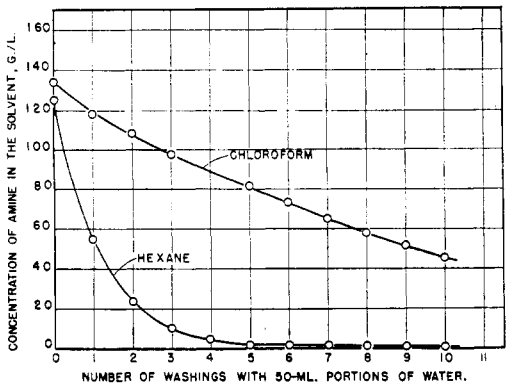

Fig. 3.

able strength, since the contacts with water were only partially effective in reducing the amine concentration in the solvent. This concept is supported, too, by the work of Smith[17] who determined the distribution coefficient for the system chloroform–water–ethylamine. Unfortunately, however, Smith's work dealt only with amine concentrations of the order of millimoles, whereas the present investigation is concerned with molar quantities.

On the other hand, the hexane–ethylamine solution, in which hydrogen bond formation can be ruled out, behaved differently toward water extraction. The curve shows that water was highly effective in reducing the amine concentration of the hexane. In fact, cold water was required for at least the first two extractions of the hexane solution, in order to reduce the vigor of the interaction between the water and the amine.

(17) H. O. Smith, *J. Phys. Chem.*, **25**, 204 (1921).

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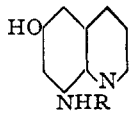
Absorption Spectra of 8-Amino-6-quinolinol Types

BY EDGAR A. STECK AND FREDERICK C. NACHOD

RECEIVED JANUARY 28, 1952

Interest in 8-(3-dimethylamino-1-methylpropylamino)-6-quinolinol (SN-191,[1] Certuna, I) led us to compare its ultraviolet absorption spectra in neutral, acid, and alkaline media with those of 8-(4-diethylamino-1-methylbutylamino)-6-quinolinol (II), 8-amino-6-quinolinol (III) and 3-hydroxy-1-naphthylamine (IV).



I, R = $CH(CH_3)CH_2CH_2N(CH_3)_2$
II, R = $CH(CH_3)CH_2CH_2CH_2N(C_2H_5)_2$
III, R = H

In Fig. 1 there are presented the absorption spectra of 8-amino-6-quinolinol (III) in acidic, basic and ethanolic solution. The comparison of

(1) All drugs identified by Survey Numbers (SN) in the files of the Antimalarial Survey have been tabulated, with antimalarial activities, in "Antimalarial Drugs, 1941–1945" (F. Y. Wiselogle, editor), Edwards Bros., Ann Arbor, Mich., 1946.

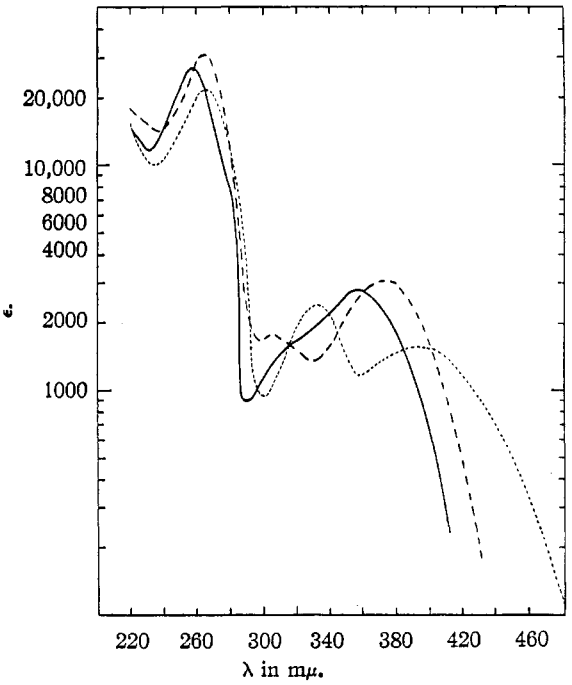


Fig. 1.—Spectra of 8-amino-6-quinolinol in: —, 95% EtOH; -------, 0.01 *N* HCl; – – –, 0.01 *N* NaOH.

these with corresponding ones of 6-quinolinol[2] shows that the 8-amino group has very little influence on the spectra. It may be noted that the spectra (Fig. 2) of 3-hydroxy-1-naphthylamine (IV), the naphthalene analog of (III), bear no simple relation to those of the contributing parents 2-naphthol[2] and 1-naphthylamine.[3] In acidic solution, the ionic contributions of (IV) cause it to be closely

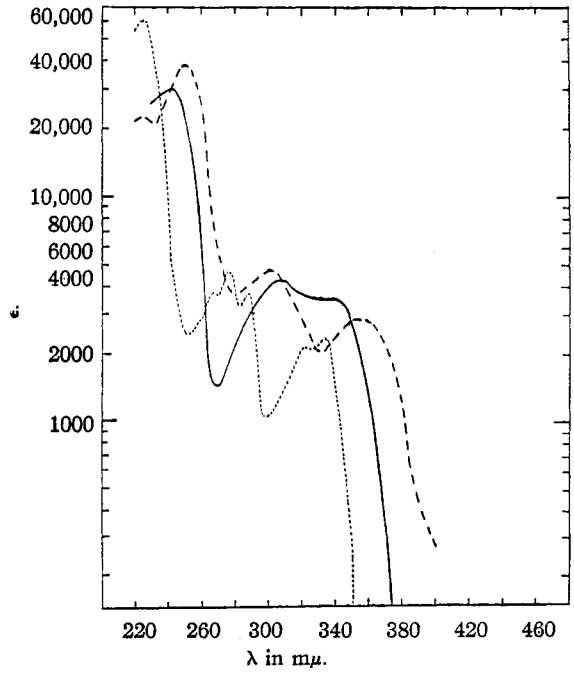


Fig. 2.—Spectra of 3-hydroxy-1-naphthylamine in: —, 95% EtOH; - - - -, 0.01 *N* HCl; – –, 0.01 *N* NaOH.

(2) G. W. Ewing and E. A. Steck, THIS JOURNAL, **68**, 2181 (1946).
(3) E. A. Steck and G. W. Ewing, *ibid.*, **70**, 3397 (1948).

similar to 2-naphthol in form; however, in alkali some fine structure is lost, and in ethanol the interaction of influences of both functional groups results in an individual spectra pattern.

Spectra of 8-(4-diethylamino-1-methylbutylamino)-6-quinolinol (II) are shown in Fig. 3; the form of the absorption curve in the case of (II) follows the general aspects of that of the parent type (Fig. 1) with variations induced by the contributions of the side-chain. The inflection in the 300–320 mμ range in ethanol for (III) is lost in (II), and the minor maximum at 308 mμ for (III) in base is de-emphasized in (II) to become an inflection. Further, there is a bifurcation of the maximum at 270 mμ shown by (III) in acid, producing twin peaks at 265 and 278 mμ in (II). All spectral curves in Fig. 3 show hypsochromic displacement when compared with those in Fig. 1. This indicates hindered resonance in (II), as expected, due to the dialkylaminoalkyl substituent on the amino group.

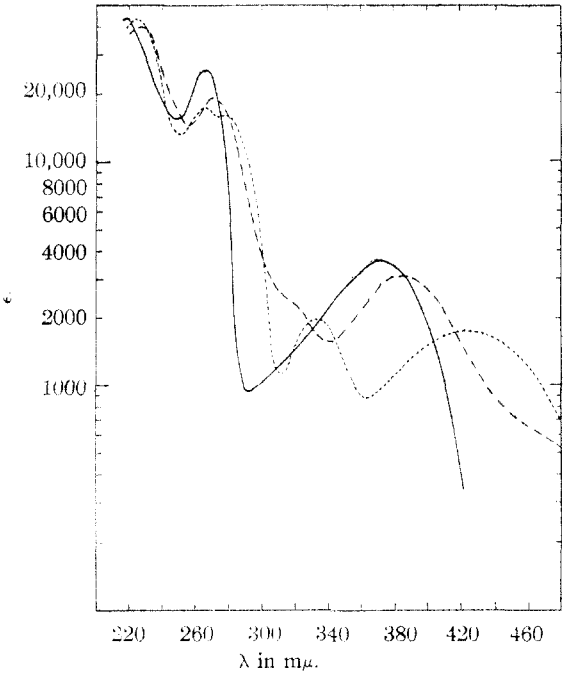


Fig. 3.—Spectra of 8-(4-diethylamino-1-methylbutylamino)-6-quinolinol in: —, 95% EtOH; - - - -, 0.01 *N* HCl; – –, 0.01 *N* NaOH.

The absorption spectra of Certuna (I) in Fig. 4, while related in shape, present a rather different picture when compared with Figs. 1 and 3. Despite close similarity of the side-chains attached to the amino groups in (I) and (II), the spectral patterns are less related than 4-amino-7-chloroquinolines bearing more variations in character as well as length of chain.[4] This is the result of differences in ease of interaction of forces in the 8-aminoquinolines with respect to the ring nitrogen. While most features of the spectrum of (I) in ethanol resemble those of (II), in the short-wave region it follows (III) in character and the sloping shoulder at *ca.* 280–300 mμ in the case of (I) may have a kindred feature in the 270–290 mμ region of (III).

(4) E. A. Steck, G. W. Ewing and F. C. Nachod, THIS JOURNAL, **70**, 3110 (1948).

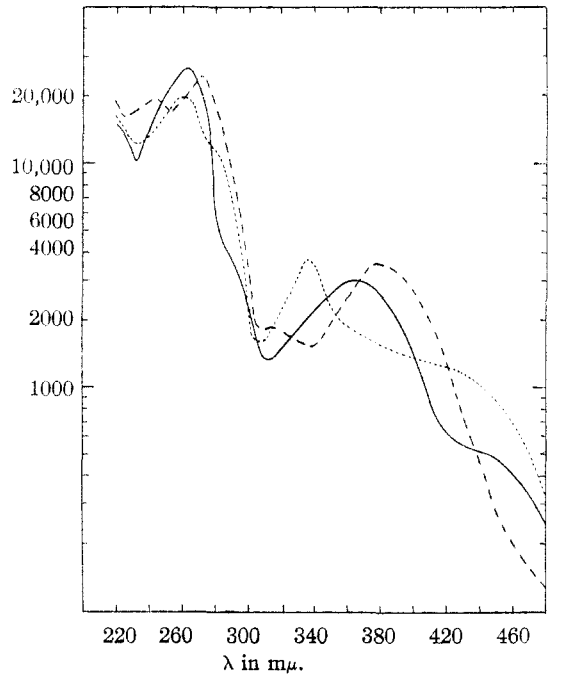


Fig. 4.—Spectra of 8-(3-dimethylamino-1-methylpropylamino)-6-quinolinol in: —, 95% EtOH; -----, 0.01 *N* HCl; – –, 0.01 *N* NaOH.

In acid solution, (I) loses much of the character shown by (II); the doublet at 265 and 278 mμ is reduced to a maximum and an inflection, and the broad maximum at 420 mμ is diminished to a mere inflection in the case of (I). While these features prevail, the maximum at 300 mμ in (II) and (III) is displaced batho- and hyperchromically in (I). Solution in alkali leads to formation of sodium salts, and while the general patterns of the spectra are more related, Certuna shows an hyperchromic displacement of the maxima in the 270 and 380 mμ regions in (II), and the maximum at 244 mμ in (I) is probably the result of bathochromic shifting of a band at shorter wave length in (II) and (III).

Experimental[5]

3-Hydroxy-1-naphthylamine.—4-Nitro-2-naphthol was prepared from 1-naphthylacetamide by the method of Morgan and Evens.[6,7] It was reduced in ethanol with 10% platinum–charcoal catalyst at 3 atm. to give 88% of 3-hydroxy-1-naphthylamine, m.p. 203.5–205° dec. The compound was sublimed twice (170°, 0.1 mm.) and then crystallized from 85% ethanol (containing traces of sodium dithionite). The white needles melted at 208.5–209°, cor. (evacuated capillary); literature,[7] m.p. 198° dec.

Anal. Calcd. for $C_{10}H_9NO$: N, 8.80. Found: N, 8.89.

8-Amino-6-quinolinol.—The demethylation of 8-amino-6-methoxyquinoline, carried out as described in the patent literature,[8] gave 8-amino-6-quinolinol (m.p. 170–172° dec.) in 85% yield. A sample was crystallized twice from ethyl acetate–hexane and then from water (containing traces of sodium dithionite) to produce the compound as pale yellow needles, m.p. 177–177.5°, dec. (lit.[5,9] 177 and 188°).

Anal. Calcd. for $C_9H_8N_2O$: N, 17.49. Found: N, 17.34.

8-(3-Dimethylamino-1-methylpropylamino)-6-quinolinol was prepared[10] from 8-(3-dimethylamino-1-methylpropyl-

(5) Analyses by Mr. K. D. Fleischer and staff of the Microanalytical Laboratories of this Institute.

(6) G. T. Morgan and E. D. Evens, *J. Chem. Soc.*, **115**, 1132 (1919).

(7) W. A. P. Challenor and C. K. Ingold, *ibid.*, **123**, 2080 (1923).

(8) F. Mietzsch and H. Klös, U. S. Patent 1,903,407.

(9) J. Mathëus, *Ber.*, **21**, 1645 (1888).

(10) E. A. Steck and W. Boehme, to be published.

amino)-6-methoxyquinoline (*cf.* ref. 11) by refluxing with hydrobromic acid.[12] The compound was used as the sulfate trihydrate, m.p. 118–120°.[10]

8-(4-Diethylamino-1-methylbutylamino)-6-quinolinol.[13]—Pamaquine base was demethylated with hydriodic acid and the product characterized[10] as the dihydriodide (m.p. 162–164°) and the methylene 1,1'-bis-(2-hydroxy-3-naphthoate) (m.p. > 250°).

The spectra were determined with a Cary recording spectrophotometer, using a dynode voltage of 4, a slit schedule of 20, and 1-cm. quartz cells. The concentrations of the solutions ranged from 0.01 to 0.200 g./l. and their spectral behavior conformed with Beer's law in all instances. The assistance of Mrs. M. Becker is gratefully acknowledged.

(11) E. C. Kleiderer, J. B. Rice and V. Conquest, Office of Publication Board, Dept. of Commerce, Washington, D. C., 1945, Report 248, p. 32.

(12) W. Kikuth, U. S. Patent 2,291,235.

(13) Swiss Patent 129,425 (to I. G. Farbenindustrie).

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Observations on Curium Valence States; A Rapid Separation of Americium and Curium[1]

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RECEIVED MARCH 24, 1952

A search for oxidation states higher than Cm(III) in aqueous solution has been made using macro amounts of curium (up to 238 μg. per experiment). Since Cm^{242} has a specific activity of *ca.* 7×10^9 α/min./microgram,[2] it was anticipated that production of hydrogen peroxide or other reducing materials might be a limiting factor in the oxidation. Consequently, americium, which does exhibit higher oxidation states (V)[3a] and (VI)[3b] in solution, was used as an internal check for oxidation. It was found that Am(III) was not oxidized to Am (VI) in the presence of curium concentrations of *ca.* 500 μg./ml. However, the oxidation of Am(III) to Am(VI) is complete at curium concentrations of *ca.* 160 μg./ml., or lower. The effect of curium α-radiation on the solution would presumably be the same for higher oxidation states of both curium and americium, and therefore could not be the limiting factor in the curium oxidation within the concentration ranges studied.

Experimental

The chemicals used were all reagent grade. The isotopes employed were Cm^{242} and Am^{241}, α-emitters of 162 day[2] and 475 year[4] half-lives, respectively.

Oxidation in Acid.—Experiments were performed with 0.1–0.3 *f* HNO_3 or $HClO_4$ solutions containing americium and curium in various weight ratios. These solutions were treated with solid ammonium peroxydisulfate and heated 1–2 hours in a water-bath at 85°. The oxidation of Am(III) to Am(VI) in the presence of curium was achieved best when the hydroxides were freshly precipitated with gaseous ammonia, dissolved in acid to give a solution of 0.1 *f* in hydrogen ion, and immediately oxidized with peroxydisulfate. Dilute acid solutions of americium and curium which had been left to stand for several hours or longer were not readily oxidized. Immediately following the oxidation, the solution was made 3–4 *f* in HF to precipitate CmF_3 and any americium still in the (III) state. (The 27 *f* HF used was pretreated with solid ammonium peroxydisulfate.) The fluoride precipitate was separated by centrifugation and washed with hot ammonium peroxydisulfate solution, 0.1 *f* in $HClO_4$ and 3 *f* in HF. The supernatant and wash were combined.

The fluoride precipitate was dissolved in 1 *f* HNO_3, saturated with H_3BO_3. Mixed $Cm(OH)_3$ and $Am(OH)_3$ were precipitated from the resulting solution with gaseous ammonia. The precipitate was dissolved in 0.2 *f* perchloric acid; Am(III) was determined in the Beckman DU spectrophotometer by observation of the 503 mμ peak (molecular extinction coefficient of 360 in 0.1 *f* $HClO_4$). Curium was determined by a total α-count after correction for the americium alphas present.

The fluoride supernatant was treated with hydrogen peroxide to reduce Am(VI) to Am(III) with consequent precipitation of AmF_3. The precipitate was dissolved as described above and americium(III) determined spectrophotometrically.

Experiments were performed with and without lanthanum as carrier for the curium. Typical results of this separation method are shown in Table I.

TABLE I

TYPICAL RESULTS FOR THE PEROXYDISULFATE SEPARATION METHOD (ONE CYCLE)

μg./ml. Cm	μg./ml. Am	μg./ml. La	Wt. fraction Cm:Am Before oxidation	Wt. fraction Cm:Am After oxidation (CmF_3)
3.7	1060	350	0.0035	0.11
82	210	800	0.39	10.0
85	28	215	3.0	19.0
160[a]	270	0	0.59	15.7
540	39[b]	0	14.0	15.8

[a] At this concentration, without lanthanum carrier, the solubility of CmF_3 limits the yield of curium in the precipitate to *ca.* 90%. [b] In the absence of curium, Am(III) is completely oxidized to Am(VI) at concentrations even as low as 11 μg./ml.

Curium was not oxidized to a fluoride-soluble state, since it was possible to precipitate CmF_3 and leave *ca.* 95% of the Am(VI) in solution. This eliminates the possibility that Cm(VI) was formed, but does not rule out the possibility of Cm(IV), which would also have an insoluble fluoride. Consequently, four experiments were performed using Zr(IV) phosphate; Cm(III) was treated with ammonium peroxydisulfate, both with and without silver catalyst, in 0.1–1 *f* acid and Zr(IV) phosphate precipitated. Since only 2–10% of the curium present was carried by zirconium phosphate, it seems evident that no Cm(IV) is formed under these conditions. (At these low acidities, the gelatinous precipitate would be expected to carry some Cm(III).)

Alkaline Oxidation.—Experiments were performed to attempt to form Cm(V) by peroxydisulfate oxidation in 2 *f*, 3 *f* and saturated K_2CO_3 solution, and to demonstrate its existence by co-precipitation with Am(V). The Am(V) precipitate contained only 0.5–2% of the curium. Concentrations ranged from 5 to 320 μg. of curium per ml. with 13 to 500 μg. of americium per ml. In this last experiment, only 2% of the curium was found in the Am(V) precipitate. It was concluded that curium is not oxidized to Cm(V) under conditions in which Am(III) is quantitatively oxidized to Am(V). Spectrophotometric examination of the carbonate supernatant was made to look for Cm(IV) or Cm(VI); only the absorption spectrum of Cm(III) was found.

The possibility of a slow step in the curium oxidation cannot be ruled out. However, the oxidation of very dilute americium solutions (4.5×10^{-5} *f*) is complete in less than an hour (Am(III) → Am(VI), 0.1 *f* H^+, peroxydisulfate). Inasmuch as Am(VI) and Am(V) undergo auto-reduction at the rate of a few per cent. an hour, due to the products of americium α-radiation,[5] and the specific activity of Cm^{242} is 1000 times that of Am^{241}, it seems likely that a sufficient concentration of reduction materials would be produced to prevent complete oxidation of americium when sufficient curium is present. However, the effect should not limit the

(1) Work done under the auspices of the AEC.

(2) G. C. Hanna, B. G. Harvey and N. Moss, *Phys. Rev.*, **78**, 617 (1950).

(3) (a) L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951); (b) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *ibid.*, **73**, 5715 (1951).

(4) B. B. Cunningham, S. G. Thompson and H. Lohr, unpublished work (1949).

(5) L. B. Asprey and S. E. Stephanou, AECU-924, November 10, 1950.