be accounted for on the basis of the general theory proposed in our paper.

KING'S COLLEGE
UNIVERSITY OF DURHAM
NEWCASTLE-UPON-TYNE 1, ENGLAND

The Electric Moments of Some Thiophene and Furan Derivatives

BY MAX T. ROGERS AND TOD W. CAMPBELL

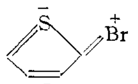
RECEIVED MARCH 14, 1955

The electric moments of several derivatives of thiophene and furan have been reported in the literature[1-3] and it has been noted that group moments indicate a greater importance of conjugation of the substituent group with the thiophene or furan ring than with the benzene ring. We have, therefore, studied the electric moments of several substances in which an electron-donating or electron-receiving group is substituted in the thiophene or furan ring and have compared the observed values with those calculated from the group moments derived from observations on benzene derivatives.

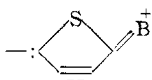
Our values are in good agreement with those reported previously for 2-bromothiophene (1.37[1] and 1.36[2]), 2-iodothiophene[1] (1.14) and 2-methylfuran[2] (0.74). Nazarova and Syrkin[3] report a lower value (1.38) for the moment of 2-furoic acid in benzene solution than we observe in dioxane solution. The comparison suggests that some association of the acid may occur in benzene solution. They report that cryoscopic data showed no appreciable association but present no data.

If the C–H moments are assumed to be 0.4 *D* (hydrogen positive) throughout, and the bond angles are taken from an electron diffraction report,[4] the moment calculated for thiophene (0.52) is just equal to the observed value. The C–S bond moment is, then, essentially zero and a similar calculation for furan gives C–O = 0.25 *D* (oxygen negative) for the bond moment within the ring. Resonance with structures placing a positive charge on the hetero-atom is important in these molecules[4] and reduces the normal C–O and C–S moments greatly. Moments were now calculated for the compounds studied here by use of the group moments and, for non-axial groups, the angles between the group moments and the bonds joining them to the ring, derived from an analysis of the available electric moments of benzene derivatives.[5] A comparison of the calculated and observed values (Table I) reveals significant differences for the 2-halothiophenes, 2-*t*-butylthiophene and 2-furoic acid and agreement within experimental error for the remaining substances.

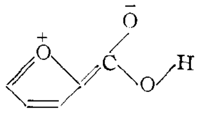
The C–Br and C–I group moments have been reduced from 1.10 and 0.90 in bromo- and iodobenzene to about 0.80 and 0.50 in 2-bromo- and 2-iodothiophene; comparable reductions occur in 2-bromo- and 2-iodofuran.[3] An important contribution of structures analogous to I to the ground state of the molecule would account for the large effect observed since this structure is in addition to resonance forms of type II. In the halobenzenes only structures energetically more comparable to II can be written. The methyl and *t*-butyl group moments also appear to be somewhat larger in 2-methylthiophene[3] and 2-*t*-butylthiophene (but not in 2-methylfuran) than in toluene and *t*-butylbenzene. A significant contribution from (hyperconjugation) structures analogous to I and II would explain this effect although it is also possible that the ring carbon atoms are more electronegative than those in benzene thus altering the portion of the group moment attributable to electronegativity differences.



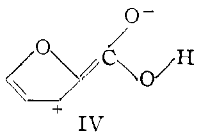
I



II



III



IV

Electron-receiving groups show a similar, though relatively less important, tendency in that the carboxyl group moment is about 0.35 *D* larger in 2-furoic acid than in benzoic acid. A comparison of calculated electric moments with observed values in the literature[1-3] revealed similar increases in group moment for the nitro group in 2-nitrofuran and 2-nitrothiophene (0.15 *D*), the aldehyde group in furfuraldehyde and 2-thiophene aldehyde (0.4 *D*), and the acetyl group in 2-acetylthiophene (0.36). An appreciable contribution of structures of type III to the normal states of these molecules would account for the observed increments. Although more favorable than forms of type IV, these structures (III) are less favorable than those of type I because of the unfavorable charge distribution.

No electric moments of substituted thiophenols have been reported so the calculated moment of 3-mercaptothiophene (Table I) was derived from bond moments (C–S = 0.80, H–S = 0.84, ∠CSH = 100°). Because of the uncertainties in this calculation no particular significance can be attached to the agreement with the observed moment of 3-mercaptothiophene.

Experimental

Materials.—Benzene and Dioxane.—The purification and physical constants of the solvents have been reported.[6]

2-Bromothiophene.—A sample of 2-bromothiophene was the gift of the Michigan Chemical Co., St. Louis, Mich. It was dried and fractionated through an efficiently packed column, b.p. 63° (38 mm.), $n^{25}\text{D}$ 1.5840, d^{25}_4 1.7030.

2-Iodothiophene.—Eastman Kodak Co. White Label material was dried and fractionated, b.p. 88° (29 mm.), $n^{25}\text{D}$ 1.6487, d^{25}_4 2.0595.

2-Methylfuran.—A sample donated by the Quaker Oats Co. was dried and fractionated, b.p. 629° (760 mm.), $n^{25}\text{D}$ 1.4302, d^{25}_4 0.9093.

---

[1] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

[2] R. Kesawni and H. Freiser, THIS JOURNAL, **71**, 218, 1789 (1949).

[3] L. M. Nazarova and Y. K. Syrkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 35 (1949); *Zhur. Obshchei Khim.*, **23**, 478 (1953).

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

[5] M. T. Rogers, unpublished results.

[6] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

TABLE I

EMPIRICAL CONSTANTS, MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND ELECTRIC MOMENTS OF SOME HETEROCYCLIC COMPOUNDS IN BENZENE SOLUTION

Compd.	ϵ_1	a	v_1	b	P_2	MR_D	μ Obsd.	μ Calcd.[a]
2-*t*-Butylthiophene	2.2716	1.093	1.14270	−0.147	60.32	42.96	0.93	0.60
2,5-Di-*t*-butylthiophene	2.2732	0.245	1.14484	−0.098	68.30	62.21	0.55	0.35
2-Iodothiophene	2.2710	2.080	1.14400	−1.585	61.15	35.02	1.13	1.48
2-Bromothiophene	2.2720	2 967	1.14500	−1.193	71.46	32.04	1.39	1.67
3-Mercaptothiophene	2.2721	1.916	1.14472	−0.502	56.09	32.58	1.07	1.08
2-Methylfuran	2.2717	0.418	1.14467	−0.039	33.21	23.33	0.70	0.71
2-Furoamide (dioxane)	2.2100	18.88	0.97284	−0.274	298.0	27.02	3.64	3.55
2-Furoic acid (dioxane)	2.2085	7.220	0.97286	−0.280	131.9	24.81	2.29	1.96

[a] Calculated by use of group moments and angles for benzene derivatives.

3-Mercaptothiophene.—A sample of 3-mercaptothiophene was the gift of Prof. R. D. Schuetz. The material was fractionated just before use, b.p. 70° (21 mm.), n^{25}D 1.6188, d^{25}_4 1.2510.

2-*t*-Butylthiophene and 2,5-Di-*t*-butylthiophene.—Samples of these compounds were provided by the Socony-Vacuum Oil Co., Paulsboro, N.J. and were used after two fractionations; 2-*t*-butylthiophene, b.p. 163° (751 mm.), n^{25}D 1.4932, d^{25}_4 0.9491; 2,5-di-*t*-butylthiophene, b.p. 212° (745 mm.), n^{25}D 1.4908, d^{25}_4 0.9137.

2-Furoic Acid and 2-Furoamide.—Eastman Kodak Co. materials were recrystallized several times before use; m.p. 134° (2-furoic acid) and 142° (2-furoamide).

Apparatus and Technique.—Dielectric constants of six solutions, ranging in mole fraction solute from 0.001 to 0.02, were measured at 25° by the heterodyne-beat method. The apparatus and technique have been described.[6] Dipole moments were computed from the molar polarizations P_2 of the solutes (at infinite dilution) obtained by the method of Halverstadt and Kumler.[7] The slopes a and b, and intercepts ϵ_1 and v_1, obtained from plots of the observed dielectric constants and molar volumes *versus* mole fraction solute, are shown in Table I along with the molar polarizations of solute P_2, the observed molar refractions MR_D (calculated values are shown for furoic acid and furoamide), and the dipole moments μ. The probable error in the electric moment values is about ±0.1 D for all compounds except 2,5-di-*t*-butylthiophene to which a probable error of ±0.2 is assigned.

---

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

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICHIGAN

Studies in Low Concentration Chemistry. XI. The Adsorption of Sulfate and Scandium Ions

BY GEORGE K. SCHWEITZER AND MARTIN R. BOMAR

RECEIVED MARCH 26, 1955

Theories of the adsorption of trace-concentration ions from aqueous solution onto polar and non-polar materials are of considerable variety and in a few cases somewhat contradictory.[1,2] In the case of ion adsorption by a polar substance, there are numerous indications that the forces of attraction are electrostatic. The degree of adsorption may be influenced by solubility relationships, lattice structure relationships, size, polarizability and the valence of the adsorbate ion as well as the degree of crystalline perfection of the adsorbent and the charge upon it.[1-8] Although less work has been done on the adsorption of ions onto non-polar materials, some theories have been advanced. The mechanism of adsorption of acids onto charcoal is considered by Kolthoff[9] to be a capillary effect caused by a reduction of interfacial tension; other investigators[10] postulate a reaction with basic oxides; still others[11] consider it to be some sort of attractive force common to all acids.

In this investigation, radiotracer studies were made of the adsorption of sulfate and scandium ions from low concentration solutions onto charcoal and various insoluble compounds. These studies included: (a) qualitative investigations on the adsorbent characteristics of numerous insoluble substances, (b) investigations of adsorption rates, (c) investigations of the effects of *p*H and acid used to adjust the *p*H upon adsorption onto charcoal, and (d) investigations of adsorption–concentration relationships.

Experimental

Materials.—Sulfur-35 as carrier-free sulfate in dilute hydrochloric acid was obtained from Oak Ridge National Laboratory. Isotopic dilutions were made with reagent grade sodium sulfate to prepare solutions of known concentrations. High specific activity scandium-46 with a known quantity of inactive scandium in dilute hydrochloric acid was obtained from the same source. Isotopic dilutions were made with scandium perchlorate which had been prepared from 99.8% scandium oxide as obtained from Research Chemicals, Inc., Burbank, California.

Neutral Norit-A Decolorizing Carbon and a number of reagent grade insoluble salts were employed as adsorbents. The chromates, sulfides, oxalates, halides were prepared by precipitation, filtration and aging for at least a day. Standard solutions were prepared from reagent grade chemicals.

Apparatus.—All sulfate adsorption experiments were carried out in 15-ml. weighing bottles stoppered with ground glass caps. Agitation of samples was effected by placing the weighing bottles on a mechanical shaker. Scandium adsorption determinations were performed in a similar manner except that 25-ml. polyethylene bottles were used for containers to avoid adsorption of the scandium by the glassware. All *p*H measurements were made with a Beckman model H-2 *p*H meter equipped with micro electrodes.

Samples for the determination of radioactivity were

---

(1) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 124–135.

(2) E. Broda, "Advances in Radiochemistry," Cambridge University Press, New York, N. Y., 1950, pp. 9–14.

(3) I. M. Kolthoff, *Analyst*, **77**, 1000 (1952).

(4) L. Imre, *Z. angew. Chem.*, **43**, 857 (1930).

(5) J. F. King and P. R. Pine, *J. Phys. Chem.*, **37**, 851 (1933).

(6) J. F. King and U. T. Greene, *ibid.*, **37**, 1047 (1933).

(7) K. Fajans and T. Erdey-Gruz, *Z. physik. Chem.*, **A158**, 97 (1931).

(8) H. Horowitz and F. Paneth, *ibid.*, **89**, 513 (1915).

(9) I. M. Kolthoff, *Rec. trav. chim.*, **46**, 549 (1927).

(10) A. King, *J. Chem. Soc.*, 889 (1935).

(11) K. D. Jain and J. B. Jha, *J. Indian Chem. Soc.*, **18**, 321 (1941).