Small and Medium Rings, 76[1]

Photorearrangement of Polycyclic Quinoxalines, Isomerisations of Isodrin-Type and Aza-Di-π-Methane Chromophores

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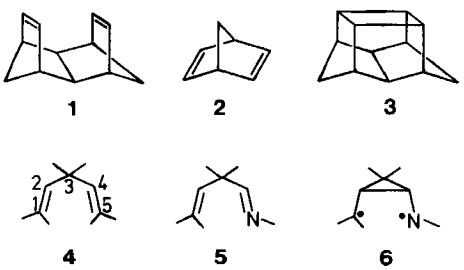
Received August 13, 1990

Key Words: Quinoxalines, multichromophoric / Sensitization, intramolecular / Cycloaddition [2π + 2π] / Quinoxaline di-π-methane rearrangement / PE Spectra

The multichromophoric polycyclic quinoxaline **11** has been synthesized starting with diketone **7**. Irrespective of whether quinoxaline **11** is irradiated in its nπ* or ππ* band, the photoproduct formed in high yield is invariably the cage compound **14**. This excitation energy transfer from the quinoxaline to the isodrin subchromophore of **11** is facilitated by a strong mixing of energy levels in these two fragments of **11**, as evidenced by the PE spectrum of quinoxaline **13**. The direct interaction of a quinoxaline chromophore with a nonconjugated double bond, i.e. an aza-di-π-methane rearrangement, is shown to occur photochemically in bicyclic quinoxaline **12**.

Much work has been devoted to the study – experimentally and theoretically – of proximal, non-conjugated chromophores, especially double bonds. Among the various combinations of chromophores that have been investigated, two special ones have attracted much attention. Isodrin-type molecules (e.g. **1**) contain two face-to-face π-bonds reminiscent of the electronic situation in norbornadiene (**2**). But, in contrast to the latter diene, a stronger spatial π overlap is conducive to a more intense through-space interaction and, additionally, cooperative through-bond coupling results in a particularly highlying π-HOMO in **1**[2a]. Photoisomerization to yield the cage compound **3** in observed with high quantum yields[2b].

Scheme 1



A second chromophore of photochemical interest is the di-π-methane moiety of β,γ-unsaturated systems (cf. **4**). The structural requirements for an efficient photorearrangement demand good interaction (homoconjugation) between centers 2 and 4 of a diene **4**[3]. Interestingly, a nitrogen atom may replace an olefinic carbon, as in **5**, without impairing the course of the reaction that is believed to lead to the product via a 1,4-diradical **6**[4] formed first.

Recently we described the unsaturated diketone **7**, prepared by [4 + 2] cycloaddition of *o*-benzoquinone to barrelene[5]. The diketone **7** underwent smooth photorearrangement at room temperature to give the cyclobutanedione **8** upon irradiation at 404 or 436 nm. No evidence for the formation of the cage compound **9** could be obtained under these conditions. Although this 1,3-acyl shift is not unexpected[6], the outcome of this photoprocess seems nevertheless remarkable. It has been reported that on irradiation of diene **1** in the presence of electron-acceptor sensitizers, under conditions where all incident light had been absorbed by the sensitizer, isomerization to the cage compound **3** has been observed[2b]. Thus, 1-cyanonaphthalene as fluorophore for example (electron affinity EA = 0.68 eV[7]) is believed to form a polar exciplex **10** with diene **1** that finally gives the product **3** by excitation energy transfer from naphthalene to the diene. Since the α-dicarbonyl unit in **7** has almost the same electron affinity as 1-cyanonaphthalene [EA(biacetyl) = 0.72 eV[8]], a similar exchange of excitation energy from the dione moiety to the diene subunit at some point of the reaction coordinate for the cycloaddition **7**→**9**, [A*···D]→ [A···D*][2b], might have been possible. However, this reaction path does not seem to be able to compete with faster 1,3-acyl shift **7**→**8**.

It is, on the other hand, possible to convert α-diketones to the corresponding quinoxalines. Although these special diazanaphthalenes show long-wavelength $n_+\pi^*_-$ excitation energies similar to their dicarbonyl counterparts[9], they are not prone to undergo 1,3-acyl shifts. Since these $n_+\pi^*_-$ transition energies are lower than the $\pi_{cc}\pi^*_{cc}$ exitations in **1** or **7** it should be possible to excite selectively the quinoxaline $n_+\pi$ transition in **11**. Thus, any transfer of energy to the

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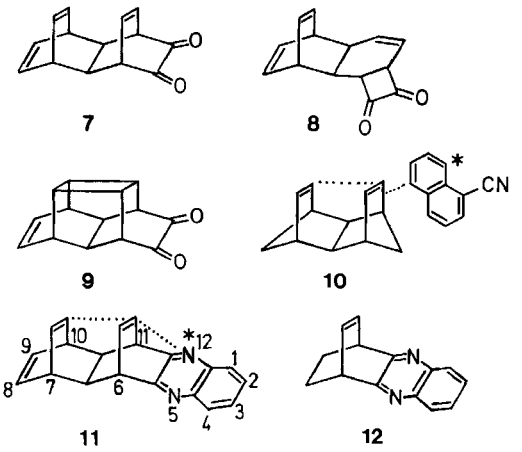
isodrin moiety in **11** could eventually result in intramolecular $[2\pi + 2\pi]$ cycloaddition and formation of the cage product.

Scheme 2



In this paper we report on the synthesis and photochemical properties of quinoxaline **11**. In order to explore the possibility that interaction between the subchromophores in **11** implies real CC-bond formation with subsequent rearrangement (e.g. a hitherto unknown di-π-methane analog), we include quinoxaline **12** in our studies.

Results

Diketone **7**[5] is treated with *o*-phenylenediamine in dichloromethane at room temperature. The yellow color of the solution disappears and, after one hour, the quinoxaline **11** is isolated in high yield. It forms colorless crystalls and is not stable above its melting point (154–157°C). After heating **11** to 170°C fragmentation takes place and and 1,4-dihydro-1,4-ethenophenazine (**13**)[10] is formed in quantitative yield.

When a solution of **11** in dichloromethane is exposed to sunlight (duran glass) for some hours, a colorless compound, m.p. 228°C, is isolated. The same product is formed within minutes during irradiation of **11** with a 100-W mercury high pressure lamp with duran filter. Complete conversion of **11** to the photoproduct is also achieved when the irradiation is carried out be means of a 1000 W Hg/Xe high pressure mercury lamp fitted with a KG1-IR filter with $\lambda \geq 380$ nm.

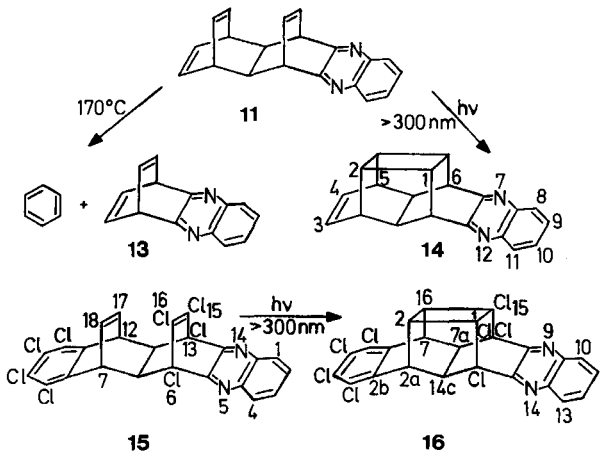
According to mass and NMR spectra the photoproduct is an isomer of **11**. It exhibits five aliphatic resonance lines and one olefinic signal (each corresponding to two hydrogen atoms) apart from the peaks typical of the quinoxaline protons. Waltz-decoupled ^{13}C-NMR spectra, H,H-COSY- and H,C-COSY-spectra confirm the cage structure **14** of the photoproduct.

Chlorine atoms do not alter the course of the photoreaction. Ouinoxaline **15** behaves similar to **11** and is rapidly transformed into cage product **16** upon irradiation with wavelengths as long as 380 nm.

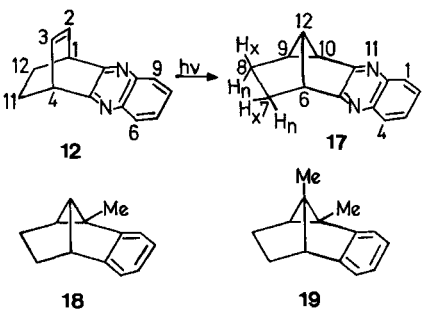
Both quinoxaline **11** and **14** display fluorescence in solution. Their absorption characteristics are very similar [**11**: $\lambda_m(\pi\pi^*)$ = 316 nm (ε = 8500), 241 (25300); **14**: $\lambda_m(\pi\pi^*)$ = 318 (8800), 239 (22700)], whereas the fluorescence quantum yields of **11** and **14** are $\Phi_F(\mathbf{14})/\Phi_F(\mathbf{11}) = 16/1$ (λ_{exc} = 296 nm). Following the change of excitation spectra and fluorescence spectra during irradiation of **11**, the maxima of each compound (320 and 390 nm, resp.) migrate towards each other, or, in other words, the Stokes shift turns out to be smaller for the more rigid cage product.

Quinoxaline **12** has been prepared from the corresponding diketone[11]. Its absorption spectrum with ππ* maxima at 314 and 237 nm is relatively insensitive to a change of solvent polarity. In cyclohexane the band at 314 nm exhibits fine structure. Irradiation of **12** with a 200-W high pressure mercury lamp in either quartz or pyrex cells leads to the same result. In carefully degassed cyclohexane or methylcyclohexane solutions (acetonitrile may also be used) the emergence of a new maximum at 320 nm, with fine structure at 335, 325, and 313 nm, is observed. Longer irradiations lead to complete decomposition. Presence of oxygen is disadvantageous, the quinoxaline chromophore of the starting material **12** is destroyed. The photoreaction is also inhibited by addition of biacetyl (**12**: 3×10^{-4} M, biacetyl: 0.1 M). It should be noted that there is a strong overlapping of absorption bands in the region 250–300 nm where biacetyl shows its second electronic transition. Longer reaction times were needed in preparative scale transformations. Addition of sensitizers (e.g. *m*-methoxyacetophenone) did not affect

Scheme 3



Scheme 4



the conversion times significantly. Isolation of the photoproduct is best achieved by preparative TLC. A colorless solid is obtained in 20% yield. The product is stable to light, i.e. the reverse photoreaction is negligible under the conditions chosen. The ^{1}H- and ^{13}C-NMR spectra indicate the complete loss of symmetry. H,C-COSY and H,H-COSY spectra suggest the structure of a dihydro-quinoxalino-semibullvalene **17**.

It is illustrative to compare relevant coupling constants in **17** with those of similar dihydro-benzosemibullvalenes **18** and **19**[12]. The entries in Table 1 show excellent agreement with published values.

Table 1. H,H coupling constants (Hz) of **17**, **19**, **18** (300 MHz, $CDCl_3$) x = *exo*, n = *endo*

J	17	19[12]	18[12]
10,12	6.3	-	-
6,12	5.4	-	5.5
9,12	6.7	-	7
10,8x	0.8	-	-
9,10	8.4	-	-
6,7x	5.4	5.5	5
6,7n	0	0	0
6,8x	-	1.3	1.3
7x,7n	11.6	11.5	11.3
7x,8x	9.4	8.8	8.8
7n,8n	6.2	6	6
7x,8n	11.6	11.5	11.3
7n,8x	0	0	0
8x,8n	13.5	13.5	12.2
8x,9	6.7	6.9	7
8n,9	1.8	2	1.4

Discussion

The electronic absorption spectrum of quinoxaline in the near UV consists of three bands, all of which can be found in the derivatives discussed here (symmetries relate to C_{2v} symmetry of quinoxaline)[9]:

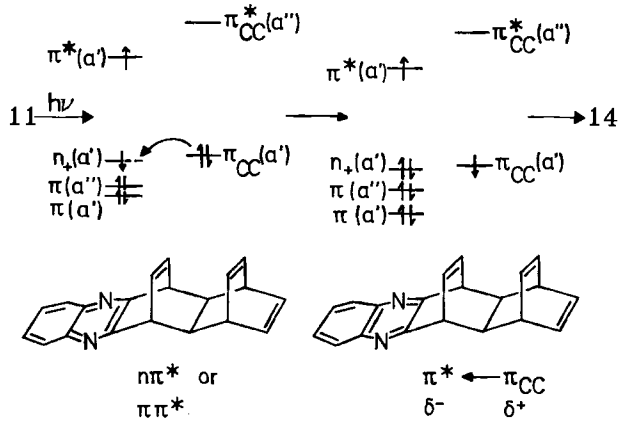
1) A symmetry-allowed $n_+\pi_+^*$ transition $^1B_1 \leftarrow {}^1A_1$ that is out-of-plane polarized and has a relatively high extinction coefficient in solution $\varepsilon(375) \approx 110\ M^{-1}\ cm^{-1}$. This electronic transition is the precise analogue of the corresponding $n_+\pi_+^*$ excitation in α-diketones, the latter being bathochromically shifted by about 50 nm.

2) The first ππ* transition begins to absorb near 320 nm. It is an allowed $^1A_1 \leftarrow {}^1A_1$ long-axis polarized excitation. The whole band is thought to be composed of the two naphthalene transitions ^1L_a and ^1L_b.

3) The most intensive absorption band is located near 240 nm.

Only absorption bands 1) and 2) are of importance in the duran glass-filtered irradiations of **11**, **12**, and **15** described above. Both the $n_+\pi_+^*$ and ππ* excitations are localized within the quinoxaline chromophore, and it remains to be answered how electronic energy is tranfered to the isodrin moiety of **11** in order to induce the intramolecular cylcoaddition. Since the $\pi_{cc}\pi_{cc}^*$ isodrin transition of **11** is presumably not excited by wavelengths longer than 300 nm [the corresponding transition in isodrin **1** itself display a relatively intense end absorption with a perceptible shoulder at 218 nm (ε 13000) and $\varepsilon_{254} = 2000$[2b]], a different explanation comes to the fore. After $n_+\pi_+^*$ or ππ* excitation of the quinoxaline part, electron transfer from the high-lying isodrin donor orbital creates an intramolecular charge-transfer situation which is conducive to cage formation (the bond order between the respective π centers increases because of lack of electron density, see Scheme 5).

Scheme 5



Such a flow of electron density from the olefinic part of the molecule to the heteroaromatic unit could be extremely facilitated in this case since both the donor (π_{cc}) and the acceptor level [n_+ or π(a')] transform as a' in the point group C_s, i.e. they strongly mix by through-space and through-bond interactions. Photoelectron spectroscopy could, in principle, support this idea. Unfortunately we have not been successful in recording the PE spectrum of **11** because of its thermal lability, only the ionization data of the

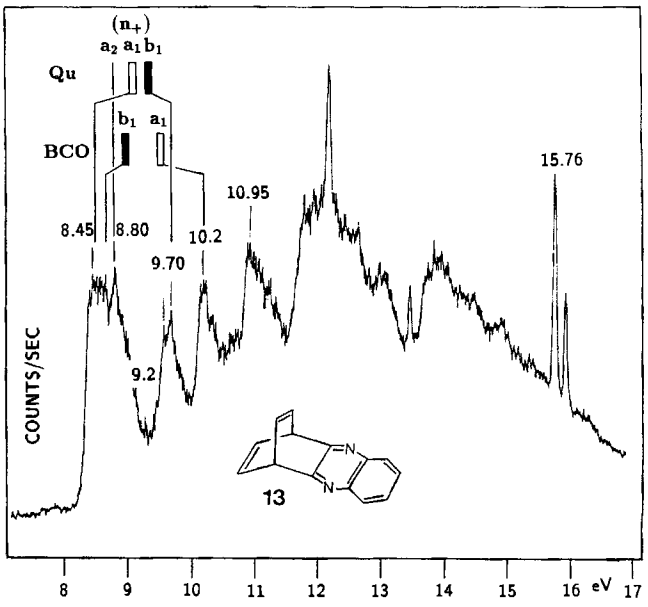


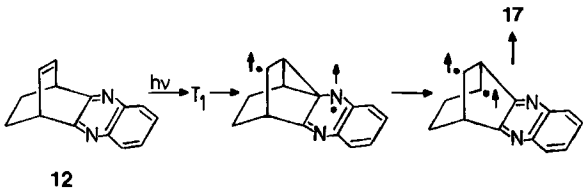
Figure 1. He(I) PE spectrum of **13**. Fragment orbitals of quinoxaline[14] (Qu) and bicyclo[2.2.2]octadiene[13] (BCO) have been used to interpret the final ionization energies and to demonstrate the strong mixing between n_+ and π levels

fragmentation products, benzene and **13**, could be obtained. On the other hand, the PE spectrum of quinoxaline **13** suffices in this respect, since **13** represents an important section of the whole molecule **11** answering the question whether mixing of n_+ and π levels takes place or not. Inspection of Figure 1 immediately shows that the PE spectrum of **13** can be rationalized by taking into account the ionization energies of the fragments quinoxaline and bicyclo[2.2.2]octadiene[13,14]. Strong mixing of levels of the same symmetry shifts the basis energies of the fragments to the positions in **13**. It is assumed that similar orbital interactions will prevail in quinoxaline **11**.

Whereas the suggested mechanism of energy transfer in **11** is reminiscent of the formation of exciplexes[15] and has been used to explain singlet-sensitization of **1** via **10**[2b], another possibility arises for the photorearrangement of quinoxaline **12**.

The formation of semibullvalene **17** is the first example of an aza-di-π-methane rearrangement that involves a quinoxaline chromophore. The photoreactivity of open-chained azahexa-2,5-dienes has been described[4,16], and very recently a report on the photorearrangement of pyrazinobarrelenes has been published[17]. It has been found that the quinoxaline chromophore in benzobarrelenes does not compete with benzene rings in vinyl-bridging reactions[18]. According to current views of the mechanism of bicyclic di-π-methane rearrangements[3,12] the photoreaction proceeds via excited triplet states. The basic mechanism seems also to be valid in the case of quinoxaline **12** (Scheme 6).

Scheme 6

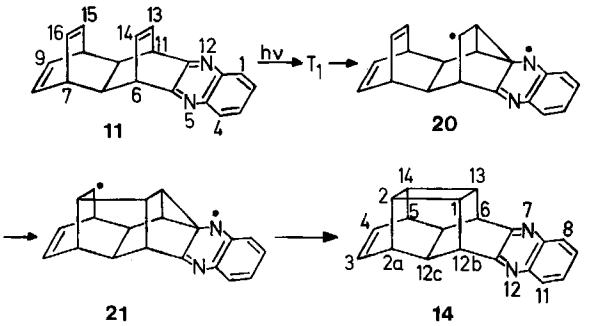


The quantum yield for singlet-triplet intersystem crossing has been determined for quinoxaline, and the value $\Phi_{ISC} = 0.27$ is nearly the same as that for naphthalene[9]. The experimental results (see above) for the conversion **12** → **17** are in agreement with the assumption of a triplet component in this photoprocess.

This propensity of the quinoxaline chromophor to participate in vinyl-bridging reactions, however, offers another interpretation for the formation of the cage product **14**. If, after excitation and intersystem crossing, quinoxaline **11** chooses the vinyl-bridging reaction coordinate, the first formed 1,4-diradical **20** will experience strong transannular bonding with the second isodrin-type π bond and immediately form diradical **21**. The decay to the ground state of **14** is obvious.

At the moment we are not able to distinguish between these alternatives and others. However, using intramolecular sensitizers, that categorically avoid vinyl-bridging, could give more experimental information.

Scheme 7



Conclusion

Quinoxaline chromophores have been found to sensitize intramolecularly [2π + 2π] cycloadditions. Energy transfer from $n_+\pi^*_+$- or $\pi\pi^*$-excited quinoxalines is not the only possible explanation since participation of the quinoxaline ring in aza-di-π-methane rearrangements has also been observed in these studies.

J. B. and R. B. gratefully acknowledge receipt of scholarships from the *Minerva Foundation*. The work done in Haifa was supported in part by the *Technion Fund for the Promotion of Research*. We also appreciate financial support by the *Deutsche Forschungsgemeinschaft*, the *Fonds der chemischen Industrie*, and the *BASF AG*.

Experimental

Melting points: SMD-20 Büchi apparatus, uncorrected. — ^{1}H NMR: Varian VXR 300, 300 MHz, Bruker WP 80, 80 MHz, Bruker WM 400, 400 MHz; ^{13}C NMR: Varian VXR 300, 75 MHz; tetramethylsilane internal standard. — IR: Perkin Elmer 710 B. — MS (70 eV): MAT 312 Finnegan and MAT 711 Varian. — UV: Cary Modell 15/50. — PE: UPG-200 Leybold-Heraeus instrument. — Irradiations: 200 W Osram HBO, 100 W Osram HBO high pressure mercury vapor lamps and a Canard-Hanovia 1000-W Hg-Xe lamp in a Schoeffel housing. — Preparative thin layer chromatography. Merck Art. 7749 silica gel 60 PF_{254} (70–230 mesh). — Elemental analyses: Institute of Pharmaceutical Chemistry of the University of Düsseldorf.

6,t-6a,7,10,t-10a,11-Hexahydro-r-6,c-11-etheno-c-7,c-10-ethenobenzo[b]phenazine (**11**): 0.150 g (0.71 mmol) of **7**[5] was dissolved in 2 ml of dichloromethane, and a solution of 0.076 g (0.71 mmol) of *o*-phenylenediamine in 2 ml of dichloromethane was added. The yellow-orange color of the solution disappeared quickly. After 1 h the solvent was rotoevaporated at 60°C to give 0.180 g (90%) of light yellow crystals, which were recrystallized yielding 0.070 g of colorless, crystals, m. p. 154–157°C (dec.) (cyclohexane). The compound is extremely sensitive to light. — IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3050, 2950, 2910, 1120, 1030, 990. — UV (dichloromethane): λ_{max} (lgε) = 316 nm (3.929) 241 (4.403). — ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 2H, 6a-, 10a-H), 3.53 (m, 2H, 7-, 10-H), 3.88 (t, 2H, 6-, 11-H), 6.06 (t, 2H, 15-, 16-H), 6.11 (t, 2H, 13-, 14-H), 6.45, (t, 2H, 8-, 9-H), 7.73 (m, 4H, 1-, 2-, 3-, 4-H). — MS (70 eV): *m/z* (%) = 284 (66) [M^+], 205 (100), 206 (87) [$M^+ - C_6H_6$].

$C_{20}H_{16}N_2$ (284.4) Calcd. C 84.48 H 5.67 N 9.85
Found C 84.55 H 5.70 N 9.80

1,2,t-2a,5,t-5a,6,t-12b,t-12c-Octahydro-r-1,c-6:c-2,c-5-ethanediylideneindeno[1,7-ab]phenazine (**14**): In a 50-ml duran-glas flask a solution of 0.070 g (0.25 mmol) of **11** in 20 ml of absol. dichlorome-

thane was irradiated with a 150-W mercury high pressure lamp for 1 h. Then the solvent was distilled off in vacuo and the solid recrystallized to give an almost quantitative yield. Further purification is performed by high vacuum sublimation (130–150°C/10^{-4} Torr). m.p. 228–230°C (dec. and sublimatin) (cyclohexan). – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (=CH), 2960 (–CH), 1495, 1395, 1210, 1030, 920, 850, 815, 790, 775, 765, 750, 690. – UV (dichloromethane): λ_{max} (lg ε) = 318.5 nm (3.944), 240 (4.356). – ^{1}H NMR ($CDCl_3$): δ = 2.06 (s, 2H, 5a-, 12c-H), 2.54 (m, 2H, 2-, 14-H), 2.81 (m, 2H, 1-, 13-H), 2.87 (m, 2H, 2a, 5-H), 3.33 (m, 2H, 6-, 12b-H), 6.35 (m, 2H, 3-, 4-H), 7.68, 8.06, (m, 4H, 8-, 9-, 10-, 11-H). – ^{13}C NMR ($CDCl_3$): δ = 39.39 (C-1, -13), 36.70 (C-2, -14), 36.67 (C-2a, -5), 43.50 (C-5a, -12c), 44.97 (C-6, -12b), 128.52, 128.60 (C-8, -9, -10, -11), 130.97 (C-3, -4), 141.95 (C-7a, -11a), 156.52 (C-6a, -12a). – MS (70 eV): *m/z* (%) = 284 (100) [M^+], 205 (52), 206 (30) [$M^+ - C_6H_6$].

$C_{20}H_{16}N_2$ (284.4) Calcd. C 84.48 H 5.67 N 9.85
Found C 84.50 H 5.67 N 9.90

6,8,9,10,11,13,15,16-Octachloro-6,t-6a,7,12,t-12a,13-hexahydro-r-6,c-13:c-7,c-12-diethenonaphtho[2,3-b]phenazine (**15**): A mixture of 2.06 g (7.06 mmol) of tetrachlorobenzobarrelene (synthesis ref.[19]) and 1.7 g (6.91 mmol) of tetrachloro-*o*-benzoquinone in 5 ml of absol. toluene was heated with stirring at 80–95 C under dry nitrogen. Exposure to light has to be avoided carefully. After about 120 min a brightening of the dark red solution occured. Heating was continued for additional 3 h. Then the precipitate was collected by filtration under nitrogen, washed with 8 ml of absol. pentane and afterward with absol. ether. The yellow crystalls were dried in a nitrogen gas flow yielding 2.42 g of an intermediary product which was extremely sensitive to moisture and light. 0.205 g (0.381 mmol) of the product was dissolved in 2 ml of dichloromethane and a solution of 0.045 g (0.416 mmol) of *o*-phenylenediamine in 2 ml of dichloromethane was added. Within 20 min the yellow color of the mixture had disappeared completely. After standing for about 12 h thc solution was filtered over a silica gel packed glas-suction filter. Evaporation of the solvent afforded a residue which was recrystallized to give 0.120 g (40%) of light tan crystals, which became colorless after washing with a small quantity of dry ether, m.p. 262–265°C (dec.) (ether/dichloromethane). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (=CH), 2990, 2910 (–CH), 1590, 1500, 1470, 1430, 1380, 1360, 1220, 1210, 1200, 1155, 1125, 1115, 1070, 1030, 1020, 980, 915, 805, 760, 715. – UV (methanol): λ_{max} (lg ε) = 317 nm (3.875).^{1}H NMR ($CDCl_3$): δ = 2.65 (s, 2H, 6a-, 12a-H), 5.05 (m, 2H, 7-, 12-H), 6.64 (t, 2H, 17-, 18-H), 7.84 (m, 4H, 1-, 2-, 3-, 4-H). – MS (70 eV): *m/z* (%) = 610 (35) [M^+], 272 (100).

$C_{24}H_{10}Cl_8O_2$ (610.0) Calcd. C 53.59 H 1.87 N 4.59
Found C 53.63 H 1.92 N 4.63

1,3,4,5,6,8,14b,15-Octachloro-1,2,t-2a,7,t-7a,8,14b,t-14c-Octahydro-r-1,c-8:c-2,c-7-ethanediylidenebenz[4,5]indeno[1,7-a,b]phenazine (**16**): 0.015 g (0.025 mmol) of **15** was dissolved in 0.8 ml of $CDCl_3$ in a NMR tube. The solution was irradiated with a 1000-W mercury/xenon lamp through a KG-1 heat filter (λ_{irr} >380 nm). The reaction was controlled by ^{1}H NMR and was complete after 15 min. After removal of the solvent the light-tan residue was washed with a small quantity of cyclohexane to give colorless crystals in quantitative yield. m.p. >300°C. – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2990 (C–H), 1490, 1440, 1395, 1390, 1380, 1320, 1295, 1240, 1210, 1175, 1020, 1005, 980, 910, 850, 775, 760 sh, 635. – UV (methanol): λ_{max} (lg ε) = 319 nm (3.903). – ^{1}H NMR ($CDCl_3$): δ = 2.65 (s, 2H, 7a-, 14c-H), 5.15 (m, 2H, 2a-, 7-H), 3.05 (t, 2H, 2-, 16-H), 8.07 (m, 4H, 10-, 11-, 12-, 13-H). – MS (70 eV): *m/z* (%) = 610 (100) [M^+], 266 (83).

$C_{24}H_{10}Cl_8O_2$ (610.0) Calcd. C 53.59 H 1.87 N 4.59
Found C 53.60 H 1.82 N 4.55

1,4-Dihydro-1,4-ethanophenazine (**12**): To a solution of 0.400 g (1.92 mmol) of bicyclo[2.2.2]oct-2-ene-5,6-dione[11] in 100 ml of dichloromethane 0.382 g of *o*-phenylenediamine (3.53 mmol) was added. After stirring at room temp. for 2 h the solvent was removed in vacuo. The residue was taken up in ether, and the solution washed with a small quantity of hydrochloric acid and with saturated aqueous $NaHCO_3$. After drying with Na_2SO_4 the solvent was removed under reduced pressure to give a solid which was recrystallized yielding 0.459 g (75%) of **12**, m.p. 145–147°C (hexane). Purification was possible by column chromatography as well (silica gel, ethyl acetate/hexene 2:1). – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2950, 1640, 1500, 1310. – UV (methylcyclohexane): λ_{max} (lg ε) = 314 nm (3.882), 307 (3.810) (sh), 302 (3.765) (sh), 237 (4.423). – ^{1}H NMR ($CDCl_3$): δ = 1.8 (m, 4H, 11-, 12-H); 4.2 (m, 2H, 1-, 4-H), 6.6 (m, 2H, 2-, 3-H); 7.7 (m, 2H, 7-, 8-H); 8.0 (m, 2H, 6-, 9-H). – ^{13}C NMR ($CDCl_3$): δ = 24.2 (C-11, -12); 42.2 (C-1, -4), 128.5 (C-6, -7, -8, -9), 134.4 (C-2, -3); 140.3 (C-5a, -9a); 158.0 (C-4a, -10a). – MS (70 eV): *m/z* (%) = 208 (57) [M^+], 180 (100), 153 (5), 103 (10).

$C_{14}H_{12}N_2$ (208.263) Calcd. 208.1000 Found 208.0999 (MS)

7,8,9,10-Tetrahydro-6,9,10-metheno-6H-cyclohepta[b]quinoxaline (**17**): 0.073 g (0.35 mmol) of **12** and 0.160 g *m*-methoxyacetophenone were dissolved in 62 ml of dry hexane in a quartz cell. The solution was carefully purged with argon and irradiated with a 1000-W mercury/xenon high pressure lamp. During the reaction a weak gas flow of argon was maintained. To follow the reaction thin layer plates (silica gel, ethyl acetate/hexane 2:1) were used. After 12 h irradiation time the reaction was interrupted, the solution filtered and the solvent removed in vacuo. The residue was a mixture of starting compound, product, sensitizer, and decomposed material. Separation by preparative thin layer chromatography (silica gel, ethyl acetate/hexane 2:1, 0.040 g per 200 × 200 mm plate) yielded 0.015 g (20%) of the expected product (third fraction) and 0.0140 g (19%) of the starting compound (second fraction). The sensitizer was recovered (first fraction). All fractions were carefully eluted with chloroform. More concentrated solutions of **12** led to remarkably bad yields. On the contrary, irradiation of a 1.3 × 10^{-4} M of **12** in hexane afforded 70% of the product as calculated from UV spectra. M.p. 105°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2960, 1570, 1410, 1330. – UV (methylcyclohexane): λ_{max} (lg ε) = 335 nm (3.886), 325 (4.013), 320 (4.050), 313 (3.948), (cyclohexane): 250 (4.381), 244 (4.445). – ^{1}H NMR ($CDCl_3$): δ = 1.27 (dddd, 1H, 8-H_n), 1.97 (dd, 1H, 7-H_n), 2.05 (ddd, 1H, 8-H_x), 2.32 (ddt, 1H, 9-H), 2.46 (ddt, 1H, 7-H_x), 2.70 (ddd, 1H, 10-H), 3.06 (dt, 1H, 12-H), 3.74 (t, 1H, 6-H), 7.6 (m, 2H, 2-, 3-H), 7.95 (m, 2H, 1-, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 23.8 (C-8); 32.6 (C-9); 33.0 (C-10); 36.8 (C-12); 42.6 (C-7), 47.7 (C-6); 128.0, 128.4, 128.6, 128.7 (C-1, -2, -3, -4); 140.9, 141.5, (C-4a, -11a); 160.5, 164.7 (C-5a, -10a). – MS (70 eV): *m/z* (%) = 208 (100) [M^+], 180 (59), 167 (18).

$C_{14}H_{12}N_2$ (208.263) Calcd. 208.1000 Found 208.0999 (MS)

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[1] Dedicated to Professor *Kurt Schaffner* on the occasion of his 60th birthday.
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