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11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene: A Probe for the Heavy Atom Effect in Solid State Photoreactions

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Abstract: The photochemistry of title compound **2** and its hydrogen halide salts was investigated in solution and in the solid state. In the solid state the halide ions were shown to cause a heavy atom effect that was not observed in solution. The orientation of the halide ions towards the chromophore was determined on the basis of the corresponding structures in the solid state as determined by X-ray crystallography. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Photoreactions carried out in the solid state show remarkable differences compared to those conducted in solution[1] and provide penetrating insights into the geometric requirements and the steric course of well-established photoreactions such as [2+2]-photocycloaddition,[2] the Norrish Type II reaction[3] and the Type B reaction of enones.[4] However, a recurring problem in solid state photochemistry is the achievement of efficient triplet energy sensitization or quenching. In solution photochemistry, the sensitizer or quencher is simply added to the reaction mixture, whereas in the solid state, these experiments require a co-crystallization of the two components, which is observed only infrequently.[5] We were able to overcome this obstacle by introducing the concept of the "ionic auxiliary" in solid state photochemistry.[6] In this approach, the chromophore under investigation is linked to a sensitizer or a metal ion by simple salt formation, and irradiation of these salts in the solid state showed that sensitization and heavy atom effects[7] could be achieved that were unique to this medium.[6]

To extend this methodology to other heavy atoms, we became interested in halide salts as a means of promoting triplet energy processes in the solid state, i.e., to investigate whether halide ions could serve as heavy atoms during irradiation of their corresponding salts with chromophores. In this respect, substituted ethenoanthracenes (dibenzobarrelenes) are ideal chromophores,[8] since their photochemistry is multiplicity-dependent. Upon direct irradiation, these compounds react from the first excited singlet state to give dibenzocyclooctatetraenes, whereas triplet sensitization leads to the formation of dibenzosemibullvalenes *via* the di-π-methane rearrangement.[8] In the present paper we describe the synthesis of an amino-substituted ethenoanthracene, namely 11,12-bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene (**2**), the preparation of its hydrogen halide salts and the investigation of the photochemistry of these materials in the solid state and solution.

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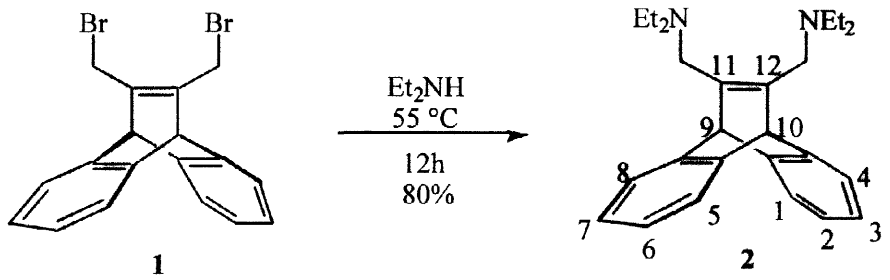
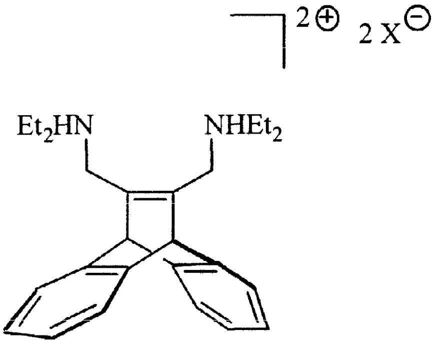


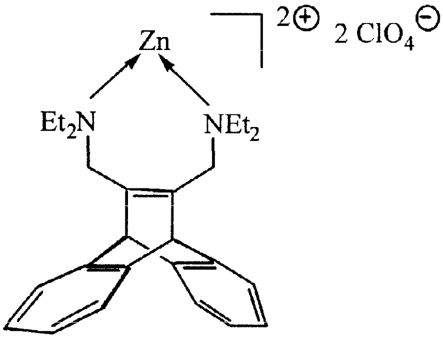
Scheme 1. Synthesis of diamine **2**

RESULTS

Synthesis. Ethenoanthracene **2** was synthesized from the known 11,12-bis(bromomethyl)ethenoanthracene **1**[9] and diethylamine (Scheme 1).[10] The bis(hydrochloride) **2·(HCl)$_2$** and the bis(hydrobromide) **2·(HBr)$_2$** were synthesized by the reaction of ethenoanthracene **2** with gaseous HCl and HBr, respectively, and the bis(hydroiodide) **2·(HI)$_2$** was obtained from salt **2·(HCl)$_2$** by ion exchange chromatography. Diamine **2** and its bis-hydrohalide salts were identified by spectroscopic analyses and by X-ray crystallography. In order to determine whether complexed metal ions could act as heavy atoms, the zinc complex **2·Zn** was synthesized from the reaction between Zn(ClO$_4$)$_2$(H$_2$O)$_6$ and **2**.[11]



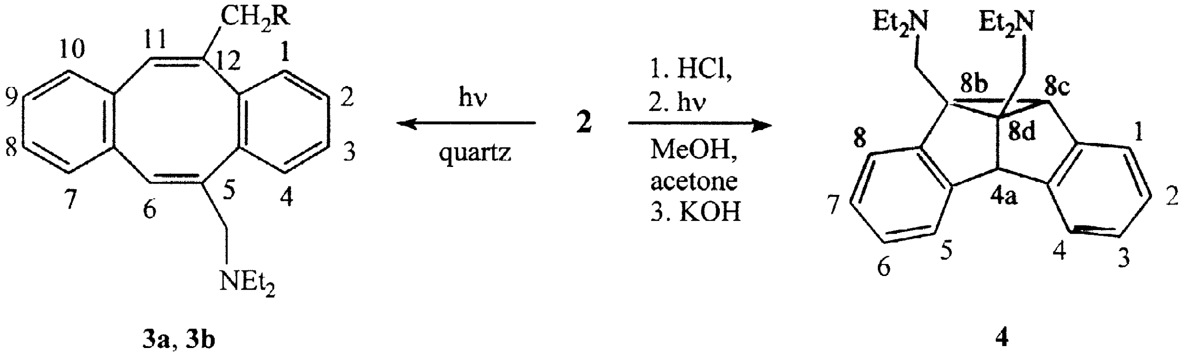
2·(HX)$_2$
(X = Cl, Br, I)



2·Zn

Solution Photolyses. Direct irradiation of diamine **2** in *n*-pentane or benzene through quartz glass gave the dibenzocyclooctatetraenes **3a** and **3b** in an 8:1 ratio, whereas in methanol or acetonitrile a ratio of **3a**:**3b** = 3:1 was observed (Scheme 2). Dibenzocyclooctatetraene **3b** could not be isolated, and the amine **3a** was obtained in low yield by acidification of the reaction mixture followed by column chromatography of the quarternary ammonium salts and subsequent treatment with base. Attempts to obtain the triplet dibenzosemibullvalene photoproduct **4** from irradiation of diamine **2** in the presence of sensitizer ketones such as acetone, benzophenone, acetophenone, *p*-

methoxyacetophenone, xanthen-9-one and thioxanthen-9-one were not successful. In each case, a complex reaction mixture was formed from which the dibenzosemibullvalene **4** could not be isolated. Instead, when compound **2** was photolyzed in the presence of benzophenone, benzopinacol could be isolated from a complex reaction mixture.[12] However, when the bis-hydrochloride salt of dibenzobarrelene **2** was irradiated through Pyrex glass (λ > 290 nm) in methanol/acetone (1:1), dibenzosemibullvalene **4** was isolated in 61% yield after basic workup and column chromatography (Scheme 2).



Scheme 2. Photolysis of diamine **2**: **3a**: R = NEt_2; **3b**: R = H

When dibenzobarrelenes **2·(HCl)$_2$** and **2·(HBr)$_2$** were photolyzed in methanol through a Vycor filter,[13] followed by basic workup, cyclooctatetraene **3b** was detected by analytical gas chromatography as the main product along with diamines **3a** and **4** and other unidentified byproducts. Moreover, cyclooctatetraene **3a** was isolated by column chromatography in 17% yield from the photoreaction mixture of dibenzobarrelene **2·(HCl)$_2$**. Irradiation of salt 2·(HI)$_2$ in methanol resulted in the formation of cyclooctatetraenes **3a** and **3b** in 35% and 23% yield, respectively, and semibullvalene **4** was not detected. The photolysis of the zinc complex of diamine **2** in methanol through quartz glass led to the formation of cyclooctatetraene **3a** in nearly quantitative yield as was determined by gas chromatography. The solution phase photolysis results are compiled in Table 1. The structural assignments of cyclooctatetraenes **3a** and **3b** and dibenzosemibullvalene **4** are based mainly on the mass spectrometric and ^{1}H and ^{13}C NMR spectroscopic data of isolated pure samples.

Solid State Photolyses. We next investigated the solid state photoreactivity of ethenoanthracene **2**, and strikingly, we observed that this chromophore is photoinert in the solid state. However, the salts of compound **2** do react in the solid state. Hydrochloride **2·(HCl)$_2$** was irradiated through quartz for 5 h (17% conversion) and after basic workup, semibullvalene **4** was identified as the sole product. The same product was identified in the solid state photolysis of hydrobromide **2·(HBr)$_2$**. The hydroiodide **2·(HI)$_2$** yielded semibullvalene **4**, too, in the course of the photoreaction (24% conversion, 79% of semibullvalene **4**), but cyclooctatetraene **3b** was also formed in 21% yield as indicated by gas chromatography. The zinc complex **2·Zn** was photolyzed in the solid state to give **3b** as the main product with semibullvalene **4** as a byproduct. The solid state photolysis results are summarized in Table 1.

Table 1.

Compound	Medium	Conversion (%)	**3a** (%)[a]	**3b** (%)[a]	**4** (%)[a]
2	*n*-pentane (quartz)	100	89	11	–
2	methanol (quartz)	100	75	25	–
2	solid (quartz)	no reaction	–	–	–
2·HCl	methanol/acetone (1:1) (pyrex)	100	–	–	>99
2·HCl	methanol (vycor)	100	6	28	<1
2·HCl	solid (quartz)	17	–	–	>99
2·HBr	methanol (vycor)	78	4	34	3
2·HBr	solid (quartz)	13	–	–	>99
2·HI	methanol (vycor)	31	35	23	–
2·HI	solid (quartz)	24	–	21	79
2·Zn	methanol (vycor)	30	>99	–	–
2·Zn	solid (quartz)	26	–	85	15

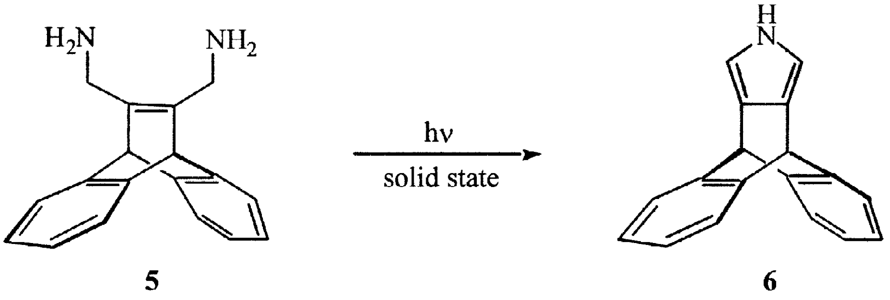
[a] Product ratios were determined by analytical gas chromatography by comparison with authentic samples. Yields were calculated relative to the corresponding conversion. Remaining components are unidentified by-products.

DISCUSSION

Whereas cyclooctatetraene **3a** is the expected singlet state photoproduct of compound **2**, the formation of photoproduct **3b** presumably results from a competing photo-induced cleavage of the C–N-bond of one diethylaminomethyl group giving a stabilized allylic radical, which further abstracts a hydrogen atom from the solvent.[14] This assumption is in agreement with the observation that the amount of cyclooctatetraene **3b** increases in solvents such as methanol or acetonitrile which possess abstractable hydrogen atoms. It was found that independent photolysis of photoproduct **3a** does not yield cyclooctatetraene **3b**, from which it may be concluded that the C–N-bond cleavage takes place either in the starting material or during the course of cyclooctatetraene formation.

The failed attempts to sensitize the photoreaction with ketones seems to be the result of a photo-induced electron transfer between the amine and the ketones giving rise to the reduction of the carbonyl group,[15] i.e. benzopinacol formation, and this reaction competes with the di-π-methane rearrangement to such a degree that formation of semibullvalene **4** becomes negligible. Solution phase irradiation of the salts of diamine **2** showed an inverse situation. Whereas direct irradiation of the salts resulted in the formation of a manifold of inseparable products, the sensitized reaction proceeded in a very clean manner. The photo-induced redox reaction was not observed, presumably because protonation of the amino groups prevents electron transfer to the ketone. The fact that cyclooctatetraene **3b** is a major product in the direct irradiation leads us to conclude that the photo-induced cleavage of C–N-bonds is even more important in ammonium salts than in amines. Such fragmentations of ammonium salts are known,[16] however this field of chemistry still needs to be investigated more systematically.

A particularly interesting observation in the course of our investigations was the photoinertness of diamine **2** in the solid state. This is in sharp contrast to the closely related primary diamine **5**, which cyclizes upon solid state irradiation to give the "pyrroloanthracene" **6** (Scheme 3).[17] Furthermore, almost all dibenzobarrelene derivatives that have been studied exhibit photoreactivity in the solid state.[8,18] To rationalize this observation, we carried out an X-ray crystal structure analysis of compound **2** (Figure 1).[19] Suitable crystals were obtained by crystallization from acetone. In the solid state, both diethylaminomethyl substituents, which are oriented towards the same aromatic ring of the anthracene moiety, have very close contacts with their environment (Figure 1). The restricted freedom of movement of compound **2** is evidenced by the crystal density, which is 2.91 x 10^{-3} mol/cm^{-3} compared to 2.02 x 10^{-3} mol/cm^{-3}, 2.57 x 10^{-3} mol/cm^{-3} and 2.46 x 10^{-3} mol/cm^{-3} for the closely related dibenzobarrelenes **2·(HCl)$_2$**, **2·(HBr)$_2$** and **2·(HI)$_2$**,[19] respectively, which are photoactive in the solid state. Direct irradiation of diamine **2** is thought to cause an initial [2+2]-photocycloaddition, so that both carbons C-11 and C-12 have to move close to the aromatic ring in the first reaction step. The "anchored" substituents at the vinyl group apparently prevent this movement, because they are locked within the lattice environment.



Scheme 3

The zinc atom in the complex **2·Zn** does not cause a measurable heavy atom effect in solution, presumably due to the relatively small atomic number of zinc; however, in the solid state there is a small heavy atom effect from the zinc atom. Such an effect from the perchlorate can be excluded, since independent studies have shown that the bis(hydroperchlorate) salt of **2** does not give any triplet photoproduct in the solid state.[20] There is almost no triplet state photoproduct formed upon irradiation of the hydrohalide salts of diamine **2** in solution, which can be explained by the formation of separated ion pairs in the polar solvent. Apparently, an external heavy atom effect is no longer effective through the distances between anion and cation. This observation is in good agreement with solution photolysis results from ionic chromophores with sensitizers or alkali metal counterions.[21] In this respect, solid state photolysis is superior to solution reactivity, because in the crystal the heavy atom and the chromophore are held close to each other by attractive ionic interactions, thus providing an efficient intersystem crossing in the course of the photoreaction. The salts **2·(HCl)₂**, **2·(HBr)₂** and **2·(HI)₂** react in the solid state upon irradiation and yield the triplet product **4**; in the case of the hydrochloride and hydrobromide salt, exlusively.

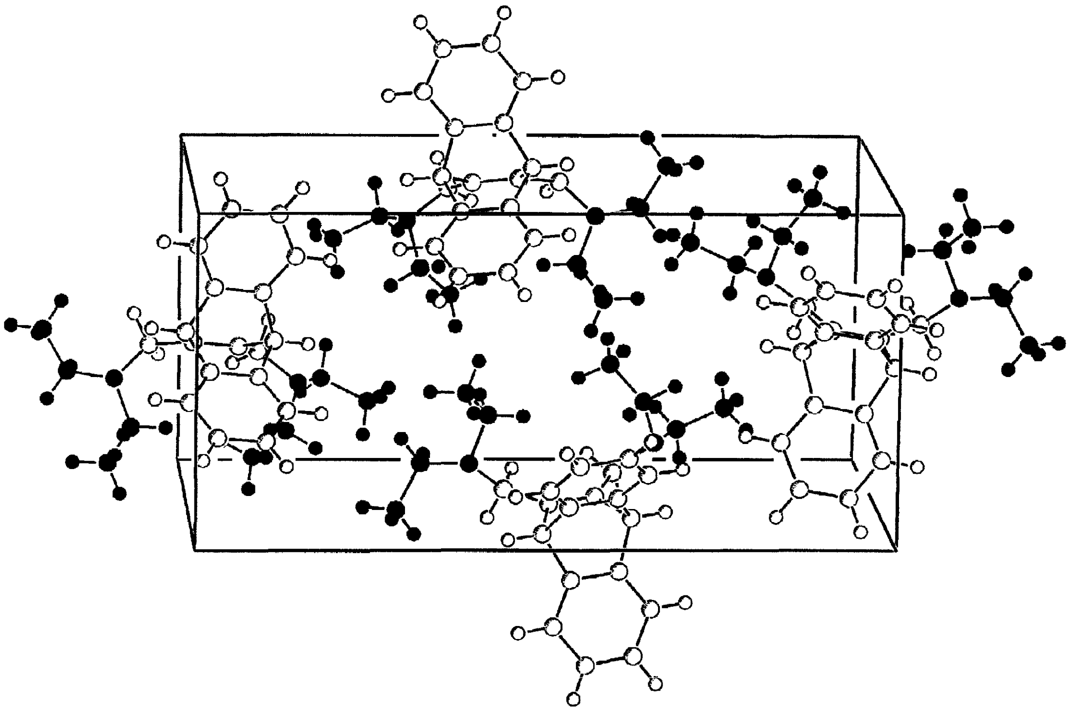


Figure 1. Structure of diamine **2** in the solid state (diethylamino groups are shaded)

To investigate the geometric relationship between the heavy atom and the chromophore further, we determined the crystal structures of these salts.[19] The overall results are summarized in Table 2. Although the benzo rings of the ethenoantracene may also be relevant for heavy atom induced intersystem crossing, we propose that the vinyl function is the more important locus of initial excitation in triplet energy transfer in the solid state photoreaction of ethenoanthracenes.[21a] Therefore, the distance **d** between the halide ion and the center of mass of the vinyl group is taken as the relative measure for the studies reported herein. Some evidence for this assumption is provided by the observation that the sensitized photoreaction of benzobarrelenes gives mainly products resulting from vinyl-vinyl bridging in the di-π-methane rearrangement.[22] We further define the angles α and β to characterize the orientation of the halide ion to the vinyl chromophore (Figure 2). For this purpose we use the center of mass, Y, of the C11–C12-bond as the reference point. Thus, α is defined as the angle between the halide ion X, Y and C11, and β is the torsion angle X-Y-C11-C9.

Figure 2. Definition of distance **d** and the angles α and β; X = Cl^-, Br^- and I^-

Table 2. Geometric parameters **d**, α and β derived from the X-ray analysis.

		d [Å]	C···X [Å][a]	α [°]	β [°]
2·$(HCl)_2$:	Cl(1)	4.63	3.51	85	159
	Cl(2)	4.93		28.5	58
2·$(HBr)_2$:	Br(1)	4.89	3.66	91	168
	Br(2)	4.79		26	87
2·$(HI)_2$:	I(1)	5.00	3.90	89	167
	I(2)	4.96		28	86.5

[a] C···X = Sum of the van der Waals radius for carbon and the ionic radius of the halide X.[23]

It can be seen from the results that there is no significant difference in the geometric relationship between the cations and anions of the three hydro halide salts in the solid state. For each compound there is one halide ion with α ≅ 90° and β ≅ 160° and one halide ion with α ≅ 28° and β ≅ 80°, respectively. The β parameter, however, deviates slightly in **2·$(HCl)_2$**. With an increasing ionic radius of the halide ion, the distance **d** between the halide ion and the vinyl chromophore increases to nearly the same extent that the ionic radius of the halide ion increases, so that the **d** parameters are also relatively comparable. In each case, this distance **d** is significantly longer than the sum of the van der Waals radius of the carbon atom and the ionic radius of the respective halide ion. In the case of the hydrochloride and hydrobromide salts of diamine **2**, the triplet state photoproduct is formed exlusively, and we therefore conclude that a distance of ca. 4.80Å provides an effect strong enough to totally suppress the singlet state photoreaction in these systems. However, a slightly greater separation of 4.95Å between heavy atom and chromophore in **2·$(HI)_2$** apparently decreases the heavy atom effect, and a considerable amount of singlet state photoproduct is formed upon irradiation in the solid state. Since the difference between this distance and the one found for the bromide salt **2·$(HBr)_2$** is smaller than the difference between the ionic radii of iodide and bromide (0.22Å),[23] and iodide as the heavier element is assumed to cause a more effective heavy atom effect,[7] it is not clear from the geometric parameters why photolysis of **2·$(HI)_2$** also yields singlet state photoproducts in the solid state. From these observations it may be tentatively concluded that it is not the *relative* distance of the heavy atom to the chromophore, i.e. the **d**/C···X ratio, but the *absolute* distance that governs the efficacy of the heavy atom effect. However, more experimental results are necessary to verify (or disprove) this hypothesis. Interestingly, in the solid state photoreaction of β,γ-unsatutrated ketones, even shorter distances between cationic heavy atoms and the chromophore give mixtures of singlet and triplet state photoproducts in the solid state,[21b] which confirms recent results in zeolites that show a higher sensitivity of the di-π-methane rearrangement towards heavy atoms compared to the oxa-di-π-methane rearrangement.[24] In summary, it seems that there is not yet enough data available for a reliable correlation of the efficiency of the heavy atom effect with solid state structure, and studies in this field represent exploratory work, so far. However, we have demonstrated that compared to photolysis in solution, halide ions serve as efficient heavy atoms in the solid state photochemistry of amine-substituted dibenzobarrelenes, and by investigating the geometric parameters in these systems, more data for the discussion of this effect is provided.

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EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AC 200 (200 MHz) instrument, and ^{13}C NMR spectra were recorded on Bruker AC 200 (50.3 MHz) or Varian XL-300 (75.4 MHz) spectrometers. C_q, CH, CH_2 and CH_3 were determined using the APT pulse sequence. ^{1}H NMR chemical shifts refer to $\delta_{TMS} = 0.0$. ^{13}C NMR chemical shifts refer to solvent signals ($CDCl_3$: $\delta = 77.0$, DMSO-d_6: $\delta = 39.5$, CD_3OD: $\delta = 49.0$). IR spectra were recorded on a Perkin Elmer 1710 FT infrared spectrometer. UV spectra were recorded on a Perkin Elmer Lambda-4B UV/VIS spectrometer. Mass spectra were recorded on a Kratos MS 80 instrument. Melting points are uncorrected. Elemental analyses were performed by Mr. P. Borda at the University of British Columbia, Department of Chemistry. Photoreactions were performed with a 450-W Hanovia medium-pressure mercury lamp at room temperature.

11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene (**2**): A solution of 6.301 g (15 mmol) of dibromide **1**[9] was refluxed in 50 mL of diethylamine for 12 h. After removal of the solvent, the crude reaction mixture was dissolved in diethyl ether and washed with 0.1 M KOH and water. After separation of the organic layer, the solvent was evaporated and the remaining brown solid was redissolved in *n*-hexane and passed through aluminium oxide (neutral) to give 4.491 g (12 mmol, 80%) of **2** as a ^{1}H NMR spectroscopically pure white solid. For further purification, compound **2** was recrystallized from dichloromethane/*n*-hexane, mp 70–71 °C. UV (CH_3OH): λ_{max} (log ε) = 272 nm (3.59), 280 (3.37). ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $^3J = 7$ Hz, 12 H, CH_3), 2.25 (q, $^3J = 7$ Hz, 8 H, NCH_2), 3.11 (s, 4 H, CH_2N), 5.26 (s, 2 H, 9-H, 10-H), 6.92, 7.27 (AA'BB'-system, 8 H, ar-H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 11.8 (CH_3), 46.4 (CH_2), 51.9 (CH_2), 53.4 (C-9, C-10), 122.5 (ar-CH), 124.1 (ar-CH), 144.5 (C_q), 146.7 (C_q). MS (EI, 70 eV), *m/z* (%): 374 [M^+] (1), 301 [$M^+ - HNEt_2$] (55), 178 [$C_{14}H_8^+$] (28), 123 [$Et_2NC_4H_3$] (100). Anal. calcd for $C_{26}H_{34}N_2$ (374.57) C: 83.37, H: 9.15, N: 7.48; found C: 83.14, H: 9.29, N: 7.44.

11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene-bis(hydrochloride) (**2·(HCl)$_2$**) and *11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene-bis(hydrobromide)* (**2·(HBr)$_2$**): Gaseous hydrochloric acid and hydrobromic acid, respectively, prepared from the reaction of H_2SO_4 and the corresponding sodium halide, was bubbled through a solution of diamine **2** in diethyl ether and a white solid precipitated immediately. The solid was collected on a sintered glass funnel and washed twice with diethyl ether to give ^{1}H NMR spectroscopically pure salts **2·(HCl)$_2$** and **2·(HBr)$_2$**, respectively, as white hygroscopic solids. **2·(HCl)$_2$**: mp 155–160 °C. IR (KBr): v;˜ = 2658 cm^{-1} (br, NH$^+$). UV (CH$_3$OH): λ_{max} (log ε) = 270 nm (3.37), 278 (3.51). ^{1}H NMR (DMSO-*d*$_6$) δ 1.28 (t, ^3J = 7 Hz, 12 H, CH$_3$), 2.90 (m, 8 H, NCH$_2$), 4.18 (br d, ^3J = 6 Hz, 4 H, CH$_2$N), 6.24 (s, 2 H, 9-H, 10-H), 7.09, 7.56 (AA'BB'-System, 8 H, ar-H), 11.30 (br s, 2 H, NH). ^{13}C NMR (50.3 MHz, DMSO-*d*$_6$) δ 8.4 (CH$_3$), 46.4 (CH$_2$), 50.4 (CH$_2$), 51.9 (C-9, C-10), 123.4 (ar-CH), 124.9 (ar-CH), 144.6 (C$_q$), 144.8 (C$_q$). MS (FAB(+), thioglycerol), *m/z* (%): 375 [M$^+$ + H] (100). **2·(HBr)$_2$**: mp 162–165 °C. IR (KBr): v;˜ = 2695 cm^{-1} (br, NH$^+$). UV (CH$_3$OH): λ_{max} (log ε) = 270 nm (3.32), 278 (3.44). ^{1}H NMR (DMSO-*d*$_6$) δ 1.28 (t, ^3J = 7 Hz, 12 H, CH$_3$), 3.00 (m, 8 H, NCH$_2$), 4.28 (d, ^3J = 6 Hz, 4 H, CH$_2$N), 5.95 (s, 2 H, 9-H, 10-H), 7.13, 7.56 (AA'BB'-System, 8 H, ar-H), 9.88 (br s, 2 H, NH). ^{13}C NMR (50.3 MHz, CD$_3$OD) δ 9.4 (CH$_3$), (one CH$_2$ signal hidden under MeOD), 52.8 (CH$_2$), 54.3 (C-9, C-10), 124.7 (ar-CH), 126.7 (ar-CH), 145.2 (C$_q$), 1446.7 (C$_q$). MS (FAB(+), thioglycerol), *m/z* (%): 375 [M$^+$ + H] (30). Anal. calcd for $C_{26}H_{36}N_2Br_2$ (536.39) C: 58.22, H: 6.76, N: 5.22; found C: 58.01, H: 6.74, N: 5.14.

11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene-bis(hydroiodide) **2·(HI)$_2$)**: A column fitted with ion exchange resin (Malinckrodt, Amberlite IRA-410 C.P.) was eluted with a saturated solution of NaI in water several times. After the resin was washed with methanol, 400 mg (0.89 mmol) of **2·(HCl)$_2$** was slowly passed through the column with methanol and the collected eluant was evaporated to dryness. Crystallization from methanol gave 450 mg (0.71 mmol, 80%) of **2·(HI)$_2$** as white crystals that turn yellow upon extended exposure to air, mp 228–232 °C (dec.). IR (KBr): v;˜ = 2657 cm^{-1} (br, NH$^+$). UV (CH$_3$OH): λ_{max} (log ε) = 270 nm (3.22), 278 (3.36). ^{1}H NMR (DMSO-*d*$_6$) δ 1.25 (t, ^3J = 7 Hz, 12 H, CH$_3$), 3.02 (m, 8 H, NCH$_2$), 4.28 (d, ^3J = 5 Hz, 4 H, CH$_2$N), 5.74 (s, 2 H, 9-H, 10-H), 7.13, 7.53 (AA'BB'-System, 8 H, ar-H), 9.88 (br s, 2 H, NH). ^{13}C NMR (50.3 MHz, CD$_3$OD) δ 8.7 (CH$_3$), 46.7 (CH$_2$), 49.9 (CH$_2$), 51.7 (C-9, C-10), 123.4 (ar-CH), 125.1 (ar-CH), 144.1 (C$_q$), 144.6 (C$_q$). MS (FAB(+), thioglycerol), *m/z* (%): 375 [M$^+$ + H] (30). Anal. calcd for $C_{26}H_{36}N_2I_2$ (630.39) C: 49.54, H: 5.76, N: 4.44; found C: 49.72, H: 5.82, N: 4.31.

11,12-Bis(diethylaminomethyl)-9,10-dihydro-9,10-ethenoanthracene-zinc(II)diperchlorate (**2·Zn**): A solution of 54 mg (0.14 mmol) of diamine **2** and 54 mg (0.14 mmol) of $Zn(ClO_4)_2(H_2O)_6$ in 25 mL of methanol were stirred for 12 h. The solvent was removed *in vacuo* and the remaining residue was redissolved in 4–5 mL of hot methanol. The insoluble precipitate was filtered off hot and crystallization at –4 °C gave 61 mg (0.09 mmol, 64%) of **2·Zn** as a white solid. mp 273–282 °C (dec.). UV (CH$_3$OH): λ_{max} (log ε) = 271 nm (3.40), 279 (3.58). ^{1}H NMR (DMSO-*d*$_6$) δ 1.10 (br t, 12 H, CH$_3$), 2.65 (br q, 8 H, NCH$_2$), 3.73 (br s, CH$_2$N), 5.44 (br s, 2 H, 9-H, 10-H), 7.07, 7.44 (AA'BB'-System, 8 H, ar-H). ^{13}C NMR (50.3 MHz, CD$_3$OD) δ 9.8 (CH$_3$), 45.4 (CH$_2$), 51.9 (CH$_2$), 53.8 (C-9, C-10), 123.0 (ar-CH), 124.7 (ar-CH), 145.0 (C$_q$), 145.4 (C$_q$). MS (EI, 70 eV), *m/z* (%): 375 [M$^+$ – Zn(ClO$_4$)$_2$ + H] (55). (FAB(+), thioglycerol), *m/z* (%): 375 [M$^+$ – Zn(ClO$_4$)$_2$ + H] (30). Anal. calcd for $C_{26}H_{34}Cl_2N_2O_8Zn$ (710.91) C: 48.88, H: 5.36, N: 4.38; found C: 48.82, H: 5.47, N: 4.24.

5,12-Bis(diethylaminomethyl)-dibenzo[ae]cyclooctene (**3a**): A solution of 283 mg (0.76 mmol) of diamine **2** in 300 mL of *n*-pentane was irradiated in a quartz immersion well for 1h 40 min. The solution turned pale yellow and small amounts of an insoluble solid precipitated. The solution was filtered, and after removal of the solvent, the remaining oil was redissolved in diethyl ether. Gaseous hydrochloric acid was bubbled through the solution and the resulting solid was collected on a filter plate. The solid was dissolved in acetone/methanol. Column chromatography (SiO_2, acetone/methanol 4:1) yielded the hydrochloride salt of **3a**, which was treated with 0.1 M KOH. The resulting suspension was extracted twice with 40 mL of diethyl ether and the combined organic layers were dried with $MgSO_4$. Evaporation of the solvent *in vacuo* yielded 30 mg (0.08 mmol, 11%) of **3a** as a green oil. ^{1}H NMR ($CDCl_3$) δ 1.03 (t, $^3J = 7$ Hz, 12 H, CH_3), 2.62 (q, $^3J = 7$ Hz, 8 H, NCH_2), 3.36 (ABX_2-system, $^2J = 15$ Hz, $^4J = 2$ Hz, 4 H, CH_2N), 6.81 (br s, 2 H, 6-H, 11-H), 6.98–7.26 (m, 8 H, ar-H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 11.9 (CH_3), 46.8 (CH_2), 60.7 (CH_2), 126.0 (CH), 126.4 (CH), 127.6 (CH), 128.3 (CH), 129.4 (br, CH) 138.2 (C_q), 140.1 (C_q), 141.6 (C_q). MS (EI, 70 eV), *m/z* (%): 374 [M^+] (22), 301 [$M^+ - HNEt_2$] (48), 230 [$M^+ - 2\ HNEt_2$] (60), 86 [$CH_2NEt_2^+$] (100). HRMS: calcd. for $C_{26}H_{34}N_2$ (M^+) 374.2722, found 374.2726.

5-(Diethylaminomethyl)-12-methyldibenzo[ae]cyclooctene (**3b**): A solution of 102 mg (0.23 mmol) of salt **2·(HCl)$_2$** in 40 mL of methanol was irradiated through a Vycor filter with stirring for 4 h. The solvent was removed *in vacuo* and the remaining oil was dissolved in water. The solution was treated with 0.1 M KOH solution and the water layer was extracted twice with diethyl ether. The organic layer was separated and dried with $MgSO_4$ and the solvent was evaporated. After column chromatography (SiO_2, methanol/ethylacetate 1:1), 13 mg (0.04 mmol, 17%) of **3b** was obtained as a colorless oil that decomposes after several weeks upon exposure to air. ^{1}H NMR ($CDCl_3$) δ 1.01 (t, $^3J = 7$ Hz, 6 H, CH_3), 2.19 (d, $^4J = 2$ Hz, 3 H, CH_3), 2.52, 2.66 (ABX_3-system, $^2J = 13$ Hz, $^3J = 6$ Hz, 4 H, NCH_2), 3.32, 3.54 (ABX_2-system, $^2J = 14$ Hz, $^4J = 2$ Hz, 4 H, CH_2N), 6.60 (br d, $^4J = 2$ Hz, 1 H, 11-H), 6.75 (br d, $^4J = 2$ Hz, 1 H, 5-H), 6.98–7.28 (m, 8 H, ar-H). ^{13} C NMR (75.4 MHz, $CDCl_3$) δ 11.5 (CH_3), 26.0 (vinyl-CH_3), 46.5 (CH_2), 60.9 (CH_2), 126.0 (CH), 126.2 (CH), 126.5 (CH), 126.7 (CH), 127.2 (CH), 127.3 (2 x CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), C_q could not be detected. MS (EI, 70 eV), *m/z* (%): 303 [M^+] (3), 288 [$M^+ - CH_3$] (5), 86 [CH_2NEt_2] (100). HRMS: calcd. for $C_{22}H_{25}N_1$ (M^+) 303.1987, found 303.1983.

rac-4b,8b,8c,8d-Tetrahydro-8b,8d-bis(diethylaminomethyl)dibenzo[a,f]cyclopropa[cd]pentalene) (**4**). A solution of 74 mg (0.13 mmol) of salt **2·(HCl)$_2$** in 4 mL of acetone/methanol (2:1) was irradiated for 13 h through a Pyrex filter. The solvent was removed *in vacuo* and the residue was dissolved in water. The solution was treated with 0.1 M KOH and after extraction with diethyl ether, the organic layer was dried with $MgSO_4$. Column chromatography (SiO_2, ethyl acetate/methanol 1:1) gave 30 mg (0.08 mmol, 61%) of diamine **4** as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, $^3J = 7$ Hz, 6 H, CH_3), 1.11(t, $^3J = 7$ Hz, 6 H, CH_3), 2.44 (q, $^3J = 7$ Hz, 4 H, NCH_2CH_3), 2.59, 2.66 (ABX_3-system, $^2J = 13$ Hz, $^3J = 7$ Hz, 2 H, NCH_2CH_3), 2.63, 3.30 (AB-system, $^2J = 13$ Hz, 2 H, vinyl-CH_2N), 2.79, 2.85 (ABX_3-system, $^2J = 13$ Hz, $^3J = 7$ Hz, 2 H, NCH_2), 2.78, 2.89 (AB-system, $^2J = 13$ Hz, 2 H, CH_2N), 2.98 (s, 1 H, 8c-H), 4.54 (s, 1 H, 4b-H), 6.97–7.20 (m, 7 H, ar-H), 7.81–7.85 (m, 1 H, ar-H). – ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.2 (CH_3), 11.8 (CH_3), 46.2 (2 CH_2), 47.6 (C-8d), 48.2 (C-8c), 51.9 (CH_2), 55.3

(CH_2), 57.2 (C-4b), 63.6 (C-8b), 120.7 (ar-CH), 121.4 (ar-CH), 124.6 (ar-CH), 126.0 (2 ar-CH), 126.0 (ar-CH), 126.1 (2 ar-CH), 138.6 (ar-C_q), 140.7 (ar-C_q), 149.9 (ar-C_q), 150.8 (ar-C_q). MS (EI, 70 eV), *m/z* (%): 374 [M^+] (3), 301 [$M^+ - HNEt_2$] (31), 288 [$M^+ - CH_2NEt_2$] (26), 86 [$CH_2NEt_2^+$] (100). HRMS: calcd. for $C_{26}H_{34}N_2$ (M^+) 374.2722, found 374.2723.

Photolysis of the Salts of Diamine 2 in Solution and in the Solid State: Degassed solutions of the salts in methanol (10^{-1} – 10^{-2} M) were irradiated at room temperature. The reaction mixtures were treated with 0.1 M KOH and after extraction with diethyl ether, the products were identified by analytical gas chromatography by comparison with authentic samples. Solid state photolyses were carried out by crushing crystals of the sample between quartz glass slides, which were sealed in a nitrogen-flushed polyethylene bag. The reaction products were removed from the quartz surface with water. The work-up procedure was similar to that of the solution photolyses. The results are summarized in Table 1. The reaction mixture resulting from irradiation of the zinc complex **2·Zn** was acidified to give the corresponding quarternary amines which were further treated with 0.1 M KOH, extracted with diethyl ether and analyzed by gas chromatography.

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