Ab initio calculation of zero-field splitting and spin-orbit coupling in ground and excited triplets of *m*-xylylene

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We report CASSCF(6,6)/cc-pVDZ optimized geometries, energies (also single-point CASPT2(6,6)/cc-pVDZ), electron spin–spin dipolar interaction (D,E) tensor, and spin-orbit coupling (SOC) for *m*-xylylene in the lowest triplet T_1 (1^3B_2), in the next triplet 1^3A_1, and in the slightly higher 2^3B_2. The zero-field splitting (zfs) parameters computed for T_1 ($D/hc = 0.013$ cm^{-1}, $E/hc = -0.003$ cm^{-1}) agree well with the observed values $|D/hc| = 0.011$ cm^{-1}, $|E/hc| < 0.001$ cm^{-1}. If $^3A_1$ is the T_2 state as calculated, its computed D/hc (-0.040 cm^{-1}) and E/hc (0.001 cm^{-1}) agree with the value $|D/hc| = 0.04 \pm 0.01$ cm^{-1} deduced from experiment assuming $E = 0$. If 2^3B_2 is the T_2 state, the experimental data need to be reevaluated, since its computed E/hc value (-0.012 cm^{-1}) is not negligible relative to D/hc (0.038 cm^{-1}). The SOC matrix elements of T_1–T_3 with the lowest and the $\pi\pi^*$ excited singlets are small (~ 0.01–0.1 cm^{-1}), while those with representative $^1\sigma\pi^*$ states are large (~ 10 cm^{-1}). The former lack one-center terms and therefore are much smaller than expected from the standard one-electron approximation. Computed SOC affects D and E slightly, and supports the proposed vibronic mechanism of intersystem crossing from T_2.

1. Introduction

m-Xylylene (**1**), a highly reactive biradical with no classical

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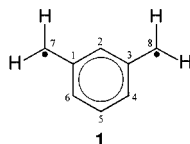
Kekulé structure, has found considerable use as a building block in magnetic organic materials.[1] It was first observed spectroscopically in 1975 by Migirdicyan and Baudet[2] in *n*-alkane polycrystalline matrices at 77 K. They determined the first electronic transition energy from the position of the fluorescence 0,0 band (22 730 cm^{-1}). According to calculations,[2–8] *m*-xylylene has a $^3B_2$ triplet ground state T_1 and two low-lying excited triplet states of different symmetries, 1^3A_1 and 2^3B_2 (here and in the following, symmetry labels refer to the space part of the electronic wave function). The computed energy separation between these excited triplets (T_2 and T_3) is very small. Most of the calculations place the 1^3A_1 state a little below the 2^3B_2 state, but some methods of calculation yield the reverse order.[5,7,8] The existence of these two close-lying triplets has not been confirmed by direct observation, but the absence of mirror-image symmetry in laser-induced fluorescence excitation spectra suggests strongly that both calculated 1^3A_1 and 2^3B_2 states are indeed present and vibronically coupled.[6,9] The energy order of the zero-order electronic states has not been established by experiment. The same general pattern of triplet state energies is found in methyl substituted *m*-xylylenes.[8]

Wright and Platz[10] found that the EPR signal intensity of *m*-xylylene follows the Curie law, in agreement with the assignment of the ground state as a triplet (T_1). They found $|D/hc| = 0.011$ cm^{-1}, $|E/hc| \le 0.001$ cm^{-1} for its zero-field-splitting (zfs) parameters, and this was later confirmed by Goodman and Berson,[11] who synthesized *m*-xylylene by an independent route. Fluorescence decay of methylated *m*-xylylene biradicals is biexponential, and this was attributed to emission from non-
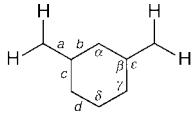
equilibrating triplet sublevels.[7,12] From the dependence of the lifetime on magnetic field strength the zfs parameter $|D/hc| = 0.04 \pm 0.01$ cm^{-1} of the excited T_2 electronic state was deduced,[13] assuming the E parameter to be negligible. This was the first zfs parameter measurement for an upper triplet state of an organic molecule; results for upper triplets of other molecules have become available more recently.[14]

The first semiempirical calculation[15] of the D parameter of the T_1 state preceded the experimental measurement[10] and overestimated the D value by a factor of three ($|D/hc| = 0.032$ cm^{-1}). This was followed by a more complete semiempirical calculation[16] that produced D values of 0.025, 0.049 and 0.053 cm^{-1} for the 1^3B_2 (T_1), 1^3A_1 (T_2) and 2^3B_2 (T_3) states, respectively. Both sets of calculations used only the spin–spin dipolar operator and assumed negligible spin-orbit coupling effects. They also made no attempt to calculate the E parameter. Even in the later calculation,[16] the D value for the T_1 state was overestimated considerably, but its increase upon excitation to the T_2 state was reproduced qualitatively. This is true regardless of whether the latter is of $^3A_1$ or $^3B_2$ symmetry, since similar D values were calculated for the 1^3A_1 and 2^3B_2 states, calculated to be closely spaced.

The purpose of the present study is threefold. First, we wish to establish whether present-day *ab initio* methods are capable of reproducing the zfs parameters of the T_1 and T_2 states more accurately. We are not aware of prior *ab initio* zfs constant calculations for higher triplet states of molecules of this size. Second, we wish to test the degree of validity of the common belief that zfs of the triplet states of planar π-electron hydrocarbons is dictated by electron spin–spin dipolar coupling and is not affected much by spin-orbit coupling. Third, we wish to find out whether the previously proposed[7] interpretation of the qualitative features of intersystem crossing from the T_2 level to low-lying singlets is supported by actually computed values of the relevant spin-orbit coupling matrix elements.

2. Method of calculation

The calculations were performed with CASSCF(6,6) wave func-

	a	b	c	d	α	β	γ	δ	ε
T_1	1.412	1.417	1.429	1.382	121.9	117.6	120.8	121.2	121.1
T_2	1.385	1.411	1.452	1.463	124.3	118.5	119.7	119.4	120.7
T_3	1.437	1.442	1.456	1.381	121.3	117.4	120.9	122.1	121.1

Fig. 1 The CASSCF(6,6)/cc-pVDZ optimized geometry of the first three triplet states of **1** (bond distances in Å and bond angles in degrees).

tions using the cc-pVDZ basis set.[17] The molecular geometry of the three lowest triplet states was optimized under constraint to C_{2v} symmetry and to C_s symmetry with state-specific CAS orbitals. The six active orbitals were of π symmetry (three a_2 and three b_1 MOs; these six π orbitals are energetically well separated from the others). The energies of the triplet states were recalculated at the CASPT2(6,6)/cc-pVDZ level at the CASSCF optimized geometries.

Geometry optimization and CASSCF calculations were done with the GAUSSIAN98 program,[18] CASPT2 calculations with the MOLCAS 4.1 program,[19] and zfs and spin-orbit coupling calculations with the *ab initio* program suite SOSS,[20] which has been presently modified to calculate the expectation values of the spin–spin Breit–Pauli operator for excited state wave functions. This modification allows the calculation of electronic spin–spin dipolar tensor and zfs parameters for any type of CI wave function. Electron spin–spin dipolar coupling and spin-orbit coupling were computed using CASSCF(6,6)/cc-pVDZ wave functions determined for each state at its optimized CASSCF(6,6) C_{2v} geometry. Both the one-electron and the two-electron parts of the spin-orbit coupling Breit–Pauli Hamiltonian were included.

In the calculation of spin-orbit coupling matrix elements between the T_1–T_3 states and $^1\sigma\pi^*$ states, the six active orbitals (two σ and four π or π^*) were those that appeared in the most important configurations in a CASSCF(10,10) calculation in which the usual space of six π orbitals was extended by adding the two σ and two σ^* orbitals that were the closest to the Fermi level. Among the lowest 25 singlet states, there were none with a significant weight of any $\pi\sigma^*$ configurations.

3. Results and discussion

Calculated triplet geometries and energies

CASSCF(6,6) optimized geometries of the three lowest triplet states subject to a C_{2v} symmetry constraint are shown in Fig. 1. The C–C bond lengths of the T_1 (1^3B_2) state are all close to ordinary aromatic bond lengths. In the T_2 (1^3A_1) state, the exocyclic C–C bonds are 3 pm shorter, the C^1–C^2 and C^2–C^3 bonds remain almost unchanged, and the other bonds are longer (C^4–C^5 and C^5–C^6 by 8 pm). The C^1–C^2–C^3 angle increases by 2.4°. Compared with the T_1 state, in the T_3 (2^3B_2) state the exocyclic bonds are all 3 pm longer than the bonds between atoms C^6, C^1, C^2, C^3, and C^4. The C–H bond lengths are constant (1.079 to 1.082 Å), as are the valence angles.

A CASSCF(6,6) optimization subject to a C_s symmetry constraint, and starting from a C_s trial geometry, led to the same C_{2v} structure for the T_1 state. However, for the T_2 and T_3 states, it ended in different C_s stationary points. CASSCF calculations for the T_2 state predict the best C_s geometry to lie 12.5 kcal mol^{-1} below the best C_{2v} geometry. However, single-point PT2 corrections to the T_2 CAS wave functions reverse this order and place the T_2 energy at the C_{2v} geometry 1.3 kcal mol^{-1} below that at the C_s geometry. In the case of the T_3 state the energy at the best CASSCF C_s geometry is 3.6 kcal mol^{-1} above that at the best CASSCF C_{2v} geometry, and the difference increases to
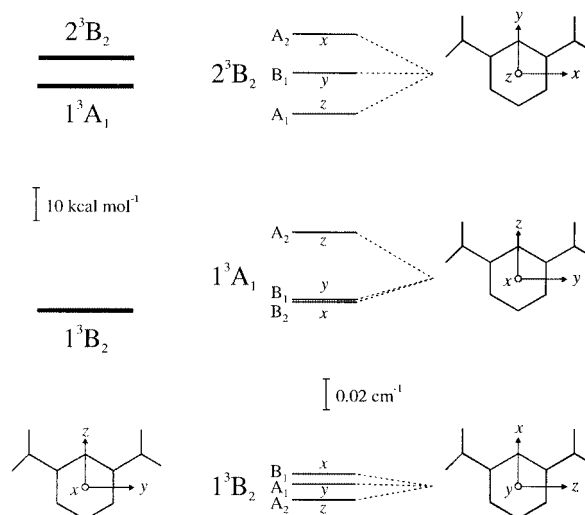
Fig. 2 CASPT2(6,6) triplet energies of **1**. Left, C_{2v} state labels for standard axis labels. Right, triplet sublevels and orientation of magnetic axes in EPR notation.

9.4 kcal mol^{-1} after single-point CASPT2 corrections. A reliable determination of the minimum geometry of the T_2 state will require a rather expensive unconstrained geometry optimization at the CASPT2 level, preferably with a larger basis set, and a vibrational frequency analysis. It is quite possible that T_2 and T_3 are two branches of a double cone surface (conical intersection). We believe that the best T_2 and T_3 C_{2v} geometries found presently are adequate for the our purposes, but realize that they need not correspond exactly to true minima in these surfaces.

Comparison with other calculations and with observed spectra

Bond lengths of the T_1 state are systematically shorter than those obtained in the pioneering UHF/STO-3G calculation of Kato *et al.*;[4] the largest difference is 3.6 pm for $r(C^4$–$C^5)$. Negri and Orlandi[6] calculated geometries for the three lowest triplet states by a modified QCFF/PI method. Their bond lengths for the T_1 state differ from the CAS values at most by 2 pm, but the trends observed upon going to higher excited triplet states are different. The T_1 distances calculated by Hrovat *et al.*[21] at the CASSCF(8,8)/6-31G* level differ from the present results by less then 1 pm.

According to our CASPT2 calculations the energy of the T_2 (1^3A_1) state is 67.2 kcal mol^{-1} above that of the T_1 (1^3B_2) ground state and the T_3 (2^3B_2) state lies 75.0 kcal mol^{-1} above the T_1 state. The observed $T_2{\rightarrow}T_1$ electronic transition energy determined from the fluorescence 0–0 band[2] is 64.8 kcal mol^{-1} and thus agrees quite well with the calculated value. The energy of the T_3 state has not yet been experimentally determined, but it cannot be much above T_2. Semiempirical π-SCF-MO-CI calculations[2] provided excitation energies of 66.9 (1^3A_1) and 79.3 (2^3B_2) kcal mol^{-1}, but the results were strongly dependent on the MOs used. Later, the transition energies were recalculated[8] for a series of methyl substituted *m*-xylylenes with adjusted semiempirical parameters. For the parent biradical they were 64.9 (2^3B_2) and 67.2 (1^3A_1) kcal mol^{-1}.

Calculated spin-dependent properties

(i) Spin–spin dipolar coupling. The zfs parameters calculated without inclusion of spin-orbit coupling are listed in Table 1 (Fig. 2). They follow the general pattern of the prior semiempirical results,[16] but are numerically smaller. Among the three lowest triplet states, the T_1 state has the smallest $|D/hc|$ value because the unpaired electrons reside far apart, primarily one on each of the exocyclic carbon atoms C^7 and C^8 (Fig. 3). As was proposed earlier[16] on the basis of semiempirical

Table 1 Calculated [CASSCF(6,6)] and experimental zfs parameters for the three lowest triplet states of **1** (in cm^{-1})

|	Calcd.			Exp.	
State	D/hc	E/hc	State	$\lvert D/hc \rvert$	$\lvert E/hc \rvert$
1^3B_2 (T$_1$)	0.013	−0.003	T$_1$	0.011 [a]	<0.001 [a]
1^3A_1 (T$_2$) [b]	−0.043 (−0.040) [c]	0.001	T$_2$	0.04 ± 0.01 [d]	0 [e]
2^3B_2 (T$_3$) [b]	0.038	−0.012		—	—

[a] Ref. 10. [b] The calculated order of the 1^3A_1 and the 2^3B_2 states could be incorrect since they are very close in energy. [c] With correction for T$_2$–S$_{12}$ spin-orbit coupling. The other results are not affected by spin-orbit coupling with the singlet states considered (Table 2). [d] Ref. 13. [e] Assumed.

Table 2 Non-zero 1-electron, 2-electron, and total spin-orbit matrix elements between the lowest triplet and the most stable and the lowest $\pi\pi^*$ and $\sigma\pi^*$ excited singlet states of **1** (in cm^{-1}) [a]

		1^1A_1 (S$_0$) [b]	1^1B_2 (S$_1$) [c]	2^1B_2 (S$_2$) [c]	2^1A_1 (S$_3$) [c]	1^1A_2 (S$_{12}$) [d]	1^1B_1 (S$_{14}$) [d]	2^1B^1 (S$_{21}$) [d]
T$_1$ (1^3B_2)	1-electron	0.0138			0.849	9.9368	17.0195	18.3706
	2-electron	−0.013			−1.0423	−5.2745	−8.8998	−9.5327
	total	0.0008 (x)			−0.1933 (x)	4.6623 (y)	8.1197 (z)	8.8379 (z)
T$_2$ ($^3A_1$)	1-electron		1.4541	0.4695		27.3672	23.2832	13.2179
	2-electron		−1.4816	−0.4803		−13.9573	−12.5189	−6.7279
	total		−0.0275 (x)	−0.0108 (x)		13.4099 (z)	10.6643 (y)	6.4900 (y)
T$_3$ (2^3B_2)	1-electron	0.1926			0.4031	17.9282	12.3315	18.9564
	2-electron	−0.1993			−0.515	−9.5159	−6.5505	−10.2365
	total	−0.0067 (x)			−0.1119 (x)	8.5159 (y)	5.7810 (z)	8.7199 (z)

[a] The label of the coupling triplet sublevel is shown in parentheses. [b] The most stable singlet. [c] $\pi\pi^*$ excited singlet. [d] $\sigma\pi^*$ excited singlet.
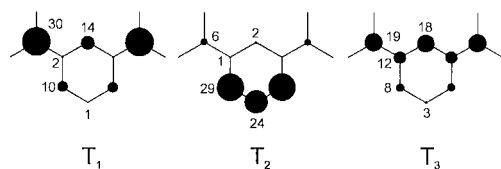
Fig. 3 CASSCF(6,6) spin populations (%) for the three lowest triplet states of **1**.

calculations, in the T$_2$ state the unpaired electrons are located in the ring, mostly on the vicinal carbons C^4, C^5, and C^6, and their proximity causes $\lvert D/hc \rvert$ to increase. The T$_x$ and T$_y$ sublevels of the T$_2$ state are very close, and the $\lvert E/hc \rvert$ parameter is only 0.001 cm^{-1}. In the T$_3$ state, the unpaired electrons are distributed over a chain of carbon atoms (C^7–C^1–C^2–C^3–C^8), which also results in a large splitting of sublevels. Compared to the T$_2$ state, in the T$_3$ state the unpaired spins are distributed in a less linear fashion and $\lvert E/hc \rvert$ is much larger.

(ii) Spin-orbit coupling. No prior results are available, and the spin-orbit interaction of the three lowest triplet states, all of which have an even number of π electrons, and the four lowest singlet states, all of which also have an even number of π electrons, was investigated first. By El-Sayed's rules,[22] spin-orbit coupling among such states should be weak, since one-center terms vanish. The four lowest singlet states are 1^1A_1 (S$_0$), 1^1B_2 (S$_1$), 2^1B_2 (S$_2$), and 2^1A_1 (S$_3$), with calculated energies 13.2, 47.2, 104.1, and 110.3 kcal mol^{-1}, respectively, relative to the T$_1$ state. The calculated energy of the S$_0$ state agrees well with the published values[21] of 12.9 and 11.7 kcal mol^{-1}, calculated at the CASSCF(8,8) and CASPT2N levels, respectively. In the C_{2v} symmetry group the singlet A$_1$ states have non-zero spin-orbit matrix elements with the T$_x$ sublevel of triplet B$_2$ states and the singlet B$_2$ states have non-zero elements with the T$_x$ sublevel of the triplet A$_1$ state, while other matrix elements vanish. Table 2 shows that even the non-zero elements are all extremely small, as expected. One-center contributions vanish by symmetry and two-center contributions are generally small, both because of the r^{-3} dependence on the distance from the atomic nucleus, and because the one- and two-electron contributions nearly cancel.

The reason for this cancellation is readily seen when NBO analysis[20] is performed. For instance, the contributions to the $\langle 1^3B_2 \lvert H^{SO} \rvert 2^1A_1 \rangle_x$ element are largely due to a pair of π-symmetry AOs located on C^6 and C^7 (C^4 and C^5) interacting either with the positive charge of the nucleus at C^1 (C^3) (one-electron contribution), or with the negative charge due to electrons at C^1 (C^3) (two-electron contribution). Since C^1 (C^3) is relatively distant, the two types of interaction approximately cancel.

Clearly, the approximate proportionality between the total, the one-electron, and the two-electron contributions to the spin-orbit coupling operators, which is the basis for the usual one-electron approximation to this operator that invokes empirical atomic constants, cannot hold for the two-center contributions. In this case, as the distance from the nucleus increases, the total spin-orbit coupling contribution goes to zero much faster than the one-electron and the two-electron parts individually, at least if the nuclear charge is approximately balanced by the electrons in its vicinity. Thus, in systems such as *m*-xylylene, in which one-center contributions vanish by symmetry, the usual empirical one-electron approximation cannot be used for spin-orbit coupling between states with equal numbers of π electrons, nor can the usual computer programs such as GAUSSIAN98. However, it is also true that in such cases spin-orbit coupling is small and can often be neglected altogether, for instance when evaluating zfs parameters. In the present case, we find that the effect of spin-orbit coupling of the T$_1$, T$_2$, and T$_3$ states with low-energy singlet states on the values of $\lvert D/hc \rvert$ and $\lvert E/hc \rvert$ is entirely negligible, less then 10^{-5} cm^{-1}.

El-Sayed's rules suggest that the matrix elements for the spin-orbit mixing of the low-lying triplet states with high-energy excited singlet states with an odd number of electrons, which are dominated by $\pi\sigma^*$ and $\sigma\pi^*$ configurations, will be larger. We have therefore attempted to identify a few representative states of this kind, both singlets and triplets, using CASCSF-(10,10)/cc-pVDZ calculations. In these, the (6,6) active space was extended by adding two σ (a$_1$ and b$_2$) and two σ^* (a$_1$ and b$_2$) orbitals. Among the resulting 25 lowest triplet states there was only one state of this type (T$_{16}$, $^3A_2$, $\sigma\pi^*$), located 270 kcal mol^{-1} above the T$_1$ state. Among the resulting 25 lowest singlet states, four states of the desired kind were found, all $\sigma\pi^*$ (energies in kcal mol^{-1}): S$_{12}$ ($^1A_2$, 279), S$_{14}$ ($^1B_1$, 289), S$_{21}$ ($^1B_1$, 334),

and S_{23} ($^1A_2$, 345). Due to the intrinsic limitations of our spin-orbit program we had to restrict the spin-orbit calculations to CASSCF(6,6) wave functions by deleting those orbitals occurring in the (10,10) active space that were either doubly occupied or unoccupied in all of the most important configurations of the interacting states. Although these four states are just a few of a large number, one can hope that their properties are representative and that they give us a glimpse of what we might expect if all of them were included.

Table 2 lists the non-zero spin-orbit coupling matrix elements between the T_1, T_2, and T_3 states and the S_{12}, S_{14}, and S_{21} states. Note that for these one-center dominated terms the usual approximate proportionality of the one-electron, two-electron, and total contributions holds well.

Only the T_y sublevel of T_1 and T_3, which are of $^3B_2$ symmetry, can couple with S_{12} ($^1A_2$), and only their T_z sublevel can couple with S_{14} and S_{21} ($^1B_1$). Similarly, only the T_z sublevel of T_2 couples with S_{12} and only its T_y sublevel couples with S_{14} and S_{21}. These matrix elements are large (~10 cm^{-1}), comparable to that in carbene.[20] However, since these singlet states are so high in energy, the effect of this spin-orbit coupling on the $|D/hc|$ and $|E/hc|$ values of T_1, T_2, and T_3 is below 0.001 cm^{-1} and negligible. The only exception is the value of $|D/hc|$ in T_2, which is reduced by 0.003 cm^{-1} by spin-orbit interaction with S_{12}. Still, this is merely a ~10% effect, beyond the present computational accuracy. However, it will not be negligible if a high-accuracy calculation is attempted in the future. With this single exception, the spin–spin dipolar $|D/hc|$ and $|E/hc|$ values given in Table 1 also represent the total presently computed values.

We realize that the cumulative effect of the many other $\sigma\pi^*$ (and probably also $\pi\sigma^*$) states located at higher energies on $|D/hc|$ and $|E/hc|$ could be larger in the absence of fortuitous compensation. Much compensation can however be expected, since there will be roughly as many $^1A_2$ states as $^1B_1$ states, and their matrix elements will be of comparable magnitude as long as the σ skeleton is approximately isotropic in the molecular plane. Then, the T_y and the T_z sublevels of low-energy triplets will be stabilized to a comparable degree. However, there is no analogous mechanism for stabilizing the T_x sublevels, and it seems that the effect of spin-orbit coupling with $\sigma\pi^*$ and $\pi\sigma^*$ states on the zfs parameters cannot be safely ignored in molecules such as **1** when high accuracy is required. An improvement of the present calculation of D and E in the direction of a larger basis set and a better description of electron correlation would thus make little sense unless spin-orbit coupling with the high-energy $\sigma\pi^*$ and $\pi\sigma^*$ states is fully included also.

Comparison with experiment

(i) Zero-field splitting. There is an element of uncertainty in the computed D and E values. First, the absolute[20] values of the calculated zfs parameters are known to be too large and to converge slowly with the quality of the basis set and with the amount of correlation introduced into the wave function. At the present level of calculation, we estimate the absolute values to be about 10% too high. Second, spin-orbit coupling with high-energy $\sigma\pi^*$ and $\pi\sigma^*$ states introduces many small corrections that are likely to mutually cancel to a considerable degree, but not perfectly, the net effect being a stabilization of the T_y and T_z sublevels relative to T_x, and a small change in the separation of T_y and T_z. The magnitude of the few contributions of this kind that we did calculate suggests that the neglect of the rest introduces an error of unknown direction in the calculation of D and E, most likely again ~10% in magnitude. It is encouraging and perhaps somewhat fortuitous that the values of zfs parameters calculated for the T_1 (1^3B_2) state are in excellent agreement with the experimental values and exceed them only by 0.002 cm^{-1}, and that the D/hc parameter of the T_2 (1^3A_1) state was calculated within the experimental error (Table

1). The assumption $E = 0$ that was made in the interpretation of the experimental data for T_2 seems well justified.

The calculated value of the $|D/hc|$ parameter for the 2^3B_2 state is close to that of the 1^3A_1 state and thus does not help to assign the observed T_2 triplet as either $^3A_1$ or $^3B_2$. The situation would change dramatically if the E parameter of T_2 could be measured, since the values calculated for 2^3B_2 and 1^3A_1 differ by an order of magnitude. If the symmetry of T_2 is not $^3A_1$ as calculated here, but instead is $^3B_2$, it would not be advisable to assume $E = 0$ in the analysis of the experimental results.

(ii) T_2 to S intersystem crossing. The observed biexponential $T_2 \rightarrow T_1$ fluorescence decays were interpreted[16] under the assumption that T_2 is of $^3B_2$ symmetry, but the conclusions for $^3A_1$ symmetry, assumed here, would be the same. It was proposed that one of the three triplet sublevels, T_x, decays slowly since its intersystem crossing to lower-energy singlets is inefficient (the spin-orbit matrix elements with the low-lying singlets are non-zero but very small). The primary decay mechanism was postulated to be $T_2 \rightarrow T_1$ internal conversion. The other two triplet sublevels, T_y and T_z, decay faster and at comparable rates, and this was attributed to vibronic intersystem crossing induced by a_2 and b_1 vibrations that mix $\sigma\pi^*$ (or $\pi\sigma^*$) character into low-energy singlet or triplet wave functions.

Our numerical results are in perfect agreement with the proposed interpretation, in that the matrix elements for purely electronic coupling of the T_x level with low-energy singlets located within ~20–40 kcal mol^{-1} are three orders of magnitude smaller than the matrix elements for coupling with $\sigma\pi^*$ singlets located one order of magnitude (~200–400 kcal mol^{-1}) higher in energy (recall that a square of the matrix element enters the rate expression), and in that there is no pronounced anisotropy differentiating the y and z directions.

Our results also leave little doubt that the lowest excited states with an odd number of π electrons are $\sigma\pi^*$ and not $\pi\sigma^*$ in character.

4. Conclusions

The following conclusions can be drawn:

(i) *Ab initio* calculations at the CASSCF(6,6)/cc-pVDZ level yield very satisfactory results for the zfs parameters of the T_1 and T_2 states of *m*-xylylene, and the method can be expected to be useful for triplet states of other organic molecules of this size.

(ii) As expected from symmetry arguments and in agreement with a long-held belief, spin-orbit coupling in *m*-xylylene has a very small effect on the zfs parameters of low-lying $\pi\pi^*$ triplets, and they are dominated by the spin-dipolar term. However, the effect of spin-orbit coupling with high-energy $\sigma\pi^*$ and $\pi\sigma^*$ states is not entirely negligible and we estimate that it introduces a ~10% uncertainty into the computed D and E values. This result is likely to be general for molecules of this type.

(iii) The non-zero spin-orbit coupling elements between the T_x sublevel of triplets with an even number of π electrons and singlets with the same number of π electrons, which do not contain one-center terms for symmetry reasons and are small as expected from El-Sayed's rule, do not follow the usual proportionality rule between the one-electron and two-electron parts and the total effect, and the cancellation of the two parts is much more pronounced than usual. The reasons for this are easily understood in qualitative terms, and we conclude that two-center terms are generally likely to be overestimated in the usual one-electron aproximation. This provides an additional argument in favor of their neglect in the simple model for spin-orbit coupling in biradicals proposed earlier.[23]

(iv) In accord with El-Sayed's rules, spin-orbit coupling matrix elements between the T_y and/or T_z sublevels of triplets with an even number of π electrons and singlets with an odd number of π electrons ($\sigma\pi^*$ excited) are large and comparable

to that in carbene. They are important for vibronically induced intersystem crossing induced by out-of-plane vibrations. This result is also likely to be general.

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