combined (total = 3.9 g.). Upon rectification through the 65-plate column there was obtained 0.6 g. of a colorless liquid, b.p. 81° (18 mm.), $n^{20}D$ 1.4180. *Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.7; sapon. equiv., 172. Found: C, 69.9; H, 11.9; sapon. equiv., 166. An S-benzylthiuronium salt was prepared from the neutral solution; m.p. 138–139° (40% yield). It did not depress the m.p. of an authentic sample of S-benzyl thiuronium acetate, m.p. 139–140°.

Isolation of *d*-2-Octanol.—Fractions 17–22, b.p. 68° (15 mm.), were combined (total = 40.1 g.); $n^{20}D$ 1.4249, lit. value,[10] $n^{20}D$ 1.4264; $[\alpha]^{25}D$ + 9.23° (*c* = 5, ethanol). A 5-g. portion, esterified with phthalic anhydride in the presence of pyridine,[10] gave a 95% yield of *d*-2-octyl hydrogen phthalate, m.p. 71–73°. This, after one recrystallization from petroleum ether (b.p. 60–70°), melted at 73–74° (lit. m.p.[9] 75°) and did not depress the m.p. of authentic *d*-2-octyl hydrogen phthalate, m.p. 74–75°. The purified ester had $[\alpha]^{25}D$ + 47.5° (*c* = 5, ethanol). (The *d*-2-octyl hydrogen phthalate obtained during the resolution of 2-octanol had $[\alpha]^{25}D$ + 47.7°). *Anal.* Calcd. for $C_{16}H_{22}O_4$: C, 69.0; H, 8.0. Found: C, 69.1; H, 8.2. The ester was hydrolyzed[9] to *d*-2-octanol; $n^{20}D$ 1.4262 (lit.[10] 1.4264), $[\alpha]^{25}D$ + 9.27° (*c* = 5, ethanol). The *d*-2-octanol used to prepare the *d*-2-octyl nitrite had $[\alpha]^{25}D$ + 9.30°.

Isolation of 2-Octyl Heptanoate.—A yellow 4-g. residue remained from the rectification of 100 g. of yellow liquid ($n^{20}D$ 1.4193). This had $n^{20}D$ 1.4285 and gave a test for esters.[20] It was rectified through the 65-plate column. There was obtained 0.7 g. of a colorless liquid; b.p. 112° at 10 mm., $n^{20}D$ 1.4320. *Anal.* Calcd. for $C_{15}H_{30}O_2$: C, 74.3; H, 12.4; sapon. equiv., 242. Found: C, 74.4; H, 12.2; sapon. equiv., 240. An S-benzylthiuronium salt was prepared from the neutral solution; m.p. 147–148° (65% yield). It did not depress the m.p. of authentic S-benzylthiuronium heptanoate, m.p. 148–149°.

Nitric Oxide.—The two wash-bottles containing 96% sulfuric acid + 65% nitric acid had absorbed 11.4 g. of nitric oxide (titration with standard permanganate).[21]

Nitrous Oxide and Nitrogen.[22]—The gases collected over potassium hydroxide totaled 6750 ml. (S.T.P.). Upon analysis in a conventional Orsat apparatus, 8% of the gas was found to be nitrous oxide (determined by slow combustion with hydrogen) and the remaining 92% was inert (nitrogen). Carbon dioxide, carbon monoxide, olefins, saturated hydrocarbons, oxygen, nitric oxide and nitrogen dioxide were all absent.

Demonstration of the Formation of Carbon Dioxide in the Thermal Decomposition of *dl*-2-Octyl Nitrite.—Ten grams of *dl*-2-octyl nitrite was decomposed at 100 ± 2° over a period of eight days in a slow stream of dry oxygen-free nitrogen. The exit gases were passed through 96% sulfuric acid, glass wool and finally through two U-tubes containing Ascarite; the Ascarite tubes gained 177 mg. (4.0 meq. of carbon dioxide). The Ascarite which reacted did not give a test for cyanide.[23] The liquid remaining in the flask weighed 7.3 g., and contained 0.9 meq. of acetic acid and 0.7 meq. of heptanoic acid.

(21) Milligan, *J. Phys. Chem.*, **28**, 544 (1924).

(22) We are indebted to Professor P. J. Elving of this department for his kind assistance in connection with the gas analyses.

Summary

The thermal decomposition of *d*-2-octyl nitrite in the liquid phase at 100° gives *optically pure d*-2-octanol in excellent yield. In addition to confirming F. O. Rice's mechanism for the pyrolysis of alkyl nitrites, this indicates that alkoxyl radicals of the type $R-\overset{R'}{\underset{H}{C}}-O\cdot$ do not rearrange to $R-\overset{R'}{\underset{\cdot}{C}}-OH$ in the liquid phase at 100°.

The other major organic product is 2-octanone. Small amounts of acetic acid, heptanoic acid, 2-octyl acetate, 2-octyl heptanoate and capronitrile are also produced. These probably arise from the cleavage of 2-octanone by nitric oxide followed by esterification of 2-octanol by the acids formed.

The gaseous products of the reaction are nitrogen, nitric oxide, nitrous oxide and carbon dioxide.

(23) Lander and Walden, *Analyst*, **36**, 266 (1911).

LAFAYETTE, INDIANA RECEIVED AUGUST 10, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Optical Crystallographic Properties of Some Sulfonamides and their Derivatives

BY RAYMOND N. CASTLE,[1] NORMAN F. WITT AND C. F. POE

The optical crystallographic properties of organic compounds are useful for purposes of identification. This is particularly true of compounds containing aromatic or heterocyclic ring systems where examples of strong dispersion of several types and strong double refraction are frequently observed. Thus the optical crystallographic properties of the sulfonamides and their derivatives should prove useful in their characterization.

Optical crystallographic studies of some of the therapeutically important sulfonamides have received the attention of several investigators. Except for sulfanilamide these data are more or less incomplete. The optical properties of sulfanilamide and of a series of Schiff bases have been determined by White.[2] Grove and Keenan[3] reported the optical properties of two forms of sulfathiazole. Prien and Frondel[4] reported the application of the optical properties of sulfanilamide, sulfathiazole and sulfapyridine, and their

(1) (a) From a portion of the dissertation submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy at the University of Colorado, August, 1944. (b) Present address: University of New Mexico, Albuquerque, New Mexico.

(2) White, unpublished thesis, University of Colorado, 1940.

(3) Grove and Keenan, THIS JOURNAL, **63**, 97 (1941).

(4) Prien and Frondel, *J. Urol.*, **46**, 784 (1941).

TABLE I

MELTING POINTS, FORMULAS AND ANALYSES

Compound	M. p., °C.[a]	Formula	N content, % Calcd.	Found
Sulfacetimide	184–184.5	$C_8H_{10}N_2O_3S$	13.08	13.07
Sulfadiazine	251–252 dec.	$C_{10}H_{10}N_4O_2S$	22.40	22.33
Sulfaguanidine monohydrate	191–191.5	$C_7H_{10}N_4O_2S\cdot H_2O$	24.13	24.09
Sulfamerazine	233.5–235	$C_{11}H_{12}N_4O_2S$	21.20	21.19
Sulfapyridine, Phase I[b]	191.5–192 sl. dec.	$C_{11}H_{11}N_3O_2S$	16.86	16.75
Sulfathiazole	173–175 (201–201.5)[c]	$C_9H_9N_3O_2S_2$	16.46	16.62
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfacetimide	231–232 dec.	$C_{16}H_{16}N_2O_5S$	8.04	7.93
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfadiazine	226–227 dec.[d]	$C_{18}H_{16}N_4O_4S$	14.57	14.56
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfaguanidine	226	$C_{15}H_{16}N_4O_4S$	16.08	16.01
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfamerazine	212	$C_{19}H_{18}N_4O_4S$	14.06	14.12
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfapyridine	204–205	$C_{19}H_{17}N_3O_4S$	10.97	11.10
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfathiazole	199–200	$C_{17}H_{15}N_3O_4S_2$	10.79	10.80
N^4-(2-Hydroxybenzylidene) sulfacetimide	212–214[e]	$C_{15}H_{14}N_2O_4S$	8.80	8.58
N^4-(2-Hydroxybenzylidene) sulfadiazine	244–245 dec.	$C_{17}H_{14}N_4O_3S$	15.81	15.82
N^4-(2-Hydroxybenzylidene) sulfaguanidine	225–226	$C_{14}H_{14}N_4O_3S$	17.60	17.45
N^4-(2-Hydroxybenzylidene) sulfamerazine	225[f]	$C_{18}H_{16}N_4O_3S$	15.21	15.21
N^4-(2-Hydroxybenzylidene) sulfapyridine	241–242[g]	$C_{18}H_{15}N_3O_3S$	11.89	11.73
N^4-(2-Hydroxybenzylidene) sulfathiazole	215–217 dec.	$C_{16}H_{13}N_3O_3S_2$	11.69	11.60
Sulfanilamide dilituarate	270[h]	$C_{10}H_{11}N_5O_7S\cdot H_2O$	19.28	19.34
Sulfacetimide dilituarate	221–222 dec.[i]	$C_{12}H_{13}N_5O_8S\cdot 1.5H_2O$	16.90	16.76
Sulfadiazine dilituarate	210–211 dec.	$C_{14}H_{13}N_7O_7S\cdot 2H_2O$	21.34	21.34
Sulfaguanidine dilituarate	255[j]	$C_{11}H_{13}N_7O_7S$	25.32	25.48
Sulfamerazine dilituarate	230–232 dec.	$C_{15}H_{15}N_7O_7S\cdot H_2O$	21.53	21.52
Sulfapyridine dilituarate	219–220 dec.[i]	$C_{15}H_{14}N_6O_7S\cdot H_2O$	19.08	18.98
Sulfathiazole dilituarate	200 dec.	$C_{13}H_{12}N_6O_7S_2\cdot 2H_2O$	18.12	18.01

[a] The melting points of the Schiff bases and the parent sulfonamides were taken in the usual capillary tubing immersed in a mechanically stirred bath. A 76 mm. immersion thermometer calibrated against a Bureau of Standards thermometer was used. The melting points of the dilituarates were determined on the bloc-maquenne apparatus and are of little value due to excessive decomposition. [b] For data on the other four phases of sulfapyridine see ref. 8. [c] Sulfathiazole is dimorphic. See ref. 3. [d] Softens at 223. [e] Softens at 208°. [f] The yellow solid turns brick red at 80–90°. [g] Softens at 237. [h] Becomes opaque at 150°. Chars rapidly at 270°. [i] Melts with evolution of gas. [j] Decomposes rapidly at 255° but does not actually melt.

acetyl derivatives to the identification of these compounds in urine. Williams and Maresh[5] presented the optical properties for five phases of sulfanilamide, for sulfaguanidine, and for their acetyl derivatives. The optical properties of sulfadiazine have been reported by Wilkerson.[6] The refractive indices of sulfanilamide, sulfapyridine and sodium sulfapyridine have been reported by Keenan.[7] More recently the optical crystallographic properties of five phases of sulfapyridine have been reported by the authors.[8]

The present communication reports the optical crystallographic properties of the following sulfanilamide derivatives: sulfacetimide (N^1-acetylsulfanilamide), sulfadiazine (2-sulfanilamidopyrimidine), sulfaguanidine (sulfanilamidoguanidine), sulfamerazine (2-sulfanilamidothiazole) and sulfapyridine (2-sulfanilamidopyridine). In addition, the optical crystallographic properties of two series of Schiff bases and of a series of dilituric acid salts of the above amines are reported. The Schiff bases were prepared from the above amines with salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde.

The melting points, formulas, and analyses are recorded in Table I, and the optical crystallographic data are recorded in Table II.

Experimental

Material.—The sulfapyridine and sulfathiazole were obtained from Merck and Company, the sulfamerazine from Sharp and Dohme, and the sulfanilamide from the Mallinckrodt Chemical Works. The sulfaguanidine was supplied by E. R. Squibb and Sons, the sulfadiazine by the Calco Chemical Division of the American Cyanamid Company, and the sulfacetimide from the Schering Corporation.[9] The salicylaldehyde was Eastman Kodak Co. no. 225 purified from the bisulfite addition compound. The 2-hydroxy-3-methoxybenzaldehyde available only as the practical product was purified by the bisulfite addition compound and thrice recrystallized from aqueous ethyl alcohol. The dilituric acid was prepared and purified by the method described in "Organic Syntheses."[10]

(5) Williams and Maresh, Abstracts of Papers, 104th American Chemical Society Meeting, September, 1942, p. 2L. No quantitative optical data are presented in the abstract.

(6) Wilkerson, THIS JOURNAL, **64**, 2230 (1942).

(7) Keenan, *J. Assoc. Offic. Agr. Chemists*, **27**, 157 (1944).

(8) Castle and Witt, THIS JOURNAL, **68**, 64 (1946).

(9) To the three firms, E. R. Squibb and Sons, Calco Chemical Division of the American Cyanamid, and the Schering Corporation who supplied the samples of sulfaguanidine, sulfadiazine and sulfacetimide, respectively, the authors wish to express sincere appreciation.

(10) "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., p. 440–441.

TABLE II

Compound	Habit and color	Pleochroism	Crystal system
Sulfacetimide	Columnar[c]		Orthorhombic
Sulfadiazine[e]	Lath shaped		Monoclinic
Sulfaguanidine monohydrate	Lath shaped		Monoclinic
Sulfamerazine	Tabular[g]		Orthorhombic
Sulfapyridine, Phase I[i]	Tabular to equant		Monoclinic
Sulfathiazole, Phase II[j]	Lath shaped		Monoclinic
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfacetimide	Deep red, acicular	Strong red-yellow Z>Y>X	Orthorhombic
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfadiazine	Brick red, tabular	Strong yellow-colorless Z>Y>X	Monoclinic
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfaguanidine	Orange, tabular	Z>Y>X	Monoclinic
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfamerazine	Brick red, columnar	Slight Z>Y>X	Triclinic (?)
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfapyridine	Brick red, tabular	Yes[l]	Monoclinic
N^4-(2-Hydroxy-3-methoxybenzylidene) sulfathiazole	Brick red, lamellar	Strong Z>Y>X	Orthorhombic
N^4-(2-Hydroxybenzylidene) sulfacetimide	Orange, acicular	Z>Y>X	Monoclinic
N^4-(2-Hydroxybenzylidene) sulfadiazine	Yellow, boat-shaped	Slight Z>Y>X	Monoclinic
N^4-(2-Hydroxybenzylidene) sulfaguanidine	Yellow, lamellar	None	Orthorhombic
N^4-(2-Hydroxybenzylidene) sulfamerazine	Yellow, tabular	Yellow, colorless Z>Y>X	Monoclinic
N^4-(2-Hydroxybenzylidene) sulfapyridine	Yellow, lamellar	None	Monoclinic
N^4-(2-Hydroxybenzylidene) sulfathiazole	Yellow, tabular	Z>Y>X	Monoclinic
Sulfanilamide dilituratc	Pinkish, tabular	None	Monoclinic
Sulfacetimide dilituratc	Lamellar	...	(?)
Sulfadiazine dilituratc	Yellow, elongated	None	Monoclinic
Sulfaguanidine dilituratc	Buff, equant	None	Triclinic
Sulfamerazine dilituratc	Yellow, columnar	None	Orthorhombic
Sulfapyridine dilituratc	Yellow, lamellar	None	Monoclinic
Sulfathiazole dilituratc	Yellow, columnar	None	Monoclinic

The sulfonamides were used without further purification for the preparation of derivatives. For determination of their optical properties sulfacetamide and sulfaguanidine were recrystallized from hot water. Sulfadiazine, sulfamerazine and sulfapyridine were recrystallized from 95% ethyl alcohol.

Preparation of the Schiff Bases.—The Schiff bases were prepared by adding the aldehyde (0.01 mole) to a hot, nearly saturated absolute alcohol solution of the sulfonamide (0.01 mole). The solutions were refluxed for varying periods of time up to three hours. In many instances crystals of the Schiff bases separated immediately. The Schiff bases from sulfacetimide, sulfaguanidine and sulfathiazole separated within five minutes. Sulfapyridine required refluxing up to one hour and sulfamerazine and sulfadiazine from one to three hours. In most instances crystals were filtered from the hot mother liquor and washed with several portions of cold alcohol. Yields were sacrificed, but by this procedure the Schiff bases were usually directly pure. When recrystallization was necessary, absolute ethyl alcohol was the solvent of choice. All Schiff bases were dried *in vacuo* at 100°.

Preparation of the Dilituratcs.—The dilituric acid (0.01 mole) dissolved in hot water or aqueous ethyl alcohol was poured into a hot solution of the sulfonamide (0.01 mole) dissolved in hot water, or hot aqueous alcohol depending upon the solubility of the particular sulfonamide. The mixture was refluxed a few minutes. The dilituratcs crystallize well on standing. Recrystallization was from hot water or hot aqueous ethyl alcohol. The dilituratcs were air-dried at room temperature.

Optical and Crystallographic Properties

Apparatus and Technique.—A Leitz petrographic microscope Model No. 30 CM was used in the present investigation. The light source was a fluorescent lamp equipped with a 15-watt G. E. Mazda Fluorescent tube, 3500° white.

The principal refractive indices α, β and γ at 25 ± 1°, were determined by the immersion method, using interference figures as a guide in selecting correctly oriented crystals. The immersion liquids used were those described by Winchell[11a] and Larsen and Berman.[11b] The optical axial angle $2V$ was calculated from the refractive indices α, β and γ, using the more exact formula suggested by Larsen and Berman.[12]

Summary

1. The optical crystallographic properties of sulfacetimide, sulfaguanidine, sulfathiazole, Phase II, sulfadiazine, sulfamerazine and sulfapyridine have been determined. Certain corrections and additions have been made to existing optical crystallographic data.

2. Two series of Schiff bases of the above sulfanilamide derivatives have been prepared and their melting points, analyses and optical crystallographic properties have been determined.

3. A series of dilituric acid salts of the above sulfanilamide derivatives have been prepared and their melting points, analyses and optical crystallographic properties have been determined.

4. The optical crystallographic properties of the sulfonamides and their derivatives are useful in their identification.

(11) (a) Winchell, "Elements of Optical Mineralogy," 5th ed., John Wiley and Sons, Inc., New York, N. Y., 1937, p. 81. (b) Larsen and Berman, "The Microscopic Determination of Nonopaque Minerals," 2nd ed., U. S. Department of the Interior, Geological Survey Bulletin No. 848, Washington, D. C., 1934, p. 42.

(12) Ref. 11b, p. 5.

TABLE II (*Continued*)

Extinction	Elongation	$2V$[a]	Optic sign	Dispersion	Refractive indices[b] α	β	γ
Symmetrical	Parallel to c	21°[d]	+	None	1.559	1.564	1.727
$Y\|\|b$, $Z\wedge c = 35°$	Parallel to b (±)	76°	+	Axial, $r>v$	1.596	1.675	1.830
$Y\|\|b$, $Z\wedge c = 17°$	Parallel to b (±)	86° ?	+	Axial, $r>v$	1.586	1.649[f]	1.731
Parallel	(±)	58°	−	Very strong, rhombic, $r>v$[h]	1.568	1.657	1.687
$Y\|\|b$, $Z\wedge c = 39°$	(±)	88°	+	Very strong axial, $r>v$	1.670	1.736	1.813
$Y\|\|b$, $X\wedge c = 23°$[k]	Parallel to b (±)	52°	−	Inclined, $r>v$	1.598	1.741	1.780
Parallel	Parallel to c (±)	Very large	+	Rhombic, $r>v$	1.507	1.682	>1.86
$Y\|\|c$, $Z\wedge a = 40°$ (?)	(±)	Large	+	Axial, $r>v$	1.563	1.695	>1.86
$Y\|\|b$, $Z\wedge c = 58°$	(±)	Small	+	Slight axial, $r>v$	1.577	1.614	>1.86
Variable (?)	(−)	Large	+	Anomalous, $r>v$	1.548	1.669	>1.86
Maximum = 21°,[m]	(+)	Very large	−	None	1.542	1.750	>1.86
Parallel	Parallel to c	Very large	+	Rhombic $r>v$	1.632	1.734	>1.86
Maximum = 12°,[m]	(±)	Very large	+	Very great axial, $r>v$	1.491	1.689	>1.86
$Y\|\|b$, $Z\wedge c = 38°$[k]	Parallel to b (±)	Large	+	Slight axial $r>v$	1.573	1.686	>1.86
Parallel	(±)	Large	+	None	1.561	1.668	>1.86
$Y\|\|b$, max. = 22°[m]	(+)	Large	+	Slight axial $r>v$	1.553	1.679	>1.86
$Z\|\|b$, $X\wedge c = 43°$	(±)	Large	+	Axial, $r>v$	1.619	1.750	>1.86
$Y\|\|b$, $Z\wedge c = 31°$	Parallel to b (±)	Large	+	Axial, $r>v$	1.601	1.735	>1.86
$X\|\|b$, max. = 40° (?)	(±)	51°	−	Very strong crossed, $v>r$	1.561	1.724	1.769
(?)	(?)	Large	−	Slight axial, $v>r$	1.399?	1.659	1.754?
(?)	(?)	Variable[n]	−	Very strong crossed, $v>r$	?	1.714	?
Variable oblique	(+)	87°	+	Axial, $r>v$	1.572	1.688	1.854
Parallel	Parallel to c (−)	40°	−	Rhombic, $v>r$	1.506	1.720	1.755
$Y\|\|b$(?), $X\wedge c = 26°$	(±)	24°	−	Axial, $r>v$	1.542	1.785	1.799°
Maximum = 10° (?)	(−)	63°	−	Strong axial, $v>r$	1.565	1.716	1.785

[a] Calcd. from α, β and γ. [b] The values of the refractive indices are accurate to ±0.002 unless otherwise noted. [c] The crystals show only the pyramid faces. [d] The calculated value appears to be too high since the isogyres scarcely separate on rotation. [e] Wilkerson[8] has published the following data: $\alpha = 1.680$, $\beta = 1.695$, $\gamma = 1.788$, $2V = 45$–46°, $Z\wedge c = 20°$?. [f] Dispersion of the β index of refraction. [g] Equant from hot water, skeleton crystals from butanol-1, and tabular from ethanol. [h] The interference figure shows characteristic purple color fringes. [i] For the details of the optical properties of sulfapyridine, Phase I–V see ref. 8. [j] Grove and Keenan[3] reported the following: $\alpha = 1.605$, $\beta = 1.733$, $\gamma > 1.733$, and parallel extinction. [k] Common orientation shows parallel extinction. [l] The absorption formula was not readily determinable. [m] The relationship of the ellipsoidal axes to the crystallographic axes was not readily determinable, thus a maximum extinction angle is reported. [n] $2V$ varies from 15 to 60° (estimated). The value for β is constant regardless of $2V$. γ varies greatly depending upon $2V$. The reason for this variation in optic axis is not understood. [o] Accuracy probably not greater than ±0.008.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. II. Compounds Containing the Sulfone Function[1]

BY EDWARD A. FEHNEL[2] AND MARVIN CARMACK

In a continuation of the work described in the preceding paper in this series,[3] we have determined the ultraviolet absorption spectra of a number of mono- and polysulfones, ketosulfones and carbalkoxysulfones in both neutral and alkaline solutions. As was anticipated on the basis of the limited spectroscopic data previously available for several simple aromatic sulfones,[4] no characteristic absorption bands attributable to the isolated sulfone function were observed in ethanol solutions in the near-ultraviolet region of the spectrum, and interaction between the sulfur-containing function and adjacent chromophores was found to be of a much lower order than in the corresponding sulfides. Strong conjugative effects were ap-

(1) Presented in part before the Division of Organic Chemistry of the American Chemical Society at the Washington meeting, August, 1948.

(2) American Chemical Society Postdoctoral Fellow, 1946–1948. Present address: Department of Chemistry, Swarthmore College, Swarthmore, Pa.

(3) Fehnel and Carmack, THIS JOURNAL, **71**, 84 (1949).

(4) (a) Chaix, *Bull. soc. chim.*, [4] **53**, 700 (1933); (b) Gibson, Graham and Reid, *J. Chem. Soc.*, **123**, 874 (1923); (c) Böhme and Wagner, *Ber.*, **75**, 606 (1942).