138. Triplet Energy of 2,2-Dimethylisoindene from Electron-Energy-Loss Spectroscopy and Photoinduced Triplet Energy Transfer

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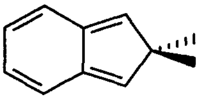
The excited electronic states of 2,2-dimethylisoindene (**1**) have been studied by electron-energy-loss spectroscopy. Its vertical gas-phase triplet (1^3B_2), and singlet (1^1B_2) excitation energies are 1.61 and 3.19 eV, respectively. The excited states are thus lowered by 0.49 eV and 1.21 eV, respectively, when compared to the corresponding states of (all-*E*)-octatetraene, which serves as a reference compound. These shifts are partially reproduced by ZINDO calculations. The spectra give no evidence for a 2^1A_g state below the 1^1B_2 state, but this lack of observation does not exclude its existence. The lowest triplet state T_1(**1**) was further characterized by flash photolysis. T_1(**1**) was observed as a transient intermediate, $\lambda \leqslant 350$ nm, with a lifetime of 8 μs in degassed hexane. The adiabatic excitation energy of T_1(**1**) was bracketed to the range of 1.1 ± 0.1 eV by energy-transfer experiments. Relationships between the energies of the lowest excited singlet and triplet states of **1** and the lowest excited doublet state of its radical cation $1^{+\cdot}$ – essentially a non-*Koopmans*' state – are discussed.

Introduction. – The title compound 2,2-dimethylisoindene (**1**) contains, from a spectroscopic point of view, a nearly unperturbed *o*-xylylene chromophore, but is much more stable than the parent compound because of steric hindrance towards dimerization [1]. It thus permits a convenient study of the electronic structure of this chromophore and its comparison with (all-*E*)-octatetraene (**2**). The π-system of both compounds consists of four conjugated C=C bonds, but already the HMO model indicates that the additional link in **1** results in a reduced HOMO-LUMO gap (0.59β for **1**, 0.69β for **2**). Thus, **1** is an example of a molecule having relatively small, unconventional chromophore with low-lying excited states [2].



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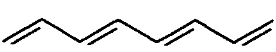

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In accordance with expectation, the absorption spectrum of **1** in 3-methylpentane glass at 77 K revealed a comparatively low-lying transition with origin at *ca.* 2.9 eV [1], corresponding essentially to a HOMO→LUMO excitation from SCF-CI calculations, and giving **1** its canary yellow color. The origin of the first absorption band of the radical cation $1^{+\cdot}$ (in 3-methylpentane glass at 77 K) lies at 1.60 eV [3]. The lack of a corresponding transition in the photoelectron spectrum of **1** and comparison with the results of calculations revealed the unusual fact that already the *first* excited doublet state of $D_1(1^{+\cdot})$ is of non-*Koopmans'* nature, *i.e.*, that this state is not well described by one of the electron configurations obtained by removing an electron from the closed-shell ground configuration of **1** [3] [4].

The present work complements existing data on the electronic states of **1**. We report triplet and singlet excitation energies in the gas phase, determined by electron-energy-loss (EEL) spectroscopy, as well as the energy, lifetime, and the absoption of the lowest triplet state of **1** in solution, determined by flash photolysis.

Experimental. – The trochoidal electron spectrometer used in the present work has been described in detail in [5]. It uses magnetically focussed trochoidal monochromators as electron-energy filters, instead of the more conventional cylindrical or hemispherical condensers, and a collision chamber with only small apertures for the incident and scattered electron beams instead of a gas nozzle. This construction results in high sensitivity and small sample consumption, an imperative prerequisite for recording a spectrum with a small amount of sample (*ca.* 20 mg). The experiment involves bombarding the sample vapor at low pressure (*ca.* 10^{-4} mbar) with a beam of electrons of varying incident energy E_i and detecting electrons scattered at a fixed residual energy E_r. The incident electrons can collisionally excite the target molecules, thereby loosing an amount of kinetic energy $\Delta E = E_i - E_r$ equal to the excitation energy. A spectrum of excited states is obtained by plotting the scattered electron I_s current against the electron loss ΔE. The collision chamber was kept at *ca.* 100° during the measurement, the resolution was *ca.* 0.045 eV, and the energy scale is accurate to within 0.03 eV.

Flash photolysis was accomplished by excitation with either an electric discharge flashlamp (1000-J electric energy, 20-µs pulse width at half height) or frequency-doubled (20 ns, 530 nm, 200 mJ) or triplet (20 ns, 353 nm, 50 mJ) pulses from a Nd glass laser. The spectrographic and kinetic detection systems and the software for transient kinetic analysis have been described in [6].

2,2-Dimethylisoindene (**1**) was synthesized by debromination of *1,3-dibromo-2,2-dimethylindan* (**3**) with lithium amalgam as described by *Dolbier et al.* [1]. The following procedural details were found to be important to achieve satisfactory results. Li (0.1 g) was cut and rolled under dry pentane and added to 20 g of Hg under Ar. The supernatant solvent was then evaporated and the reaction vessel evacuated. All subsequent operations were done under vacuum (< 1 Pa). Formation of the amalgam from the heterogeneous mixture was accelerated by ultrasonic treatment. After 40 min, a degassed soln. of **3** (0.5 g) in 5 ml of dry pentane was slowly added to the amalgam, and the mixture was stirred at r.t. After 15 min, the solvent and the yellow product were evaporated at r.t. and recondensed. Markedly improved yields were obtained, when the dark grey residue was then extracted repeatedly by addition of degassed pentane (10 ml), ultrasonic treatment for 10 min, and evaporation until the supernatant solvent remained colorless (5–10 extractions). The combined extraxts were slowly freed from the solvent at –55°. The residue contained, in addition to yellow **1**, an unknown volatile grey material, possibly Hg. Separation of **1** from this material was achieved by repeated sublimation at –20°. The purified solid product **1** (71 mg, 30% yield) could be stored indefinitely under vacuum at –70°. Solid **1** should be handled at temperatures below 0° to avoid decomposition.

Isoindene **1** reacts instantly with 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (NPTD) to give the expected *Diels-Alder* adduct. M.p.: 163–164°. ^{1}H-NMR ($CDCl_3$, TMS): 0.90 (*s*, 3 H); 1.60 (*s*, 3 H); 4.90 (*s*, 2 H); 6.75–6.85 (*m*, 2 H); 7.2–7.5 (*m*, 7 H). MS: 319 (M^+). This reaction was used to determine the extinction coefficient of **1** in benzene soln. The extinction coefficient of a fresh sample of NPTD (*Fluka*, *purum*, > 98%) in dry benzene was determined as $\varepsilon(\lambda_{max} = 540 \text{ nm}) = 222 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$. A weighted, *ca.* twofold excess of NPTD was added to a soln. of **1** (*ca.* 10^{-3} M) in benzene (10 ml) the extinction of which at 400 nm had been measured with a 1-mm cell. The yellow color of **1** was rapidly quenched upon dissolution of NPTD, and subsequently the red color of NPTD developed. The extinction of excess NPTD was then measured at 540 nm and used to calculate the amount of reacted NPTD. Three such determinations gave $\varepsilon(\mathbf{1}, 400 \text{ nm}) = 3060 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$. As a test of this procedure, known amounts of tetracene were 'titrated' in the same way. Single measurements were accurate to within ± 10%.

Results. – *EEL Spectroscopy.* Energy-loss spectra were recorded at several residual energies and a representative spectrum is shown in *Fig. 1*. It was recorded at low residual energy and thus shows both triplet and singlet electronically excited states [5]. The more intense band, peaking at 3.19 eV, persists even at higher residual energies and must correspond to the singlet excited state 1^1B_2. The lowest vibrational level appears at

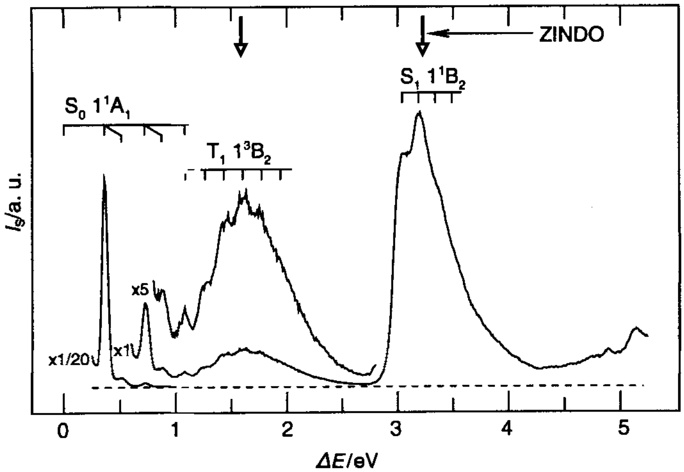

Fig. 1. *Electron-energy-loss spectrum of 2,2-dimethylisoindene* (**1**), *that is plot of the scattered electron current* I_s (in arbitrary units) vs. *the electron-energy loss* ΔE, *recorded with a residual energy of 3.5 eV.* Results of ZINDO calculations are indicated by vertical arrows.

3.04 eV, in agreement with the matrix absorption value of 2.85 eV [1], if allowance is made for a bathochromic shift of 0.19 eV in the matrix. The spectra show no evidence for another singlet excited state below the 1^1B_2 state, although a 2^1A_1 state could be the lowest excited singlet state of **1**, analogous to the 2^1A_g state of (all-*E*)-octatetraene reported in [7]. Our earlier EEL measurements of **2** failed to disclose this state [8], and we, therefore, cannot exclude a similar failure in the case of **1**. Nevertheless, we shall henceforth use the symbol S_1 to denote the 1^1B_2 state at 3.19 eV.

The broader band, peaking at 1.61 eV, becomes less intense at higher residual energies, indicating that it corresponds to the lowest triplet state 1^3B_2 of **1**. Its vibrational structure with a spacing of *ca.* 0.15 eV (1200 ± 150 cm^{-1}) is consistent with the excitation of a C=C streching vibration, as would be expected for a π-π^* excitation. The observed transition energies are given in *Table 1.*

Table 1. *Experimental* (band maxima in eV ± 0.03 eV) *and Calculated* (ZINDO) *Energies for the Lowest Triplet* T_l (1^3B_2 and 1^3B_u) *and the Singlet* S_l (1^1B_2 and 1^1B_u) *States of* **1** (this work) *and* **2** ([8])

Compound	$E(T_l)$		$E(S_l)$		$E(S_l) - E(T_l)$	
	exp.	calc.	exp.	calc.	exp.	calc.
(all-*E*)-Octatetraene (**2**)	2.10	2.15	4.40	3.91	2.30	1.76
2,2-Dimethylisoindene (**1**)	1.61	1.59	3.19	3.23	1.58	1.62

The signal below 1 eV is due to excitation of high vibrational levels of the electronic ground state of **1**, with C–H and C=C stretching vibrations being active. Unfortunately, these peaks partially overlap with the triplet band, making it impossible to localize with certainty its origin, *i.e.*, the adiabatic triplet energy. Either 1.08 eV or 1.26 eV are possible values.

Flash Photolysis. Flash photolysis of a 5×10^{-4} M solution of **1** in degassed hexane with a 20-ns laser pulse at 353 nm (3.51 eV) gave rise to transient bleaching of the absorption of **1** in the range of 360–440 nm (2.82–3.44 eV), and transient absorption at shorter wavelengths, $\lambda \leqslant 350$ nm ($\geqslant 3.87$ eV). No absorption changes were detected above 440 nm ($\leqslant 2.82$ eV). Part of the transient bleaching and all of the transient absorption decayed by first-order kinetics with a rate of 1.3×10^5 s^{-1}. The energy-transfer experiments described below clearly identify this transient intermediate as the lowest triplet state of **1**.

Flash photolysis of polycyclic aromatic hydrocarbons produces well-known, characteristic triplet-triplet absorptions in the visible region [9]. The decay rate of these transient absorptions was accelerated in the presence of **1**, indicating triplet-energy transfer to occur from the aromatic hydrocarbons to **1**. For reasons of solubility, benzene was used as a solvent in all experiments. The energy transfer rate, k_{et}, was calculated by comparison of the observed decay rates of the aromatic hydrocarbon triplets in the presence, k^{Q}_{obs}, and absence, k^{0}_{obs}, of quencher **1**: $k_{et}[Q] = k^{Q}_{obs} - k^{0}_{obs}$.

Decay kinetics of the transient aromatic triplets in the absence of quencher **1** usually contained a second-order contribution due to triplet-triplet annihilation. To avoid this complication, a sufficient amount of **1** was always added such that the observed decay was cleanly-first-order due to dominant decay by the energy-transfer process. Under these circumstances the ill-defined contribution k^{0}_{obs} was negligible, *i.e.*, $k_{et}[Q] \approx k^{Q}_{obs}$. The reactivity of **1** did not allow determination of its amount by weighing. The quencher was thus added from a stock solution of known extinction, and the concentration [Q] was calculated using the extinction coefficient $\varepsilon(\mathbf{1}, 400 \text{ nm}) = 3060 \pm 200$ M^{-1}cm^{-1} (see *Experimental*). This value is in agreement with previous estimates for the extinction coefficient of *o*-xylylene [10].

The energy-transfer rate constants thus determined were in the range expected [11] for exothermic triplet-energy transfer, $\log(k_{et}/\text{s}^{-1}) = 9.5 \pm 0.2$, except for the sensitizers with the lowest triplet energy (*Table 2*). The triplet energies of the top five aromatic hydrocar-

Table 2. *Rate Constants for Triplet-Energy Transfer between Various Benzenoid Aromatic Hydrocarbon Donors and* **1** *in Degassed Benzene at Ambient Temperature* (23 ± 2°)

Sensitizer	$\log(k_{et}/\text{s}^{-1})$[a])	$E(T_1)$/eV[b])	λ_{obs}/nm[c])	λ_{exc}/nm[d])
Dibenz[*a,h*]anthracene	9.5	2.27	580	conv.
Benz[*a*]anthracene	9.3	2.05	485	conv.
Anthracene	9.5	1.85	420	conv.
Dibenzo[*a,i*]pyrene	9.7	1.75	490	conv./353
Tetracene	9.4	1.28	485	conv.
Violanthrene	9.4	1.20	550	conv.
Isoviolanthrene	9.1	1.10	625	530
Dibenzo[*a,l*]pentacene	9.1	1.06	545	530
Benzo[*a*]pentacene	6.8	0.95	520	530
Pentacene	< 6.5	0.86	500	530

[a]) Average energy-transfer rate constants from *ca.* 10 individual measurements. In most cases, 2–3 different solutions were prepared independently. Standard error ± 0.1 log units.

[b]) Triplet energies; sources are given in the text.

[c]) Wavelengths of maximum triplet-triplet absorption used for observation of triplet decay rates.

[d]) Excitation source: 'conv.' indicates conventional electric discharge, numbers indicate laser wavelengths.

bons [12] listed in *Table 2* and of pentacene [13] are known accurately. The triplet energies of violanthrene, isoviolanthrene, dibenzo[*a,l*]pentacene, and benzo[*a*]pentacene were estimated by empirical correlation with the energies of the ^1L_a band (0–0 transition) in benzene solution (*Fig. 2*). Such an interpolation should yield values accurate to ± 0.04 eV due to the structural similarity of all compounds considered. As predicted by the correlation, the triplet-state energies of isoviolanthrene and dibenzo[*a,l*]pentacene are very similar: both triplet states co-exist in equilibrium in solutions containing both compounds at similar concentrations, and energy transfer can be observed directions by flash photolysis.The relative ordering of the triplet energies of the last three entries in *Table 2* was verified by the observation of 'irreversible' energy between neighboring pairs.

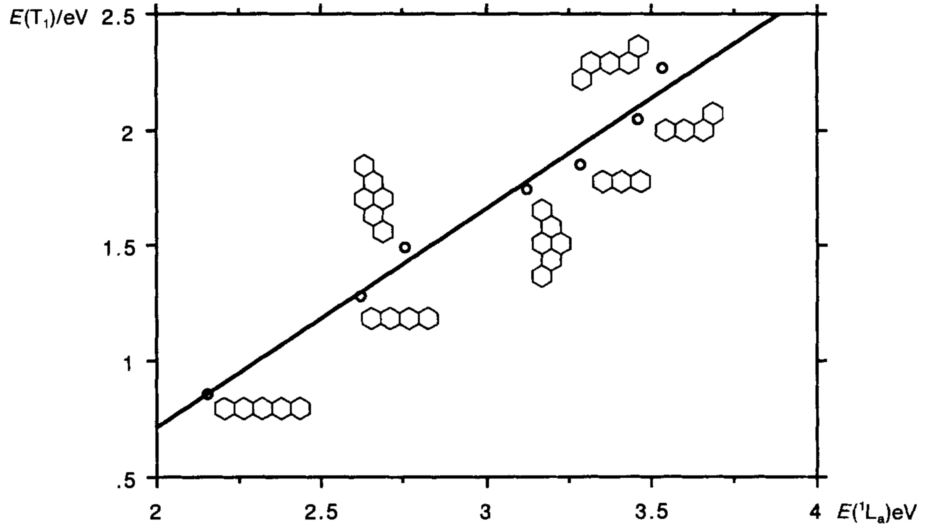

Fig. 2. *Correlation between 0–0 energies of the ^1L_a bands* ($E(^1L_a)$) *of polycyclic aromatic hydrocarbons in benzene solution and the energies of their lowest triplet state,* $E(T_1)$. The slope and intercept of the linear regression line are 0.95±0.06 and (−1.18±0.18) eV, respectively. This linear relation was used to calculate the triplet energies of violanthrene, isoviolanthrene, dibenzo[*a,l*]pentacene, and benzo[*a*]pentacene given in *Table 2*.

Balzani et al. have developed a simple model function for the dependence of energy-transfer rates in fluid solution on the spectroscopic energy difference between donor and acceptor [11]. *Balzani*'s function (Eqn. 29 in [11]) was adjusted to the measured values of k_{et} (*Table 2*, excluding pentacene) by nonlinear least-squares fitting. The solid line drawn in *Fig. 3* is the best fit obtained with the following values for the two adjustable parameters: Energy of T_1(**1**) equal to 1.10 ± 0.01 eV, $k^0_{en} = (0.91 \pm 0.24) \times 10^{10}$ s^{-1}. The parameters $k_d = 1 \times 10^{10}$ M^{-1} s^{-1} and $k_{-d} = 1.2 \times 10^{10}$ s^{-1} (benzene), and ΔG^{+} (0) = 0.062 eV for polycyclic arenes were taken from [11] and held constant. (The reader is referred to [11] for the definition of these parameters.)

The last entry of *Table 2* shows that energy transfer from triplet pentacene to **1** is immeasurably slow, indicating that this process is endothermic. We, therefore, seeked evidence for the reverse process, *i.e.*, energy transfer from triplet **1** to pentacene. To this

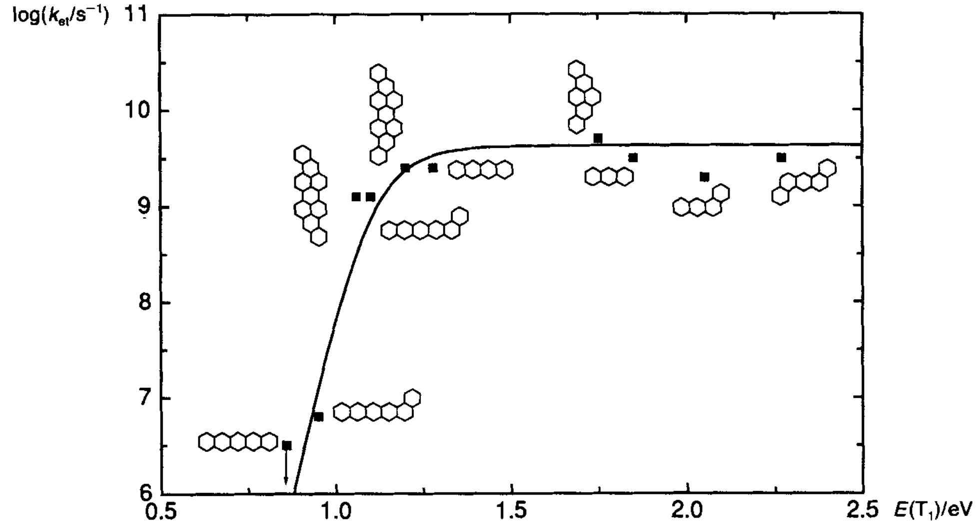

Fig. 3. *Correlation of triplet energies,* $E(T_1)$, *of polycyclic aromatic hydrocarbon sensitizers with observed rate constants,* k_{et}, *of triplet-energy transfer to isoindene.* The solid line is the best fit of *Balzani*'s function (Eqn. 29 in [11]) to the experimental data. Fitting parameters are given in the text. The point shown for pentacene is an upper limit and was not included in the fitting procedure.

end, we used a degassed benzene solution containing benzophenone (5×10^{-3} M), **1** (7×10^{-4} M), and pentacene (1.6×10^{-5} M). Under these conditions, most of the exciting light at 353 nm was absorbed by benzophenone. The transient absorbance waveform at 500 nm showed a rapid rise during the laser pulse. The initial absorbance then decayed to about half of its intensity with a rate of *ca.* 3×10^{6} s^{-1} but subsequently rose again to nearly its original intensity with a rate of *ca.* 1.5×10^{5} s^{-1}, before it finally decayed on a much longer time scale. In the absence of **1**, the intermediate rise was not observed, and the slow decay was much weaker. In the absence of pentacene, the initial absorbance decayed completely with a first-order rate of 3×10^{6} s^{-1}. The latter solution, when monitored at 320 nm, showed a biexponential decay curve with rates of 3×10^{6} s^{-1} and 1.1×10^{5} s^{-1}. These experiments clearly show that **1** serves as a triplet-energy relay between benzophenone and pentacene: The initial rise in absorbance is due to the immediate formation of triplet benzophenone ($\lambda_{max} = 530$ nm) and a small amount of triplet pentacene through direct excitation. Triplet benzophenone is quenched predominantly by **1** whose concentration exceeds that of pentacene by a factor of forty. Hence, the time-resolved rise in absorbance observed between 1 and 5 µs after the laser pulse may be attributed to energy transfer from triplet **1** (which does not absorb at the observation wavelength of 500 nm) to pentacene. The rate of this rise is close to the decay rate of triplet **1** in the absence of pentacene, since the concentration of pentacene (1.6×10^{-5} M) was too low to reduce the lifetime of **1** substantially. Despite its low efficiency, energy transfer from triplet **1** to pentacene is easily detected by the intermediate rise in absorbance at 500 nm thanks to the extremely high extinction coefficient of triplet pentacene. The final slow decay corresponds to the decay of triplet pentacene. Similar results were obtained with a mixture containing fluorenone, **1**, and pentacene.

Discussion. – The data compiled in *Table 1* illustrate the effect of the additional link in the *o*-xylylene chromophore (in comparison with a linear tetraene) by comparing the energies of triplet and singlet states originating from HOMO-LUMO excitation in **1** and **2**. A lowering of the excited state energies as well as a reduction of the triplet/singlet (T_1/S_1) splitting are observed experimentally. ZINDO calculation [14] including all singly excited configurations in the CI expansion were performed for the S_1 and T_1 states of **1** and **2**. (The energies of the T_1 states were taken as the difference of the S_0 and T_1 total energies.) We note from *Table 1* a satisfactory agreement between theory and experiment except for S_1(**2**), the energy of which is considerably underestimated.

Molecules with very small HOMO-LUMO gaps have triplet ground states and are diradicals. Molecules with somewhat larger HOMO-LUMO gaps have the normal excited state ordering, that is a singlet ground state, but some of the diradical-like properties remain conserved and they may, therefore, be called diradicaloids (*cf. e.g.* [2] for a discussion of this topic). The question arises whether the reduced HOMO-LUMO gap makes **1** a diradicaloid. It has been proposed that this term should be applied to molecules with a lowest triplet state of less than 100 kJ/mol (*ca.* 1 eV) above S_0 [15], hence **1** approaches, but does not quite reach this limit.

The first intense triplet absorption band observed in the flash photolysis experiment of **1** lies to the *blue* of the first ground-state absorption band, like those of the extended linear acenes. This finding agrees well with predictions for the triplet-triplet absorption spectrum of *o*-xylylene calculated by a semiempirical PPP SCF CI model [16]. The parity-forbidden $T_1(1^3B_2)$–$T_2(2^3B_2)$ transition is calculated to lie at 2.4 eV (515 nm). This energy would cause the T_2 state to be hidden under the high-energy tail of the S_1 band in the spectrum of *Fig. 1*, where it cannot be identified as a separate peak. The first transition of oscillator strength ($f = 0.25$) is $T_1(1^3B_2)$–$T_5(3^3B_2)$ at 4.2 eV (293 nm), in agreement with the experimental absorption observed for **1** ($\lambda \leqslant 350$ nm).

The rates of triplet energy transfer from various sensitizers to **1** given in *Table 2*, and the observation of triplet energy transfer from **1** to pentacene prove that the adiabatic triplet energy of **1** is lower than that of violanthrene (1.2 eV), higher than that of pentacene (0.86 eV), and very close to those of isoviolanthrene and dibenzo[*a,l*]pentacene (both 1.1 eV). In view of the uncertainty in the triplet energies of the reference compounds, we propose an energy of T_1(**1**) to be 1.1 ± 0.1 eV. Although the energy-transfer experiments were done with benzene solutions, the triplet energies of the reference compounds were determined in apolar rigid glassy matrices at 77 K. Therefore, the above value refers to these conditions. The solvent shift is thus expected to be small, allowing comparison with the gas phase EEL value of 1.08 eV.

Ten years ago, *Kumar et al.* have proposed the value of 1.0 ± 0.1 eV as an estimate of the triplet energy of non-bridged *o*-xylylenes and of the enols of 2-methylbenzaldehyde and 2-methylacetophenone, based on the observation of triplet energy transfer from the enol triplets to β-carotene [17]. We have previously shown [18] that these triplets decay to a mixture of (*Z*)- and (*E*)-isomers of the ground-state enols, although they must have been generated initially as the (*Z*)-isomers. Calculations had suggested that the relaxed geometries of these enol triplets were essentially coplanar, but experimental evidence was put forward that equilibrium between the (*Z*)- and (*E*)-conformers was reached within 100 ns in the triplet state [18]. The fact that the triplet energy of the bridged compound **1** is quite similar to those of the non-bridged enols indicates that rotation of one of the two methylene groups *does not* substantially stabilize the triplet state of *o*-xylylenes.

A simple approximate relation has been proposed for the singlet and triplet energies ($E(S_1)$ and $E(T_1)$) of a neutral molecule and the doublet energy $E(D_1)$ of its radical cation, provided all three transitions correspond to the HOMO-LUMO promotion, and that further conditions are met (the 'SDT rule' [3]). The relation states that D_1 should lie between T_1 and S_1 or, quantitatively, $E(D_1) = [E(T_1) \times E(S_1)]^{1/2}$. While this relation has been remarkably well satisfied in the case of stilbene systems [19] a systematic study of benzenoid hydrocarbons indicated that predictions of D_1 are on the average too low by *ca.* 0.35 eV [20]. Applying the above relation yields $E(D_1) = 2.26$ eV for isolated $\mathbf{1}^{+\cdot}$ using the energies of T_1(**1**) and S_1(**1**) from *Table 1*. The experimental vertical value in the gas phase can be estimated as $E(D_1) = 1.9$ eV from the center of gravity of the double-peaked band in the matrix spectrum of $\mathbf{1}^{+\cdot}$ at *ca.* 1.7 eV [3] and allowing for a matrix shift of *ca.* 0.2 eV. Hence, $E(T_1) < E(D_1) < E(S_1)$ is satisfied, but there is a quantitative disagreement with theory by about the amount established in [20], indicating that a deviation of this magnitude may generally be expected as a consequence of the assumptions underlying the 'SDT-rule' [3].

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