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AN EFFICIENT CHEMILUMINESCENT HYDRAZIDE: BENZO(ghi)PERYLENE-1,2-DICARBOXYLIC ACID HYDRAZIDE

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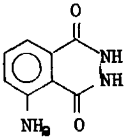
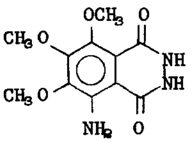
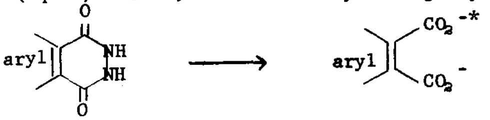
The chemiluminescence of organic cyclic hydrazides has been extensively studied and many such compounds have been synthesized in efforts to increase the efficiency of light production.[1] The best known example of this class, luminol (I),[2] has a chemiluminescence efficiency of only 1.25%.[3]


I

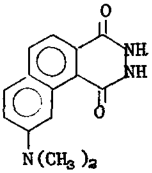

II

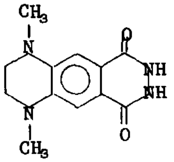
The chemiluminescent reactions are oxidative in nature and the corresponding carboxylates are the light emitters (eq. 1). Thus, the efficiency of light production is a resultant of the



(1)

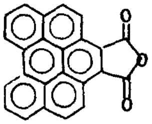
selectivity of the organic reactions, the efficiency of cross-over to the excited state energy surface, and the efficiency of fluorescence[5] of the carboxylates. It would be preferable to study each of these variables separately;[6] however, empirical approaches (probably involving two or more of the above variables) have been moderately successful. These approaches include the use of energy transfer,[7] and the use of electron releasing substituents. Thus, in the latter category, compounds II[8] and III[9] were found to be 30% and 150% more efficient than luminol (I) itself. Not


III

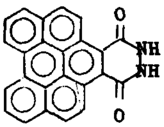

IV

all such substitutions are effective, since compound IV did not prove to be very efficient in light production.[10] We now report on an efficient cyclic hydrazide based on the perylene ring system.

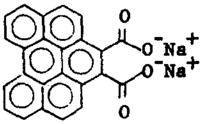
Perylene and maleic anhydride in nitrobenzene yielded anhydride V,[11] which was converted into hydrazide VI with hydrazine. The emission spectrum for the chemiluminescence of hydrazide VI in aqueous DMSO with base and oxygen is given in Fig. 1 along with the fluorescence spectrum of the corresponding carboxylate VII; the match in the spectra indicates that the carboxylate is the light emitter in the chemiluminescence.[1] The quantum yield of emission proved to be 7.3%, the highest value found yet for a hydrazide. Since the fluorescence quantum yield for VII was 14%,[12] it is apparent that with about 50% of the molecules the oxidation of hydrazide VI yielded an excited state of VII.



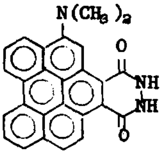
V



VI



VII



VIII

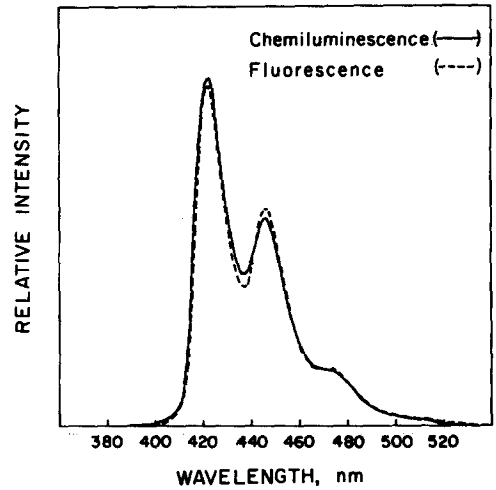


Figure 1. Emission spectra (solvent: 30 mole % water and 70 mole % DMSO).

Compound VIII was then prepared to test the effect of a substituent. 3-Nitroperylene[13,14] was reduced, and the resulting amine was alkylated with dimethyl sulfate. Condensation with maleic anhydride (and oxidation with nitrobenzene) followed by hydrazide formation yielded compound VIII.[15] Oxidation of VIII in aqueous DMSO led to light emission at 526 mμ. The efficiency of emission was about 7%,[16] a value near that found for compound VI. In this example, the effect of the substituent may have been damped by the steric effect of the peri hydrogen leading to an inhibition of resonance of the dimethylamino group.[1]

Experimental

Benzo(ghi)perylene-1,2-dicarboxylic Acid Anhydride (V) was prepared by the method of Clar.[11]

Benzo(ghi)perylene-1,2-dicarboxylic Acid Hydrazide (VI). The anhydride (50 mg, 0.14 mmol) and 95% hydrazide (1 ml) were degassed under vacuum and sealed in a glass tube which was heated at 125° for 6 hr. The resulting suspension was cooled and the yellow precipitate was filtered. The brownish-yellow solid was washed with dilute acetic acid, chloroform, and then ether to give the hydrazide (41 mg, 0.11 mmol, 79%). Further purification of the hydrazide was achieved by sublimation at 320° (.005 Torr) to give a yellow solid, mp over 350°; Calcd: C, 79.99; H, 3.36; N, 7.77. Found: C, 79.72; H, 3.27; N, 7.58.

3-(N,N-Dimethylamino)perylene. 3-Aminoperylene (prepared by the method of Dewar and Mole[13]) (43 mg, 0.15 mmol) and dimethyl sulfate (520 mg, 4 mmol) in acetone (25 ml)were refluxed in the presence of potassium carbonate (0.5 g) for 24 hr. The resulting mixture was hydrolyzed with water to remove the excess dimethyl sulfate, and then purified by column chromatography (silica gel, eluted with benzene) to give the title compound (40 mg, 0.13 mmol, 80%). Sublimation at 170° (10^{-2} Torr) gave the pure compound, mp 166-168°C; Calcd: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.25; H, 5.75; N, 4.67.

4-(N,N-Dimethylamino)benzo(ghi)perylene-1,2-dicarboxylic Acid Hydrazide (VIII). 3-(N,N-Dimethylaminoperylene (75 mg, 0.25 mmol) and maleic anhydride (75 mg, 0.75 mmol) in 3 ml of nitrobenzene were refluxed for 1.5hr. After being cooled at 5°C overnight, the precipitate was filtered and washed with chloroform and benzene to give dark brown crystals (47 mg, 0.14 mmol, 55%); ν_{max}^{KBr} 1820, 1755 cm^{-1} (anhydride). The anhydride (32 mg, 0.08 mmol) and 95% hydrazine (1 ml), after being degassed and sealed in a glass tube, were heated at 125° for 6 hr. The resulting mixture was poured into 50 ml of water and acidified with acetic acid to pH 5. The precipitate (28 mg, 0.07 mmol, 85%) was filtered and sublimed at 300° (10^{-2} Torr) to give the hydrazide, mp over 350°; Calcd: C, 77.41; H, 4.25. Found: C, 77.11; H, 4.33.

Acknowledgements

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5. To date, emission from the singlet state is the rule.[1]
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15. The structure shown for VIII is probably correct, although we cannot rule out the isomeric structure with the dimethylamino group substituting the *peri* position.
16. Uncorrected for phototube response. The corrected value would be about 20% higher.