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SYNTHESIS OF [2]PARACYCLO[2]PARACYCLO[2](1,8)-NAPHTHALENOPHANE-9-ENE-1,17-DIYNE

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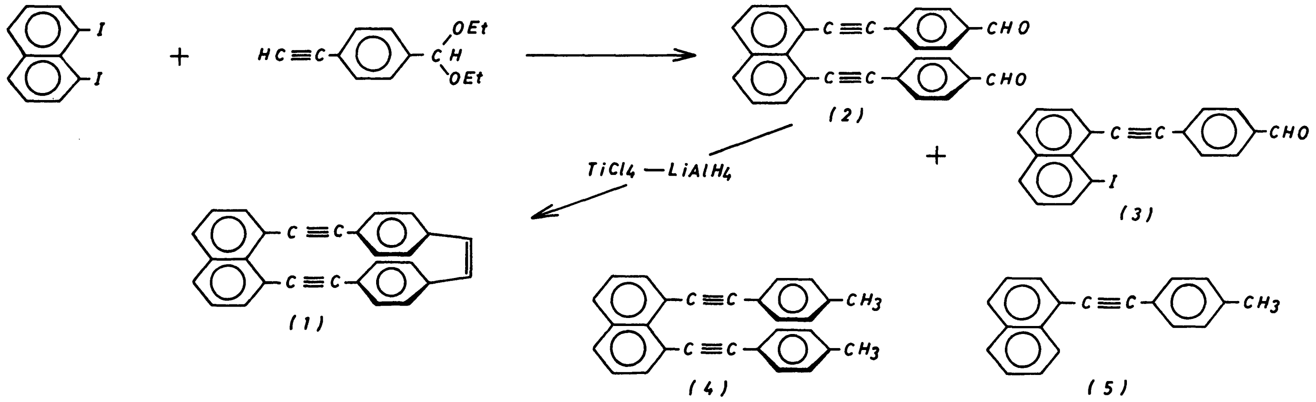
[2]Paracyclo[2]paracyclo[2](1,8)naphthalenophane derivative having transannular π-electronic interactions was synthesized.

In view of the increasing interest in phane compounds,1) Bieber and Vögtle2) reported the synthesis of [0]paracyclo[2]paracyclo[0](1,8)naphthalenophane derivatives. In this paper we wish to report preliminary results on the preparation of [2]paracyclo[2]paracyclo[2](1,8)naphthalenophane-9-ene-1,17-diyne (1) having transannular π-electronic interactions.

In the presence of $(Ph_3P)_2PdCl_2$ and CuI, a palladium-catalyzed substitution3) of 1,8-diiodonaphthalene with p-ethynylbenzaldehyde diethyl acetal led to the formation of 1,8-bis(p-formylphenylethynyl)naphthalene [(2), colorless needles, mp 168-169 °C, 35% yield. ^{1}H-nmr ($CDCl_3$): δ 7.42-7.98 (m, 14H, Ar-H) and 9.98 ppm (s, 2H, -CHO). $\nu_{C=O}$ 1700 and $\nu_{C\equiv C}$ 2200 cm^{-1}. MS: m/e 384 (M^+)] and 1-(p-formylphenylethynyl)-8-iodonaphthalene [(3), colorless needles, mp 113-115 °C, 42% yield. ^{1}H-nmr ($CDCl_3$): δ 7.36-7.95 (m, 10H, Ar-H) and 9.95 ppm (s, 1H, -CHO). $\nu_{C=O}$ 1700 and $\nu_{C\equiv C}$ 2200 cm^{-1}. MS: m/e 382 (M^+)]. The intermolecularly titanium-induced reductive coupling of 2 with $TiCl_4$-$LiAlH_4$-Bu_3N4) pro-



ceeded to the formation of phane compound 1 [pale yellow crystals, mp 239-241 °C (dec), 7.5% yield. ^{1}H-nmr ($CDCl_3$): δ 6.39 (s, 8H, benzene ring H), 7.18 (s, 2H, -CH=CH-), and 7.40-7.76 ppm (m, 6H, naphthalene ring H). $\nu_{CH=CH\ (cis)}$ 730 cm^{-1}. MS: m/e 352 (M^+)].

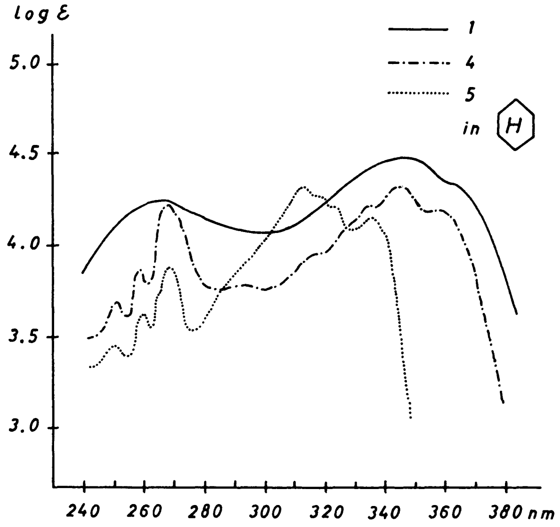


Fig. 1. UV spectra of 1, 4, and 5.

The structure of phane compound 1 was determined on the basis of IR, NMR, and MS spectra and the elementary analyses. The NMR signal of the benzene ring protons in 1 (δ 6.39 ppm) is shifted to up-field by about 0.5 ppm, compared with that of the reference compound, 1,8-bis(p-tolylethynyl)naphthalene (4) (δ 6.92 (d) and 7.23 ppm (d)). Since the benzene ring protons of 1 probably are deshielded by the bridging vinylene group, this phenomenon indicates that the two benzene rings in 1 are held face to face in more close proximity by the vinylene bridge than in 4. Moreover, as shown in Fig. 1, the absorption bands of 1 show an increase of intensity and a disappearance of fine structure of the bands compared with the spectrum of 4, indicating that there is more strong transannular π-electronic interaction in former system than in latter.

On the other hand, the NMR signals of benzene ring protons in 4 are somewhat shifted to up-field, compared with those of monosubstituted analog, 1-(p-tolylethynyl)-naphthalene (5) (δ 7.12 (d) and 7.42 ppm (d)). In addition, in the electronic spectra of 4 and 5, the longest wavelength band of 4 appears at longer wavelength by 32 nm than that of 5. This red shift and an increase of intensity in the spectrum of 4 may be caused by the transannular π-electronic interaction between the two chromophores in 4.

References

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