

## THE VISCOSITY DEPENDENCE OF THE FLUORESCENCE QUANTUM YIELD OF MESOIONICS

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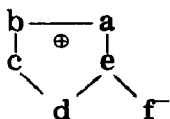
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### Summary

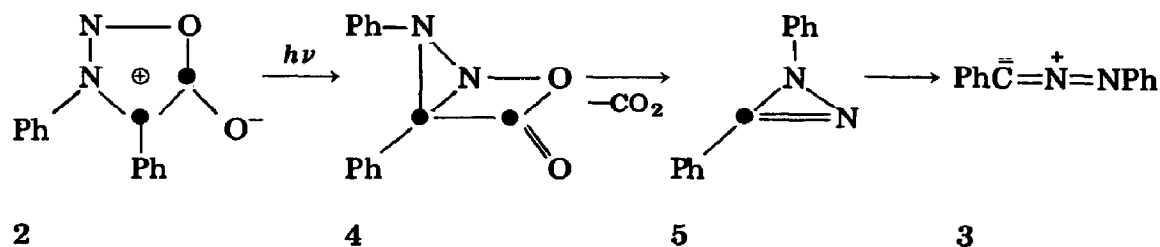
The fluorescence quantum yields for diphenylsydnone and the related mesoionics, 1,4-diphenyl-1,2,4-triazol-3-one and 1,4,5-triphenyl-1,2,4-triazol-3-one, are sensitive to the viscosity of the medium. The viscosity can be changed by either changing the solvent or varying the temperature of a single solvent. The viscosity dependence of the fluorescence quantum yield for diphenylsydnone is identical for the two methods, indicating little or no activation barrier other than that required for motion of the phenyl groups.

The heterocycles known as mesoionics, of general structure



1

are photochemically reactive [1 - 6]. The photochemical result as exemplified by the behavior of diphenylsydnone 2



2

4

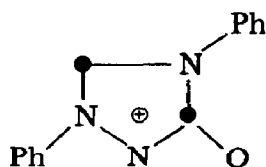
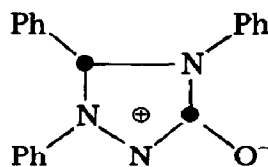
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3

is the loss of  $\text{CO}_2$  and rearrangement to yield, as the first trappable species, a nitrilimine, 3. Reasonable intermediates in the reaction pathway are the diaza lactone 4 and the 1-*H*-diazirine 5.

Eber *et al.* [7] have recently investigated the photophysical behavior of **2** and other sydnones. On the basis of the similarity of quantum yields for decomposition of 3-methylsydnone by direct irradiation and benzophenone sensitization, they concluded that the photoreaction proceeded from the triplet state. Since the fluorescence lifetimes and quantum yields showed Arrhenius behavior ( $\Delta E_a = 760 \text{ cm}^{-1}$ ), they postulated a triplet level above the lowest singlet state to which thermally activated intersystem crossing occurs followed by rearrangement.

We have observed that the fluorescence quantum yields of **2** and of the mesoionics 1,4-diphenyl-1,2,4-triazol-3-one **6** and 1,4,5-triphenyl-1,2,4-triazol-3-one **7**

**6****7**

vary as a function of the viscosity of the medium (Table 1 and Fig. 1). With the published viscosities of ethanol as a function of temperature [11, 12], the data from Eber *et al.* [7] can also be plotted against  $\ln \phi_F^{-1}$  (Fig. 2). Since the slope of  $\ln \phi_F^{-1}$  versus  $\ln \eta$  is the same for the experiments in which the viscosities were changed by temperature ( $m = -0.63 \pm 0.04$ ) and by solvent ( $m = -0.61 \pm 0.14$ ), there is no evidence that there is any activated process other than that associated with the solvent viscosity. The slopes obtained for the  $\ln \phi_F^{-1}$  versus  $\ln \eta$  correlations for **2** and **7** agree with that expected from the Förster-Hoffman derivation [13] ( $m = -0.67$ ) but the slope for **6** is significantly less ( $m = -0.29 \pm 0.02$ ). Viscosity-dependent emission yields have been widely observed [14 - 20] and can be

TABLE 1

Fluorescence quantum yields for **2**, **6** and **7** as a function of solvent viscosity

| Solvent           | Viscosity (25 °C)<br>(cP) | $\phi_f^a$ |          |          |
|-------------------|---------------------------|------------|----------|----------|
|                   |                           | <b>2</b>   | <b>6</b> | <b>7</b> |
| Glycerol          | 954 <sup>b</sup>          | 0.0825     | 0.118    | 0.84     |
| Ethylene glycol   | 17.4 <sup>c</sup>         | 0.0226     | 0.047    | 0.076    |
| <i>n</i> -butanol | 2.58 <sup>c</sup>         | 0.00229    | 0.0226   | —        |
| Isopropyl alcohol | 2.036 <sup>c</sup>        | 0.00197    | 0.0207   | —        |
| Ethanol           | 1.08 <sup>c</sup>         | —          | 0.0168   | —        |
| Methanol          | 0.547 <sup>b</sup>        | —          | 0.0137   | —        |

<sup>a</sup>The quantum yields were measured by the method given in ref. 8.

<sup>b</sup>Values taken from ref. 9.

<sup>c</sup>Values taken from ref. 10 and corrected to 25 °C.

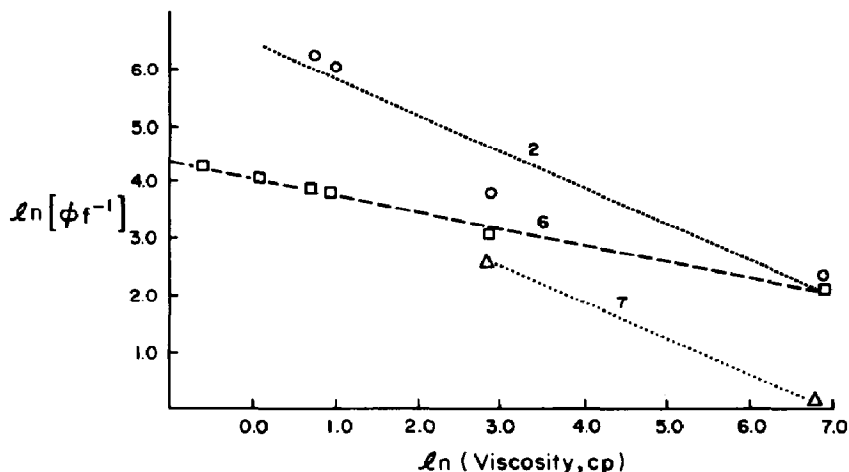


Fig. 1. Correlation of the fluorescence yields of 2, 6 and 7 with viscosity.

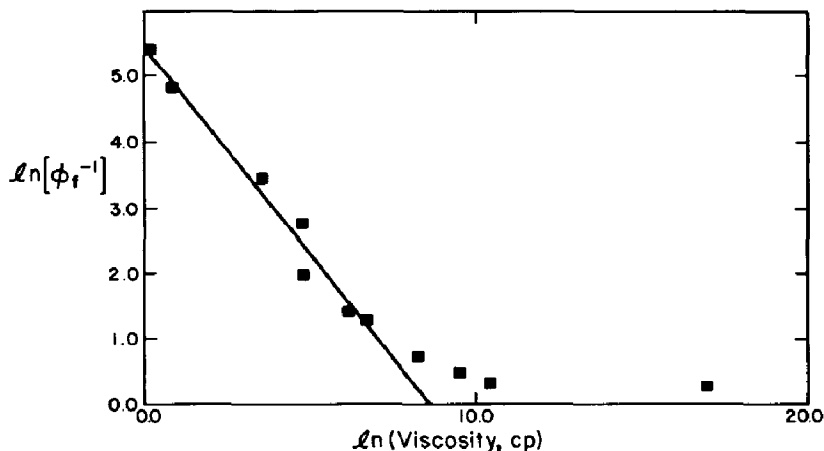


Fig. 2. Correlation of the fluorescence yield of 2 with the viscosity of ethanol at various temperatures.

used to uncouple photochemical reactions requiring molecular motion from the radiationless process of internal conversion [18]. Griebel [20] has recently critically examined the theoretical basis for the viscosity-fluorescence yield relationships.

We interpret the viscosity dependence of the fluorescence of the mesoionics as indicative of the molecular motion required for 2, 6 and 7 to cross from the lowest singlet state to the strained ring intermediates, *e.g.* 4, which can then partition between ground state and fragmentation. The viscosity dependences for 2 and 7 are similar, since two phenyl rings need to move past each other, whereas 6 can move the pendant ring without the steric effect of a nearby ring and therefore a smaller free volume is required.

In conclusion, the photophysical behavior of the mesoionics 2, 6 and 7 is best explained by a reaction profile which requires internal molecular motion in much the same way as olefinic isomerizations.

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