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Characterization of the triplet state of aromatic esters and nitriles. Evaluation of the steric effect on the triplet of methyl mesitoate¹

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The phosphorescence emission and electron spin resonance spectra of methyl mesitoate (**1**) and mesitonitrile (**2**) have been studied in order to assess the steric effect (inhibition of resonance) in the former. The triplet energy of **1** (80.5 kcal mol⁻¹) is considerably higher than that of **2** (74.2 kcal mol⁻¹) while the zero-field splitting parameters are very similar (**1**, $D/hc = 0.127$ cm⁻¹, $E/hc = 0.013$ cm⁻¹; **2**, $D/hc = 0.127$ cm⁻¹, $E/hc = 0.006$ cm⁻¹). The triplet energy and zero-field splitting parameters of *o*-, *m*-, and *p*-methyl toluate and *o*-, *m*-, and *p*-tolunitrile are also reported.

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On a étudié les spectres d'émission phosphorescence et de résonance paramagnétique électronique du mésitoate de méthyle (**1**) et du mésitonitrile (**2**) afin de déterminer l'effet stérique (inhibition à la résonance) dans le premier. L'énergie de l'état triplet de **1** (80.5 kcal mol⁻¹) est beaucoup plus élevée que celle de **2** (74.2 kcal mol⁻¹) alors que les paramètres de couplage à champ zéro sont très similaires (**1**, $D/hc = 0.127$ cm⁻¹, $E/hc = 0.013$ cm⁻¹; **2**, $D/hc = 0.127$ cm⁻¹, $E/hc = 0.006$ cm⁻¹). On rapporte aussi l'énergie de l'état triplet et les paramètres de couplage à champ zéro pour les *ortho*-, *mé*ta- et *para*-toluates de méthyle et les *ortho*-, *mé*ta et *para*-tolunitriles.

[Traduit par le journal]

Introduction

Electron spin resonance (esr) spectroscopy can give useful information about the effects (steric and electronic) of substituents on electronically excited triplet states (**1**). The zero-field splitting parameters (D and E) obtained from the esr spectrum are intrinsic properties of the triplet. Furthermore, in the best of cases, hyperfine splitting may be discernible in which case information about the unpaired electron distribution can be obtained. In contrast, other sources of information, for example, singlet-triplet absorption, phosphorescence emission, and triplet-triplet absorption, of course, involve transitions between two states and substituent effects on these spectra result from perturbations of both initial and final states. The usefulness of esr for providing information on the effect of substituents on stable (ground state) triplet molecules is also well established (**2**).

We have reported (**1c**) results of a study on the esr and phosphorescence emission spectra of methyl benzoates with electron-withdrawing substituents (cyano- and carbomethoxy-) from which it was possible to conclude that the lowest triplet of these compounds has π, π^* character. It was also clear, from the relatively small value of D (compared with that for benzene for example) that considerable spin density was distributed onto the carbomethoxy and cyano groups. We have now extended this study to include methyl mesitoate and mesitonitrile in an attempt to assess the steric-effect (inhibition of resonance) on the zero-field splitting parameters and triplet energy.

It is well known that the carboxyl carbonyl of methyl mesitoate cannot be coplanar with the phenyl ring in the ground state and therefore resonance interaction is reduced.⁴ On the other hand, the nitrile function, being linear, is not prevented from being planar with the ring in mesitonitrile and resonance and inductive interaction with the ring are uninhibited. This classic concept, established over thirty-five years ago, has

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⁴X-Ray analysis of mesitoic acid (hydrogen-bonded dimer) indicates the carboxyl group is twisted out of plane of the ring by 48.4° (**3**) while *o*-toluic acid (hydrogen-bonded dimer) is almost planar (**4**).

been used to explore the importance of steric effects in several diverse systems (5).

An example of the difference in steric interaction in methyl mesitoate and mesitonitrile which is most pertinent to the present discussion is the comparison of the ultraviolet absorption spectra of these compounds, first reported by Fehnel and Wepster (6). These spectra are shown in Figs. 1 and 2. Figures 1a and 1b allow a comparison of the absorption spectra of methyl benzoate and cyanobenzene

in the primary (1L_a) and secondary (1L_b) absorption band regions. The similarity of the spectra indicates a resonance interaction involving the carbomethoxy and cyano substituents in both compounds. Figures 2a and 2b show the same absorption regions for methyl mesitoate and mesitonitrile. While the spectrum of mesitonitrile still indicates the strong resonance interaction between the cyano group and the phenyl ring, the spectrum of methyl mesitoate is very different from that of methyl benzoate and reflects the diminished resonance interaction. The lowest triplet has the 1L_a configuration; therefore, the steric effect on the corresponding singlet evident in Fig. 2a should be compared with that on the triplet (7).

Results and Discussion

The spectral (electron spin resonance and phosphorescence emission) characteristics of the triplet states of the substituted methyl benzoate esters and cyanobenzenes studied here are summarized in Table 1.

It is apparent, from the overall similarity of the data, that a π, π^* triplet is involved in every case. In particular, the phosphorescence lifetime which varies between 1 and 5 s is too long for an n, π^* state. We assume, therefore, that the differences that do exist can be considered as substituent effects on the 3L_a (or $^3B_{1u}$) state (7).

Since the triplet energy of methyl benzoate ($77.9 \text{ kcal mol}^{-1}$) and cyanobenzene ($77.0 \text{ kcal mol}^{-1}$) are similar, the difference in the triplet energy of methyl mesitoate ($80.5 \text{ kcal mol}^{-1}$) and mesitonitrile ($74.2 \text{ kcal mol}^{-1}$), that is, $6.3 \text{ kcal mol}^{-1}$, can be attributed to the steric effect in the former. The triplet energy of methyl mesitoate is in fact comparable to that of mesitylene ($79.8 \text{ kcal mol}^{-1}$) or isodurene ($79.6 \text{ kcal mol}^{-1}$) (8).

The observed steric effect upon the absorption and emission spectra are, of course, the combined influence on both the ground state and on the excited singlet and triplet states, respectively. The increase in triplet energy of methyl mesitoate relative to mesitonitrile and methyl benzoate is interpreted to mean that while the ground state energy of methyl mesitoate may be raised by the lack of resonance interaction, the excited state energy is raised even more and the result is a net increase in the transition energy.

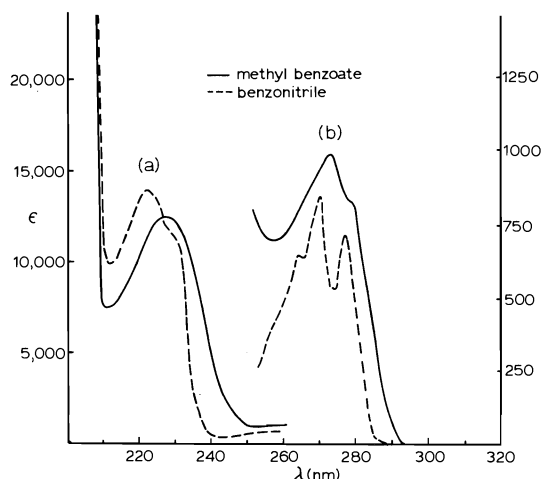


FIG. 1. The primary band (a, left axis of ordinates) and secondary band (b, right axis of ordinates) of the ultraviolet absorption spectra of methyl benzoate and benzonitrile in ethanol solution.

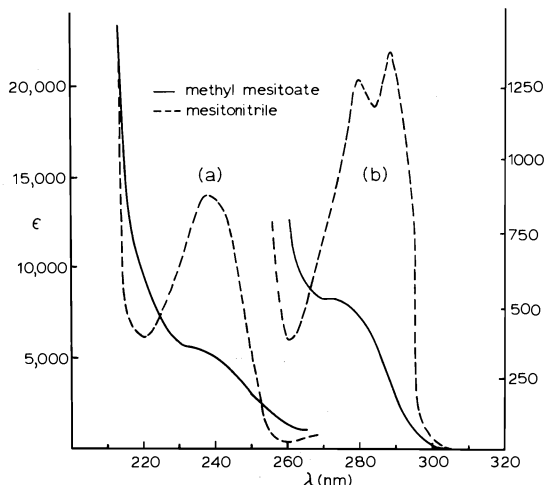


FIG. 2. The primary band (a, left axis of ordinates) and secondary band (b, right axis of ordinates) of the ultraviolet absorption spectra of methyl mesitoate and mesitonitrile in ethanol solution.

TABLE 1. Zero-field splitting parameters and phosphorescence energies for the triplet of some substituted methyl benzoates and cyanobenzenes

Compound	τ_{Phos} (s)	E_T (kcal mol ⁻¹)	D/hc (cm ⁻¹)	E/hc (cm ⁻¹)	D^*/hc (cm ⁻¹) ^a	Reference
Methyl benzoate	2.7	77.9	0.133	0.011	0.134	<i>b</i>
Methyl- <i>o</i> -toluate	2.2	77.5	0.120	0.023	0.126	<i>c</i>
Methyl- <i>m</i> -toluate	4.2	75.9	0.120	0.035	0.134	<i>c</i>
Methyl- <i>p</i> -toluate	3.8	76.4	0.123	0.009	0.124	<i>c</i>
Methyl mesitoate	1.2	80.5	0.127	0.013	0.129	<i>c</i>
Cyanobenzene	3.7	77.0	0.135	0.005	0.135	<i>c</i>
	0.04	76.7	0.137	0.007	0.138	<i>d, e</i>
	—	—	0.134	0.019	0.138	<i>f, g</i>
	—	—	0.136	0.006	0.139	<i>h, i</i>
<i>o</i> -Tolunitrile	3.9	75.9	0.133	0.014	0.135	<i>c</i>
<i>m</i> -Tolunitrile	4.7	75.3	0.130	0.022	0.135	<i>c</i>
<i>p</i> -Tolunitrile	3.9	75.8	0.131	0.006	0.131	<i>c</i>
	—	76.1	0.136	0.005	0.136	<i>d, e</i>
	—	—	0.134	0.022	0.139	<i>f, g</i>
Mesitonitrile	—	74.2	0.127	0.006	0.127	<i>c</i>
	—	—	0.127	0.019	0.132	<i>f, g</i>

^aCalculated [$D^* + (D^2 + 3E^2)^{1/2}$].^bReference 1a.^cThis work.^dIn 1,4-dibromobenzene crystals at 77 K.^eReferences 1g, 1h.^fIn 2-methyltetrahydrofuran at 77 K.^gReferences 1i, 1j.^hReference 1e.ⁱIn ethanol at 77 K.

We look next to the zero-field splitting parameters for direct evidence on the structure of the triplet.

The decrease in the D value from that for benzene (0.158 cm⁻¹ (9)) to that for methyl benzoate (0.133 cm⁻¹) is taken as an indication of the greater average separation of the electrons in the triplet of methyl benzoate. Assuming the point dipole approximation, the D value of benzene is equivalent to an average separation of the electrons of 2.02 Å; while that of methyl benzoate is equivalent to 2.14 Å.⁵ The same increase in the average separation of the electrons is observed with cyanobenzene. The trend to lower D values continues with mesitonitrile indicative of the ability of a methyl substituent to take on spin density.

If the carbomethoxy moiety is prevented from becoming coplanar with the phenyl ring in the triplet of methyl mesitoate, the D value should increase relative to that of mesitonitrile and approach that of mesitylene itself. Such is not the case; methyl mesitoate has the same D value as mesitonitrile (within experimental error) and the value is considerably smaller than that for mesitylene ($D/hc = 0.140$ cm⁻¹ (10)).

⁵The average separation of the electrons in the triplet was estimated using the equation $D = (3/4)g^2\beta^2 \times (1/r^3)$ (ref. 1a).

There are several possible explanations for this result; one is that in the triplet the carbomethoxy moiety is able to twist enough toward the plane of the phenyl ring so that electron delocalization can occur. That is, the steric interactions may not be severe enough to prevent the triplet of methyl mesitoate from becoming planar enough to allow delocalization of the electrons to an extent similar to that of mesitonitrile. This, of course, would be at the expense of energy reflected in the increased triplet energy. To test this possibility we attempted to obtain the esr spectrum from the triplet of methyl 1,3,5-tri-*tert*-butylbenzoate. However, the esr spectrum and the phosphorescence emission spectrum of this compound indicate that more than one species is present; we believe this ester to be photochemically reactive, and have thus far been unable to characterize the triplet.

Experimental

The procedure and apparatus used have been described previously (1c, 2c).

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