k and *l*. The mixing coefficient of ψ_i into the p orbital of the carbon atom is given by the expression $(c_{ik} + c_{il})\beta/[\alpha - (\alpha + n_i\beta)] = -(c_{ik} + c_{il})/n_i$, while that of ψ_j, the antibonding MO paired with ψ_i, is given by $(c_{ik} + c_{il})/n_i$. Therefore, these MO's are mixed into the p orbital to the same extent but with opposite signs. Since ψ_i and ψ_j have the same coefficients at the starred atoms and coefficients of the same magnitude but opposite sign at the unstarred atoms, the contribution of the odd AH to the resulting NBMO occurs only at the unstarred atoms, the set to which the lone carbon is not bonded. If the carbon is instead bonded to one or more of the unstarred atoms, the mixing coefficients for ψ_i and ψ_j are the same. Thus, the NBMO that results from the mixing has coefficients only at the starred atoms of the odd AH, just those atoms where the NBMO of the odd AH, which survives unaltered after union, also has nonzero coefficients.

(9) W. T. Borden, *Chem. Commun.*, 881 (1969).

(10) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 5968 (1975).

(11) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).

(12) (a) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975); (b) W. T. Borden, *J. Am. Chem. Soc.*, **98**, 2695 (1976); (c) W. T. Borden and E. R. Davidson, *J. Chem. Phys.*, **64**, 663 (1976).

(13) Planar D_{3h} trimethylenemethane actually possesses a pair of degenerate singlet states of E′ symmetry. Although one of them may be described as having an allyl plus p wave function,[12] the other resembles an ethylene weakly interacting with two radicals.[12b,c] However, it is easily shown[12b,c] that the latter is merely a linear combination of two other allyl plus p type wave functions in which the two remaining peripheral carbons are chosen to bear the noninteracting p orbital. A physical explanation of this mathematical fact can be given in terms of the potential surface for the singlet: E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977).

(14) In the NBMO's of odd AH's carbon atoms with coefficients of opposite sign are separated by $4n - 3$ others. If the union of an additional carbon to two such atoms occurs, a ring of $4n$ atoms is formed.

(15) The experimental results of A. S. Kende and E. E. Riecke, *J. Am. Chem. Soc.*, **94**, 1397 (1972), on the preferred course of thermal rearrangement of a 2-vinyl-1-methylenecyclopropane are consistent with this expectation.

(16) Obvious routes for the laboratory preparation of **7**, necessary to test experimentally these theoretical predictions, include cleavage, either thermal or photochemical, of the very weak σ bond of the zero bridge in 2,4-dimethylenebicyclo[1.1.0]butane, and extrusion of nitrogen, again either thermally or photochemically induced, from 5,6-dimethylene-3,4-diazabicyclo[2.1.1]hexene.

(17) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(18) Since the MO's for the singlet and triplet differ, the optimum geometries for these two states are also expected to differ.[12,13] More specifically, the π bonding between the ring and the exocyclic methylene groups is stronger in the triplet than in the singlet; consequently, the bonds to these groups should be shorter in the former than in the latter state. A determination of the optimum geometry for each state is planned.

(19) E. R. Davidson, *Chem. Phys. Lett.*, **21**, 565 (1973).

(20) The NBMO's do not transform together to form the basis for a degenerate representation of the point group; indeed, D_{2h} has no degenerate representations.

(21) J. H. Meadow and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 4383 (1976).

(22) Ab initio studies of trimethylenemethane[12c] indicate that in AH's like **2** and **7**, either the MO's of the triplet or the lowest open shell singlet can be used to carry out CI, since both give the same calculated energy.

(23) J. N. Murrell and A. Hinchcliffe, *Mol. Phys.*, **11**, 101 (1966), have shown that in dinegative ions of aromatic π systems intraorbital electron correlation plays an important role in causing a ^{1}A state to fall below the triplet in some large molecules.

(24) Brillouin's theorem in open shell systems is discussed by R. Manne, *Mol. Phys.*, **24**, 935 (1972).

(25) This diradical, also known as 2,2′-bisallyl, is implicated in the degenerate rearrangement of 1,2-dimethylenecyclobutane and the dimerization of allene.[26] Triplet **8** has been observed by P. Dowd, *J. Am. Chem. Soc.*, **92**, 1066 (1970).

(26) J. J. Gajewski, *J. Am. Chem. Soc.*, **97**, 3457 (1975), and references therein.

(27) As the molecule twists about the bond connecting the two allylic fragments, the out-of-phase combination of localized NBMO's is progressively stabilized by spiroconjunction, relative to the in phase, until at 90° the former combination lies below the latter. At a twist angle of about 40° they are calculated to be degenerate.[28]

(28) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(29) The choice of the set of NBMO's for the triplet is arbitrary, since for two electrons of the same spin any orthonormal linear combination of their MO's gives the same wave function. See ref 4b, pp 176–178, for a discussion.

(30) At rhomboid, as well as at square, geometries of **1** there is a singlet state in which the electrons are so localized.

(31) Although this calculation was carried out with an open shell SCF program,[19] the wave function in eq 10 for this singlet shows that it is really a closed shell state of A_g symmetry in D_{2h}. While it is obvious that the first two terms on the second line of eq 11 have this symmetry, it is perhaps less apparent that the second two terms possess it as well. However, since any D_{2h} symmetry operation that does not take ψ_2 and $\psi_{2'}$ each into a multiple of itself takes them into each other, and since open shell singlets have spatial wave functions that are invariant to orbital interchange, it is clear that these latter two terms also have A_g symmetry, as of course they must. The triplet wave function changes sign on interchange of ψ_2 and $\psi_{2'}$; so it does not belong to A_g in D_{2h}. The singlet wave function $|\psi_S{}^{\alpha}\psi_A{}^{\beta}\rangle + |\psi_A{}^{\alpha}\psi_S{}^{\beta}\rangle$ has the same symmetry in D_{2h} as the triplet but is of much higher energy, since it is equivalent to $|\psi_2{}^2\rangle - |\psi_{2'}{}^2\rangle$.

(32) M. J. S. Dewar and J. W. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).

(33) As noted previously,[12] Dewar's SCF results for the planar singlet grossly overestimate its energy, since the half-electron method, used in setting up the Fock operator, does not lead to the correct set of MO's for this species.

(34) The π bond order between the cisoid terminal atoms in **8** is negative, a consequence of the positive bond orders within the allylic fragments and between the central atoms. The negative π bond order between these terminal atoms suggests a preference for a conrotatory mode of interconversion of **8** with 1,2-dimethylenecyclobutane, in agreement with the results of stereochemical studies.[26] It should be noted, however, that the preferred geometry for **8** is probably not a planar one.[26,28]

(35) For example, 1,8-naphthoquinodimethane belongs to the same class of diradical as trimethylenemethane (**2**). Nevertheless, in a bridged 1,8-naphthoquinodimethane that has been recently studied experimentally [C. R. Watson, R. M. Pagni, J. R. Dodd, and J. E. Bloor, *J. Am. Chem. Soc.*, **98**, 2551 (1976)] the triplet appears to be 0.2 kcal/mol higher in energy than the lowest singlet.

(36) G. Hall, private communication.

(37) NOTE ADDED IN PROOF. Geometry optimization for the different states of 1,3-dimethylenecyclobutadiene (**7**) shows that the triplet is, indeed, the ground state but that ^1A_g, rather than $^1B_{2u}$, is the singlet state of lowest energy. A detailed description of the potential surface for this very interesting molecule will be submitted for publication shortly.

P-Type Delayed Fluorescence from Rubrene

Don K. K. Liu and Larry R. Faulkner*

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801.

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Abstract: An absorbance transient assigned to the lowest rubrene triplet can be sensitized by energy transfer from flash-excited anthracene or benzophenone. In acetonitrile this transient showed a first-order lifetime of 80–120 μs. Delayed fluorescence from rubrene was observed, and its intensity at all times was proportional to the square of the triplet absorbance. These results show that rubrene undergoes triplet–triplet annihilation to produce the emitting singlet. An attempt was made to locate the energy of the rubrene triplet by using various electron acceptors as quenching agents. The results are consistent with a triplet energy between 1.04 and 1.29 eV.

Delayed fluorescence from fluid solutions of aromatic hydrocarbons generally arises as the result of bimolecular triplet–triplet annihilation. This type of emission, known as P-type delayed fluorescence,[1,2] requires that the sum of the excitation energies of the interacting triplets at least approximate that of the first excited singlet. Whether the lowest rubrene (5,6,11,12-tetraphenylnaphthacene) triplet possesses sufficient energy to undergo this process has long been questioned.[3-6] Despite electrochemiluminescence studies[4] that seem to indicate that rubrene does yield delayed fluorescence, direct spectroscopic observations of the phenomenon have never been reported.

Until very recently, even the lowest triplet energy was in doubt.[3-6,9,10] However, Rumyantsev, Lesin, and Frankevich[11] have reported that it lies at 1.21 eV in rubrene microcrystals. This value was obtained from the activation energy of magnetic field effects on singlet exciton fission. Even though their result applies strictly only to crystalline material, it should be a very good estimate of the solution-phase triplet energy if rubrene adheres to the patterns observed in other aromatic hydrocarbons.

The first excited singlet state lies at 2.36 eV as determined by the location of the 0,0 absorption maximum in acetonitrile. Thus the data of Rumyantsev et al. indicate that delayed fluorescence is virtually thermoneutral, rather than endothermic, and may yet be directly observed. Experimental studies have been hampered by the near unit quantum efficiency for rubrene's fluorescence in fluid media.[1,2] Since the intersystem crossing efficiency is virtually zero, significant triplet concentrations can be generated only by sensitization. In steady state measurements, there is accordingly some danger of confusing the delayed fluorescence arising from the homomolecular annihilation of two rubrene triplets and that caused by the heteromolecular annihilation of rubrene and sensitizer triplets. Flash techniques are less susceptible to such problems; hence we have chosen them for our attempts to test the viability of triplet-triplet annihilation in the rubrene system. We have observed a delayed emission that appears to arise from this source.

In addition, we have performed a series of experiments toward the determination of the energy of the lowest rubrene triplet in acetonitrile. Triplet energies are usually evaluated by means of phosphorescence spectra, singlet-triplet absorption spectra, or studies of triplet-triplet energy transfer involving compounds of known triplet energies.[1,2] For various experimental reasons, these techniques are not feasible for rubrene, hence we have approached the problem instead by studying electron transfer reactions in which the rubrene triplet participates.

It has been shown that the electron donor and acceptor properties of an electronically excited molecule are enhanced,[12-14] and one frequently finds that excited molecules undergo redox interactions that will not occur in the absence of excitation. For example, the rubrene triplet $^3R^*$ may react in a polar solvent with an acceptor A,

$$^3R^* + A \rightarrow R^+ + A^- \qquad (1)$$

The free energy for this reaction can be written in terms of the standard potentials for the A/A^- and $R^+/^3R^*$ couples,

$$-\Delta G^\circ = E^\circ(A/A^-) - E^\circ(R^+/^3R^*) \qquad (2)$$

To a first approximation, $E^\circ(R^+/^3R^*)$ differs from the corresponding ground state potential $E^\circ(R^+/R)$ by the excitation energy to the lowest triplet,[12-14,22] $\Delta E(^3R^*)$; hence we have,

$$E^\circ(R^+/^3R^*) = E^\circ(R^+/R) - \Delta E(^3R^*) \qquad (3)$$

Substitution of (3) into (2) then gives,

$$\Delta E(^3R^*) + \Delta G^\circ = E^\circ(R^+/R) - E^\circ(A/A^-) \qquad (4)$$

This relation shows that $\Delta E(^3R^*)$ can be evaluated from ground state electrochemical data if an acceptor can be found such that ΔG° for reaction 1 is approximately zero. By observing the sensitized triplet absorption transient following flash excitation of rubrene in the presence of oxidizing agents of varying strengths, we can observe their abilities to quench the triplet via (1). Thus we can find the acceptor reduction potential for which $\Delta G^\circ \simeq 0$, hence find the triplet excitation energy. The usefulness of this approach is evaluated below.

Experimental Section

The flash instrument was constructed in the conventional kinetic recording geometry. The excitation source consisted of two EG & G FX-142C-4.5 flashlamps connected in series to a bank of high voltage capacitors totaling 4 μF. The flashlamps were fired by the overvoltage method using a triggered spark gap as a high-voltage holdoff switch. The discharge voltage was selectable over an operating range of 6 to 15 kV, giving a range of flash energies of 72 to 450 J per flash. A discharge of 300 J usually proved sufficient for excitation of the rubrene samples. The full width at half-maximum for such a pulse was about 10 μs. The flashlamps were mounted parallel to a cylindrical quartz sample cell (100 mm long, 21 mm in diameter) with UV transmitting Corning glass filters (C. S. 7-51) between the lamps and the cell. Some of the experiments were performed using externally triggered Xenon Corp. FP5-100C flashlamps. These were operated using a 12 μF capacitance charged to a voltage ranging from 2 to 10 kV.

Collimated light from a 150 W xenon arc lamp was used as the monitoring beam. Detection of both emission and absorption was accomplished with a Bausch and Lomb high-intensity UV-vis monochromator and a gated[15] Hamamatsu R269 photomultiplier. The photomultiplier output was converted to a voltage via a fast current follower, and this voltage was sent through a 4 μs, 8-bit A/D converter to a Data General Nova 820 minicomputer operating in the direct memory access mode. Data collection was initiated by a signal from a phototransistor monitoring the flash event or from the flash-controlling logic. Points along the transients were acquired at 7- or 8-μs intervals.

Rubrene from Aldrich Chemical Co. was sublimed in vacuo at 250 °C prior to use. Benzophenone, *p*-benzoquinone, and *p*-dichlorobenzene were also obtained from Aldrich and were sublimed in vacuo at 30 °C. 2,4,7-Trinitrofluorenone, 2-bromo-6-chloro-*p*-benzoquinone, *p*-chloranil, and tetrabromo-*o*-benzoquinone were purchased from Aldrich and recrystallized from ethanol before use, as was the 2,5-dichloro-*p*-benzoquinone purchased from Eastman Organic Chemicals. Anthracene (Aldrich Gold Label, blue-violet fluorescence) was used without further treatment. Fisher spectrograde benzene and Matheson Coleman and Bell spectrograde acetonitrile were used as solvents. The benzene was prepared by passage through activated alumina followed by fractional distillation from calcium hydride. Acetonitrile was treated by passage through a column of activated alumina into a storage vessel.[16]

Solutions were prepared by first degassing the solvent by five to ten freeze-pump-thaw cycles on a high vacuum line and then distilling it into a volumetric flask connected to the sample cell. The flask was maintained at 77 K during pumping to avoid losses through sublimation of the sample compounds contained in the flask. Two to five additional freeze-pump-thaw cycles were performed with the solution, then approximately 0.5 atm of high purity helium was introduced. After stirring, the solution was transferred into the optical cell, which was then sealed by a Teflon stopcock and removed from the vacuum line.

Delayed fluorescence measurements required a two-step procedure. The first was to record the emission intensity of a deaerated solution of rubrene and sensitizer at the prompt fluorescence maximum (553 nm). Then the sample was exposed to a chamber containing 4 mL of air at atmospheric pressure. The air was allowed to equilibrate with the solution and the headspace volume of 45 mL and the emission was measured again. The difference between the two transients provided the delayed fluorescence intensity. This procedure was needed to differentiate the fairly short-lived delayed fluorescence from prompt fluorescence and scattered light arising from the flashlamp afterglow. Limiting the exposure of the sample to oxygen minimized its effect on the prompt fluorescence intensity of rubrene. The aerated sample was handled in a darkened room to avoid photoperoxidation of the rubrene before flashing.

For the determination of the rubrene triplet energy, samples consisted of rubrene, sensitizer, and quencher, as indicated in Table 1. Absence of transient absorption at 472 nm and 505 nm, attributed to triplet-triplet absorption (see transient spectrum below), was taken to indicate quenching of the rubrene triplet species.

Table I. Rubrene Triplet Lifetimes in Acetonitrile

Rubrene concn × 10^5 M	Quencher	Quencher concn × 10^5 M	Sensitizer[a]	Sensitizer concn × 10^4 M	Triplet lifetime, μs[b]
2.1[c]			B	23	120
3.9			B	22	94
4.2			A	5.9	106
3.6	*p*-Dichlorobenzene[d]	49	A	0.55	80
3.9	*p*-Benzoquinone	9.8	B	23	90
3.8	*p*-Benzoquinone	9.4	A	0.53	104
3.5	2,4,7-Trinitro-9-fluorenone	5.9	B	23	78
3.1	2,5-Dichloro-*p*-benzoquinone	29	B	21	Q
4.0	2,5-Dichloro-*p*-benzoquinone	10	A	0.56	Q
3.8	2-Bromo-6-chloro-*p*-benzoquinone	8.6	A	0.54	Q
2.0[c]	*p*-Chloranil	8.1	B	23	Q
3.5	Tetrabromo-*o*-benzoquinone	1.9	A	0.57	Q

[a] B = benzophenone, A = anthracene. [b] From linear segment of log plot of absorbance change. Q = quenched. [c] Benzene used as solvent. [d] Used to check possible heavy-atom effect on lifetime.

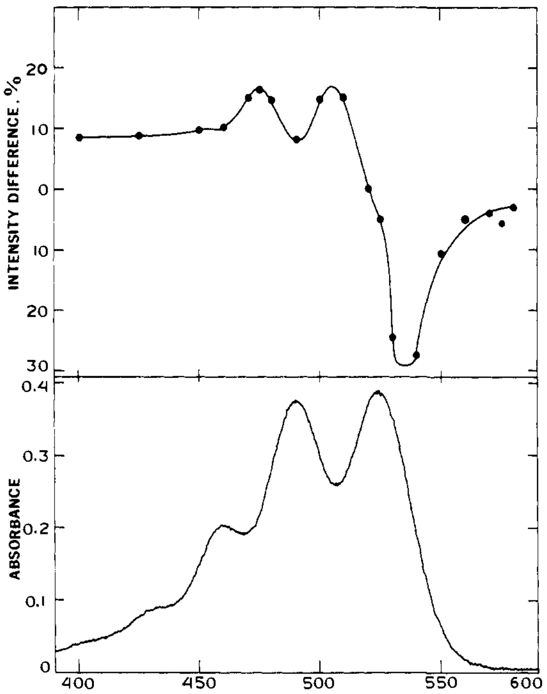

Figure 1. Top: Transmission change 250 μs following initiation of flash excitation of a benzene solution of rubrene (2.6×10^{-5} M) and benzophenone (1.1×10^{-3} M). Flash energy, 380 J. Bottom: Absorption spectrum of rubrene in acetonitrile (3.3×10^{-5} M).

Results and Discussion

Figure 1 shows a transmission spectrum obtained 250 μs following flash excitation of a benzene solution containing rubrene and benzophenone. The vertical axis represents the percentage change in the transmittance of the solution at the specified wavelength. The upward direction indicates an increase in the absorption of the sample. The spectrum obtained using anthracene as the sensitizer in acetonitrile solution was essentially the same. It was also the same as that obtained by Yildiz, Kissinger, and Reilley[9] using benzophenone and biacetyl as sensitizers. From this correspondence, we can conclude that the transient absorption is due to rubrene triplets generated by triplet-triplet energy transfer.

Figure 1 also shows the ground state absorption spectrum of rubrene in acetonitrile. Note that the transient and ground state spectra overlap strongly and that minima in the transient spectrum correspond to ground state absorption maxima as may be expected if both triplet and ground state species are present at the same time. Depopulation of the ground state probably causes the increased solution transmittance between 520 and 570 nm, where the triplet apparently does not absorb as strongly. This bleaching effect accounts in conventional terms for the transmittance increase, which was previously ascribed by Yildiz et al.[9] to triplet-triplet fluorescence excited by the analyzing lamp. In support of our position, we note that the bleaching does not extend outside rubrene's ground state absorption band.

Since the triplet and ground state spectra overlap, precise determinations of triplet concentrations and absorptivities could not be obtained. If one assumes a triplet molar absorptivity of zero at the photobleached 535-nm wavelength, the fractional conversion at the time corresponding to the spectrum in Figure 1 would be about 7%.

Transient spectra were also obtained for acetonitrile solutions of benzophenone and anthracene individually and in mixtures with the electron acceptors *p*-benzoquinone and 2,5-dichloro-*p*-benzoquinone. The pure sensitizer solutions gave the expected benzophenone ketyl radical[17] and anthracene triplet[18] spectra while the quinone-containing mixtures gave spectra of the appropriate semiquinone radical or radical ion.[19]

Kinetic data were obtained from the transmission transients following flash excitation by assuming that the absorbances due to ground and triplet state rubrene were always additive and that the sum of ground state and triplet concentrations always equalled the total rubrene concentration. This leads directly to the expression

$$[^3R^*] = \frac{\log (I_i/I(t))}{b(\epsilon_T - \epsilon_G)} \tag{5}$$

where $[^3R^*]$ is the triplet rubrene concentration, I_i and $I(t)$ are the intensities of the monitoring light source passing through the sample solution before and during the light-generated transient, b is the length of the light path in the solution, and ϵ_T and ϵ_G are the rubrene triplet and ground state molar absorptivities. Typical data are shown in a semilogarithmic format in Figure 2. At times beyond ~200 μs, the plot is virtually linear and indicates an apparent first-order lifetime of 83 μs. The nonlinearity seen at earlier times probably reflects a second-order contribution from triplet-triplet annihilation (see below). A series of samples produced similar plots with apparent lifetimes averaging about 100 μs. The relative standard deviation in an individual lifetime due to deviations of the experimental points from the fitted curve was generally less

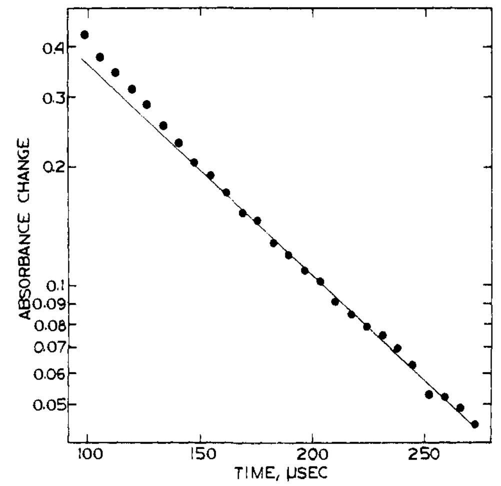

Figure 2. Semilogarithmic plot of the change in absorbance at 472 nm following flash excitation of rubrene (2.6×10^{-5} M) and anthracene (9.0×10^{-5} M) in acetonitrile vs. time. Straight line corresponds to τ = 82 μs. Flash energy, 290 J.

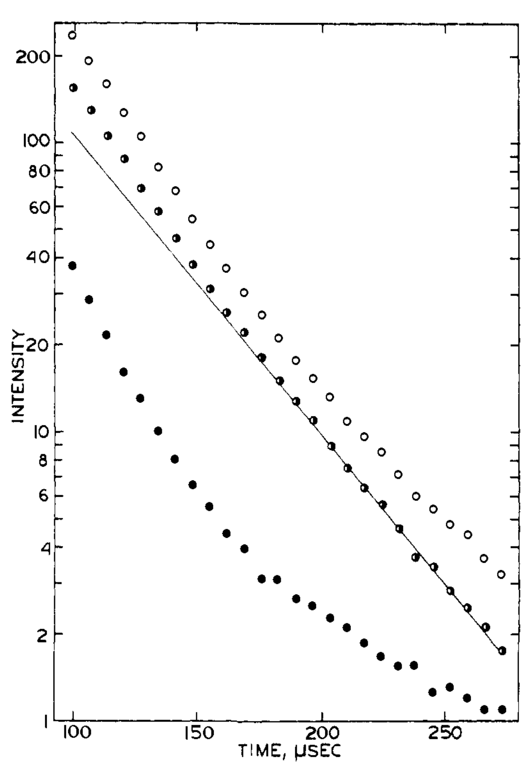

Figure 3. Semilogarithmic plot of emission transients at 553 nm of the deaerated (○) and oxygen quenched (●) rubrene solution and their difference (◐) vs. time. Straight line corresponds to a 42-μs lifetime.

than 2%. However, the apparent lifetime varied by as much as 20 μs from the 100 μs average from sample to sample.

Rather intense, but predictably short-lived, delayed fluorescence from rubrene solutions was measured by the method described earlier. Figure 3 shows typical emission transients recorded at 553 nm before (open circles) and after (filled circles) exposure to oxygen. Their difference (half-filled circles) is taken as the delayed fluorescence. These results were obtained from the same sample represented in Figure 2.

The oxygen admitted to the system may have three effects:[2] quenching of delayed fluorescence, quenching of prompt fluorescence, and photoperoxidation of rubrene. Since we assume that oxygen in the amounts used quenches only the longer lived triplet molecules, it is important that neither of the latter two effects measurably alters the prompt fluorescence intensity. As a test, a sample containing rubrene, anthracene, and 2,5-dichloro-*p*-benzoquinone (which is shown below to quench rubrene triplet) was subjected to the procedure used to measure delayed fluorescence. No difference in emission intensity between the aerated and deaerated solution was seen. This indicates that the amount of air admitted to the sample has a negligible effect on the prompt fluorescence.

As noted earlier, the observed emission could be the result of either rubrene triplet-triplet annihilation or mixed rubrene-anthracene triplet-triplet annihilation of the type observed by Parker[1,20] for a mixture of anthracene and tetracene. That is, the reaction

$$^3\mathrm{An}^* + {}^3\mathrm{R}^* \xrightarrow{k_{\mathrm{md}}} {}^1\mathrm{R}^* + \mathrm{An} \xrightarrow{\Phi_f} \mathrm{R} + \mathrm{An} + h\nu \qquad (6)$$

would result in delayed rubrene emission with exactly the same spectral distribution as that from the homomolecular reaction. These processes can, however, be separated on the basis of kinetic behavior.

The results of Figure 2 show that the rubrene triplet decays approximately exponentially in the available time domain, thus

$$[^3\mathrm{R}^*] \simeq [^3\mathrm{R}^*]_0 e^{-t/\tau} \qquad (7)$$

where τ is the first-order triplet lifetime. On the other hand, if we assume that the anthracene triplets are rapidly quenched, the anthracene triplet concentration should be proportional to the rate of light absorption, I_a, at all times during the period of observation. That is,

$$[^3\mathrm{An}^*] = \beta I_a \qquad (8)$$

where β is related to the anthracene triplet formation efficiency and the rate of decay.

The assumption of fast quenching is reasonable, for the anthracene triplet lifetime is mainly controlled by energy transfer to rubrene. If that transfer is diffusion limited (i.e., $k_{\mathrm{et}} \simeq 2 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in acetonitrile at 25 °C),[1] then the anthracene triplet lifetime in a solution containing 3×10^{-5} M rubrene would be less than 2 μs. In any case, anthracene triplet-triplet absorption could not be detected in the transient spectrum of rubrene sensitized by anthracene.

The intensity of P-type delayed fluorescence caused by rubrene triplet-triplet annihilation should always depend upon the square of the instantaneous triplet concentration. Since rubrene has unit fluorescence efficiency[1,2]

$$I_{\mathrm{DF}} = \alpha k_s [^3\mathrm{R}^*]^2 \qquad (9)$$

where I_{DF} is the observed delayed fluorescence intensity, α is a geometric factor, and k_s is the rate constant for the process

$$^3\mathrm{R}^* + {}^3\mathrm{R}^* \xrightarrow{k_s} {}^1\mathrm{R}^* + \mathrm{R}$$

Likewise, the observed intensity of delayed emission arising from anthracene-rubrene mixed triplet-triplet annihilation is given by

$$I_{\mathrm{MDF}} = \alpha k_{\mathrm{md}} [^3\mathrm{An}^*][^3\mathrm{R}^*] \qquad (10)$$

Substituting eq 7 into 9 and 8 into 10 gives us

$$I_{\mathrm{DF}} = \alpha k_s [^3\mathrm{R}^*]_0{}^2 e^{-2t/\tau} \qquad (11)$$

$$I_{\mathrm{MDF}} = \alpha k_{\mathrm{md}} \beta I_a [^3\mathrm{R}^*] \qquad (12)$$

The semilogarithmic plot of the delayed fluorescence transient (Figure 3) resembles that for absorbance (Figure 2) in showing (1) a linear region at later times and (2) positive deviations from the linear relation at earlier times. In the linear region, the emission lifetime is 42 μs, which is exactly the value

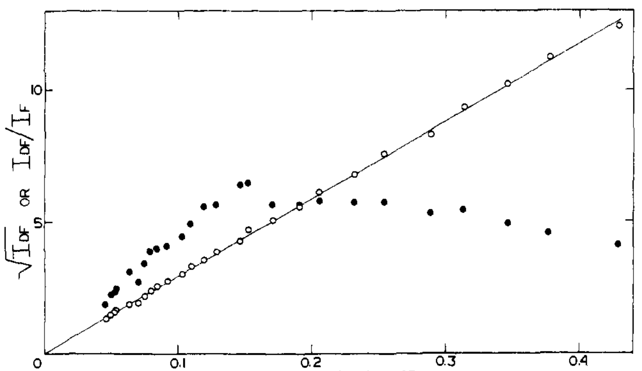

Figure 4. Plot of the square root of the delayed fluorescence intensity (○) and the ratio of delayed and prompt fluorescence intensities (●) vs. the absorbance change at 472 nm.

expected, on the basis of eq 11, for the homomolecular annihilation of rubrene triplets that are known from Figure 2 to decay with $\tau = 83\ \mu s$.

The dependence of the measured delayed fluorescence intensity upon the square of the rubrene triplet concentration over the entire period of observation can be verified in the following manner. Since the absorbance change, $\log I_i/I(t)$, is proportional to $[^3R^*]$ (eq 5), eq 9 predicts that a plot of $(I_{DF})^{1/2}$ vs. $\log I_i/I(t)$ should be linear with a zero intercept if homomolecular annihilation is the source of the delayed emission. On the other hand if the observed delayed emission is due to mixed annihilation, eq 12 predicts that a plot of I_{MDF}/I_F vs. $\log I_i/I(t)$ will be linear with a zero intercept since the intensity of prompt fluorescence, I_F, should be proportional to I_a. In Figure 4, both the square root of the observed delayed fluorescence and the ratio of delayed to prompt fluorescence are plotted against the absorbance change for the same sample used for Figures 2 and 3. It is quite clear that the dependence of the measured delayed emission upon the rubrene triplet concentration is of the form expected from homomolecular, rather than heteromolecular, annihilation. This result and the dynamic comparison cited just above indicate conclusively that the observed delayed emission is due to rubrene–rubrene triplet–triplet annihilation.

Table I summarizes the results of the electron-transfer quenching experiments, and Table II lists the pertinent standard potentials. Since 2,5-dichloro-*p*-benzoquinone (Cl_2BQ) and all stronger acceptors completely quenched the rubrene triplet, while 2,4,7-trinitrofluorenone (TNF) and the still weaker acceptor *p*-benzoquinone did not, the acceptor potential for which $\Delta G° = 0$ in a quenching reaction appears to lie between −0.18 and −0.43 V vs. SCE. According to eq 4, we can therefore estimate the triplet energy as being between 1.04 and 1.29 eV. These limits are consistent with the value determined by Rumyantsev et al.[11] and with the known tetracene triplet energy of 1.28 eV.

A more precise estimate may possibly be derived from the second-order rate constant for incomplete quenching of the triplet by TNF. With an accounting for the uncertainty in the apparent first-order rate constants of triplet decay in the absence of quencher, a value of k_q between 1.3×10^7 and $8.5 \times 10^7\ M^{-1}\ s^{-1}$ can be calculated from the shortening of the lifetime in the presence of TNF. Rehm and Weller[13] have shown that k_q values for electron-transfer quenching of singlets in acetonitrile depend systematically upon $\Delta G°$ for the quenching reaction. From their observed relationship and the limiting rate constants for TNF, we obtain $\Delta G° = 0.14 \pm 0.03$ eV, which gives a triplet energy of 1.15 ± 0.03 eV.

Despite the excellent agreement with expectations, this triplet energy is still suspect to some degree, because the quenching systems are rather complex. For example, the quenchers may interfere with sensitization of rubrene by quenching benzophenone or anthracene triplets through energy-transfer or electron-transfer interactions. An interference of this sort potentially complicates any application of this technique for the evaluation of triplet energies; hence it is important that the evaluation not be wholly based on the complete disappearances of the triplet transient in the presence of a given set of quenchers. Evidence from systems in which the transient is only partially quenched (e.g., with TNF in this case) must certainly be included.

Table II. Standard Potentials in Acetonitrile

Compd (M)	$E°(M/M^-)$, V vs. SCE
p-Benzoquinone[a]	−0.51
2,4,7-Trinitro-9-fluorenone	−0.43
2,5-Dichloro-*p*-benzoquinone[a]	−0.18
2-Bromo-6-chloro-*p*-benzoquinone	−0.09
p-Chloranil[a]	+0.01
Tetrabromo-*o*-benzoquinone[b]	+0.15
Rubrene cation radical[c]	+0.86

[a] M. E. Peover, *Trans. Faraday Soc.*, **58,** 1656 (1962). [b] Estimated from charge-transfer data: E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63,** 3183 (1975). [c] H. Tachikawa and A. J. Bard, *Chem. Phys. Lett.*, **26,** 246 (1974).

In any case, our results and those of Rumyantsev et al.[11] leave little doubt that rubrene resembles tetracene in possessing a triplet energy that is virtually half that of the singlet. Much discussion has followed Parker's observations that P-type delayed fluorescence from tetracene is extremely weak in fluid solutions,[1,20] and his results have usually been rationalized by invoking a triplet energy that is slightly less than half that of the singlet, so that annihilation leading to delayed fluorescence would require thermal activation.[1,2,20,21] That possibility also applies to rubrene. An interesting alternative is that the homomolecular annihilation processes involving both rubrene and tetracene yield singlets without activation, but the latter displays weak emission in steady state experiments with mechanical chopping because the triplet lifetime is short. We recorded rubrene triplet lifetimes of ~100 μs in this work, and similar values were reported by Yildiz et al.[9] These small values are not enforced by the medium, for we observe first-order lifetimes in excess of 1 ms for anthracene in the same solvent under the same conditions. Our present results permit no comment about the efficiency of singlet production in rubrene's homomolecular triplet annihilation. We can state only that the annihilation occurs and that it is approximately thermoneutral.

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The Electronic Structures and Spectra of Benzocyclobutenes and of Biphenylene Derivatives

H. Vogler and G. Ege*

Contribution from the Institut für Organische Chemie, Universität Heidelberg, D-6900 Heidelberg, Im Neuenheimer Feld 7, West Germany. *Received September 24, 1976*

Abstract: The UV-vis spectra of the benzocyclobutenes **1–6,** of the dications and dianions of **1** and **2**, and of the biphenylene derivatives **7** as well as of the phenanthrocyclobutenes **8** have been studied by means of PPP calculations. The agreement between experimental and theoretical transition energies and moments for the few known compounds is very good, so that our predictions for the yet unknown compounds are reliable. For the benzocyclobutenes **2** we obtain in agreement with experiment a hypsochromic shift of the lowest transition with increasing number of annelated benzene rings. This is in contrast to the bathochromic shift of the acene series. For the benzobicyclobutenes **4** we also obtain a hypsochromic shift whereas the series **6** and the dications and dianions of **2** show a bathochromic shift with increasing number of benzene rings. The calculated properties of 1,2-diphenylphenanthro[1]cyclobutene (**8b**) and of the isomeric nonalternant hydrocarbons **9** are different from the properties of a compound synthesized by Bergmann and Agranat[1] to which they ascribed the formula **8b**. We suggest for this compound the structure of the butatriene **12.**

For compounds **1–8** many calculations of ground state properties are to be found in the literature[2–8] but according to our knowledge the UV–vis spectra of such compounds have not yet been treated with more sophisticated methods than the Hückel scheme.[5] We have calculated singlet transition energies and moments using the PPP method[9] with the parametrization of Pancíř, Matoušek, and Zahradník.[10] Compared to standard treatments and parametrizations, this method, which utilizes a single set of parameters based on atomic spectral data, gave a better agreement between theory and experiment, including both ground-state properties and electronic spectra for a number of conjugated compounds.[10] Since we are dealing with pure hydrocarbons we use the all-β (AB) approximation.[10] The excited states have been obtained by a limited configuration interaction between 50 configurations, which are the lowest excited singlet configurations selected lexicographically. We shall restrict our discussion to the lowest transitions, because we did not take into consideration doubly excited configurations which are important for the higher excited states. The theoretical extinction coefficients ϵ are obtained from the calculated oscillator strengths f using the relationship[10,11] $\log \epsilon = \log f + 4.5$. The geometry was determined in an iterative manner from the calculated bond orders ("SC procedure"). The starting geometry consists of regular polygons with all bond lengths equal to 1.397 Å and exo bonds bisecting the bond angle. Only resonance integrals and electron repulsion integrals between neighbors were adjusted in this procedure. Compounds with phenyl ligands have been studied with distortion angles $\varphi = 0$ and 90° between the plane of the phenyl group and the plane of the rest of the molecule. The results for $\varphi = 90°$ do not differ significantly from those for the corresponding hydrocarbons without phenyl ligands. Therefore, we only discuss our results for $\varphi = 0°$.

All the calculated transition energies and extinction coefficients together with the experimental values are given in Table I.

Results

Benzocyclobutenes 1–6. The compounds **1c** and **1d** have not yet been synthesized. **1a** and **1b** have been detected as reactive intermediates.[12,13] Calculations on the ground-state stability show that only **1c** might be isolable.[8] On the contrary the synthesis of **2b**[14] and **2c**[15] has been reported as well as that of the tetramethyl derivative **2a′**.[16] Some portion of the stability of **2a–2c** must be related to the steric hindrance to dimerization offered by the phenyl groups.[8] Perhaps the introduction of other bulky groups might allow the isolation of **1a** and **1b.** The distortion angle φ of the phenyl groups in **2a–c** is not known. The calculated longest wavelength absorption in **2b** and **2c** differs from the experimental values less than 0.1 eV. Also the difference between theoretical and experimental extinction coefficients is satisfactory. In **2a–c** a distortion angle $\varphi = 90°$ would shift the lowest transition about 0.5 eV to higher energies (cf. **1a–c**) and the extinction coefficients would be considerably reduced. Therefore, one can suppose that in **2b** and **2c** the phenyl groups are in conjugation with the rest of the molecule. The phenyl groups in **2a′** are certainly a little distorted, since the experimental transition energy is about the mean value of **2a** ($\varphi = 0°$) and **1a.** The experimental extinction coefficient of **2a′** is also smaller than the calculated one of **2a.** The experimental value of the lowest transition in **2b′** (3.10 eV, $\log \epsilon = 3.7$)[17] is shifted by 0.38 eV to higher energy compared to that of **2b.** In a test calculation of **2b′** the two phenyl groups and the two carboxy groups on the benzene ring reduce the calculated lowest transition energy of **2b** less than 0.05 eV. In **1b** the lowest transition energy is nearly unchanged only if either the two phenyl groups or the two carboxy groups are added to the benzene ring. Altogether they would reduce the transition energy of **1b** by 0.27 eV. Therefore, we can conclude that in **2b′** all four phenyl groups are highly distorted. With the increasing number of benzene rings in **2** the calculated and experimental lowest transition is shifted to higher energies as opposed to the acene series which shows a bathochromic shift.[18]