

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment and Resonance in Heterocyclic Molecules Containing Nitrogen and Sulfur

BY P. F. OESPER, G. L. LEWIS AND C. P. SMYTH

Because of the use of dipole moment in studying resonance and color in dyes derived from benzothiazole,¹ it seemed desirable to investigate the dipole moments and structures of benzothiazole itself and some simple derivatives and related compounds. It has seemed appropriate to consider at the same time the moment and structure of 2-nitrothiophene.

Purification of Materials

Benzene.—The purification was carried out in the usual manner,² the material being shaken with concentrated sulfuric acid, washed, dried over sodium wire, and distilled.

2-Nitrothiophene.—This substance was prepared by Mr. L. C. Felton and recrystallized by Mr. E. C. Hurdis in this Laboratory.

Benzothiazole.—Material from the Eastman Kodak Company was redistilled; b. p. 228.5–229.5°. 2-Mercaptobenzothiazole, 2-methylmercaptobenzothiazole, and N-methylbenzothiazolethione were given us by Dr. L. G. S. Brooker of the Eastman Kodak Company. 2-Methyl-4,5-diphenyloxazole, 4-methyl-2-mercaptobenzothiazole and 6-methyl-2-mercaptobenzothiazole were prepared and purified by Mr. A. B. Jennings.

Experimental Results

The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus previously described,³ and the densities were determined with an Ostwald-Sprengel pycnometer in a manner described previously.⁴ The dielectric constants, ϵ , and the densities, d , of benzene solutions containing mole fraction, c_2 , of the compound indicated are given in Table I, the polarizations, P_2 , being listed in the last column. Table II lists in the second column the values of MRD , the molar refraction for the D sodium line. For the first three substances, these were obtained from the densities and refractive indices measured for the solutions, and, for the remaining substances, the values were calculated from that of benzothiazole and the following atomic refraction values: carbon, 2.4; hydrogen, 1.1; single-bonded sulfur,

7; double-bonded sulfur, 8.5. The third column gives the polarizations, P_∞ , obtained by extrapolation to $c_2 = 0$ of the values of P_2 in Table I,

TABLE I
DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS AT 25°

c_2	ϵ	d	P_2
2-Nitrothiophene			
0.00000	2.2769	0.87398	...
.00314	2.3528	.87567	376
.00532	2.4081	.87692	378
.00804	2.4786	.87840	379
.01020	2.5375	.87959	380
2-Methyl-4,5-diphenyloxazole			
.00000	2.2769	.87403	...
.01029	2.3232	.88060	127
.02027	2.3608	.88701	121
Benzothiazole			
.00000	2.2769	.87396	...
.02362	2.3581	.88513	81.4
.04245	2.4257	.89391	81.9
.07416	2.5412	.90858	81.8
.1366	2.7642	.93654	80.2
2-Mercaptobenzothiazole			
.000000	2.2751	.87275	...
.000836	2.2951	.87336	372
.001124	2.3004	.87355	364
.001402	2.3075	.87370	373
.001696	2.3124	.87387	357
2-Methylmercaptobenzothiazole			
.00000	2.2751	.87275	...
.00154	2.2806	.87382	93
.00526	2.2934	.87637	91.6
.00943	2.3068	.87921	90.1
.01076	2.3108	.88010	89.4
4-Methyl-2-mercaptobenzothiazole			
.00000	2.2760	.87261	...
.00113	2.3022	.87348	378
.00176	2.3152	.87395	364
6-Methyl-2-mercaptobenzothiazole			
.00000	2.2763	.87294	...
.00134	2.3116	.87401	421
.00000	2.2743	.87295	...
.00153	2.3156	.87404	432
N-Methylbenzothiazolethione			
.00000	2.2751	.87275	...
.00214	2.3457	.87436	516
.00556	2.4598	.87996	507
.00978	2.5955	.87695	489
.01480	2.7643	.88377	477

(1) Brooker, Sprague, Smyth and Lewis, *THIS JOURNAL*, **62**, 1116 (1940); Brooker, White, Keyes, Smyth and Oesper, *ibid.*, **63**, 3192 (1941); Brooker and Sprague, *ibid.*, **63**, 3203 (1941).

(2) Smyth and Walls, *ibid.*, **54**, 1854 (1932).

(3) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(4) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).

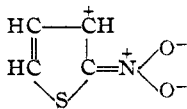
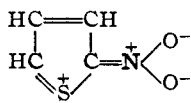
and the fourth column gives the dipole moments calculated in the usual manner. The probable errors in the moment values are about 1% for 2-nitrothiophene, benzothiazole, and N-methylbenzothiazolethione, 5% for 2-methyl-4,5-diphenyloxazole, and 2 to 3% for the other substances. A second less accurate set of measurements upon 2-methylmercaptobenzothiazole gave $P_{\infty} = 90$ as compared to the value 93 in Table II. As the solvent was not very carefully purified for some of the measurements, small differences in the data for different samples of benzene are apparent in Table I.

TABLE II
MOLAR REFRACTIONS, POLARIZATIONS (AT 25°) AND DIPOLE MOMENTS

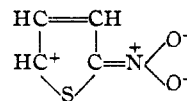
Substance	MR _D	P _∞	μ × 10 ¹⁸
2-Nitrothiophene	32.0	380	4.12
2-Methyl-4,5-diphenyloxazole	74	134	1.7
Benzothiazole	39.5	82.5	1.45
2-Mercaptobenzothiazole	47	380	4.00
2-Methylmercaptobenzothiazole	51.5	93	1.42
4-Methyl-2-mercaptobenzothiazole	51.5	380	4.00
6-Methyl-2-mercaptobenzothiazole	51.5	430	4.30
N-Methylbenzothiazolethione	53	534	4.84

Discussion of Results

In connection with electron diffraction measurements, Schomaker and Pauling⁵ have shown how the lowering of the dipole moment from 1.87 for tetrahydrothiophene to 0.54 for thiophene corresponds to contributions to the structure of the latter of resonating forms containing a charge on the sulfur atom. Neglecting, for the time being, any effect of the nitro group upon resonance in the ring and assuming the thiophene moment to be 0.6 acting in the line bisecting the CSC angle, the moment due to the nitro group to be equal to that just measured by one of us in benzene solution for 2-nitropropane, 3.4, and the angles of the ring to be those found by means of electron diffraction,⁵ the moment calculated for the molecule is 3.6 as compared to 4.1 observed. The nitro group moment used here includes the inductive effects in 2-nitropropane, which should differ little from the direct effects in 2-nitrothiophene. Evidently, polar structures analogous to those for nitrobenzene contribute to that of 2-nitrothiophene, such structures being



(5) Schomaker and Pauling, *THIS JOURNAL*, **61**, 1769 (1939).



Contributions from these structures will, obviously, raise the moment above that calculated with the moment for 2-nitropropane. The moment of nitrobenzene in the vapor state and also in solution is about 0.5 higher than the values found for the nitropropanes in the vapor state⁶ and in solution. If 3.9 is used instead of 3.4 for the moment due to the nitro group, the moment value calculated for 2-nitrothiophene is 4.1, in exact agreement with the observed value. It may, therefore, be concluded that the amount of the contributions of these polar structures is approximately the same as that of the roughly analogous polar structures in nitrobenzene and that the amount of double bond character in the carbon-nitrogen bond is about the same in the two molecules.

No precise calculation of a moment for benzothiazole was possible because of the large number of resonating structures which may contribute to its structure and because of some uncertainty as to the valence angles. The CSC angle was taken as 91°, the value found for it in thiophene,⁵ and values of 110°, 116° and 113° were used for the S—C—C, the S—C—N, and the C—N—C angles of the ring, which was assumed to be planar. The moment due to the sulfur bonds was taken equal to that of tetrahydrothiophene, 1.9, and acting in the line bisecting the angle between the bonds, and the moment due to the nitrogen bonds was taken as 2.2, equal to that of quinoline, which is close to that of pyridine, and acting in the line bisecting the nitrogen bond angle. The value 2.2 may be high because of resonance in the quinoline molecule and, probably, does not act exactly in the bisector of the nitrogen angle because the two nitrogen bonds, presumably, do not have equal amounts of double bond character. After correction for the H—C bond moments, the moment calculated for the molecule on the basis of these approximations had a value 1.0 and a direction nearly that of the C—H bond of the heterocyclic ring. If the thiophene moment had been used instead of that of tetrahydrothiophene, the calculated moment would have been higher than the observed instead of lower. It would appear that, among the many resonating polar structures which may contribute to the structure

(6) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

of benzothiazole, those with a positively charged sulfur are most important and, among these, that with the negative charge on the 2-carbon would contribute most to raising the moment above the value calculated without regard for these polar structures.

The moment of 2-methyl-4,5-diphenyloxazole is about 0.2 higher than that of benzothiazole. The moment of tetrahydrofuran is 0.2 lower than that of tetrahydrothiophene, and, as the oxygen bond moments are largely opposed to the nitrogen bond moments, this lower value would tend to cause the resultant moment of the 2-methyl-4,5-diphenyloxazole molecule to be nearly 0.2 higher than that of benzothiazole. Consideration of this rather small moment with the rather small value for benzothiazole suggests, though it does not prove, that neither molecular structure receives large contributions from polar structures.

It is, at first, surprising that the moment of 2-methylmercaptobenzothiazole is, practically, the same as that of benzothiazole, for the moment of the benzothiazole nucleus acting nearly in the direction of the carbon to mercapto sulfur bond should be re-enforced by the mercapto group moment, which, account being taken of its angle, should raise the total resultant moment by about 1.0. If the mercapto sulfur acts as a source of electrons which are fed back into the ring structures to form various resonating structures with the mercapto sulfur positively charged, the lowering of the moment below the expected value can result from small contributions from these polar structures.

The isomer with the methyl group on the nitrogen has a moment more than three times as large as that of the molecule with the methyl on the mercapto sulfur, primarily, because of the presence of the thiocarbonyl group. The moment calculated for this molecule is about 4.4. The normally used thiocarbonyl bond moment⁷ value is high because of a large contribution from a C^+-S^- structure. There should be fairly stable contributing structures in which the positive charge on this carbon has moved over to the nitrogen or to the sulfur of the adjacent ring, particularly, the structure with positive nitrogen. Contributions from these structures should raise the moment to such an extent that one might expect a resultant value a little higher than the observed one.

(7) Smyth, *THIS JOURNAL*, **60**, 183 (1938).

The moment of 2-mercaptobenzothiazole should be close to that of 2-methylmercaptobenzothiazole instead of being not much lower than that of N-methylbenzothiazolethione, as the replacement of the mercaptan hydrogen by a methyl group should have only a small effect upon the moment. Evidently, the compound exists largely in a lactam form, in which the migration of the hydrogen from the sulfur to the nitrogen leaves a structure like that of the thione with correspondingly large moment. This is borne out by the similarly large moments of the 4- and the 6-methyl-2-mercaptobenzothiazole, the value for the first of which happens to be identical with that of 2-mercaptobenzothiazole, than which it should be a very little higher because of the methyl group. The difference expected between the two moments is, however, no greater than the possible experimental error in the values, which is large because of the low solubilities of these compounds. Moving the methyl group from the 4 to the 6 position brings the small moment associated with a methyl group attached to a benzene ring, as in toluene, more nearly in line with the principal moment of the molecule and, therefore, raises the resultant moment to the expected value. The moments of these mercaptobenzothiazoles give an exceptionally clean-cut indication of the existence of the substances mainly in the lactam form with the mercaptan hydrogen on the nitrogen.

The writers wish to express their gratitude to Mr. L. C. Felton and Mr. E. C. Hurdis of this Laboratory and, especially, to Mr. A. B. Jennings of this Laboratory and Dr. L. G. S. Brooker of the Kodak Research Laboratories for preparation and purification of substances studied in this work.

Summary

The dipole moments of 2-nitrothiophene, 2-methyl-4,5-diphenyloxazole, benzothiazole, 2-mercaptobenzothiazole, three different methylmercaptobenzothiazoles, and N-methylbenzothiazolethione have been measured in benzene solution. The moment of 2-nitrothiophene shows resonance like that in thiophene and in nitrobenzene, the carbon-nitrogen bond having about the same amount of double-bond character as that in nitrobenzene. The rather small moments of 2-methyl-4,5-diphenyloxazole and benzothiazole are consistent with each other and show resonance with contributions, probably small, from, at least,

some of the several polar structures which may be written for these molecules. The moment of *N*-methylbenzothiazolethione shows that contributions from structures involving polarity in the thiazole ring raise the moment only a little above the large value calculated from the normal group moments. The large moments of 2-mer-

captobenzothiazole and 4- and 6-methylmercaptobenzothiazole as compared to the small moment of 2-methylmercaptobenzothiazole show that the former substances exist mainly in the lactam form with the hydrogen on the nitrogen rather than on the sulfur.

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The Potential of the Ytterbic-Ytterbous Ion Electrode

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According to Walters and Pearce,¹ the ytterbic-ytterbous ion electrode potential is -0.578 volt (negative charge on electrode). Although this value is in essential agreement with the prediction of Latimer,² several considerations throw doubt on its validity.

First, the value of Walters and Pearce would lead to the prediction that ytterbic ions should be reducible by zinc (normal potential -0.76 volt). However, a series of experiments³ by W. A. Taebel⁴ in this Laboratory failed to verify this prediction. Over fifty attempts to reduce aqueous ytterbic chloride solutions by shaking with zinc dust, liquid zinc amalgams and solid amalgamated zinc using various concentrations of hydrochloric acid in the presence and absence of ammonium sulfate, over a temperature range of 0° to 100° failed to give any evidence of reduction. Passage of ytterbic chloride solutions through a Jones reductor into a standard iodine solution showed no measurable reduction of the iodine. Attempts to catalyze the reduction by the presence of other oxidation-reduction systems likewise failed.

Second, it was pointed out in a previous publication⁵ that the polarographic half-wave potential for the reduction of trivalent ytterbium or europium ions to the corresponding divalent ion should be very nearly equal to the normal electrode potential, provided that the reduction process at the dropping mercury electrode is reversible. The half-wave potential for europium was found to

be in agreement with the normal potential given by McCoy.⁶ The half-wave potential for ytterbium, however, was found to be -1.169 volts referred to the normal hydrogen electrode.⁵ Logarithmic analysis of the current voltage curves showed only slight deviations from the theoretical slope (based on reversible electrode behavior) for both europium and ytterbium.

Third, the determinations of Walters and Pearce were made by using a platinum indicator electrode in solutions containing ytterbic and ytterbous ions in a $1 N$ potassium chloride, $1 N$ acetic acid medium. The platinum electrode in such a solution can possess a hydrogen electrode function and assume a potential determined partly by hydrogen ions and partly by the ytterbium. It is well known that divalent ytterbium reacts fairly rapidly in acid solution to produce hydrogen and trivalent ytterbium. Kolthoff and Miller⁷ have shown that when two different potential determining systems exist in the same solution and are not in oxidation-reduction equilibrium, the potential of an electrode in the solution is a function of the potentials of both systems and also depends upon the relative concentrations of the potential-determining substances. The resulting potential, lying between the individual potentials of the two systems and not characteristic of either system, is called a mixed potential.

The dropping mercury electrode, owing to its high hydrogen over-voltage, should be a suitable indicator electrode for the ytterbic-ytterbous systems in solutions of moderate acidity. Preliminary experiments showed that solutions of divalent ytterbium are too unstable to permit accurate polarographic measurements. The step-

(1) G. C. Walters and D. W. Pearce, *THIS JOURNAL*, **62**, 3330 (1940).

(2) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938, p. 269.

(3) Unpublished experiments, private communication.

(4) Present address, Westinghouse Electric and Manufacturing Co., Bloomfield, N. J.

(5) H. A. Laitinen and W. A. Taebel, *Ind. Eng. Chem., Anal. Ed.*, **13**, 825 (1941).

(6) H. N. McCoy, *THIS JOURNAL*, **58**, 1578 (1936).

(7) I. M. Kolthoff and C. S. Miller, *ibid.*, **62**, 2171 (1940).