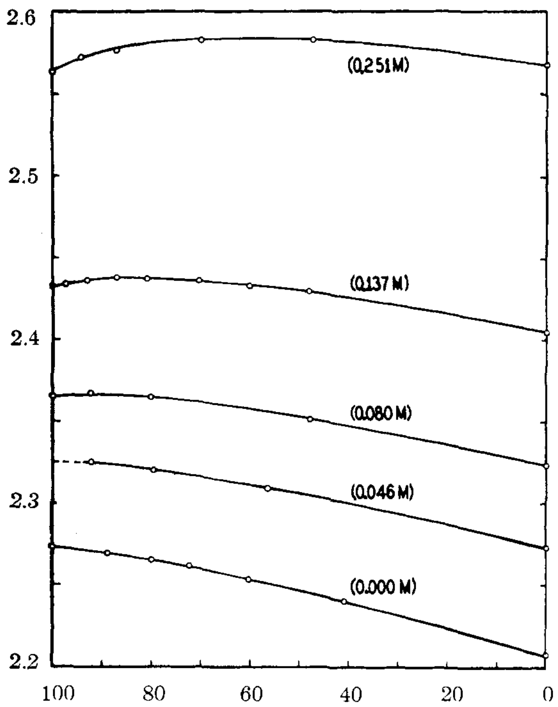

Fig. 1.—Dielectric constant curves for equimolar solutions of *p*-chloroaniline in mixed benzene–dioxane solvent.

Data derived from the 0.251 M line did not fit in well, due to excessive concentration, and were not used.

All solutions were weighed so that concentrations could also be expressed in terms of weight fraction solute, w_2. Plots of w_2 *vs.* solvent composition were made for each solute line. Densities were determined for several solutions on the 0.137 M line, as well as at several solvent compositions, to permit a plot from which $\Delta d/w_2$ values were obtained.

Data were abstracted from the various plots to permit calculation of electric moments in the following solvent environments: 100% dioxane, 80-20, 60-40, 40-60 and 20-80. The following illustrated the general procedure. For solutions in dioxane values of $\Delta\epsilon$ were taken from each equimolar line to the solvent line. Each such value was divided by w_2 to yield $\Delta d\epsilon/w_2$. These were then extrapolated to $M = 0$ to yield $\Delta\epsilon/w_{2\infty}$. From the density graph $\Delta d/w_2$ was obtained which was sufficiently accurate to be used as $\Delta/w_{2\infty}$. From these data the moment in dioxane solution was calculated.

In a completely similar manner moments were calculated for the other solvent compositions. The moments are plotted in Fig. 2.

Extrapolation to 100 mole % benzene yielded a moment of 2.98 in agreement with a value previously determined in benzene solution.[1]

Several alternate methods of handling the data were tried with essentially equivalent results. Individual moments might also have been determined in several mixed solvent environments without requiring equimolar conditions; however, the method used was more flexible and informative.

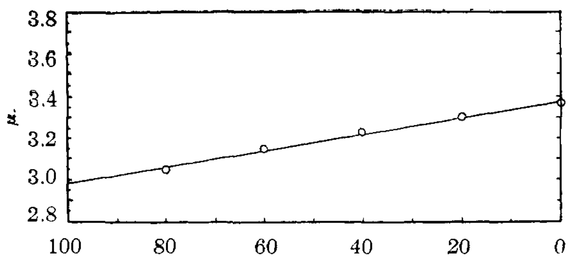

Fig. 2.—Electric moments of *p*-chloroaniline as a function of mixed solvent environment.

Two solute lines (but no solvent line) were run for *p*-nitroaniline, a compound only slightly soluble in benzene. A value of 31.7 for $\Delta\epsilon/w_2$ between the two lines was in agreement with a value of 31.7 between benzene solutions of approximately equal concentration reported earlier.[1]

Some data by Few and Smith[2] for aniline in mixed benzene–dioxane solvent, determined in connection with an association study, were converted for analysis by one of the alternate extrapolation methods. A value of 2.93 for $\Delta\epsilon/w_{2\infty}$ was obtained in agreement with 2.93 based on other work in benzene solution by the same authors.[3]

Moments by extrapolation should be of value in connection with the following points: (1) benzene solution moments may be had for many compounds not soluble in benzene; (2) solutes which associate in benzene solution (carboxylic acids, amides, etc.) may possibly yield reliable moments by extrapolation; (3) mixed solvents of benzene and a polar solvent (such as morpholine) may prove of value.

Experimental data on *p*-chloro- and *p*-nitroaniline, and other compounds currently being studied will be reported in a later paper.

[2] A. V. Few and J. W. Smith, *J. Chem. Soc.*, 2781 (1949).

[3] A. V. Few and J. W. Smith, *ibid.*, 753 (1949).

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The Dielectric Constant of Liquid Trifluoroacetic Acid[1]

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There are two widely different sets of data for the dielectric constant of liquid trifluoroacetic acid in the literature: those of Simons and Lorentzen,[3] who report large values and an abnormal positive temperature coefficient, and those of Dannhauser and Cole,[4] who report lower values and a negative temperature coefficient. Prior to the appearance of the more recent publication, we had conducted measurements on this material as part of a program to study the effects of hydrogen bonding on the dielectric properties of various substances. Since special precautions were taken to avoid contamination of this corrosive material, and the dielectric

[1] Presented before the Division of Physical and Inorganic Chemistry, 125th meeting, American Chemical Society, March, 1954.

[2] Predoctoral Fellow, National Science Foundation, 1952-1953.

[3] J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **72**, 1426 (1950).

[4] W. Dannhauser and R. H. Cole, Jr., *ibid.*, **74**, 6105 (1952).

constant is important in discussions of the solvent properties,[5] we are reporting these results, which are in general agreement with one set of values, but which deviate significantly from both.

Experimental

Trifluoroacetic Acid.—Anhydrous material was prepared from the sodium salt by the method given by Norton.[6] A second distillation was carried out over sulfuric acid in a desiccated fractionating column. The middle cut was obtained at the normal boiling temperature within a 0.1° range. The observed melting point, $-15.2 \pm 0.05°$, agrees with the literature value.[7]

Method.—For preliminary measurements, we employed coaxial cylindrical electrodes made of gold plated brass. These electrodes were visibly attacked, and large drifts in measured values of capacitance and conductance were observed. Subsequently, another coaxial cell was fabricated from platinum and used in all the measurements. The spacing between electrodes of this cell was approximately 1.5 mm., and its air capacity was 17.8 $\mu\mu f$. Electrical measurements were made with a wide range capacitance–conductance bridge which incorporates the best features of two recent bridges[8,9] and which will be described elsewhere.

The results reported here were obtained after pouring the freshly distilled acid into the cell, with precautions to minimize exposure to moisture from the air, since the dry material is highly hygroscopic. No greases were used on the ground-glass joints of the cell because they are attacked by the acid. The values for the dielectric constant were reproducible, indicating negligible uptake of water during the course of the measurements. Nevertheless, further checks of the possible effect of water were made. These included a separate measurement at 25° on a sample which was distilled in a dry atmosphere directly into the cell, which gave agreement within 0.05 dielectric constant unit, and separate measurements on a sample to which small portions of water were deliberately added. It was concluded that the probable error from moisture uptake is less than 0.1 unit. The precision of the measurements was within 0.05 unit.

The measurements were made at a frequency of 20 kc./sec., after it had been established that the capacitance and conductance were substantially independent of frequency between 100 c.p.s. and 100 kc. The results, together with those of the earlier investigators, are presented in Table I.

TABLE I

DIELECTRIC CONSTANT OF TRIFLUOROACETIC ACID

Temp., °C.	Dielectric constant		
	Simons and Lorentzen	Dannhauser and Cole	This research
−10	. .	9.16	9.54 ± 0.1
0	29.5	8.90	9.21
10	34.5	8.65	8.90
20	39.0	8.42	8.55
30	44.5[a]	8.22	8.26
40	. .	8.02	. .
50	. .	7.83	. .

[a] Extrapolated value.

Discussion

Our values for the dielectric constant are very different from those of Simons and Lorentzen, and are in qualitative agreement with those of Dannhauser and Cole. The former authors did not evaluate electrode polarization effects which could cause anomalies since nickel electrodes were employed; the latter authors observed a large electrode polarization effect at low frequencies, probably because their stainless steel electrodes would be slowly attacked by the acid. With the platinum electrodes used in this research, no electrode polarization difficulties were encountered. Our conductivity values agreed, within experimental error, with those of Dannhauser and Cole.

The differences between our results and those of Dannhauser and Cole are larger than the estimated probable errors, particularly at the lower temperatures. We find $d\epsilon/dt$ equals −0.032 dielectric constant unit per degree throughout the temperature range; Dannhauser and Cole's results give a temperature coefficient which increases as the temperature is raised, and has the value −0.020 at 25°.

There is evidence for an unusually large atomic polarization in the symmetrical carboxylic acid dimers. The mechanism of this polarization, which is of general interest where hydrogen bonds are involved, will be discussed in a forthcoming publication.[10] An approximate treatment of the dielectric properties of the liquid already has been published.[11] This treatment assumes that the atomic polarization is negligible, and that all of the orientation polarization can be ascribed to a low concentration of a "self-ionized" highly polar rigid dimer species. Since, in addition to the atomic polarization, one cannot rule out the possibility of significant contributions from non-cyclic polar dimers, and higher polymers, a definitive evaluation of the relative importance of the various possible configurations in the liquid state remains to be made.

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(5) J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **74**, 4746 (1952).

(6) T. R. Norton, *ibid.*, **72**, 3527 (1950).

(7) F. Swartz, *Bull. sci. roy. acad. Belg.*, **8**, 343 (1922).

(8) R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Instr.*, **20**, 252 (1949).

(9) C. T. O'Konski, THIS JOURNAL, **73**, 5093 (1951).

(10) C. T. O'Konski, to be published.

(11) F. E. Harris and B. J. Alder, *J. Chem. Phys.*, **21**, 1306 (1953).

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Addition Compounds of Silicon Tetrahalides

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Silicon tetrahalides frequently have been reported to form addition compounds or coördinate covalent links with donor molecules. In such compounds one would expect (1) that their stability would be affected by the acid and base strengths but would depend to a greater extent on steric interference as Sisler has shown in his investigations of addition of oxygen bases to group IV halides[2]; (2) that addition would be reversible; and (3) that the coördination number of the central silicon atom would not exceed six.

We have found that although silicon tetrafluoride decomposes formamide at room temperature, with N,N-dimethylformamide (DMF) it forms a white solid of composition $SiF_4 \cdot 2DMF$. This solid sublimes readily at 100° in vacuum, is not hygroscopic, is insoluble in hydrocarbon solvents, and is decomposed by water liberating DMF. The infrared spectrum (Fig. 1A) is similar to that of DMF (Fig. 1B) in that the carbonyl absorption band is retained, but differs in that at 750 cm.$^{-1}$ a very intense band and shoulder appear. The supposed addition compound $SiF_4 \cdot 2NH_3$ (Fig. 1C) absorbs

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(1) Du Pont Fellow at Harvard University, 1953–1954.

(2) H. H. Sisler, E. E. Schilling and W. D. Graves, THIS JOURNAL, **73**, 426 (1951). See also A. B. Burg, *ibid.*, **76**, 2674 (1954), on the addition of trimethylamine to chlorosilanes.