

Photochemical Reactions of Bromoanthracenes with N,N-Dimethylaniline in Solution

Jan Fulara* and Tadeusz Latowski**⁺

* Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

** Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland

Z. Naturforsch. **36b**, 846-851 (1981); received June 25, 1980

Photochemical Reactions, Bromoanthracenes

Major products of the photolysis of 9-bromoanthracene and 9,10-dibromoanthracene in benzene and acetonitrile as well as photochemical reaction products of the two bromoanthracenes with N,N-dimethylaniline in these solvents have been isolated and identified. The mechanisms of partial reactions are discussed and attention is paid to the medium effect on the photochemical transformations.

Both excimers and exciplexes have attracted the attention of molecular physicists and photochemists over the last decade. Owing to the use of laser photolysis, measurements of short-lived photocurrents, and pulse spectrofluorimetry, it became possible to satisfactorily explain photophysical processes occurring in molecular systems [1]. Excimers and exciplexes provide important steps of many photochemical reactions. Photochemical reactions of a variety of aromatic hydrocarbons have been shown to be preceded by excimer formation [2, 3].

The exciplexes, first detected in systems comprising aromatic hydrocarbons and tertiary aromatic amines [4], have frequently been observed in many classes of organic compounds. In articles [5, 6], numerous examples of photochemical reactions are reported for which exciplexes have been shown or postulated to provide intermediate steps.

The exciplexes of anthracene with tertiary amines, which were carefully studied, proved to be photochemically active. The products and/or kinetics of these reactions were studied by Yang and co-workers [7], Saltiel, and co-workers [8] and Pac and Sakurai [9].

One of us (T. L.) together with his co-workers, studied the products and kinetics of a variety of photochemical reactions between N,N-dimethylaniline (DMA) and bromobenzene [10] as well as between DMA or other tertiary aromatic amines and chlorinated methanes [11]. The results of these studies, as well as those by Tasa, Pac, and Sakurai [12], revealed that exciplexes provided initial steps

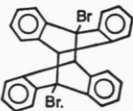
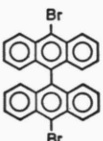
of these reactions. Photochemical activity of systems including halogenated aliphatic and aromatic hydrocarbons is determined by high lability of radical anions of these compounds. In the hitherto studied systems containing halogenated benzenes [10] or chlorinated methanes [11], the electron donor (aromatic amine) was first excited. In the case of halogenated anthracenes the situation may be reversed. According to Weller's suggestion [13], the excitation of the acceptor instead of donor should not affect the nature of the exciplex formed between the halogenated compound and the amine.

In this article the results of the study of the photolysis of 9-bromoanthracene (BA) and 9,10-dibromoanthracene (DBA) and reactions of these compounds with DMA in benzene and acetonitrile are presented.

Results and Discussion

A. Photolysis of the bromoanthracenes in solution

The photolysis of BA in benzene afforded the following compounds:

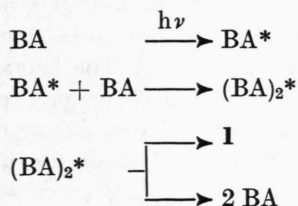
No.	Formula	% Yield (wt.%)
1		90.7
2		1.3

⁺ Reprint requests to Dr. T. Latowski.

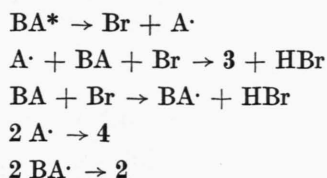
No.	Formula	% Yield (wt. %)
3		3.8
4		3.1

and hydrogen bromide. Similar products were obtained in 1,4-dioxane. In acetonitrile, **1** was the major product, along with small amounts of more than ten other compounds detected by thin-layer chromatography. In the dioxane medium, compounds **2**, **3** and **4** were absent.

Photodimerization is a common process for aromatic hydrocarbons, in particular for anthracene and its derivatives [3]. Halogenated anthracenes were found to form photodimers in solution, their yields decreasing in the series 9-fluoroanthracene > 9-chloroanthracene > 9-bromoanthracene [14]. The photodimerization of anthracene was shown to proceed from the excited singlet state *via* an excimer as the intermediate step [2, 15]. The mechanism of the formation of **1** can be outlined as follows:



The low yields of **2**, **3** and **4** are indicative of the homolytic dissociation of the C-Br bond in the bromoanthracene molecule. These yields, being lower than in the case of bromobenzene [16], are presumably due to enhanced ability of the bromoanthracene to cope with the consequences of the π -electron excitation. The reactions affording **2**, **3** and **4** can be written as follows:



The low yields of **2**, **3** and **4** show that the photolysis of BA is not competitive for the photodimerization process.

The photolysis of 9,10-dibromoanthracene (DBA) in acetonitrile affords a variety of products in low yields. Photodimers were not observed. The photochemical activity of DBA was markedly lower than that of BA.

B. Photochemical reactions of bromoanthracene with DMA in solution

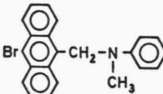
The following products were formed during irradiation of BA with DMA in acetonitrile:

No.	Formula	% Yield (wt. %)
5		65.2
6		2.9
7		13.5
8		9.0
9		4.0
10		3.3
11		1.3
12		0.4

and hydrogen bromide.

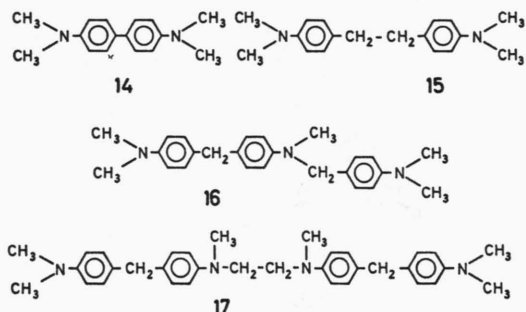
In the benzene medium, the reactivity of the BA-DMA system was markedly lower. The products included 1, 2, 3 and 4 which were found also during photolysis of BA in this solvent (section A), and 7 whilst 5, 11 and 12 were absent.

The photochemical reaction of DBA with DMA in acetonitrile gave the following products:

No.	Formula	% Yield (wt. %)
BA		70
7		13.4
11		1.2
9		7.2
13		8.2

and hydrogen bromide.

To learn whether or not DBA reacts with 7, which is formed in high yield in the photochemical reaction between DBA and DMA in acetonitrile, major products of the photochemical reaction in this system were investigated. The following products were found:

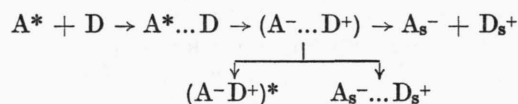


These products indicate that the main pathway of the photochemical reaction of the bromoanthracenes with DMA and 7 in acetonitrile is photoreduction to anthracene and 9-bromoanthracene, respectively.

There are some reports on the photoreduction of DBA and 9,10-dichloroanthracene (DCA) by diethylamine and triethylamine [17] as well as aniline, N-methylaniline and DMA [18] in heptane and methylcyclohexane, where also the formation of BA or CA is observed. In benzene, radical transformations predominate owing to the nonpolar nature of this solvent.

The system anthracene - DMA in acetonitrile behaves unlike those just described. The photochemical reaction in this system affords the following products [9]: the photodimer of anthracene (in a low yields), 9,10,9',10'-tetrahydro-9',9'-bianthryl (10 to 20%), 9,10-dihydroanthracene (5-10%), and 9 (60 to 65%). In all these compounds the molecule of anthracene is hydrogenated at positions 9,10.

To elucidate the differences in the photochemical behavior of anthracene and bromoanthracene in the presence of DMA and 7, and to suggest the mechanism of the formation of the products in our systems, let us consider primary photophysical processes occurring in the exciplexes of the type aromatic hydrocarbon (A)-aromatic amine (D) in the polar medium [19]:



where $A^* \cdots D$ is the encountering complex, $(A^* \cdots D^+)$ is the unrelaxed CT complex, $A_s^- \cdots D_s^+$ is the solvated ion pair, A_s^- , D_s^+ are the free radical ions, and $(A-D^+)^*$ is the relaxed exciplex.

The radical anion of anthracene A_s^- and the radical cation DMA_s^+ , which are formed upon ionic photodissociation of the exciplex, become precursors of the photoproducts.

In the case of bromoanthracenes, the radical anions $BA^{\cdot-}$ and $DBA^{\cdot-}$ dissociate to produce the bromide ion and the aryl radical. The heterolytic dissociation of bromoanthracene occurs presumably either within the unrelaxed CT complex or in the ion pair. The aryl radical and the radical cation of the amine in the solvent cage are precursors of further transformations in these systems which can be represented as follows:

- $\{BA^{\cdot-} + DMA^{\cdot+}\} \rightarrow \{A^{\cdot} + DMA^{\cdot+} + Br^-\}$
- $\{DBA^{\cdot-} + DMA^{\cdot+}\} \rightarrow \{BA^{\cdot} + DMA^{\cdot+} + Br^-\}$
- $\{DBA^{\cdot-} + 7^{\cdot+}\} \rightarrow \{BA^{\cdot} + 7^{\cdot+} + Br^-\}$

The anthryl ($A^{\cdot}$) and 9-bromoanthryl ($BA^{\cdot}$) radicals are acceptors of hydrogen which is produced mostly from the methyl groups of the amines. Anthracene and 9-bromoanthracene arise by splitting off hydrogen by the $A^{\cdot}$ or $BA^{\cdot}$ radical:

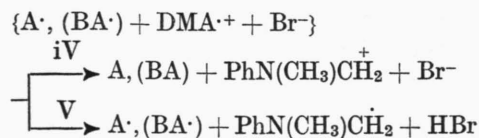


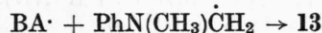
Table. R_f values and color of spots in TLC of the identified photochemical reaction products.

Compound	R_f values	H:EE PE:EE	10:1* 10:1	H:EE PE:EE	1:1* 1:1	Color of spots in iodine vapors	under the Hg lamp
	H* PE						
1	—	—	—	—	—	—	—
2	0.47*	—	—	—	—	—	pale-orange
3	0.33	—	—	—	—	—	—
4	0.30*	—	—	—	—	—	yellow
5	0.24	—	—	—	—	—	—
6	0.23*	—	—	—	—	—	pale-yellow
7	0.18	0.87	—	—	—	pale-brown	blue
8	—	0.50	—	—	—	brown	—
9	—	0.23*	—	0.54*	—	navy blue	—
10	—	0.18	—	0.44	—	violet	—
11	—	0.45	—	—	—	green	yellow
12	—	0.06	—	0.37	—	violet	—
13	—	—	—	—	—	navy blue	—
14	—	—	—	—	—	navy blue	—
15	—	0.61*	—	—	—	yellow	pale yellow
16	—	—	—	0.44	—	blue	—
17	—	—	—	0.44	—	blue	—
	—	—	—	0.39	—	blue	yellow
	—	—	—	0.33	—	blue	yellow

H = hexane; EE = ethyl ether; PE = petroleum ether.

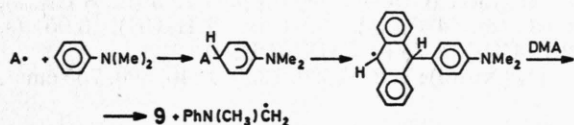
* The work was supported in part under project 03.10.7 of the Polish Academy of Science.

Product 13, formed by recombination of these radicals



is indicative of the presence of the two radicals, *i.e.* of pathway V.

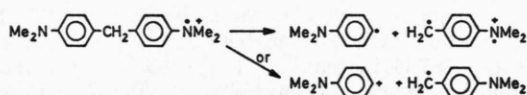
The anthryl radical ($\text{A}^\bullet$) may combine with DMA to give 9:



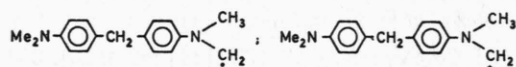
The remaining products of the photochemical reactions of BA and DBA with DMA in acetonitrile (6, 7, 8, 10, 11 and 12) may arise either by subsequent transformations of the $\text{PhN}(\text{CH}_3)\dot{\text{C}}\text{H}_2$ carbocation or the $\text{PhN}(\text{CH}_3)\dot{\text{C}}\text{H}_2$ radical. These transformations are analogous to those described for the reactions of DMA with bromobenzene [10] and chlorinated methanes [11].

Quite dissimilar are the fates of the transformations in the system DBA-7, whose precursors are the $\text{BA}^\bullet$ radical and the $7^{+\bullet}$ radical cation. The composition of the products suggests that in this

system the radical cation $7^{+\bullet}$ decomposes to give two fragments:



Further, similarly as in the case of DMA, hydrogen is split off 7 or the radical cation of 7 by the $\text{BA}^\bullet$ radical to give BA and the following species:



The reactive species formed during decomposition of $7^{+\bullet}$ and in reaction (iii) react with each other to give 14-17.

Experimental Section

Reagents

N,N-Dimethylaniline (manufactured by POCh, Gliwice, Poland) was of analytical reagent grade. It was additionally purified by the earlier reported procedure [11]. 9-Bromoanthracene (Fluka AG, Busch SG) was doubly crystallized from ethanol followed by final purification by column chromatography on silica gel using hexane as the eluant.

9,10-Dibromoanthracene was doubly crystallized from ethanol. The purity of the reagents was monitored by TLC.

Acetonitrile (B. D. H., England) was first distilled over a Vigreux column, the first benzene-containing fractions being rejected, followed by purification using the procedure described in [20]. Dioxane (analytical reagent; POCh, Gliwice) was first purified by crystallization, the lower-melting fractions being rejected, and then by the procedure described in [21]. Spectroscopic-grade benzene (Loba-Chemie) was used as supplied. Hexane (Reakhim, U. S. S. R.) petroleum ether (POCh, Gliwice) and ethyl ether (POCh, Gliwice) were purified by distillation.

Procedure

The solutions to be irradiated were outgassed either by bubbling argon for approx. 30 min or by freeze-pump-thaw cycles. The irradiations were carried out in round-bottom flasks fitted with stop-cocks to cut off air, or in sealed Pyrex ampuls, using the filtered (liquid filter made of BiCl_3 in 6 N HCl) radiation of a medium pressure Hg lamp Q-400. The mixture of photoproducts was separated and analyzed by TLC and column chromatography on silica gel (Merck) using appropriate developing systems.

The isolated products were identified either based on their MS, NMR, IR and UV spectra [22] or by comparison of the spectra with those of authentic samples.

Mass spectra were run on a Varian MAT-711 spectrometer. ^1H NMR spectra were obtained on a Tesla BS 487 C instrument operated at 80 MHz. IR spectra were taken with a Perkin-Elmer Model 257 spectrophotometer, and the UV spectra with a Specord UV-VIS spectrophotometer (G. D. R.).

Spectroscopic characteristics of the photochemical reaction products

Photodimer of 9-bromoanthracene (1)

MS (EI, 70 eV) m/e : 434, 432 (1:1) (M-HBr), 354 (M-2 $\times$ HBr), 258, 256 (1:1) (M/2), 177 (C_{14}H_9).

^1H NMR ($\text{C}_6\text{D}_6/\text{TMS}$) δ ppm: 7.75–6.65 (m, H_{arom}), 6.67–6.54 (m, H_{arom}), 5.25–5.13 (m, C-H).

IR (KBr): 1475, 1460, 1295, 1165, 1050, 855, 830, 780, 760, 695, 625 cm^{-1} .

10,10'-Dibromo-9,9'-bianthryl (2)

MS (EI, 70 eV) m/e : 514, 512, 510 (1:2:1) (M), 432, 430 (1:1) (M-HBr), 433, 431 (M-Br), 350 (M-2 $\times$ HBr), 176 (C_{14}H_8).

^1H NMR (CDCl_3/TMS) δ ppm: 8.70, 8.55 (d, 4 H_{arom}), 7.58–7.38 (m, 4 H_{arom}), 7.12–7.00 (m, 8 H_{arom}).

IR (KBr): 1580, 1445, 1270, 1165, 1102, 1032, 927, 760, 662 cm^{-1} .

UV (CHCl_3) λ : 404, 383, 362, 345 nm.

10-Bromo-9,9'-bianthryl (3)

MS (EI, 70 eV) m/e : 434, 432 (1:1) (M), 353 (M-Br), 352 (M-HBr), 258, 256 (1:1) ($\text{C}_{14}\text{H}_9\text{Br}$), 176 (C_{14}H_8).

^1H NMR (CDCl_3/TMS) δ ppm: 8.65–8.53 (m, 3 H_{arom}), 8.08, 7.98 (d, 2 H_{arom}), 7.58–7.23 (m, 4 H_{arom}), 7.05–6.96 (m, 8 H_{arom}).

IR (KBr): 1585, 1442, 1270, 1030, 925, 895, 845, 792, 760, 737, 695, 650 cm^{-1} .

UV (CHCl_3) λ : 400, 387, 381, 368, 350 nm.

9,9'-Bianthryl (4)

MS (EI, 70 eV) m/e : 354 (M), 177 (C_{14}H_9).

^1H NMR (CDCl_3/TMS) δ ppm: 8.88 (s, 2 H_{arom}), 8.11, 8.00 (d, 4 H_{arom}), 7.73–7.25 (m, 4 H_{arom}), 7.03–6.98 (m, 8 H_{arom}).

IR (KBr): 1447, 1265, 1017, 892, 862, 737, 690 cm^{-1} .

UV (CHCl_3) λ : 391, 370, 351 nm.

Anthracene (5), N-methylaniline (6), N,N,N',N'-tetramethyl-*p,p'*-diaminodiphenylmethane (7), crystal violet (11), and methyl violet (12) were identified by comparison of their NMR, IR and UV spectra, and of R_f values, with those of the corresponding authentic samples.

N,N,N'-Trimethyl-*p,p'*-diaminodiphenylmethane (8)

^1H NMR (CCl_4/TMS) δ ppm: 6.15–6.85 (m, 8 H_{arom}), 3.60 (s, 2 H- CH_2), 3.15 (s, 1 H-NH), 2.69 (s, 6 H-N- CH_3), 2.63 (s, 3 H-N- CH_3).

IR (film): 3450, 2890, 2800, 1620, 1445, 1320, 1260, 840, 800 cm^{-1} .

9-*p*-Dimethylaminophenyl-9,10-dihydroanthracene (9)

^1H NMR (CDCl_3/TMS) δ ppm: 7.23 (m, 8 H_{arom}), 6.63 (m, 4 H_{arom}), 5.10 (s, 1 H-CH), 3.95 (s, 2 H- CH_2), 2.75 (s, 6 H-N(CH_3) $_2$).

IR (Nujol): 1620, 1520, 1330, 1240, 800, 755 cm^{-1} .

Leuco derivative of crystal violet (10)

^1H NMR (CCl_4/TMS) δ ppm: 6.90–6.40 (m, 12 H_{arom}), 3.60 (s, 1 H-CH), 2.75 (s, 18 H-N(CH_3) $_2$).

IR (film): 3450, 2940–2920, 2800, 1620, 1360, 1080, 820 cm^{-1} .

N-Methyl-N-9-(10-bromoanthryl)-methyleaniline (13)

MS (FD) m/e : 376, 374 (1:1), (EI, 70 eV) m/e : 376, 374 (1:1) (M), 271, 269 (1:1) (M- PhNCH_2), 189 (M-NPh CH_2 -HBr).

^1H NMR (CCl_4/TMS) δ ppm: 8.05–8.43 (m, H_{arom}), 7.38–6.90 (m, H_{arom}), 5.04 (s, H- CH_2), 2.38 (s, H-N- CH_3).

IR (Nujol): 1610, 1515, 1480–1450, 1340, 1120, 770, 750, 690 cm^{-1} .

N,N,N',N'-Tetramethylbenzidine (14)

MS (HR) *m/e*: 240.1627, calcd. for $C_{16}H_{20}N_2$ 240.1628.

1,2-Bis[N,N-dimethyl-p-aminophenyl]ethane (15)

MS (HR) *m/e*: 268.1940, calcd. for $C_{18}H_{24}N_2$ 268.1942.

N-Methyl-N-(N',N'-dimethyl-4'-aminobenzyl)-4-(N'',N''-dimethyl-4''-aminobenzyl)aniline (16)

MS (HR) *m/e*: 373.2488, calcd. for $C_{25}H_{31}N_3$ 373.2520.

1H NMR (CCl_4/TMS) δ ppm: 6.75–6.24 (m, H_{arom}), 3.48 (s, $H-CH_2$), 2.98 (s, $H, -N-CH_2$), 2.63 (m, $H, N-CH_3$).

IR: 1625, 1335, 1075, 850 cm^{-1} .

UV λ max 350 nm.

1,2-Bis[N,N,N'-trimethyl-4,4'-diamino-1,1'-methylenediphenyl]ethane (17)

MS (HR) *m/e*: 506.3381, calcd. for $C_{34}H_{42}N_4$ 506.3413.

IR: 1625, 1530, 1330, 1175, 820 cm^{-1} .

-
- [1] M. Gordon and W. R. Ware, The Exciplex, Academic Press, London 1975.
- [2] M. D. Cohen, A. Ludmer, and V. Yakhot, Chem. Phys. Lett. **38**, 398 (1975).
- [3] J. B. Birks, Rep. Prog. Phys. **38**, 903 (1975).
- [4] H. Leonhardt and A. Weller, Z. Elektrochem. **67**, 791 (1963).
- [5] R. S. Davidson, in R. Foster (ed.): Molecular Association, Vol. 1, p. 215, Academic Press, London 1975.
- [6] A. Lablache-Combier, Bull. Chem. Soc. Fr. **1972**, 4791.
- [7] N. X. Yang, D. M. Shold, and B. J. Kim, J. Am. Chem. Soc. **98**, 6587 (1976).
- [8] J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, J. Am. Chem. Soc. **99**, 884 (1977).
- [9] C. Pac and H. Sakurai, Tetrahedron Lett. **1969**, 3829.
- [10] T. Latowski, Zesz. Nauk. WSP Gdańsk, Mat. Fiz. Chem. **8**, 189 (1968); M. Grodowski and T. Latowski, Tetrahedron **30**, 767 (1974).
- [11] T. Latowski and B. Zelent, Roczniki Chem. **48**, 831 (1974); *ibid.* **51**, 1405 (1977); *ibid.* **51**, 1709 (1977); *ibid.* **51**, 1883 (1977); T. Latowski, M. Przytarska, and B. Zelent, *ibid.* **51**, 995 (1977); T. Latowski and K. Wyrzykowska, *ibid.* **49**, 833 (1975); K. Wyrzykowska, M. Grodowski, K. Weiss, and T. Latowski, Photochem. Photobiol. **28**, 311 (1978); T. Latowski and B. Zelent, J. Org. Chem. **44**, 3559 (1979).
- [12] T. Tosa, C. Pac, and H. Sakurai, Tetrahedron Lett. **1969**, 3655; C. Pac, T. Tosa, and H. Sakurai, Bull. Chem. Soc. Jpn. **45**, 1169 (1972).
- [13] H. Knibe and A. Weller, Z. Phys. Chem. (N. F.) **55**, 99 (1967); A. Weller, Pure Appl. Chem. **16**, 115 (1968).
- [14] R. Lapouyade, H. Bonas-Laurent, and R. Calas, C. R. Acad. Sci. Paris, Ser. C **1968**, 1674.
- [15] E. J. Bowen, Adv. Photochem. **1**, 23 (1963).
- [16] J. Szychliński, Roczniki Chem. **35**, 1709 (1961).
- [17] O. M. Soloveichik and B. L. Ivanov, Zh. Org. Khim. **10**, 2404 (1974).
- [18] O. M. Soloveichik, B. L. Ivanov, and M. Kuzmin, *ibid.* **12**, 859 (1976).
- [19] N. Mataga and N. Nakashima, Spectrosc. Lett. **8**, 275 (1975).
- [20] J. F. O'Donnel, J. T. Ayres, and C. K. Maim, Anal. Chem. **37**, 1161 (1965).
- [21] A. J. Vogel, Preparatyka Organiczna, Warszawa 1964, p. 179.
- [22] R. M. Silwerstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds, 3ed., ed. russian transl. Moscow 1972.