

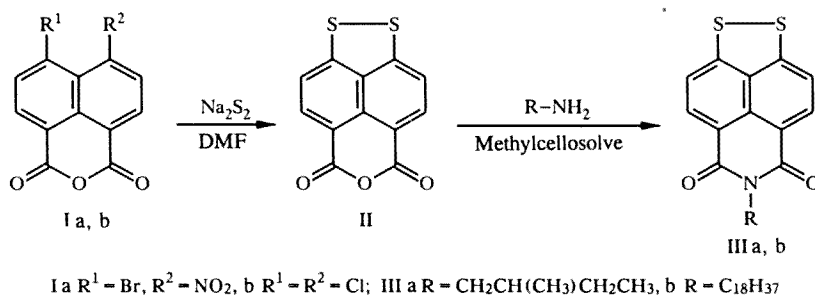
SYNTHESIS OF N-ALKYL 4,5-DITHIONAPHTHALIMIDES

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Introduction of electron donor substituents in position 4 or 5 of naphthalic anhydride or naphthalimide causes the appearance of luminescence. For example, 4-dialkylaminonaphthalic anhydrides luminesce effectively in the yellow-green region of the spectrum ($\lambda_{\max}$ in toluene in the 480-505 nm region, quantum yield φ 0.4-0.7) with a large Stokes shift [1].

4,5-Dithionaphthalic anhydride (II) and N-alkyl 4,5-dithionaphthalimides (IIIa and b) have been synthesized to elucidate the effect of sulfur atoms on the luminescent properties of these compounds. The anhydride II was synthesized from 4-bromo-5-nitro- (Ia) or 4,5-dichloronaphthalic anhydride by reaction with sodium disulfide in DMF. The yield of the anhydride was almost independent of the starting material (34% from Ia and 32% from Ib).

The anhydride was converted to the corresponding imide (IIa, b) by boiling with the primary amine in methyl cellosolve.



Compounds II, IIIa and IIIb did not show luminescence in DMF. This may indicate that the electron donor S-S group is insufficiently conjugated with the strongly electron accepting perianhydride (or imide) groups in compounds II, IIIa and IIIb.

4,5-Dithionaphthalic Anhydride (II, $\text{C}_{12}\text{H}_4\text{O}_3\text{S}_2$). Yield 34%, m.p. 330°C (dec.) (from toluene). IR spectrum (Nujol): 1764, 1730, 1686, 1594, 1562, 1502 cm^{-1} . UV spectrum in DMF, $\lambda_{\max}$ (lg ϵ): 283 (4.38), 340 (2.36), 470 nm (4.49). ^1H NMR spectrum ($\text{DMSO}-d_6$): 7.84 (2 H, d, 3-, 6-H), 8.29 (2 H, d, 2-, 7-H).

N-(2-Methylbutyl) 4,5-Dithionaphthalimide (IIIa, $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}_2$). Yield 90%, m.p. 184-186°C. IR spectrum (Nujol): 2920, 2855, 1625, 1575, 1530 cm^{-1} . UV spectrum in DMF, $\lambda_{\max}$ (lg ϵ): 468 nm (4.17). ^1H NMR spectrum (CDCl_3): 0.91 (3H, d, $-\text{CHCH}_3$), 0.94 (3 H, t, CH_3), 1.15, 1.54 (2 H, m, CH_2), 1.98 (2 H, d, NCH_2), 7.44 (2 H, d, 3-, 6-H), 8.39 ppm (2 H, d, 2-, 7-H).

N-Octadecyl 4,5-Dithionaphthalimide (IIIb, $\text{C}_{30}\text{H}_{41}\text{NO}_2\text{S}_2$). Yield 96%. M.p. 110-113°C. IR spectrum (Nujol): 2920, 2835, 1625, 1575, 1500 cm^{-1} . ^1H NMR spectrum (CDCl_3): 1.09 (3 H, m, CH_3), 1.13 (32 H, m, $(\text{CH}_2)_{16}$), 4.11 (2 H, t, NCH_2), 7.43 (2 H, d, 3-, 6-H), 8.40 ppm (2 H, d, 2-, 7-H). UV spectrum in DMF, $\lambda_{\max}$ (lg ϵ): 468 nm (4.39).

REFERENCES

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