

# On the Electronic Spectra of *o*- and *m*-Xylylenes and Their Methylated Derivatives. An Experimental and Theoretical Study<sup>1</sup>

E. Migirdicyan\*<sup>2a</sup> and J. Baudet<sup>2b</sup>

*Contribution from the Laboratoire de Photophysique Moléculaire du C.N.R.S., Université Paris-Sud, 91405 Orsay, France, and the Laboratoire de Biochimie Théorique, Institut de Biologie Physico-Chimique, 75005 Paris, France. Received April 7, 1975*

**Abstract:** Resolved spectra of *o*- and *m*-xylylenes and their methylated derivatives trapped in suitable *n*-alkane polycrystalline matrices at 77 K are presented. These biradicaloid species are photolytically produced from the corresponding methylbenzenes. As with benzyl type radicals, the fluorescence spectra of *m*-xylylene diradicals can be analyzed using the vibrational modes and frequencies of their parent aromatic compounds. In contrast, the vibrational envelopes of the fluorescence spectra of *o*-xylylenes are indicative of important geometrical change in going from the first excited to the ground electronic state. This observed behavior is what might be expected from the excitation of a polyene molecule. The energies of the first electronic excited states of *o*- and *m*-xylylenes determined from 0,0 bands of their fluorescence spectra are compared with the results of SCF-CI calculations using various molecular orbital bases.

Matrix isolation has been a powerful tool for the study of reactive molecular fragments which normally have only a transient existence in the gas or liquid phases at room temperature. The technique provides a means to prepare detectable concentrations of trapped species and has been extensively used to study organic as well as inorganic radicals<sup>3a</sup> characterized by one unpaired electron. For example, the benzyl radical and its methylated derivatives can be generated "in situ" by uv photolysis of the corresponding methylbenzenes dispersed in glassy or crystalline matrices at 77 K. Under these conditions, the splitting of a methyl C-H bond in the parent aromatic molecule produces a trapped aromatic radical and a hydrogen atom. The latter diffuses rapidly from the site of dissociation and recombines with other hydrogen atoms or reacts with the solvent. Benzyl type radicals are identified either by absorption<sup>3b,c</sup> or by the more sensitive technique of emission spectroscopy.<sup>4</sup>

In comparison to the systematic investigations of these monoradicals, the optical spectroscopy of aromatic biradicaloid species has received little attention. Here we report spectroscopic and theoretical data on the energies and the probabilities of the electronic transitions of *o*- and *m*-xylylenes (*o*- and *m*-benzoquinodimethanes) resulting from the dissociation of CH bonds on two different methyl groups of *o*- and *m*-xylenes, respectively. As with benzyl type radicals, these species are photolytically generated "in situ" in a rigid matrix where they are trapped at 77 K. They are formed at low concentrations so that their detection is only possible by the very sensitive technique of luminescence.

It was previously reported<sup>5</sup> that 2537 Å photolysis of glassy methylcyclohexane solutions of methylated benzene derivatives at 77 K gives rise to two new emission spectra, A and B, in addition to the fluorescence of benzyl type radicals. Spectra A and B can be distinguished by their different vibrational structures. They both start at higher energies (400–440 nm) than the green fluorescence of polymethylbenzyl radicals (470–490 nm). Although A and B are in the same wavelength range, they can be separated by selective excitation with radiation of appropriate wavelength. These blue emissions have lifetimes less than 10<sup>-3</sup> sec and are therefore probably fluorescence. A and B emissions can no longer be excited after thawing and recooling irradiated samples, which shows that the emitting species are unstable in the melted solutions above 77 K. Of these two spectra, only the poorly resolved emission A is present

in photolyzed solutions of ortho-methyl-substituted benzenes, e.g., *o*-xylene and 1,2,3-trimethylbenzene, whereas only the well-resolved emission B is present when the parent molecules have two methyl substituents in meta position such as *m*-xylene and mesitylene. Emissions A and B are both absent in photolyzed solutions of *p*-xylene and toluene, while they are both present in photolyzed solutions of the other polymethylbenzenes containing methyl substituents in ortho as well as in meta position. On the basis of these observations, emissions A and B were attributed respectively to *o*- and *m*-xylylenes.

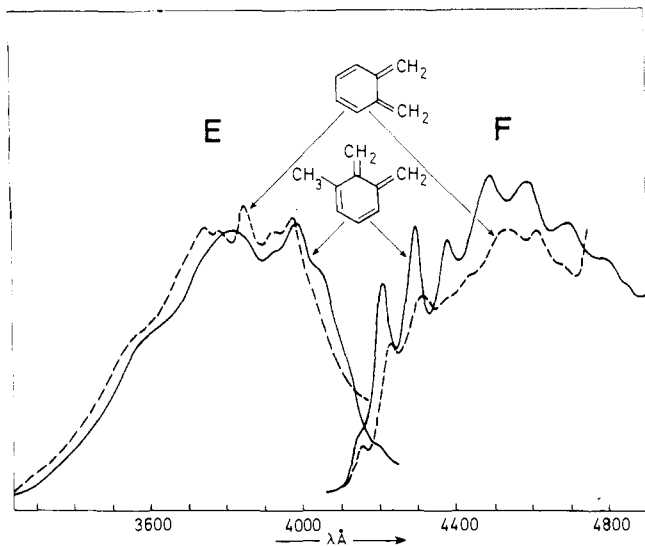
Flynn and Michl<sup>6,7</sup> have recently reported the photochemical synthesis of *o*-xylylene from six different precursors. Their arguments demonstrate that the common photoproduct derived from all these precursors is *o*-xylylene. Their published absorption, emission, and excitation spectra of this species in rigid glassy EPA at 77 K are similar to the emission A and its excitation spectrum which we have previously recorded from photolyzed glassy solutions of *o*-xylylene in methylcyclohexane at 77 K.<sup>5</sup> The results of Flynn and Michl support our assignment of emission A to *o*-xylylene and, consequently, our assignment of emission B to *m*-xylylene. This represents, to our knowledge, the first spectroscopic observation of the *m*-xylylene biradical.

The increasing interest raised by recent theoretical studies on biradicaloid species<sup>8,9</sup> led us to repeat our experiments under conditions where better resolved spectra of *o*- and *m*-xylylenes can be recorded in order to compare the energies and intensities of their electronic transitions determined spectroscopically with theoretical values.

The energies of the electronic states of *o*- and *m*-xylylenes were previously calculated by a self-consistent-field (SCF) molecular orbital (MO) method with configuration interaction (CI).<sup>10</sup> For both species, the basis used for CI was the SCF MO's of the ground state. The results showed that the ground state of the meta isomer is a triplet while that of the ortho is a singlet. The agreement between experimental<sup>5</sup> and theoretical<sup>10</sup> results was good for the first electronic singlet-singlet transition of *o*-xylylene but poor for the first electronic triplet-triplet transition of *m*-xylylene. We report here improved calculations leading to a better agreement between experimental and theoretical results.

## Spectroscopic Results

**Resolved Electronic Spectra of *o*- and *m*-Xylylenes.** In the glassy matrices previously used,<sup>5-7</sup> the distribution of solute



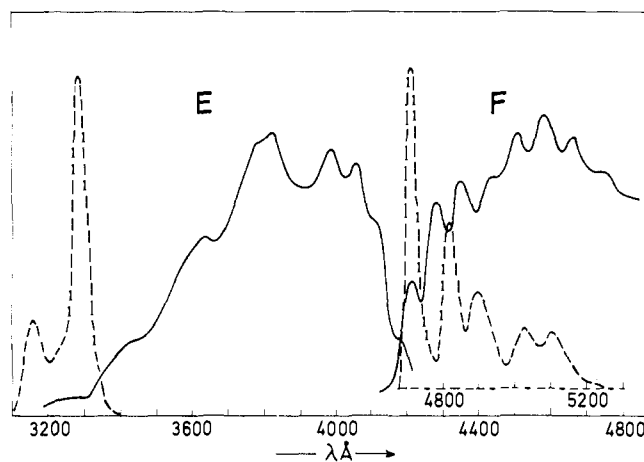
**Figure 1.** Electronic spectra of *o*-xylene (dashed line curves) and of 1-methyl-*o*-xylene (full line curves) produced by photolysis of respectively *o*-xylene and 1,2,3-trimethylbenzene in *n*-pentane at 77 K: F, fluorescences excited by 3600–3700 Å radiations; E, excitation spectra of the fluorescences at 4600 Å.

species among a great variety of sites resulted in solute spectra consisting of broad bands. In contrast, suitable normal alkane polycrystalline matrices are known<sup>11,12</sup> to provide only a small number of distinct lattice sites which can be occupied by aromatic guest molecules or trapped species generated from them by photolysis. In these Shpolskii matrices, the solute-solvent interaction is reduced to a minimum since the solvent-excited state lying above 50,000  $\text{cm}^{-1}$  is much higher in energy than the excited state of the trapped species. Previous reports from different laboratories<sup>11–17</sup> have established that spectra consisting of sharp bands are expected for trapped species located in well-defined sites of the crystalline normal alkane matrix, when the carbon skeleton chain length of the linear paraffin equals the longest dimension of the carbon skeleton of the aromatic solute.

*o*- and *m*-xylenes as well as their methylated derivatives were produced by uv photolysis of the corresponding polymethylbenzenes dispersed in normal alkane solutions frozen at 77 K. According to the number and position of the substituents on the aromatic ring, the sharpest spectra for xylenes were obtained in either *n*-pentane or *n*-hexane frozen at 77 K.

Concerning the characterization of species, the results obtained in the present experiments are similar to those previously observed in rigid glasses;<sup>5</sup> besides benzyl type radicals, *o*-xylenes are the only emitting species produced from *o*-xylene and 1,2,3-trimethylbenzene, while *m*-xylenes are the only emitting fragments generated from *m*-xylene and mesitylene. Methylated *o*- and *m*-xylenes (*o*- and *m*-durylenes) are both formed during uv photolysis of durene solid solutions, whereas no emission attributable to *o*- and *m*-xylenes can be excited in uv photolyzed solutions of *p*-xylene at 77 K. The most suitable matrices are found to be frozen *n*-hexane for species formed from durene and frozen *n*-pentane for species formed from the other polymethylbenzenes studied. For a given matrix, the fluorescence spectra of monoradicals and biradicaloid species produced photochemically from the same parent molecule are not always equally well resolved.

**First Electronic Transition Energies of *o*- and *m*-Xylenes.** Figures 1 and 2 show the fluorescence (F) and excitation (E) spectra of *o*-xylene and its methylated deriva-



**Figure 2.** Electronic spectra of *o*-durylene (full line curves) and of duryl radical (dashed line curves) produced by photolysis of durene in *n*-hexane at 77 K: F, fluorescences excited by 3600-Å (*o*-durylene) and by 3300-Å (duryl radical) radiations; E, excitation spectra of the fluorescences at 4750 Å (*o*-durylene) and at 4885 Å (duryl radical).

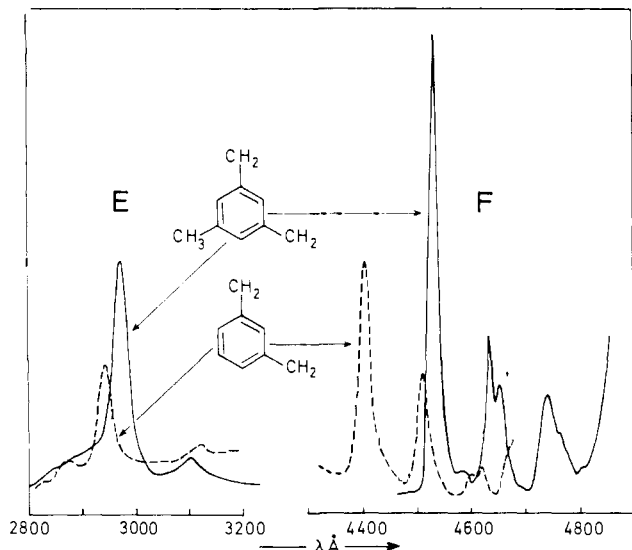
**Table I.** First Electronic Transition Energies of *o*- and *m*-Xylenes and Their Methylated Derivatives Trapped in *n*-Pentane at 77 K

| Parent molecules        | First electronic transition energies |                                  |
|-------------------------|--------------------------------------|----------------------------------|
|                         | <i>o</i> -Xylenes                    | <i>m</i> -Xylenes                |
| <i>m</i> -Xylene        |                                      | 22730 $\text{cm}^{-1}$ (2.81 eV) |
| <i>o</i> -Xylene        | 24130 $\text{cm}^{-1}$ (2.99 eV)     |                                  |
| Mesitylene              |                                      | 22100 $\text{cm}^{-1}$ (2.74 eV) |
| 1,2,3-Tri-methylbenzene | 24100 $\text{cm}^{-1}$ (2.99 eV)     |                                  |
| Durene                  | 23850 $\text{cm}^{-1}$ (2.96 eV)     | 22430 $\text{cm}^{-1}$ (2.78 eV) |

tives trapped in either *n*-pentane (Figure 1) or *n*-hexane (Figure 2) at 77 K. These spectra are not equally well-resolved, the used matrices probably being more suitable for methylated derivatives than for *o*-xylene itself. All the spectra presented in Figures 1 and 2 are nevertheless better resolved than those obtained in previous experiments carried out in rigid glasses.<sup>5–7</sup> In particular, it is possible here to separate out and define fluorescence 0,0 bands, which are the shortest wavelength emission bands, since hot bands are suppressed in spectra of species trapped in solid solutions at low temperatures. The overall shapes of F and E spectra have approximately mirror image symmetry. For each *o*-xylene derivative, the E spectrum certainly involves the first electronic transition since it starts in the region of the corresponding fluorescence 0,0 band. It may also include a close-lying higher transition similar to the case of benzyl-type radicals,<sup>18</sup> since calculations have predicted a second excited singlet state energetically very close to the first one (see later).

Figure 3 presents the fluorescence (F) and excitation (E) spectra of *m*-xylene and 3-methyl-*m*-xylene trapped in *n*-pentane at 77 K. Particularly noteworthy is the difference in vibrational structures of the spectra corresponding to ortho and meta isomers. The E spectra of *m*-xylenes consist essentially of band features in the 2800–3200 Å region. However, the excitation spectrum in the visible region was too weak to be detected in our experimental conditions, in contrast to the case of the *o*-xylene biradicaloid species.

The first electronic transition energies of xylenes determined from the positions of their fluorescence 0,0 bands are listed in Table I. The imprecision in determination of  $\nu_{\text{max}}$  is 30  $\text{cm}^{-1}$  ( $\sim 0.004$  eV) for *o*-xylenes and 15  $\text{cm}^{-1}$  ( $\sim 0.002$

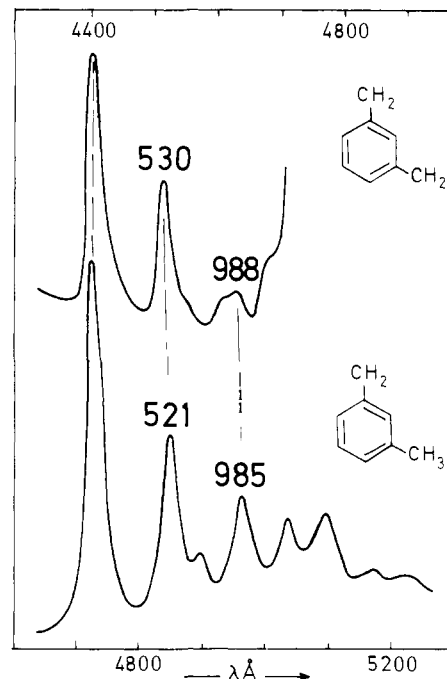


**Figure 3.** Electronic spectra of *m*-xylylene (dashed line curves) and 3-methyl-*m*-xylylene (full line curves) diradicals produced by photolysis of respectively *m*-xylylene and mesitylene in *n*-pentane at 77 K; F, fluorescences excited by 2950-Å (*m*-xylylene) and 2970-Å (3-methyl-*m*-xylylene) radiations; E, excitation spectra of the fluorescences at 4420 Å (*m*-xylylene) and at 4530 Å (3-methyl-*m*-xylylene).

eV) for *m*-xylylenes. These values all refer to experiments carried out in polycrystalline *n*-pentane matrices where the solute-solvent interactions are approximately the same for all the species involved. The values reported in this table show that the effect of methyl substitution on the aromatic ring is to decrease the energy of the first excited states of *o*- and *m*-xylylenes, in agreement with expectations for  $\pi\pi^*$  transitions.

**Vibronic Analysis of Fluorescence Spectra of *m*- and *o*-Xylylenes.** Figure 4 shows the fluorescence spectra of *m*-xylylene (upper curve) and *m*-xylyl monoradical (lower curve) produced together from *m*-xylylene in *n*-pentane at 77 K. The fluorescence spectrum of *m*-xylylene can be observed only in a small wavelength range (4400–4700 Å) because of the presence, in the same spectrum, of the intense *m*-xylyl radical fluorescence starting at 4740 Å. In Figure 4 the two F spectra are shifted with respect to each other so that their 0,0 bands coincide. The striking feature of these fluorescence spectra is the great similarity of their vibrational structure. In particular the two main vibronic bands of *m*-xylylene at 530 and 988  $\text{cm}^{-1}$  and those of the *m*-xylyl radical at 521 and 985  $\text{cm}^{-1}$  have frequencies very close to the ground state vibrational modes 6a(538  $\text{cm}^{-1}$ )/6b(514  $\text{cm}^{-1}$ ) and 1 (998  $\text{cm}^{-1}$ ) of *m*-xylylene (Pitzer and Scott's notation<sup>24</sup>). Similarly, the fluorescence vibronic bands at 517, 610, and 1006  $\text{cm}^{-1}$  in 3-methyl-*m*-xylylene correspond approximately to ground state normal modes 6 (515  $\text{cm}^{-1}$ ), 12 (575  $\text{cm}^{-1}$ ), and 1 (998  $\text{cm}^{-1}$ ) of mesitylene,<sup>24</sup> the greater discrepancy between fluorescence and infrared data for the second vibronic band resulting from its poor separation from the first one (see Figure 3).

Little information is directly available on ground state vibrational modes and frequencies of organic free radicals since their infrared and Raman spectra are generally not known. Leach and his coworkers, however, have established, by the method of isodynamic molecules, that it is possible to analyze the well-resolved solid state fluorescence spectrum of benzyl radical<sup>19,20</sup> and its methylated derivatives<sup>21–23</sup> using the vibrational frequencies of their parent aromatic compounds. The results obtained in the present study show that this method of isodynamic molecules can be extended to *m*-xylylene and 3-methyl-*m*-xylylene since it



**Figure 4.** Fluorescence spectra of *m*-xylylene diradical (upper curve,  $\lambda_{\text{exc}} = 2950 \text{ \AA}$ ) and of *m*-xylyl monoradical (lower curve,  $\lambda_{\text{exc}} = 3230 \text{ \AA}$ ) produced by photolysis of *m*-xylylene in *n*-pentane at 77 K.

is possible to analyze the fluorescence spectra of these species using the vibrational frequencies of *m*-xylylene and mesitylene, respectively. This indicates that *m*-xylylene type diradicals keep the aromatic character of methylated benzene derivatives, as was already the case for benzyl type monoradicals.

The situation is different for *o*-xylylene and its methyl-substituted derivatives. The vibrational envelopes of the fluorescence spectra of these species are indicative of important geometrical change in going from the first excited to the ground electronic state. The observed behavior is what might be expected from the excitation of a polyene molecule and is very different from that of the *o*-xylyl monoradical and its methylated derivatives. This is illustrated in Figure 2 which shows the fluorescence (F) and excitation (E) spectra of *o*-durylene (full line curve) and of duryl monoradical (dashed curve) produced together from durene in *n*-hexane at 77 K. Here again, the two F spectra are shifted with respect to each other so that their 0,0 bands coincide. Our resolved fluorescence spectra of *o*-xylylenes trapped in *n*-alkane matrices at 77 K (see Figures 1 and 2) present a vibrational progression at about 400  $\text{cm}^{-1}$  which could be due to the in-plane bending mode of the  $\text{CH}_2$  substituent since this frequency is of the same order of magnitude as those attributed to this mode at 417  $\text{cm}^{-1}$  in propylene<sup>25</sup> and at 361  $\text{cm}^{-1}$  in benzyl radical<sup>20</sup> trapped in frozen cyclohexane.

### Theoretical Results

In our previous work on the electronic structure of xylylene biradicaloid species,<sup>10</sup> the CI calculation performed in the basis of the singlet MO's led to the conclusion that *m*-xylylene ground state is a triplet and its first electronic triplet-triplet transition is at 3.25 eV. The excitation energies obtained with the MO's of the triplet configuration were very similar, the first excited state being slightly lowered at 3.13 eV, a value which is still too large with respect to the experimental energy of 2.81 eV reported in the present work.

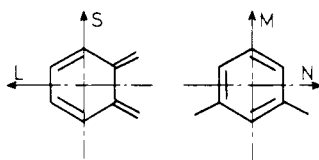
As compared to the usual better performance of a basis of triplet MO's, such a disappointing result is not too surprising. In another work on electronic spectra of doublet states, it was found for the benzyl radical<sup>26</sup> that the excitation energies obtained with the MO's coming from the SCF treatment of the first quadruplet instead of the doublet ground state configuration are in much better agreement with experiment. This suggested to us to calculate the electronic triplet-triplet transitions of *m*-xylylene, using the MO's coming from the SCF treatment of the first quintet. The first triplet-triplet transition energy is then found at 2.90 eV with an oscillator strength of 0.017 in satisfactory accordance with the experimental evidence.

A possible rationalization of the better performance of quintet MO's for calculating the excitation energies of benzene derivatives is as follows: for an  $8\pi$ -electron system, the SCF treatment of the lowest quintet configuration involves 6 MO's instead of 5 in the lowest triplet, and the upper MO's assigned to the 4 unpaired electrons are precisely the ones which are correlated to the  $\pi$  and  $\pi^*$  degenerate MO's of benzene. The benzene degeneracy is lost in *m*-xylylene, but the configurations  $\Phi(4 \rightarrow 6)$  and  $\Phi(5 \rightarrow 6)$  are still very close and this implies that the fifth and sixth MO's have to be considered on an equal footing in the SCF process, as it is the case for the quintet. Moreover, this treatment assigns a particular role to the benzene ring when calculating the first electronic transitions and is somewhat related to the localization technique used by Flynn and Michl<sup>6,7</sup> for that purpose.

In our previous calculations on *o*-xylylene, the first and second transitions were predicted to be at 2.95 and 3.09 eV in a CI calculation starting with the MO's of the SCF closed-shell treatment, and 2.83 and 2.99 eV starting with the MO's of the lowest triplet. According to the values of the oscillator strengths, the first transition should be almost entirely forbidden, whereas the second one could be more easily observed.

### Correlation between Experimental and Theoretical Results

The observed and calculated transition energies as well as the calculated oscillator strengths and directions of transition moments of *o*- and *m*-xylylenes are listed in Table II. The axes of xylylenes are defined as follows:



The agreement between experimental and theoretical values of electronic transition energies is good within 0.1 eV for both species, although the use of a molecular basis appropriate to benzenic compounds is less justified in the case of an ortho than in a meta isomer.

The calculated energies of the two lowest electronic transitions of *o*-xylylene have very close values, and this raises the question as to how meaningful is the ordering of states predicted by a theory involving so many approximations and parameters.

According to Kasha's rule, the emissions of polyatomic molecules in condensed media proceed generally from the lowest states of each multiplicity. Therefore, the observed energies displayed in Table II refer unambiguously to the first electronic transitions, these values being determined from the fluorescence 0,0 bands of xylylenes. In the present work, the oscillator strengths of xylylenes were not measured but only calculated. Flynn and Michl,<sup>6,7</sup> however,

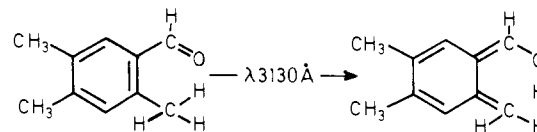
**Table II.** Energies, Oscillator Strengths, and Theoretical Directions of Electronic Transitions of *o*- and *m*-Xylylenes

| Biradicaloid species | Nature               | Electronic transitions |              |          |                                  |          |   |
|----------------------|----------------------|------------------------|--------------|----------|----------------------------------|----------|---|
|                      |                      | Obsd                   | Energies, eV |          | Theoretical oscillator strengths |          | Theoretical direction of transition moment <sup>a,b</sup> |
|                      |                      |                        | <i>a</i>     | <i>b</i> | <i>a</i>                         | <i>b</i> |   |
| <i>o</i> -Xylylene   | $S_1 \leftarrow S_0$ | 2.99                   | 2.95         | 2.83     | 0.009                            | 0.006    | Along L axis  |
|                      | $S_2 \leftarrow S_0$ |                        | 3.09         | 2.99     | 0.185                            | 0.141    | Along S axis  |
| <i>m</i> -Xylylene   | $T_1 \leftarrow T_0$ | 2.81                   | 3.13         | 2.90     | 0.026                            | 0.017    | Along N axis  |
|                      | $T_2 \leftarrow T_0$ |                        | 3.15         | 3.44     | 0.012                            | 0.002    | Along M axis  |

<sup>a</sup> CI with the basis of the SCF MO's of the ground state. <sup>b</sup> CI with the basis of the SCF MO's of the first triplet state (*o*-xylylene) or the first quintet state (*m*-xylylene).

were able, in their experiments, to estimate 0.06 as the value of the oscillator strength of the first electronic transition of *o*-xylylene. This observed value is closer to that calculated here for the second electronic transition  $S_2 \leftarrow S_0$  (about 0.2) than for the first transition  $S_1 \leftarrow S_0$  (about 0.01) suggesting that our calculations give a reverse order of the  $S_1$  and  $S_2$  states of *o*-xylylenes. This conclusion is similar to that reached by Flynn and Michl who compared their experimental and theoretical results, using a slightly different  $\pi$ -electron method.

Additional evidence in favor of the reversal of  $S_1$  and  $S_2$  states of *o*-xylylenes is provided by the polarized absorption spectra of the methylated hydroxy-*o*-xylylenes produced from the photoenolization of 2,4,5-trimethylbenzaldehyde and 2,5- or 2,4-dimethylbenzaldehyde oriented in a durene single crystal<sup>27</sup> according to the reaction



These photoenols are methylated *o*-xylylenes where one methylene H atom is replaced by a hydroxy group. They are detected by their broad absorption ( $\lambda_{\max} \sim 4000 \text{ \AA}$ ) located in the same wavelength range as the Franck-Condon envelope of the excitation spectrum of *o*-xylylene and its methylated derivatives (see Figure 3). In all the cases, the broad absorptions are found to be polarized along the short S axis of the photoenols, suggesting that the presence of two or three methyl substituents on the aromatic ring does not influence appreciably the direction of the transition moment. If in addition we neglect the effect of the hydroxy substituent on the direction of transition moment, then the first  $S_1 \leftarrow S_0$  transition of the photoenol determined experimentally has the same direction as the theoretical transition  $S_2 \leftarrow S_0$  of *o*-xylylene, again suggesting a reversal of  $S_1$  and  $S_2$  states in the theoretical calculations.

The calculated oscillator strengths of the first electronic transitions of *m*-xylyl monoradical and *m*-xylylene diradical are respectively 0.016<sup>28</sup> and 0.017. These very close values provide additional support in favor of the great structural similarity between these species. This also explains why it is so difficult to detect, in both cases of *m*-xylyl and *m*-xylylene, the visible excitation spectrum corresponding to the first electronic transition, in experimental conditions where the fluorescence spectrum and the uv excitation spectrum corresponding to a higher electronic transition are easily recorded. In contrast, the visible excitation spectrum of *o*-xylylene is detected in the same experimental conditions as its fluorescence spectrum. This is consistent with the fact that the corresponding transition of this species has a higher oscillator strength than the first transition of *m*-xylylene.

provided that the fluorescence quantum yields of both isomers are of the same order of magnitude.

### Experimental Section

**Materials.** Merck UVASOL *n*-pentane and Eastman Kodak spectrograde S 1135 *n*-hexane were used without further purification. No emission lying in the spectral region of *o*- and *m*-xylylenes fluorescence was detected from these solvents frozen at 77 K before and after photolysis with Hg 2537 Å radiation. Durene (Eastman Kodak 2295) was purified by column chromatography on Woelm neutral aluminum oxide. Purest samples commercially available of *o*-xylene (Eastman Kodak S276), *m*-xylene (Eastman Kodak S275), *p*-xylene (Eastman Kodak S277), 1,2,3-trimethylbenzene (Fluka), and mesitylene (Fluka) were used without further purification. The purity of aromatic compounds was checked by gas-liquid chromatography on a Perkin Elmer F6 apparatus using a Benton didecylphthalate column. For each compound, the analysis reveals the presence of other methylated benzene derivatives at concentrations of less than 1% and therefore should not interfere with our experimental results.

**Procedure.** Solid solutions at 77 K of methylated benzene derivatives at concentrations of 3 to 6 × 10<sup>-3</sup> M in *n*-pentane or *n*-hexane were prepared from the deaerated room-temperature solutions by rapid freezing, thus favoring a good dispersion of the solute molecules. The mixed crystals were then photolyzed with Hg 2537 Å radiation emitted by a Gallois low-pressure Ar-Hg lamp and absorbed exclusively by the aromatic compound. The species thus produced photochemically and trapped in the matrix were then detected by their fluorescence and excitation spectra using an experimental set-up already described elsewhere.<sup>29</sup> The exciting source was a high-pressure xenon lamp Osram XBO 150 W. All the spectra presented in this work were not corrected for the variation with wavelength of either source intensity or photomultiplier sensitivity.

**Theoretical Method.** Since the spectra observed in the present work are attributed to biradicaloid species of π type, we have limited the theoretical investigations to the electronic spectra of their π-electron system, using the calculation method described in an earlier paper.<sup>30</sup> Basically, our method consists in determining the π MO as a linear combination of 2pπ carbon orbitals, the coefficients of which are given by a SCF treatment performed on the singlet, triplet, or quintet configuration of lowest energy in the frame of the closed-shell or restricted open-shell theory of Roothaan. In our treatment, the overlap integrals  $S_{pq}$  are retained from the beginning, and the effective nuclear charges  $\zeta_p$  and valence state ionization potentials included in the expression of the core integrals  $\alpha_p$  are evaluated from atomic-spectroscopy data. The core resonance integrals  $\beta_{pq}$  are assumed to be of the general form  $\beta_{pq} = k_{pq}S_{pq}$ , with a proportionality factor  $k_{cc}$  fitted on the spectrum of an appropriate reference compound (benzene). The one-center bielectronic Coulomb integrals are extracted from atomic-spectroscopy tables according to Julg's recipe<sup>31</sup> and the nuclear effective charges  $\zeta_p'$  derived from those values are introduced into the theoretical formulas for the other Coulomb integrals, the remaining bielectronic integrals being estimated through the Mulliken-Ruedenberg approximation. Starting with the input data defined in this way, the zero-differential overlap (ZDO) approximation is applied not to the integrals over the primitive 2p<sub>π</sub> atomic orbitals, but to integrals over corresponding Löwdin orthogonalized

orbitals, and a monoconfigurational SCF treatment of the ground and lower excited states is performed, the result of which is then improved by CI. More precisely, the occupied and virtual MO's of the preceding treatment are used in order to construct a basis of singlet or triplet configurational functions including all the nonexcited Slater determinants and the most important diexcited ones with 0, 2, and 4 unpaired electrons (i.e., 52 components for the singlets and 46 for the triplets). It should be added that the final results of the CI calculation may depend on the choice of the starting MO's coming either from the SCF treatment of the lowest singlet configuration or from the lowest triplet or quintet, in so far as the set of configurational wave functions is incomplete.

**Acknowledgment.** The authors would like to thank Dr. G. Berthier and Dr. S. Leach for their stimulating discussions as well as for their valuable criticism of the manuscript.

### References and Notes

- (1) This work was presented at the 5th I.U.P.A.C. Symposium on Photochemistry, Enschede, Holland, July 21-27, 1974.
- (2) Université Paris-Sud; (b) Institut de Biologie Physico-Chimique.
- (3) (a) A. M. Bass and H. P. Broida, Ed., "Formation and Trapping of Free Radicals," Academic Press, New York, N.Y., 1960; (b) I. Norman and G. Porter, *Proc. R. Soc. London, Ser. A*, **230**, 399 (1955); (c) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).
- (4) L. Grajcar and S. Leach, *C. R. Hebd. Seances Acad. Sci.*, **252**, 1014 (1961).
- (5) E. Migirdicyan, *C. R. Hebd. Seances Acad. Sci.*, **266**, 756 (1968).
- (6) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **95**, 5802 (1973).
- (7) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **96**, 3280 (1974).
- (8) L. Salem, 4th I.U.P.A.C. Symposium on Photochemistry, Baden-Baden, 1972, p 317.
- (9) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
- (10) J. Baudet, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 191 (1971).
- (11) E. V. Shpolskii, A. A. Il'ina, and L. A. Klimova, *Dokl. Akad. Nauk SSSR*, **87**, 935 (1952).
- (12) E. V. Shpolskii, *Sov. Phys.-Usp. (Engl. Transl.)*, **3**, 372 (1960); **5**, 522 (1962); **6**, 411 (1963).
- (13) T. N. Bolotnikova, *Opt. Spectrosc. (USSR)*, **7**, 138 (1959).
- (14) S. Leach, *J. Phys. C*, **28**, 134 (1967); *Mem. Soc. R. Sci. Leige, Collect.* **5**, **20**, 179 (1970).
- (15) L. A. Klimova, A. I. Ogloblina, and E. V. Shpolskii, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **34**, 1361 (1970).
- (16) C. Pfister, *Chem. Phys.*, **2**, 171, 181 (1973).
- (17) M. Lamotte and J. Jousset-Dubien, *J. Chem. Phys.*, **61**, 1892 (1974).
- (18) M. C. Tomas-Magos Cossart, Thèse, 1973, Orsay.
- (19) L. Grajcar and S. Leach, *J. Chim. Phys. Phys.-Chim. Biol.*, **61**, 1523 (1964).
- (20) L. Watmann-Grajcar, *J. Chim. Phys. Phys.-Chim. Biol.*, **66**, 1023 (1969).
- (21) S. Leach, A. Lopez-Campillo, R. Lopez-Delgado, and M. C. Tomas-Magos, *J. Phys. C*, **28**, 147 (1967).
- (22) S. Leach and E. Migirdicyan, *C. R. Hebd. Seances Acad. Sci.*, **264**, 156 (1967).
- (23) S. Leach and E. Migirdicyan, *Chem. Phys. Lett.*, **1**, 21 (1967).
- (24) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 803 (1943).
- (25) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N.J., 1945, p 355.
- (26) M. Suard and J. Baudet, *J. Chim. Phys. Phys.-Chim. Biol.*, **67**, 1088 (1970).
- (27) E. Migirdicyan, A. Despres, V. Lejeune, and S. Leach, *J. Photochem.*, **3**, 383 (1975).
- (28) C. Branciard-Larcher, E. Migirdicyan, and J. Baudet, *Chem. Phys.*, **2**, 95 (1973).
- (29) E. Migirdicyan, *J. Chem. Phys.*, **55**, 1861 (1971).
- (30) G. Berthier, J. Baudet, and M. Suard, *Tetrahedron, Suppl.* **2**, **19**, 1 (1963).
- (31) A. Julg, *J. Chim. Phys. Phys.-Chim. Biol.*, **55**, 413 (1958); **56**, 235 (1959).