J. Am. Chem. Soc. **1986**, *108*, 1853-1860

Methyl Substitution Effects on the Electronic Structures and Spectra of *m*-Xylylene Biradicals

V. Lejeune,[†] A. Despres,[†] E. Migirdicyan,*[†] J. Baudet,[‡] and G. Berthier[‡]

Contribution from the Laboratoire de Photophysique Moléculaire du CNRS,[§] Bâtiment 213, Université Paris-Sud, 91405 Orsay, Cedex, France, and Laboratoire de Biochimie Théorique, Institut de Biologie Physico-Chimique, 75005 Paris, France. *Received April 4, 1985*

Abstract: The effect of methyl substitution on the electronic properties of *m*-xylylene biradical has been studied by spectroscopic as well as theoretical methods. The biradicals are generated in situ by UV photolysis of the corresponding methylbenzenes dispersed in *n*-hexane at 5–10 K. Quasi-line fluorescence and excitation spectra of these fragments have been obtained by site-selective laser experiments. In most cases, the vibrational structures of fluorescence and excitation spectra do not present mirror-image symmetry, which is explained by the existence of two close-lying excited triplet states which can interact vibronically. The electronic energies have been determined experimentally from the fluorescence origin bands for the first transition and theoretically by using a SCF MO method with configuration interaction, the participation of the methyl groups to the π-electron system being introduced according to the hyperconjugation theory. Correlations between spectroscopic and theoretical data are discussed, particularly in cases where the parent molecules give rise to several isomeric biradicals.

The first studies on organic compounds containing two unpaired electrons date back to the beginning of the century with the discovery of Chichibabin,[1] Thiele,[2] and Schlenk[3] hydrocarbons. The first two compounds, which have diphenylmethyl groups attached in the para positions, can also be represented by a quinoid form in which the two unpaired electrons become paired. In contrast, the quinoid form cannot be assumed for the Schlenk hydrocarbon where the diphenylmethyl groups are substituted in the meta position. According to the classical susceptibility measurements,[4] and later to the EPR experiments[5] carried out over a wide temperature range, the three hydrocarbons are characterized by low-lying singlet and triplet states. Whereas the paramagnetism of the first two compounds decreases as the temperature is reduced, that of the Schlenk species remains significant even at very low temperatures. Therefore Chichibabin and Thiele hydrocarbons are biradicaloids having a diamagnetic singlet ground state with a thermally accessible triplet level, while the Schlenk hydrocarbon is a true biradical with a triplet ground state, like oxygen. Susceptibility and EPR measurements have also been performed on conjugated radicals having three unpaired electrons which interact to give a quartet ground state.[6]

A number of photochemical transformations are known to proceed via the intermediary of biradicalar species. Unlike the Chichibabin, Thiele, and Schlenk hydrocarbons which are stable, these intermediates are often highly reactive species. In fluid systems, they are generally difficult to observe and characterize because of their short lifetimes controlled by the rate at which they undergo intersystem crossing.[7,8] Most frequently, the biradicals are detected by indirect techniques involving the CIDNP method[9] or chemical reactions (hydrogen abstraction, electron transfer to paraquat dications, etc...) used as the monitoring process.[10] In the particular case of intramolecular hydrogen abstraction reactions such as the photoenolization of *o*-alkyl carbonyl compounds[11,12] or the Norrish type II reaction of phenyl alkyl ketones,[13,14] the biradicalar species have been directly observed by laser flash photolysis and identified by absorption spectroscopy.

When the photolysis is carried out in organic solutions at low temperatures, the biradicals produced "in situ" from appropriate precursors can be trapped in the matrix and directly observed by EPR and optical spectroscopy. In a previous report,[15] we have described the site-selected fluorescence and excitation spectra of *m*-xylylene biradical and some of its methylated derivatives trapped in Shpolskii matrices at 5–10 K. Xylylenes, alias benzoquinodimethanes, result from the photodissociation of CH bonds on two different methyl groups of the corresponding methylated benzenes. While the ortho and para isomers are biradicaloid species with a singlet ground state, the meta isomer is a triplet ground state biradical for which no classical Kēkulē structure can be written. The experimental evidence for the triplet character of *m*-xylylene in the ground state has been provided by the ESR experiments of Wright and Platz[16] who have prepared detectable amounts of this species by exhaustive photolysis of a diazo derivative of *m*-xylene in ethanol frozen at 77 K. The chief aim of the present work is to study the whole series of methyl-substituted biradicals in order to understand the effect of the methyl group on the electronic properties of *m*-xylylene, the prototype of aromatic biradicals.

Biradicalar species are characterized by the presence of two degenerate or nearly degenerate nonbonding orbitals occupied by two electrons. When the paramagnetic centers located in distinct parts of the compound interact by electron exchange through a small residual conjugation, the system has low-lying singlet and triplet states whose splitting and ordering depends on the case under consideration. However, when the exchange interaction between the two odd electrons is smaller than the hyperfine interaction between odd electron spin and nuclear spin, the system is better described as two doublet states.[17] For aromatic biradicals such as *m*-xylylene, the electron interaction should be rather large because the radical centers are connected to each other through a benzene ring. In addition to the EPR method, optical spectroscopy may be used to distinguish between fragments having

---

[†] Université Paris-Sud.

[‡] Institut de Biologie Physico-Chimique.

[§] Associē ā l'Universitē de Paris-Sud.

(1) Chichibabin, A. E.; *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1810.

(2) Thiele, J.; Balhorn, H. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1463.

(3) Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 661.

(4) Muller, E.; Muller-Rodloff, J. *Ann. Phys.* (*Leipzig*) **1935**, *517*, 134.

(5) Hutchison, C. A., Jr.; Kowalsky, A.; Pastor, R. C.; Wheland, G. W. *J. Chem. Phys.* **1952**, *20*, 1485.

(6) Kothe, G.; Ohmes, E.; Brickmann, J.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 938.

(7) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

(8) Caldwell, R. A.; *Pure Appl. Chem.* **1984**, *56*, 1167.

(9) de Kanter, F. I. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

(10) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252.

(11) Porter, G.; Tchir, M. F. *J. Chem. Soc. D* **1970**, 1372; *J. Chem. Soc. A* **1971**, 3772.

(12) Lutz, H.; Breheret, E.; Lindqvist, L. *J. Chem. Soc. A* **1973**, *69*, 2096.

(13) Faure, J.; Fouassier, J. P.; Lougnot, D. J.; Salvin, R. *Nouv. J. Chim.* **1977**, *1*, 15.

(14) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.

(15) Lejeune, V.; Despres, A.; Migirdicyan, E. *J. Phys. Chem.* **1984**, *88*, 2719.

(16) Wright, B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628.

(17) Briere, R.; Dupeyre, R. M.; Lemaire, H.; Morat, C.; Rassat, A.; Rey, P. *Bull. Soc. Chim.* **1965**, 3290.

0002-7863/86/1508-1853$01.50/0

singlet, triplet, and doublet ground states.

The UV photolysis of methylated derivatives of benzene dispersed in organic glasses or Shpolskii matrices at low temperatures gives rise to benzyl-type monoradicals together with *o*- and/or *m*-xylylene biradical species.[18,19] These fragments can be distinguished by the energies and the vibrational structures of their emission and excitation spectra. While the fluorescence of benzyl-type monoradicals starts around 4700–4900 Å, those of *o*- and *m*-xylylenes have origin bands near 4100–4200 and 4400–4600 Å, respectively. The emissions of *o*-xylylene biradicaloids show vibrational structures typical of polyenes with progressions of the CH_2 substituent in-plane bending modes around 400 cm^{-1} and of the C—C and the C=C stretching modes near 1270 and 1530 cm^{-1}, respectively.[20] In contrast, the fluorescence of benzyl-type monoradicals[21] and of *m*-xylylene biradicals can be analyzed by using the vibrational modes and ground-state frequencies of parent molecules, which indicates that these fragments have aromatic character. For *m*-xylylene biradicals, the activity of these modes depends on the number and the position of methyl groups on the aromatic ring.[22] This is particularly noticeable for mode 6b which derives together with mode 6a from the splitting of the benzene e_{2g} mode 6 on lowering the symmetry from D_{6h} to C_{2v}. While the totally symmetric mode 6a is observed in the fluorescence spectra of all the *m*-xylylenes, mode 6b is absent in the spectra of some biradicals.

m-Xylylene is a planar C_{2v} symmetry species. Theory[19,23] predicts that this biradical has a triplet ground state of B_2 symmetry and two close-lying triplet excited states having A_1 and B_2 symmetries, with molecular axes defined according to Mulliken's convention. The two possible transitions 2^3B_2–1^3B_2 and 1^3A_1–1^3B_2 with small oscillator strengths (vide infra) are both theoretically allowed on the basis of orbital symmetry. Only totally symmetric vibrations having intensity distribution governed by the Franck–Condon principle are expected to be active in such allowed transitions. The presence in the fluorescence spectra of the non totally symmetric in-plane mode 6b having b_2 symmetry suggests the existence of vibronic coupling, through this mode, between excited A_1 and B_2 triplet states, giving rise to a forbidden component in the first electronic transition of these biradicals.[15]

The energy gap ΔE between the two close-lying excited A_1 and B_2 triplet states of *m*-xylylene has not been measured experimentally, but it is reasonable to assume that ΔE will vary with the methyl substitution on the aromatic ring, leading eventually to an inversion of excited states. In our previous report,[15] we have attempted to determine the symmetry of the fluorescent level by using a procedure developed by Albrecht[24] in the frame of Herzberg–Teller theory.[25] For C_{2v} species with ground state of B_2 symmetry, modes having b_2, a_2, and a_1 symmetries are expected for a A_1 emitting level, while modes having a_1, b_1, and b_2 symmetries are predicted for a B_2 emitting level. The distinctive modes between the two cases have therefore a_2 and b_1 symmetries. Such modes have not been observed unambiguously in the fluorescence spectra of *m*-xylylene biradicals and consequently this kind of argument is unable to predict the symmetry of their fluorescent state.

In the present paper we extend the site-selection spectroscopy of *m*-xylylene[15] to the whole series of polymethyl-*m*-xylylene biradicals, in order to study the effect of methyl substitution on the transition energies of these species. To confirm our experimental assignments on the basis of theoretical arguments, we have calculated the energies and oscillator strengths of these transitions, using a π-electron SCF MO method with CI.

Experimental Section

Merck UVASOL *n*-hexane was used without further purification. The purest samples commercially available of 1,2,3-trimethylbenzene (Aldrich T 7320-2), 1,2,3,4-tetramethylbenzene (prehnitene, K & K Laboratories), pentamethylbenzene (Aldrich-Janssen), and hexamethylbenzene (Eastman-Kodak 2294) were used without further purification.

The biradicals were generated "in situ" by UV photolysis (200-W Osram Hg lamp) of the corresponding methylated benzenes (concentration $c = 3.10^{-3}$ M) dispersed in *n*-hexane frozen at 5–10 K. The experimental setup for site-selected fluorescence and excitation spectra was the same as that described previously.[15] Solutions in ethanol of coumarin 440, 460, and 480 (Exciton) and coumarin 307 (Lambda-Physics) were used as lasing media, and the laser line width was 6 cm^{-1}. The excitation spectra were not corrected for variation in laser intensity.

Spectroscopic Results

The photodissociation of two CH bonds on two different methyl groups of the methylated benzenes can produce one or several isomeric biradicals, according to the positions of methyl groups on the aromatic ring. When the parent hydrocarbon gives rise to only one biradical, unique and well-resolved fluorescence and excitation spectra are obtained, leading to unambiguous energy evaluation of the excited electronic levels of the fragments. This is the case for biradicals produced from *m*-xylene, mesitylene, pseudocumene, 1,2,3-trimethylbenzene, durene, prehnitene, and hexamethylbenzene. In contrast, isodurene can lose two H atoms in symmetrical 1,3-positions or in 1,5-positions, thus producing two geometrically distinct dimethyl-*m*-xylylenes. Similarly three isomeric trimethyl-*m*-xylylenes can be generated from pentamethylbenzene. If the biradicals thus produced absorb at different wavelengths, the contribution of each isomeric species to the global fluorescence emitted from the mixture can be separated by selective excitation, leading to the energy determinations of the excited electronic levels of the biradicals. In order to establish correlations between these spectroscopic energies and the particular isomer involved, we have performed molecular orbital calculations.

Since the calculations refer to isolated species, the results should be compared with spectroscopic data obtained under conditions such that solvent–solute interactions are negligible. The interactions are reduced to a minimum when the excited state of the solvent molecule is much higher in energy than the excited state of the biradical. These conditions are fulfilled for Shpolskii systems where the biradicals dispersed in frozen *n*-alkanes display quasi-line electronic spectra at very low temperatures.[15] Under conventional broad-band excitation, the fluorescence spectra of *m*-xylylenes incorporated in Shpolskii matrices at 5–20 K generally present a multisite structure even when the parent hydrocarbon yields only one isomeric species.[22] This is due to the distribution of biradicals in several crystallographically well-defined lattice sites of the matrix, leading to a frequency distribution of about 100 cm^{-1} at most for the transition origin. This structure can be considerably simplified by using narrow-band laser excitation where only the fragments that have an absorption energy coincident with the laser frequency are selectively excited. The sharp electronic spectra presented here correspond to biradicals located in the most prominent sites of Shpolskii matrices either before or after annealing of the samples.

(A) Spectroscopic Determinations of the First Triplet–Triplet Transition Energies of *m*-Xylylene Biradicals. When the UV photolysis of the parent molecule gives rise to only one geometrically well-defined biradical, all the fluorescence bands have the same excitation spectrum. This has already been observed for biradicals generated from *m*-xylene, mesitylene, durene, and pseudocumene whose site-selected fluorescence and excitation spectra have been presented in Figures 1 and 2 of ref 15. This is also true for biradicals produced from 1,2,3-trimethylbenzene, 1,2,3,4-tetramethylbenzene, and hexamethylbenzene whose quasi-line fluorescence and excitation spectra in the visible are displayed here in Figure 1.

When the photolysis of the polymethylbenzene yields several isomeric biradicals, the fluorescence and excitation spectra of each species contribute to the total spectra recorded from the sample.

---

(18) Migirdicyan, E.; *C. R. Hebd. Seances Acad. Sci.* **1968**, *266*, 756.

(19) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

(20) Despres, A.; Lejeune, V.; Migirdicyan, E.; Siebrand, W. *Chem. Phys. Lett.* **1984**, *111*, 201.

(21) Grajcar, L.; Leach, S. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1523.

(22) Lejeune, V.; Despres, A.; Migirdicyan, E. "Proceedings of the International Conference on Photochemistry and Photobiology", Alexandria, Egypt, Jan 5–10, 1983.

(23) Baudet, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 191.

(24) Albrecht, A. C. *J. Chem. Phys.* **1960**, *33*, 156.

(25) Herzberg, G.; Teller, E. *Z. Phys. Chem., Abt B* **1933**, *21*, 410.

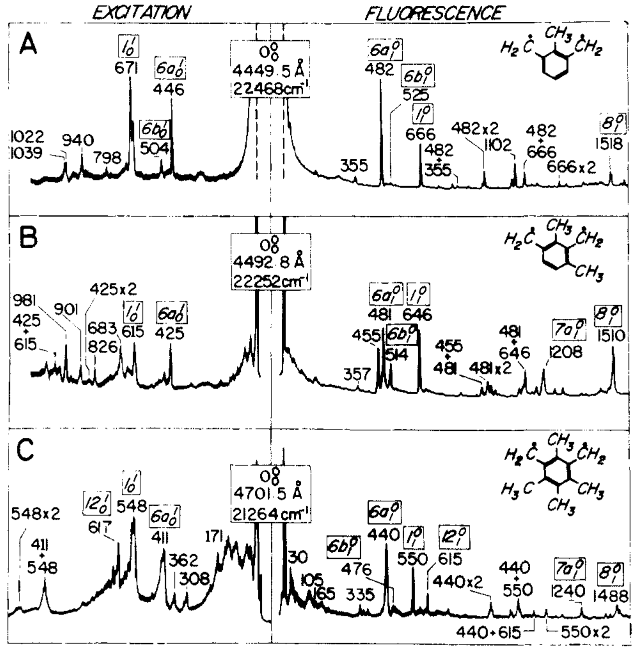


Figure 1. Site-selected fluorescence and excitation spectra of biradicals generated from 1,2,3-trimethylbenzene (A), prehnitene (B), and hexamethylbenzene (C) isolated in *n*-hexane frozen at 5–10 K. The emissions are excited with laser lines corresponding to the origins of the transition. The excitation spectra are obtained by monitoring the fluorescence origin bands for A and B and the first vibronic band at 4801 Å for C while scanning the dye laser.

For the three fragments produced from pentamethylbenzene, the situation is particularly favorable since their fluorescence spectra are well separated in energy. Three intense fluorescence spectra F_1, F_2, and F_3 with origin bands at respectively 4510, 4653.7, and 5089 Å are emitted from the photolyzed solutions of pentamethylbenzene in *n*-hexane at 5–10 K. They are shown in Figure 2 together with the corresponding excitation spectra E_1, E_2, and E_3.

In all the cases, the longest wavelength excitation band is coincident, within an experimental uncertainty of about 1 Å, with the shortest wavelength fluorescence band, thus confirming its attribution to the 0,0-transition.

For all the *m*-xylylene biradicals, the origin band is the most intense in the fluorescence and excitation spectra. The frequency of this origin band corresponds to the energy of the first triplet–triplet transition of the biradicals.

(B) Vibronic Structures of the Electronic Spectra of *m*-Xylylene Biradicals. (1) **Site-Selected Fluorescence Spectra.** As for the biradicals studied in ref 15, the quasi-line fluorescence spectra presented in Figures 1 and 2 have been analyzed by correlation with the vibrational modes and ground-state frequencies of the parent molecules. According to the data published by Varsanyi[26] for polymethylbenzenes, the most reasonable assignments for the vibronic bands are indicated on the Figures 1 and 2 by using the Pitzer and Scott notation.[27] Modes 6a and 6b are expected to appear around 400–600 cm^{-1}. The intense fluorescence bands with frequencies around 440 and 480 cm^{-1} have been systematically attributed to the totally symmetric mode 6a, since they show two-member progressions for all the biradicals. The weaker bands at 470–560 cm^{-1} presenting one-quantum activity are assigned to mode 6b. Particularly noteworthy is the negligibly small activity of this vibration in the fluorescence spectrum of the biradical produced from 1,2,3-trimethylbenzene, as was already the case for *m*-xylylene and for *m*-durylene-h_{12} and -d_{12} (see curves A and B in Figure 1 of ref 15). Let us discuss the particular case of the biradical formed from hexamethylbenzene (HMB). The frequency of the e_{2g} mode 6 is 450 cm^{-1} in HMB.[28] This vibration splits into modes 6a and 6b on lowering the symmetry from D_{6h} (HMB) to C_{2v} (biradical). The intense fluorescence band at 440 cm^{-1} from the origin observed in curve C of Figure 1 is attributed to mode 6a since it shows a two-member progression. The weak band at 476 cm^{-1} probably corresponds to mode 6b. Weak fluorescence bands at 310–360 cm^{-1} are observed for four biradicals out of six. They have been tentatively assigned to the C–CH_3 in-plane bending vibrations 9, 15, or 18.

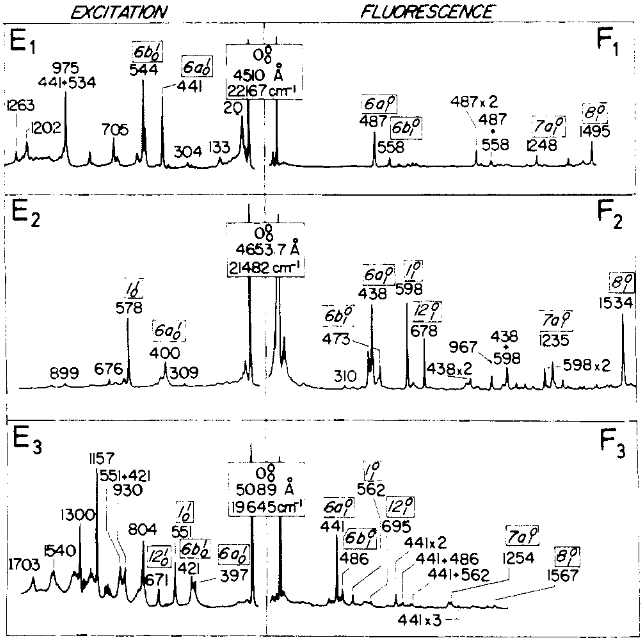


Figure 2. Site-selected fluorescence F_1, F_2, and F_3 and excitation E_1, E_2, and E_3 spectra of biradicals generated from pentamethylbenzene isolated in *n*-hexane frozen at 5–10 K. The emissions are excited with laser lines corresponding to the intense excitation bands at 4422 Å for F_1, at 4532 Å for F_2, and 4807 Å for F_3. The excitation spectra are obtained by monitoring the fluorescence vibronic bands at 4611 Å for E_1, at 4805 Å for E_2, and the origin band for E_3.

(2) **Laser-Induced Fluorescence Excitation Spectra.** The vibrational structures of emission and absorption—or excitation—spectra of aromatic compounds having sparsely spaced electronic levels generally present mirror-image symmetry. This is not always observed for *m*-xylylene biradicals. On the low-frequency side, it is often possible to establish correspondence between two strong excitation bands and two strong fluorescence vibronic bands attributed to modes 6a and 1. These modes have frequencies which are slightly lower in the first excited than in the ground state. Mode 6b is weakly active in the excitation spectra of most species except in one biradical generated from pentamethylbenzene (see curve E1, Figure 2) where it appears with high intensity. At frequencies higher than about 800 cm^{-1} from the origin, there often appear intense excitation bands which are neither progressions of fundamentals nor combinations between two frequencies. Such features are expected for species presenting two close-lying excited states of different symmetry, as is the case for *m*-xylylene biradicals. The excitation spectra presented in Figures 1 and 2 result probably from the overlapping of A_1 and B_2 electronic manifolds which can interact vibronically through the inducing mode 6b of b_2 symmetry. The vibronic levels of one manifold will be mixed with levels of appropriate symmetry of the other manifold, resulting in level shifts and intensity redistribution. At energies close to that of the second excited state, the excitation spectrum will exhibit anomalous spacings as well as intensities and hence will no longer present mirror image symmetry with the fluorescence spectrum.

Theory

(A) Computational Background. It is well established that an ab initio calculation of spectroscopic quality for electronic tran-

---

[26] Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1969.

[27] Pitzer, K. S.; Scott, D. W. *J. Am. Chem. Soc.* **1943**, *65*, 803.

[28] Schnepp, O.; McClure, D. S. *J. Chem. Phys.* **1957**, *26*, 83.

sition energies and oscillator strengths requires extensive CI computations starting with large basis sets of AO's. Treatments of that sort have been presented for unsaturated prototype molecules, as acetylene, ethylene, or even benzene (see, e.g., ref 29), but systems somewhat larger remain out of range in the present state of the art in quantum chemistry.

To deal with aromatic molecules, semiempirical methods involving appropriate parametrizations for π–π^* transitions are convenient. In this respect, all valence electron methods, as CNDO-S[30] or INDO-S[31] are rather successful. However, the ZDO approximation used from the outset in such calculations implies that for the π-electron subsystem we are satisfied with pictures more or less similar to those of earlier treatments neglecting overlap for π-electrons (i.e., the primitive Hückel method or the PPP method). On this point, the main feature of the model for an alternant hydrocarbon is the π–π^* pairing of the occupied and virtual MO's. This arrangement is responsible for a two by two degeneracy between excited configurations involving an electron from a π orbital or toward its π^* counterpart, and so the π–π^* excited states have to be primarily described by a zero-order CI mechanism between degenerate configurations, hence a π spectrum consisting in pairs of accidentally forbidden and allowed transitions with the same symmetry. This classical picture, initially found in the study of the closed-shell molecules[32] and monoradicals,[33] can be extended to alternant biradicals (see below) and is preserved in subsequent CI mixings between singly excited states.[34]

Departures from the paired-configuration model arise when, first of all, overlap integrals are reintroduced in the theory. This has been achieved in connection with molecular spectroscopy for π-electron methods (for a review, see ref 35), but the same refinement in all valence electron computations seems to be much less attractive: Overlap is rather the first step toward calculations simulating the ab initio results obtained with minimal basis sets valid for the ground state only. Here, we have limited ourselves to π-electron computations based on a theoretical scheme we have previously used for studying the electronic transitions of mono- and biradicals[36,19,23] derived from benzene.

Basically, the electronic energy levels of the *m*-xylylene biradicals are determined by an SCF-CI method using molecular orbitals ϕ_i constructed from the eight $2p\pi$ atomic orbitals χ_p of the carbon framework and, if methyl substituents are present, the pair of pseudo-$2p\pi$ orbitals associated with each CH_3 group in the Mulliken hyperconjugation theory.[37] The doubly occupied and virtual MO's, as well as the two singly occupied MO's, come from a Roothaan open-shell treatment for triplet ground states.[38] Mono- and diexcitations are included in the CI process.

To include overlap, we replace the primitive basis χ by an orthogonalized one λ through the Löwdin transformation $\lambda = S^{-1/2}\chi$ (S being the matrix of overlap integrals S_{pq} between the χ orbitals), and we evaluate the bielectronic and core integrals in the new basis, using the following recipes:[39]

(i) The ZDO hypothesis of the PPP methods is well verified by the $2p\pi$ Löwdin orbitals so that the Coulomb integrals $(pp;pp)_\lambda$ and $(pp;qq)_\lambda$ in the new basis are the only ones to be computed from the whole set of bielectronic integrals in the old basis. To do that, it is sufficient to have the primitive one-center and two-center Coulomb integrals and to approximate the remaining multicentric integrals by a Mulliken–Ruedenberg formula involving only linear terms in S_{pq}.[40] The former $(pp;pp)_\chi$ are determined from atomic spectroscopy data, the latter $(pp;qq)_\chi$ from their theoretical expression, using effective nuclear charges $\zeta^*_{\rm red}$ fitted on the experimental one-center integrals. For overlap integrals S_{pq}, standard Slater–Zener exponents are taken.

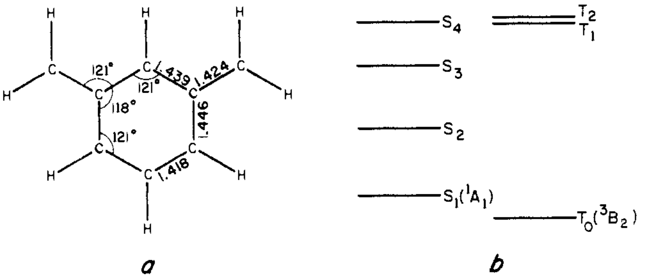


Figure 3. (a) Equilibrium geometry for the 1^3B_2 state of *m*-xylylene.[42] (b) Energy level diagram for the first computed singlet and triplet states.

(ii) The primitive one-center integrals α_p are evaluated from appropriate valence-state ionization potentials W_p as in usual π-electron theories, i.e., for a carbon

$$\alpha_p = W_p - \sum_{q \neq p} (pp;qq)_\chi$$

The two-center resonance integrals β_{pq} are written in the form

$$\beta_{pq} = \tfrac{1}{2}S_{pq}(\alpha_p + \alpha_q) + \epsilon_{pq}$$

with a correction factor ϵ_{pq} assumed to be proportional to S_{pq}: $\epsilon_{pq} = -kS_{pq}$. At the first order of an expansion in S, the ϵ_{pq}'s can be identified to resonance integrals over the λ basis and, so, they play the same role as the β parameters of the PPP model. In spite of its formal analogy with the latter theory, however, the present calculation method takes overlap into account, because the whole set of integrals included in the theory are evaluated in the primitive atomic basis and then subjected to the appropriate Löwdin transformation. In consequence, the degeneracies between paired configurations are lifted, and nonzero oscillator strengths arise for accidentally forbidden transitions.

(iii) In the case of the *m*-xylylene biradical itself, the energy spectrum depends on the following semiempirical parameters: the W_p's of the various types of carbon atoms, the $(pp;pp)$ integral of the $2p\pi$ orbital of carbon, and the k factor characterizing a pair of bonded or nonbonded carbons. The values used in the present study are W_p(secondary carbon) = −11.05 eV; W_p(tertiary carbon) = −11.27 eV; W_p(quaternary carbon) = −11.49 eV; $(pp;pp)_C$ = 10.13 eV; $K_{C\text{-}C}$ = 8.525 eV (hence $\zeta^c_{\rm red}$ = 0.951, instead of 1.59 for overlap integrals).

In the case of methyl-substituted biradicals, the parameters of the pseudo-$2p\pi$ orbital attributed to the hydrogens of each CH_3 come from previous calculations on propylene[41] and toluene.[36] Their values are $W_p(H_3)$ = −9.55 eV, W_p(primary carbon) = −10.83 eV; $(pp;pp)$ = 8.75 eV, and $k_{C\text{-}H_3}$ = 5.0 eV (hence $\zeta_{\rm red}$ = 0.583 eV instead of 1).

(B) Molecular Geometries. As input data for the *m*-xylylene geometry, we have taken the theoretical structure determined by Kato et al.[42] using ab initio LCAO–UHF calculations for the triplet ground state. The C_{2v} optimized geometry exhibits bond lengths longer than in a benzene ring (Figure 3a) with distorsions whose effect on the computed vertical energy transitions is appreciable (about 0.1–0.2 eV). The same skeleton was maintained in the methyl-substituted biradicals, the C–CH_3 bond being symmetric with respect to the ortho ring carbons. The methyl carbon atom and the H_3 pseudo-atom are in the *m*-xylylene plane, at 1.50 and 2.14 Å from the adjacent ring carbon, respectively.

---

(29) Peyerimhoff, S. D.; Buenker, R. J. *Adv. Quantum Chem.* **1975**, *9*, 69.

(30) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.

(31) Krogh-Jespersen, K.; Ratner, K. *J. Chem. Phys.* **1976**, *65*, 1305. Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223.

(32) Dewar, M. J. S.; Longuet-Higgins, H. C. *Proc. Phys. Soc., London, Sect. A* **1954**, *67*, 795.

(33) Pople, J. A. *Proc. Phys. Soc., London, Sect. A* **1955**, *68*, 81.

(34) Pariser, R. *J. Chem. Phys.* **1956**, *24*, 250.

(35) Jug, K. *Theor. Chim. Acta* **1969**, *14*, 91.

(36) Branciard-Larcher, C.; Migirdicyan, E.; Baudet, J. *Chem. Phys.* **1973**, *2*, 95.

(37) Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41.

(38) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

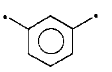
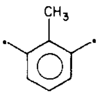
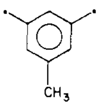
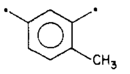
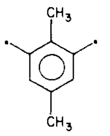
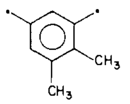
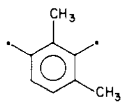
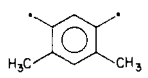
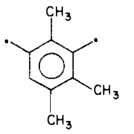
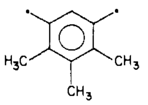
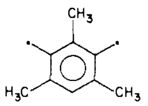
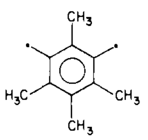
(39) Berthier, G.; Suard, M.; Baudet, J. *Tetrahedron* **1963**, *19*, S2, 1.

(40) Ruedenberg, K. *J. Chem. Phys.* **1951**, *19*, 1433.

(41) Levy, B.; Berthier, G. *J. Chim. Phys.* **1966**, *63*, 1375.

(42) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.

Table I. Theoretical Transition Energies[a] of *m*-Xylylene Biradicals

biradical		T_1–T_0		T_2–T_0		T_5–T_0	S_1–T_0
	B_2	2.813 (0.005)	A_1	2.915 (0.020)	A_1	4.188 (0.125)	0.295
	B_2	2.769 (0.001)	A_1	2.968 (0.025)	A_1	4.146 (0.102)	0.329
	A_1	2.764 (0.017)	B_2	2.970 (0.010)	A_1	4.295 (0.135)	0.302
		2.889 (0.013)		2.897 (0.027)		4.203 (0.234)	0.318
	A_1	2.749 (0.024)	B_2	2.917 (0.004)	A_1	4.275 (0.085)	0.353
		2.739 (0.029)		3.033 (0.016)		4.294 (0.218)	0.315
		2.768 (0.003)		2.878 (0.033)		4.134 (0.197)	0.377
	A_1	2.896 (0.033)	B_2	3.069 (0.028)	A_1	4.202 (0.314)	0.310
		2.666 (0.038)		2.885 (0.005)		4.234 (0.169)	0.372
	A_1	2.743 (0.035)	B_2	3.075 (0.022)	A_1	4.257 (0.271)	0.297
	A_1	2.878 (0.035)	B_2	2.996 (0.009)	A_1	4.104 (0.251)	0.348
	A_1	2.695 (0.041)	B_2	2.989 (0.008)	A_1	4.193 (0.218)	0.349

[a] In eV; oscillator strength for each of the three spin components of T_0 and T_i in parentheses.

(C) π–π^* Theoretical Spectra of *m*-Xylylene Biradicals. Starting with the MO basis obtained in the SCF treatment of the *m*-xylylene triplet states, the π–π^* spectrum of each biradical was computed by performing mono- and biexcitations (giving configurations with at most four singly occupied MO's) from the ground-state configuration. In the case of *m*-xylylene itself, the CI mixing includes 172 triplet and 153 singlet spin-adapted functions for the whole set of occupied and virtual MO's. If there are n additional CH_3 groups in a methyl-substituted biradical ($1 \leq n \leq 4$), the electron energy spectrum involves n bonding π-orbitals of low energy and at its top n antibonding π^*-orbitals, which are well localized on the CH_3's. We have excluded them from the excitation processes, in order to have the same number of configurations as in *m*-xylylene and to avoid any size problem in the CI treatment.

As concerns the characteristics of the ground state, no change except an average energy lowering of 0.4 eV results from CI, i.e., a triplet state T_0 belonging to the B_2 representation (Mulliken's notation) for a C_{2v} nuclear framework. The first singlet S_1 is about 0.3 eV higher and the first two excited triplets T_1 and T_2, in the visible region, are about 2.8 and 2.9 eV above T_0 (see Figure 3b). The next triplets are much higher.

As shown in Table I, six *m*-xylylene compounds—out of eight belonging to the C_{2v} point group exactly—have A_1 and B_2 states as first and second excited triplets, respectively (the exceptions being *m*-xylylene itself and 2-methyl-*m*-xylylene). In any case, however, the oscillator strength of a 1^3A_1–1^3B_2 transition is found to be larger than the value computed for a 2^3B_2–1^3B_2 transition.

We have not been able to establish a significant relationship between the number and position of CH_3 groups attached to *m*-xylylene and the variation of the first transition energies. However, it is interesting to discuss how our own calculations deviate from the predictions of theories without overlap.

Within the paired-configuration model, the π–π^* electronic transitions of an even alternant biradical with two nonbonding MO's can be derived from a special configurational mixing closely related to the one developed for monoradicals. The only difference arises from the consideration of two π nonbonding levels—instead

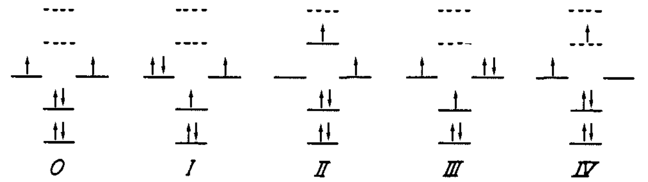


Figure 4. Dominant configurations for the ground and for the first excited electronic states of a C_s biradical.

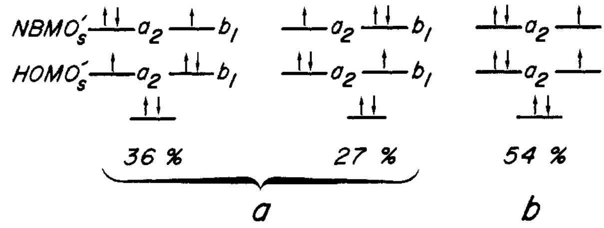
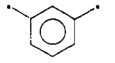
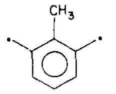
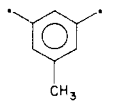
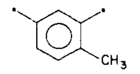
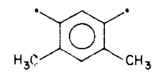
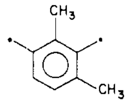
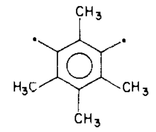


Figure 5. The most important configurations in the (a) 2^3B_2 and (b) 1^3A_1 states of *m*-xylylene.

Table II. First Electronic Transition Energies of *m*-Xylylene Biradicals in Cases Where the Parent Molecule Gives Rise to Only One Biradical

	transition energies, eV		
biradical	calcd (t)	obsd (e)	Δ_{t-e}, eV
	2.81	2.82	-0.01
	2.77	2.78	-0.01
	2.76	2.73	0.03
	2.89	2.80	0.09
	2.90	2.77	0.13
	2.77	2.76	0.01
	2.69	2.64	0.05

of one in a monoradical—in transitions involving some doubly occupied π-MO or its virtual π^* counterpart (see Figure 4). For the ground state, the leading term of the CI expansion is the standard configuration $|0\rangle$ of the biradical where the bonding levels are fully occupied and the nonbonding levels contain two unpaired electrons. In our computations, the SCF configurations $|0\rangle_{SCF}$ of the *m*-xylylene biradicals have weights c_0^2 equal to 0.92 or more. For the lowest excited states, leading terms formed by well-balanced mixtures of four configurations like $|I\rangle$, $|II\rangle$, $|III\rangle$, and $|IV\rangle$ have to be considered. If the nonbonding MO's belong to two different irreducible representations, the four components are distributed into two groups, $|I\rangle$, $|II\rangle$ and $|III\rangle$, $|IV\rangle$, corresponding to electronic states of different symmetry (case of C_{2v} biradicals).

The preceding HOMO–LUMO picture via the nonbonding MO's works reasonably well in aromatic compounds provided that we take account of the proximity of the last two doubly occupied levels as well as the first two virtual ones in benzenic compounds. The former arise from the splitting of the benzene e_{1g} level and the latter from the e_{2u} when the symmetry of the nuclear framework is lowered from D_{6h} to say C_{2v}. The corresponding pairs of π–π^* MO's, of a_2 and b_1 types, can be involved in two pairs of A_1 and B_2 monoexcited configurations with each nonbonding MO. If both nonbonding MO's are considered, this process will give rise to two excited states of different symmetry (i.e., the 2^3B_2 and 1^3A_1 states of *m*-xylylene) whose leading term will have four components, two coming from the first pair of π–π^* MO's and two coming from the second pair. In the case of less symmetrical biradicals, the two excited triplets cannot be separated, and their CI wavefunctions have more or less mixed leading terms.

Our treatment, whose results are summarized in Table I, modifies the former picture in the following way: (i) As is well-known, overlap raises the orbital energies of the virtual orbitals. Consequently, an excitation toward a LUMO may be disfavored with respect to excitation from the corresponding HOMO, and the configuration of type $|II\rangle$ may be less important than the configuration of type $|I\rangle$ in the lowest excited triplets. (ii) The two nonbonding MO's are not exactly equivalent, and one of the configurations of type $|I\rangle$ may prevail over the other.

As a general rule in the series of *m*-xylylene compounds, the first two excited triplets can be qualitatively described by a very small number of excitations. In the C_{2v} biradicals, the 2^3B_2 wavefunction has only two large components (Figure 5a), whereas one configuration contributes for more than half to the 1^3A_1 wavefunction (Figure 5b). The nonzero values of the oscillator strengths of the corresponding transitions (see Table I) are closely connected with this situation. However, if we add the contributions of all the HOMO–LUMO configurations included in the leading terms of the paired model corresponding to the first excited triplets of *m*-xylylene for instance, we obtain 77% and 80% of the total CI wavefunctions (and more than 90% if we take into account those coming from the monoexcited configurations with four singly occupied MO's). This means that our treatment preserves a good part of the usual π models neglecting overlap.

Relationship between Experiment and Theory in *m*-Xylylene Biradicals

(A) Assignment of the First Electronic Transition. The first electronic transition energies of *m*-xylylene biradicals were determined experimentally from the fluorescence origin bands and theoretically from the energy differences between the first electronic excited level and the ground state.

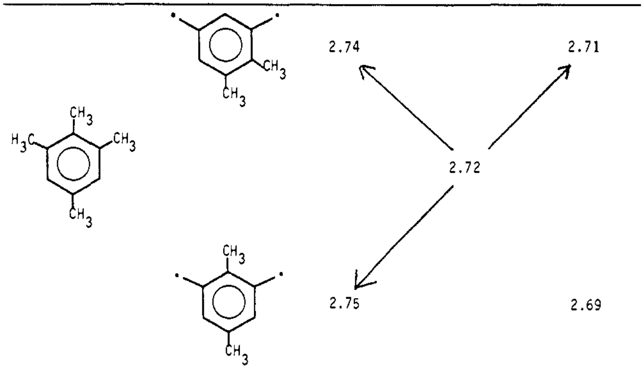
When the methylated derivative of benzene gives rise to only one geometrically well-defined *m*-xylylene biradical, one can directly compare the experimental and calculated energies for the first electronic transition of these species. The results presented in Table II show that the agreement between the two sets of data is generally good within 0.15 eV. This uncertainty is about an order of magnitude higher than the distribution of fluorescence origin bands corresponding to biradicals in different lattice sites.

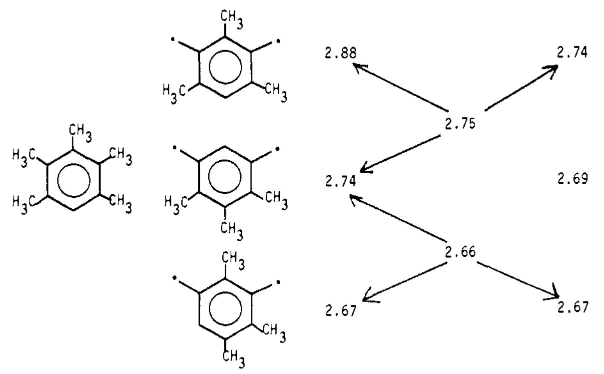
When the symmetry of the parent molecule is such that photolysis can produce several isomeric biradicals, spectroscopic data provide two or three transition energies but it is not possible a priori to assign each of these values to a particular isomer. In contrast, computation data directly give the transition energies of the isomeric biradicals, but the approximations used in the calculations introduce an uncertainty which is difficult to evaluate. However, the Δ_{t-e} values listed in Table II suggest that this uncertainty should be lower than 0.15 eV. Hence we consider that the attribution of a given transition energy to a particular biradical will only be meaningful in cases where the differences in energy values of the various isomers involved are higher than 0.15 eV. From the results displayed in Table III for the calculated as well as observed transitions energies of *m*-xylylene biradicals, it is obvious that correlation between theory and experiment requires further discussion.

Two isomeric biradicals are expected to be generated from isodurene. The emission spectrum of photolyzed solutions of this compound in *n*-hexane at 5 K presents four sharp bands at 4542 (2.728 eV), 4551.2 (2.723 eV), 4553.5 (2.721 eV), and 4563.5 Å (2.715 eV) and a number of more intense bands starting at λ

Table III. First Electronic Transition Energies of Methylated *m*-Xylylenes in Cases Where the Parent Molecule Gives Rise to Several Isomeric Biradicals

parent molecule	biradical	transition energies, eV calcd	obsd	empirical





> 4740 Å attributed to benzyl-type monoradicals. The four sharp bands can correspond to the fluorescence origins of either one or two geometrically distinct isomers distributed in four different lattice sites since the energies of 2.75 and 2.74 eV calculated for the first transition of the two biradicals are too close to allow a distinction. The energy gaps between the first two transitions calculated for the two isomers are 1350 and 2370 cm^{-1}. It would therefore be expected that the excitation spectra which extend up to 1500 cm^{-1} will present different structures for the isomeric biradicals since the perturbation introduced by the second excited state will not affect them in the same way. The laser-induced fluorescence and excitation spectra detected from the four different lattice sites are all identical with the corresponding spectra depicted in curves E of respectively Figures 1 and 2 of ref 15. This suggests that the observed spectra all belong to only one isomer trapped in four different lattice sites, but the relative positions of the two CH_3 on the ring cannot be precisely stated without further discussion (vide infra).

The photodissociation of one or two CH bonds from methyl groups in pentamethylbenzene leads to the formation of three benzyl-type monoradicals and three biradicals. The calculated energies for the first transition are 2.44, 2.41, and 2.24 eV in monoradicals[36] and 2.88, 2.74, and 2.67 eV in biradicals (see Table I). Only three fluorescence F_1, F_2, and F_3 out of the six expected spectra are emitted from the photolyzed solutions of pentamethylbenzene in *n*-hexane at 5–10 K. F_1 and F_2 with origin bands at respectively 4510 (2.75 eV) and 4653.7 Å (2.66 eV) could reasonably be assigned to two isomeric trimethyl-*m*-xylylene biradicals, as shown in Table III. F_3 with an origin at 5089 Å (2.44 eV) can be attributed either to the last trimethylated biradical or to one of the tetramethylbenzyl monoradicals. The first assignment is questionable since the difference of 0.23 eV between theoretical and experimental values is larger than the uncertainty of 0.15 eV generally found for *m*-xylylene biradicals. In addition no striking feature allowing any distinction between monoradicals and biradicals has been revealed from the vibronic structures of the fluorescence F_1, F_2, and F_3 and the excitation E_1, E_2, and E_3 spectra presented in Figure 2.

Table IV. Empirical Formulation of the Effect of Methyl Substitution on the Observed Transition Energies of *m*-Xylylene Biradicals

$$E_{\mathrm{emp}} = E_0 - \sum\epsilon$$

with $\sum\epsilon = 0.04n_1 + 0.09n_2 + 0.02n_3$

CH_3 positions[a]	n_1	n_2	n_3	$\sum\epsilon$	E_{emp}	E_{obsd}
0	0	0	0	0	2.82[b]	2.82[b]
2	1	0	0	0.04	2.78	2.78
5	0	1	0	0.09	2.73	2.73
4 (=6)	0	0	1	0.02	2.80	2.80
4,6	0	0	2	0.04	2.78	2.77
2,4	1	0	1	0.06	2.76	2.76
2,4,5,6	1	1	2	0.17	2.65	2.64
4,5	0	1	1	0.11	2.71	2.72
2,5	1	1	0	0.13	2.69	–
2,4,6	1	0	2	0.08	2.74	2.75
4,5,6	0	1	2	0.13	2.69	–
2,4,5	1	1	1	0.15	2.67	2.66

[a] For the first seven compounds, see Table II; for the next five compounds, see Table III. [b] E_0.

Siebrand[43] has attempted to formulate the effect of methyl substitution on the observed transition energies by an empirical additivity rule. In the monosubstituted biradicals, the three distinguishable positions for a methyl group, namely, 2, 4 (=6), and 5 correspond to red-shifts of 0.04, 0.02, and 0.09 eV, respectively. The data listed in Table IV show that the transition energies of polymethylated species can be obtained within 0.01 eV by simply adding these contributions such as

$$\sum\epsilon(\mathrm{eV}) = 0.04n_1 + 0.09n_2 + 0.02n_3$$

where n_1, n_2, and n_3 represent the number of methyl substituents in respectively the three distinguishable positions mentioned above. It is interesting to notice that such a procedure leads to a unique assignment of the spectra, when several isomeric biradicals are produced from a given parent molecule. For example, the observed transition energy of 2.72 eV detected for the biradical produced from isodurene has been attributed to the asymmetrical 4,5-dimethyl *m*-xylylene, while the comparison between experimental and theoretical values did not allow any assignment (see Table III). Similarly spectra F_1 and F_2 emitted from the photolyzed solutions of pentamethylbenzene have been attributed to 2,4,6- and 2,4,5-trimethyl-*m*-xylylene, respectively (see Table III). As a consequence of these correlations, fluorescence F_3 can safely be attributed to a benzyl-type monoradical generated from pentamethylbenzene.

(B) Symmetry of the First Excited Triplet State vs. Vibronic Structure of the Fluorescence Spectra. The theoretical data collected in Table I indicate that the perturbation introduced by the electronic effect of methyl substitution is different for $^3B_2$–$^3B_2$ and $^3B_2$–$^3A_1$ transitions. As a consequence, the energy gaps between the two close-lying excited $^3B_2$ and $^3A_1$ states as well as the ordering of these levels depends significantly on the number and the position of methyl groups on the aromatic ring. In true C_{2v} biradicals, the theoretical symmetry of the first excited level is B_2 for the fragments generated from *m*-xylene and 1,2,3-trimethylbenzene and A_1 for the others. On the other hand, mode 6b is absent or has negligibly small activity in the fluorescence spectra of biradicals generated from *m*-xylene, 1,2,3-trimethylbenzene, and durene (*m*-durylene) while this mode is present with a weak intensity in the spectra of all the other species. It is therefore tempting to correlate the presence of mode 6b in the fluorescence with biradicals having an emitting level of symmetry A_1 and not B_2, except for *m*-durylene whose first excited level has A_1 symmetry. In the latter species, however, the ordering of excited states predicted by theory may be questionable since the uncertainty Δ_{t-e} = 0.13 eV found for the first transition (see Table II) is nearly as large as the gap $T_2 - T_1$ = 0.17 eV. This correlation

---

[43] Siebrand, W., personal communication.

seems to be in contradiction with the qualitative prediction of Herzberg–Teller theory[25] where mode 6b having b_2 symmetry should appear in $^3B_2$–$^3B_2$ as well as in $^3A_1$–$^3B_2$ transitions, as mentioned in the introduction. In order to account for that, explicit calculation[44] of vibronic coupling matrix elements should be made. Given the relative oscillator strengths of the first two electronic transitions (see Table I) and the presence of mode 6b in the more intense emission (i.e., $^3A_1$–$^3B_2$), this borrowing mechanism should involve higher $^3A_1$ excited states having large oscillator strengths f, as, for example, level T_5 whose f is larger than 0.1 in most cases (see Table I).

Conclusion

Information obtained from vibronic structures of fluorescence spectra and from quantum chemical calculations reveals some parentage between *m*-xylylene biradicals and benzyl-type monoradicals. In both cases, the two first electronic transitions, involving doublet D states for monoradicals and triplet T states for biradicals, are close in energy and have very low oscillator strengths. However theory predicts three or four singlet states between the ground and the lowest excited triplet state in biradicals (see Figure 3b), whereas no excited electronic level is found below the fluorescence state in benzyl-type radicals, the first quadruplet state being at least 1 eV above the first excited doublet.[36] The presence of singlet levels below the emitting triplet introduces in biradicals new relaxation paths for radiationless transitions to the ground state T_0, such as $T_1 \rightarrow S_n$ (n = 1–3, 4) and $S_0 \rightarrow T_0$ intersystem crossings together with $T_1 \rightarrow T_0$ and $S_n \rightarrow S_0$ internal conversions. In monoradicals, the $D_1 \rightarrow D_0$ internal conversion is the only process to compete with the $D_1 \rightarrow D_0$ fluorescence.

Let us now discuss the theoretically determined ordering of the two close-lying excited $^3B_2$ and $^3A_1$ states. For *m*-xylylene, this ordering depends on the approximations used in the calculations. For example, the symmetry of the lowest excited triplet T_1 changes from A_1 to B_2 when the number of configurations used in the CI increases from 54 to 172. The question then arises, what is the meaning of the ordering predicted for the two close-lying excited $^3B_2$ and $^3A_1$ states of *m*-xylylene biradicals and its dependence with methyl substitution as depicted in Table I? Moreover, the empirical additivity rule found on the observed transition energies for the whole series of methylated *m*-xylylene biradicals could be interpreted as an indication that the lowest excited triplet is of the same symmetry in all the molecules tested. To clarify the situation, we intend to determine the symmetry of the fluorescent state of *m*-xylylene biradicals by means of the multistep photoselection technique.[45]

Acknowledgment. We are grateful to Dr. Siebrand who, as a referee, suggested to us the empirical additivity rule.

Registry No. 1,2,3-Trimethylbenzene biradical, 100859-21-0; prehnitene biradical, 100859-22-1; hexamethylbenzene biradical, 100859-23-2.

---

(44) Orlandi, G. *Chem. Phys. Lett.* **1976**, *44*, 277.

(45) Johnson, P. M.; Albrecht, A. C. *J. Chem. Phys.* **1968**, *48*, 851.

Formation of Ionic Transition Metal Carbonyl Cluster Fragments by Ion–Molecule Reactions. 2. The $Co(CO)_3(NO)$ and $Ni(CO)_4$ Systems

DonnaJean Anderson Fredeen and David H. Russell*

Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843. *Received September 10, 1985*

Abstract: The ion–molecule reaction chemistry of $Co(CO)_3(NO)$ and $Ni(CO)_4$ is presented. Ionic cluster fragments of the type $M_x(CO)_y(NO)_z^+$ are formed from the reaction of the fragment ion $M(CO)_a(NO)_b^+$ with its respective neutral. The relative reaction rate and electron deficiency of the ionic cluster fragments are used to estimate the bond order of the ionic cluster fragments. Comparison of the $Cr(CO)_6$, $Fe(CO)_5$, $Co(CO)_3(NO)$, and $Ni(CO)_4$ systems shows that the ionic cluster fragments can be divided into two catagories: (1) ionic cluster fragments with simple polyhedral structures and (2) ionic cluster fragments which exhibit unusual binding of the ligands and/or metals, resulting in ionic cluster fragments with high bond orders. These two classes of ionic cluster fragments are discussed in terms of the interrelationship of the reactivity/electron deficiency model and the cluster valence molecular orbital model developed by Lauher.

In a recent paper,[1] we reported on the formation of ionic cluster fragments of $Cr_x(CO)_y^+$ and $Fe_x(CO)_y^+$ by gas-phase ion–molecule reactions. In this report, we wish to extend this work to include ionic cluster fragments of $Ni_x(CO)_y^+$ and $Co_x(CO)_y(NO)_z^+$. Although the ion–molecule chemistry of these various transition-metal carbonyl systems are quite similar, there are substantial differences in the degree of coordination saturation/unsaturation for many of the ionic cluster fragments formed.

In our previous paper, we attempted to review the most pertinent literature on the gas-phase ion–molecule chemistry of ionic cluster fragments of transition metals as well as bare metal ions. Although such a review will not be duplicated here, we would like to reemphasize the earlier work by Ridge.[2] On the basis of studies of anionic cluster fragments of $Fe(CO)_5$, Ridge postulated a direct relationship between the electron deficiency and reactivity for ionic cluster fragments. That is, the reactivity increases as the electron deficiency (degree of coordination unsaturation) of an ionic cluster fragment increases. On the basis of this concept, Ridge suggested that the $Fe_2(CO)_x^-$ (x = 5–7) ionic cluster fragments contain a double metal–metal bond.

In our first paper,[1] Ridge's data analysis method was applied to the $Cr_x(CO)_y^+$ and $Fe_x(CO)_y^+$ cluster fragments. For example, the reaction of $Fe(CO)^+$ with neutral $Fe(CO)_5$ gives rise to product ions having reactivities that follow the predicted electron deficiencies assuming simple polyhedral structures. Conversely, the reaction of Fe^+ with $Fe(CO)_5$ gives rise to product ions having sharp discontinuities between reactivity and electron deficiencies.

---

(1) Fredeen, DonnaJean Anderson; Russell, David H. *J. Am. Chem. Soc.* **1985**, *107*, 3762.

(2) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.

0002-7863/86/1508-1860$01.50/0