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# Structure–Reactivity Factors for Exciplex Isomerization of Quadricyclene and Related Compounds

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*Summary* The quadricyclenes (**1**) and (**3**) are equally effective in exciplex isomerization although other cage hydrocarbons do not undergo efficient reaction when sensitized by aromatic fluorophores; irradiation of charge-transfer complexes of (**1**) and (**3**) and electron-deficient alkenes results in efficient valence but not geometrical isomerization.

SEVERAL groups have studied the quenching of aromatic fluorophores by the strained hydrocarbon, quadricyclene (**1**). Quenching leads to efficient valence isomerization [(**1**)→(**2**)][1] and is understood in terms of the interaction of quadricyclene as an electron donor and the excited fluorophores as electron acceptors.[2] We have extended this study to quadricyclene derivatives and structurally varied sensitizers, and to a new mode of photosensitization for these systems involving irradiation of ground-state charge transfer (CT) complexes.

In the Table are shown Stern-Volmer data ($k_q\tau$ values) for the quenching of sensitizer fluorescence by (**1**) and (**3**), rate constants ($k_q$) obtained using literature values for sensitizer lifetimes ($\tau$), and sensitizer excited state reduction potentials ($E_{red}$*). From linear reciprocal plots ($1/\phi$ *vs.* 1/[quencher]) of quantum yields† for the isomerizations (**1**)→(**2**) and (**3**)→(**4**), intercept:slope ratios ($i:s$) and limiting quantum efficiencies ($\phi_{lim}$, $1/i$) were calculated. Reasonable agree-

TABLE. Fluorescence quenching and quantum yield data for valence isomerization.[a]

| Quencher | Sensitizer | $E_{red}$*[b] | $k_q\tau$/l mol$^{-1}$ | $k_q$/l mol$^{-1}$ s$^{-1}$ × 10$^{-9}$ | $i:s$ | $\phi_{lim}$ |
|---|---|---|---|---|---|---|
| (1) | 9,10-Dicyanoanthracene | 2·1 | 151·0 | 10·1 | 177·0 | 0·33 |
| | 1-Cyanonaphthalene | 1·9 | 113·0 | 12·6 | 73·5 | 0·71 |
| | 9-Cyanoanthracene | 1·4 | 92·6 | 7·12 | 81·6 | 0·31 |
| | Anthracene | 1·3 | 4·82 | 0·98 | 4·74 | 0·65 |
| | Biacetyl | 1·4 | 2·10 | 0·37 | 2·92 | 0·27 |
| (3) | 9,10-Dicyanoanthracene | 2·1 | 53·7 | 3·58 | 61·7 | 0·28 |
| | 1-Cyanonaphthalene | 1·9 | 42·0 | 4·67 | (10·0)[c] | (0·40)[c] |
| (6) | 1,4-Dicyanobenzene | 2·6 | 56·7 | 5·85 | 70·9 | 0·03 |

[a] Hexane or cyclohexane solution, room temperature. [b] $E_{red}* = E_{1/2}(red) + E_{00}$ using ground state reduction potentials (*V vs.* SCE; principal references: D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259; H. Beens and A. Weller, *Acta Phys. Polon.*, 1968, **4**, 593; E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, 1967, **47**, 2557) and singlet excitation energies. [c] See footnote ‡.

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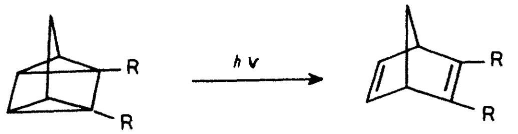
† Quantum yields were determined for nitrogen-purged solutions using a Rayonet reactor and either RUL 3000 (280—320 nm) or RUL 3500 (330—380 nm) lamps, and valerophenone/acetophenone actinometry (P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, 1972, **94**, 7480).

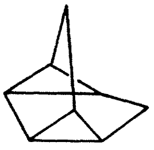
ment between $k_{qT}$ and $i:s$ values confirmed that quadricyclene isomerization is predominately sensitized by fluorophore singlets.‡

Other strained hydrocarbons were examined as potential electron donors. Homoquadricyclene (**5**) was an ineffective fluorescence quencher but other modest donors, (**6**) (vertical ionization potentials[3] in eV, IP$_V$, 8·90), (**7**), (**8**) (IP$_V$ 9·18), and (**9**) (IP$_V$ 9·78) quenched the fluorescence of the most potent acceptor, 1,4-dicyanobenzene (DCB) ($k_{qT}$ 56·7, 14·0, 31·7, and 5·4 l mol$^{-1}$, respectively). Isomerization of (**7**)—(**9**) to dicyclopentadiene or cyclo-octa-1,5-diene did not accompany fluorescence quenching but DCB was a modest sensitizer for the isomerization (**6**)→(**5**) (see Table).



(1) R = H (2)

(3) R = $CO_2Me$ (4)



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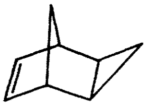

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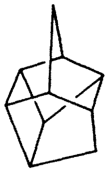

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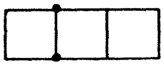

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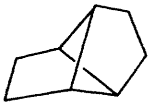
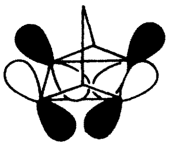


(9)

Fluorescence quenching constants obtained in our study extend the trend[2] which reflects electron donor–acceptor (EDA) relationships among sensitizer–quencher pairs. Quenching rates depend not only on $E_{red}^*$ but also on the oxidation potential of quenchers [for (**1**) and (**3**), $E_{1/2}$(ox) 0·91 and 1·64 V *vs.* standard calomel electrode (SCE)[4]]. Limiting quantum efficiencies for isomerization of (**1**) and (**3**) are relatively high and in the range found for sensitization of (**1**) by other aromatic sensitizers.[1]§ Notably, differences in exciplex binding for (**1**) and (**3**) (reflected in the quenching constants) do not result in very different quantum yields for ring opening. That a rather nonspecific EDA interaction is responsible for isomerization is supported by the effectiveness of biacetyl, an 'n,$\pi^*$' singlet sensitizer, in driving the reaction.

Along with exciplex binding, other factors that, in principle, control the partitioning of exciplex to isomeric products include the thermodynamics[5] of ring opening and the kinetics of the mutual polarization of exciplex partners (*i.e.*, changes in bond order resulting from EDA interaction). Features of the highest occupied molecular orbitals (HOMO) for the present series of isomerizable donor substrates appear to be relevant. The HOMO of (**1**) [and presumably of (**3**)], an AS ($C_{2v}$) combination of Walsh orbitals (**10**),[6] contributes strongly to transannular bonding (that bonding lost in the ring opening), unlike the situation with the nonisomerizable (**8**) in which the $a_u(\sigma)$ HOMO (**11**) is more delocalized and is cross-ring anti-bonding.[3a] A corollary of this pattern is the exciplex perturbation of (**6**) in which the bond order is increased by removal of electron density from a transannular anti-bonding HOMO.[3b]

Irradiation of charge-transfer complexes of quadricyclenes provided a novel entry for sensitized isomerization. A weak CT complex ($\lambda_{max}$ 286 nm, $K_{CT}$ *ca.* 0·1 l mol$^{-1}$, $\epsilon$ *ca.* 300¶) was obtained on addition of fumaronitrile (in excess) to methylene chloride solutions of (**1**). Irradiation of the complex using a monochromator (313 nm) gave (**2**) ($\phi$ 0·22) but geometrical isomerization of fumaronitrile was not observed. Irradiation of a complex of (**1**) and maleonitrile



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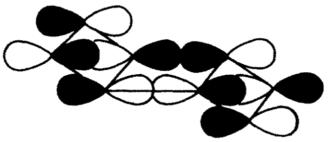

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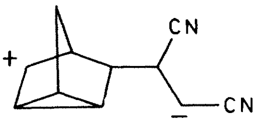

(12)

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‡ The match of $k_{qT}$ and $i:s$ was not satisfactory for 1-cyanonaphthalene/(**3**): the reciprocal quantum yield plot showed a slight upward curvature. A steeper concentration dependence could have been the result of exciplex quenching (H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, 1976, **98**, 2002) by (**3**) at high quencher concentration.

§ Sensitizer decomposition was observed (u.v. spectrophotometry) for 9,10-dicyanoanthracene, 9-cyanoanthracene, and anthracene, with limiting quantum yields in the range 0·02—0·04. Photoaddition of anthracene and (**1**) has been reported (T. Sasaki, K. Kanematsu, I. Audo, and O. Yamashita, *J. Am. Chem. Soc.*, 1977, **99**, 871). Biacetyl disappearance was more pronounced ($\phi$ 0·2—0·3) at low and high [(**1**)], suggesting bimolecular reaction of biacetyl singlets and triplets.

¶ Values for $K_{CT}$ and $\epsilon$ are estimates since saturation criteria (D. A. Deranleau, *J. Am. Chem. Soc.*, 1969, **91**, 4044) for graphical analysis could not be met.

produced similar results with $\phi$ [(**1**)→(**2**)] 0·4. The absence of geometrical isomerization shows that, if intermediates such as (**12**) are important in valence isomerization, their lifetimes must be short with respect to the period of a rapid bond rotation. The complex of (**3**) and tetracyanoethylene ($\lambda_{max}$ 387 nm) on photolysis at 366 nm in $CH_2Cl_2$ gave (**4**) with moderate efficiency ($\phi$ 0·10).

The isomerization of excited complexes of (**1**) shows an interesting solvent dependence which suggests that outright electron transfer is not required for photosensitization in non-polar media. Limiting quantum yields for reaction [(**1**)→(**2**)] sensitized by 1-cyanonaphthalene are as follows: hexane (0·74), dioxan (0·17), acetonitrile (0·11), and 80% acetonitrile–water (0·07). We are presently investigating this limitation of exciplex isomerization under conditions in which radical-ion-pair formation is more likely.

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