Photochemistry of Tetrabenzo[*c,e,i,k*][1,2,7,8]tetraazacyclododecine in 2-Propanol

Erich Tauer*, Karl-Heinz Grellmann, and Angelika Heinrich

Max-Planck-Institut für Biophysikalische Chemie, Abteilung Spektroskopie,
Postfach 2841, W-3400 Göttingen, F.R.G.

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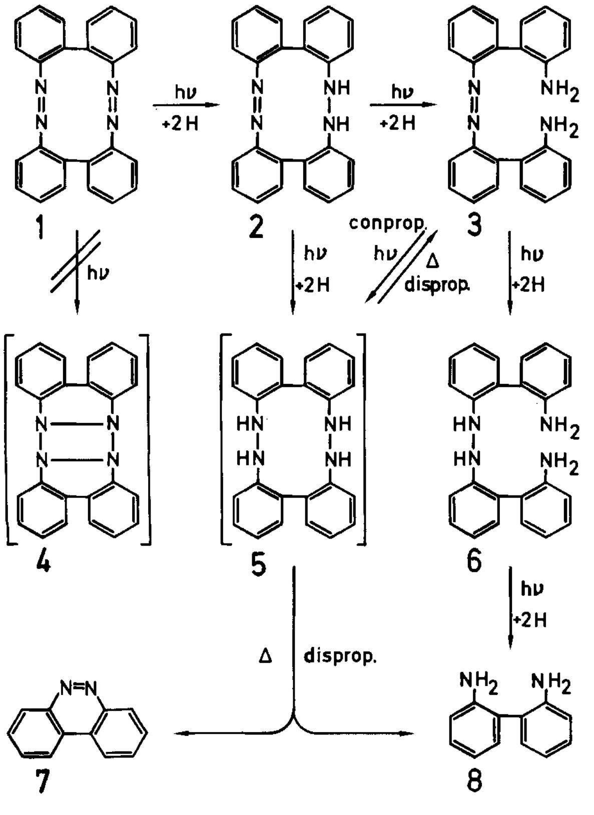
The photochemical properties of the tetraazacyclododecine **1** were investigated. The *trans,trans* isomer $\mathbf{1}_{tt}$ can be photoisomerized yielding the stable *cis,cis* isomer $\mathbf{1}_{cc}$. The isomerization requires two photons and proceeds via the unstable *trans,cis* isomer $\mathbf{1}_{tc}$. In nitrogen-purged 2-propanol as solvent **1** yields five stable photoproducts as a result of a number of consecutive photoreduction reactions. Our attempts to convert **1** by light into the tetraazetidine **4** were not successful.

As pointed out recently by Ritter et al.[1], the synthesis of a stable tetraazetidine (a compound with a four-membered, only nitrogen-containing ring) has not yet been realized. By studying the *trans-cis* photoisomerization reaction of an azobenzenophane, Ritter et al. obtained indirect evidence for the formation of such a four-membered ring system, which had a lifetime of only a few minutes.

We tried to synthesize a tetraazetidine photochemically by starting from the hitherto unknown tetrabenzo[*c,e,i,k*][1,2,7,8]tetraazacyclododecine (**1**) in the hope that it can be photoisomerized to **4** (cf. Scheme 1). Exploratory irradiation experiments with solutions of **1** in 2-propanol showed that benzo[*c*]cinnoline (**7**) was formed in about 20% chemical yield. This appeared to be a promising observation because the precursor of **7** could have been **4**. However, a more detailed analysis revealed that the conversion of **1** into **7** takes place in a number of steps *without* involving **4** as intermediate. In this paper we describe the details of this reaction sequence which is, in addition, accompanied by a *trans-cis* photoisomerization of **1**.

Scheme 1



Results

1. *trans-cis* Photoisomerization

The synthesis of **1** from *trans*-2,2′-dibromoazobenzene yields presumably the *trans,trans* isomer ($\mathbf{1}_{tt}$), which is most probably more stable than the *cis,cis* isomer ($\mathbf{1}_{cc}$). If a vigorously stirred suspension of $\mathbf{1}_{tt}$ in air-equilibrated methanol is irradiated with an incandescent lamp through a 390-nm cut-off filter, the orange-colored crystal suspension slowly dissolves and yellow crystals precipitate. (The photoreactions described in the next paragraph are to a large extent quenched by oxygen.) Because of the very poor solubility of the product, it is possible to convert the suspension of the starting material almost quantitatively into the photoproduct, which we assign to the *cis,cis* isomer $\mathbf{1}_{cc}$. So far, this assignment is based on the identical molecular weights of starting material and photoproduct, and on the melting point of $\mathbf{1}_{cc}$, which is identical with that of $\mathbf{1}_{tt}$. The latter observation is in all probability due to the fact that above 200°C $\mathbf{1}_{cc}$ is *thermally* converted into $\mathbf{1}_{tt}$: If a sample of $\mathbf{1}_{cc}$ is heated in an open capillary, the yellow color of the crystals turns at about 200°C into orange (without melting) and the orange crystals melt at 308–310°C like $\mathbf{t}_{tt}$. A similar color change around 200°C is observed when a *mixture* of $\mathbf{1}_{tt}$ and $\mathbf{1}_{cc}$ is heated, and the melting point shows *no depression*.

Since the absorption spectra of $\mathbf{1}_{cc}$ and $\mathbf{1}_{tt}$ differ significantly in the visible region, it is possible to show that the

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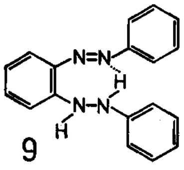
$1_{tt} \rightarrow 1_{cc}$ isomerization requires *two* photons: If a solution of 1_{tt} is irradiated for a short period of time the absorbance around 430 nm decreases. In the dark, the absorbance reverts with a halflife of about 6 hours (at 25 °C) to the original value, provided only a small fraction of 1_{tt} is photolyzed, in order to avoid appreciable excitation of the photoproduct. We presume that under these conditions the *trans,cis* isomer (1_{tc}) is formed. Like in the case of azobenzenophanes[1,2] the *trans,cis* isomer is thermally unstable. Contrary to our expectation, 1_{tc} does not decay to 1_{tt} *and* 1_{cc}, but exclusively to 1_{tt}, and a second photon is required to convert 1_{tc} into 1_{cc}. Prolonged irradiation of 1_{tt} leads to the formation of a stationary mixture of 1_{tt},1_{tc}, and 1_{cc}, whereby part of the *cis,cis* isomer may precipitate because it is much less soluble than 1_{tt}. This poor solubility of 1_{cc} makes a quantitative study of the photoisomerization reaction difficult.

2. Photoreduction of 1

All photoreduction experiments described in this paragraph were carried out in 2-propanol as solvent. The solutions were purged with oxygen-free nitrogen. The solubility of 1_{tt} in 2-propanol is poor; saturated solutions contain about 70 mg/l. Prolonged irradiation of such a solution leads quickly to a mixture of 1_{tt},1_{tc}, and 1_{cc} and, much more slowly, to a complex mixture of stable reaction products. Fortunately, however, it turned out that these photoproducts were formed in consecutive steps; this facilitated the analysis of the overall reaction considerably. If the time dependence of the photoreaction is monitored by TLC, the first observable photoproduct is 9,10-dihydrotetrabenzo[*c,e,i,k*][1,2,7,8]tetraazacyclododecine (**2**) (cf. Scheme 1). If only a small fraction of **1** is photolyzed, the chemical yield of **2** amounts to >90%. **2** can be isolated, it forms red crystals. Considering the fact that **2** contains a hydrazo group, this compound is amazingly stable. 2-(Phenylazo)hydrazobenzene (**9**) is also a remarkably stable hydrazo compound. It was synthesized by Ruggli et al.[3] who proposed that hydrogen bonds between the azo and hydrazo groups stabilize this compound. However, if this was also the reason for the stability of **2**, the NMR signal of the NH proton should be located at much lower fields than observed.



9

Irradiation of a solution of **2** yields 2′,2‴-azobis([1,1′-biphenyl]-2-amine) (**3**) as the main product and, in addition, biphenyl-2,2′-diamine (**8**) and benzo[*c*]cinnoline (**7**). The ratio of the chemical yields of the three photoproducts **3**, **7**, and **8** is roughly ≈3.5:1:1. **3** is also stable and forms red crystals.

Long-wavelength irradiation ($\lambda \geq 320$ nm) of the azo compound **3** yields as the main product 2′,2‴[1,2-hydrazinediyl]bis([1,1′-biphenyl]-2-amine) (**6**) (which does not absorb at $\lambda \geq 320$ nm) and again, like in the case of **2**, as minor products **7** and **8**. The ratio of the chemical yields is **6**:**7**:**8** ≈ 6:1:1. The hydrazo compound **6** forms colorless crystals which are stable at room temperature. In solution **6** is, in the presence of oxygen, slowly oxidized to **3**.

Finally, irradiation of a solution of **6** yields in a clean reaction the diamine **8**. The chemical yield of this reaction is 83%. The photoproducts **2**, **3**, **6**, **7**, and **8** can also be isolated if a solution of **1** is irradiated for prolonged times.

The structures of **2**, **3**, and **6** were determined by elemental analysis and by UV and NMR spectroscopy. The molecular masses were determined by mass spectrometry. The isolated compounds **7** and **8** were compared with authentic samples (mixed melting points, no depression). Compounds **1**, **2**, **3**, and **6** have not yet been described.

Discussion

The first report on the photoreduction of azo compounds appeared already in 1949 in a paper by Blaisdell[4]. He showed that azobenzene is photoreduced first to hydrazobenzene and in a second step to aniline. Obviously, to some extent **1** behaves analogously (cf. Scheme 1): The main reaction sequence is the stepwise photoreduction of one azo moiety yielding **3**, followed by the photoreduction of the second half via **6** yielding finally **8**. Since the intermediate photoproducts **2**, **3**, and **6** are stable compounds which can be photolyzed separately, the postulation of the reaction sequence **1** → **2** → **3** → **6** → **8** in Scheme 1 is straightforward. However, it does, of course, not explain why the formation of the benzocinnoline **7** is observed when solutions of **2** or of **3** are photolyzed.

In the case of **2** the formation of **7** can be easily explained by assuming a second reaction sequence in which the *azo* moiety of **2** is photoreduced to yield **5**. The bishydrazo derivative **5** is most probably unstable, and we assume that it disproportionates thermally to **7** and **8** yielding the two products in equimolar ratio, as found experimentally.

While the occurence of two photoreduction pathways (**2** → **5** and **2** → **3**) is not astonishing in the case of **2**, it is somewhat surprising that the photolysis of **3** also yields, in addition to **6**, the two products **7** and **8**. We assume that **3** is not only photoreduced to the main product **6**, but that it also *conproportionates in the excited state* to **5**, yielding finally **7** and **8** in an equimolar ratio.

It is conceivable that the bishydrazo compound **5** disproportionates *thermally* not only to **7** and **8**, but also to **3**, as indicated in Scheme 1. If this is the case, the photoreduction of **2** to **3** may proceed partly or entirely via **5**. With the available experimental data it is not possible to decide to which extent the indirect route **2** → **5** → **3** is responsible for the formation of **3** from **2**. It would be interesting to investigate whether **5** can be prepared from **2** at low temperatures, where it is presumably more stable, and to study the decay of **5** at elevated temperatures.

Under our experimental conditions (nitrogen-purged 2-propanol as solvent, excitation wavelength $\lambda_{exc} \geq 300$ nm, room temperature) benzo[*c*]cinnoline (**7**) is formed *only* from **2** and **3**, *but not* from **1**. Therefore, the tetraazetidine

4 cannot be a precursor of **7**. If the photocyclization reaction **1** → **4** takes place at all, **4** must be thermally unstable and revert to **1**. Unfortunately, it is not possible to perform in 2-propanol low-temperature photolysis experiments with **1** because of solubility problems.

Experimental

UV: Perkin-Elmer Model 320. – ^{1}H NMR: Bruker WP 80 CW. – MS: Varian MAT CH 17. – Melting points: uncorrected, determined in open capillaries.

Photochemical Preparation of Compounds **2, 3, 6, 7,** *and* **8** *in Gram Amounts:* A suspension of 2 g of **1** in ≈2*l* of 2-propanol was irradiated with a 125-W Hg-immersion lamp with a Solidex filter. The solvent was purged with nitrogen (oxygen content ≤2 ppm). The progress of the photoreaction was monitored by TLC. The yield of a particular photoproduct could be optimized to some extent by varying the exposure time. The retention values of starting material **1** and photoproducts on the TLC plates (SiO_2, toluene/ethyl acetate, 3:1) were : **1** = 0.67, **2** = 0.60, **3** = 0.42, **6** = 0.51, **7** = 0.33, **8** = 0.36. The isolated photoproducts **2, 3,** and **6** were photolysed under the same conditions as **1**.

trans,trans-Tetrabenzo[c,e,i,k][1,2,7,8]tetraazacyclododecine ($\mathbf{1}_{tt}$): 6.8 g (0.02 mol) of 2,2′-dibromoazobenzene[5] and 6.35 g (0.1 mol) of activated copper bronze[6] were suspended under nitrogen in 50 ml of dimethylformamide, vigorously stirred and boiled under reflux for 8 h. After cooling 250 ml of H_2O was slowly added, the precipitate filtered, washed with H_2O and dried. Chromatographic purification (SiO_2, toluene) yielded 2.5 g (70%) of $\mathbf{1}_{tt}$. Orange crystals, m.p. 309–310 °C (from toluene). – UV (2-propanol): λ_{max} (lg ε) = 430 nm (3.19), 288 (4.13), 258 (sh) (4.29). – ^{1}H NMR ($CDCl_3$): δ = 6.7–7.8 (m, arom. H). – MS (70 eV): *m/z* = 360 [M^+].

$C_{24}H_{16}N_4$ (360.4) Calcd. C 79.98 H 4.47 N 15.54
Found C 80.10 H 4.47 N 15.58

trans → *cis Photoisomerization of* $\mathbf{1}_{tt}$: 600 mg (1.67 mmol) of $\mathbf{1}_{tt}$ was suspended in 2l of air-equilibrated methanol in a 2-l round-bottom pyrex glass flask and with vigorous stirring irradiated with a slide projector (100-W tungsten lamp) through the flask and a GG 395 Schott filter. Within 3 d the orange crystals of $\mathbf{1}_{tt}$ dissolved and the much less soluble, yellow crystals of $\mathbf{1}_{cc}$ precipitated. The filtered crystals were washed with methanol and dried. Yield: 556 mg (92.7%) of yellow crystals of $\mathbf{1}_{cc}$, m.p. 308–310 °C (like $\mathbf{1}_{tt}$). On heating, the yellow color of the crystals changed around 200 °C to orange. A mixed melting point of $\mathbf{1}_{tt}$ and $\mathbf{1}_{cc}$ showed no depression. – UV (methanol): λ_{max} (lg ε) = 407 nm (3.02), 226 (4.57). – MS (70 eV): *m/z* = 360 [M^+]. Because of its poor solubility, it was not possible to take a ^{1}H NMR of $\mathbf{1}_{cc}$.

$C_{24}H_{16}N_4$ (360.4) Calcd. C 79.98 H 4.47 N 15.54
Found C 79.85 H 4.46 N 15.37

9,10-Dihydrotetrabenzo[c,e,i,k][1,2,7,8]tetraazacyclododecine (**2**): A suspension of 2.0 g of $\mathbf{1}_{tt}$ in 2*l* of 2-propanol was irradiated as described above. The optimal exposure time was about 3 h. The volume of the suspension was reduced to about 500 ml, unreacted $\mathbf{1}_{tt}$ (1.67 g) was separated from the solution by filtration, and then the solvent was evaporated. Chromatography of the residue (SiO_2, toluene/ethyl acetate, 3:1) afforded 88 mg (27%) of **2**. It formed red crystals, m.p. 180–181 °C (from 2-propanol). – UV (2-propanol): λ_{max} (lg ε) = 434 nm (4.10), 320 (sh) (3.92), 302 (4.04), 250 (4.53). – ^{1}H NMR ($CDCl_3$): δ = 3.4 (br. s, 2H, NH), 6.5–8.6 (m, 16H, arom. H). – MS (70 eV): *m/z* = 362 [M^+].

$C_{24}H_{18}N_4$ (362.4) Calcd. C 79.54 H 5.01 N 15.46
Found C 79.07 H 4.94 N 15.63

2′,2‴-Azobis([1,1′-biphenyl]-2-amine) (**3**): 790 mg (2.17 mmol) of **2** was dissolved in 2*l* of 2-propanol and the solution irradiated as described above for 3 h. After evaporation of the solvent chromatography of the residue (SiO_2, cyclohexane/ethyl acetate, 1:1) afforded 311 mg (39.4%) of **3** besides 84 mg (10.6%) of **7** and 91 mg (11.5%) of **8**. The compound **3** formed red crystals, m.p. 161–163 °C (from C_6H_{12}). – UV (2-propanol): λ_{max} (lg ε) = 301 nm (4.16). – ^{1}H NMR ($CDCl_3$) δ = 3.45 (s, 4H, NH), 6.7–7.5 (m, 16H, arom. H). – MS (70 eV): *m/z* = 364 [M^+].

$C_{24}H_{20}N_4$ (364.5) Calcd. C 79.10 H 5.53 N 15.37
Found C 79.08 H 5.62 N 15.24

2′,2‴-[1,2-Hydrazinediyl]bis([1,1′-biphenyl]-2-amine) (**6**): 900 mg (2.47 mmol) of **3** was dissolved in 2*l* of 2-propanol and the solution irradiated as described above for 24 h. After the evaporation of the solvent chromatography of the residue (SiO_2, cyclohexane/ethyl acetate, 1:1) furnished 620 mg (68.9%) of **6** besides 88 mg (9.8%) of **7** and 99 mg (11.0%) of **8**. The compound formed colorless crystals, m.p. 197–198 °C (from 2-propanol). – UV (2-propanol): λ_{max} (lg ε) = 295 nm (406). – ^{1}H NMR ($CDCl_3$): δ = 3.6 (br. s, 4H, NH_2), 5.7 (br. s, 2H, NH), 6.5–7.3 (m, 16H, arom. H). – MS (70 eV): *m/z* = 366 [M^+].

$C_{24}H_{22}N_4$ (366.5) Calcd. C 78.66 H 6.05 N 15.29
Found C 78.58 H 6.10 N 15.34

CAS Registry Numbers

$\mathbf{1}_{cc}$: 133871-02-0 / $\mathbf{1}_{tt}$: 133870-99-2 / **2**: 133886-88-1 / **3**: 133871-00-8 / **6**: 133871-01-9 / **7**: 230-17-1 / **8**: 1454-80-4 / 2,2′-dibromoazobenzene: 15426-16-1

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