at low temperature using a liquid N₂ trap. The solvent was distilled from a –78° bath and collected at –196°. Pressures of approximately 10⁻³ Torr were required to remove propane and/or DME.

Low-Temperature Kinetics. The kinetics of the decomposition of **7** were measured by monitoring the loss in peak height of the 358-nm azo uv absorption (actual wavelength monitored was 365 nm in order to minimize absorption by product). A constant temperature between –60 and –40° was maintained in a quartz dewar with flat windows, which contained the sample solution in a Suprasil cell, by a stream of cold nitrogen gas which was boiled from liquid nitrogen. The boiling was controlled by a thermocouple located inside the dewar but outside the cell, employing a Capacitrol temperature controller (Barber-Coleman Co.) and a cartridge heater. The temperature within the solution inside the cell was monitored using a copper–constantan thermocouple and was constant within ±0.5°. The voltages were read using a Fluke 881A dc differential voltmeter, accurate to 1 μV. The data obtained were evaluated using a least squares computer program written by Dr. K. Vorhees. The individual logarithmic plots contained 18–25 points and were linear over a minimum of 3 half-lives with correlation coefficient at least 0.9996. The values of the resulting rate constants were (units of 10⁻⁴ sec⁻¹, temperature in parentheses): 5.20 (–30.65); 5.34 (–39.85); 3.15 (–42.44); 2.47 (–44.17); 2.13 (–44.95); 1.39 (–47.89); 0.964 (–50.06); 0.626 (–52.40); 0.468 (–54.98); 0.257 (–56.77); 0.246 (–60.16); 0.175 (–60.20). The Eyring parameters were calculated using a program written by R. Hargrove. Error limits were estimated.

Method of Calculation. Calculations employed the standard version of the PPP method using a program described elsewhere.³⁷ Results b in Figure 2 were obtained using all singly excited con-

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(37) J. Downing, J. Michl, P. Jørgensen, and E. W. Thulstrup, *Theor. Chim. Acta*, **32**, 203 (1974).

figurations (SCI), all bond lengths equal to 1.40 Å, parameters as in ref 38. Results c in Figure 2 were obtained using SCI and bond lengths obtained from bond orders iterated to self-consistency using the method of ref 39. In this procedure, "single" bonds in structure 2 converged to 1.45 Å, "double" bonds to 1.36 Å. These values are very close to those reported for fulvene,⁴⁰ another cyclic polyene with a single classical structure.

Calculations reported in Tables I and II and results a in Figure 2 used 126 singlet-projected configurations and parameters of ref 38, except that the Ohno-Klopman expression⁴¹ was used for two-center electron repulsion integrals. Bond lengths were equal to 1.40 Å. Closed-shell SCF procedure was used for 2 and 15; Hückel MO's were used for 14. Configurations were selected to span a basis invariant to transformation of the delocalized frontier orbitals to a localized form. The following assignments of space parts (and all linearly independent spin functions possible for each of the assignments) were used (orbitals are numbered 1 through 8 in order of increasing energy). First, configurations with six electrons in the orbitals 1, 2, 3, 6, 7, and 8 were set up: ground configuration, all singly excited ones, and only those doubly excited ones involving excitation from or to orbitals 2, 3, 6, and 7. Each of these was then combined with each of the three possible arrangements of two electrons in orbitals 4 and 5 to give a total of 76 configurations. Second, configurations with seven electrons in the orbitals 1, 2, 3, 6, 7, and 8 were combined with the eighth electron in either 4 or 5. These were obtained by adding the seventh electron to orbital 6, 7, or 8 with 1, 2, and 3 doubly occupied and to orbital 6 or 7 with 1 and either 2 or 3 doubly occupied, the other (3 or 2), and either 6 or 7 being singly occupied (22 configurations). Third, configurations with five electrons in the orbitals 1, 2, 3, 6, 7, and 8 were combined with the two possible ways of assigning three electrons to orbitals 4 and 5. These 22 configurations (5-3 partition) are paired by the hole-particle relationship to those listed just above (7-1 partition). Fourth, configurations with six electrons in orbitals 1, 2, 3 and the remaining two in 6 and 7, as well as those with six electrons in orbitals 1, 4, 5 and remaining two in 2 and 3, were included (six in all).

Very similar results were obtained with other choices of parameters and configuration selection methods, including SECI-2²⁷ (up to 139 configurations).

Oxidation of 6 to 7 and 11. A solution of 150 mg (0.88 mmol) of the hydrochloride¹⁵ of 6 in 10 ml of absolute methanol was cooled under a nitrogen blanket with stirring to ca. -30°. To this cooled solution were added several drops of a saturated solution of KOH in methanol until the solution was distinctly basic to pH paper (pH ~9). The solution was further cooled to ca. -90° in a Dry Ice-ethanol bath to which liquid nitrogen was periodically added. Over a period of 30 min 9 drops (ca. 90 mg, 0.84 mmol) of *tert*-butyl hypochlorite were added. Care was taken during the addition of the hypochlorite to make sure that the solution remained basic. The cold solution from above was quickly transferred to a precooled flask (-78°) suitable for attachment to a vacuum line. The methanol was then removed at -78° (5×10^{-6} Torr) into a trap held at -196°. The residue remaining after re-

moval of the methanol was taken up in 2 ml of cold (-78°) DME and was quickly transferred to a low temperature (-80 to -90°) chromatographic column of Florisil (or silica gel) which had been prewashed with cold propane. The column was then eluted with propane containing increasing percentages of DME. The volumes used were 150 ml of propane, 175 ml of 95:5 propane/DME, 175 ml of 88:12 propane/DME, 500 ml of 80:20 propane/DME, and 100 ml of DME. The propane and 95:5 and 88:12 propane/DME elutions contained either no uv absorbing material or small amounts of the known spiro dimer 3. Elution with 80:20 propane/DME and removal of the solvent by low-temperature distillation as above afforded 7 as a white solid: mp -9 to -7° dec; uv (-100°, ether) λ_{\max} 358 nm (broad band, $\epsilon_{\max} \sim 100$), 265 and 271 nm, (sharp peaks, $\epsilon_{\max} \sim 1000$). Intensities were estimated by warming up and measuring the spectrum of 3 which was formed. For nmr see text.

Elution of the low-temperature column with DME gave a solution having strong uv absorptions at 312 and 230 nm. The DME solution was added to a cold solution of methanol and allowed to warm to room temperature. Removal of the methanol under vacuum produced a yellowish solid having uv, nmr, and ir spectra identical with those of an authentic sample of 11 prepared according to ref 25 (*cf.* ref 24).

Thermolysis of 7. When a solution of 7 was warmed above -40°, its uv and pmr spectrum rapidly changed to those of the spiro dimer 3.

Photolysis of 7 in Glass Matrix. The photolytic conversion of 7 to 2 was accomplished by two different procedures in either EPA, ethyl ether, or 2-MTHF, all of which make a glass at -196°. A cold (-78°) solution of 7, approximately 10^{-2} - 10^{-3} M, was placed in a low-temperature quartz cell (3-mm path length). The solution was further cooled to -196° forming a glass matrix. The glassy solution of VII was then irradiated with the collimated beam of a 200-W high-pressure mercury lamp equipped with a 345-nm cut-off filter (Corning Glass Co.). After 15-20 min of irradiation the characteristic absorption spectrum of 7 disappeared and was replaced by that of 2. Alternatively, the glassy solution of 7 described above was irradiated with a low-pressure mercury lamp. After approximately 3-4 min of irradiation the characteristic spectrum of 7 was replaced by that of 2. This latter procedure is the method of choice since complete conversions are more easily achieved.

Photolysis of 2. A ca. 10^{-2} solution of 2 in a low-temperature quartz cell (3-mm path length) was irradiated at -196° with a high-pressure mercury lamp equipped with a 345-nm cut-off filter. After 24 hr of irradiation, the uv spectrum of 2 had disappeared and was replaced by that of 5 (authentic sample²⁷). Warming of the solution to room temperature followed by glc retention time comparison on two different columns (column A, 25°; and column B, 85°) with an authentic sample²⁷ completed the identification of 5.

Photolytic Preparation of 2 from 5, 8, 9, 10, and *o*-Xylene. Solutions of the above compounds in EPA were placed in low-temperature quartz cells and irradiated with a low-pressure mercury lamp for various periods of time. In all cases, the characteristic uv absorption spectrum of 2 was observed along with other uv absorption peaks, and the emission and excitation spectra were identical with that of 2 prepared from 7.

Examples of the degrees of conversion obtained with the various precursors are given in the following (precursor, concentration, irradiation time, estimated per cent conversion to II): *o*-xylene, 2×10^{-2} M, 2 hr, 0.2%; 5, 2.9×10^{-2} M, 3 hr, 2%; 8, 3.3×10^{-3} M, 3 hr, 40%; 9, 4×10^{-3} M, 0.5 hr, 10%; 10, 2.3×10^{-3} M, 3 hr, 30%. No attempts were made to maximize the per cent conversion by variation of initial concentration and irradiation time.

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