Multipolar Complexes. I. The Dimerization of Nitrobenzene[1]

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Evidence of dimerization of nitrobenzene and nitrosobenzene in carbon tetrachloride solution is presented based upon fluorine nuclear magnetic resonance shielding (F-n.m.r.) in their p-fluoro derivatives. This evidence is found to be consistent with literature data on the concentration dependence of the dielectric constant of dilute solutions of nitrobenzene in carbon tetrachloride and with literature data on the freezing point lowering in dilute solutions of nitrobenzene in benzene. The present F-n.m.r. shielding results together with earlier detailed investigations of solvent effects lead to the conclusion that the structure and bonding interaction involved in the nitrobenzene dimer represents a generalized behavior which has been classified as multipolar complexing.

In previous papers detailed investigations were made of substituent and solvent effects on the F-n.m.r. shielding parameters of *meta-* and *para-*substituted fluorobenzenes.[2] For many *meta-*substituted and $-R$ ($+M$) *para-*substituted fluorobenzenes in dilute solutions of pure solvents, the relatively large shielding paramaters relative to internal fluorobenzene were found to be solvent insensitive to on the order of the experimental error. The exceptional cases were interpreted as involving solvent modification of the intramolecular screening effect of the substituent.

In contrast, $+R$ ($-M$) *para-*substituted fluorobenzenes generally show substantial effects on shielding relative to internal fluorobenzene with changes in solvent polarity. These solvent effects are also presumed to result from solvent modification of the substituent intramolecular shielding effect. In the valence bond representation, these observed solvent effects have been qualitatively accommodated in terms that the contribution of II to the ground electronic state is enhanced by increasing solvent polarity.
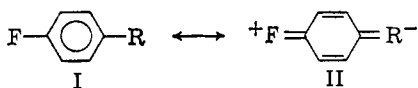
The much greater medium sensitivity exhibited by the $+R$ *para-*substituted fluorobenzenes than by their *meta* isomers is expected. This is indicated by previous generalized correlations of substituent effects[2] $\int_{H}^{m-X} = -7.10\sigma_I + 0.60$ p.p.m.; $\int_{H}^{p-X} = -29.5\sigma_R^0 - 7.1\sigma_I + 0.60$. It is especially evident in the F-n.m.r. shielding of the monofluoro trityl cation and anion[3]

	$\int_{H}^{m}$, p.p.m.	$\int_{H}^{p}$, p.p.m.
cation	-2.6	-28.6
anion	$+3.5$	$+17.0$

In theoretical treatments, the F-n.m.r. intramolecular shielding has been directly related to the molecular orbital theory π-electron charge density localized at the fluorine atom and at the bonded (aromatic) carbon atom in the ground electronic state.[4,5] According to Hückel MO theory (and modifications), changes in π-electron density are generally about an order of magnitude greater at the *para-* than the *meta-*carbon atom.

In this and subsequent papers in this series we report the results of investigations which attempt to determine the origin (mechanism by which II is enhanced) of the polar solvent effects on F-n.m.r. shielding of the $+R$ *para-*substituted fluorobenzenes. In this paper we report the investigation of F-n.m.r. shielding in the binary system CCl_4–*p*-fluoronitrobenzene which has been carried out over the complete composition range. A similar study for the system CCl_4–*p*-fluoronitrosobenzene is also reported.

The most commonly employed model of polar solvent effects is that of Kirkwood.[6] The electrostatic work arising from the mutual polarization of a continuous medium of fixed dielectric constant and the electric field of a generalized multipole charge distribution within a simplified molecular cavity is calculated.

A quite different model of the origin of polar solvent effects is the notion that at least a substantial part of these effects arises through equilibria involving complex formation between the polar solute molecule and only one solvent molecule. In 1928 Höjendahl proposed a mobile equilibrium between monomeric and dimeric nitrobenzene (the latter with zero dipole moment) to account for dielectric constant as a function of composition in the binary system nitrobenzene–benzene.[7] Piekara developed a detailed theory of such binary mixtures in which the proposal of the existence of a "transitory aggregate" with the second molecule in antiparallel orientation to the first is the principal feature required to explain the effect of electric field strength on the dielectric constant and several other physical properties.[8] Bellamy has favored specific complexes in the interpretation of solvent effects on

(1) This work was supported in part by the National Science Foundation, the Office of Naval Research, and the U. S. Atomic Energy Commission.

(2) R. W. Taft, *et al., J. Am. Chem. Soc.*, **85**, 709, 3146 (1963).

(3) R. W. Taft, *et al.*, Abstract of Papers, Applied Spectroscopy Conference, Cleveland, Ohio, Sept. 30, 1964, paper 91.

(4) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

(5) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963); R. W. Taft, *et al., ibid.*, **38**, 380 (1963).

(6) J. G. Kirkwood, *ibid.*, **2**, 351 (1934).

(7) Hojendahl, Thesis, Copenhagen, 1928, cited in C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, N. Y., 1931, p. 173.

(8) A. Piekara, *Proc. Roy. Soc.* (London), **A172**, 360 (1939); *Acta Physiol. Polon.*, **10**, 107 (1950); *J. Chem. Phys.*, **29**, 1297 (1958).

infrared frequency shifts.[9] Saum proposed association of nitriles through opposed dipole pairs based upon heats of vaporization and viscosity comparisons.[10] Ritchie, et al.,[11] have proposed formation of 1:1 complexes between nitriles and polar molecules in carbon tetrachloride based principally upon the interpretation of the concentration dependence of the infrared nitrile integrated absorption intensities. Dannhauser and Flueckinger[12] have interpreted the Kirkwood correlation factor, g, and its temperature coefficient for pure nitriles in terms of pair association of antiparallel dipoles. Jakobsen and Brasch have recently reported far infrared vibrational frequencies (50–100 cm.$^{-1}$) in polar liquids which are attributed to association complexes.[13]

The results of this investigation provide a clean-cut choice between these two different models for the polar solvent effect on the F-n.m.r. shielding of p-fluoronitrobenzene and p-fluoronitrosobenzene.

Experimental

Shielding measurements were carried out essentially as described previously.[2] For p-fluoronitrobenzene and p-fluoronitrosobenzene shifts were measured relative to 2% 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB) as an internal standard, using the sideband method. The average value of eight sweeps (four in each the upfield and downfield directions) was taken. Shielding parameters were obtained with an average standard deviation of ±0.0125 p.p.m. Spectra at low concentrations (0.02–0.08 M) were obtained with a Varian HA-100 spectrometer operating at 94.1 Mc. We are indebted to Mr. Jerry Holcomb for the courtesies extended us in use of this equipment at the Pittsburgh airport. A capillary of external TCTFCB in CCl₄ was used as the frequency-lock reference to obtain the shielding parameters relative to 4% internal TCTFCB. It was found necessary to apply a correction of −0.11 p.p.m. to all shielding obtained with HA-100 to give agreement with HR-40 results. This correction at least in part is probably due to the higher temperatures involved.

In order to obtain the shielding parameter of p-fluoronitrobenzene at each composition, shielding parameters for fluorobenzene relative to internal TCTFCB were obtained from solutions containing 0.52 M fluorobenzene, 2% TCTFCB, and varying concentrations of CCl₄ and the polar component.

Sample preparation was carried out by adding appropriate volumes of two stock solutions to a sample tube (14-mm. length; 5-mm. o.d.) using Hamilton microsyringes for the additions. The sample tube was then sealed off. The two stock solutions were made up with equal concentrations of TCTFCB (and fluorobenzene if used) in carbon tetrachloride and in the polar component. These stock solutions we prepared by weighing the desired amounts of the standards into a 5- or 10-ml. volumetric flask and then adding the

particular solvent to the mark. It has been assumed that the volumes of the mixed solvents are the sums of the volumes of the components.

Carbon tetrachloride (Fisher Spectranalyzed) was distilled through an N–F spinning-band column retaining only the middle fraction, b.p. 76.5° at 732 mm. (lit.[14] b.p. 76.8° at 760 mm.).

p-Fluoronitrobenzene (Penisular Chem Research, Inc.) was distilled under reduced pressure through an N–F spinning-band column, b.p. 43–45° at 2 mm. (lit.[15] b.p. 86.6° at 14 mm.).

p-Fluoronitrosobenzene was prepared by applying the method of Vogel[16] for the preparation of nitrosobenzene from nitrobenzene to p-fluoronitrobenzene. This procedure gave better yields than did the method reported by Olah, et al.[17] A crude product, m.p. 37.5–39.5°, was obtained. Vacuum sublimation gave a 31% yield of a pale yellow solid, m.p. 39.0–40.5° (lit.[18] m.p. 39°).

3,4-Difluoronitrobenzene was prepared by the nitration of o-difluorobenzene (Aldrich Chemical Co.). Seven grams (0.061 mole) was added dropwise over 10 min. to a mixture of 3.6 ml. of concentrated nitric acid and 10 ml. of concentrated sulfuric acid at −8°. The mixture was kept at this temperature with vigorous stirring for an additional 45 min. and then allowed to slowly attain room temperature. The reaction mixture was poured onto ice and allowed to stand until the ice melted. The diluted reaction mixture was extracted with three 50-ml. portions of ether, and the combined ether extracts were washed with water and 10% sodium carbonate and dried over anhydrous sodium sulfate and Drierite. The ether solvent was removed, giving 7.1 g. of crude product. Distillation under reduced pressure gave 5.3 g. of a middle cut, b.p. 53.5–54.0 at 3 mm. (lit.[18] b.p. 80–81° at 14 mm.).

1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane was generally used as obtained from Peninsular Chem Research, Inc. Equivalent results were obtained with a vacuum sublimed sample.

Results

Table I lists the shielding results obtained for the binary system CCl₄–p-fluoronitrobenzene. Figure 2 gives the shielding parameter ($f_H^{p-NO_2}$) of p-fluoronitrobenzene relative to internal fluorobenzene plotted vs. its concentration in carbon tetrachloride (open circles are experimental points; the line is a smoothed curve through these points).

In order to obtain an independent check on these results which avoided the use of the internal fluorobenzene reference, the binary system CCl₄–3,4-difluoronitrobenzene was studied. Table II lists the shielding parameter, $f_{m-NO_2}^{p-NO_2}$, obtained from the two fluorine signals over the entire composition range.

(9) L. J. Bellamy and H. E. Hallam, Trans. Faraday Soc., 55, 220 (1959).

(10) A. M. Saum, J. Polymer Sci., 42, 57 (1960).

(11) C. D. Ritchie, et al., J. Am. Chem. Soc., 84, 4687 (1962); 86, 1571 (1964).

(12) W. Dannhauser and A. F. Flueckinger, J. Phys. Chem., 68, 1814 (1964).

(13) R. J. Jakobsen and J. W. Brasch, J. Am. Chem. Soc., 86, 3571 (1964).

(14) A. Weissberger, et al., "Organic Solvents," Vol. III, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1955.

(15) F. K. Beilstein, "Handbuch der organischen Chemie," Band 5, II, p. 180.

(16) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., New York, N. Y., 1956, p. 630.

(17) G. Olah, A. Pavlath, and I. Kuhn, Acta Chim. Acad. Sci. Hung., 7, 65 (1955).

(18) J. G. McNally and J. R. Byers, Jr., U. S. Patent 2,391,179 (Dec. 18, 1945); Chem. Abstr., 40, 2635 (1946).

Table I. Shielding Parameters for p-Fluoronitrobenzene in Binary Mixtures with Carbon Tetrachloride at 25°

Concn., M	$-f_{c\text{-}b}^{H},a$ p.p.m.	$f_{c\text{-}b}^{p\text{-}NO_2},b$ p.p.m.	$f_{H}^{p\text{-}NO_2},c$ p.p.m. (obsd.)	$f_{H}^{p\text{-}NO_2},d$ p.p.m. (calcd.)
0.020	1.25	10.68	9.43	9.43
0.046	1.24	10.68	9.44	9.45
0.060	1.23	10.70	9.47	9.45
0.080	1.23	10.70	9.47	9.46
0.113	1.22	10.69	9.47	9.48
0.157	1.20	10.69	9.49	9.50
0.227	1.17	10.71	9.54	9.54
0.339	1.14	10.73	9.59	9.60
0.453	1.10	10.76	9.66	9.66
0.566	1.07	10.78	9.71	9.71
0.679	1.04	10.80	9.76	9.75
0.905	0.98	10.81	9.83	9.84
1.13	0.93	10.84	9.91	9.91
1.60	0.84	10.88	10.04	10.04
1.81	0.81	10.87	10.06	10.07
2.26	0.75	10.91	10.16	10.15
4.52	0.58	10.96	10.38	10.35
5.66	0.53	10.97	10.44	10.38
6.79	0.52	11.00	10.48	10.43
9.05^e	0.52	11.03	10.51	10.50

^{a} Shielding of fluorobenzene relative to internal tetrachlorotetrafluorocyclobutane (c-b). ^{b} Shielding of p-fluoronitrobenzene relative to internal tetrachlorotetrafluorocyclobutane (c-b). ^{c} Shielding of p-fluoronitrobenzene relative to internal fluorobenzene. ^{d} Calculated with the following parameters: $f_0 = -9.43$ p.p m.; $f_{\lim} = 11.2$ p.p.m.; $K_d = 4.0\ M$. ^{e} Liquid p-fluoronitrobenzene.

Table II. Shielding Parameter for 3,4-Difluoronitrobenzene in Binary Mixtures with Carbon Tetrachloride at 25°

Concn., M	$-f_{3\text{-}F}^{4\text{-}F},a$ p.p.m. (obsd.)	$-f_{3\text{-}F}^{4\text{-}F},b$ p.p.m. (calcd.)
0.151	5.61	5.62
0.211	5.63	5.64
0.302	5.67	5.68
0.362	5.72	5.71
0.453	5.74	5.74
0.604	5.77	5.78
0.755	5.80	5.81
0.906	5.83	5.85
1.21	5.91	5.91
1.51	5.95	5.95
2.11	6.04	6.02
2.42	6.09	6.05
3.02	6.14	6.10
6.04	6.31	6.22
9.06^c	6.42	6.31

^{a} Shielding parameter for 4-F relative to 3-F of substrate, ^{b} Calculated with following parameters: $f_0 = -5.53$ p.p.m.; $f_{\lim} = -6.80$ p.p.m.; $K_d = 3.8\ M$. ^{c} Liquid 3,4-difluoronitrobenzene.

In Table III are given shielding parameters, $f_{H}^{p\text{-}NO}$, obtained for p-fluoronitrosobenzene in carbon tetrachloride solutions from 0.020 to 3.00 M.

Discussion

In Figure 1 are plotted the previously obtained[2] shielding parameters, $f_{H}^{p\text{-}NO}$, for p-fluoronitrosobenzene in a variety of pure solvents relative to internal fluorobenzene at high dilution $vs.$ the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. While a qualitative correspondence between the two parameters is apparent, it is clear that the dielectric function is inadequate for a quantitative treatment of the F-n.m.r. solvent effects. The situation is not improved by using the dielectric function[6] $(\epsilon - 2)/(2\epsilon + 2)$ or a similar modification;

Table III. Shielding Parameters for p-Fluoronitrosobenzene in Carbon Tetrachloride Solutions at 25°

Concn., M	$-f_{c\text{-}b}^{H},a$ p.p.m.	$-f_{c\text{-}b}^{p\text{-}NO},b$ p.p.m.	$-f_{H}^{p\text{-}NO},c$ p.p.m. (obsd.)	$-f_{H}^{p\text{-}NO},$ p.p.m. (calcd.)
0.020	1.25	12.30	11.05	11.04
0.040	1.25	12.29	11.04	11.04
0.060	1.24	12.30	11.06	11.05
0.080	1.24	12.29	11.05	11.06
0.113	1.24	12.30	11.06	11.08
0.150	1.22	12.32	11.10	11.09
0.188	1.22	12.33	11.11	11.11
0.225	1.22	12.33	11.13	11.13
0.300	1.19	12.34	11.15	11.16
0.375	1.18	12.36	11.18	11.19
0.450	1.17	12.38	11.21	11.21
0.525	1.14	12.39	11.25	11.25
0.600	1.14	12.40	11.26	11.27
0.675	1.11	12.41	11.30	11.30
0.750	1.11	12.42	11.31	11.32
1.13	1.04	12.49	11.45	11.43
1.50	0.99	12.54	11.55	11.53
1.88	0.96	12.58	11.62	11.62
2.25	0.92	12.60	11.68	11.69
3.00	0.86	12.68	11.82	11.82

^{a} Shielding of fluorobenzene relative to internal tetrachlorotetrafluorocyclobutane (c-b). ^{b} Shielding of p-fluoronitrosobenzene relative to internal tetrachlorotetrafluorocyclobutane (c-b). ^{c} Shielding of p-fluoronitrosobenzene relative to internal fluorobenzene. ^{d} Calculated with the following parameters: $f_0 = -11.03$ p.p.m.; $f_{\lim} = -14.07$; $K_d = 12.4\ M$.

neither is there noticeable improvement using functions,[19,20] $e.g.$

$$\left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{(n\mathrm{D})^2 - 1}{2(n\mathrm{D})^2 + 1}\right] \text{ or }$$

$$\left[C_1\frac{\epsilon - 1}{2\epsilon + 1} + C_2\frac{(n\mathrm{D})^2 - 1}{2(n\mathrm{D})^2 + 1}\right]$$

The F-n.m.r. shielding data for the nitroso compound is used in this comparison because of its high solvent sensitivity. Quite equivalent scatter patterns are obtained with the shielding parameters for other $+R$ $para$-substituted fluorobenzenes.[2]

The results shown in Figure 1 do not support the notion that the F-n.m.r. polar solvent effects are due primarily to the dielectric action of bulk solvent. Figure 2, on the other hand, illustrates the precision with which the shielding results for the binary system CCl_4-p-fluoronitrobenzene may be described by the assumption of a mobile equilibrium between monomeric and dimeric nitrobenzene. The closed circles in Figure 2 are points calculated for a dimer dissociation constant, $K_d = 3.76\ M$, and a shielding parameter, $f_{H}^{\text{dimer}} = -11.14$ p.p.m. ($\Delta_{\text{dimerization}} = -1.7$ p.p.m.). We believe the quality of fit leaves little doubt that the major cause of the concentration dependence of $f_{H}^{p\text{-}NO_2}$ is to be attributed to the formation of a weakly stable dimer, the lifetime of which is short ($<10^{-2}$ sec.) compared to the time scale of the F-n.m.r. measurement.

The assumption of precisely medium independent values for dimer dissociation constant and shielding parameter is unreasonable, of course, for the entire

(19) E. G. McRae, $J.$ $Phys.$ $Chem.$, 61, 562 (1957); $Spectrochim.$ $Acta$, 12, 192 (1958).
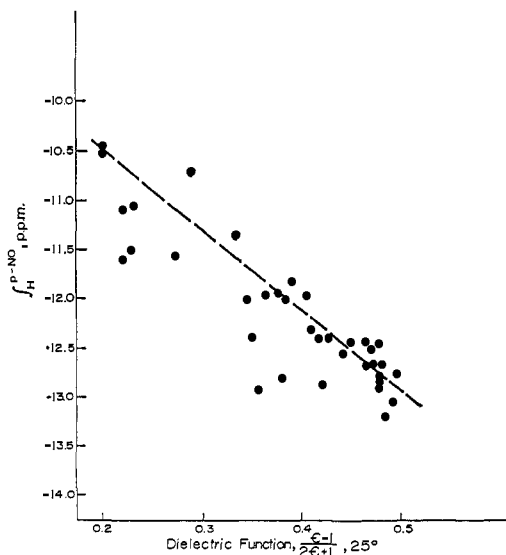(20) A. D. Buckingham, $Proc.$ $Roy.$ $Soc.$ (London), A248, 169 (1958).

Figure 1. Relationship between the shielding parameter, $f_H^{p\text{-}NO_2}$ for p-fluoronitrosobenzene and the dielectric constant function, $(\epsilon - 1)/(2\epsilon + 1)$, for organic liquids.

range of composition. It will be noted in Figure 2 that measurable deviations occur only at concentrations exceeding about 2 M in the polar component. This result has proven to be very general. Consequently, we have utilized a program written for the Pennsylvania State University IBM computer (7074) which obtains best fit of the experimental shielding parameters in terms of best values of the dissociation constant and (limiting) shielding parameter for the presumed dimer. Table IV lists these parameters obtained from the data

Table IV. Dissociation Constants and Shielding Parameters for Dimers in Carbon Tetrachloride at 25°

Solute	K_d, M	$-f_H^{monomer}$, p.p.m.	$-f_H^{dimer, a}$, p.p.m.
p-FC$_6$H$_4$NO$_2$	4.0 ± 0.3	9.43 ± 0.02	11.2 ± 0.2
3,4-Di-FC$_6$H$_3$NO$_2$	3.8 ± 0.4	5.53 ± 0.03^b	6.8 ± 0.2^b
p-FC$_6$H$_4$NO	12.4 ± 4.0	11.03 ± 0.02	14.1 ± 0.5

^{a} Shielding parameter/unit fluorobenzene derivative. ^{b} Shielding of 4-F relative to 3-F.

of Tables I–III based upon shielding measurements made up to but not exceeding 2.2 M in the polar component. Tables I–III also list valuse of f_H calculated by the best-fit parameters. For solutions below 2.2 M, deviations from experimental values are within the experimental error. The computer program is described in generalized terms in the Appendix.

The results in Table IV indicate that there is no measurable effect of a 3-F substituent on the nitrobenzene dimer stability. Since the 3-F substituent is known with great generality to produce larger effects than the 4-F substituent on reaction equilibria and rates,[21] it is implied that a value of $K_d \cong 4.0$ applies as well for unsubstituted nitrobenzene in CCl$_4$ at 25° (and of $K_d \cong 10$ for unsubstituted nitrosobenzene).

Physical properties of binary nitrobenzene–carbon tetrachloride or benzene mixtures from the literature

(21) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 186–192.
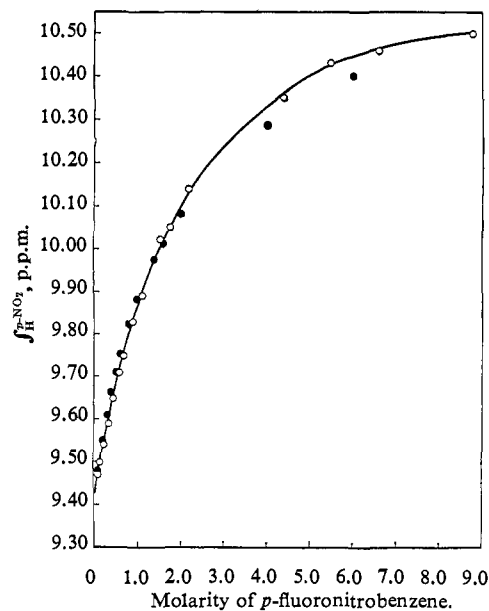

Figure 2. Shielding parameter ($f_H^{p\text{-}NO_2}$) for p-fluoronitrobenzene in binary mixtures with carbon tetrachloride: O, experimental values; ●, calculated values. The fit of concentration dependence by assumption of dimer formation: from $K_{dissocn} = [p\text{-}FC_6H_5NO_2]^2/$ $[p\text{-}FC_6H_5NO_2:p\text{-}FC_6H_5NO_2] = 3.76$ moles/l. and $f_{lim} -11.14$ p.p.m.

may be cited as confirmatory evidence of dimer formation. The dimer dissociation constant implied from our F-n.m.r. shielding studies permits an *a priori* calculation of the dielectric constant of dilute solutions of nitrobenzene in CCl$_4$ at 25° if we assume (with Hojendahl[7]) that the dimer has no permanent dipole moment.

The system is regarded as a ternary mixture of monomer, dimer, and CCl$_4$, for which the molar polarization, P_{mix}, is obtained additively from the partial molar polarizations of the components[22]: $P_{mix} = N_{mono}P_{mono} + N_{di}P_{di} + N_{CCl_4}P_{CCl_4}$. Values of P_{di} and P_{CCl_4} are obtained (by the relation of Lorentz and Lorenz) as the molar refractions[22]

$$P_d = R_M = \frac{(nD)^2 - 1}{(nD)^2 + 2} \times \frac{M}{\rho}$$

Values of 31 and 28, respectively, are obtained from the refractive index, density, and molecular weights.

For nitrobenzene monomer $P_{mono} = P_d + P_u = R_{di}/2 + 4\pi N\mu^2/9kT = 344$, using the literature value for the permanent dipole moment of nitrobenzene. With the values of P_{mono}, P_{di}, and P_{CCl_4} given, P_{mix} and the dielectric constant, ϵ, may be computed at any composition for which $K_d = 4.0$ M is valid.

$$\epsilon_{mix} = \frac{2P_{mix}\rho_{mix} + M_{av}}{M_{av} - P_{mix}\rho_{mix}}$$

Table V lists values of the dielectric constant, ϵ_{calcd}, so obtained. The agreement with interpolated values of ϵ_{obsd} is quite satisfactory up to approximately 2 M nitrobenzene in CCl$_4$. The cause for deviations above this concentration is uncertain but may be associated with deviations from the additive relationship assumed for the molar polarization of the mixture. It may also

(22) *Cf.* D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 276–278.

be significant that these deviations set in at about the same concentration level noted above for the shielding results, e.g., Figure 2. The calculated values of ϵ are not strongly dependent upon the assumption of $\mu_{di} = 0$. For example, $\epsilon_{calcd} = 5.71$ for 12% (wt.) $C_6H_5NO_2$ if it is assumed that $\mu_{di} = 1.0$ D. Nevertheless, it appears that $\mu_{di} = 0$ gives better agreement with the experimental values. The values of ϵ_{calcd} are sharply dependent upon the value of K_d and it appears that this method may be the one of choice in obtaining accurate K_d values.

Table V. Calculation of the Concentration Dependence of the Dielectric Constant of Dilute Solutions of Nitrobenzene in Carbon Tetrachloride at 25°

Concn., M	$C_6H_5NO_2$, % (wt.)	ϵ_{calcd}[a]	ϵ_{obsd}[b]
0.000	0.0	2.23	2.25 ± 0.02
0.128	1.0	2.47	2.50 ± 0.05
0.256	2.0	2.70	2.72 ± 0.05
0.509	4.0	3.19	3.24 ± 0.05
0.759	6.0	3.71	3.78 ± 0.06
1.25	10.0	4.79	4.88 ± 0.08
1.49	12.0	5.47	5.45 ± 0.08
2.04	14.2	7.02	6.25 ± 0.10

[a] Calculation as described in text. [b] Interpolated values (with estimated uncertainties) from data given by H. Sadek and R. M. Fuoss, J. Am. Chem. Soc., 76, 5905 (1954); J. Timmermans, "The Physicochemical Constants of Binary Systems," Vol. 1, Interscience Publishers Inc., New York, N. Y., 1959, p. 787.

Freezing point depression measurements for nitrobenzene–benzene mixtures were found by Bury and Jenkins[23] to be nonideal. The data of these authors is presented in Table VI for benzene solutions up to 1.293 m in nitrobenzene. Listed in Table VI are the freezing point depression observed, $(T_f)_{obsd}$, the ideal solution value, $(T_f)_{ideal}$, and the calculated freezing point depression, $(T_f)_{calcd}$, obtained on the assumption of dimer formation with $K_d = 2.5$ M at a mean temperature of approximately 3°. The agreement between $(T_f)_{obsd}$ and $(T_f)_{calcd}$ is excellent. If the assumption is made that K_d has essentially the same value in benzene and CCl_4 solutions, one obtains from the mean values at 3° 2.5, based upon the Bury and Jenkins data, and at 25° 4.0, based upon our F-n.m.r. shielding results, an order of magnitude estimate of the enthalpy of dimerization of nitrobenzene of -3000 cal./mole.

Table VI. Calculation of Freezing Point Depression for Dilute Solutions of Nitrobenzene in Benzene

Concn., m	$(\Delta T_f)_{ideal}$	$(\Delta T_f)_{obsd}$[a]	$(T_f)_{calcd}$[b]
0.105	0.53	0.51	0.51
0.165	0.84	0.80	0.80
0.260	1.32	1.23	1.23
0.373	1.89	1.72	1.73
0.485	2.46	2.22	2.20
0.596	3.05	2.68	2.69
0.734	3.73	3.27	3.24
1.089	5.54	4.65	4.65
1.293	6.55	5.39	5.42

[a] Data of C. R. Bury and H. O. Jenkins, ref. 23. [b] Based on $K_d = 2.5$ M.

(23) C. R. Bury and H. O. Jenkins, J. Chem. Soc., 688 (1934).

The following F-n.m.r. shielding results from the present and previous investigations[2] are relevant to the question of the structure and the nature of the interaction involved in complexes such as the nitrobenzene dimer. The downfield shift of the shielding parameter, f_H^{p-X}, for a given +R para-substituted fluorobenzene (relative to internal fluorobenzene) between cyclohexane and a polar liquid (cf. Table VII) is similar but actually somewhat greater for polar functions attached to methyl than to phenyl groups. These results appear to indicate comparable stability of aliphatic and aromatic derivatives.

As discussed previously,[2] substantial downfield shifts, e.g., those listed in Table VII, are observed only for strongly polar +R para substituents with charges on peripheral atoms. For a given +R para-substituted fluorobenzene the downfield shift between cyclohexane and a pure polar solvent tends to parallel rather closely the group dipole moment of the polar function in the solvent (cf. Table VII). Also Table IV indicates that the nitro group with the larger dipole moment than that of the nitroso group forms the more stable dimer.

The apparent identity of K_d for nitrobenzene, p-fluoronitrobenzene, and 3,4-difluoronitrobenzene indicates that the dimerization involves localized polar groups rather than the entire molecule. Thus the nitro group moment must be very similar for these three compounds, whereas the molecular dipole moment is substantially less for the latter two compounds. Ritchie has presented a similar argument in terms of negligible meta- and para-substituent effects on the dissociation constants for benzonitrile–DMSO complexes.[11]

These observations lead us to the picture that the weak bonding involved is quite general and is largely electrostatic interaction between charged multicentered groups (e.g., NO_2, $COCF_3$, SO_2F, etc.), which are paired so that their resultant dipole moments are opposed. We propose the name multipolar complex for pairs held together by such an interaction. This structural arrangement carries with it the feature that the hydrocarbon residues in the complexes will be oriented to minimize nonbonded repulsions between these residues. The proposed structure and interaction appears to be generally consistent with the previous evidence and proposals in ref. 7–13.

The mutual polarization of the opposed-pair group resultant dipole moments will act to provide some additional stability to the multipolar complex. If both polar groups are attached to p-fluorophenyl labels it is reasonable to expect that this mutual polarization will induce a polarization of the relatively mobile benzene π-electrons (to which p-F-n.m.r. is especially sensitive) in the direction expected for a greater apparent contribution of resonance form II ($^+F=C_6H_4=R^-$) in the complex than the substrates. Thus, for example, multipolar complex formation between p-fluoronitrobenzene and p-fluoronitrosobenzene is expected and has been observed[24] to produce downfield shifts for the fluorine atoms of both compounds. This observation appears to be general for multipolar complexing[24] and rules out a predominant contribution

Table VII. Solvent Effects on the Shielding Parameters for Some $+R$ para-Substituted Fluorobenzenes Relative to Fluorobenzene[a]

Solvent	μ, D	$-f_H^{p\text{-}NO}$, p.p.m.	$-f_H^{p\text{-}NO_2}$, p.p.m.	$-f_H^{p\text{-}SO_2F}$, p.p.m.	$-f_H^{p\text{-}COCF_3}$, p.p.m.
CH₃CN	3.94	12.80	10.35	13.55	13.10
C₆H₅CN	4.39	12.65	10.45	...	...
C₆H₅NO₂	4.21	12.65	10.50	13.45	13.20
CH₃NO₂	3.50	12.90	10.55	13.60	13.15
HCON(CH₃)₂	3.80	12.85	10.30	13.50	12.95
(CH₃)₂CO	2.80	12.45	10.10	13.35	12.95
C₆H₅N	2.25	12.55	10.25	13.55	12.90
1-Fluorohexane	1.90	11.54	9.79	12.76	12.54
CH₃CO₂C₂H₅	1.76	12.00	9.85	13.00	12.85
(C₂H₅)₂O	1.15	11.35	9.65	12.70	12.65
Cyclohexane	0.0	10.50	9.20	12.20	12.00

[a] Data of ref. 2.

from covalent interactions of the electron-pair donor-acceptor type.[25] Double p-fluorophenyl label experiments[26] have shown (without exception[2,24]) that, when the latter interactions are involved, the p-F of the electron-pair acceptor is shifted to higher field strength whereas that of the donor is moved to lower field.

It should be noted that our proposed multipolar dimer of nitrosobenzene is to be distinguished from the dimer which has been observed in the crystalline state.[27] The latter has the structure shown below and is colorless.

$$\text{C}_6\text{H}_5 \quad \text{O}$$
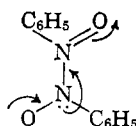
The formation of this dimer in solution could not reasonably account for the F-n.m.r. shielding results. Further, nitrosobenzene and p-fluoronitrosobenzene have characteristic blue colors in their melts and in solutions of organic solvents. For the latter compound, absorption maxima have been observed[28] at 742, 306, and 281 mμ. None of these bands show any major concentration or solvent dependence,[28] implying that the formation of the multipolar complex alters only very slightly the ultraviolet spectra.

While the qualitative concepts are in apparent accord, the dissociation constants listed in Table IV are an order of magnitude greater than those obtained by Saum[10] and in some of the most recent work of Ritchie.[29] The dissociation constants for nitriles obtained by Dannhauser,[12] however, are of comparable magnitude to the K_d values of Table IV. This situation clearly demands further study.

In the next paper in this series kinetic polar solvent effects are considered in terms of generalized multipolar complex formation.

Appendix

Computer Program for Parameter Refinement. We here describe the fitting of observed F-n.m.r. shifts in terms of equilibrium constants for various sorts of

complexing of the substrate (substituted fluorobenzenes), e.g., with polar solvent and with itself to form dimers. The statistical procedure is a general one, applicable to cases where the observable is an average over the contributing species, i.e., where the time scale of the measurement is slow in comparison with the rates of interconversion of the species in equilibrium.

To illustrate the procedure in detail, for the system substituted fluorobenzene, D, in polar solvent, S, forming the 1:1 complex, SD
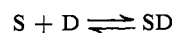
$$\text{S} + \text{D} \rightleftharpoons \text{SD}$$

$$K_{\text{dissocn}} = K = [\text{S}][\text{D}]/[\text{SD}]$$

we fit the observed F-n.m.r. shift, f_H, in the polar solvent by the following equation (1) where f_{lim} is the

$$f_H = \frac{[\text{SD}]}{[\text{D}_0]} f_{\text{lim}} + \frac{[\text{D}_0] - [\text{SD}]}{[\text{D}_0]} f_0 \quad (1)$$

(limiting) shift of the complex relative to internal fluorobenzene (or other appropriate standard) and f_0 is the shift of the uncomplexed substrate, relative to the same standard, measured in pure nonpolar solvent. The polar solvent is a binary mixture of this nonpolar solvent and the polar component, D.

Adopting the symbolism, $F = f_H$, $A = f_{\text{lim}}$, $B = f_0$, and $y = $ concentration of [SD] in moles/liter, we have

$$F = \frac{y}{[\text{D}_0]} A + \frac{[\text{D}_0] - y}{[\text{D}_0]} (B) \quad (2)$$

and

$$y^2 - ([\text{S}_0] + [\text{D}_0] + K)y + [\text{S}_0][\text{D}_0] = P(y) = 0 \quad (3)$$

Upon initial specification of K, A, and B, e.g., obtainable from plots of f_H vs. [D₀] or [S₀], and knowing [S₀] and [D₀] we generate a value of F. Our purpose is to minimize by least-squares procedures the difference between the calculated and observed values of F as a function of all or some of the parameters K, A, and B, i.e., $\sum_i (\Delta F_i)^2 = $ minimum, where the index i runs over the data points for various [S₀]$_i$ and [D₀]$_i$.

The Gauss–Newton statistical procedure is employed for the nonlinear, least-squares fitting.[30,31] We may

(25) R. S. Mulliken and W. B. Person, Ann. Rev. Phys. Chem., 13, 107 (1962).
(26) R. W. Taft and J. W. Carten, J. Am. Chem. Soc., 86, 4199(1964).
(27) K. Nakamoto and R. E. Rundle, ibid., 78, 113 (1956).
(28) P. Hagan, Undergraduate Thesis, Pennsylvania State University, June 1962.
(29) Private communication from C. D. Ritchie; C. D. Ritchie, R. Uschold, and A. L. Pratt, to be published.

(30) For a discussion of the Gauss–Newton method with emphasis on details of convergence and initial parameter choice see W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, pp. 150–157.
(31) H. O. Hartley, Technometrics, 3, 269 (1961).

expand F in eq. 2 in a Taylor series about the value obtained from the initially specified parameters, F^0

$$F' = F^0 + \sum_p \frac{\partial F^0}{\partial X_p} \Delta X_p + \frac{1}{2!}\sum_{p,q} \frac{\partial^2 F^0}{\partial X_p \partial X_q} \Delta X_p \Delta X_q + \cdots \quad (4)$$

where the X_p values are the parameters K, A, and B which are to be optimized. If our initial assumptions of values for the latter are reasonable, we may truncate eq. 4 after the first-order sum term, which linearizes our statistical problem.

Therefore

$$F_i' \text{ (comp.)} - F_i \text{(obsd.)} = \Delta F_i' = \Delta F_i^0 + \sum_p \frac{\partial F_i^0}{\partial X_p} \Delta X_p \quad (5)$$

and

$$\frac{1}{2}\frac{\partial \sum_i (\Delta F_i')^2}{\partial X_j} = \sum_i \Delta F_i^0 \frac{\partial F_i^0}{\partial X_j} + \sum_i \sum_p \frac{\partial F_i^0}{\partial X_p}\frac{\partial F_i^0}{\partial X_j} \Delta X_p = 0 \quad (6)$$

Here, $\partial F_i^0/\partial A = (y^0/[D_0])_i$, $\partial F_i^0/\partial B = (([D_0] - y^0)/[D_0])_i$, and $\partial F_i^0/\partial K = (\partial F_i^0/\partial y)(\partial y/\partial K) = ((A - B)/[D_0])_i(y^0/P'(y^0))_i$, where $P'(y) = \partial P(y)/\partial y$.

The problem is now one of solution of eq. 3 in terms of y and then of the simultaneous equations (6); the latter yield the values for X_p. Since $X_p' = X_p + \Delta X_p$, new values for A, B, and K are obtained. Using these, the procedure is repeated until either all parameters converge or the standard deviation for fitting converges within prespecified limits between consecutive cycles.

The procedures adopted have been illustrated for the special case of 1:1 SD complexing; however, several other complexing situations of interest can also be considered upon minor changes in parts of the analysis. For example, for dimerization of the solute, $K_{dissocn} = [D]^2/[D_2]$, the only change required in the above analysis is in eq. 3, i.e.

$$4y^2 - (4[D_0] + K)y + [D_0]^2 = P(y) = 0 \quad (7)$$

and in the partial derivatives, $\partial F_i/\partial K$, derived from it. Further, for cases where more than one process of importance occurs, e.g.

$$S + D \rightleftharpoons SD$$
$$2S \rightleftharpoons S_2$$
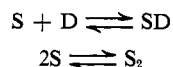
two equilibrium constants enter but eq. 1, 2, 5, and 6 still apply. With this understanding, the Fortran coded program constructed for use on the IBM 7094 (and later modified for the IBM 7074) was written as a main program with a set of subroutines one for each complexing case. The former, completely general for all cases of interest, accepts the initial parameter choices, sets up eq. 6, solves them, and tests the new parameter values. The subroutines generate only the appropriate partial derivative sums which are used in eq. 6.

The following statistical quantities are derived directly: the data variances, $V_i = \Delta F_i$, correct to the first-order sum term in ΔX; the parameter variances, equivalent to σ^2: goodness of fit (GoF) $= \sum_i V_i^2/(ND - NP)$, where ND is the number of data and NP the number of parameters fitted (the standard deviation of fitting is obtained from this quantity); the interparameter correlation coefficients, ρ_{pq}. The absolute value of this quantity is between 0 and 1; the closer to one, the stronger is the linear dependence of X_p on X_q.

Carbalkoxynitrenes. The Photolytic Decomposition of Gaseous Alkyl Azidoformates[1]

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The photolytic decomposition of gaseous ethyl and methyl azidoformates has been studied with regard to carbalkoxynitrene formation and other modes of decomposition. Chemical trapping and product analysis show that the nitrenes are produced when light is used whose energy is above about 95 kcal./mole, but below 130 kcal. Transient spectra show absorption by NCO. From the appearance time of NCO and the dependence of the NCO spectrum on partial pressure of a chemical trapping agent, limits on the nitrene lifetime are set at about 3×10^{-7} and 10^{-5} sec. At higher photolysis energies transient N_3 is also observed, and the product pattern indicates that a transient but unobserved CO_2N_3 may be present.

Introduction

Transient polyatomic species supposedly containing monovalent nitrogen (nitrenes) have been identified in