Laboratories, for the high temperature mass spectrometric analyses.

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

The Fluorides of Titanium: X-Ray Powder Data and Some Other Observations

BY KARL S. VORRES[1] AND FREDERIC B. DUTTON

RECEIVED MAY 28, 1954

Titanium trifluoride, prepared from the tetrachloride by reduction with aluminum in the presence of $AlCl_3$[2] and subsequent conversion with HF, was oxidized with chlorine. The resulting TiF_3Cl is a yellow powder which sublimes more readily than TiF_4, reacts with water to form a clear acid solution, and dissolves slightly in chloroform but neither in benzene nor in carbon tetrachloride. It hydrolyzes readily, and the air-stable product obtained by atmospheric hydrolysis and subsequent drying, both from it and from TiF_4, appears to be $TiOF_2$. The material so obtained and the oven-dried (100°) product of treating TiO_2 with 50% aqueous HF gave identical powder diffraction patterns. TiF_4 was prepared from the tetrachloride and anhydrous HF following Ruff[3] and others, and was purified by sublimation.

X-Ray powder diffraction data (Table I) were obtained for all the fluorides except TiF_3Cl, which was very finely divided and gave unsatisfactory patterns. Our data for TiF_4 disagree with the ASTM data[4]; these have previously been reported to be unreliable,[5] and comparison with the $TiOF_2$ pattern (see Table I) now shows that the original sample must have been predominantly $TiOF_2$. Except for $d = 2.18$ and $d = 1.20$, all the $TiOF_2$ lines of $d > 0.900$ appear in the ASTM data in proper position and sequence of intensity, and the three strongest $TiOF_2$ lines are the three strongest ASTM TiF_4 lines.

The $TiOF_2$ lines may be given simple-cubic indices, and the report of a complete structural investigation is in press.[6]

TABLE I

X-RAY POWDER DIFFRACTION DATA

TiF_3		TiF_4				$TiOF_2$	
		Obsd.		ASTM			
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
4.23	1	8.5	12	6.50	10	3.76	100[b]
3.84	100	6.0	8	5.45	3	2.67	13
3.57[a]	45	4.00	85	4.75	2	2.18	<1
3.11	10	3.79	1	4.35	2	1.89	31[b]
2.71[a]	25	3.68	100	3.80	100[b]	1.69	32[b]
2.31	6	3.09	35	3.56	2	1.54	7
2.08	100	2.68	10	3.40	2	1.34	13
1.92[a]	45	2.35	2	3.22	20	1.26	11
1.80	85	2.22	4	2.68	12.5	1.20	1
1.72[a]	45	2.01	10	2.35	3	. .	<1
1.62	1	1.89	70	2.18	6	1.09	3
1.57	1	1.72	20	1.90	40[b]	1.050	3
1.36[a]	4	1.69	20	1.70	40[b]	1.012	3
1.28	50	1.63	30	1.61	4	.949	<1
1.089	45	1.50	2	1.55	6	.921	4
1.042	20	1.39	17	1.485	1	.895	1
0.9033	6	1.34	17	1.345	12.5	. . .	<1
.8287	20	1.28	20	1.266	10	.850	4
.8074	15	1.25	2	1.098	2	.829	4
		1.04	1	1.054	2	. . .	<1
		1.00	1	1.015	2		
				0.921	2		

[a] Diffuse line. [b] Strongest lines.

---

(1) Department of Chemistry, University of Southern California, Los Angeles, California.

(2) O. Ruff and F. Neuman, *Z. anorg. Chem.*, **128**, 81 (1923).

(3) O. Ruff and Richard Ispen, *Ber.*, **36**, 1777 (1903).

(4) X-Ray Diffraction Data Cards, American Society for Testing Materials, Philadelphia, Pa.

(5) H. M. Haendler, S. F. Bartrom, R. S. Becker, W. J. Bernard and S. W. Bukata, THIS JOURNAL, **76**, 2177 (1954).

(6) K. S. Vorres and Jerry Donahue, *Acta Cryst.*, in press.

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

Metal–Amine Coördination Compounds. IV. Copper(I) Complexes

BY RONALD T. PFLAUM[1] AND WARREN W. BRANDT

RECEIVED DECEMBER 2, 1954

The copper(I) coördination compounds described are formed in the reaction of the copper(I) ion with 1,10-phenanthroline, 2,2′-bipyridine, 2,2′,2″-terpyridine and 2,2′-biquinoline. Compounds of the first two chelating agents have received considerable attention in the past. Since the first observations on the color reaction,[2] many investigators have examined the absorption characteristics and the application of the complexes to the analytical determination of copper.[3–5] The formula of the 1,10-phenanthroline complex[4] and the stability of the 2,2′-bipyridine compound[6] have been determined, whereas the stability of the copper(I)–1,10-phenanthroline complex has not been evaluated.

The selectivity of 2,2′-biquinoline for the copper(I) ion accounts for the interest in it. This selectivity and the characteristics of the 2,2′-biquinoline complex in various non-aqueous solvents have been studied by several investigators.[4,7–9] Studies on substituted 1,10-phenanthroline reagents, which also exhibit selectivity for the copper(I) ion, have been carried out.[10–12] Most of the work has been done in immiscible alcoholic media with the emphasis toward application of the complexes to the determination of the copper.

No work has been reported on the copper(I)–2,2′,2″-terpyridine complex. An examination of

(1) An abstract of a thesis submitted by Ronald T. Pflaum to the Graduate School of Purdue University, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Present address, Dept. of Chem., State University of Iowa.

(2) G. Tartarini, *Gazz. chim. ital.*, **63**, 597 (1933).

(3) M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 116 (1945).

(4) J. Hoste, *Anal. Chim. Acta*, **4**, 23 (1950).

(5) W. H. McCurdy and G. F. Smith, *Analyst*, **77**, 846 (1952).

(6) E. I. Onstott and H. A. Laitinen, THIS JOURNAL, **72**, 4724 (1950).

(7) J. G. Breckenridge, R. W. J. Lewis and L. A. Quick, *Can. J. Research*, **17B**, 258 (1939).

(8) J. Hoste, *Research*, **1**, 713 (1948).

(9) J. Gillis, *Anal. Chim. Acta*, **8**, 97 (1953).

(10) G. F. Smith and W. H. McCurdy, *Anal. Chem.*, **24**, 371 (1952).

(11) G. F. Smith and D. H. Wilkins, *ibid.*, **25**, 510 (1953).

(12) A. R. Gahler, *ibid.*, **26**, 577 (1954).

this reagent with the copper(I) ion would be worthwhile. This investigation was concerned with such an examination together with a study of the above-mentioned complexes in aqueous and in non-aqueous media. Inasmuch as the systems are colored, the study was largely spectrophotometric in nature.

Experimental

Materials Used.—The 2,2′-bipyridine, 2,2′,2″-terpyridine, 2,2′-biquinoline and 1,10-phenanthroline reagents were obtained from the G. Frederick Smith Chemical Company. Hydroxylamine hydrochloride was obtained from the Eastern Chemical Company.

Standard solutions of copper(II) sulfate were prepared from the recrystallized salt and standardized by electrodeposition. All other inorganic chemicals were reagent grade quality.

Technical grade solvents were redistilled before use.

Spectrophotometric Data.—A General Electric automatic recording spectrophotometer and a Beckman Model B spectrophotometer were used to obtain absorptimetric data. All measurements were made in matched 1.0-cm. cells.

Study of the Color Reaction.—Studies on the color reactions resulting from the chelation of the copper(I) ion with the above-mentioned reagents were carried out on solutions containing the reagent, copper(II) ion, a reductant, and an inorganic base. Solutions containing 5×10^{-5} to 1×10^{-3} M copper(II) ion were used in this work. Sodium hydrogen sulfite, sodium hyposulfite, hydroxylamine hydrochloride and hydrazine sulfate were employed as reductants. Ammonium and sodium hydroxides were used to increase the *p*H of the solutions in order to favor maximum color formation. Measurements of *p*H were made on a Beckman Model H-2 *p*H meter standardized at *p*H 7 with a commercial buffer solution. The effects of the variables on the color reaction were determined spectrophotometrically.

Effect of Non-aqueous Solvents.—The effects of miscible organic solvents on the copper(I) complexes were studied on solutions containing 50% by volume of the non-aqueous solvents. The effects of immiscible solvents were determined on the colored extracts resulting from the extraction of the absorbing complex out of an aqueous phase into the non-aqueous solvent. Spectrophotometric analysis was employed to ascertain the effect of the organic medium on the coördination compounds.

Determination of Formulas.—Formulas for the 2,2′-bipyridine and 1,10-phenanthroline complexes were determined by the method of continuous variations.[13] Stock solutions of 4×10^{-4} M copper(II) ion and the reagents were prepared and aliquots mixed in the appropriate ratios. Hydroxylamine hydrochloride was used for the reduction of the copper(II) to copper(I) ion. Adjustments in *p*H were made with dilute sulfuric acid and dilute ammonium hydroxide. For the studies of the complex in an immiscible solvent, the color developed was extracted into isoamyl alcohol. Ethanolic solutions (20% ethanol) were prepared for the study of the complexes in a miscible solvent. Absorption measurements were made on the resulting solutions at selected wave lengths. Formulas were determined from a plot of corrected absorbance values against the mole fraction of copper(I) ion.

Results and Discussion

The Color Reaction.—The effects of copper concentration, reagent, solvent, reductant, *p*H and oxygen were determined in connection with a study of the color reactions. The definition of these variables accounts for most of the chemical phenomena observed. The effects of reagent and of non-aqueous solvents will be discussed in following sections.

It was found that complex formation occurred over a *p*H range of 5 to 9. Optimum formation was obtained using hydroxylamine hydrochloride as the reductant and either ammonium or sodium hydroxide to a *p*H of 7.5 to 9.0. The presence of oxygen in the systems interfered with this formation. The colors of the 1,10-phenanthroline, 2,2′-bipyridine and 2,2′,2″-terpyridine complexes, which were changed from the normal orange or purple hues to green on the addition of air or oxygen, were regenerated upon standing or on expellation of dissolved oxygen with a stream of nitrogen.

In the 1,10-phenanthroline system, changes in hue were observed with changes in copper concentration. Typical curves illustrating changes from purple to yellow on dilution of the complex are shown in Fig. 1. It is apparent that Beer's law is not obeyed and one would expect the changes in hue to be due to variations in the coördination of the metal ion with the reagent. A study of the species involved indicated that amine coördination changes did not occur. It is possible that the phenomena are due to associations of the chelated molecules in the more concentrated solutions. This viewpoint is substantiated by precipitate formation in these solutions after a period of two hours. A solvation explanation is also possible since changes in hue and precipitation can be eliminated by the addition of a miscible solvent to the colored system. This was the basis for the use of non-aqueous solvents in the determination of copper as proposed by Moss and Mellon.[3]

Effect of Non-aqueous Solvents.—The effects of non-aqueous solvents upon the absorption characteristics of the complexes were determined and the results are presented in Table I. Values of wave lengths of maximum absorption are accurate to ±1 mμ. All of the miscible solvents examined are listed, whereas only those immiscible solvents that extracted the complexes are included. Such common solvents as benzene, toluene, carbon tetrachloride and ether did not extract the colored species.

TABLE I

ABSORPTION MAXIMA (mμ) FOR COPPER(I) COMPLEXES IN PRESENCE OF NON-AQUEOUS SOLVENTS

Solvent	Bipyridine	Terpyridine	Phenanthroline	Biquinoline
Water	435	435	408	ppt.
Dimethylformamide[a]	435	430	433	546
Dioxane[a]	435	430	435	545
Ethanol[a]	435	430	435	545
Methyl carbitol[a]	435	430	435	545
Tetrahydrofuran[a]	438	435	438	550
Amyl alcohol	435	430	435	545
Isoamyl alcohol	435	430	435	545
n-Hexyl alcohol	435	430	435	545
Aniline	..[b]	..[b]	..[b]	548
Bromobenzene	..[b]	..[b]	..[b]	553
Chloroform	435	430	435	..
Nitrobenzene	435	435	430	553

[a] 50% solvent in aqueous system. [b] No extraction.

It is postulated that the variations observed with variations in the solvent medium are due to coördination tendencies between the chelated molecule and the solvent. Differences in the magnitude of the wave length shifts indicate differences in the degree of solvation. Solvation

---

(13) P. Job, *Compt. rend.*, **180**, 938 (1925).

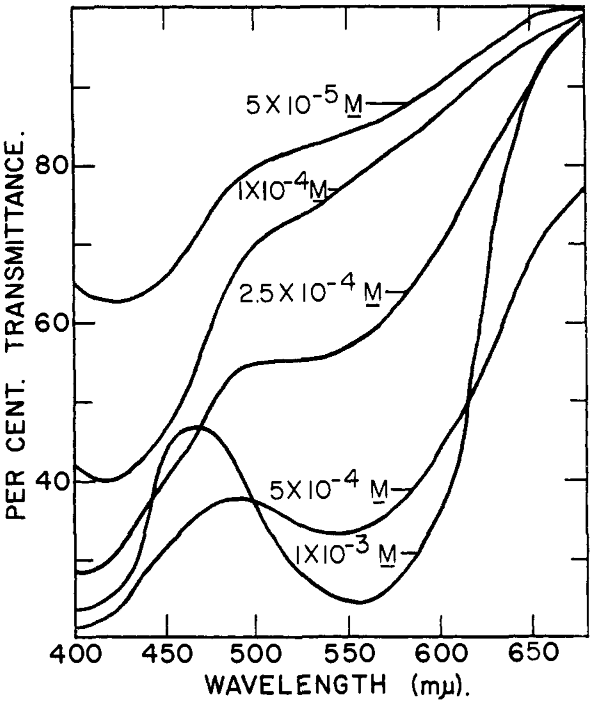

Fig. 1.—Effect of dilution of the copper(I)–1,10-phenanthroline system.

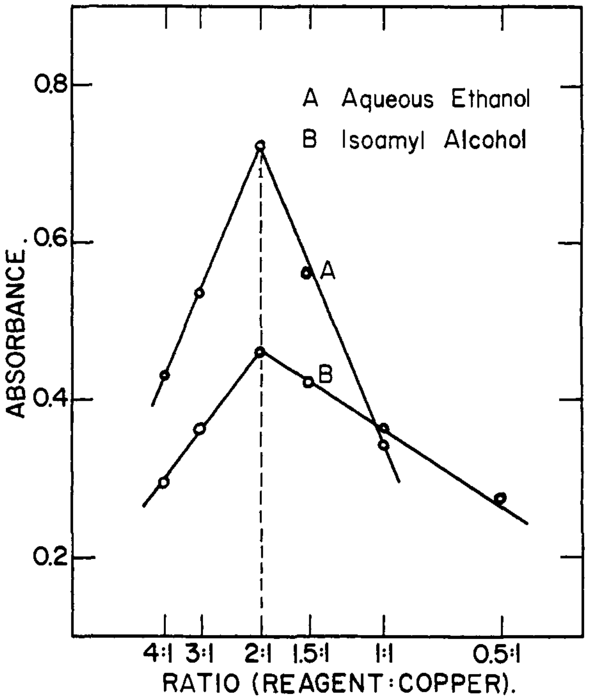

Fig. 2.—Continuous variations studies of copper(I)–1,10-phenanthroline system.

reactions would explain the excellent extractability of the complexes into immiscible solvents.

Determination of Formulas and Spectrophotometric Data.—Formulas for the copper(I)–1,10-phenanthroline, 2,2′-bipyridine and 2,2′,2″-terpyridine complexes in aqueous ethanolic and in isoamyl alcoholic media were determined in this investigation. Continuous variations plots for the phenanthroline system are shown in Fig. 2. (Measurements of absorbance were made at 435 mμ.) A 2:1 complex is apparent for this system. A 2:1 complex was also found for the 2,2′-bipyridine system in the same media. Only one molecule of 2,2′,2″-terpyridine was found to coördinate with the copper(I) ion.

In addition to the above work, the phenanthroline complex in an aqueous medium was investigated in order to assign formulas to the purple and orange species mentioned in a preceding section. It was found that a 2:1 complex existed as the absorbing species in the two colored solutions. Such a result was anticipated inasmuch as identical species were observed on the addition of ethanol or isoamyl alcohol to these systems.

TABLE II

ABSORPTIMETRIC DATA ON IRON(II) AND COPPER(I) COMPLEXES

Reagent	Max.		a_m	
Pyridine	$Fe(py)_x^{++}$ ..[a]	$Cu(py)_x^{+}$ 405	$Fe(py)_x^{++}$ ..	$Cu(py)_x^{+}$ 100
Bipyridine	$Fe(bipy)_3^{++}$ 522	$Cu(bipy)_2^{+}$ 435[b]	$Fe(bipy)_3^{++}$ 8650	$Cu(bipy)_2^{+}$ 4500
Terpyridine	$Fe(trpy)_2^{++}$ 552	$Cu(trpy)^{+}$ 430[b]	$Fe(trpy)_2^{++}$ 12,500	$Cu(trpy)^{+}$ 3250
Phenanthroline	$Fe(phen)_3^{++}$ 510	$Cu(phen)_2^{+}$ 435[b]	$Fe(phen)_3^{++}$ 11,100	$Cu(phen)_2^{+}$ 7000
Biquinoline	$Fe(biqu)_x^{++}$ ..[c]	$Cu(biqu)_2^{+}$ 545	$Fe(biqu)_x^{++}$ ..	$Cu(biqu)_2^{+}$ 5500

[a] Precipitate formed. [b] Complex in isoamyl alcohol. [c] No complex formed.

Values of wave lengths of maximum absorption and molar absorptivities for the complexes studied are presented in Table II. Spectra for some of the complexes are shown in Fig. 3. The data show the variations that exist in the iron(II) and copper(I) systems as a result of increased coördination and

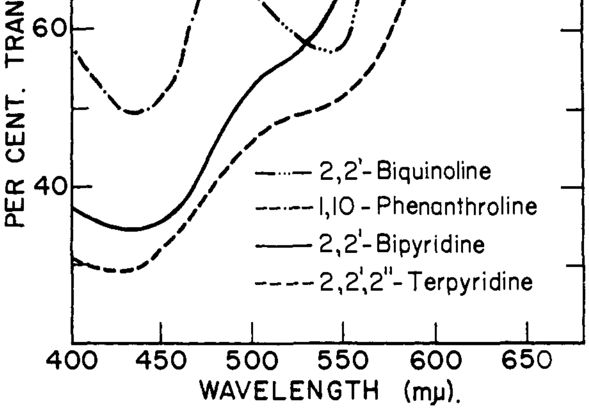

Fig. 3.—Spectra of copper(I)–amine complexes.

steric requirements of the ligands. Inasmuch as comparisons and correlations have been reported to exist in the iron(II) and copper(II) metal–amine coördination compounds,[14] it was of interest to observe whether similar correlations could be made in the present situation.

In the matter of wave lengths of maximum absorption, the copper(I) system of complexes shows a much smaller variation than does the iron(II) system. This is reasonable in light of the apparent influence of the solvent system on the copper complexes. Only the copper(I)–2,2′-biquinoline complex shows a large deviation. This is not surprising in view of the unique character of this reagent. (2,2′-Biquinoline gives a specific reaction with the copper(I) ion under most conditions.)

The magnitude of the molar absorptivities do not follow the same pattern in the compounds of the two metallic ions. The value of the copper(I)–2,2′,2″-terpyridine complex appears to be abnormally small. This may be related to the different number of coördination positions filled in the two metal ions, and possibly to the inherent differences in steric requirements of the reagents. Thus, there is a danger in predicting color intensity and sensitivity on the basis of the nature of the reagent alone when comparing dissimilar ions such as iron(II) and copper(I).

Acknowledgment.—The authors wish to thank the United States Atomic Energy Commission for the research grant which made this work possible.

[14] R. T. Pflaum and W. W. Brandt, THIS JOURNAL, **76**, 6215 (1954).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

The Electric Moments of Mono- and Diacetylferrocene

BY H. H. RICHMOND AND HENRY FREISER

RECEIVED OCTOBER 14, 1954

Much interest has centered about the structure of the recently discovered dicyclopentadienyliron, or ferrocene, and similar compounds. The "molecular sandwich" structure proposed by Wilkinson, *et al.*,[1] to explain the unique stability of ferrocene has received support by X-ray diffraction studies[2] and is generally accepted as correct.

Considerable attention has been devoted to the electronic structure of ferrocene. Jaffe[3] concluded from his molecular orbital calculations that in ferrocene there are eight bonding and one nonbonding orbitals. All the orbitals are filled resulting in a diamagnetic ferrocene having the rare gas configuration. The eight bonding molecular orbitals indicate that the iron atom is bound to each of the cyclopentadienyl radicals by four covalent bonds.

Jaffe concluded that there was no barrier to the free rotation of the cyclopentadienyl groups.

More recently, Moffitt[4] described the ferrocene structure in terms of one covalent bond between the iron atom and each of the two cyclopentadienyl groups. This description helps explain the "aromatic" properties of ferrocene. Moffitt, like Jaffe, predicted the free rotation of the two organic rings.

The study of the dipole moments of mono- and diacetylferrocene was undertaken as a means of obtaining experimental evidence for free rotation of the organic rings in ferrocene.

Experimental

Purification of Benzene.—Nitration grade benzene, supplied by the Pittsburgh Coke and Chemical Co., was fractionally crystallized twice by partial freezing in an ice–water bath and decanting the unfrozen benzene. The remaining frozen benzene after melting was stirred at 40–50° with an equal volume of 96%, reagent grade sulfuric acid for several hours and the process repeated until the sulfuric acid layer was colorless. After the acid layer was removed, the benzene was washed with water and then with sodium bicarbonate solution. The benzene was then dried, first, by azeotropic distillation followed by refluxing over sodium and finally fractionally distilled, a central fraction boiling within 0.1° being collected, whose freezing point was 5.5°. The benzene was stored over sodium in the absence of air.

Preparation of Materials.—The monoacetylferrocene, m.p. 89–90°, and the diacetylferrocene, m.p. 130–131°, both of which were well-defined crystalline red solids, were supplied by Drs. R. B. Woodward and M. Rosenblum of Harvard University.

Measurements and Calculations.—The equipment used for the measurement of dielectric constant was based on the heterodyne beat method.[5,6] It consisted of a Clough–Brengle Beat Frequency Audio Oscillator Model 179A modified by replacing a portion of the capacitance by a General Radio Precision Condenser 722F, and a dielectric cell in parallel. The equipment and measurement procedure have been reported in detail.[7,8] The density measurements were made in a 100-ml. flask type pycnometer equipped with calibrated capillary necks, in a manner similar to that reported.[9]

The molar refractions of the acetylferrocenes were calculated from the molar refraction of ferrocene which was determined[10] to be 46.8.

The dielectric constants, densities, weight fractions are given in Table I, along with the empirical constants, and molar polarizations were calculated from them. The molar polarizations were calculated by the Debye method as modified by Halverstadt and Kumler.[11] The empirical constants α and β were obtained graphically from the equations relating the dielectric constants, ϵ_{12}, and the specific volumes V_{12} as linear functions of the weight fraction of the solute

$$\epsilon_{12} = \epsilon_1 + \alpha w_2; \; V_{12} = V_1 + \beta w_2$$

The polarization was then calculated from the equation

$$P_{2\infty} = \frac{3\alpha V_1}{(\epsilon_1 + 2)^2} + (V_1 + \beta)\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

The electric moment was then calculated from

$$\mu = 0.01281 \times 10^{-18} \sqrt{(P_{2\infty} - MR_{\mathrm{D}})T}$$

Discussion of Results

There are a number of values reported for the

---

[1] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

[2] (a) J. D. Dunitz and L. L. Orgel, *Nature*, **171**, 121 (1953); (b) P. F. Eiland and R. Pepinsky, THIS JOURNAL, **74**, 4971 (1952); (c) E. O. Pischer and W. Pfab, *Z. Naturforsch*, **7B**, 377 (1952).

[3] H. H. Jaffe, *J. Chem. Phys.*, **21**, 156 (1953).

[4] W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

[5] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931, Chapter 3.

[6] C. P. Smyth, "Physical Methods of Organic Chemistry," Vol. I, Part II, Ed. by Arnold Weissberger, Interscience Publ., Inc., New York, N. Y., 1949, p. 1633.

[7] A. J. Weith, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **70**, 805 (1948).

[8] R. K. Keswani, M.S. Thesis, "Dipole Moments of Certain Substituted Thiophenes," University of Pittsburgh, Pittsburgh, Pa., 1948.

[9] H. Freiser and W. L. Glowacki, THIS JOURNAL, **70**, 2575 (1948).

[10] R. B. Woodward and M. Rosenblum, private communication.

[11] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).