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# 5,6,8,9-TETRAAZA[3.3]PARACYCLOPHANE, TRANSANNULAR EFFECT ON THE n → π* TRANSITION

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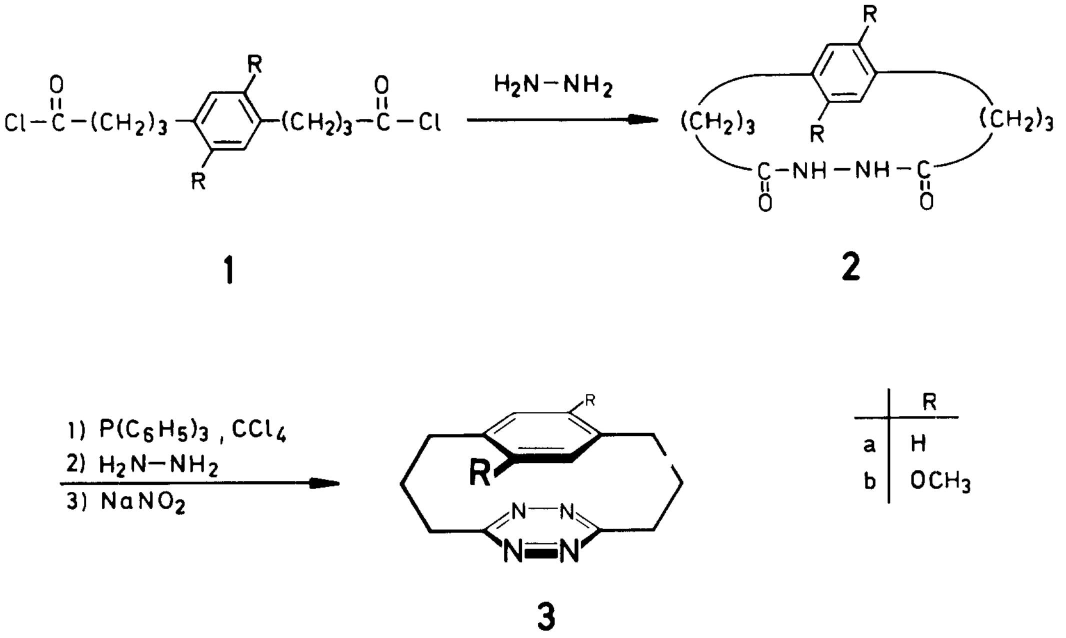
Summary: 5,6,8,9-Tetraaza[3.3]paracyclophane (3a) and the corresponding 14,17-dimethoxy derivative 3b were prepared. 3a and 3b exist as chair and boat conformers, the boat form being energetically favoured. Transannular interaction in 3a and 3b leads to a hypsochromic shift of the first n → π* absorption.

Series of cyclophanes with donor and acceptor groups suitably attached to the aromatic rings show the dependence of the charge transfer (CT) absorption on distance, orientation and mutual fixation of the donor and acceptor components [1]. In all these cases π → π* transitions are investigated. Less is known, however, about transannular effects on n → π* transitions. Such studies require a clear n → π* absorption band. s-Tetrazines provide a n → π* band at about 550 nm polarized perpendicular to the plane of the molecule [2] which is almost completely separated from π → π* and further n → π* transi-



1

2

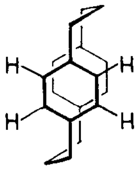
3

| | R |
|---|---|
| a | H |
| b | OCH$_3$ |

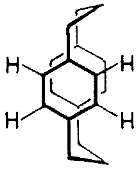
tions. For the present study, therefore, we combined s-tetrazine as acceptor with benzene or 1,4-dimethoxybenzene as donors in a [3.3]paracyclophane framework to give 3a and 3b.

The synthesis of 3a started from the diacid dichloride 1a[3] which was cyclized with hydrazine to give 4,7-diketo-5,6-diaza[10]paracyclophane (2a) in 20% yield [dilution method, toluene/triethylamine, tetrahydrofuran; from toluene colourless crystals, m.p. 283-284°C (dec.); MS: m/z = 246 (100%, $M^+$)]. From 2a following the three step reaction sequence of R. Appel[4a], H. Wamhoff[4b] et al. the target compound 5,6,8,9-tetraaza[3.3]paracyclophane (3a) was obtained in low yield [0.6%; from ligroin red crystals, m.p. 90-91°C; MS: m/z = 240 (90%, $M^+$); $^1$H-NMR ($CD_2Cl_2$, 360 MHz, 303 K): $\delta$ = 2.3-2.45 (m; 4H, $CH_2$), 2.65-2.75 (m; 4H, $CH_2$), 3.35-3.45 (m; 4H, $CH_2$), 6.78 (s; 14,15,17,18-H)].

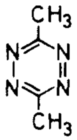
The required diacid dichloride 1b was prepared from the parent diester[1d] (hydrolysis and reaction of the diacid with thionyl chloride). Subsequent treatment of 1b in analogy to 1a afforded in 15% yield 2b [from methanol colourless crystals, m.p. 206-207°C (dec.); MS: m/z = 306 (100%, $M^+$)] which was then cyclized in 5% yield to the 14,17-dimethoxy-5,6,8,9-tetraaza[3.3]paracyclophane (3b) [from diethyl ether red crystals, m.p. 140-141°C; MS: m/z = 300 (100%, $M^+$); $^1$H-NMR ($CD_2Cl_2$, 360 MHz, 303 K): $\delta$ = 2.1-2.3 (m; 4H, $CH_2$), 2.4-2.6 (m; 2H, $CH_2$), 3.0-3.15 (m; 2H, $CH_2$), 3.18-3.5 (m; 4H, $CH_2$), 3.77 (s; 6H, $OCH_3$), 6.23 (s; 15,18-H)].



**3a** (chair)



**3a** (boat)



**4**

According to the $^1$H-NMR spectra 3a and 3b exist as a mixture of boat and chair conformers. Below -80°C the arene protons of 3a are observed as two AA'BB' systems or approximately, disregarding the long range couplings ($^4J_{HH}$ and $^5J_{HH} \leq 1.5$ Hz), as one AB system for the chair [($CD_2Cl_2$, 14,15,17,18-H) $\delta$ = 6.84, 6.92 (AB quartet, $^3J_{AB}$ = 7.8 Hz)] and two $A_2$ signals for the boat form [$\delta$ = 6.57 (s), 7.04 (s)]. The boat form is energetically preferred (boat:chair ≅ 66:34). The two arene protons of 3b appear at low temperature as four singlet signals [($CD_2Cl_2$, 15,18-H, 183 K) $\delta$ = 5.99 (36%), 6.29 (26%), 6.38 (3%), 6.49 (36%)]. We assign the two dominant signals of equal intensity to the arene protons of the boat form. The signal at $\delta$ = 6.29 (26%) apparently represents the arene protons of the chair conformer with the propylene bridge arranged anti to the methoxy substituents and the small signal at $\delta$ = 6.38 (3%) the arene protons of the energetically unfavoured chair conformer with syn arrangement of the bridge. Again the boat form is preferred (boat:chair ≅ 72:29).

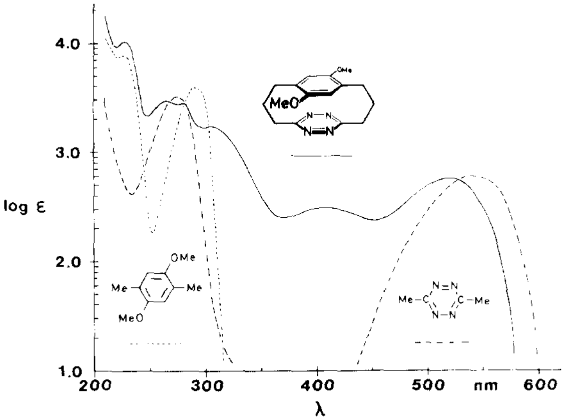


Fig. 1. Electron spectra of 3b, 4, and 1,4-dimethoxy-2,5-dimethylbenzene in dioxane.

Table 1. Electron spectra ($\lambda_{\max}$) of 4, 3a, and 3b in dioxane

| | $\lambda_{\max}$[nm](log $\varepsilon$) |
|---|---|
| 4 | 541 (2.78), 273 (3.47) |
| 3a | 522 (2.67), 335sh (2.57), 328 (2.62), 260 (3.45), 215 (4.09) |
| 3b | 518 (2.76), 405 (2.49), 302 (3.23), 280 (3.44), 263 (3.47), 228 (4.02) |

Table 2. Solvent dependence of $\lambda_{\max_1}$ [nm]

| | 2-Methylbutane | Dioxane | DMSO |
|---|---|---|---|
| 4 | x) | 541 | 537 |
| 3a | 525 | 522 | 518 |
| 3b | 523 | 518 | 516 |

x) Vibronic fine structure

The electron spectrum of the subunit 3,6-dimethyl-s-tetrazine (4) shows the characteristic n → π* absorption at 540 nm followed by a strong band at 273 nm (fig. 1). As compared to 4 the first n → π* transition of the cyclophanes 3a and 3b is found at shorter wavelength, 522 or 518 nm (table 1). This hypsochromic shift is only little affected by the π-donor property of the arene subunit (3a → 3b: ca. 4 nm). Furthermore the first n → π* absorption of 3a, 3b and 4 also exhibits the solvent dependence characteristic for n → π* transitions, namely, increasing hypsochromic shift with increasing solvent polarity (table 2). This solvent effect is of the order of 10 nm. The observed hypsochromic shift of the first n → π* absorption in 3a and 3b, corresponding to an increase of excitation energy of about 2 kcal·mol$^{-1}$, can be attributed to a transannular interaction. This effect on the n → π* band, however, is significantly smaller than charge transfer interactions concerning π → π* transitions. In the electron spectrum of 3b (fig. 1), for example, the absorption band at 405 nm represents a charge transfer absorption (π → π*). The bathochromic shift of 116 nm with respect to the first π → π* absorption (289 nm) of the 1,4-dimethoxy-2,5-dimethylbenzene donor subunit corresponds to a decrease of the excitation energy of about 28 kcal·mol$^{-1}$.

The electron spectra of the model compounds 3a and 3b show that not only π → π* transitions but also n → π* absorptions are effected by transannular interactions. In these examples the transannular effect on the first n → π* band of the acceptor subunit is reverse to the transannular effect on the first π → π* band of the donor subunit.

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