five field strengths, varying from 8,000 to 13,500 gauss, and the arithmetic mean of the values was used.

Method.—A weighed amount of adsorbent (about 7 g.) was agitated for about an hour with 10 ml. of a standard solution of the paramagnetic salt, the mixture filtered through sintered glass, the adsorbent washed several times with water, dried in an oven (110° for charcoal and 140° for silica gel) for two hours and transferred to the susceptibility tube for measurement. The filtrate and washings were combined and analyzed, the amount of salt adsorbed being determined by difference. The susceptibility of the pure adsorbent was determined in a separate experiment. When ferrous (or ferric) salts were studied the drying was carried out in an inert atmosphere and special analyses were made to determine whether any oxidation (or reduction) had occurred in handling.

Analytical methods used were as follows: (a) ferrous iron was determined by titration with cerate, (b) ferric ion was reduced in a silver reductor and the ferrous ion titrated with cerate, (c) nickel was determined gravimetrically with dimethylglyoxime, (d) cobalt was titrated potentiometrically with ferricyanide in ammonium citrate–ammonium hydroxide solution, (e) manganous ion was titrated potentiometrically with permanganate in a neutral pyrophosphate solution.

Materials.—Eimer and Amend Co. C.P. charcoal was treated with concd. sulfuric acid to remove materials which reduced cerate, washed several times with water and dried at 110° for two hours. Silica gel from Davisson Chemical Co. was used directly and showed no change in susceptibility after treatment with water and redrying at 140° for two hours. Both adsorbents were shown to be reasonably free of ferromagnetic impurities by the small change in susceptibility observed with varying field strength.

Results.—The gram susceptibilities of the adsorbed salts were calculated by the additivity rule from the observed gram susceptibilities of the mixtures, the analytical data and the susceptibility of the pure adsorbent. In each case measurements were made on several samples treated in various ways, and the values so obtained were averaged. The mean values of the gram atomic susceptibilities of the adsorbed paramagnetic metal atoms are shown in Table I along with the corresponding magnetic moments, in Bohr magnetons, calculated on the assumption that the molecular field constant Δ is zero. The range of magnetic moments commonly observed for the ion in solution or in simple salts is given for comparison, and an average value of the amount of metal ion adsorbed is shown for each ion studied. The diamagnetism of the anions has been neglected. The probable error in χ_A for the adsorbed salt is about 15% so the magnetic moments are, in general, reliable to only about ± 0.4; this precision is adequate for the purpose of the present work.

In a separate series of experiments it was shown that the charcoal used was a good adsorbent for base, a poor adsorbent for acids and, when equilibrated with a neutral salt solution (KCl), hydrogen ion was liberated from the charcoal but no change in the chloride ion concentration occurred. This indicates that the charcoal is a low-tempera-

TABLE I

THE MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS
OF ADSORBED IONS

Adsorbent	Adsorbate	Amount adsorbed[a]	χ_A, c.g.s. units $\times 10^{+6}$	μeff., adsorbed salt	μeff.[b] typical salts
Charcoal	NiCl$_2$	4.5	3,930	3.08	2.9–3.4
Charcoal	CoCl$_2$	4.6	10,100	4.96	4.4–5.2
Charcoal	CoSO$_4$	2.0	10,470	5.05	4.4–5.2
Charcoal	MnSO$_4$	4.5	15,450	6.13	5.2–5.96
Charcoal	FeSO$_4$	1.8	13,400	5.69	5.0–5.5
Charcoal	Fe$_2$(SO$_4$)$_3$	2.6	16,750	6.24	5.4–6.0
Charcoal	None	...	−0.462[c]	..	...
Silica gel	NiCl$_2$	7.2	4,660	3.32	2.9–3.4
Silica gel	FeSO$_4$	0.7	10,110	4.93	5.0–5.5
Silica gel	Fe$_2$(SO$_4$)$_3$	2.5	8,400	4.50	5.4–6.0
Silica gel	None	...	−0.317[c]	...	...

[a] Milligrams of metal per gram of adsorbent. [b] See ref. 3, pp. 79 and 99. [c] Gram susceptibility.

ture air-activated material which behaves as though it were a cation exchanger.[4]

Discussion

The paramagnetic cations studied here evidently do not lose their paramagnetism when adsorbed on sugar charcoal or on silica gel. This is in qualitative agreement with the results of Bhatnagar, et al.,[2] for silica gel but is contrary to their findings in the case of charcoal. Since their charcoals were strongly paramagnetic and so must have contained paramagnetic (and possibly ferromagnetic) impurities, it seems possible that the losses in paramagnetism they observed resulted from desorption of impurities in the charcoal.

The magnetic moments observed here for the adsorbed ions are within the normal range of values observed for the corresponding ion in solution or in a simple salt,[3] with the exception of adsorbed ferrous and ferric ions. The origin of the discrepancies for these ions are not known but may be associated with the formation of surface oxides or hydroxides of iron. Since, in every case, the covalent complexes of the ions have much smaller magnetic moments (or are diamagnetic),[5] we conclude that the ions are held on the surface by essentially ionic bonds. This would be expected for cations adsorbed on silica gel since they presumably displace hydrogen ions from acidic hydroxyl groups on the silica gel surface. A similar ion-exchange mechanism for the adsorption of cations on charcoals which have been activated in air at low temperatures ($<600°$) has been postulated.[4] The charcoal surface would thus be covered by a surface oxide characterized by acidic hydroxyl groups which could exchange hydrogen ions with the cations in solution and the ions so adsorbed would be held by an essentially ionic bond to an oxygen atom of the surface.[6−8] Our results are in agreement with this hypothesis.

(4) See, for example, B. Steenberg, "Adsorption and Exchange of Ions on Activated Charcoal," Almquist and Wiksells, Uppsala, 1944.

(5) L. Pauling, "Nature of the Chemical Bond," Second Ed., Cornell University Press, Ithaca, N. Y., 1940.

(6) H. L. Bennister and A. King, *J. Chem. Soc.*, 991 (1938).

(7) J. Wilson and T. R. Bolam, *J. Colloid Sci.*, **5**, 550 (1950).

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Some Nitrogen Derivatives of Dibenzothiophene

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It has been shown that 3-acetylaminodibenzothiophene and 3-acetylaminodibenzothiophene-5-oxide are carcinogenic to rats.[2] For this reason N-substituted derivatives of 3-aminodibenzothiophene have been prepared. The isomeric 2-substituted derivatives have also been synthesized for comparison.

(1) Cancer Research Laboratory, University of Florida, Gainesville, Fla.

(2) E. C. Miller, J. A. Miller, R. B. Sandin and R. K. Brown, *Cancer Research*, **9**, 504 (1949).

Experimental[3]

2-Benzenesulfonylaminodibenzothiophene.—To an ice-cold solution of 4 g. (0.02 mole) of 2-aminodibenzothiophene,[4] m.p. 132–133°, in 20 ml. of pyridine was added dropwise 3.0 ml. (0.024 mole) of benzenesulfonyl chloride. The violet solution was refluxed for one hour. The mixture was cooled and then poured into 200 ml. of dilute hydrochloric acid. A brown oil precipitated. Within two hours the oil solidified. Two crystallizations from acetic acid gave 5.1 g. (76%) of lustrous white crystals, m.p. 171–172°. The compound was soluble in alcohol, acetone, benzene, pyridine and acetonitrile. It was moderately soluble in chloroform and very slightly soluble in heptane.

Anal. Calcd. for $C_{18}H_{13}NO_2S_2$: N, 4.13; S, 18.9. Found: N, 4.03; S, 18.9.

3-Benzenesulfonylaminodibenzothiophene.—This compound was prepared from 3-aminodibenzothiophene,[5] m.p. 124–125°, by the procedure used for the 2-isomer. Crystallization from chlorobenzene and then alcohol gave 71% colorless needles, m.p. 198–199°.

Anal. Calcd. for $C_{18}H_{13}NO_2S_2$: N, 4.13; S, 18.9. Found: N, 4.06; S, 18.8.

3-(N⁴-Acetylsulfanilamido)-dibenzothiophene.—The same procedure was followed as for the other sulfonamines. Slightly more than a molar equivalent of pure *p*-acetylaminobenzenesulfonyl chloride[6] was used. Crystallization from aqueous acetic acid gave a 78% yield of colorless crystals, m.p. 269–270°.

Anal. Calcd. for $C_{20}H_{16}N_2O_3S_2$: N, 7.07. Found: N, 6.94.

2-(N⁴-Acetylsulfanilamido)-dibenzothiophene.—Crystallization from acetic acid gave a 58% yield of colorless crystals, m.p. 215–216°.

Anal. Calcd. for $C_{20}H_{16}N_2O_3S_2$: N, 7.07. Found: N, 6.93.

2-Sulfanilamidodibenzothiophene.—To 1.5 g. (0.0038 mole) of 2-(N⁴-acetylsulfanilamido)-dibenzothiophene suspended in 40 ml. of boiling alcohol was added slowly 15 ml. of concentrated hydrochloric acid. The clear solution was refluxed for one hour. Colorless needles precipitated. An almost quantitative yield of the hydrochloride was obtained, m.p. 252 dec. To the hydrochloride suspended in water an excess amount of dilute ammonium hydroxide was added. The gummy precipitate was crystallized out of methanol. Colorless crystals (1.2 g., 90%) were obtained, m.p. 175–176°.

Anal. Calcd. for $C_{18}H_{14}N_2O_2S_2$: N, 7.91. Found: N, 7.87.

3-Sulfanilamidodibenzothiophene.—To a suspension of 1.0 g. (0.0025 mole) of 3-(N⁴-acetylsulfanilamido)-dibenzothiophene in 40 ml. of boiling alcohol was added 15 ml. of concentrated hydrochloric acid. The mixture was refluxed an hour. Charcoal was added to the clear solution. The mixture was refluxed an additional half-hour and filtered hot. Dilute ammonium hydroxide was added to the clear hot solution until a definite turbidity was formed. The solution was allowed to cool. The crystals were collected on a buchner funnel and washed with water. Colorless microcrystals (0.80 g., 90%) were obtained, m.p. 254–255° dec.

Anal. Calcd. for $C_{18}H_{14}N_2O_2S_2$: N, 7.91. Found: N, 7.97.

***n*-Propyl N-2-Dibenzothienylcarbamate.**—To an ice-cold solution of 1.00 g. (0.005 mole) of 2-aminodibenzothiophene in 10 ml. of pyridine was added dropwise 1.85 g. (0.015 mole) of *n*-propyl chlorocarbonate. The mixture was allowed to stand at ice-water temperature for 30 minutes and was then poured into cold dilute hydrochloric acid. Crystallization from heptane gave 0.72 g. (51%) of colorless glistening needles, m.p. 117.5–119°.

Anal. Calcd. for $C_{16}H_{15}NO_2S$: S, 11.23. Found: S, 11.10.

***n*-Propyl N-3-Dibenzothienylcarbamate.**—This compound was prepared from 3-aminodibenzothiophene by the

procedure used for the 2-isomer. Crystallization from heptane gave an 84% yield of colorless crystals, m.p. 103–104°.

Anal. Calcd. for $C_{16}H_{15}NO_2S$: S, 11.23. Found: S, 11.48.

2-(*o*-Carboxybenzoylamino)-dibenzothiophene.—To a suspension of 9.4 g. (0.064 mole) of phthalic anhydride in 80 ml. of warm xylene, a solution of 12 g. (0.06 mole) of 2-aminodibenzothiophene in 80 ml. of warm xylene was added. The mixture was warmed for half an hour and then allowed to stand at room temperature for half an hour. The pasty precipitate was collected on a buchner funnel and dissolved in 10% sodium hydroxide solution. The filtered solution was acidified with dilute hydrochloric acid. Crystallization of the precipitate from methanol gave 10 g. (48%) of colorless microcrystals, m.p. 208–210° dec.

Anal. Calcd. for $C_{20}H_{13}NO_3S$: S, 9.22. Found: S, 9.39.

3-(*o*-Carboxybenzoylamino)-dibenzothiophene.—This compound was prepared from 3.0 g. of 3-aminodibenzothiophene by the procedure used for the 2-isomer. Crystallization from methanol gave 2.9 g. (57%) of colorless microcrystals, m.p. 286–289° dec.

Anal. Calcd. for $C_{20}H_{13}NO_3S$: S, 9.22. Found: S, 9.42.

2-Benzalaminodibenzothiophene.—A solution of 0.20 g. (0.001 mole) of 2-aminodibenzothiophene in 3 ml. of alcohol was refluxed for 15 minutes with 0.10 ml. (0.001 mole) of benzaldehyde. Solidification took place when the cooled supersaturated solution was scratched or seeded. Crystallization from aqueous methanol gave 0.23 g. (80%) of colorless plates, m.p. 121–122°.

Anal. Calcd. for $C_{19}H_{13}NS$: S, 11.2. Found: S, 11.0.

3-Benzalaminodibenzothiophene.—This compound was prepared from 3-aminodibenzothiophene by the procedure used for the 2-isomer. Crystallization from hexane gave a 90% yield of yellow needles, m.p. 160°.

Anal. Calcd. for $C_{19}H_{13}NS$: S, 11.2. Found: S, 11.1.

3-(4'-Dimethylaminobenzalamino)-dibenzothiophene.—A solution of 0.40 g. (0.002 mole) of 3-aminodibenzothiophene in 8 ml. of alcohol was refluxed for one hour with 0.30 g. (0.002 mole) of *p*-dimethylaminobenzaldehyde. The Schiff base was precipitated by adding the cooled mixture to excess water. Two crystallizations from methyl cellosolve gave 0.53 g. (80%) of yellow crystals, m.p. 195–196°.

*Anal.* Calcd. for $C_{21}H_{18}N_2S$: S, 9.70. Found: S, 9.51.

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Preparation of Lithium Fluoborate

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In the course of studying the reaction of lithium aluminum hydride with boron trifluoride etherate[2] it became necessary to prepare a quantity of pure lithium fluoborate. In addition to the well-known methods of preparing lithium fluoborate from aqueous solutions,[3] Baumgarten and Bruns[4] prepared lithium fluoborate in milligram quantity by the reaction of gaseous boron trifluoride with lithium carbonate heated at 300°.

$$3Li_2CO_3 + 9BF_3 \xrightarrow{300°} 6LiBF_4 + 3CO_2\uparrow + (BOF)_3\uparrow \quad (1)$$
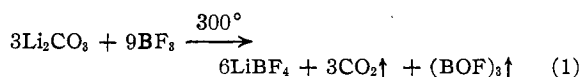
The product was found to contain about 4% lithium fluoride. This impurity can be attributed to

(1) Research Department, Mathieson Chemical Corporation, Pasadena, California.

(2) I. Shapiro, H. G. Weiss, M. Schmich, Sol Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(3) Since fluoborate ion is known to hydrolyze, the lithium fluoborate that can be obtained from an aqueous solution is of questionable purity.

(4) P. Baumgarten and W. Bruns, *Ber.*, **72B**, 1753 (1939).

(3) All melting points are uncorrected.

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(5) R. K. Brown, R. G. Christiansen and R. B. Sandin, *ibid.*, **70**, 1748 (1948).

(6) S. Smiles and J. Stewart, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 8.