[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY UNIVERSITY OF PITTSBURGH]

Electric Moments and Structure of Substituted Thiophenes. I. Certain Halogenated Derivatives[1]

BY RAM KESWANI AND HENRY FREISER

Interest in the structure of thiophene and in the influence of substituents upon that structure has prompted the initiation of a program for the determination of the dipole moments of substituted thiophenes. Aside from thiophene[2] itself and 2-nitrothiophene,[3] no measurements of dipole moments of members of this interesting heterocyclic family have been reported. The measurement of thiophene and 2-nitrothiophene have been repeated here for purposes of comparison. The work reported here on certain of the halogenated thiophenes represents the first phase of the program.

Experimental

Purification of Materials.—Jones and Laughlin reagent-grade benzene was distilled in a three-foot glass helices-packed fractionating column and a central portion boiling within 0.03° was collected. It was found to have a density of 0.868231 g./ml. and a refractive index (n_D) of 1.49475, both measured at 30°.

Socony-Vacuum 99 mole per cent. thiophene was shaken with hydrochloric acid, washed, dried, and carefully distilled in the three-foot column. Fractions boiling at 82.5° at 747.1 mm. within a range of 0.02° were collected for use; d^{30}_4 1.04760, n^{30}_D 1.5214.

The 2-chlorothiophene, 2-bromothiophene and 2,5-dichlorothiophene, which were obtained from the Michigan Chemical Corporation, were dried and fractionated prior to use. The boiling points obtained were 126.28-126.30° at 736.7 mm., 150.6-150.7° at 734.7 mm., and 160.0-160.1° at 734.0 mm. respectively, while the corresponding densities and refractive indices (n_D) measured at 30.0° were 1.27316 g./ml. and 1.5432, 1.69288 g./ml. and 1.5815, and 1.42901 g./ml. and 1.5575, respectively.

2-Nitrothiophene was prepared by the method of Babasinian[4] under the direction of Dr. M. F. Dull. It was recrystallized twice from petroleum ether without any change in freezing point which was found from melting curves to be 42.6°. This value differs from that reported by Steinkopf,[5] but is in good agreement with that obtained by Von Seemann and Lucas.[6]

2-Iodothiophene and tetrabromothiophene were also prepared under the direction of Dr. M. F. Dull from directions given by Steinkopf.[5] The 2-iodothiophene was purified by fractional crystallization followed by vacuum distillation; b. p. at 13 mm. 65.0°, d^{30}_4 2.04926 g./ml.

The tetrabromothiophene was recrystallized until no further change in its melting point, 117°, was observed.

Measurements and Calculations.—The dielectric constants were measured at a frequency of 250 kilocycles with a heterodyne beat apparatus consisting of a Clough-Brengle Beat Frequency Audio Oscillator Model 179A whose variable frequency oscillator circuit was modified by the replacement of some of the original capacitance by a General Radio Precision Condenser 722 F and a dielectric cell in parallel. The measurement procedure has been reported elsewhere.[7] The cell, similar in design to that previously reported,[7] was constructed of stainless steel and Teflon. The densities of the liquids and solutions were measured in flask-type pycnometers of 20 ml. and 100 ml. capacities, respectively, in a manner similar to that previously reported,[8] with an estimated accuracy better than one part in 100,000. The dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction, f_2, of the substance indicated are given in Table I.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES OF BENZENE SOLUTIONS MOLAR REFRACTIONS, POLARIZATIONS AT 30° AND DIPOLE MOMENTS

f_2	ϵ	d	P_2	MR_D	P_∞	$\mu \times 10^{18}$
	Thiophene			24.36	30.1	0.53
0.00000	2.2627	0.868231	...			
.04560	2.2816	.875494	29.9			
.04954	2.2810	.876139	29.2			
.05022	2.2838	.876247	30.0			
.06531	2.2911	.878696	30.2			
	2-Nitrothiophene			31.55	393	4.23
0.002974	2.3364	0.869920	388.4			
.005919	2.4105	.871588	385.2			
.006646	2.4277	.871999	381.7			
.007522	2.4486	.872497	378.4			
	2-Chlorothiophene			29.37	81.0	1.60
0.01249	2.3040	0.873441	82.9			
.01946	2.3260	.876350	78.3			
.02526	2.3439	.878770	77.7			
.03707	2.3822	.883776	76.3			
	2-Bromothiophene			32.10	70.0	1.37
0.01130	2.2952	0.878260	70.9			
.01687	2.3104	.883164	70.0			
.03075	2.3504	.895450	70.0			
.03427	2.3607	.898573	70.0			
	2-Iodothiophene			37.2	63.1	1.14
0.01462	2.2954	0.888006	63.1			
.02131	2.3101	.897053	62.8			
.02564	2.3207	.902917	63.3			
	2,5-Dichlorothiophene			34.50	59.7	1.12
0.008979	2.2806	0.874630	60.0			
.01403	2.2895	.877633	59.9			
.02539	2.3106	.885248	59.4			
.03244	2.3225	.889088	59.5			
	Tetrabromothiophene			55.5	66.5	0.73
0.004296	2.2693	0.881420	64.8			
.006934	2.2742	.889442	67.2			
.01187	2.2837	.904428	67.6			

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(1) This work is abstracted from a portion of the thesis to be submitted by Ram Keswani to the University of Pittsburgh in partial fulfillment of the requirements for the Master of Science degree.

(2) H. de V. Robles, *Rec. trav. chim.*, **58**, 111 (1939).

(3) P. F. Oesper, G. L. Lewis, and C. P. Smyth, THIS JOURNAL, **64**, 1130 (1942).

(4) V. S. Babasinian, *ibid.*, **50**, 2749 (1928).

(5) W. Steinkopf, "Die Chemie des Thiophenes," Theodor Steinkopf, Dresden, 1941.

(6) C. Von Seemann and C. C. Lucas, *Can. J. Research*, **19B**, 292 (1941).

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

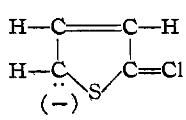
(8) H. Freiser and W. L. Glowacki, *ibid.*, **70**, 2575 (1948).

along with the molar polarization, P_2, in the fourth column. This table also lists in the fifth column the values of MR_D, the molar refraction for the sodium D line, obtained directly for thiophene, 2-chloro-, 2-bromo and 2,5-dichlorothiophene, from the solutions of 2-nitrothiophene and for the remaining substances the values were calculated from that of thiophene and the following atomic refraction values: hydrogen 1.1, iodine 13.9, and bromine 8.8_7.

The sixth column gives the polarization, P_∞, obtained by extrapolation to $f_2 = 0$ of the values of P_2 in Table I, and the seventh column gives the dipole moments calculated in the usual manner. When the P_2 values showed no trend with concentration, the average value was taken as P_∞. The precision of the electric moment determination is about 1%.

Discussion of Results

The values of the moments of thiophene and 2-nitrothiophene are in good agreement with those previously reported.[2,3] In order to evaluate structural influences in the 2-halothiophenes the observed moment values were compared to those calculated on the basis of vector addition. The calculations were made in the following manner: The angles taken for the bonds in the thiophene nucleus were those obtained by Schomaker and Pauling[9] by electron diffraction studies on the thiophene itself. The halogen–carbon bond moment was assumed to act in the line bisecting the bond angle of the corresponding ring carbon atom while the sulfur bond moment, taken to be 0.53, was assumed to act in the line bisecting the CSC angle. Because the chemical properties of the halothiophenes resemble those of the corresponding halobenzenes, the values of the carbon–halogen bond moments were taken to be those in monohalogenbenzenes ($\mu_{C-Cl} = 1.58$, $\mu_{C-Br} = 1.48$, and $\mu_{C-I} = 1.25$). The values thus calculated for 2-halothiophenes are 1.76, 1.67, and 1.45 for 2-chloro, 2-bromo- and 2-iodothiophene, respectively. The over-all agreement between these calculated values and those experimentally determined is fair and confirms the belief that the carbon–halogen bonds in the thiophene series are very similar to those in the benzene series, making structures such as



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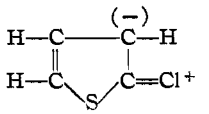
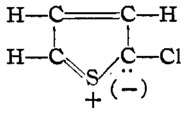
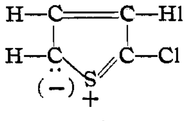


as well as



and



of significance in the description of the ground state of 2-chlorothiophene.

The calculated values of the moments of the 2-halothiophenes while in general agreement with the observed values are somewhat higher than the latter, being about 0.16 D higher for 2-chlorothiophene and twice that, about 0.31, in the case of the corresponding bromo- and iodine derivatives. These deviations may well be compared with similar deviations observed in ortho disubstituted benzene derivatives which are attributed to mutual inductive effects, since the 2-substituted thiophenes are structurally similar to the ortho disubstituted benzenes with the sulfur considered as one of the substituents. Mutual inductance of the two groups will cause a decrease in the moments of these compounds from the calculated values. It is possible that the smaller deviations encountered in the case of the chlorothiophene might be related to the greater importance of structures involving a double bond between carbon and halogen in the case of chlorine over that of the bromine or iodine. These structures as pictured above would tend to make the sulfur more negative in chlorothiophene than in thiophene itself.

The moment of 2,5-dichlorothiophene calculated in the manner mentioned above was found to be in exact agreement with the experimentally observed result. It must be observed, however, that because of the geometrical relationships in this compounds, the two C–Cl bonds meeting at an angle of 158°, the net moment is not at all sensitive to changes in the C–Cl bond moment. Also because of the importance of structures similar to that shown above for 2-chlorothiophene in which C–Cl has double bond character, the negative deviation expected in the 2,5-dichlorothiophene because of mutual inductive interaction is possibly counter-balanced by the resulting increase in negative character of the sulfur.

The value calculated for the moment of tetrabromothiophene in the manner explained above is 1.37 D acting in the direction opposite to the thiophene moment. The large difference between this and the observed value of 0.73 D may be accounted for on the basis of the mutual inductive effects of the four bromine atoms which are all close together. A similar negative deviation is encountered in the case of 1,2,3-trichlorobenzene whose observed moment, 2.31 D,[10] is 0.85 unit lower than that calculated by vector addition. Likewise, the observed moment of 1,2,3,4-tetrachlorobenzene, 1.90 D,[11] is 0.84 unit lower than that calculated by vector addition and 0.36 unit lower than the observed value of *o*-dichlorobenzene[12] with which, according to calculations based on vector addition, the value of tetrachlorobenzene should coincide. These cases lend weight to the above argument.

Summary

1. Dielectric constants and densities at 30° are reported for benzene solutions of thiophene, 2-

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[9] V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939).

[10] J. A. A. Ketelaar, *Rec. trav. chim.*, **59**, 757 (1940).

[11] C. P. Smyth and G. L. Lewis, THIS JOURNAL, **62**, 721 (1940).

[12] E. Fischer and F. Rogowski, *Physik. Z.*, **40**, 331 (1939).

nitrothiophene, 2-chlorothiophene, 2-bromothiophene, 2-iodothiophene, 2,5-dichlorothiophene and tetrabromothiophene.

2. The dipole moments for these compounds, calculated by use of the Debye equation, have been found to be 0.53, 4.23, 1.60, 1.37, 1.14, 1.12 and 0.73, respectively.

3. The dipole moment values show the general resemblance of the structures of these substituted thiophenes to those of the corresponding benzene derivatives. Deviations between observed moment values and those calculated on the basis of vector additivity have been attributed largely to dipole-polarizability interactions. The possibility of decreased participation of the sulfur electrons in the thiophene ring resonance for the chloro-derivatives is also considered.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Viscosity–Molecular Weight Relations for Various Synthetic Rubbers[1]

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Introduction

Houwink[4] and Flory[5] have shown that the relation between the intrinsic viscosity of a high-polymer solution and the molecular weight of the polymer is of the form

$$[\eta] = KM^a \qquad (1)$$

where in the case of polyvinyl acetate compounds[4] and polymethacrylate[4] $a \sim 0.6$ and in the case of polyisobutylene[5] $a = 0.64$. More recently the authors[6] have shown that for natural rubber, the relation is

$$[\eta] = 5.02 \times 10^{-4} M^{0.667} \qquad (2)$$

In this paper, we are reporting viscosity–molecular weight relations for four more polymers: a butadiene–styrene copolymer (Buna S), sodium polymerized polybutadiene, a butadiene–acrylonitrile copolymer (Buna N), and neoprene. As will be shown, these measurements confirm the hypothesis that for these essentially linear polymers a is very close, if not equal to, two-thirds.

Experimental

Materials.—The rubber samples used in these experiments were kindly supplied by the Firestone Tire and Rubber Company of Akron, Ohio. The Buna S (GR-S) was of three kinds: one of low degree of conversion (100% soluble), one of medium degree of conversion (53.5% soluble) and one of high degree of conversion (32% soluble). The polybutadiene was polymerized with sodium according to methods similar to those used in the preparation of Russian SK.[7]

The toluene used was the commercial solvent dried with calcium chloride.

Fractionation.—Unlike natural rubber, the synthetic rubbers are not subject to rapid oxidative degradation in solution, so some of the precautions reported in the previous paper[6] are unnecessary. The rubbers were dissolved in toluene and fractionally precipitated[8] by methanol; in some cases fractions were refractionated into subfractions. Anti-oxidant ("Agerite," aldol - α - naphthylamine), although possibly unnecessary for these synthetics, was added to all solutions.

In certain polymers, a portion of the soluble fraction consists of "microgel," a material which is not easily removed by slow extraction with good solvents in the absence of agitation, but is more or less easily dissolved by energetic shaking, leaving only the insoluble cross-linked "macrogel." A second portion of the 100% soluble polymer was fractionated as follows: After extraction of the acetone-soluble fraction (9.0%) the rubber was dried under vacuum and then extracted with toluene in an atmosphere of carbon dioxide. Agitation of the mixture was avoided in order to minimize dispersion of the "microgel." At intervals of several days the supernatant liquid was carefully pipetted out and additional toluene added with as little disturbance to the swollen "microgel" at the bottom as possible. After much of the "sol" had been extracted in this way, fresh toluene was added and the mixture shaken. One or two shakes sufficed to bring the "microgel" into solution indicating that, for this sample at least, the bonds between the molecules of "microgel" are extremely weak. The resulting solution was completely stable, no material settling out after even a month's standing.[9] The "sol" and "microgel" portions were separately fractionated. A sample of the "macrogel" was degraded and solubilized by oxidation at high temperatures and subsequently fractionated.

Measurements.—The molecular weights of the fractions were calculated from osmotic pressures measured in a Flory-type osmometer, while solution viscosities were determined in an Ostwald viscosimeter. The details of these procedures were reported in the previous paper.[6]

For Buna N, the viscosity relation for various solvents was determined in the following manner: After measurements of the osmotic pressure and the viscosity in toluene, a sample of each fraction was dried in vacuum at room temperature and redissolved successively in acetone, chloroform and benzene[10] and its intrinsic viscosity in each of these solvents determined.

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[1] This research was carried out during 1943 on a grant from the Reconstruction Finance Corporation, Office of Rubber Reserve, for fundamental research on the physical properties of synthetic rubbers.

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[4] R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940–1941).

[5] P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[6] W. C. Carter, R. L. Scott and M. Magat, *ibid.*, **68**, 1480 (1946).

[7] For details of the preparation of SK see A. Talalay and M. Magat, "Synthetic Rubber from Alcohol," Interscience Publishers, New York, N. Y., 1945.

[8] In the fractionations of GR-S, the inhibitor, anti-oxidant and the lowest molecular weights were extracted with acetone before the remainder of the soluble material was extracted with toluene.

[9] No significance should be attached to the relative amounts of "sol," (23%) and "microgel" in view of the crude method of separation; the "microgel" portion undoubtedly contains some "sol."

[10] No significant oxidative degradation was observed in Buna N fractions, unlike natural rubber where the breakdown is rapid, or Buna S where the breakdown is slow but appreciable.