cribed to the formation of electrostatically associated neutral ion pairs. At high concentrations in isopropyl ether, the tetrachloroferrate ion[2] may be largely associated in the form of triple ions such as $[H_3O^+{\cdot}4H_2O\ FeCl_4^-H_3O^+{\cdot}4H_2O]^+$ and $[FeCl_4^-\ H_3O^+{\cdot}4H_2O\ FeCl_4^-]^-$, associated in neutral iron pairs as $[H_3O^+{\cdot}4H_2O\ FeCl_4^-]$, and dissociated to a lesser extent as the ions $H_3O^+{\cdot}4H_2O$ and $FeCl_4^-$. With dilution, the conductance would be expected to go through a minimum as the triple ions dissociated and the concentration of neutral ion pairs increased. The final increase in conductance would follow an increased dissociation of neutral ion pairs with high dilution. Thus, the appearance of such minima in the conductance–dilution curves of the ethereal phases of the iron extraction system provides supporting experimental evidence for the "polymerization" theory which Myers, Metzler and Swift[5] have proposed to account for the variation in the iron distribution coefficient with total iron concentration in ethereal extraction of iron from aqueous solution having constant initial hydrochloric acid concentrations.

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GEOMETRIC CONSIDERATIONS OF TETRAZOLE DERIVATIVES FROM DIPOLE MOMENT DATA

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Hill and Sutton[1] in their study of electric dipole moments of some sydnones applied vector addition to the solution of geometric problems. From known moments and moments of aromatic compounds differing only by *para* substitution, they deduced various angles between substituted phenyl bonds and the direction of the dipole moments of the parent compound. A qualitative picture of the hybrid nature of tetrazoles was recently reported by Kaufman, *et al.*[2] The purpose of the present study was to investigate the geometry of tetrazoles by means similar to those of Hill and Sutton. With this idea in mind, chloro-, bromo- and nitrophenyltetrazoles were prepared and their dipole moments measured in benzene solution at 25°.

Experimental

Preparation and Purification of Materials.—Mallinckrodt analytical reagent grade benzene was purified by crystallizing twice, rejecting a small portion each time, and then fractionally distilling after standing several days over freshly cut and ribboned sodium. All was rejected but the center cut which was re-distilled in the same manner before use. The specific volume parameter for the solvent was obtained for each run from a least squares examination of the specific volume, weight fraction data and was found to be constant to ±0.02%.

Tetrazoles.—All were prepared from amide and hydrazoic acid by a method similar to that described by Harvill, *et al.*[3] Analytical data are presented in Table I. All tetrazoles were sublimed twice before making any physical measurements.

Amides.—These were prepared in the usual manner. In Table I, the melting points of the amides are listed; all were recrystallized twice from ethanol.

Physical Measurements and Calculations.—This experimental part is essentially that of Kaufman, *et al.* The apparatus was calibrated with benzene, the dielectric constant of which was taken to be 2.2750 at 25°.[4] The calculated data are presented in Table II, where ϵ_1 and V_1, the dielectric constant and the specific volume of the solvent, respectively, are the intercepts while α and β are the slopes of the straight lines obtained by plotting solution dielectric constant and specific volume, respectively, against weight fraction of solute.[5] P_∞ is the solute polarization at infinite dilution calculated from the Halverstadt and Kumler relationship[6] while R_2 is the molar refraction of the solute for the D-sodium line and μ is the dipole moment calculated from the approximate Debye equation

$$\mu = 0.01281 \times 10^{-18}\,[(P_\infty - R_2)T]^{1/2} \qquad (1)$$

Discussion

From the known moments of nitrobenzene (3.97 *D*), 1-phenyl-5-methyltetrazole (5.64 *D*) and 1-*p*-nitrophenyl-5-methyltetrazole (3.20 *D*) it follows that the angle between the phenyl–NO_2 bond and the moment of 1-phenyl-5-methyltetrazole is approximately 34°. Therefore, 34° is also the angle between the phenyl–N bond and the moment of 1-phenyl-5-methyltetrazole. In the following manner, Kofod, *et al.*,[7] obtained a value of 0.8 *D* for the Ph–N bond assuming a value of 1.3 *D* for the H–N bond. The experimental value for unsubstituted pyrrole is 1.80 *D* while that of N-phenylpyrrole is 1.32 *D*. Therefore, since the two rings are co-linear, the Ph–N bond must be 0.48 *D* less than the H–N bond or 0.8 *D*. Similarly the CH_3–N bond is 0.12 *D* more than the H–N bond or 1.42 *D*.

If the value of 0.8 *D* for the phenyl-N moment in 1-phenyl-5-methyltetrazole is utilized, a value of 5.00 *D* for the moment of 5-methyltetrazole and 39° for the angle between the phenyl–N bond and the moment of 5-methyltetrazole is obtained. From a similar treatment of 1-methyl-5-*p*-nitrophenyltetrazole (3.87 *D*) the following information was obtained. The angle between the phenyl–NO_2 bond and, therefore, the phenyl–C bond and the moment of 1-methyl-5-phenyltetrazole is approximately 43°. The angle between the phenyl–C bond and the moment of 1-methyltetrazole is approximately 45° while the dipole moment of 1-methyltetrazole is calculated to be 5.45 *D*. The experimental value of 5.38 *D* was reported for this compound by Jensen and Friediger.[8]

From the above data, predictions about the moments of phenyltetrazoles differing only by *para* substituents may be made; *e.g.*, from the known moments of chloro- (1.59) and bromobenzene

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TABLE I

ANALYTICAL DATA

Tetrazole	Recrystallization	M.p., °C.	M.p., °C. lit		C	H	X
1-Ethyl-5-*p*-chlorophenyl-	Sublim.	82.7–83.8	....	Calcd.	51.80	4.35	16.99
				Found	51.33	4.24	17.1
1-*p*-Chlorophenyl-5-methyl-	ETOH-needles	88.5–89.4	....	Calcd.	49.37	3.62	18.21
				Found	49.47	3.59	18.1
1-*p*-Bromophenyl-5-methyl-	H_2O-needles, cyclohexane-plates	116.7–118	....	Calcd.	40.19	2.95	33.43
				Found	40.01	3.07	33.9
1-*p*-Bromophenyl-5-ethyl-	ETOH-plates	92.6–93.6	....	Calcd.	42.70	3.58	31.58
				Found	42.62	3.29	32.2
1-Methyl-5-*p*-nitrophenyl-	CH_2Cl_2–ETOH prisms	123.4–124.4	123–126[a]				
1-*p*-Nitrophenyl-5-methyl-	CH_2Cl_2-plates	132.3–132.7	130–135[a] 132–133[b]				
Amide							
p-Nitroacetanilide		(uncorr.) 214.8–215.6	215.9[c]				
p-Chloroacetanilide		179.6–179.8	178.4[c], 179.0[d]				
p-Bromoacetanilide		168.5–168.8	167[e]				
N-Ethyl-*p*-chlorobenzamide		109.0–110.2	....				
N-Ethylbenzamide		68.4–69.8	70–71[g], 67[h]				

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TABLE II

CALCULATED DATA

Tetrazole	ϵ	V_1	α	β	P_∞	R_2	μ
1-*p*-Nitrophenyl-5-methyl-	2.2805	1.14412	5.60	−0.38	261.9	52.0	3.20
1-Methyl-5-*p*-nitrophenyl-	2.2865	1.14543	8.19	− .49	354.7	47.9	3.87
1-Ethyl-5-*p*-chlorophenyl-	2.2920	1.14528	12.22	− .39	523.0	55.7	4.78
1-*p*-Bromophenyl-5-ethyl-	2.2748	1.14543	9.53	− .50	501.8	57.7	4.66
1-*p*-Chlorophenyl-5-methyl-	2.2874	1.14429	10.95	− .37	442.9	50.7	4.38
1-*p*-Bromophenyl-5-methyl-	2.2866	1.14512	9.25	− .54	456.9	51.9	4.45

(1.57),[9] the moments of 1-*p*-bromophenyl-5-methyl- and 1-*p*-chlorophenyl-5-methyltetrazole were calculated to be 4.43 and 4.41 *D*, respectively. The observed moments (Table II) are 4.45 and 4.38 *D*, respectively.

Assuming the simplest geometry for the tetrazole ring (a regular pentagon with all substituent bonds co-linear with a ring axis) the dipole moment of 5-methyltetrazole would have a direction somewhat as illustrated in Fig. 1. Figure 2 shows the dipole moment of 1-methyltetrazole. Knowing the direction of the moment in 5-methyltetrazole, it is interesting to note that the direction of the 1-methyltetrazole could be predicted easily, qualitatively, by considering the addition of the $^{+}C–N^{-}$ dipole. It is also of interest to note that the information illustrated in Fig. 2 agrees very well with the resonance structures depicted for 2-ethyltetrazole by Kaufman, *et al.*[2]

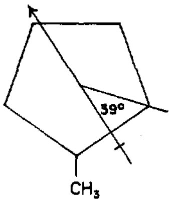

Fig. 1.

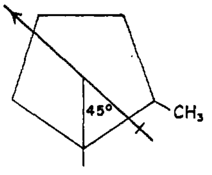

Fig. 2.

Acknowledgment.—We wish to thank Dr. Richard Knipe for his interesting discussions and suggestions.

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ALCOHOLIC FERRIC PERCHLORATE SOLUTIONS[1]

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Solutions of ferric perchlorate in alcohol, acetone and many other organic solvents are much more intensely yellow colored than aqueous solutions of comparable concentration and acidity. Rabinowitch and Stockmayer[3] have suggested that, in the case of alcoholic solutions, this color intensification might be due to ferric perchlorate complex ion[4] or to alcoholysis. These same solvents also intensify the yellow color of ferric bromide and the red color of ferric thiocyanate solutions[5]; the latter has been utilized in the colorimetric determination of iron.[6]

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] Radio Corporation of America, Needham Heights, Mass.

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