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CHROMOPHORIC SYSTEMS BASED UPON THROUGH-BOND INTERACTION V[1]

Charge-Transfer Interaction via Five Sigma-bonds

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Introduction

The conformational requirements for efficient through-bond interaction between π- or n-electron systems have been predicted by Hoffmann c.s.[2].
For interaction over three sigma-bonds these predictions have been extensively verified from UV absorption spectra[3], photoelectron spectra[4] and chemical properties[5] of suitable model compounds.
We have recently shown that through-bond interaction between a π-electron system with electron acceptor properties and a π- or n-electron system with electron donor properties separated by three sigma-bonds leads to the occurrence of a so called "sigma-coupled transition" with strong charge-transfer character[3b]. This phenomenon is exemplified by the absorption spectrum of 1 (see Fig. 1) which -as compared to the reference molecules 2 and 3- shows a strong sigma-coupled transition at 294 nm (ε = 2860) due to through-bond interaction[3b] between the electron rich S-atom and the electron deficient 1,1-dicyanovinylidene system (see Fig. 1).

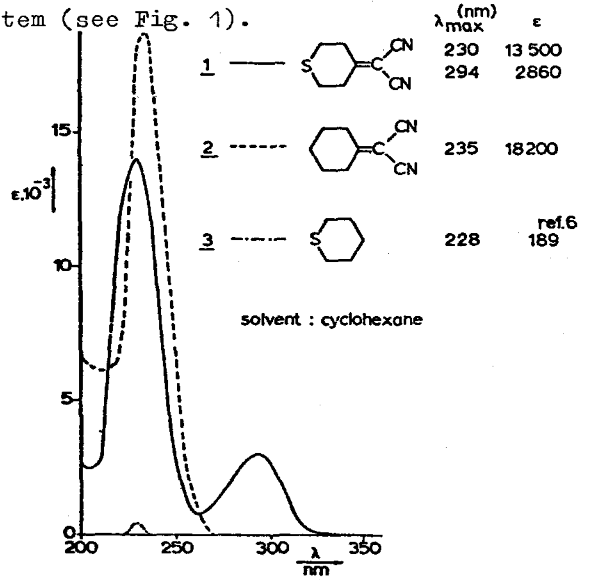
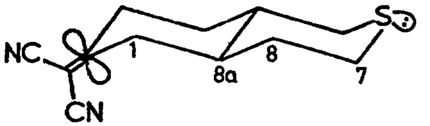


Fig. 1

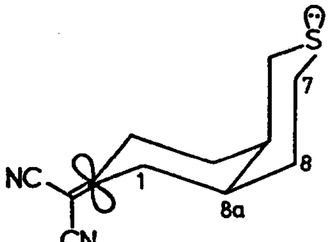
Reports on through-bond interaction over more than three sigma-bonds are scarce[7]. It seemed interesting to test whether through-bond donor-acceptor interaction as displayed by 1, can also be extended beyond three sigma-bonds in a conformation favouring through-bond interaction. The present paper reports on the observation of such interaction over five sigma-bonds.

Results and Discussion

Compounds 4 and 5 were synthesized (see experimental); their UV absorption spectra are shown in Fig. 2.

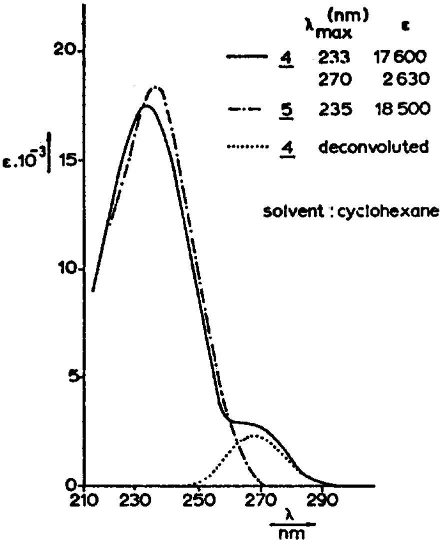


4



5

Fig. 2



The spectrum of 5 resembles the sum spectrum of the separate chromophores as represented by 2 and 3 in Fig. 1. The trans-fused isomer 4 however shows a readily detectable new long-wavelength absorption (λ_{max} = 270 nm; ϵ_{max} = 2630 after deconvolution) which we attribute to a through-bond electron donor--acceptor interaction.

The observation of this interaction for 4 and its absence in 5 are in full agreement with the predictions made by Hoffmann c.s.[2] and recently elaborated by Brunck and Weinhold[8]. Of special importance seems the parallel orientation of the C(1)-C(8a) and C(7)-C(8) bonds in 4 as opposed to their nearly perpendicular orientation in 5. The shorter wavelength of the sigma-coupled transition in 4 as compared to 1 may be attributed to the larger charge-separation -and therefore higher energy- of a charge-transfer excited state in 4.

The present results support the conformational requirements predicted[2,8] for long-range through-bond interaction and furthermore show how CT interaction may differentiate between stereoisomers containing appropriately spaced electron-donating and -accepting fragments.

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Experimental

Melting- and boiling points are uncorrected. IR spectra were recorded on a Unicam SP 200 spectrometer, UV spectra on a Cary 14 instrument, (deconvolution of overlapping absorption bands was achieved with a DuPont-310 curve resolver). ^{13}C-NMR spectra on a Varian XL-100 Fourier-transform spectrometer with TMS as an internal reference, MS spectra on a AEI MS-9 instrument at 70 eV.

Synthesis of 1 and 2 was reported in ref. 1.

4-Thiacyclohexanone (6) was prepared according to ref. 9.

4-Thiacyclohexanone-morfolineenamine (7) was prepared by the procedure of Stork c.s.[10]; b.p. 116°/0.1 mm Hg.

6-Thia-2,3,4,4a,5,6,7,8-octahydronaphthalene-2-one (8) was prepared from 7 analogous to the method described for octalone-2[10]. The reaction product contained some β,γ-unsaturated product but was used without separation of isomers.

6-Thia-perhydronaphthalene-2-one trans (9) and cis (10). Hydrogenation of 8 in an ethanol-THF mixture over Pd/C (10%) gave a mixture of 9 and 10 with 9 as the predominant component (~ 90%). The attribution of the cis conformation to 10 is based upon the upfield shift of its ^{13}C-NMR resonances[11] as compared to 9. Recrystallization from methanol yielded 9 in pure form while pure 10 was obtained from the mother liquor by preparative GLC on an OV-225 column (length 3 m Ø 7 mm, 10%, T = 200°, V = 60 ml/min).

9: M.p. 99°-101° (Found: C 63.6, H 8.2, S 19.0; calc. for $C_9H_{14}OS$ (M = 170.27): C 63.48, H 8.29, S 18.83 %).

IR (KBr) C=O: 1700 cm^{-1}.

^{13}C-NMR ($CDCl_3$): 48.33, 42.68, 42.44, 41.42, 35.66, 32.62, 33.40, 27.88 (C=O not observed).

MS: 170 (100), 67 (50.5), 55 (61.9%).

10: M.p. 86°-87°.

IR(KBr) C=O: 1700 cm^{-1}.

^{13}C-NMR ($CDCl_3$): 210.39, 46.75, 39.50, 38.01, 35.58, 32.15, 28.76, 27.4, 26.76.

MS: 170 (100), 109 (66.2%).

Trans-6-thiaperhydronaphthylidene-2-malonitrile (4). This compound was obtained by condensation of 9 with malonitrile in refluxing benzene, with piperidine as a catalyst, during 30 minutes. Purification was achieved by column chromatography over silica with $CHCl_3$ as an eluent followed by repeated crystallization from ethanol. M.p. 101.5°-102.5° (Found: C 66.1, H 6.4, N 12.8, S 14.8; calc. for $C_{12}H_{14}N_2S$ (M = 218.3): C 66.02, H 6.46, N 12.83, S 14.69%).

IR ($CHCl_3$) C=N: 2230, C=C: 1600 cm^{-1}.
MS: 218 (100%).

Cis-6-thiaperhydronaphthylidene-2-malonitrile (5) was prepared as described for 4 and recrystallised from n-butanol. M.p. 112°-114° (Found: C 66.0, H 6.5, N 12.8, S 14.6%).
IR ($CHCl_3$) $C\equiv N$: 22.30, C=C: 1600 cm^{-1}.
MS: 218 (100%).

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