UCRL-17188

University of California
Ernest O. Lawrence Radiation Laboratory

AN N. M. R. METHOD FOR THE DETERMINATION OF RELATIVE ACIDITIES OF WEAK ACIDS IN LIQUID AMMONIA

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Inorganic Chemistry

UCRL-17188
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

AN N.M.R. METHOD FOR THE DETERMINATION OF RELATIVE ACIDITIES OF WEAK ACIDS IN LIQUID AMMONIA

Thomas Birchall and William L. Jolly

July 1966

An N.M.R. Method for the Determination of Relative Acidities of Weak Acids in Liquid Ammonia

Thomas Birchall and William L. Jolly

Department of Chemistry of the
University of California and the
Inorganic Materials Research Division of the
Lawrence Radiation Laboratory,
Berkeley, California 94720

Abstract

An n.m.r. method for the establishment of a scale of acidities of weak acids in liquid ammonia is described. A pK range of 6.6 units has been covered using substituted anilines. The relative values fit a Hammett $\sigma\rho$ plot with $\rho = -5.3$. A new σ value for 4-fluorine of -0.05 is proposed for these systems.

Introduction

In recent years there has been an increasing interest in strongly basic systems and in the determination of the acidities of very weak acids.[1-5] The acidities studied cover an enormous range of about 30 pK

(1) R. Stewart and J. P. O'Donnell, J. Am. Chem. Soc., 84, 493(1962); Can. J. Chem., 42, 1681, 1694(1964).

(2) K. Bowden and R. Stewart, Tetrahedron, 21, 261(1965) and refs. therein.

(3) A. Streitwieser, Jr. and H. F. Koch, J. Am. Chem. Soc., 86, 404 (1964).

(4) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons and A. H. Pudjaatmaka, J. Am. Chem. Soc., 87, 384(1965).

(5) A. Shatenshtein, J. Am. Chem. Soc., 59, 432(1937).

units, and no one solvent system has been used in their determination. In general, as an acid becomes weaker, the solvent system must become more basic in order to achieve a measurable ionization. The solvent systems used include aqueous hydroxide, pyridine,[1] dimethyl sulphoxide-alcohol mixtures,[2] cyclohexylamine,[3] and liquid ammonia,[5,6] to mention

(6) E. C. Fohn, R. E. Cuthrell and J. J. Lagowski, Inorg. Chem., 4, 1002(1965); Inorg. Chem., 5, 1002(1966).

just a few. The principle disadvantage of most of these solvent systems is that they only cover a limited range of 5 or 6 pH units.[1]

However, the high basicity and low ionization constant of liquid ammonia (10^{-27} at 25°)[7] indicate that this would be a suitable solvent in which

(7) W. L. Jolly and C. J. Hallada, Chapter 1 in Non-Aqueous Solvent Systems, T. C. Waddington, ed., Academic Press, Ltd., London, 1965.

to study acid dissociation. Recently a study of acid dissociation in liquid ammonia has been reported by Lagowski and coworkers,[6] who used a spectrophotometric technique.

The high volatility of ammonia makes it necessary either to work at low temperatures, as did Lagowski,[6] or to study the solutions under pressure, as we have chosen to do. N.M.R. is ideally suited for determining the concentrations of protonic species in sealed tubes, and we have used this technique to determine the relative acidities of some anilines covering a range of 6.5 pK units. Evidence will be presented to show that this method can be used to extend this range by at least 5 pK units at the weaker end of the scale. However, extension to the more acidic region where some direct measurements have been made[6] seems unlikely because of the tendency of the stronger acids to form complexes.[8]

(8) K. L. Servis, J. Am. Chem. Soc., 87, 5495(1965) and refs. therein.

The principle disadvantages of the spectrophotometric method are the complicated apparatus needed for the determinations and the fact that amide ion absorbs strongly at 350 mμ and so obscures absorption bands in

this region.[6] Solvent absorption has also been found to be troublesome in the determination of the acidities of anilines in dimethylsulphoxide solutions.[9]

---

(9) R. Stewart and D. Dolman, private communication.

Experimental

Chemicals. All of the substituted anilines except 4-cyanoaniline were obtained commercially; 4-cyanoaniline was kindly donated by Dr. R. Stewart of the University of British Columbia. The anilines were purified by recrystallization from suitable solvents, or by drying followed by distillation, until the literature melting or boiling points were obtained.

Commercial synthetic ammonia was dried and stored over sodium in a glass vessel attached to the vacuum line until required.

Preparation of Samples. All samples were prepared using standard vacuum line techniques in the following manner. The two acids to be compared were placed in a glass tube (A, Figure 1) fitted with a break-off seal and glass-enclosed magnet. This tube was evacuated, sealed and attached by glassblowing to the vessel shown in Figure 1. The apparatus was thoroughly dried by flaming under high vacuum, transferred to a dry bag where a small piece of freshly cut sodium was introduced via B under an atmosphere of dry argon, then transferred back to the vacuum line and evacuated thoroughly. Pure dry ammonia from the reservoir was then distilled into the vessel, and the apparatus was then sealed at B.

The reaction between sodium and ammonia was allowed to proceed to completion at room temperature to give $NaNH_2$ and hydrogen. It was found necessary to catalyze this reaction with minute amounts of platinum introduced into the n.m.r. tube by previously washing this tube with a 10^{-4} M solution of chloroplatinic acid, drying and subsequent decomposition by heating. The reaction of sodium with ammonia was generally complete in 12-24 hours, as evidenced by the complete discharge of the deep blue color of the solvated electron; if the tubes were not "platinized" reaction times up to three months were observed.

Once reaction was complete, the hydrogen produced in the reaction was removed via C, collected and measured by means of a Toepler pump. The hydrogen determination gave a direct measure of the sodium amide in the vessel, and although it was not needed in the calculation, it served as a check on the results since the total amount of acid ionized should equal the amount of amide ion. After the hydrogen had been removed, break-off seal A was broken, and the acids were distilled down into the n.m.r. tube. The tube was sealed off at the constriction, the mixture warmed to room temperature when equilibrium was rapidly achieved and the n.m.r. spectrum recorded on a Varian A60 spectrometer at 31°C.

The final solutions were approximately 0.5 M in each acid and in sodium amide; however deliberate variations from these values for a given pair of acids gave the same relative acidity within experimental error.

Analysis of N.M.R. Spectra. The method adopted to set up the relative acidity scale was simply that of adding two acids, HA and HB, to a suspension of sodium amide in liquid ammonia, allowing the mixture to come to equilibrium, and then measuring the ratios $(HA)/(A^-)$ and $(HB)/(B^-)$.

Using the relation $\Delta pK = \log [(HB)/(B^-)] - \log [(HA)/(A^-)]$, the value of ΔpK for the two acids was calculated. This was then repeated for another pair of acids, HB and HC, and so on until the required range was covered.

The ratios acid/anion were obtained from an examination of the n.m.r. spectrum of the solution at equilibrium. Fortunately, the spectra were simple because of rapid proton exchange between the acids studied and their anions. Thus only two, rather than four, groups of peaks were observed, each group being a time-averaged combination of an acid and its anion. Having previously obtained n.m.r. spectra of both the acid alone and the anion alone, it was an easy matter to calculate the ratio acid/anion from the spectrum of a mixture of the two, because the n.m.r. spectrum resulting from two species undergoing rapid chemical exchange depends only upon the n.m.r. parameters of the species and upon their relative amounts.[10]

---

(10) J. A. Pople, W. G. Schnieder and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, New York, 1959, p. 218.

A typical spectrum is shown in Figure 2. This is the spectrum which results when 4-methylaniline and 3,5-dimethylaniline are added to a suspension of sodium amide in liquid ammonia. The "quartet" of peaks centered at -6.29 p.p.m. arises from an average of the ring protons of 4-methylaniline and its anion, while the two peaks at -5.77 and -5.49 p.p.m. arise from the ring protons of 3,5-dimethylaniline and its anion. Removal of a proton from an aniline results in a shift to higher field of all the

peaks in the spectrum due to the increased shielding from the negative charge on the molecule. The ring protons are the most sensitive to the negative charge and shifts to higher field of ~1 p.p.m. are observed. Since the negative charge on the nitrogen will effect the shielding at the ring positions via both inductive and conjugative effects the shielding will be different at the various ring positions, and it is found that the shift to higher field is in the order para > ortho > meta. The effect is illustrated in Figure 2 for 4-methylaniline by the two sets of quartets (A and B) below the actual spectrum; the set (A) to lower field represents the ring protons of the unionized acid, while the set (B) to higher field represents the spectrum of the completely ionized acid. It is seen that the ortho and meta proton resonances have moved apart. This behavior is more obvious in the case of 3,5-dimethylaniline (the lines above the actual spectrum) where the ortho and para protons (C) have almost the same chemical shift in the parent acid but are quite different in the anion (D and E). In our measurements we have used this shifting apart of the aromatic part of the spectrum to determine the extent of ionization because this eliminates the need for a reference point from which to measure chemical shifts. However, the acids aniline and 3-trifluoromethylaniline have complicated n.m.r. spectra which change drastically as δ/J changes, thus making the spectra rather more difficult to analyze. We found it more convenient, in these two cases, to use chemical shifts relative to an external reference of tetramethylsilane to estimate the extent of ionization. In the cases where the acidities were sufficiently close, cross checks were carried out, and agreement better than 0.1 pK unit in all cases, and to 0.05 pK unit in most cases, was obtained.

Discussion

Introduction of substituents into the ring of an aromatic acid changes the electron density at the acidic center, and thus the acidity is changed. In this way large changes in the strength of a parent acid can be produced. We have used a series of substituted anilines to cover a range of 6.6 pK units. The data are shown in Table I. The acidities are all relative to that of 2,5-dichloroaniline, the strongest acid for which we have quantitative data. The effect of substituents upon the acidity is illustrated in a conventional Hammett $\sigma\rho$ plot (Figure 3) for the meta and para substituted compounds. We have used σ values compiled by Barlin & Perrin[11] for all substituents except 4-cyano (for which we

(11) G. B. Barlin and D. D. Perrin, Quart. Revs., 20, 75(1966).

have used the σ^- value of 1.00 which has been used to fit experimental results for the dissociation of anilinium ions[12]). Some disubstituted

(12) J. Clark and D. D. Perrin, Quart. Revs., 18, 295(1964).

compounds are also included in this plot by assuming additivity of the σ constants. A good straight line correlation is obtained with a ρ value of -5.3. The high ρ value indicates that the acidity of the aniline is extremely sensitive to the substituent.

One noticeable feature of this Hammett plot is a lower acidity for 4-fluoroaniline than would have been predicted from the σ value of a

para fluorine. Obviously the electron withdrawing ability of fluorine is counteracted by a much stronger effect due to conjugation with the ring with the result that the electron density on the nitrogen is increased rather than reduced. This effect of a para fluorine has also been observed in the pK values of phenol and anilinium ions.[13]

---

(13) A. I. Biggs and R. A. Robinson, J. Chem. Soc., 388(1961).

Streitwieser[3] has suggested that a σ^- component should be added to the normal σ for 4-fluorine and we propose that a σ value of -0.05 should be used for this substituent when considering acidities of anilines, anilinium ions, phenols and other related systems.

Since a nitro group in the para position can conjugate with the acidic center a σ^- should be used to obtain correlation on a Hammett type plot: a value of 1.26 for use with anilines has been suggested.[12] Using this value we would predict that 4-nitroaniline would be 1.05 pK units more acidic than 2,5-dichloroaniline. However we were unable to obtain any overlap between 2,5-dichloroaniline and 4-nitroaniline in anhydrous ammonia, and our data indicated that, for these two acids, $\Delta pK > 3$. Stewart and Dolman[8] have found a difference of 3.8 pK units for this pair of acids. The ability of a nitro group to transmit its effect to the reactive center appears to be greater in anhydrous liquid ammonia than it is in the aqueous systems used to establish the σ^- constants.

The dissociation of these anilines may be regarded as the second ionization of the corresponding anilinium ion, and it is of interest to compare the effect of substituents upon the two dissociations.

Figure 4 shows a plot of the anilinium ion acidity versus the aniline acidity and a remarkably good correlation is obtained. The slope of the line (0.53) shows the greater sensitivity to the substituent of the aniline acidity over that of the anilinium ion acidity.

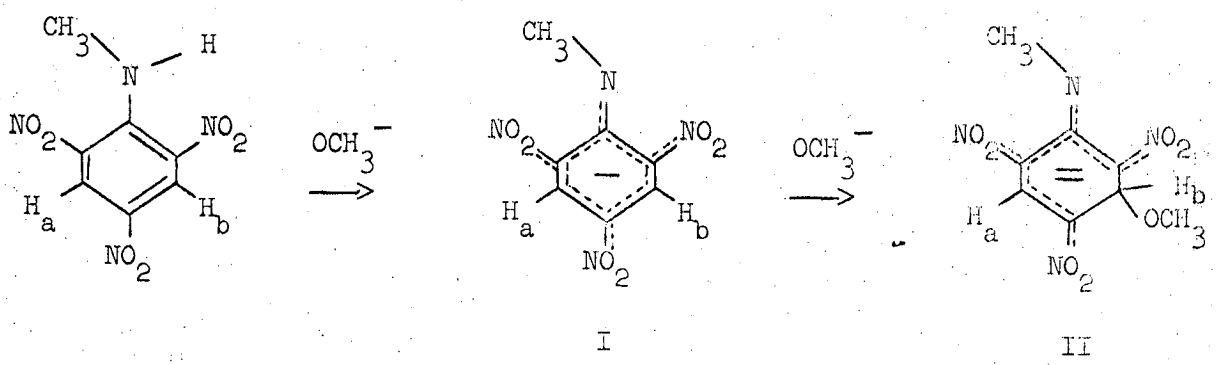
Complex Formation

Attempts were made to study stronger acids in the hope that we would be able to extend our scale of relative acidities to include nitroanilines and acids such as o and p-nitroacetanilide (whose pK's were recently determined directly in liquid ammonia[6]). We would then be able to put our scale on an absolute basis. Unfortunately the susceptibility of nitroanilines to complex formation has prevented us from extending the measurements to acids stronger than 2,5-dichloroaniline. For example, a solution of 4-nitroaniline, 2,4-dimethyl-6-nitroaniline and sodium amide in liquid ammonia gave an n.m.r. spectrum which had only two very broad structureless peaks in the aromatic region of the spectrum. Presumably partial ionization of each acid had occurred but complex formation occurs between anions, with rapid exchange resulting in a broadening of the spectrum.

The nature of the complexes formed between nitroanilines and base has been clarified as a result of some n.m.r. studies of Crampton and Gold[14] and Servis.[9] This former group examined the changes which occurred

(14) M. R. Crampton and V. Gold, Proc. Chem. Soc., 298(1964); Chem. Commun., 256(1965).

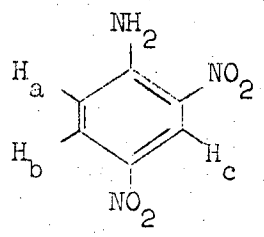
in the n.m.r. spectra of some polynitroanilines in dimethylsulphoxide upon the addition of base. They concluded that anion I



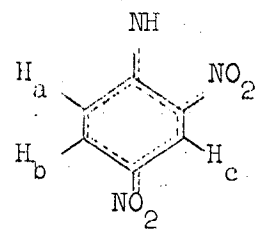
was first formed, and that this was converted into II upon the addition of more than one equivalent of base. However, they were unable to observe a signal due to H_b and concluded that rapid exchange of OCH_3^- at that site was occurring. Servis[8] in a later communication reported on the reactions of some 1-substituted trinitrobenzenes with methoxide and was able to observe signals due to both H_a and H_b.

During the course of our measurements we have found that even 4-nitroaniline is subject to complex formation of the above type and that 2,4-dinitroaniline forms di-negative anion complexes in which exchange is slow.

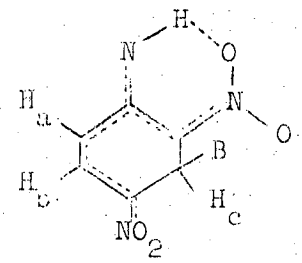
Table II gives the n.m.r. parameters for solutions of 2,4-dinitroaniline III in liquid ammonia containing various amounts of base. A solution of this acid in plain



III



IV



V

ammonia gives an n.m.r. spectrum which consists of an AB quartet for H_a and H_b and a doublet for H_c, with each component of B being further split by spin-spin coupling with H_c. The NH_2 proton signal is not visible because of rapid exchange with anion present. Lagowski[6] has shown that this acid is ionized in plain liquid ammonia. Addition of one equivalent of base (e.g. NaOH) results in complete removal of one proton to give the anion IV, and the n.m.r. signals arising from the ring protons show a shift to higher magnetic field. It should be noted that the basic n.m.r. pattern of the acid is retained in the spectrum of the anion and at all intermediate stages of ionization, as was found for the other anilines. Profound changes in the spectrum occur as the base concentration is further increased. A new set of peaks grows in at the expense of those due to the anion, and when two equivalents of base have been added only the new set remains. The spectrum of the resulting solution is shown in Figure 5 and is assigned to a complex having structure V. The AB quartet of H_a and H_b is retained, but shifted to higher magnetic field as a result

of the extra negative charge, and H_c is now found to resonate at a higher magnetic field than H_a. This shift is ten times the shift undergone by H_b and is best explained by a rehybridization at the 3-carbon from sp^2 to sp^3. This change is accompanied by a reduction in the spin-spin coupling between H_b and H_c. The new broad peak observed at lowest field is assigned to the NH proton internally hydrogen bonded to the 2-nitro group: this peak is present when OCH_3^- or NH_2^- are used instead of OH^-. The areas of the peaks due to NH, H_b, H_a and H_c are in the expected 1:1:1:1 ratio. Water produced in the ionization of the aniline gives rise to the peak at -4.55 p.p.m., and this peak presumably also includes the signal from the proton of the OH group at the 3-position, proton exchange causing a merging of these two types of hydrogen.

Proton removal occurs when 4-nitroaniline is treated with base in liquid ammonia; but whereas sodium hydroxide produces no further interaction, excess amide does. A collapse in the spectrum of the ring protons occurs, implying attack of one or more ring positions by amide ion.

These phenomena illustrate the stronger basicity of liquid ammonia compared to the solvents used by other investigators[9,13] who observed addition of base to aromatic systems only with trinitro compounds. It is clear that addition occurs to dinitro and probably even mononitro compounds in liquid ammonia.

Other Acids

Recent interest in the acidities of carbon compounds[2,4] has led us to examine a few of these, in a preliminary manner, in the hope that we will be able to obtain good data for both nitrogen and carbon acids in the same solvent. We have examined solutions of the following acids in liquid ammonia in the presence of sodium amide: indene, fluorene, triphenylmethane, diphenylmethane and toluene. With the exception of toluene all of these acids can be completely ionized with excess amide ion. Literature data[4] indicate that diphenylmethane is ~11 pK units weaker than fluorene, and it appears that fluorene is at the more acidic end of our aniline scale.[1,2] It follows that we should be able to extend our scale by at least another 5 pK units, since diphenylmethane can be completely ionized in liquid ammonia. Toluene cannot be detectably ionized, even with high concentrations of potassium amide, so it appears that the limit to our scale lies somewhere between toluene and diphenylmethane.

Acknowledgments

The authors wish to thank Drs. R. Stewart and D. Dolman for making their data available to us in advance of publication.

This work was supported by the United States Atomic Energy Commission.

Table I

Relative Acidities of Some Substituted Anilines

Substituent	pK for Anilines	Literature Values for pK's of Anilinium Ions
2,5-dichloro	0	1.52[b]
3,5-bistrifluoromethyl	0.06	
4-cyano	0.34	1.74[d]
2,4-dichloro	1.16	2.01[b]
3,4-dichloro	2.45	2.56[b]
3-trifluoromethyl	3.22	3.49[c]
4-chloro	4.34	3.89[a]
-	5.65	4.60[a]
4-fluoro	5.88	4.65[a]
3,5-dimethyl	6.22	4.91[e]
2,5-dimethyl	6.26	4.61[f]
4-ethyl	6.43	
4-methyl	6.58	5.08[a]

[a] Reference 13.

[b] R. A. Robinson, J. Res. Natl. Bur. Std. A68, 159 (1964).

[c] A. Bryson, J. Am. Chem. Soc. 82, 4858 (1960).

[d] M. M. Fickling, A. Fischer, B. R. Mann, J. Parker, and J. Vaughan, J. Am. Chem. Soc. 81, 4226 (1959).

[e] B. M. Wepster, Rec. Trav. Chim. 76, 335 (1957).

[f] R. N. Beale, J. Chem. Soc. 2494 (1954).

Table II

N.M.R. Spectra of Solutions of 2,4-Dinitroaniline

in Liquid Ammonia Containing Various Bases

Base(B^-)	-δ p.p.m. from External T.M.S.					J_{AB}, c/s	J_{BC}, c/s
	NH	H_C	H_B	H_A	HB/B^- [a]		
None[b]	-	8.83	8.08	7.09	-	9.64	2.87
OH^- 1 equiv.	-	8.63	7.25	6.56	-	9.7	2.9
OH^- > two equiv.	11.22	5.24	6.95	5.59	4.55	10.22	0.75
OMe^- > two equiv.	11.25	5.23[c]	7.02	5.59	3.10	10.29	-
NH_2^- > two equiv.	~11.0	5.19	6.94	5.52	-	10.22	0.69

[a] Time-averaged signal of rapidly exchanging proton.

[b] These are the n.m.r. parameters for a solution of this acid in plain liquid ammonia and not of the unionized acid.

[c] Slow OMe^- exchange results in broadened H_C peak.

Figure Captions

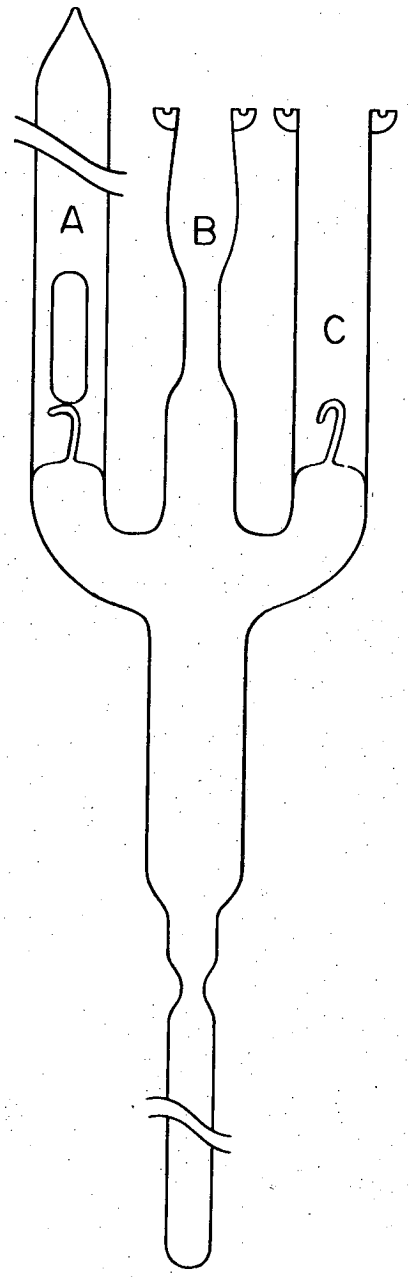
Figure 1. Vessel used for the preparation of samples.

Figure 2. N.m.r. spectrum of a solution of 4-methylaniline, 3,5-dimethylaniline, and their anions in liquid ammonia.

Figure 3. Hammett $\sigma\rho$ plot for relative acidities of substituted anilines.

Figure 4. Acidities of substituted anilinium ions (ordinate) plotted against the relative acidities of the parent aniline (abscissa).

Figure 5. N.m.r. spectrum of a solution of 2,4-dinitroaniline in liquid ammonia containing more than two equivalents of sodium hydroxide.



MUB-11366

Fig. 1

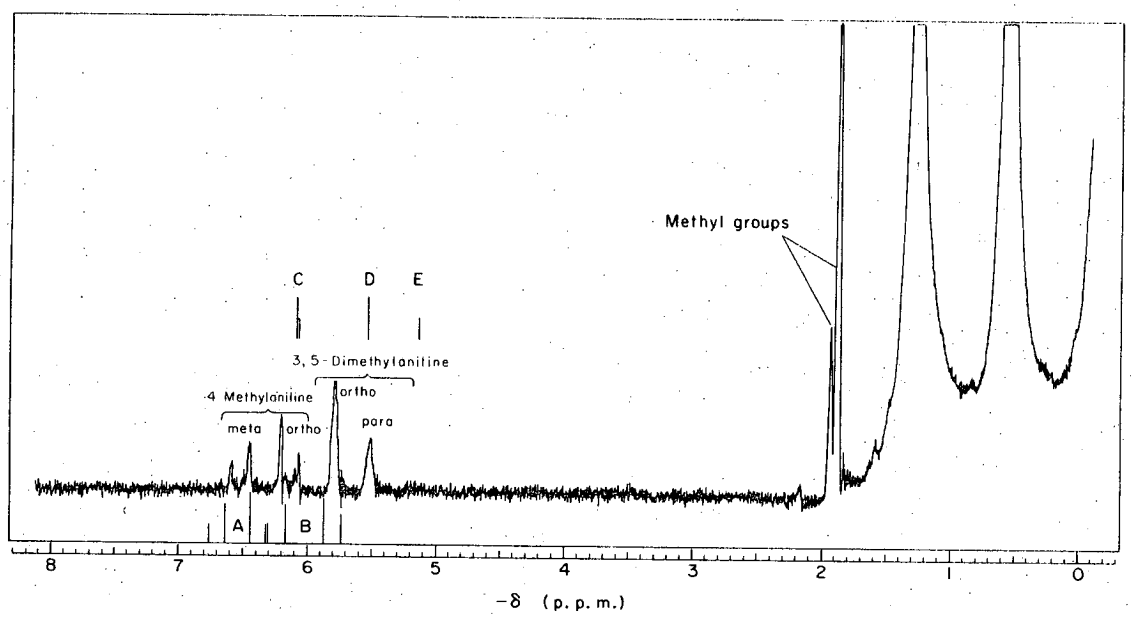
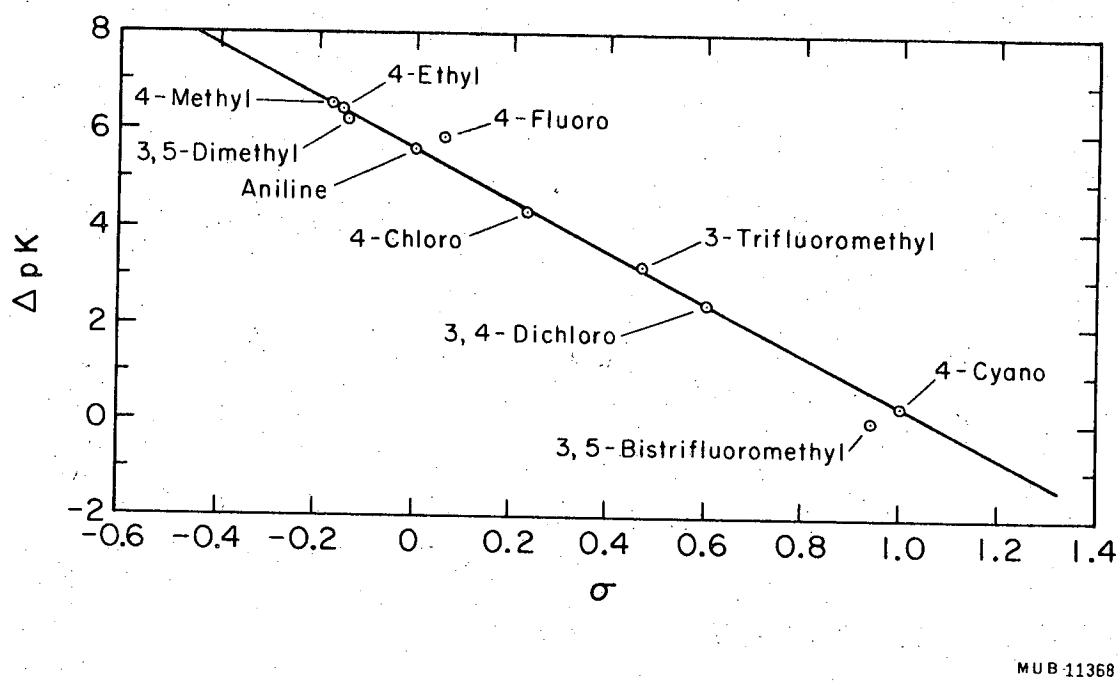
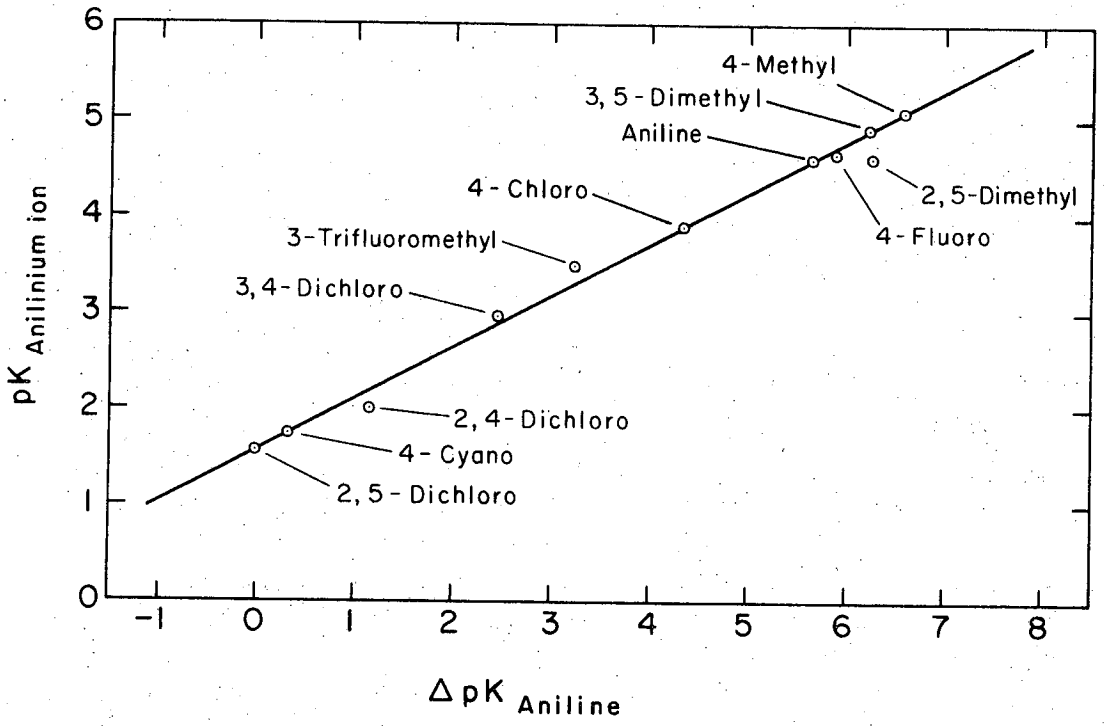

Methyl groups
C
D
E
3, 5 - Dimethylaniline
ortho
4 Methylaniline
meta
ortho
para
A
B
8
7
6
5
4
3
2
1
0
-δ (p. p. m.)

Fig. 2



MUB 11368

Fig. 3



MUB-11369

Fig. 4

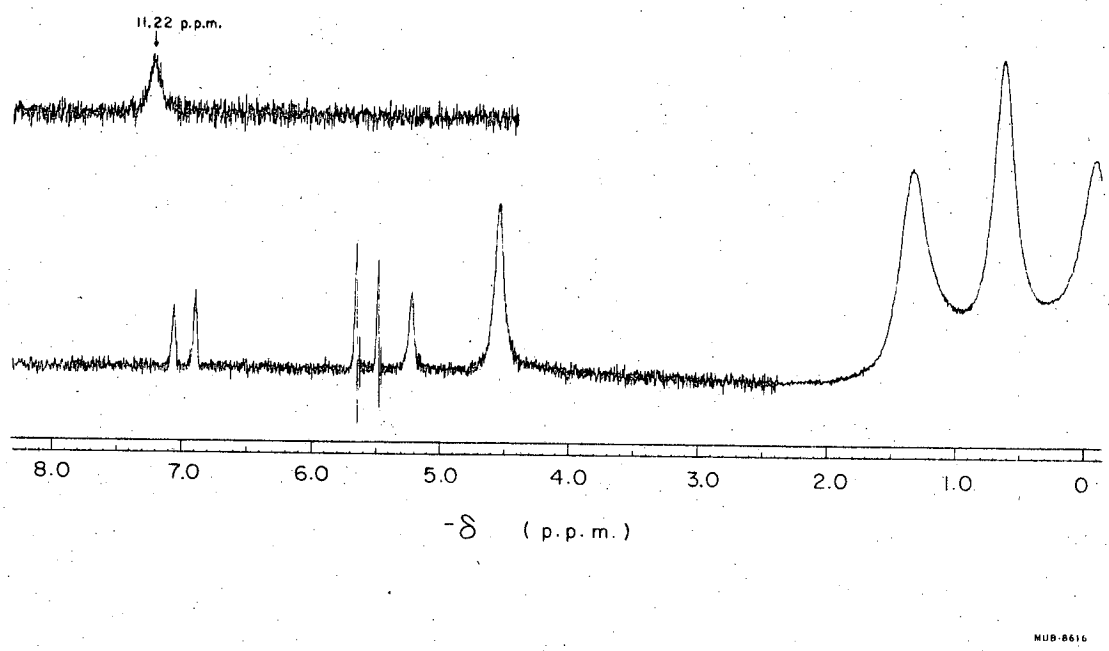


Fig. 5

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.