Thermochimica Acta, 64 (1983) 155–165
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A THERMOCHEMICAL APPROACH TO THE ANALYSIS OF ANILINE–FORMALDEHYDE REACTIONS

K. KISHORE and K.N. SANTHANALAKSHMI

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 12 (India)

(Received 2 November 1982)

ABSTRACT

The analysis of reaction and reaction products of 4:1, 2:1 and 1:1 stoichiometric reactions of aniline (AN) and formaldehyde (F) has been undertaken based purely on thermochemical considerations. Data on the enthalpy of formation and reaction are obtained from combustion and solution calorimetry. The same have been obtained by adopting Benson's theoretical thermochemical calculations. The computed and experimental ΔH_f^0 and ΔH_r^0 data are obtained for different possible reaction products of AN and F. Among them, compounds *NN'*-diphenyl methylenediamine and anhydroformaldehyde aniline are identified as the reaction products of 4:1, 2:1 and 1:1 AN/F reactions. The structures of the products were further confirmed by spectral data. It was concluded that the thermochemical evaluation of structures yielded information about the nature of the products of AN and F reactions which agreed with experimental data and the results of other authors.

INTRODUCTION

The study of reaction and reaction products of AN and F gained importance from an early date, analogous with that of phenol-, urea-, and melamine reactions with formaldehyde. Similar to the resin forming reactions, the course of AN and F reactions depends strongly on the reaction stoichiometry, pH and temperature of the experimental conditions [1]. Also, the reactions of AN and F can be classified as, firstly, high molecular weight resin forming reactions induced by acid catalysts, and secondly, low molecular weight bases forming reactions conducted in the absence of acid catalysts. A good rationalisation of acid induced reactions of AN and F at pH 7.0 was carried out by Wagner [2]. Recently a brief survey of AN and F reactions has been presented by Manuel and Le Blanc [3]. It may be seen that, despite substantial experimental work and extensive literature available on the subject, little is known regarding the mechanistic aspects of AN and F reactions involving different molar stoichiometric ratios, particularly in the case of reactions conducted in the absence of acid catalysts. The same is seen regarding the thermochemical properties of the respective reaction products.

0040-6031/83/$03.00

TABLE 1

R_f values of some aniline–formaldehyde reaction products

AN/F ratio	Compound	R_f value
4:1	A	0.75±0.01
2:1	B	0.75±0.02
1:1	C	1.0 ±0.02

The main objective of the present work was to obtain a reasonably complete set of thermochemical data for a couple of AN and F reactions and to ascertain the validity of the formation of the reaction products on the basis of thermochemistry. To begin with, 4 : 1, 2 : 1 and 1 : 1 stoichiometric reactions of AN and F were chosen for the present investigation. Experimental techniques like combustion calorimetry and solution calorimetry were utilised to determine the enthalpy values of the reaction and reaction products. The thermochemical characterisation was further verified by spectral analysis.

EXPERIMENTAL

Materials

Aniline (B.D.H.A.R.), fractionally distilled over zinc dust at 183–184°C, was used. Formaldehyde solution (B.D.H. assay 37–41% w/v), whose exact w/v % value was determined by sodium sulphite method [4], was used as such to react with aniline. The solid compounds obtained from 4 : 1, 2 : 1 and 1 : 1 molar ratio reactions of AN and F were separated from the reaction mixture, dried and subjected to the following analyses.

TABLE 2

Nitrogen estimation of AN and F reaction products from combustion calorimetry

Compound	Wt. (mg)	Vol. NaOH (0.1065 N) (ml)	Total wt. N_2 (g)	Correction for N_2 in O_2 gas	N in the compound (wt.%)
A	0.19965	33.7	0.0319	0.0037	14.14±0.20
B	0.37680	60.95	0.0577	0.0037	14.32±0.20
C	0.23995	38.13	0.0361	0.0037	13.52±0.20

TLC studies

The solid residues were found to be soluble in benzene. The solutions were subjected to TLC analysis adopting the standard method. Single neat spots were obtained from 2:1 and 1:1 AN/F reaction products while a single spot was obtained in the case of 4:1 AN/F product after the removal of excess unreacted aniline. Table 1 gives the R_f values of the respective spots. For convenience, the compounds from 4:1, 2:1 and 1:1 AN/F reactions could be designated as A, B and C, respectively.

Elemental analysis

The C and H% analysis data of compounds A, B and C were determined on a Perkin-Elmer Coleman carbon–hydrogen analyser instrument. The procedure and the method of operation were carried out as described in the manufacturer's manual. The nitrogen contents of the compounds were determined by two methods; the first was by subtracting the percentages of carbon and hydrogen from 100 and the second involved combustion calorimetry. The compound was burned in an atmosphere of oxygen (25 atm pressure). After combustion, the N_2 and various oxides of nitrogen produced were converted into nitric acid by the 4–5 ml of water which had been added to the bomb before combustion. The bomb and its contents were shaken well and the aqueous solution was titrated against standard sodium hydroxide solution. The oxygen gas used for pressurising the bomb contained nitrogen as impurity. The correction for this was estimated by the above method using standard benzoic acid samples (NBS sample, Parr, Moline, U.S.A.). The correction was found to be 0.0165 g HNO_3 for 25 atm O_2 gas in the bomb which was kept constant in all the experiments. Tables 2 and 3 give the estimation of nitrogen in the samples and the elemental analysis data of samples A, B and C, respectively.

TABLE 3

Elemental analysis data of the AN and F reaction products

Element (%)	A[$C_{13}H_{14}N_2$]		B[$C_{13}H_{14}N_2$]		C[$C_{21}H_{21}N_3$]	
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
C	78.56 ± 0.01	78.79	78.80 ± 0.01	78.79	80.00 ± 0.01	80.02
H	6.77 ± 0.06	7.07	6.98 ± 0.08	7.07	6.65 ± 0.07	6.66
N	14.14 [a]	14.14	14.32 [a]	14.14	13.52 [a]	13.32

[a] Determined from combustion calorimetry.

Calorimetric procedures

The bomb calorimeter (Toshniwal, India) was employed for the combustion (in the presence of O_2) studies. The calorimetric and calculation procedures adopted were the same as mentioned elsewhere [5]. The temperature measurements were done on a tenjunction teflon coated (outer diameter 0.1 in., Omega, U.S.A.) chromel–alumel thermopile by feeding the mV output to a strip-chart recorder (Omniscribe, Digital Electronics Ltd., Bombay) to record the temperature (0.001°C accuracy) vs. time curve. The corrected temperature was calculated by Rossini's method [5]. All the weighings of the pelletised samples were carried out on a semi-micro Mettler electrobalance to an accuracy of 0.01 mg. Weighings were reduced to masses and molecular weights were obtained from the table of atomic weights [6].

The energy equivalent of the bomb calorimeter was determined from the combustion of standard benzoic acid samples (thermochemical grade, Parr, Moline, U.S.A.) with a certified energy of combustion of -26.435 kJ g^{-1}, under standard calorimetric conditions. Each combustion run of samples A, B, C and benzoic acid was repeated at least five times under the same conditions. The value of energy equivalent of the empty calorimeter was found to be 514.6392 cal $°C^{-1}$. The combustion data of compounds A, B and C are presented in Tables 4 and 5 where m is the mass, E is the value of energy equivalent of the empty calorimeter plus the amount of water in the bomb and calorimetric bucket, ΔT is the corrected temperature rise, q_N, q_f and q_{cot} are the energy corrections for the formation of HNO_3, combustion of fuse and combustion of cotton, respectively. The value of q_N used for

TABLE 4

Heat of combustion data of compounds A and B isolated from the 4:1 and 2:1 AN/F reactions

Exptl.	A		B	
	1	2	1	2
m(compd.) (g)	0.19965	0.37625	0.37680	0.20065
m(fuse) (g)	0.02230	0.03400	0.02390	0.00905
m(cotton) (g)	0.01400	0.02285	0.02135	0.01945
E(cal $°C^{-1}$)	2663.2392	2378.6392	2446.8392	2277.9392
q_N(cal)	3.6135	3.6135	3.6135	3.6135
q_f(cal)	31.9577	48.7247	34.2506	12.9694
q_{cot}(cal)	58.5072	95.4921	89.2234	81.2832
ΔT(corrected)(°C)	0.677	1.412	1.364	0.801
$-\Delta H_c^0$(cal g^{-1})	8559.6523	8553.6662	8520.1321	8605.7777
$-\Delta H_c^0$(kcal $mole^{-1}$)	1694.8012	1689.6659	1686.9862	1703.9440
Mean (ΔH_c^0)(kcal $mole^{-1}$)	1694.0 ± 5.3		1695.2 ± 8.5	

TABLE 5

Heat of combustion of compound C isolated from the 1 : 1 AN/F reaction

Exptl.	1	2	3
m(compd.)(g)	0.23995	0.20510	0.24948
m(fuse)(g)	0.01860	0.00995	0.02965
m(cotton)(g)	0.01275	0.01180	0.01090
E(cal °C^{-1})	2462.6392	2457.2892	2458.4892
q_N(cal)	3.6135	3.6135	3.6135
q_f(cal)	26.6553	14.2591	42.4908
q_{cot}(cal)	42.4595	49.3132	45.5520
ΔT(corrected)(°C)	0.875	0.746	0.912
$-\Delta H_c^0$(cal g^{-1})	8632.0367	8610.1994	8619.8729
$-\Delta H_c^0$(kcal mole^{-1})	2719.0216	2712.2128	2715.2600
Mean	2715.6 ± 2.6 kcal mole^{-1}		

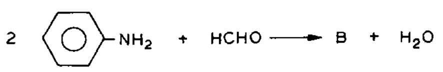
compounds A, B and C is the same as obtained in the benzoic acid runs.

The 4 : 1, 2 : 1 and 1 : 1 stoichiometric reactions of AN and F are exothermic in nature. The respective enthalpies of reaction of AN and F were measured using an adiabatic solution calorimeter which was assembled in the laboratory. The detailed procedure and the calculations involved have been described in detail elsewhere [7].

RESULTS AND DISCUSSION

It has already been qualitatively shown from the enthalpy of reaction data that AN and F yield various products when reacted in different molar stoichiometries [7]. The 4 : 1 and 2 : 1 AN/F reactions fall in the category of reactions of AN and F in excess AN. In the 2 : 1 AN/F molar reaction no residual AN or F was found to remain unreacted. In 4 : 1 AN/F reaction, some excess unreacted aniline remained. Based on the R_f values of A and B (Table 1), it may be seen that the values coincide with each other. Also, Table 6 shows that ΔH_c^0 values were found to be identical for compounds A and B. The ΔH_r^0 values of the 4 : 1 and 2 : 1 AN/F reactions calculated with respect to 1 mole of F (Table 7) seem to tally with each other; also, compounds A and B possess identical melting points (62.0 ± 0.05°C). Based on the above results it may be said that compounds A and B are the same.

The thermochemical approach was adopted to determine the structures of the products. The molecular formula of compound B derived by balancing the number of C, H, N and O atoms of reactants and products was found to be $C_{13}H_{14}N_2$, i.e., for 2 : 1 AN/F reaction



(1)

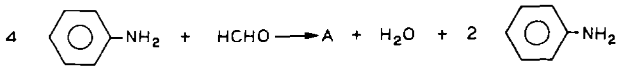
TABLE 6

ΔH_f^0 and ΔH_c^0 data of aniline and formaldehyde reaction products

Compound	$-\Delta H_c^0$(298 K) (kcal mole^{-1})	ΔH_f^0(298 K) (kcal mole^{-1})
A	1694.9 ± 5.3	34.75 ± 0.15
B	1695.2 ± 8.5	34.99 ± 0.15
C	2715.6 ± 2.6	84.30 ± 0.15

Molecular weight of B = $C_{12}H_{14}N_2 + CH_2O - H_2O = C_{13}H_{14}N_2$

In the case of the 4 : 1 AN/F reaction, the amount of unreacted AN separated by steam distillation was found to be half the original amount taken before the start of the reaction. Therefore, for the 4 : 1 AN/F reaction



(2)

The molecular formula of A would be deduced as $C_{13}H_{14}N_2$, i.e. compounds A and B possess the same molecular formula. The elemental analysis data obtained both by calculation and experimental method (Table 3) seem to agree well. The nitrogen weight percents obtained from bomb calorimetric data (Table 3) for A and B coincide with that value calculated from the formula $C_{13}H_{14}N_2$. The ΔH_f^0 values of compounds A and B were calculated from the ΔH_c^0 values based on the molecular formula $C_{13}H_{14}N_2$ (Table 6). In order to do so, the ΔH_f^0 values [$\Delta H_f^0(CO_2, g) = -94.051 \pm 0.01$ kcal mole^{-1}; $\Delta H_f^0(HNO_3, l) = -13.797 \pm 0.01$ kcal mole^{-1} and $\Delta H_f^0(H_2O, l) = -68.315 \pm 0.01$ kcal mole^{-1}] from ref. 8 were used.

Among the numerous possible structures written in concurrence with the molecular formula $C_{13}H_{14}N_2$, only those structures which would be the possible products of AN and F in that desired stoichiometric reaction are listed in Table 8. In order to fix one among the possible structures of compounds A and B, the ΔH_f^0 values of structures A1–A6 have been calculated using Benson's method of thermochemical calculations [9]. Table 8

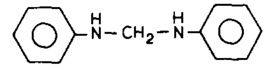
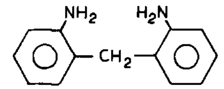
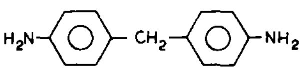
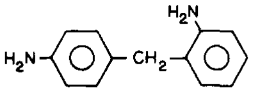
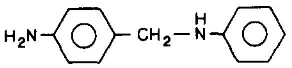
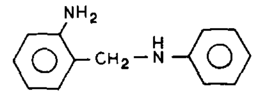
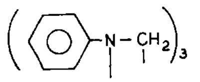
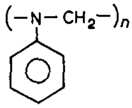
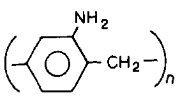
TABLE 7

Heats of reaction data of AN and F reactions determined by solution calorimetry

Molar ratio (AN/F)	$-\Delta H_r^0$(298 K) (kcal mole^{-1} AN)	$-\Delta H_r^0$(298 K) (kcal mole^{-1} F)
4 : 1	2.7002 ± 0.0038	10.7992 ± 0.0065
2 : 1	5.2493 ± 0.0253	10.7206 ± 0.0188
1 : 1	13.7567 ± 0.0044	13.7494 ± 0.0003

TABLE 8

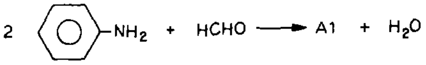
Data on heats of formation of compounds

No.	Structure	M.p. (°C)		ΔH_f^0(298.15 K) (calcd. by Benson's method) (kcal mole^{-1})	ΔH_r^0(298 K) (calcd. from Benson's ΔH_f^0 values) (kcal mole^{-1})
		Exptl.	Lit.		
A1		65 (for both A and B)	65	36.24±0.05	−10.860±0.05
A2			158		
A3			92	20.64±0.05	−26.46 ±0.05
A4			88		
A5					
A6				25.84±0.05	−21.250±0.05
C1		141 (for C)	141	80.07±0.05	−13.065±0.05
C2				36.19±0.05 kcal/mole of monomer	−3.605±0.05
C3				3.34±0.05	−27.415±0.05

presents the ΔH_f^0 values of A1–A6. On comparing the results presented in Tables 6 and 8, i.e. those values obtained theoretically and experimentally, respectively, it is seen that the ΔH_f^0 value calculated for compound A1 agrees well with that of the experimentally determined value of compound A (or B). Thus, it may be inferred that structure A1, viz. *NN'*-diphenyl methylenediamine, corresponds to the structure of compounds A and B.

For further thermochemical and experimental confirmation of the structures of the reaction products of the 4 : 1 and 2 : 1 AN/F reactions, ΔH_r^0 values were analysed as follows. Assuming each of the structures from A1 to A6 to be the sole product (only single compounds are detected in TLC) in each of the 4 : 1 and 2 : 1 AN/F reactions, the ΔH_r^0 values were calculated using the calculated ΔH_f^0 values of the reactants and products. The following typical calculation serves to illustrate this method.

For the 2 : 1 AN/F reaction



(3)

$$\Delta H_r^0(298\text{ K}) = \Delta H_f^0(\text{A1}) + \Delta H_f^0(\text{H}_2\text{O}) - 2\Delta H_f^0(\text{AN}) - \Delta H_f^0(\text{F})$$

$$= 36.24 - 68.315 - 2 \times 7.34 + 35.9$$

$$= -10.85 \pm 0.05 \text{ kcal mole}^{-1}$$

$$\Delta H^0_{\text{r(observed)}} = -10.721 \pm 0.019 \text{ kcal mole}^{-1}\text{F}$$

$$\text{or } -5.249 \pm 0.025 \text{ kcal mole}^{-1}\text{A}$$

Likewise, the calculated ΔH_r^0 values using each of the ΔH_f^0 values of A1–A6 are listed in Table 8. It may be seen from Tables 7 and 8 that the calculated and experimental ΔH_r^0 values for the structure A1 are in good agreement, thus supporting the inference made previously.

However, in order to verify the results obtained from the thermochemical predictions, spectral analysis of compounds A and B was carried out. Figures 1 and 2 present the IR and NMR spectra of compounds A and B, respectively. Individual IR and NMR spectra of A and B are found to be the same. The IR spectrum contains a single band around 3500–3310 cm^{-1} corresponding to secondary $\rangle$N–H stretching, and a weak band around 1580 cm^{-1} corresponding to secondary $\rangle$N–H bending. No evidence for the presence of a primary amino group was detected. Among the structures A1–A6, A2, A3 and A4 possess only primary amino groups, while A5 and A6 possess secondary and primary amino groups, and A1 possesses only a

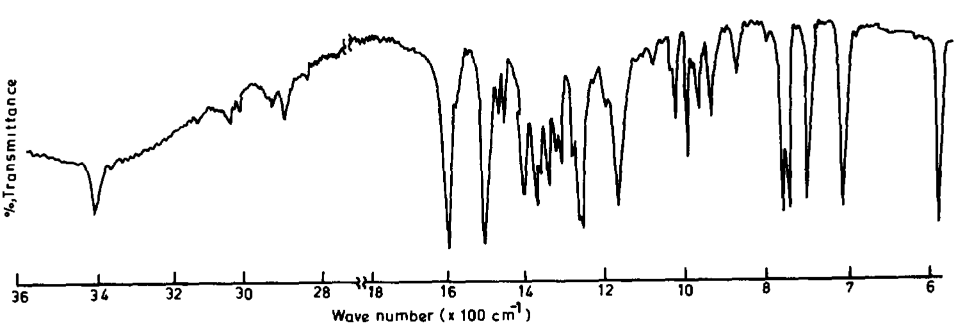


Fig. 1. IR spectrum of compounds A and B in KBr pellet.

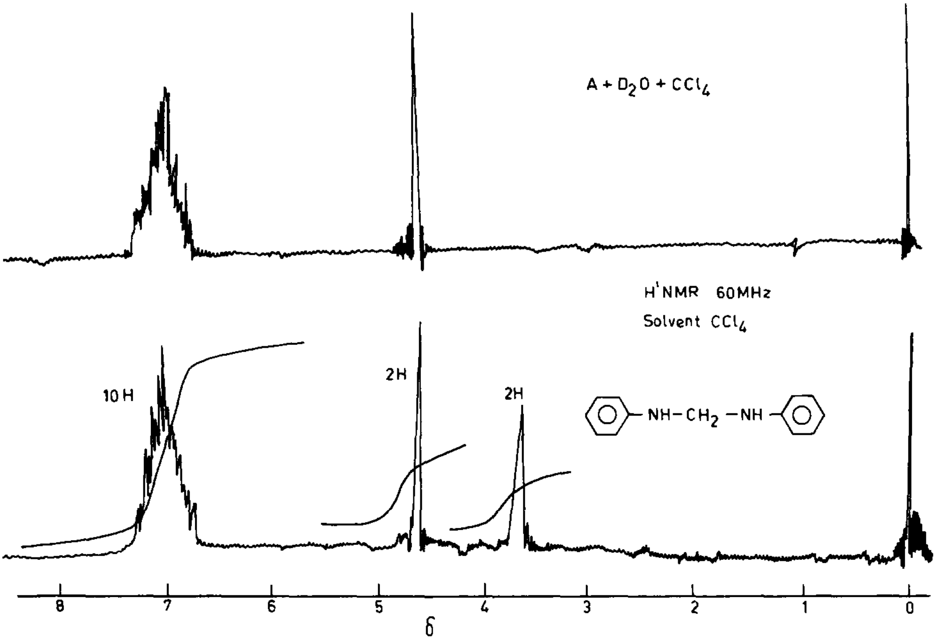
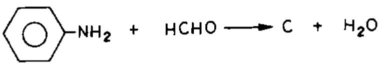


Fig. 2. H^1 NMR spectrum of compounds A and B.

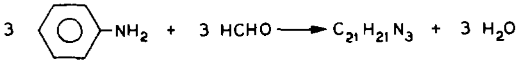
secondary amino group. The bands observed in various regions of IR of compounds A and B best fit the structure A1. In the case of the H^1NMR spectrum (Fig. 2) of compound A (which is the same as that of B), when treated with D_2O the peak at 3.70δ vanishes, thus confirming the presence of amino groups. The proton intensity ratio of the three peaks in H^1NMR would be 5 : 1 : 1, 4 : 1 : 2, 4 : 1 : 2, 4 : 1 : 2, 9 : 2 : 3 and 9 : 2 : 3 for structures A1, A2, A3, A4, A5 and A6, respectively. Thus, a close examination of the H^1NMR spectrum of compound A clearly indicates that the observed spectral results are consistent with structure A1, supporting the inference made from thermochemical considerations.

In the 1 : 1 AN/F stoichiometric reaction wherein equimolar proportions of AN and F are reacted to form product C, no unreacted excess AN or F could be detected. TLC analysis ensured a single compound whose R_f value is given in Table 1. The m.p. of the recrystallised compound C was found to be 141 ± 0.1°C. The molecular formula of compound C, determined from the following reaction by balancing the C, H, N and O atoms of the reactants and products, is C_7H_7N



(4)

However, its m.p. corresponds to that of the trimeric Schiff's base (methyleneaniline) which is reported in the literature [2]. Hence, the molecular formula of C could be corrected to $C_{21}H_{21}N_3$, which agrees with the equation



(5)

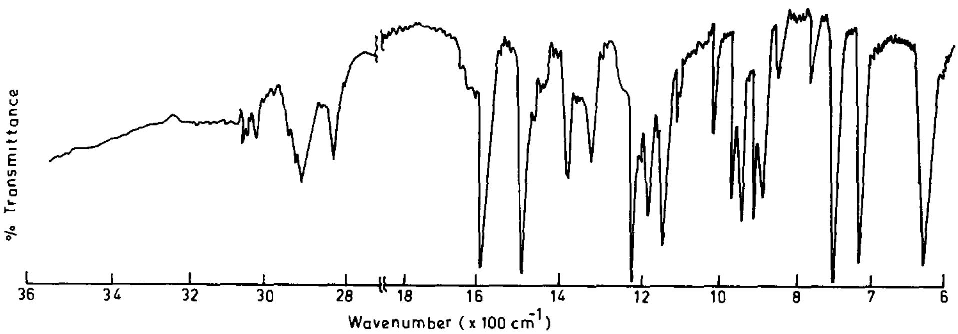


Fig. 3. IR spectrum of compound C (anhydroformaldehyde aniline) in KBr pellet.

The elemental analysis data calculated using this formula agree well with that obtained from experiment (Tables 2 and 3). The ΔH_f^0 value calculated from the ΔH_c^0 value using the molecular formula $C_{21}H_{21}N_3$ is given in Table 6. In agreement with the molecular formula, the possible structures C1, C2 and C3 are listed in Table 8. On comparing Tables 6 and 8 it is seen that the calculated ΔH_f^0 value of C1 agrees with the experimental ΔH_f^0 value of C. Also, by assuming each of the compounds C1, C2 and C3 as the products, the ΔH_r^0 values of the 1 : 1 AN/F reaction were calculated (Table 8). The calculated ΔH_r^0 value for compound C1 agrees well with the experimental ΔH_r^0 value (Tables 7 and 8) for the 1 : 1 AN/F reaction. These thermochemical observations indicate the structure C1 for compound C.

Figures 3 and 4 present the IR and H^{1}NMR spectra, respectively, of compound C obtained from the 1 : 1 AN/F reaction. The IR spectrum of compound C taken in KBr pellet agrees well with that reported by Mehdi [10] for anhydroformaldehyde aniline (trimeric Schiff's base). In the H^{1}NMR spectrum (Fig. 4) no evidence for free –OH or –NH_2 groups is seen. The sharp singlet at 4.8δ and multiplet at 7.0δ present with the proton intensity ratio 1 : 2.5 agree with the structure of C1. These spectral observations do not favour structure C2. The possibility of the polymeric structure C3 is ruled out because compound C has a sharp melting point and low molecular weight. Thus, for compound C obtained from the 1 : 1 AN/F reaction, the structure is C1, which is supported both by spectral and thermochemical data.

It is clearly evident from the present investigation that the structural inferences obtained based purely on thermochemical data agree quite well with those derived from spectral data, i.e. application of the thermochemical approach has been verified as appropriate for compounds whose spectral data (viz. IR and H^{1}NMR) are easily accessible. However, in the case of aniline–formaldehyde reactions conducted in the presence of acid catalysts, infusible, insoluble and hard polymeric resinous materials are obtained and any chemical and spectral analysis carried out to predict the structure has been rendered futile. In such circumstances, a thermochemical approach

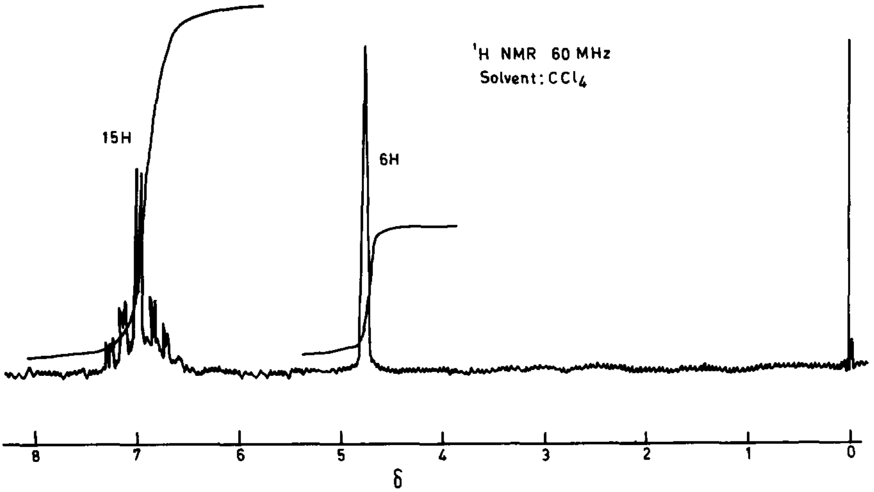


Fig. 4. H^1 NMR spectrum of compound C (anhydroformaldehyde aniline).

would certainly serve as a better tool of analysis and establish a new method of confirmation of the products of complex reactions.

REFERENCES

1 I. Wiesner, Collect. Czech. Chem. Commun., 38 (1973) 1473.
2 E.C. Wagner, J. Org. Chem., 19 (1954) 1862.
3 D.F. Manuel and J.R. LeBlanc, Kinet. Mech. Polym., 3 (1972) 157.
4 J.F. Walker, Formaldehyde, American Chemical Society Monograph Series, Reinhold, New York, 3rd edn., 1964, pp. 383, 483.
5 F.D. Rossini (Ed.), Experimental Thermochemistry, Interscience, New York, 1956.
6 Commission on Atomic Weights of IUPAC, Pure Appl. Chem., 47 (1976) 80.
7 K. Kishore and K.N. Santhanalakshmi, Thermochim. Acta, 53(3) (1982) 263.
8 CODATA values: J. Chem. Thermodyn., 7 (1975) 1; 8 (1976) 603.
9 S.W. Benson, Thermochemical Kinetics, Wiley, New York, 2nd edn., 1976.
10 S. Mehdi, Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., 132 (1970) 366.