

ternary electrolyte. Cyanides are much weaker salts in pyridine than are iodides.⁷

Summary

Both iodine and cyanogen iodide dissolve in pyridine to give solutions whose electrical conductivity increases with time to give maximum values. The experimental evidence indicates that reaction between solvent and solute results in the primary formation of a non-conducting addition compound which in time changes over to a true quaternary pyridonium salt. In the case of iodine the extraordinarily high value for the molecular conductivity at infinite solution can only be explained by the formation of a ternary salt.

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Electric Moments of Hydrazine and its Derivatives¹

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In a discussion of the structure of azo compounds as revealed by the measurement of their dipole moments, Bergmann, Engel and Sandor³ arrive at the conclusion that hydrazo compounds probably also possess a *trans*-configuration, first, because azotoluene and hydrazotoluene form mixed crystals, and, second, because the former has a zero electric moment and must therefore possess a structure of highest symmetry. While their statement "that only similarly constituted substances can form mixed crystals" is not a question for dispute, it nevertheless seemed highly improbable that a definite comparison between the structures of these two classes of compounds, based on this one observation, was permissible. That hydrazo compounds might easily assume the *trans*-configuration in solid mixtures in which this form is forced upon it by the symmetry of the other component is very probable. That they should prefer this structure exclusively, say in dilute benzene solution, seemed questionable in view of the fact that the >N-N< linkage in hydrazo compounds permits free rotation, that is, theoretically allows a variety of positions of the substituents with respect to each other, whereas the positions of groups in azo compounds with -N=N- linkage is presumably fixed.

That this objection to Bergmann's postulation is correct is conclusively

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³ Bergmann, Engel and Sandor, *Ber.*, **63**, 2572 (1930).

proved by our experimental results. Hydrazobenzene possesses an appreciable electric moment, whereas it should have zero moment if it assumed only the *trans*-configuration, that is, if the substituents were fixed in a position of highest symmetry.

We have also measured the dielectric constants of dilute benzene solutions of hydrazine and several of its derivatives in order to determine the effect of substitution upon the dipole moment of the parent hydronitrogen.

Experimental

Apparatus and Method.—The dielectric constants of the various binary solutions were measured in the apparatus designed and used by Ulich and Nespital,⁴ based on the resonance principle and employing a crystal controlled oscillator. For a detailed description of the apparatus and its operation reference is made to the original articles.⁴

The various concentrations were prepared either by the direct addition of the solute to the benzene solution in the condenser cell, or by the preparation of standardized stock solutions in benzene which were pipetted to the solution in the cell. In the latter case an equal amount of solution was always removed from the cell before the addition of the standard solution, so that the volume of liquid remained constant throughout a single series of measurements.

Benzene was used exclusively as the non-polar solvent. Carbon disulfide and carbon tetrachloride had to be eliminated from consideration because of the interaction of these solvents with hydrazine and its derivatives.

All substances were carefully purified either by recrystallization from appropriate solvents, or by distillation under reduced pressure.

Evaluation of the Experimental Data.—The polarization of a binary liquid mixture may be calculated in accordance with Debye⁵ from the equation

$$P_{1,2} = P_1X_1 + P_2X_2 = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_1X_1 + M_2X_2}{d} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_{1,2}}{d}$$

in which $P_{1,2}$ is the molar polarization of the binary liquid mixture; P_1 and P_2 , X_1 and X_2 , M_1 and M_2 , the molar polarizations, mole fractions and molecular weights of the solvent and solute, respectively; ϵ , the dielectric constant of the solution; d , the density of the solution; $M_{1,2}/d$, the average molecular volume of the solution.

The density of the most concentrated solution of each series of measurements was determined and $M_{1,2}/d$ calculated for this concentration. The values for the less concentrated solutions were obtained by interpolation. Only in the case of hydrazine were all $M_{1,2}/d$ values determined by interpo-

⁴ Ulich and Nespital, *Z. physik. Chem.*, **16B**, 227 (1932).

⁵ "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929. See also C. P. Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, No. 55, The Chemical Catalog Co., Inc., New York, 1931.

lation between the molecular volumes of pure hydrazine and of pure benzene, assuming a linear variance of $M_{1,2}/d$ with X_2 . Where the densities of the pure substances were available, theoretical values for $M_{1,2}/d$ were calculated in the same way and for control compared with those found by direct density measurements.

The molar polarization of the solute, P_2 , was calculated on the basis of the above equation in the following form: $P_2 = (P_{1,2} + P_1X_2 - P_1)/X_2$. P_∞ was obtained by extrapolation of the P_2 values to infinite dilution (where $X_2 = 0$). The electric moments were then calculated on the basis of the equation, $\mu = 0.01273 \times 10^{-18} \sqrt{P_M T}$, in which P_M is the polarization due to the permanent moment of the molecule and T , the absolute temperature. P_M was obtained by correcting P_∞ for the induced polarization, $P_E + P_A$, due to deformation of the molecule by the applied electric field. P_E was obtained either by adding together the individual atomic refractivities (D-line) with suitable allowance for variance in type of linkage or, where density and refractive index were available, by application of the Lorenz-Lorentz expression. P_A was arbitrarily taken as 15% of P_E in accordance with the suggestion of K. L. Wolf.⁶

The experimental data⁷ are summarized in the tables.

TABLE I
HYDRAZINE,⁸ N₂H₄, $t = 18^\circ$

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.002147	2.297	88.52	26.719	83
.00700	2.323	88.24	27.007	85
.007496	2.327	88.21	27.052	86
.008116	2.330	88.18	27.085	87

$$P_\infty = 80-83$$

TABLE II
PHENYLHYDRAZINE, C₆H₅NHNH₂

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.004061	2.309	88.63	26.925	107
$t = 17.5^\circ$.008557	2.326	88.68	27.183	95
.01390	2.351	88.73	27.551	95

⁶ Wolf, *Physik. Z.*, 5, 227 (1930).

⁷ The following values for pure benzene were used

t	ϵ	$M_{1,2}/d$	P_1
18°	2.286	88.64	26.597
20°	2.282	88.86	26.605

⁸ The anhydrous hydrazine employed had been prepared for use in making conductivity measurements by Dr. H. Hilgert (Thesis, Rostock, 1932). Its specific conductivity was $\kappa_{25^\circ} = 1 \times 10^{-6}$. Due to its slight solubility in benzene, only very dilute solutions could be prepared. The presence of a trace of moisture in the solvent, or exposure of the benzene solution to the air, rapidly caused the solution to become cloudy. In Table I each concentration, X_2 , represents a separately prepared stock solution of hydrazine in benzene. Each ϵ -value represents an average of several measurements, each time with fresh portions of the same stock solution.

TABLE II (Concluded)

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.003701	2.303	88.63	26.839	93
$t = 17.5^\circ$.01226	2.340	88.71	27.389	92
	.02531	2.394	88.84	28.184	90
	.003502	2.301	88.79	26.858	100
$t = 19^\circ$.008476	2.320	88.83	27.142	91
	.01646	2.350	88.91	27.592	87

 $P_\infty = 97-107$

TABLE III

 α, α -PHENYLMETHYLHYDRAZINE, $C_6H_5(CH_3)NNH_2$, $t = 18.5^\circ$

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.009341	2.335	88.92	27.384	111
	.01475	2.368	89.04	27.886	114
	.004733	2.310	88.81	26.994	110
	.01028	2.341	88.94	27.475	112
	.01751	2.381	89.10	28.087	112

 $P_\infty = 112$

TABLE IV

 α, α -DIPHENYLHYDRAZINE, $(C_6H_5)_2NNH_2$, $t = 20^\circ$

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.003408	2.303	89.08	26.976	136
	.007541	2.326	89.40	27.404	133
	.01197	2.347	89.71	27.799	126
	.004367	2.309	89.17	27.089	137
	.01002	2.336	89.57	27.599	126

 $P_\infty = 141$

TABLE V

HYDRAZOBENZENE, $C_6H_5NHNHC_6H_5$, $t = 18^\circ$

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.000671	2.289	88.69	26.655	113
	.002155	2.297	88.79	26.801	121
	.005893	2.316	89.06	27.156	121
	.001115	2.291	88.72	26.693	113
	.003583	2.305	88.90	26.949	124
	.009952	2.332	89.35	27.473	115

 $P_\infty = 117$

TABLE VI

BENZALDEHYDE PHENYLHYDRAZONE, $C_6H_5CH:NNHC_6H_5$, $t = 19^\circ$

	X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
	0.002029	2.297	88.91	26.837	143
	.006142	2.327	89.25	27.371	152
	.01136	2.362	89.69	28.006	150
	.003235	2.309	89.01	27.040	162
	.006871	2.334	89.31	27.490	156
	.01110	2.362	89.67	27.999	153

 $P_\infty = 157$

TABLE VII
 BENZALAZINE, $C_6H_5CH:NN:CHC_6H_5$, $t = 18^\circ$

X_2	ϵ	$M_{1,2}/d$	$P_{1,2}$	P_2
0.003585	2.295	89.02	26.842	95
.005947	2.300	89.27	26.989	93
.01219	2.313	89.93	27.378	91

$P_\infty = 95$

 TABLE VIII
 ELECTRIC MOMENTS OF HYDRAZINE AND ITS DERIVATIVES

Substance	P_∞	P_E	$P_E + P_A^9$	P_M	μ^{10}
(1) Hydrazine	80-83	8.9	10.2	69.8-72.8	1.83-1.85
(2) Phenylhydrazine	97-107	34.1	39.2	57.8-67.8	1.65-1.79
(3) α,α -Phenylmethylhydrazine	112	38.6	44.4	67.6	1.79
(4) α,α -Diphenylhydrazine	141	58.3	67.1	73.9	1.87
(5) Hydrazobenzene	117	58.6	67.4	49.6	1.53
(6) Benzaldehydophenylhydrazone	153	61.4	70.6	82.4	1.97
(9) Benzalazine	95	64.1	73.7	21.3	1.00 ¹¹

Discussion.—Our values for phenylhydrazine vary somewhat, but if the upper limit is considered as being more nearly the correct one, it is evident that the moments of (2), (3) and (4) do not vary greatly from one another and are practically identical with that of hydrazine itself. This result is not at all surprising if one considers that free rotation around the axis of the N—N linkage is possible in hydrazine and those of its derivatives where such rotation is not hampered by the size of the substituent groups. The observed differences may rest in part with the manner in which the P_A values have been approximated. There is reason to assume that hydrocarbon groups give a relatively smaller P_A contribution than has arbitrarily been assigned to them in the above table on the basis of Wolf's suggestion. Consequently, the differences in the dipole moments of the first four substances lie within the limits of the experimental and calculative errors of our method.

That benzaldehyde phenylhydrazone should have a higher moment might also be expected, since it undoubtedly possesses a less symmetrical structure than any of the above substances. If the moment for benzalazine is assumed to be due to the relative positions of the $C_6H_5CH=$ groups, the low moment may be explained as resulting from the fact that the two substituent groups oscillate preferentially in a sector around the *trans*-position and that, because of the size of these groups, complete rotation around the N—N axis is prevented.¹²

⁹ $P_A = 15\%$ of P_E . See Ref. 6.

¹⁰ In Debye units ($= 10^{-18}$ e. s. u.).

¹¹ Hassel and Naeshagen, *Tids. Kemi Bergvesen*, 7, 84 (1930), give the value 0.89.

¹² It has been suggested that the presence of the conjugated system may be re-

Summary

The dielectric constants of dilute benzene solutions of hydrazine and several of its derivatives have been measured and their dipole moments calculated.

sponsible for the low electric moment of benzalazine. This possible explanation is, however, somewhat speculative since nothing is known about the effects of such systems.

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Synthetic Glycerides. IV. Esters of Aromatic and Aliphatic Acids

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The general purpose of our investigation has been stated in previous communications.¹ The structural relationships found for fatty acid esters of glycerol have been in agreement with Fischer's² findings which showed that methods of preparation which were expected to yield β -monoglycerides gave α -monoglycerides, and that methods which were thought to yield α,β -diglycerides produced α,α' -diglycerides. However, Abderhalden and Eichwald³ and Bergmann⁴ apparently succeeded in preparing α,β -diglycerides of aromatic acids by an indirect and difficult method using propylamines.

Several investigators⁵ have continued to use methods which give compounds of different structure than that assigned.⁶

Helferich and Sieber,⁷ by the use of triphenylmethyl (trityl) ethers of glycerol, prepared the β -mono-(*p*-nitrobenzoate) and the β -monobenzoate (probably the first true β -esters of glycerol), and the α,β -dibenzoate.

Bergmann and Carter⁸ prepared β -monopalmitin, the first fatty acid ester of this type, by the catalytic reduction of β -palmito- α,α' -benzylidene glycerol.

In the present investigation the β -mono-(*p*-nitrobenzoate) and the α,β -dibenzoate of glycerol were prepared by the method of Helferich and Sieber and their identity established by their ready conversion, when

(1) Roche, Averill and King, *THIS JOURNAL*, **51**, 866 (1929); **52**, 365 (1930); Robinson, Roche and King, *ibid.*, **54**, 705 (1932).

(2) Fischer, *Ber.*, **53**, 1621 (1920).

(3) Abderhalden and Eichwald, *ibid.*, **49**, 2095 (1916).

(4) Bergmann, *Z. physiol. Chem.*, **137**, 27, 47 (1924).

(5) Heiduschka and Schuster, *J. prakt. Chem.*, **120**, 145 (1928); Thomson, *Trans. Roy. Soc. Canada*, **20**, 445 (1926); Whitby, *ibid.*, **13**, 255 (1919); *J. Chem. Soc.*, **129**, 1458 (1926); Delaby and Dubois, *Compt. rend.*, **187**, 767 (1928).

(6) Fairbourne, *J. Chem. Soc.*, 372 (1930).

(7) Helferich and Sieber, *Z. physiol. Chem.*, **175**, 311 (1928).

(8) Bergmann and Carter, *ibid.*, **191**, 211 (1930).