

PHOTODIMERIZATION OF BENZENE
—PHOTOCHROMISM OF LAYERED DITHIACYCLOPHANE—¹⁾

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Summary: A novel cage compound was obtained by irradiation of a quadruple-layered dithiacyclophane and showed thermally reverse reaction.

Benzene is well-known to be photochemically inert, though condensed aromatic hydrocarbons such as anthracene²⁾ and naphthalene³⁾ undergo ready photodimerization. Cyclophanes whose aromatic rings are fixed with each other at close distances often provide unusual intramolecular cycloadditions.⁴⁾ Here we report on a novel photodimerization of the benzene nuclei of layered dithiacyclophane 1.⁵⁾

In order to explore a new type of multilayered cyclophane, we attempted the photodesulfurization of dithiacyclophane 1, but found that, instead, an unexpected photoreaction took place. Thus, irradiation of 1 in dry benzene with a high pressure mercury lamp for 8 hrs in a nitrogen atmosphere led to the formation of a sparingly soluble material in 83% yield, colorless fine crystals from chloroform, mp > 300 °C(dec). It was assigned to be a polycyclic cage structure of 2 as follows.⁶⁾ The MS spectrum of 2 exhibits the completely same pattern as that of 1, suggesting that they are isomeric with each other and thermally reverse reaction takes place during the measurement. On the other hand, NMR and UV spectra of 2 are quite different from those of 1, respectively (Figs. 1 and 2). The NMR spectrum of 1 has a typical feature of cyclophane, that is, the aromatic protons absorb in very high field (δ 5.67 as a singlet for the inner benzene and δ 6.30 as an A₂B₂ multiplet for the outer benzene) due to the magnetic shielding of the other benzene rings.⁷⁾ However, spectrum of 2 demonstrates, instead of the inner

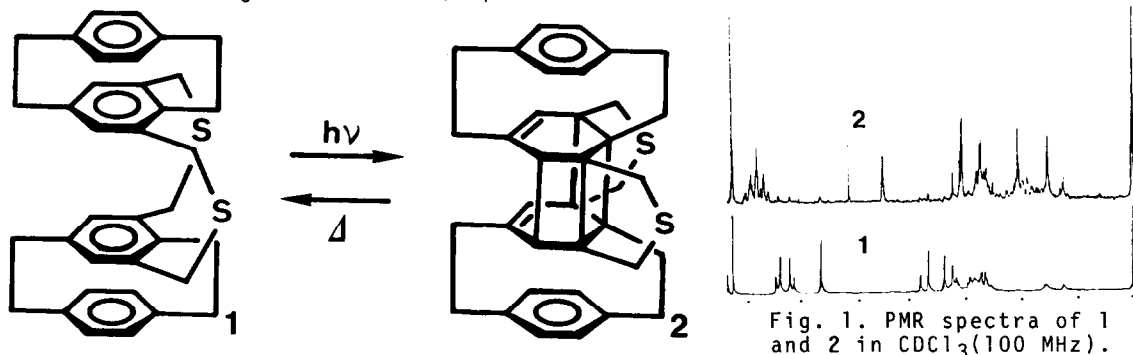


Fig. 1. PMR spectra of 1 and 2 in CDCl₃(100 MHz).

benzenoid signal, the appearance of an olefinic signal at δ 4.53 and an allylic methine signal at δ 2.08, which are connected by a very small long-range coupling. In addition, the signals of the outer benzenoid protons are unsymmetrical and at the ordinary resonance positions (δ 6.8-6.9) of alkyl benzenes. The disappearance of the inner benzenes of 1 on irradiation is also pointed out from the UV spectral change. Although UV spectrum of 1 shows a significant bathochromic effect due to a strong transannular π -electronic interaction between the stacked benzenes, that of 2 is characteristic of simple, isolated benzene chromophores. These data strongly support that the two inner benzenes of 1 undergo an intramolecular photocycloaddition to form cage compound 2. The carbon skeleton of 2 also agrees with ^{13}C -NMR data consisting of eighteen signals.⁸⁾

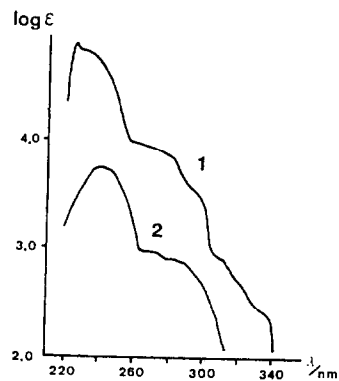


Fig. 2. UV spectra of 1 and 2 in CH_2Cl_2 .

Cage compound 2 was relatively stable at room temperature, but when heated at 90°C in THF, it reverted to 1 with a half-life of 30 min. and completely in 4 hrs. Its conversion in solid state required much higher temperature (200°C).

Although such polycyclic cage compounds were previously found for syn-dimerization of naphthalene derivatives,³⁾ the present reaction is, to our knowledge, the first example of photodimerization of benzene nuclei. The unusual photoreaction is presumably attributable to the excimer-like structure of 1, i.e., face-to-face stacking and close proximity of the inner benzenes. Furthermore, it should be noted that the strain release of the [2.2]paracyclophane framework of 1 in the valence-bond tautomerization compensates the loss of the resonance energy of the inner benzenes.⁹⁾

References and Notes

- 1) Layered Compounds LXX. Part LXIX: F.Hama, Y.Sakata, and S.Misumi, *Nucleic Acid Res.*, Spec. Publ., **10**, 73 (1981).
- 2) A.Mustafa, *Chem. Rev.*, **51**, 1 (1952); T.Laird, *Chem. & Ind.*, 186 (1978) and references cited therein.
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- 4) H.H.Wasserman and P.M.Keehn, *J. Am. Chem. Soc.*, **89**, 2770 (1967); **98**, 2374 (1969); T.Toyoda, A.Iwama, T.Otsubo, and S.Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 3300 (1976) and references cited therein.
- 5) The synthesis of dithiacyclophane 1 will be reported elsewhere.
- 6) Satisfactory elemental analysis was given for 2.
- 7) T.Otsubo, S.Mizogami, Y.Sakata, and S.Misumi, *Bull. Chem. Soc. Jpn.*, **46**, 3831 (1973).
- 8) These signals were assigned by off-resonance technique as follows; six signals at δ 22.51, 30.16, 32.75, 34.99, 44.58, 44.69 for secondary sp^3 -carbons of bridged methylenes; one signal at δ 48.73 for tertiary sp^3 -carbons of allylic methine; three signals at δ 46.00, 51.12, 61.21 for bridgehead quaternary sp^3 -carbons; five signals at δ 128.31, 129.33, 130.64, 130.89, 135.22 for tertiary sp^2 -carbons of benzenes and olefins; three signals at δ 132.79, 136.20, 140.00 for bridgehead quaternary sp^2 -carbons of benzenes and olefins.
- 9) The strain energy of [2.2]paracyclophane (ca. 30 Kcal/mol) is almost comparable to the resonance energy of benzene; R.H.Boyd, *Tetrahedron*, **22**, 119 (1966); K.Nishiyama, M.Sakiyama, S.Seki, H.Horita, T.Otsubo, and S.Misumi, *Bull. Chem. Soc. Jpn.*, **53**, 869 (1980).