Notiz / Note

A Macrocyclic Tetraazapolyene – Synthesis and Configuration

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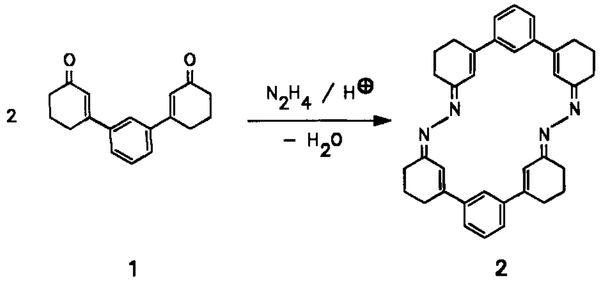
Received October 31, 1990

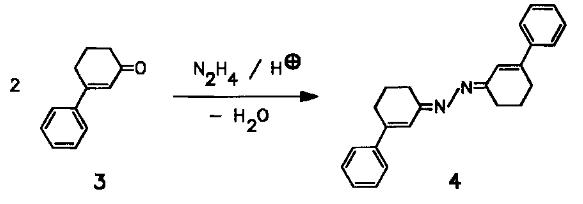
Key Words: Azines / Bis(azines) / Macrocycles / Tetraazapolyenes

The new macrocyclic bis(azine) **2** forming yellow microcrystals has been prepared in 72% yield by treating the diketone **1** with hydrazine hydrate under high-dilution conditions. In contrast to the UV/Vis spectrum of the "open-chain" azine **4**, that of **2** shows characteristic features of a polyene chromophore containing (Z)-configurated double bonds.

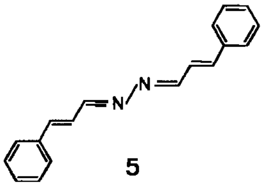
In contrast to azines of normal ring size, which are the object of many studies in heterocyclic chemistry, papers dealing with macrocyclic azines and bis(azines) are hardly found in the chemical literature[1]. One reason for this situation may be that the most common procedure for azine formation – the acid- or base-catalyzed reaction of an aldehyde or a ketone with hydrazine – is an equilibrium reaction. Furthermore, the use of bifunctional carbonyl compounds normally leads to the formation of polycondensed material which may be used as yellow pigment[2].

We have now succeeded in preparing the macrocyclic bis(azine) **2** by treating the diketone **1**[3] with hydazine hydrate in ethanol under acid-catalysis conditions[4]. The yield of the macrocycle (72%) is remarkable when compared with that of the "open-chain" analog **4** (83%) which has been prepared under similar conditions with the exception of high dilution. The obtained yields of cyclization products may be due in part to the low solubility of the diazine **2**, which shifts the equilibrium of azine formation towards the desired product, and to the absence of important steric interferences. The rigid-group principle, too, might play a role, as it has already been observed for the McMurry coupling of diketone **1**[5].





In the context of our concept of modifying classical chromophores by incorporating them into macrocyclic structures[5,6], we have investigated the electronic absorption of the yellow macrocyclic diazine **2** and compared it to that of its "open-chain" analog **4** and of the unclamped cinnamalazines **5** and **6**.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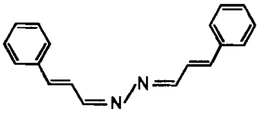
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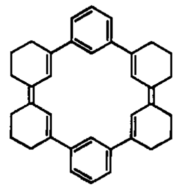
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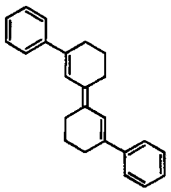
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The UV/Vis spectra of both azines **2** and **4** exhibit no fine structure and – in contrast to 1,8-diphenyloctatetraene[7] and cinnamalazine **5**[8] (poor vibrational structure) – coincide with those of the clamped polyenes **7** and **8**[5].

The most striking feature of the electronic absorption spectrum of the cyclic bis(azine) **2**, when compared to that of its "open-chain" analog **4**, is the occurrence of an intense additional band at λ = 282 nm. This band has been found to be characteristic of the presence of (Z)-configurated double bonds within a polyene chain[9] and can also be observed in the case of the cyclopolyene **7**[5] and the (Z) isomer **6** of cinnamalazine (λ = 277 nm; hexane)[8]. In fact, two of the four C=N bonds of **2** must have a (Z) configuration to allow the macrocyclic structure to be formed. As the spectrum of **4** lacks a "*cis* peak", we conclude that this azine adopts an *all*-(*E*) configuration.

The longest wavelength absorption of the macrocycle **2** (λ = 329 nm; 1,4-dioxane; qualitative spectrum due to low solubility) is blue-shifted by 16 nm when compared to that of the "open-chain" analog **4** (λ = 345 nm, ε = 47100; dioxane). A similar, even more

Chem. Ber. **124** (1991) 671–672 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/0303–0671 $ 3.50+.25/0

important hypsochromic shift (23 nm) has been observed in the transition from the "open-chain" diphenylhexatriene **8** to the macrocyclic hydrocarbon **7**[5]. This large shift may be due in both cases to a serious deviation from coplanarity in the cyclic (aza)polyenes **2** and **7**. On the other hand, the difference between the absorption maxima of the (*E*) and (*Z*) isomer of cinnamalazine (**5** and **6**, respectively) is only 2–3 nm (hexane)[8].

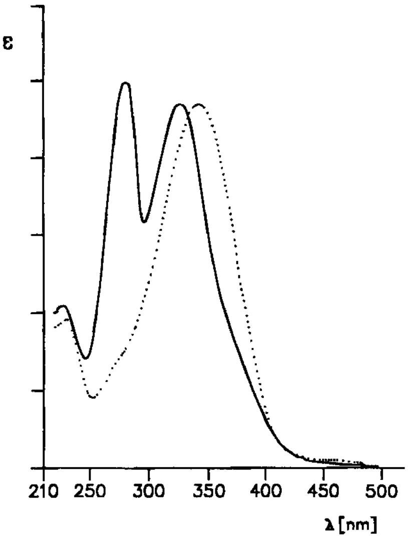

Figure 1. Qualitative absorption spectra of cyclodiazine **2** (——) and monoazine **4** (·····) (1,4-dioxane, T = 289 K); the extinctions of the longest wavelength absorptions have been set equal arbitrarily

Cinnamalazine **5**, which lacks additional clamping of the polyene chain, exhibits an absorption maximum at λ = 338 nm (ε = 68000; hexane)[8] or 346 nm (ε = 65000; ethanol)[10]. If solvent effects are taken into account, there is hardly a difference in the location of the longest wavelength band of the azines **4** and **5**. The extinction coefficient, however, is considerably smaller in the case of the clamped chromophore (**4**), just as it has been noticed for the polyenes 1,6-diphenyl-1,3,5-hexatriene[11] and **8**[5].

The synthesis of the cyclobis(azine) **2** is remarkable insofar as a macrocycle is the main product in a reaction performed under equilibrium conditions. Iso- and terephthalaldehyde are converted into only polymeric products under the same reaction conditions. Macrocyclic bis(azines) of the type described here may be interesting compounds as electron donors in charge-transfer complexes and in the formation of organic conductors[12].

Experimental

Melting points: uncorrected. – IR: Unicam SP-1100 IR spectrometer (Pye Unicam). – UV: CARY-219 spectrophotometer (Varian Associates). – ^{1}H NMR: WH-200 (200 MHz) (Bruker Physik AG). – MS: MS-50 (AEI). – Elemental analyses: Mikroanalytisches Laboratorium, Institut für Organische Chemie und Biochemie, Universität Bonn.

3-Phenylcyclohex-2-ene-1-one Azine (**4**): **3** (1.72 g, 10 mmol) and 100% hydrazine hydrate (0.25 g, 5 mmol) are dissolved in ethanol (20 ml). After addition of a drop of concd. HCl, the reaction mixture is heated at reflux for ca. 1.5 h. During this time, yellow-orange crystals separate from the solution. They are filtered off and recrystallized from 2-propanol or small amounts of THF to yield 1.41 g (83%) of pure **4**, m.p. 187–188°C. – IR (KBr): $\tilde{\nu}$ = 700 cm^{-1} (vs), 760, 770 (d, vs), 1620 (m). – UV (dioxane): λ_{max} (ε) = 345 nm (47100). – ^{1}H NMR (200 MHz, CDCl$_3$, δ = 7.25): δ = 1.95 (quint, ^3J = 6.25 Hz, 4H, CH$_2$), 2.62–2.72 (m, 8H, CH$_2$), 6.81 (s, 2H, olefinic CH), 7.27–7.47 (m, 6H, aromatic CH), 7.52–7.59 (m, 4H, aromatic CH). – ^{13}C NMR (50.27 MHz, CDCl$_3$): δ = 22.02 (CH$_2$), 25.4 (CH$_2$), 27.85 (CH$_2$), 125.03 (CH), 125.50 (CH), 128.37 (CH), 128.56 (CH), 140.31 (C), 147.88 (C), 161.93 (C=N).

$C_{24}H_{24}N_2$ (340.47) Calcd. C 84.67 H 7.10 N 8.23
Found C 84.18 H 7.10 N 8.09
Calcd. 340.1939 Found 340.1944 (MS)

7,8,24,25-Tetraazaheptacyclo[29.3.1.1^{2,6}.1^{9,13}.1^{14,18}.1^{19,23}.1^{26,30}]tetraconta-1(35),2(36),6,8,13(37),14,16,18(38),19(39),23,25,30(40),31,33-tetradecaene (**2**): 1.2 l of ethanol and 6 drops of concd. HCl are heated to reflux in a 2-l flask fitted with a two-component dilution-principle apparatus[13]. Solutions of **1** (2.66 g, 10 mmol) and 100% hydrazine hydrate (0.5 g, 10 mmol), each in 250 ml of ethanol, are added dropwise over a period of 8 h, after which time the reaction mixture is heated at reflux for 1 additional hour. After cooling to room temp., the formed yellow precipitate is filtered from its suspension, washed thoroughly with ethanol, and dried in vacuo to yield 1.89 g (72%) of pure **2**. The cyclodiazine **2** is sparingly soluble in all common organic solvents. It can be recrystallized from large amounts of pyridine; m.p. >300°C (dec.). – IR (KBr): $\tilde{\nu}$ = 700 cm^{-1} (w), 800 (m), 905 (m), 980 (w), 1590, 1615 (d, m). – UV (dioxane): λ_{max} = 282 nm, 329. – ^{1}H NMR (200 MHz, CDCl$_3$, δ = 7.25; all signals are broadened): δ = 2.10 (quint, ^3J = 6.6 Hz, 8H, CH$_2$), 2.48–3.50 [br. m including: δ = 2.72 (t, ^3J = 5.6 Hz) and 2.83 (t, ^3J = 5.0 Hz), 16H, CH$_2$], 7.33–7.55 (m, 8H, CH) 7.93 (s, 2H, CH), 8.31 (s, 2H, CH).

$C_{36}H_{36}N_4$ (524.71) Calcd. N 10.68 Found N 10.51
Calcd. 524.2940 Found 524.2942 (MS)

CAS Registry Numbers

1: 95020-74-9 / **2**: 131193-64-1 / **3**: 10345-87-6 / **4**: 131193-65-2

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