(3) Bhura, D. C., Tandon, S. G., *J. Chem. Eng. Data*, **14**, 278 (1969).
(4) Gupta, V. K., Tandon, S. G., *J. Indian Chem. Soc.*, **46**, 831 (1969).
(5) Bhura, D. C., Tandon, S. G., *J. Chem. Eng. Data*, **16**, 106 (1971).
(6) Agrawal, Y. K., Tandon, S. G., *J. Chem. Eng. Data*, **16**, 371 (1971).
(7) Agrawal, Y. K., Tandon, S. G., *J. Chem. Eng. Data*, **16**, 495 (1971).
(8) Agrawal, Y. K., Tandon, S. G., *J. Indian Chem. Soc.*, **46**, 397 (1971).
(9) Gupta, V. K., Tandon, S. G., *J. Indian Chem. Soc.*, **48**, 753 (1971).
(10) Gupta, V. K., Tandon, S. G., *J. Chem. Eng. Data*, **17**, 248 (1972).
(11) Agrawal, D. R., Tandon, S. G., *J. Chem. Eng. Data*, **17**, 257 (1972).
(12) Weissberger, A., Proskauer, E. S., Riddick, J. A., Toops, E. E., Jr., "Technique of Organic Chemistry", Vol. VII, A., Weissberger, Ed., Interscience, New York, N.Y., 1955.
(13) Wagner, R. B., Zook, H. D., "Synthetic Organic Chemistry", Wiley, New York, N.Y., 1953.

Received for review February 28, 1978. Accepted August 3, 1978.

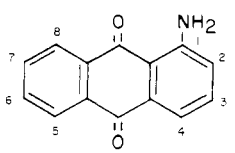
Synthesis and Fluorescence Properties of Halogenated Aminoanthraquinones

Jules Weinstein,† Richard C. Clapp,* Masato Nakashima, and John A. Sousa

U.S. Army Natick Research and Development Command, Natick, Massachusetts 01760

Derivatives of 1-aminoanthraquinone containing the heavy atoms bromine and iodine have been prepared, and their relative fluorescence intensities in three solvents have been determined. The results demonstrate that the fluorescence of 1-aminoanthraquinone can be significantly reduced by appropriate substitution.

In an attempt to identify groups that would reduce or control the level of fluorescence in aminoanthraquinones, we have prepared a number of derivatives of 1-aminoanthraquinone (**1**)



1

containing the heavy atoms bromine and iodine. Although various bromo derivatives of 1- and 2-aminoanthraquinone have been described and are important intermediates in the synthesis of anthraquinone dyes (*1*), to our knowledge no iodo derivatives of an aminoanthraquinone have been reported. Application of the Sandmeyer reaction to the preparation of the 4-chloro and 4-bromo derivatives of 1-aminoanthraquinone has been reported (*2*), and we have employed this reaction for the preparation of 1-amino-4-iodoanthraquinone. 1-Amino-4-(benzoylamino)-anthraquinone, prepared from 1,4-diaminoanthraquinone by monobenzoylation, was converted to 1-(benzoylamino)-4-iodoanthraquinone through the diazonium salt. Removal of the benzoyl group by hydrolysis yielded 1-amino-4-iodoanthraquinone. 1-Amino-5-iodoanthraquinone was prepared from 1,5-diaminoanthraquinone by the same sequence of reactions.

Attempts to prepare 1-amino-2-iodoanthraquinone from 2-amino-1-(benzoylamino)anthraquinone in a similar manner were unsuccessful since the starting material underwent cyclization to an imidazole under the reaction conditions required for the Sandmeyer reaction. Although 1-amino-2-bromoanthraquinone is readily obtained by bromination of 1-aminoanthraquinone, attempts to iodinate 1-aminoanthraquinone under a variety of conditions were not successful.

The fluorescence spectra of the iodo derivatives were measured, and the intensities of the fluorescence bands at the peaks relative to the fluorescence intensity of 1-aminoanthraquinone were determined. Since light emission intensity was found to be strongly influenced by environment, measurements were carried out in three solvents: benzene (nonpolar), acetonitrile (polar), and ethanol (polar and hydrogen bonding). The data, normalized to the same scale, are given in Table I, together with data obtained for some bromo derivatives of 1-aminoanthraquinone. The results demonstrate that the fluorescence intensity of 1-aminoanthraquinone can be significantly reduced by the introduction of bromine or iodine. The combination of a halogen atom and an acetyl or benzoyl substituent on the amino group is particularly effective in reducing the intensity.

Experimental Section

Melting points were obtained in capillary tubes in a Mel-Temp apparatus and are corrected. The fluorescence spectra were determined in a Perkin-Elmer MPF-3 spectrofluorometer equipped with a correction attachment and the infrared spectra in Perkin-Elmer spectrometers, Models 267 and 521. Merck-Darmstadt silica gel, 0.05–0.2 mm, 70–325 mesh ASTM, was used for column chromatography. TLC was carried out on plates of silica gel GF with benzene as eluent for the iodo derivatives. Elemental analyses were performed by Midwest Microlab, Indianapolis, Ind., and were in agreement with theoretical values and have been submitted for review.

1-Amino-4-iodoanthraquinone. 1-Amino-4-(benzoylamino)anthraquinone was prepared by treatment of 1,4-diaminoanthraquinone with a slight excess of benzoyl chloride in nitrobenzene and pyridine at 140 °C (*3*).

To 6 mL of concentrated sulfuric acid at 20 °C was added 1.71 g (5.0 mmol) of 1-amino-4-(benzoylamino)anthraquinone with stirring over 25–30 min. Sodium nitrite (375 mg, 5.4 mmol) was then added over 20–25 min, and stirring at 20 °C was continued for 2 h. The reaction mixture was added in portions to 200 g of ice and 100 mL of water, and after 10–15 min of stirring the mixture, the brown precipitate of diazonium salt was filtered off and washed once with ice water. To a vigorously stirred mixture of the brown precipitate and 950 mL of water was added 3.4 g (20 mmol) of potassium iodide. After the resulting mixture had been stirred at room temperature for 1.5 h and on the steam bath for 1 h, cooling and filtration afforded 1.83 g (81% crude yield) of 1-(benzoylamino)-4-iodoanthraquinone, melting from 175 to 190 °C.

A 500-mg portion of the 1.83 g and 3 mL of concentrated sulfuric acid were heated on the steam bath for 25 min. The cooled mixture was poured onto ice, and filtration gave 387 mg of a dark red solid. A 250-mg portion of this product was chromatographed in benzene solution on a silica gel column with benzene as eluent. An orange-red band was collected from the

† Deceased May 7, 1976.

Table I. Relative Fluorescence Intensities of Substituted Anthraquinones[a]

compd	solvent		
	ethanol	aceto-nitrile	benzene
1-NH_2	74.0	177	501
1-NH_2-4-I	3.28	3.11	4.31
1-$NHCOCH_3$-4-I	9.18	7.06	18.6
1-$NHCOC_6H_5$-4-I	1.02	2.22	5.26
1-NH_2-5-I	13.5	14.8	15.5
1-$NHCOCH_3$-5-I	3.70	3.35	8.52
1-$NHCOC_6H_5$-5-I	7.40	4.77	9.02
1-NH_2-2-Br	106	191	346
1-NH_2-4-Br	34.8	35.1	26.9
1-NH_2-2,4-diBr	19.7	15.1	9.45
1-CH_3NH	10.2	16.0	55.7
1-CH_3NH-4-Br	12.4	18.2	38.8
1-CH_3NH-2,4-diBr	5.78	3.39	8.34
1-$NHCOCH_3$	55.0	149	192
1-$NHCOCH_3$-4-Br	4.59	3.53	3.26
1-$NHCOC_6H_5$-4-Br	5.33	4.59	4.11

[a] Excitation wavelength was 467 nm.

column, and removal of the benzene, followed by crystallization from aqueous ethanol, yielded 150 mg (49% yield from 1-amino-4-(benzoylamino)anthraquinone) of 1-amino-4-iodoanthraquinone as small red needles: mp 208–210 °C; IR (KBr) 3430, 3300, 1660, 1630, 1600, 1530, 1270, 720 cm^{-1}.

1-(Benzoylamino)-4-iodoanthraquinone. A 254-mg portion of the 1.83 g of crude 1-(benzoylamino)-4-iodoanthraquinone from the preparation above was dissolved in benzene, and the solution was chromatographed on a silica gel column with benzene as the eluting solvent. A yellow band was collected, and concentration of the eluate afforded 187 mg of orange solid. Crystallization from benzene–heptane gave 128 mg (43% yield) of orange hairlike crystals: mp 207–209 °C; IR (KBr) 1690, 1680, 1630, 1580, 1485, 1325, 1250, 700 cm^{-1}.

1-(Acetylamino)-4-iodoanthraquinone. A solution of 49.2 mg of 1-amino-4-iodoanthraquinone in 4 mL of acetic anhydride was refluxed for 30 min. Filtration of the cooled solution yielded 49.1 mg (89%) of small orange needles, 242–244 °C. Crystallization from ethanol gave 42.4 mg of product: mp 243–245 °C; IR (KBr) 1690, 1665, 1630, 1570, 1480, 1325, 1250, 720 cm^{-1}.

1-Amino-5-iodoanthraquinone. 1-Amino-5-(benzoylamino)anthraquinone was prepared from 1,5-diaminoanthraquinone by the same procedure as was used for the monobenzoylation of 1,4-diaminoanthraquinone. It was purified (mp 246–248 °C; lit. (*4*) 244–245 °C) by crystallization from ethanol.

1-Amino-5-(benzoylamino)anthraquinone (796 mg, 2.33 mmol) was diazotized in concentrated sulfuric acid with 175 mg (2.53 mmol) of sodium nitrite under the conditions used for the 1,4 isomer. Treatment of the diazonium salt with 1.6 g (9.6 mmol) of potassium iodide by the procedure previously used yielded 906 mg of crude 1-(benzoylamino)-5-iodoanthraquinone. A 500-mg portion of this material was hydrolyzed with concentrated sulfuric acid, and crystallization of the product from ethanol afforded 189 mg (42%) of small orange-red needles: mp 211–213 °C; IR (KBr) 3460, 3330, 1665, 1630, 1600, 1535, 1255, 705 cm^{-1}.

1-(Benzoylamino)-5-iodoanthraquinone. A solution of 40 mg of 1-amino-4-iodoanthraquinone and 0.15 mL of benzoyl chloride in 2 mL of chlorobenzene was refluxed for 10 min. The precipitate that separated on cooling was filtered off and washed with ethanol: 44.4 mg (85%), mp 257–260 °C. Crystallization from benzene–heptane gave yellow-orange needles: mp 259–261 °C; IR (KBr) 1670, 1630, 1580, 1525, 1255, 700 cm^{-1}.

1-(Acetylamino)-5-iodoanthraquinone. A solution of 100 mg of 1-amino-5-iodoanthraquinone in 6 mL of acetic anhydride was refluxed for 30 min. Crystallization of the 101 mg (90%) of precipitate, mp 240–242 °C, afforded yellow-orange needles: mp 242–244 °C; IR (KBr) 1690, 1665, 1635, 1580, 1515, 1260, 705 cm^{-1}.

Preparation of Bromine Derivatives. 1-Amino-2-bromoanthraquinone was prepared by the bromination of 1-aminoanthraquinone in acetic acid (*5*). The 1,4 isomer and its benzoyl derivative were obtained from 1-amino-4-(benzoylamino)-anthraquinone by the Sandmeyer reaction (*2*); treatment with acetic anhydride afforded the acetyl derivative. 1-(Methylamino)-4-bromoanthraquinone was prepared by the bromination of 1-(methylamino)anthraquinone in pyridine (*6*). Bromination of 1-(methylamino)anthraquinone with 2 mol of bromine in acetic acid–pyridine afforded 1-(methylamino)-2,4-dibromoanthraquinone (*7*), purified by column chromatography on silica gel. 1-Amino-2,4-dibromoanthraquinone was obtained from Aldrich and crystallized from ethanol.

Literature Cited

(1) K. Venkataraman, "The Chemistry of Synthetic Dyes", Academic Press, New York: 1952, Vol. 2; 1971, Vol. 5.
(2) K. K. Mozgova, *J. Gen. Chem. USSR (Engl. Transl.)*, **19**, 755 (1949).
(3) German Patent 522 787; *Chem. Abstr.*, **25**, 3672 (1931).
(4) E. Hefti, *Helv. Chim. Acta*, **14**, 1404 (1931).
(5) German Patent 160 169; *Chem. Zentralbl.*, 1447 (1905).
(6) C. V. Wilson, "Organic Syntheses", Coll. Vol. III, Wiley, New York, 1955, p 575.
(7) A. Tundo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **15**, 84 (1957); *Chem. Abstr.*, **52**, 4185 (1958).

Received for review August 11, 1978. Accepted October 7, 1978.