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[2.2](4,4')BENZOPHENONO(2,6)NAPHTHALENOPHANE: SYNTHESIS, STRUCTURE, AND SPECTROSCOPIC STUDY

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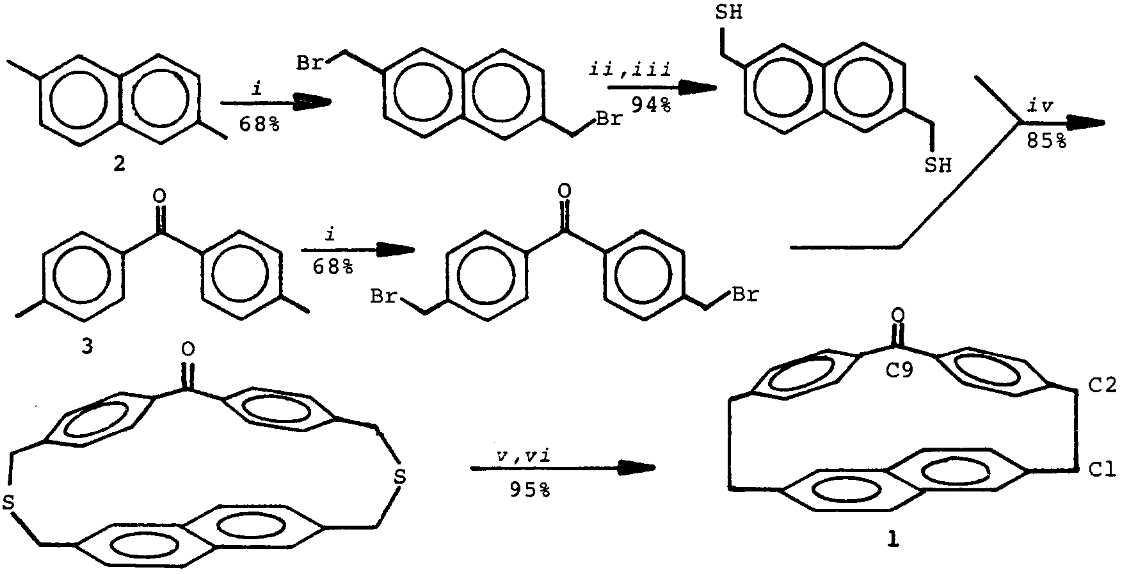
Summary: The synthesis of [2.2](4,4')benzophenono(2,6)naphthalenophane (**1**), the parent member of a series of stacked sensitizer-acceptor cyclophanes, is reported along with its x-ray structure and the absorption and emission spectra.

Our interest in energy transfer between nonconjugated chromophores[1] coupled with the development of synthetic applications of photoextrusion reactions[2] has culminated in the synthesis of [2.2](4,4')benzophenono(2,6)naphthalenophane (1).[3] The synthetic route to **1** was accomplished in the five steps illustrated in the Scheme from 2,6-dimethylnaphthalene (2) and 4,4'-dimethylbenzophenone (3) in an overall yield of 35%. The key steps of cyclization to the dithiacyclophane and photoextrusion of sulfur dioxide were accomplished in excellent yield further illustrating the value of this general route to aryl cyclophanes.[4]

Scheme: Synthesis of Cyclophane 1



i) NBS/CCl_4/Δ; *ii)* $(H_2N)_2CS$/EtOH; *iii)* KOH/MeOH-H_2O; *iv)* KOH/EtOH/benzene; *v)* *m*CPBA/$CHCl_3$; *iv)* hν/benzene

The ketone 1 was obtained as a crystalline solid, mp 169-170°C.[4] The infrared carbonyl absorption of 1 occurs at 1670 cm^{-1}, indicating strain in the cyclophane framework. The ^1H nmr spectrum displays an AA'BB' multiplet at 3.10 ppm for the two sets of four methylene protons and a multiplet at 6.80 ppm for the fourteen aromatic protons. The ^{13}C nmr reveals only fourteen resonances as expected with a structure that possesses a C_2 axis of symmetry. The carbonyl carbon (C9) appears at 200 ppm and the four methylene carbons (C1, C2, C16 and C17) appear as two absorptions at 35.1 and 34.5 ppm while the 22 remaining aromatic carbons appear as eleven absorptions between 142 and 125 ppm.

The ultraviolet absorption spectrum and the fluorescence and phosphorescence emission spectra of cyclophane 1 are given in figure 1 along with the spectra of 2 and 3. The absorption spectrum of 1 displays fine structure similar to those of the two reference chromophores except that the three sharp bands between 290 and 320 nm of the dialkylnaphthalene have been bathochromically shifted by about 14 nm. Fluorescence emission was observed at 350 nm, in the same region as that of 2,6-dimethylnaphthalene but was 17 times weaker. Singlet lifetime measurements for 1 and 2 using the Berlman method[5] gave values of 41 and 39 ns, respectively.

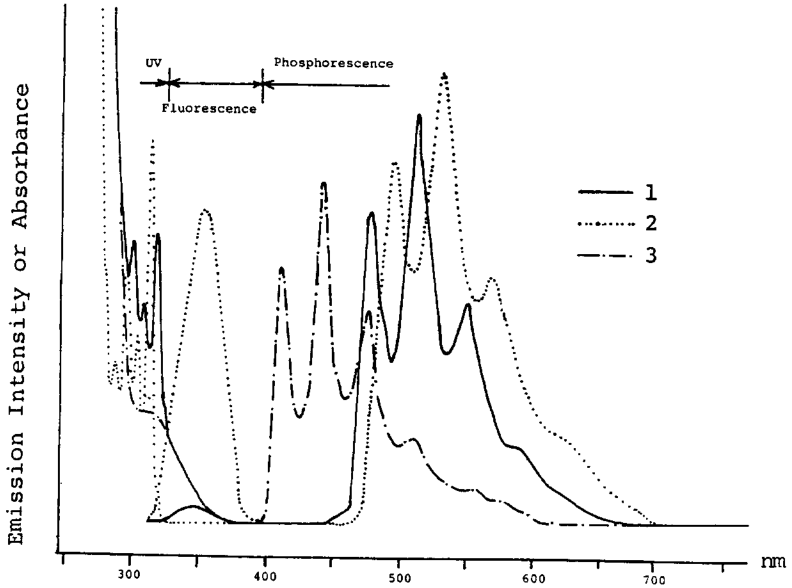


Figure 1. UV, fluorescence, and phosphorescence spectra of 1, 2, and 3.

Most interesting was the phosphorescence emission at 77 K which appeared as a five-band pattern very similar to that of 2 but shifted by ca 25 nm. Triplet lifetime measurements[5] for 1 gave a value of 2.69 s, very close to the value of 1.81 s measured for 2. The lifetime of 3 is 5.7 ms. Thus, although the position of the triplet emission spectrum appears to be intermediate between that expected from the two contributing chromophores, the lifetime measurements clearly indicate that the naphthyl chromophore is the greater contributor to the lowest triplet state of 1.

As indicated by the spectra, especially the phosphorescence emission, the cyclophane structure does sufficiently distort the chromophores so that the triplet excited state is higher in energy by 3 Kcal/mol. The extent of this distortion, however, is most vividly revealed in the x-ray structure of 1.[8,9] In the ORTEP drawing shown in Figure 2, the two phenyl rings of the benzophenone unit are extended along the long axis above the plane of the naphthalene ring. The whole upper region of the cyclophane is canted toward one side of the naphthalene ring as shown in the end view (Fig. 2b). The carbonyl of the benzophenone moiety is tilted even farther to the side and shows considerable thermal motion, presumably in order to maintain at least a portion of the resonance interaction with the two phenyl rings. This is consistent with the ultraviolet absorption spectrum of 1 in which the n,π^* band tails to 400 nm with no apparent decrease in intensity.

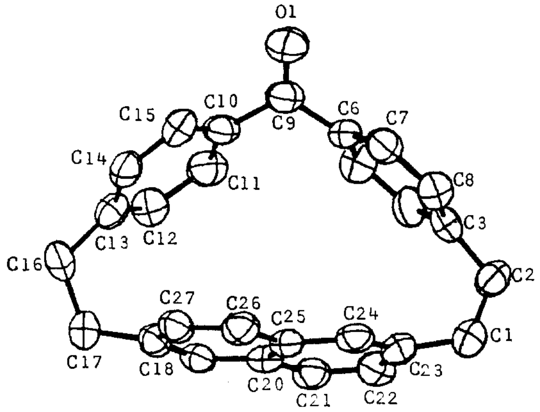


Figure 2a. [2.2](4,4')Benzophenono(2,6)naphthalenophane

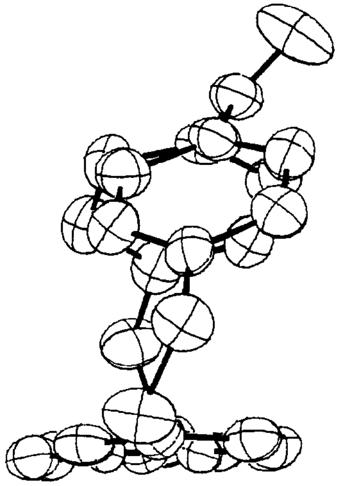


Figure 2b. End view of 1.

The high efficiency of energy migration from the benzophenone chromophore to the naphthalene triplet state *via* the singlet manifold, intersystem crossing and then triplet energy transfer, illustrated in Figure 3, is assured by the proximity of the stacked donor-acceptor groups. The cyclophane displays, in addition to a very strong phosphorescence, a reluctance to be reduced to the benzhydrol-naphthalene cyclophane under ordinary irradiation conditions in 2-propanol. This reduction is rapidly effected, however, by

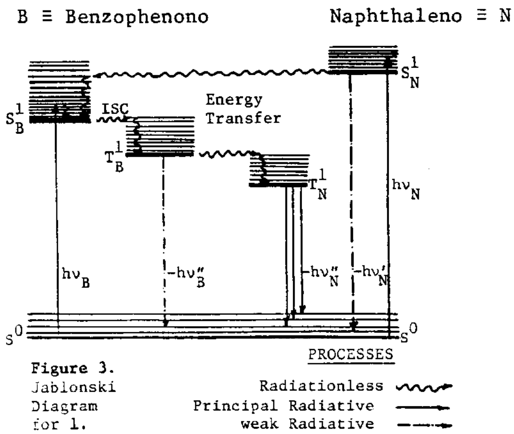


Figure 3. Jablonski Diagram for 1.

treatment of 1 with $NaBH_4$. Work is in progress which will extend the chemical and photochemical information concerning 1 and to extend the series.

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2. Givens, R. S. *Org. Photochem.* 1981, *5,* 227; Givens, R. S.; Olsen, R. J.; Wylie, P. L. *J. Org. Chem.* 1979, *44,* 1608 and references therein.

3a. Taken, in part, from the Master's Thesis of MKV, the University of Kansas, Lawrence, KS (1983).

b. Keehn, P. M.; Rosenfeld, S. M. "Cyclophanes" *Organic Chemistry* 45-I *1984* provides a comprehensive review of cyclophane structure and chemistry.

4. All new compounds gave satisfactory elemental analyses. Spectral data (nmr, ir, uv and ms) were consistent with the proposed structures.

5. Berlman, J. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd Edition, Academic Press, New York, NY (1971).

6. Lifetime measurements were obtained using a Molectron Model UV-1000 Pulsed Nitrogen Laser (337 nm, 700 Kwatt output, pulse width 15 ns) as the source and a EG and E Princeton Applied Research Optical Multichannel Analyzer (OMA-II). Measurements were carried out at the Phillips Research Center.

7. Rabalais, J. W.; Wahlborg, A.; McGlynn, S. P. *J. Mol. Spectrosc.* 1970, *36,* 155.

8a. Crystal Data: (Recrystallized from hexane) monoclinic space group $P2_1/c$; $a = 10.92(1)$; $b = 11.15(1)$, $c = 19.10(2)$Å; $\beta = 119.6(8)$; $Z = 4$; $R = 0.070$, $R_\omega = 0.060$; $D_c = 1.188$ Mg m^{-3}. Unpublished studies of Dr. R. Sheldon and D. Delatore, University of Kansas.

b. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Rd., Cambridge, CB2 iEW, UK. Any request should be accompanied by the full literature citation for this communication.

9. For a survey of crystal structures of cyclophanes, see Keehn, P. M., Chapter 3, reference 3.

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