Temperature Dependent Fluorescence of 'Tunable Fluorophore-Fissile Bond' Systems Based on 1-Phenyl, 3-Aryl Δ^2-Pyrazolines as a Means of Quantitating Photofission Processes

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The activation energy for the C(5)-N(1) bond homolysis in the lowest excited singlet state of the 1-Phenyl, 3-Aryl, 5-(2'-Phenyl ethenyl) Δ^2-pyrazolines as deduced from the temperature dependence of the fluorescence quantum yield (Φ_F) can be combined with the corresponding singlet energy to give a constant value of 75.5 kcal mol^{-1} as the total photofission energy. The corresponding value for 1,3-Diphenyl, 5-(2'-Iodo phenyl) Δ^2-pyrazoline significantly exceeds the bond dissociation energy (BDE) of the aryl carbon-iodine linkage.

Molecules with two or more essentially unconjugated moieties are crucial to the study of energy- and electron transfer photoprocesses.[1] We now demonstrate that photofission can also be profitably examined if the energy donor and acceptor components are chosen to be a fluorophore and a fissile bond respectively as in **1**. The systems **2** and **4** employ the optical brightener family of 1-phenyl, 3-aryl, Δ^2-pyrazolines[2] as the fluorophore module. Their lowest excited singlet states have internal charge transfer (ICT) character[3] (**5**) which allows remote substitutional tuning of the singlet energy (E_S) to provide a controlled variable driving force for bond fission. The fissile bond in **2** is the N(1)-C(5) bond whose σ orbital system is orthogonal to the fluorophore π system with a node at N(1), whereas **4** possesses a fissile C-I bond external to the fluorophore. This general situation mimics some aspects of the environmentally and technologically important photofissions of aryl halides[4] and ketones.[5]

The photofission of the C(5)-N(1) bond in Δ^2-pyrazolines is known.[6] Low Φ_F values of some 1,3-diphenyl, Δ^2-pyrazolines (at 20 °C) also allows us to deduce that the C(5)-N(1) bond can undergo photohomolysis in competition with fluorescence. Φ_F decreases sharply with the increasing ability of 5-substituents to stabilize an adjacent free valency, δE_π.[7] Φ_F = 0.80,[8] 0.83,[8] 0.19,[8] 0.043 and δE_π is proportional to 0.00, 0.24, 0.37, 0.40 for 5-unsubstituted, 5-phenyl, 5,5-diphenyl and 5-(2'-phenyl ethenyl) cases respectively. The last case which is representative of system **2** clearly shows the development of free radical character at C(5) after photoexcitation. The second case, representative of system **3**, shows no such photohomolysis. In the cases where homolysis occurs, the fission site is not C(4)-C(5) since 4,5-diphenyl disubstitution causes no reduction in Φ_F (0.82[8]), compared to the 5-phenyl case. The fission is homolytic since the 5-phenyl, 5-(4'-methoxy phenyl) case[9] gives little

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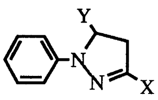

2; Y = 2-phenyl ethenyl
3; Y = phenyl
4; X = phenyl,
Y = 2-iodo phenyl

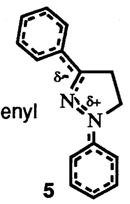

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Table 1. Fluorescence-derived parameters for **2** and **3**[a]

2 or **3**, X =	E_S[b]	Φ_F (3)	Φ_F (2)	E_a[b]	$(E_S + E_a)$[b]
ethenyl[16]	76.2	0.84	-	-	-
4-OMe phenyl	73.2	0.84	0.012	1.5	74.7
4-NH_2 phenyl	72.9	0.81	-	-	-
phenyl	72.6	0.83	0.035	3.3	75.9
4-MeCONH phenyl	71.8	0.80	0.050	3.8	75.6
4-Br phenyl	70.7	0.79	0.20	5.1	75.8
4-pyrazol-1'-yl phenyl	69.8	0.81	0.25	5.6	75.4
4-Ph phenyl	69.3	0.84	0.43	6.4	75.7
4-(1',2',4'-triazol-1'-yl) phenyl	69.1	0.78	0.43	6.1	75.2
2-phenyl ethenyl	68.2	0.84	-	-	-
4-CN phenyl	66.6	0.91	0.89	-[c]	-
4-Ph 1,3-butadienyl[17]	64.9	0.84	0.92	-[c]	-

[a] 10^{-5}M **2** and **3** in aerated hexane at 30.0 °C. E_a values are obtained *via* equation,[11] $\log \{[\Phi_F(3)/\Phi_F(2)] - 1\} = -E_a/2.3RT + \text{constant}$, by measurement of $\Phi_F(2)$ over the temperature range 15-60 °C. $\Phi_F(3)$ is temperature independent (<5%) over this same range. $\Phi_F(2)$ and $\Phi_F(3)$ are measured by taking Φ_F = 1.00 for 9,10-diphenylanthracene in cyclohexane.[18] Several $\Phi_F(3)$ values are available in Ref. 19. This is also a leading reference for the preparation of **3** (except where noted otherwise) and, by analogy, of **2**. E_S values are evaluated from the crossing point of the fluorescence excitation and emission spectra (corrected and normalized) of **3** according to the mirror symmetry relation.[20] Electronic absorption (S_0->S_1) and emission spectral parameters of corresponding members of **2** and **3** are nearly identical except for Φ_F. [b] Units = kcal mol^{-1}. [c] Temperature dependence of $\Phi_F(2)$ too small to allow accurate quantitation.

change in Φ_F (0.26) compared to the 5,5-diphenyl case which rules out cation formation at C(5). The polarity of the Δ^2-pyrazoline excited singlet (**5**) makes anion generation at C(5) unlikely.

The data (Table 1 and Figure 1) show the sigmoidal dependence of Φ_F (**2**) at 30 °C upon E_S.[10] Φ_F (**3**) are near unity and independent of E_S. This lack of photofission makes **3** useful as control compounds. In contrast to the temperature independence of Φ_F (**3**), Φ_F (**2**) below the plateau alone are measurably dependent on temperature and can be analyzed to yield activation energies for homolysis from the lowest excited singlet state (E_a). The remarkable finding is that ($E_s + E_a$) is essentially constant for **2**. ($E_s + E_a$) appears to be characteristic for the photohomolysis of the C(5)-N(1) bond in **2** and is the total energy needed from the nearby energy reservoir, *i.e.* the excited fluorophore and from the heat bath. To compare the total photofission energy ($E_s + E_a$) with thermally derived bond dissociation energy (BDE), we turn to a different but related example **4**. Here[11] $E_s + E_a = 72.6 + 3.8 = 76.4$ kcal mol^{-1}. In contrast, BDE = 64 kcal mol^{-1} for aryl C-I bonds.[12] This discrepancy must be contrasted with the agreement of BDE values with ($E_T + E_a$) for several aryl halides[13] (E_T = triplet energy). The extra energy requirement for the fission of a bond from a proximal but separate singlet excited state is explained by RRKM (Rice-Ramsperger-Kassel-Marcus) theory.[14] The fraction of the total photofission energy required, i.e. the BDE must flow from the donor π system to the acceptor σ system across the node and any additional intervening spacers within the singlet state lifetime[15] which is much shorter than that for a triplet. Such an inequality of the BDE (a thermodynamic quantity) and the total photofission energy in the lowest excited singlet state is reminiscent of the electrochemical overpotential phenomenon, where the potential needed to effect a redox reaction exceeds the thermodynamic value due to kinetic limitations of the electrode process.

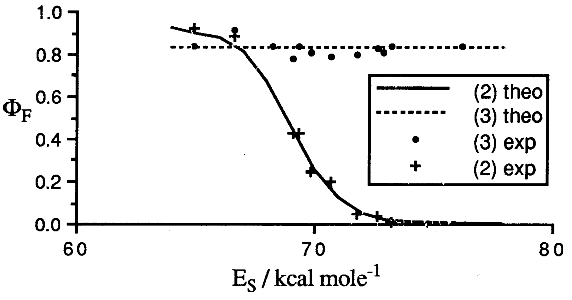

Figure 1. Φ_F versus E_S profiles for **2** and **3**[a]

[a] The full line represents function $\log[(0.92/\Phi_F) - 1] = 0.43\,E_S - 29.4$. This form can be predicted by analysis of the competition between fluorescence and other de-excitation channels including temperature dependent bond homolysis of the Arrhenius type along with the separate equation $E_S + E_a = 75.5$. The broken line is described by the function $\Phi_F = 0.83$.

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