

may lie in the presence of traces of nitrogenous bases in the phosphite used at that time.

The esters, whose constants are shown in Table I, were obtained in yields of 84% or better. The products were finally purified by distillation through a 15-plate ring-packed fractionating column.

Determination of Viscosity.—The determinations were made conventionally in an Ostwald viscosimeter at 32 and 52°, the results being correlated with water standard.

Determination of Dielectric Constants.—The determinations were made at 32° by means of the Sargent Oscillometer, Model V, which was calibrated with carefully purified substances, whose dielectric constants had been accurately established earlier.⁵ The dielectric constants of the phosphonates fell within the substantially linear portion of the calibration curve of the instrument. Thus it was possible to determine the relative values of the dielectric constants of any two substances to four, or even five, significant figures from the readings of the instrument. However, the actual accuracy of the determinations was obviously limited by the accuracy of the values taken as standards, a situation that has been common in such determinations.

Calculation of the Dipole Moments.—The dipole moments were calculated by the Böttcher equation and the results are shown in Table I. The values of the dipole moments are estimated to be accurate within 0.02 *D*.

Acknowledgment.—We wish to acknowledge the financial aid of the Research Corporation in the form of a Frederick Gardner Cottrell grant for partial support of this work.

(5) E. Treiber, J. Schurz and H. Koren, *Monatsh.*, **82**, 32 (1951).

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The Anisotropic Rate of Photographic Development of Single Crystals of Silver Chloride^{1,2}

BY HENRY LEIDHEISER, JR., AND FRANCES H. COOK

RECEIVED SEPTEMBER 28, 1953

The purpose of this communication is to describe some preliminary experiments which show that the rate of photographic development of silver chloride is dependent upon the crystal face exposed at the surface.

Large single crystals of silver chloride³ were machined in the form of spheres, $\frac{5}{8}$ " in diameter, with a small shaft for handling.⁴ These spheres were etched to a depth of approximately 0.01" by agitating slowly in 1% sodium cyanide solution; X-ray photographs taken at grazing incidence and by back reflection indicated that the strains introduced by the machining operation were removed by

(1) This research was conducted under Contract No. AF 33(616)-323 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

(2) When this manuscript was first submitted for publication, the reviewer suggested that we await the publication of the article by H. D. Keith and J. W. Mitchell, *Phil. Mag.*, **44**, 877 (1953), which describes a very extensive study of the formation of free silver on single crystals of silver bromide. Resubmission of this manuscript was postponed until copies of the article could be obtained. Of particular pertinence to the experiments reported herein is the statement by Keith and Mitchell: "Under comparable conditions, the surface density of reduction centers is usually greater on (111) than on (100) surfaces and the rate of reduction at individual centers appears higher."

(3) The crystal ingots were purchased from the Harshaw Chemical Co., Cleveland, Ohio. See H. C. Kremers, *J. Opt. Soc. Am.*, **37**, 337 (1947).

(4) See H. Leidheiser, Jr., and A. T. Gwathmey, *Trans. Electrochem. Soc.*, **91**, 97 (1947), for a description of the single crystal method of study.

this etching. Smooth and strain-free surfaces were obtained by rotating the crystal and lightly pressing against it a strip of wool flannel moistened with 1% sodium cyanide solution. The surfaces so obtained had the microscopic and macroscopic appearance of plate glass.

The polished crystal was washed thoroughly in water and allowed to dry. After additional exposure to artificial light at ordinary room lighting conditions, the crystal was immersed in a photographic developer such as Ansco Finex-L maintained at 5–7°. The crystal faces making small angles with the (111) plane rapidly became covered with minute grains of silver while the (100) face and the faces making small angles with the (100) plane remained free of silver for much longer periods of time. The (110) faces and surrounding area had an intermediate activity. The relative order of activity of the faces was the same in Eastman developers Dektol and DK-50. When a heavy deposit of silver was formed and the crystal was immersed in nitric acid, the silver was removed most rapidly from the (100) faces and surrounding areas.

X-Ray analysis at grazing incidence of the silver deposits indicated that on the same crystal the degree of preferred orientation of the deposit on the (100) face was greater than that of the deposit on the (111) face. The electron microscope observations made by Keith and Mitchell relative to the formation of filamentous silver in some cases and the formation of geometric figures in other cases were confirmed in this study.

It is not known at the present stage of progress whether the results reported herein represent differences in the rate of development of the latent image or simply differences in the fogging behavior of the crystal faces. An answer to this problem is being sought. Consideration will also be given in future studies to an analysis of the role of trace impurities such as silver oxide and silica on the results.

Additional experiments have indicated that the rate of etching of silver chloride crystals in acid fixing solution is also dependent on the crystal face exposed at the surface. Experimental work on the photographically important properties of silver chloride crystals is being continued.

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Relationships between the Absorption Spectra of the 8-Quinolinol Chelates of the Group IIIb Metals and the Acidic Species of 8-Quinolinol

BY THERALD MOELLER AND FRED L. PUNDSACK

RECEIVED AUGUST 3, 1953

In the course of investigations of the 8-quinolinol and 5,7-dihalo-8-quinolinol chelates of the Group IIIb metals,^{1,2} marked similarities between the absorption spectra of solutions of these compounds in "neutral" non-aqueous solvents and the spectra of acidic aqueous solutions of the reagents were noted.² Although the absorption spectra of acidic,

(1) T. Moeller and A. J. Cohen, *THIS JOURNAL*, **72**, 3546 (1950).

(2) F. L. Pundsack, Doctoral Dissertation, University of Illinois (1952).

neutral and alkaline solutions of 8-quinolinol have been described by several investigators,³⁻⁸ the only similarities to the spectra of derived metal chelates which have been reported are some resemblances between 8-quinolinol spectra in cyclohexane and copper(II) 8-quinolinol chelate spectra in chloroform.⁶ Any resemblances involving the acidic species of 8-quinolinol appear to have been overlooked.

Inasmuch as similarities in absorption spectra are often pertinent to structure evaluation, detailed comparisons of these absorption spectra were made.² The lack of absolute agreement among recorded values as summarized in Table I prompted a redetermination of the spectra of 8-quinolinol in acidic and alkaline media and an evaluation of the effects of acid and alkali concentration changes. Since the absorption data for the Group IIIb 8-quinolinol chelates,¹ upon which the original comparisons were based, were obtained for chloroform solutions and thus did not permit accurate evaluations below 260 m μ , comparative measurements were made upon solutions of the gallium(III) chelate in 95% ethanol over the range 250-600 m μ . Although comparisons are made herein only between 8-quinolinol and its gallium chelate, the relationships pointed out apply equally well to the derivatives of the other Group IIIb elements and to the halo-substituted 8-quinolinol systems.

TABLE I
ABSORPTION SPECTRA DATA FOR 8-QUINOLINOL

Acidic solution λ , m μ	"Neutral" solvent		Alkaline solution		Ref.	
	log ₁₀ ^a	λ , m μ	log ₁₀	λ , m μ		
250	4.54	240	4.60	255	4.54	3 ^{b,c}
310	3.30	310	3.48	340	3.48	
320	3.30			355-360	3.48	
355-360	3.30					
310	3.09	305	3.46	335	3.38	4 ^{b,c}
355	3.24			365	3.42	
250	4.60	242	4.62	253	4.50	6 ^c
318-319	3.23	320	3.38	345	3.43	
358	3.23					
310	3.20	265	3.46	335	3.46	7,8 ^{d,e}
320	3.20	310	3.42	355	3.45	
360	3.22					
250	4.63	240	4.60	253	4.48	This study
309	3.20	308	3.47	335	3.44	
319	3.20			353	3.43	
358	3.22					

^a Logarithm of molecular extinction coefficient. ^b 0.01 N HCl, 95% C₂H₅OH, 0.01 N NaOH. ^c 0.1 N HCl, C₆H₁₁O₂, 0.1 N NaOH. ^d Aqueous buffers: pH 1.44, 6.96, 12.40. ^e Values estimated from graphic representations.

Experimental

Reagents.—The 8-quinolinol used was an Eastman

- (3) G. W. Ewing and E. A. Steck, *THIS JOURNAL*, **68**, 2181 (1946).
 (4) K. G. Stone and L. Friedman, *ibid.*, **69**, 209 (1947).
 (5) H. Irving, J. A. D. Ewart and J. T. Wilson, *J. Chem. Soc.*, 2672 (1949).
 (6) J. P. Phillips, W. H. Huber, J. W. Chung and L. L. Merritt, Jr., *THIS JOURNAL*, **73**, 630 (1951).
 (7) R. Näsänen, P. Lumme and A. L. Mukala, *Acta Chem. Scand.*, **5**, 1199 (1951).
 (8) R. Näsänen, *ibid.*, **5**, 1293 (1951).

Kodak Co. product which had been recrystallized from ethanol. Other chemicals were of reagent quality.

Apparatus.—Spectrophotometric measurements were made with a Cary Recording Spectrophotometer, employing 5-cm. cells.

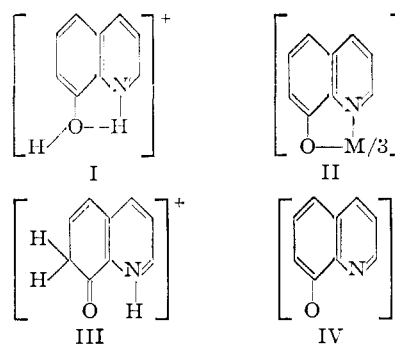
Procedure.—A standard acidic solution of 8-quinolinol was prepared by dissolving 3.130 mg. of the reagent in 50 ml. of 0.1060 N hydrochloric acid. Two solutions, containing, respectively, 11.60 and 1.16 mg. of 8-quinolinol per liter, were prepared by dilution with 0.1060 N hydrochloric acid. The first of these was used at wave lengths greater than 300 m μ ; the second at wave lengths less than 300 m μ . A standard alkaline solution of 8-quinolinol was prepared by dissolving 10.00 mg. of the reagent in 100 ml. of 1.0 N sodium hydroxide. Two solutions, containing, respectively, 20.00 and 1.20 mg. of 8-quinolinol per liter of 0.1 N sodium hydroxide, were obtained by appropriate dilution. The first of these was used at wave lengths greater than 300 m μ ; the second at wave lengths less than 300 m μ . A standard solution of the gallium(III) chelate^{1,2} was prepared by dissolving 72.0 mg. of the complex in 100 ml. of 95% ethanol. Two solutions, containing, respectively, 14.40 and 0.58 mg. of the chelate per liter, were prepared by dilution. The first of these was used at wave lengths greater than 300 m μ ; the second at wave lengths less than 300 m μ .

Discussion

The observed effects of acidic and alkaline conditions upon the absorption spectrum of 8-quinolinol, as summarized in Table I, are generally similar to those previously reported³⁻⁸ and of the same general magnitude. Variations in acid concentration between 0.1 and 0.002 N and in alkali concentration between 0.1 and 0.05 N had no significant effect upon the spectra, suggesting the presence of but a single absorbing species in each pH region.

The apparent similarity between the spectrum found for acidic solutions and those given for chloroform solutions of the 8-quinolinol chelates of the tripositive Group IIIb metals¹ is perhaps more directly shown by data obtained for the gallium(III) chelate in 95% ethanol, where absorptions at 258 (5.27),⁹ 320 (3.86), 336 (3.92), and 380 (4.21) m μ were noted. The essential differences amount to bathochromic shifts and increases in absorption intensities with the gallium chelate.

It is reasonable to assume that in systems as closely comparable as these absorptions in the same spectral regions result from structural similarities. This suggests that in acidic media the added proton functions in essentially the same fashion as do the metal ions in the neutral chelates forming in effect a type of chelated structure, as is indicated in formulas I and II. This structure amounts to a hydrogen bonded arrangement and appears, on the basis of spectral evidences, to be more probable



(9) Values in parentheses represent logarithms of equivalent extinction coefficients.

than the one previously proposed^{4,6} and given in formula III.

Similarities in the absorption spectra of 8-quinolinol in alkaline and "neutral" media (except for bathochromic shifts) support this view. The sodium derivative of 8-quinolinol is very soluble in water and insoluble in materials such as benzene or chloroform,¹⁰ suggesting that it is a salt rather than a chelate. This evidence and the well-known fact that sodium ion does not commonly add complexing groups indicate that the appearance of a structure comparable to II in alkaline solutions of 8-quinolinol is most unlikely. A structure as is shown in formula IV is more probable. In neutral solvents, the absence of a structure comparable to II may be due to an enhanced tendency toward intermolecular hydrogen bonding rather than intramolecular. In such media, a structure like that given in IV with the proton on the oxygen alone would then seem reasonable.

Acknowledgment.—Support received from the Office of Naval Research and from the National Science Foundation is gratefully acknowledged.

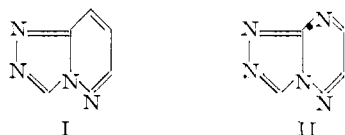
(10) P. Süe and G. Wétroff, *Bull. soc. chim.*, [5] **2**, 1002 (1935).

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The Synthesis of Some *s*-Triazolo(4,3-*b*)-*as*-triazines¹

BY E. C. TAYLOR, JR., W. H. GUMPRECHT AND R. F. VANCE
RECEIVED OCTOBER 10, 1953

In view of the significant purine-inhibitory activity which has been observed for a number of derivatives of heterocyclic systems related to the purine ring system²⁻⁶ it seemed of considerable interest to investigate the chemical and biological properties of heterocyclic systems retaining some gross structural similarity to the purines but less closely related than the majority of compounds previously studied. A few derivatives of one such system, *s*-triazolo(4,3-*b*)pyridazine (I), have been reported to be extremely toxic.⁷ The present paper reports the preparation of several derivatives of a closely related ring system, *s*-triazolo(4,3-*b*)-*as*-triazine (II).



(1) Abstracted from part of the thesis presented by W. H. Gumprecht to the University of Illinois in partial fulfillment of the degree of Bachelor of Science in Chemistry.

(2) R. O. Roblin, Jr., J. O. Lampen, J. P. English, Q. P. Cole and J. R. Vaughan, Jr., *THIS JOURNAL*, **67**, 290 (1945).

(3) G. H. Hitchings, G. B. Elion, H. VanderWerff and E. A. Falco, *J. Biol. Chem.*, **174**, 765 (1948).

(4) G. H. Hitchings, G. B. Elion, E. A. Falco, P. B. Russell, M. B. Sherwood and H. VanderWerff, *ibid.*, **183**, 1 (1950).

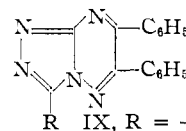
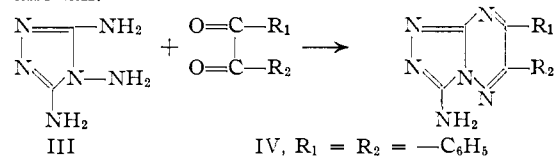
(5) R. L. Thompson, M. L. Wilkin, G. H. Hitchings, G. B. Elion, E. A. Falco and P. B. Russell, *Science*, **110**, 454 (1949).

(6) E. A. Falco, G. H. Hitchings, P. B. Russell and H. VanderWerff, *Nature*, **164**, 107 (1949).

(7) C. Bülow, *Ber.*, **42**, 2208 (1909). A reinvestigation of these compounds is in progress in these laboratories.

A few derivatives of *s*-triazolo(4,3-*b*)-*as*-triazine have been reported by Hoggarth,^{8,9} who condensed several 3,4-diamino-1,2,4-triazoles with benzil and biacetyl to give the appropriately substituted triazolotriazines. However, the requisite triazoles had been prepared only in poor yield and often as only one of many products by the reaction of hydrazine with 1-benzoylmethylthioisothiosemicarbazide, 1,4-dibenzoylthiosemicarbazide, N,N'-dithiocarbamylhydrazine and similar compounds, and the condensation reactions were employed only for the purpose of furnishing confirmatory evidence for the vicinal diamino grouping in the triazoles concerned.

A more attractive approach leading directly to *s*-triazolo(4,3-*b*)-*as*-triazines more suitably substituted for possible biological activity has been found to involve the condensation of α,β -dicarbonyl compounds with guanazine (3,4,5-triamino-1,2,4-triazole) (III), readily available from the condensation of hydrazine with cyanogen bromide. Successful condensations with benzil, biacetyl, *p,p'*-dichlorobenzil, phenanthrenequinone and pyruvic acid to give the appropriately substituted 3-amino-*s*-triazolo(4,3-*b*)-*as*-triazines (IV-VIII) were carried out; unsuccessful attempts were made to effect condensation with glyoxal and alloxan.



R IX, R = -SH; X, R = -SCH₃

IV, R₁ = R₂ = -C₆H₅
V, R₁ = R₂ = -CH₃
VI, R₁ = R₂ = -C₆H₄Cl-*p*
VII, R₁ = R₂ = phenanthro(9,10-*c*)
VIII, R₁ = -OH, R₂ = -CH₃

Unsuccessful attempts were made to convert 3-mercapto- (IX) and 3-methylmercapto-6,7-diphenyl-*s*-triazolo(4,3-*b*)-*as*-triazine (X) to the 3-amino derivative IV with alcoholic ammonia or with potassium amide. This behavior is consistent with the reported failure of 3-methylmercapto-5-phenyl-1,2,4-triazole to react with ammonia¹⁰ and parallels the observed unreactivity of numerous heterocyclic thioamides and S-alkylisothioamides with amines.¹¹

Preliminary tests carried out with the organism *Leuconostoc mesenteroides* P-60 showed that compounds IV, V, VIII, IX and X were inactive either as purine substitutes or as antagonists at the concentrations employed. Compounds VI and VII were too insoluble to be tested under the conditions employed.

(8) E. Hoggarth, *J. Chem. Soc.*, 614 (1950).

(9) E. Hoggarth, *ibid.*, 4817 (1952).

(10) E. Hoggarth, *ibid.*, 1160 (1949).

(11) (a) F. H. S. Curd, M. I. Davis, E. C. Owen, F. L. Rose and G. A. P. Tvey, *ibid.*, 720 (1946); (b) F. H. S. Curd, J. K. Landquist and F. L. Rose, *ibid.*, 775 (1947); (c) A. F. Crowther, F. H. S. Curd, D. N. Richardson and F. L. Rose, *ibid.*, 1636 (1948); (d) R. de B. Ashworth, A. F. Crowther, F. H. S. Curd and F. L. Rose, *ibid.*, 581 (1948); (e) H. C. Carrington, *ibid.*, 684 (1947); (f) H. L. Wheeler and G. S. Jamieson, *Am. Chem. J.*, **32**, 342 (1904); (g) F. E. King and T. J. King, *J. Chem. Soc.*, 943 (1947); (h) P. B. Russell, G. B. Elion, E. A. Falco and G. H. Hitchings, *THIS JOURNAL*, **71**, 2279 (1949).