Pergamon

Tetrahedron 56 (2000) 6867–6875

TETRAHEDRON

Solid-State Photolysis of Anthracene-Linked Ammonium Salts: The Search for Topochemical Anthracene Photodimerizations

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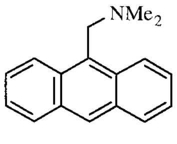
Received 7 January 2000; accepted 20 February 2000

Abstract—The reaction of 9-*N,N*-dimethylaminomethylanthracene **1** with aromatic carboxylic acids gave crystalline salts (**2a**, **2b**, **3a** and **3b**), which were irradiated in the solid state. Whereas salt **3a** was selectively transformed to the dimer **4a**, the other salts were photoinert. The results were rationalized on the basis of X-ray structure analysis. In the presence of oxygen, solid-state irradiation of anthracene salt **3b** leads to selective photooxygenation. The selectivity of both solid-state photoreactions was not observed in solution. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The performance of photoreactions in the crystalline state and the continuing improvement of this methodology have provided access to selectivities in solid-state photoreactions that are not observed in solution photochemistry.[1] The investigation of the solid-state structures of the photoactive compounds and comparison with their reactivity have led to fundamental knowledge of the geometric requirements and the steric course of well-established photoreactions.[2] Due to the dense packing in the crystal lattice, solid-state reactions proceed with a minimum of atomic or molecular motion. Therefore, any reaction in the crystalline state is proposed to take place with the least motion.[3] Such a control of the solid-state reactivity by the packing arrangement of the crystal is known as the topochemical postulate. However, the photodimerization of several crystalline anthracene derivatives has been shown to be non-topochemical,[3a,4] because the product formation could not be directly correlated with the observed solid-state structure. Reasonable explanations of these striking exceptions from the topochemical postulate are based on observations, that the reactions of the anthracene derivatives take place at defect sites[5] or on the surface[6] of the crystals. Since *one* of the factors which cause non-topochemical behaviour may be the *relatively* high degree of mobility of the chromophores in the crystal lattice, the introduction of attractive ionic interactions by salt formation[7] may be useful to achieve a topochemical reaction. Thus, a positively or negatively charged chromophore must remain in the close proximity of its counter ion, which should restrict its mobility. Moreover, ionic interactions are considered to be strong and are often accompanied by hydrogen bonding. These forces may lead to a more selective crystallization process which could reduce the formation of defect sites.

Ammonium salts of the easily available aminomethyl-substituted anthracene derivative **1** with selected aromatic carboxylic acids were chosen as photoactive model compounds, which may photodimerize on irradiation.[8] We report the investigation of the photochemistry of selected crystalline salts of amine **1** and the correlation of the solid-state reactivity with their crystal structure.



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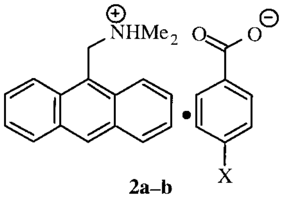
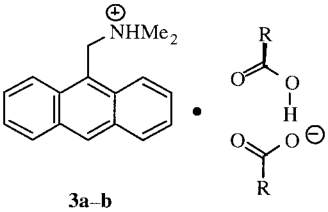


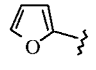
2a–b

2a: X = NO_2; **2b**: X = CH_2OH

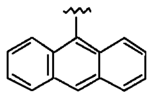


3a–b

3a: R =



3b: R =



Results

Synthesis

9-Dimethylaminomethylanthracene (**1**) and its hydrochloride salt **1·HCl** were synthesized according to literature

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Keywords: solid-state photolysis; topochemical anthracene photodimerization.

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PII: S0040-4020(00)00508-1

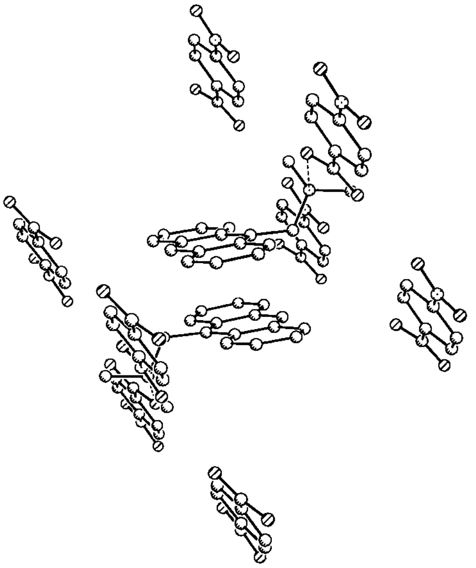


Figure 1. Structure of salt **2a** in the solid state.

procedure.[9] The salts of amine **1** were obtained by addition of the corresponding aromatic carboxylic acid to the amine **1** and subsequent crystallization from methanol/ethyl acetate, ethyl acetate or ethyl acetate/*n*-hexane. Whereas the salts **2a** and **2b** crystallized in an amine-acid ratio of 1:1, crystallization of a mixture of amine **1** with 2-furancarboxylic acid or 9-anthracenecarboxylic acid yielded solid samples of ammonium salts **3a** and **3b** with an amine-acid ratio of 1:2. This ratio was observed on crystallization from all the employed solvents and solvent mixtures; even when a 1:1 mixture of the two components was used. With 4-nitrobenzoic acid, the intentional use of an amine-acid ratio of 1:2 for the salt formation resulted in crystallization of the 1:1 salt **1b**. Attempts to prepare crystalline salts by the reaction of the amine **1** with anisic acid, 4-bromobenzoic acid or naphthylacetic acid failed, because these salts were obtained as viscous oils at room temperature. With phenylacetic acid, an amorphous solid was obtained by slow solidification of the initially precipitated viscous oil at −4°C. ^{1}H NMR-spectroscopic analysis showed an amine-acid ratio of 1:2. However, this salt could not be obtained analytically pure.

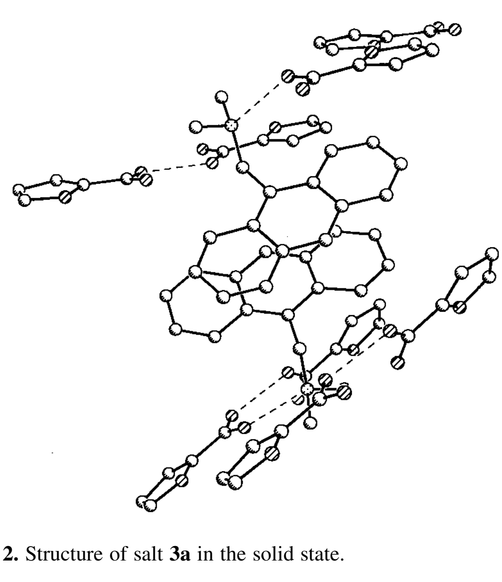


Figure 2. Structure of salt **3a** in the solid state.

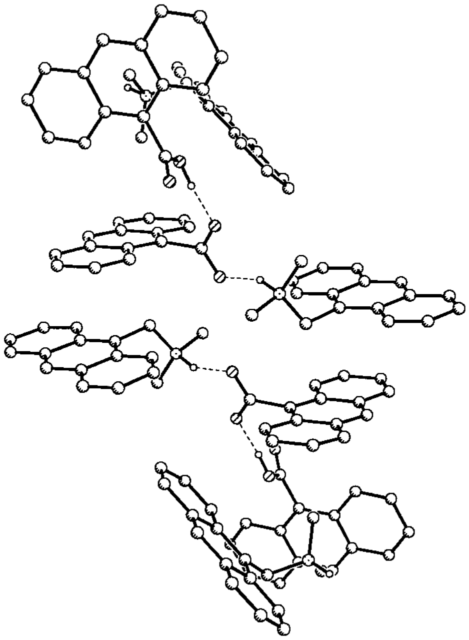


Figure 3. Structure of salt **3b** in the solid state.

Solid-State Structures

The ammonium salt **2a** crystallized in the space group P$\bar{1}$ (from methanol/ethyl acetate). The aromatic carboxylate ions form an almost planar layer in the crystal lattice, and the anthracene moieties are arranged perpendicular to this plane (Fig. 1). Moreover, the ammonium functionality is embedded in the anionic aromatic layer by hydrogen bonding to the carboxylate group, whereas two anthracene moieties arrange as closest pairs with a head-to-tail orientation. The molecular planes of the two anthracene molecules are almost coplanar.

Single crystals of salt **3a** were obtained by crystallization from ethyl acetate. Interestingly, the achiral compound crystallizes in the chiral space group P1. In the solid state, one furancarboxylate moiety and one free acid molecule form hydrogen-bonded, nearly planar complexes, which build up a distorted layer within the crystal lattice (Fig. 2). Like in the solid-state structure of salt **2a**, the ammonium functionalities are hydrogen bonded to the carboxylate ions. The connection of the ammonium substituent with the carboxylate layer results in the formation of stacks of anthracene chromophores which are located between two furan layers. The anthracene moieties are arranged as pairs of closest molecules in a head-to-tail orientation.

The ammonium salt **3b** also crystallizes in an amine-acid ratio of 1:2 (Fig. 3). Resembling the solid-state arrangement of salt **3a**, three molecules are connected by hydrogen bonding: One free carboxylic acid moiety is hydrogen bonded to the carbonyl functionality of the carboxylate, whereas the negatively charged oxygen atom of the latter is connected to the ammonium hydrogen atom. But compared to salt **3a**, the molecular planes of the aromatic substituents of the acid and the carboxylate are not coplanar but perpendicular towards

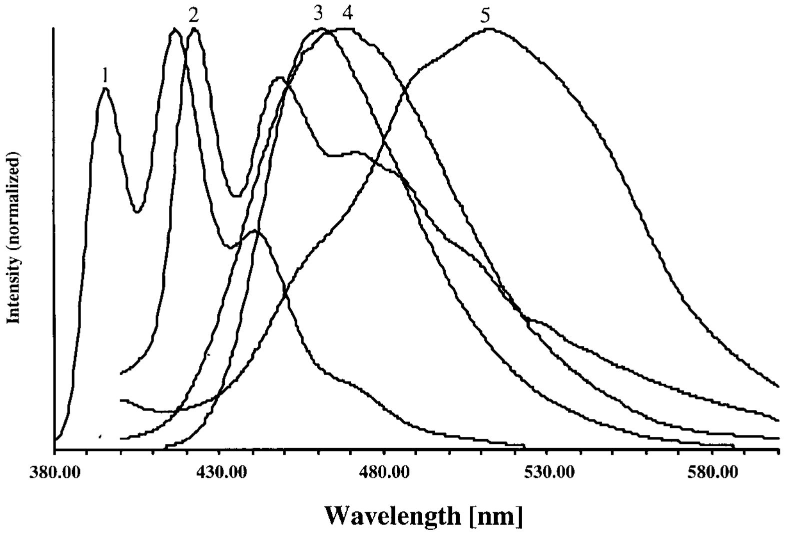


Figure 4. Emission spectra of the anthracene derivatives **1**, **2b**, **3a** and **3b.** 1: **3a** in MeOH (10^{-5} M); 2: crystalline **1**; 3: crystalline **2b**; 4: crystalline **3b**; 5: crystalline **3a**.

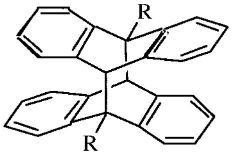
each other. Moreover, there is no head-to-tail oriented pair of two ammoniummethyl-substituted anthracene moieties in the solid-state. Instead, the closest coplanar arrangement of two anthracene chromophores consists of one ammoniummethyl-substituted anthracene and one anthracene carboxylate molecule; however, these molecules are significantly twisted towards each other and separated by relatively large distances.

Solid-State Emission Spectra

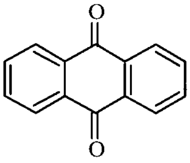
Fig. 4 shows the solid-state emission spectra of the amine **1**, and its salts **2b**, **3a** and **3b** compared with the fluorescence spectrum of salt **3a** in methanol. The solution spectrum of salt **3a** resembles the one observed for unsubstituted anthracene. The solid-state emission of the amine **1** also exhibits a structured fluorescence pattern; however, the band maxima at longer wavelength are significantly broadened. The solid-state emission spectra of the salts **2b** and **3b** exhibit one broad, red-shifted emission band at λ=462 nm and λ=470 nm, respectively, whereas salt **3a** emits with a very broad band at λ=513 nm. The salt **2a** does not emit in the solid state.

Solid-State Photolyses

The free amine **1** was crystallized from *n*-hexane or methanol, and irradiation of both solid samples did not result in a photoreaction. The solid hydrochloride salt **1·HCl**, which was crystallized from methanol/ethyl acetate, was also photoinert. However, irradiation of a thoroughly ground crystalline sample of salt **3a** (λ>320 nm) gave the head-to-tail dimer **4a** in almost quantitative yield as was determined by ^{1}H NMR spectroscopy. Small amounts (<5%) of non-isolable, unidentified byproducts were also detected. Bulk single crystals exhibited a very slow reaction under the same conditions. For example, after 8 h of irradiation the ground sample showed a monomer/dimer ratio of ca. 1:1, whereas on photolysis of the bulk single crystal under the same conditions, a 10:1 ratio was observed. Several filters were employed to investigate the wavelength-dependency of the photolysis of salt **3a**: With every filter used (Schott GG 395, WG 360, WG 320, WG 295), the result of the photoreaction did not change.



4a–c



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4a: R = $CH_2NMe_2H^{\oplus}$

4b: R = CH_2NMeH; **4c**: $COO^{\ominus}$

The salts **2a**, **2b** and **3b** did not react on solid-state irradiation (λ>320 nm); however, in the case of the anthracene salt **3b**, small amounts of anthraquinone **5** were detected by ^{1}H NMR spectroscopy. When the irradiation of a solid sample of anthracene salt **3b** was conducted in an oxygen-gas atmosphere, enhanced formation of anthraquinone **5** was observed. No other product could be detected under these conditions. When the salts **2b** and **3a** were irradiated under oxygen-gas atmosphere, only trace amounts of anthraquinone **5** were detected by ^{1}H NMR spectroscopy; even after prolongued irradiation times. In the case of compound **3a**, the formation of the dimer **4a** was observed under these conditions, but the reaction rate is significantly slower than under inert-gas atmosphere. Irradiation of anthracene salt **2a** in the presence of oxygen did not result in anthraquinone formation.

The head-to-tail structure of the dimer **4a** was deduced from the characteristic signal of the bridgehead protons in the ^{1}H NMR spectrum, because the observed shift of δ=3.88 is comparable to the reported one for the closely related aminomethyl-substituted anthracene dimer **4b** (δ=3.70).[8] The bridgehead proton of the head-to-head dimer is expected give a ^{1}H NMR signal at higher field, as was observed for the head-to-head isomer of dimer **4b** (δ=4.15).[8] Moreover, the head-to-tail connection was confirmed by a NOE effect between the bridgehead proton and the opposite methylene group. The characteristic signals

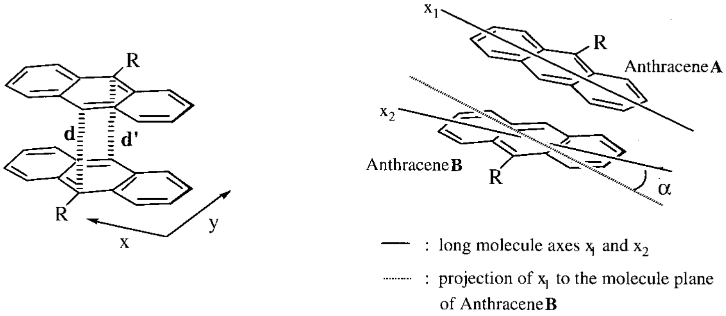


Figure 5. Definition of the geometric parameters **d**, x, y and α.

of the bridgehead carbon atoms (C-9: δ=57.9; C-10: 62.7) further confirmed the dimeric structure.

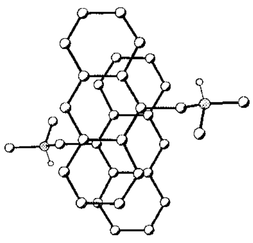
For comparison, the ammonium salts **1·HCl**, **3a** and **3b** were also irradiated in solution. After 2 h of irradiation of salt **3a** in methanol, the dimer **4a** was the main product (>90%; conversion 40%). However, ^{1}H NMR-spectroscopic analysis of the crude reaction mixture revealed that several byproducts were also formed in small amounts. At full conversion, these byproducts accumulate; and additional byproducts were formed. The dimer **4b** could not be isolated from the reaction mixture. Irradiation of anthracene salt **3b** in DMSO-d_6 under inert-gas atmosphere also yielded a complex reaction mixture. It was shown by ^{1}H NMR-spectroscopic analysis of the photolysate, that the head-to-tail dimer **4c** was formed as the main product, which was indicated by a singlet at δ=5.70 whose shift is comparable to the one of the head-to-tail dimer of 9-anthracenecarboxylic acid (δ=5.63).[10] Irradiation of salt **3b** in oxygen-saturated DMSO-d_6 also yielded the dimer **4c** among other unidentified byproducts. Anthraquinone **5** was only formed in trace amounts (>5%) under these conditions. Irradiation of the hydrochloride salt **1·HCl** in methanol gave the head-to-tail dimer as main product; but as observed in the case of salt **3a**, several byproducts were also formed in small amounts.

Discussion

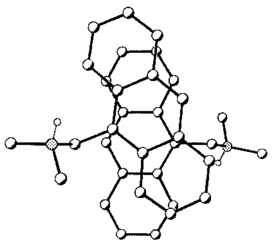
The ammonium salt **3a** represents one of the few achiral molecules that crystallize in chiral space groups. Such a behaviour is rarely observed,[1c,11] and in most cases, there is no correlation between the tendency of a molecule to crystallize in a chiral space group and a distinct structural feature. Since the other ammonium salts **2a** and **3b**, crystallize in achiral space groups, the ammoniummethyl-substituted anthracene moiety is unlikely to be a general structural element that forces crystallization in a chiral one. However, it should be noted, that other achiral, 9-substituted anthracene derivatives are known, that crystallize in chiral space groups.[12] Another remarkable property of salts **3a** and **3b** is their crystallization in an amine-acid ratio of 1:2. The solid-state structure analysis of salts **3a** and **3b** reveals that the association of a carboxylate functionality with one carboxylic acid molecule is the basic structural element of this arrangement, which has also been observed with other carboxylates.[13] Interestingly, the formation of this solid-state structure is independent from the solvent and from the amine-acid ratio which is present in solution. Thus, the crystallization process of the salts **3a** and **3b** results from a selective self-assembly in the solid state. It may be assumed that this self-organization depends on the acidity of the carboxylic acid; however, the salt of amine **1** with 4-nitrobenzoic acid (pK_a=3.41), whose pK_a value is comparable with the one of 2-furancarboxylic acid (pK_a=3.23), does not crystallize in an amine-acid ratio of 1:2 – even when such a ratio was initially used for crystallization.

In contrast to the salt **3a**, the anthracene salt derivatives **1·HCl**, **2a**, **2b** and **3b** did not dimerize on irradiation in the solid state. These observations may be explained by the arrangement of the chromophores in the crystalline state. Thus, the photoinertness of the solid samples may be caused by a large separation between the reaction centers of two anthracene moieties, whereas the photodimerization of salt **3a** should result from a favorable arrangement of the chromophores in the crystalline medium. The solid-state structure analysis of salts **2a** and **3a** reveals that both salts form crystal lattices in which two anthracene molecules arrange as a close coplanar pair in a distorted head-to-tail orientation. According to structure-reactivity correlation studies on the solid-state photodimerization of anthracene and its derivatives,[4] we defined the parameters **d**, Δx, Δy and α to obtain a quantitative analysis of the solid-state arrangement (Fig. 5). The distances **d** and **d**′ between the opposite reactive *meso* positions (i.e. C-9 and C-10), which may form the new C–C bonds in the photodimerization, were taken as structural parameters, whose ideal value should be **d**<420 pm.[3a,4] The deviation from an ideal superposed position of two anthracene molecules was quantified by the shift (Δx and Δy) of one molecule with respect to another along the long and the short molecule axes, x and y. In the case of a perfect superposition, the ideal values are Δx=Δy=0 pm. Moreover, the parameter α defines the twisting angle between two anthracene molecules, i.e. the deviation from a parallel orientation of the long molecule axes x_1 and x_2 (Fig. 5). Thus, α is the angle between the long molecule axes of two anthracene molecules which are projected to one molecule plane.[14] The ideal angle α should be 0°. The observed structural features of compounds **2a** and **3a** (Table 1) reveal that in both salts, the distances **d** between the *meso* positions of the anthracene moieties are smaller than 400 pm. These distances are generally considered to be suffiently short for a photodimerization in the solid state.[4] However, in both cases, the anthracene frameworks have to move significantly in order to achieve

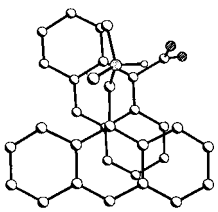
Table 1. Geometric parameters **d**, **d′**, Δx, Δy and α of the salts **2a**, **3a** and **3b** derived from X-ray analysis



2a



3a



3b

	2a	3a	3b
d [pm]	386.4	354.8	501.7
d′ [pm]	386.4	393.5	397.7
Δx [pm]	1.44	1.20	[a]
Δy [pm]	1.10	0.29	[a]
α [deg]	0	23.40	77.5

[a] Since the molecule axes are nearly perpendicular towards each other, the determination of Δx and Δy is not useful.

a perfect superposition of the π systems, which is a necessary prerequisite for a photodimerization. To achieve a better overlap, one anthracene moiety of salt **2a** has to shift along both molecule axes for more than 100 pm (Δx and Δy), whereas the aromatic rings of salt **3a** only have to shift significantly along *one* molecular axis (Δx) along with a twist (α=23.4°) of the two molecules towards each other. Although, such deviations from an ideal arrangement of the two chromophores may hinder the photodimerization in the solid state, the photoreaction must not necessarily be suppressed. Wang and Jones showed for example, that such a deviation from the ideal superposition does not inhibit a photodimerization, because shifts along the molecular axes larger that 100 pm still allow the solid-state photodimerization of acridizinium salts, whose structure is closely related to anthracene.[15]

To rationalize the photoreactivity of the salts **2a** and **3a**, it is helpful to further investigate the interaction between the ionic centers of the molecules. The packing diagram reveals that the ammonium moiety is embedded in the dense layer which is formed by the aromatic carboxylate counterions. This arrangement is likely to be governed by attractive ionic interactions and by hydrogen bonding between the protonated amine and the carboxylate oxygen atom. Thus, in addition to the steric constraints of the crystal packing, the ammonium functionality is ‘anchored’ within the counterion layer, which should further restrict the freedom of movement of the anthracene moiety in the crystal lattice. Considering this ‘fixed’ ammonium functionality, the least hindered motion of the anthracene moiety may result from a rotation around the CH_2–C_{ar} bond or around the N–CH_2 bond. The latter leads to a twisting of the anthracene moieties towards each other rather than to a translatory shift. In the case of salt **1·HCl**, such a motion results in a less favorable arrangement of the two chromophores, because the improvement of the Δx value will be accompanied by a significant increase of the angle α. Thus, the combination of the significant deviation from an ideal superposition of two anthracene molecules with their restricted mobility should result in the suppression of the dimerization. In the case of salt **3a**, the twisting of one anthracene moiety may lead to a more favorable orientation of the two chromophores towards each other, because the values for Δx and α become smaller during the twisting movement and should thus facilitate the photodimerization.

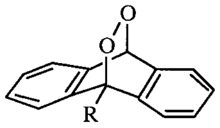
The observed relatively slow solid-state photoreaction of salt **3a** shows that the geometric arrangement of the chromophores is far from being ideal and may be close to the limit beyond which a photoreaction is no longer possible. It was observed, that the reaction is getting slower with prolongued reaction times and that the bulk single crystal has a significantly lower conversion compared to carefully ground solid samples. Since the photodimer does not absorb at wavelengths higher that λ=300 nm, this photoproduct does not act as an internal light filter which may slow down further photoreactions. These observations lead to the conclusion, that the reaction does not take place at a defect side, since such reactions were shown to get faster after an induction period.[4] However, it cannot be excluded, that the photoreaction proceeds mostly on the surface of the solid, a phenomenon which is frequently observed in solid-state photochemistry.[1b,1e]

In contrast to the observed solid-state structures of salts **2a** and **3a**, X-ray structure analysis of salt **3b** shows that the anthracene moieties of this compound do not form close coplanar pairs with a parallel alignment of the π systems. The closest anthracene pair observed consists of one ammoniummethyl-substituted and one 9-anthracenecarboxylate. However, the separation between the *meso* positions is rather large (**d**=397.7 and 501.7 pm). Furthermore, the molecules are severely twisted towards each other by 77.5°. Consequently, a solid-state photodimerization is not expected due to a highly unfavorable orientation of the chromophores.

A reasonable correlation between the solid-state reactivity and the solid-state emission spectrum of the chromophores was observed. The photoinert salts **2b** and **3b** exhibit a broad emission band at λ=460–470 nm, which is suggested to be a red-shifted monomer emission. Such a bathochromic shift compared to the emission in solution may result from partial overlap of the chromophore with the π system of another anthracene moiety. Thus, by comparison with the salts **2b** and **3b**, it may be concluded that the more pronounced red-shift of the solid-state emission of salt **3a** results from a stronger overlap between the opposing π systems of the chromophores. In fact, this assumption was confirmed by X-ray structure analysis results of salts **3a** and **3b**. The significant shift of the emission band of salt **3a** may be caused by excimer formation, since the observed band shift maximum at $\lambda=513$ is comparable to the known excimer emission of anthracene derivatives.[16c] Such a correlation of the red-shift of the solid-state fluorescence band with the degree of intermolecular $\pi-\pi$ interaction has already been observed for several alkenes and polycyclic aromatic molecules,[16] and may serve as an efficient tool to evaluate the orientation of two π systems towards each other in the solid state. From these results, it may be deduced that two anthracene moieties of the solid salt **2b** are overlapping to almost the same extend than the ones of salt **3b**. The emission spectrum of the amine **1** represents an ensemble of a nearly 'undisturbed' anthracene emission and a band which may result from fluorescence of one anthracene chromophore which partially overlaps with a neighboring aromatic π system. Moreover, the latter broad band may also result from exciplex formation of the amine functionality and the anthracene chromophore.

Irradiation of salt **3a** in methanol gave dimer **4a** as main reaction product only at low conversion. At full conversion, a considerable number of byproducts was formed. This may be due to the formation of the head-to-head dimer and additional reaction pathways which result from a photo-induced cleavage of the CH_2–N bond. Such photocleavage reactions of benzylammonium salts are known to yield a variety of photoproducts.[17] On solid-state photolysis of salt **3a**, this reaction pathway is obviously suppressed.[18] However, it is not clear whether the initially formed radicals quickly recombine or whether these reactive intermediates are not formed at all in the solid state. In order to trap the radicals with an alcohol functionality, the 4-hydroxymethyl-substituted benzoate was used as counter ion. It was proposed that salt **2b** arranges in a similar crystal lattice than **2a**, so that the hydroxy fuctionality may be positioned in the near vicinity of the formed radicals. However, no trapping product was observed on irradiation of salt **2b**, so that it may be concluded that the radicals which result from a photo-induced C–N-bond cleavage are not formed.

Although the anthracene salt **3a** does not photodimerize in the solid state, a remarkably selective reaction to give anthraquinone **5** was observed under oxygen-gas atmosphere. It is already known that autoxidation of solid anthracene yields anthraquinone **5** as reaction product,[19] and 9,10-dicyanoanthracene is photooxygenated to anthraquinone **5** in solution. Moreover, it has also been reported that anthracene peroxide rearranges to anthraquinone on X-ray irradiation in the solid state.[20] Thus, we assume that the initially formed photoproduct of salt **3b** may be the endoperoxide **6**[21] which subsequently rearranges to the anthraquinone **5**. The thermally-induced transformation of 9-substituted anthracene peroxides to anthraquinone with the loss of the substituent has been obsereved;[22] however, the yields are relatively low and additional rearrangement products are also formed in solution. Since the formation of such rearrangement products requires significant molecular motion, we assume that in the case of endoperoxide **6**, the corresponding reaction pathways are suppressed by the steric constraints in the crystal lattice. Thus, the formation of anthraquinone **5** from solid-state irradiation of salt **3b** under oxygen-gas atmosphere represents a highly selective reaction. This selectivity is even more remarkable considering the observation that photolysis of salt **3b** in an oxygen-saturated solution only gave trace amounts of anthraquinone **5**. Analysis of the reaction mixture showed that both the carboxy- and the ammoniummethyl-substituted anthracene were consumed during anthraquinone formation. Thus, all three anthracene moities per salt unit are photooxygenated in the solid state. At this stage, the distinct mechanism of this reaction is not quite clear and further experiments to isolate the intermediate peroxide **6** and to identify subsequent reaction intermediates are necessary.



6

$R = CH_2\overset{\oplus}{N}Me_2H, CO\overset{\ominus}{O}, \text{ or } COOH$

The formation of the peroxide **6** requires the presence of singlet oxygen, since the reaction between singlet-state anthracene and triplet oxygen is spin forbidden. The singlet oxygen may result from a photosensitization of ground-state triplet oxygen by a singlet-excited anthracene chromophore. The efficiency of this process is likely to be caused by the presence of three anthracene chromophores per salt molecule. That such a high density of anthracene molecules may be required for an efficient photooxidation is shown by the observation that the other anthracene salts **2a**, **2b** and **3a** only yielded traces of anthraquinone **5** under the same conditions.

In conclusion, most derivatives of salts of 9-*N*,*N*-dimethylaminomethylanthracene **1** with selected aromatic carboxylic acids are photoinert in the solid state. In the case of salt **2a**, it was shown that the suppressed reactivity is mainly caused by attractive ionic interactions and hydrogen bonding which restricts the freedom of movement of the anthracene chromophores, which need to move significantly for a photodimerization. However, the photoactive salt **3a** represents one example for a selective solid-state photoreaction, because irradiation of crystalline samples gave almost exclusively the head-to-tail dimer **4a**, whereas solution photolysis yielded a large number of products. The transformation of anthracene salt **3b** to anthraquinone **5** under oxygen-gas atmosphere also represents a highly selective solid-state photoreaction. Since it was shown that the anthracene molecules may act as photosensitizers in the solid state and no disturbing photodimerization takes place, this structural feature may offer new opportunities for selective solid-gas-phase photoreactions.[23]

Table 2. Crystallographic data of compounds **2a**, **3a** and **3b**

	2a	**3a**	**3b**
empirical formula	$C_{24}H_{22}N_2O_4$	$C_{27}H_{25}NO_6$	$C_{47}H_{37}NO_4$
formula weight	402.44	459.48	679.78
crystal size [mm]	0.5×0.5×0.4	0.5×0.4×0.4	0.3×0.3×0.1
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	P1	$P2_1/c$
a [pm]	760.44(9)	835.73(14)	1421.75(22)
b [pm]	1077.32(13)	1116.39(21)	1667.67(25)
c [pm]	1223.88(15)	1374.19(23)	1569.39(24)
α [°]	97.595(7)	76.659(14)	90
β [°]	97.465(7)	73.967(14)	108.966(21)
γ [°]	92.959(7)	69.180(15)	90
V [nm^{-3}]	0.9830(2)	1.1392(3)	3.5190(9)
Z	2	2	4
ρ_c [Mgm^{-3}]	1.360	1.340	1.283
μ_c [mm^{-1}]	0.093	0.095	0.08
F(000)	424	484	1432
θ range [°]	3.20 to 22.45	3.12 to 22.51	3.00 to 22.51
no. reflns. measd.	2905	5898	4987
no. unique reflns.	2563	5898	4585
no of restraints	0	3	0
no of parameters	278	622	480
$R1^a$ [$I>2\sigma(I)$]	0.0386	0.0492	0.1305
$R1^a$ [$I>4s(I)$]	0.0321	0.0347	0.0544
$wR2^b$ (all data)	0.0913	0.0820	0.1218
g_1; g_2^c	0.0536; 0.2048	0.0473; 0.0040	0.0486; 0
extinction coefficient	0.029(3)	0.0100(13)	0.00219(42)
largest diff peak and hole (e nm^{-3})	139 and −154	146 and −132	172 and −168

[a] $R_1 = \dfrac{\sum \lVert F_o| - |F_c \rVert}{\sum |F_o|}$

[b] $wR2 = \sqrt{\dfrac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$

[c] $w = \dfrac{1}{\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P}$; $P = \dfrac{(max(F_o^2, 0) + 2F_c^2)}{3}$

Most notably, no example for a non-topochemical solid-state reaction was observed, because the photochemical behaviour of the crystalline salts **2a** and **3a**,**b** could be successfully correlated with their solid-state structures.

Experimental

General Methods. ^{1}H NMR and ^{13}C NMR: Bruker AC 200 (^{1}H NMR: 200 MHz; ^{13}C NMR: 50.3 MHz); ^{1}H NMR chemical shifts refer to $\delta_{TMS}=0.0$. ^{13}C NMR chemical shifts refer to solvent signals (DMSO-d_6: $\delta=39.5$; CD_3OD: $\delta=49.2$, $CDCl_3=77.0$). UV: Hitachi U-3200 spectrophotometer. Fluorescence: Perkin–Elmer LS50 spectrometer. Solid-state fluorescence spectra were recorded with a Front Surface Accessory, Perkin–Elmer. Emission spectra were recorded with an excitation wavelength of $\lambda_{ex}=380$ nm (with salt **3a** in methanol: $\lambda_{ex}=370$ nm) Elemental analyses were performed by Mr. C.-P. Kneis at the University of Würzburg, Institute of Inorganic Chemistry. Melting points were determined with a Büchi B-545 and are uncorrected.

9-*N*-Dimethylaminomethylanthracene 1 (mp 65–66°C) and its hydrochloride **1·HCl** (mp 252–254°C, dec.) were synthesized according to Marcus and Fitzpatrick.[9]

X-Ray Crystallography. All data were collected from shock-cooled crystals on an Enraf–Nonius CAD4 four circle diffractometer (graphite–monochromated Mo-Kα radiation, $\lambda=71.073$ pm) equipped with a low temperature device at 193(2) K.[24] No absorption correction was employed. The structures were solved by direct methods (SHELXS-97[25]) and refined by full-matrix least squares methods against F^2 (SHELXL-97[26]).

All non-hydrogen atoms were refined with anisotropic displacement parameters. The following hydrogen atoms were located by difference Fourier syntheses and refined isotropically: H1N bonded to N1 in **2b**. H1O and H2O bonded to O1 and O2, and H1N and H2N bonded to N1 and N2, respectively, in **3a**. H1N bonded to N1 and H1O bonded to O4 in **3b**. All other hydrogen atoms of the molecules were assigned ideal positions and refined isotropically using a riding model with U_{iso} constrained to 1.2 or 1.5 times the U_{eq} of the parent atom. Additional crystallographic data of the refinements and the data collections of compound **2a**, **3a** and **3b** are given in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138799 (**2a**), CCDC-138800 (**3a**) and CCDC-138801 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

Photolysis in solution and in the solid state. The solution photolyses were performed in deoxygenated solvents with a 150 W mercury high-pressure lamp (Heraeus TQ 150). Solid-state irradiations were carried out with a 500 W mercury high-pressure lamp (Heraeus TQ) with the crystalline samples crushed between Pyrex slides in argon-flushed polyethylene bags or by distributing the ground solid on the inner walls of a test tube (DURAN glassware). If not stated otherwise, the samples were placed without further cooling ca. 5 cm in front of the cooling mantle of the lamp. The photolysate was analyzed by means of ^{1}H NMR. In preparative runs the solid samples (20–40 mg) were placed in a flask (DURAN glassware) and flushed with argon. During photolysis the flask was frequently removed and placed in a sonic bath for 1–2 minutes.

***N*-9-Anthracenylmethyl-*N*,*N*-dimethylammonium 4-nitrobenzoate (2a).** To a mixture of 75 mg (0.32 mmol) of amine **1** in 3 mL of ethyl actetate were added 58 mg (0.32 mmol) of 4-nitrobenzoic acid in 2 mL of methanol. The solution was stirred at 50°C for 10 min, concentrated to ca. 2–3 mL and cooled slowly to −4°C to give 99 mg (0.25 mmol, 74%) of salt **2a** as bright yellow prisms, mp 159–160°C. UV (MeOH): λ_{max} (log ϵ)203 (4.23), 215 (4.25), 250 (4.57), 331 (3.50), 347 (3.75), 365 (3.92), 384 (3.89). ^{1}H NMR (CD_3OD) δ 2.89 (s, 6 H, NCH_3), 5.31 (s, 2 H, CH_2N), 7.51–7.72 (m, 4 H, ar-H), 8.01–8.18 (m, 6 H, ar-H), 8.40 (dd, J=9 Hz, 1 Hz, 2 H, ar-H), 8.68 (s, 1 H, ar-H). ^{13}C NMR (CD_3OD) δ 44.1 (NCH_3), 54.1 (CH_2N), 122.9 (ar-C_q), 124.1 (ar-CH), 124.6 (ar-CH), 126.8 (ar-CH), 129.1 (ar-CH), 130.9 (ar-CH), 131.4 (ar-CH), 132.2 (ar-CH), 133.0 (ar-C_q), 144.6, (ar-C_q), 150.6 (ar-C_q), 172.1 (C=O), one ar-C_q not detected. Anal. calcd for $C_{24}H_{24}N_2O_4$ (459.50) C: 71.63, H: 5.51, N: 6.96; found C: 71.25, H: 5.36, N: 6.59.

N-9-Anthracenylmethyl-N,N-dimethylammonium 4-hydroxymethyl benzoate (2b). A mixture of 70 mg (0.46 mmol) of amine **1** and 108 mg (0.46 mmol) of 4-hydroxymethylbenzoic acid was dissolved in 5 mL of methanol/ethyl acetate (1:1). Slow evaporation of the solvent at room temp. gave 121 mg (0.33 mmol, 68%) of salt **2b** as yellow cubes, mp 150–151°C. ^{1}H NMR (CD_3OD) δ 2.71 (s, 6 H, NCH_3), 4.63 (s, 2 H, CH_2OH), 5.04 (s, 2 H, CH_2N), 7.36 (d, J=8 Hz, 2 H, ar-H), 7.49–7.68 (m, 4 H, ar-H), 7.91 (d, J=8 Hz, 2 H, ar-H), 8.10 (dd, J=9 Hz, 1 Hz, 2 H, ar-H), 8.41 (d, J=9 Hz, 2 H, ar-H), 8.63 (s, 1 H, ar-H).). ^{13}C NMR (CD_3OD) δ 44.7 (NCH_3), 54.6 (CH_2N), 65.0 (CH_2OH), 125.0 (CH), 125.3 (C_q), 126.6 (CH), 127.5 (CH), 128.5 (CH), 130.8 (CH), 130.9 (CH), 131.2 (CH), 132.9 (C_q), 133.1 (C_q), 135.4 (C_q), 146.5 (C_q), 173.4 (C=O). Anal. calcd for $C_{25}H_{25}NO_3$ (387.9) C: 77.49, H: 6.50, N: 3.61; found C: 77.25, H: 6.40, N: 3.67.

N-9-Anthracenylmethyl-N,N-dimethylammonium 2-furancarboxylate·2-furancarboxylic acid complex (3a). A mixture of 121 mg (0.51 mmol) of amine **1** and 115 mg (1.03 mmol) of 2-furancarboxylic acid was dissolved in 3 mL of ethyl acetate. The solution was refluxed for 10 min and then cooled slowly to −4°C to give 185 mg (0.41 mmol, 78%) of salt **3a** as pale yellow prisms, mp 97–98°C. UV (MeOH): $\lambda_{\max}$ (log ϵ)=336 (3.45), 350 (3.75), 368 (3.89), 386 (3.81). ^{1}H NMR (CD_3OD) δ 2.93 (s, 6 H, NCH_3), 5.38 (s, 2 H, CH_2N), 6.48 (dd, J=2 Hz, 3 Hz, 2 H, ar-H), 7.02 (dd, J=3 Hz, 1 Hz, 2 H, ar-H), 7.49–7.69 (m, 6 H, ar-H), 8.09 (d, J=9 Hz, 2 H, ar-H), 8.39 (d, J=9 Hz, 2 H, ar-H), 8.65 (s, 1 H, ar-H). ^{13}C NMR (CD_3OD) δ 43.9 (NCH_3), 53.8 (CH_2N), 112.7 (ar-CH), 117.0 (ar-CH), 121.9 (ar-C_q), 124.5 (ar-CH), 126.8 (ar-CH), 129.2 (ar-CH), 130.9 (ar-CH), 132.5 (ar-CH), 132.9 (ar-C_q), 133.0 (ar-C_q), 146.6 (ar-CH), 149.5 (ar-C_q), 164.5 (C=O). Anal. calcd for $C_{27}H_{25}NO_6$ (459.50) C: 70.58, H: 5.48, N: 3.05; found C: 70.30, H: 5.24, N: 3.05.

N-9-Anthracenylmethyl-N,N-dimethylammonium 9-anthracenecarboxylate·9-anthracenecarboxylic acid complex (3b). To a mixture of 65 mg (0.28 mmol) of amine **1** in 1 mL of ethyl acetate were added 122 mg (0.56 mmol) of 9-anthracenecarboxylic acid in 3 mL of methanol. Slow evaporation of the solvent at room temp. yielded 131 mg (0.19 mmol, 69%) of salt **3b** as pale yellow plates, mp 218–220°C (dec.). UV (MeOH): $\lambda_{\max}$ (log ϵ) 218 (4.44), 248 (4.55), 330 (3.78), 346 (4.08), 364 (4.25), 384 (4.20). ^{1}H NMR (DMSO-d_6) δ 2.45 (s, 6 H, NCH_3), 4.62 (s, 2 H, CH_2N), 7.58–7.73 (m, 12 H, ar-H), 8.10–8.24 (m, 10 H, ar-H), 8.59 (d, J=8 Hz, 2 H, ar-H), 8.70 (s, 1 H, ar-H), 8.76 (s, 2 H, ar-H). ^{13}C NMR (DMSO-d_6) δ 44.4 (NCH_3), 53.5 (CH_2N), 124.9, 125.1, 125.3, 125.6, 126.1, 126.6, 126.8, 127.6, 128.0, 128.2, 128.5, 128.9, 130.6, 130.8, 130.9, 131.4, 170.6 (C=O). Anal. calcd for $C_{47}H_{37}NO_4$ (679.8) C: 83.04, H: 5.49, N: 2.06; found C: 82.60, H: 6.32, N: 2.45.

Photolysis of salt 1·HCl in methanol. A solution of 68 mg (0.25 mmol) of hydrochloride **1·HCl** in 10 mL of methanol was irradiated for 6 h at $\lambda > 320$ nm. ^{1}H NMR-spectroscopic analysis showed that all starting material was consumed. The photodimer **4a** was formed as main product among several byproducts as indicated by a multitude of additional ^{1}H NMR signals in the aromatic region and at δ2.5–4.5 (in CD_3OD). On concentration of the solution by evaporation of solvent, a white solid precipitated, which was washed three times with ca. 5 mL of ethyl acetate to give 31 mg of dimer **4a** as white solid (0.06 mmol, 46%). mp 248–250°C (dec.) UV (MeOH): $\lambda_{\max}$ (log ϵ)=2.03 (4.32), 216 sh (4.11), 254 (3.11), 296 (zero-onset). ^{1}H NMR (CD_3OD) δ 2.63 (s, 12 H, NCH_3), 4.03 (s, 2 H, 9-H), 4.58 (s, 4 H, CH_2N), 6.94–7.17 (m, 18 H, ar-H). ^{13}C NMR (D_2O/CD_3OD, 5:1) δ46.2 (NCH_3), 57.3 (C-9), 59.1 (CH_2N), 61.6 (C-10), 127.6 (ar-CH), 127.8 (ar-CH), 128.5 (ar-CH), 129.7 (ar-CH), 140.7 (ar-C_q), 142.5 (ar-C_q).

Basification of the dimer with aqueous NaOH and subsequent extraction with dichloromethane gave the free amine whose ^{1}H NMR spectrum was identical with the one obtained from the photodimer of amine **1**.

Photodimerization of amine 1. A solution of 45 mg (0.19 mmol) of amine **1** was irradiated for 6 h in 8 mL of *n*-hexane ($\lambda > 320$ nm). During photolysis, a yellow solid precipitated, which was washed twice with 4 mL of *n*-hexane. The remaining solid was crystallized from methanol/dichloromethane to give 26 mg (0.05 mmol, 58%) of the head-to-tail photodimer. ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 12 H, NCH_3), 3.69 (s, 4 H, CH_2N), 3.81 (s, 2 H, 10-H), 6.70–7.00 (m, 16 H, ar-H).

Photodimerization of salt 3a in the solid state. The salt **3a** was crystallized from ethyl acetate, and the crystals were thoroughly ground. A portion of 20 mg (0.04 mmol) was placed on the inner wall of a DURAN test tube and irradiated at 10°C ($\lambda > 320$ nm) for 32 hours. Analysis of the crude reaction mixture by ^{1}N-NMR spectroscopy showed that the photodimer has formed almost quantitatively (>95%, conversion 78%). ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 12 H, NCH_3), 3.88 (s, 2 H, 9-H), 4.50 (s, 4 H, CH_2N), 6.52 (dd, J=2 Hz, 3 Hz, 4 H, ar-H), 6.84–6.97 (m, 14 H, ar-H), 7.22–7.28 (m, 6 H, ar-H), 7.58 (dd, J=2 Hz, 1 Hz, 6 H, ar-H). ^{13}C NMR (CD_3OD) δ46.0 (NCH_3), 57.9 (C-9), 59.4 (CH_2N), 62.7 (C-10), 112.8 (ar-CH), 117.1 (ar-CH), 127.7 (ar-CH), 128.0 (ar-CH), 128.3 (ar-CH), 129.8 (ar-CH), 141.6 (ar-CH), 143.1 (ar-C_q), 146.7 (ar-C_q), 149.5 (ar-C_q), 164.1 (C=O).

The identity of the photodimer was confirmed by basification with aqueous 0.1N NaOH, extraction with deuterochloroform and comparison of the ^{1}H NMR spectrum with an authentic sample of the head-to-tail dimer of amine **1**.

Photolysis of salt 3b in the solid state under oxygen-gas atmosphere. A ground sample of salt **3b** (15 mg) was placed on the inner walls of a DURAN test tube, which was subsequently fitted with a septum. Syringe needles were used as inlet and outlet to maintain a permanent flow of oxygen-gas over the sample. The solid was irradiated $\lambda > 320$ nm for 8 hours. During that period the solid sample turned deep yellow. Analysis of the crude reaction mixture by ^{1}N NMR spectroscopy showed that anthraquinone **6** was formed almost exclusively (>95%, conversion 30%). Anthraquinone **6** was identified by comparison with an authentic sample: ^{1}H NMR (DMSO-d_6) δ 8.04, 8.32 (AA'BB' system, 8 H, ar-H).

Acknowledgements

This work was generously financed by the Bundesministerium für Bildung und Forschung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. Constant encouragement and generous support by Prof. W. Adam is gratefully appreciated. We thank A. Ancev for assistance with the synthetic work (IAESTE exchange student from the University of Skopje, Macedonia).

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