Kinetics of the nucleophilic substitution reactions of methyl 2,4-dichloro-3,5-dinitrobenzoate with piperidine, piperazine, morpholine and thiomorpholine in methanol and benzene

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The kinetic of the nucleophilic substitution of methyl 2,4-dichloro-3,5-dinitrobenzoate with piperidine, piperazine, morpholine and thiomorpholine in methanol and benzene were determined spectrophotometrically at different amine concentrations and at temperatures ranging from 25 to 45 °C. The second order rate constants and the thermodynamic parameters show that the reactions are not amine catalysed and are greatly dependent of the nature of solvent and amine. UV, IR, ^{1}H NMR, and elemental analysis are used to prove the aminodechlorination at C–2.

Keywords: 2,4-dichloro-3,5-dinitrobenzoate, methanol, benzene, secondary cyclic amines

Evidence for the S_NAr mechanism of aromatic nucleophilic substitution came from studies of the base catalysis of reactions involving amine nucleophiles.[1-14] A series of papers have revealed that the kinetics are greatly dependent of the ring size of nucleophiles *e.g.* pyrrolidine, piperidine, etc. as well as the nature of solvent.[5,9,15,16] The formation of the Meisenheimer intermediate in the reaction of methyl 4-methoxy-3,5-dinitrobenzoate with piperidine in DMSO is rate-limiting.[17]

We report here the reaction of some secondary cyclic amines *e.g.* piperidine, piperazine, morpholine and thiomorpholine with methyl 2,4-dichloro-3,5-dinitrobenzoate 1 in methanol and benzene. Compounds of this kind exhibit antimicrobial activity and act as antithrombotic agents.[18] This drew our interest to investigate the reaction rates, to discuss a plausible mechanism for the titled reaction and to determine which chlorine atom (at C–2 or C–4) is substituted by amine.

Experimental

Melting points are uncorrected. The UV spectra were recorded on a Shimadzu 160-A instrument. IR spectra were recorded on a Perkin Elmer 1430 ratio recording IR spectrophotometer using potassium bromide pellets. The ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on a JEOL 500 MHz spectrometer. Elemental analyses were performed at the microanalytical laboratory in the Faculty of Science, Cairo University, Egypt.

Synthesis of 2,4-dichloro-3,5-dinitrobenzoic acid: 2,4-dichloro-3,5-dinitrobenzoic acid was prepared by heating 2,4-dichlorobenzoic acid (10 g, 0.035 mol.) with a mixture of conc. H_2SO_4 (50 ml) and conc. HNO_3 (20 ml) for 10 h at 140 °C. The reaction mixture was cooled and poured into ice-cold water. The product was crystallised twice from benzene–petroleum ether (60–80 °C) as yellow crystals, m.p. 220 °C, yield 85 %. Anal. Calc. for $C_7H_2Cl_2N_2O_6$: C, 29.9; H, 0.7; N, 10.0. Found C, 29.85; H, 0.5; N, 9.95. ^{1}H NMR (DMSO-d_6) δ: 8.76 ppm (1H, H-6). IR (KBr), 3092 cm^{-1} (br, O-H); 1719 cm^{-1} (C = O) and 1555, 1382 cm^{-1} (*asym* and *sym* NO_2). UV λ_{max} = 225 nm (ε = 14980 M^{-1}cm).

Synthesis of methyl 2,4-dichloro-3,5-dinitrobenzoate **1**: A solution containing (5 g, 0.018 mol) of 2,4-dichloro-3,5-dinitrobenzoic acid was mixed with 20 ml absolute MeOH solution containing 1 ml conc. H_2SO_4, and refluxed for 3 h. It was then poured onto Na_2CO_3 solution. The solid formed was crystallised from MeOH as yellow crystals, yield 95 %, m.p. 79 °C. Anal. Calc. for $C_8H_4Cl_2N_2O_6$: C, 32.5; H, 1.35; N, 9.5. Found C, 32.6; H, 1.3; N, 9.2. ^{1}H NMR ($CDCl_3$) δ: 8.58 ppm (s, 1H, H-6), 3.99 (s, 3H, –$COOCH_3$). IR (KBr) 1741 cm^{-1} (C=O ester), 1559 cm^{-1} (–NO_{2asym}), 1340 (–NO_2 sym). UV λ_{max} = 227 nm (ε = 16250 M^{-1}cm).

Methanol and benzene were purified as reported.[19]

CAUTION: Methanol is toxic and causes blindness and death when ingested, inhaled or absorbed through the skin. Benzene is a volalile, colourless, highly flammable liquid, b.p. 80.1 °C. It is acutely toxic by inhalation, ingestion or dermal exposure. It irritates skin and eyes and is a known human carcinogen.

Piperidine, morpholine and thiomorpholine were distilled over sodium hydroxide pellets through a 25 cm fractionated column.

CAUTION: These amines can affect you when breathed in and passing through your skin. They can irritate the nose, throat, lungs, eyes and skin. Most of them are skin allergy, flammable, corrosive and explosive chemicals.

Reaction products

General procedure: A mixture of methyl 2,4-dichloro-3,5-dinitrobenzoate (0.25 g, 0.85 mmol) and the desired amine (molar ratio 1: 2) was stirred in 20 ml methanol and left overnight at room temperature. The reaction mixture was poured onto cold water and the precipitate formed was crystallised from the appropriate solvent.

Methyl 4-chloro-2-(N-piperidyl)-3,5-dinitrobenzoate 2: Yellow needles from MeOH–H_2O; yield 95 %, m.p 82 °C. Anal. Cal. for $C_{13}H_{14}Cl\ N_3O_6$: C, 45.4; H, 4.1; N, 12.2. Found: C, 45.6; H, 3.9; N, 11.85. ^{1}H NMR ($CDCl_3$) δ: 8.34 ppm (s, 1H, H-6), 3.94 ppm (s, 3H, –$COOCH_3$); 3.05 ppm (s, 4H, 2 α-CH_2N); 1.59 ppm (s, 6H, β and γ-CH_2N). IR (KBr): 1730 cm^{-1}(C = O ester), 1545 cm^{-1} (–NO_2 asym), 1347 cm^{-1} (NO_2 sym). UV λ_{max} = 221 nm (ε = 12230 M^{-1}cm), 302 nm (ε = 6500 M^{-1} cm), 362 nm (ε = 2300 M^{-1}cm).

Methyl 4-chloro-2-(N-piperazinyl)-3,5-dinitrobenzoate **3**: Yellow needles from MeOH-H_2O; yield 95 %, m.p 220 °C (dec.). Anal. Calc. for $C_{12}H_{13}Cl\ N_4O_6$: C, 41.8; H, 3.8; N, 16.25. Found: C, 42.0; H, 3.3; N, 16.55. ^{1}H NMR ($CDCl_3$) δ: 8.21 ppm (s, 1H, H-6), 4.00 (s, 3H, –$COOCH_3$); 3.09 ppm (s, 4H, α-CH_2–N-adjacent to aromatic moiety), 3.08 ppm (d, *J* = 2.8Hz, 2H, β-CH_2N) 2.88 ppm (d, *J* = 4.5Hz, 2H, β–CH_2–N–), 1.85 ppm (br s, 1H, N–H). IR (KBr): 3416 cm^{-1} (NH), 1728 cm^{-1} (C = O ester), 1541 (–NO_2 asym), 1339 cm^{-1} (–NO_2 sym). UV λ_{max} = 219 nm (ε = 8960 M^{-1}cm), 302 nm (ε = 5880 M^{-1}cm), 362 nm (ε = 4030 M^{-1}cm).

Methyl 4-chloro-2-(N-morpholyl)-3,5-dinitrobenzoate **4**: Yellow needles from MeOH-H_2O, yield 95 %, m.p 96 °C, Anal. Cal. for $C_{12}H_{12}Cl\ N_3O_7$: C, 41.7; H, 3.5; N, 12.2. Found: C, 41.8; H, 3.2; N, 12.2. ^{1}H NMR ($CDCl_3$): δ, 8.20 ppm (s, 1H, H-6), 3.93 ppm (s, 3H, $COOCH_3$) 3.67 ppm (t, *J* = 4.6 Hz, 4H, CH_2O); 3.12 ppm (t, *J* = 4.6 Hz, 2H, CH_2N), 3.09 ppm (t = 4.6 Hz, 2H, –CH_2N). IR (KBr): 1723 cm^{-1} (C = O ester), 1543 cm^{-1} (–NO_2 asym), 1356 cm^{-1} (–NO_2 sym). UV λ_{max} = 220 nm (ε = 10820 M^{-1} cm), 302 nm (ε = 6770 M^{-1} cm), 362 nm (ε = 4150 M^{-1}cm).

Methyl 4-chloro-2-(N-thiomorpholyl)-3,5-dinitrobenzoate **5**: Yellow needles from MeOH-H_2O, yield 95 %, m.p. 92 °C. Anal. Cal. for $C_{12}H_{12}Cl\ N_3O_6S$: C, 39.8; H, 3.6; N, 11.6. Found: C, 40.0; H, 3.8; N, 11.9. ^{1}H NMR ($CDCl_3$) δ: 8.37 ppm (s, 1H, H-6); 3.97 ppm (s, 3H, COOCH3), 3.34 ppm (m, 4H, α-CH_2N), 2.61 ppm (br s, 4H, α-CH_2S). IR (KBr): 1723 cm^{-1} (C = O ester), 1545 cm^{-1} (NO_2 asym), 1355 cm^{-1} (–NO_2 sym). UV λ_{max} = 222 nm (ε = 12170 M^{-1}cm), 302 nm (ε = 5360 M^{-1}cm), 362 nm (ε = 3250 M^{-1}cm).

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Kinetic measurements

The kinetic runs were carried out under pseudo first-order conditions by using 5×10^{-5} mol dm^{-3} of **1** and different concentrations of piperidine, piperazine, morpholine and thiomorpholine, ranging from 0.03 to 0.8 mol dm^{-3} in methanol and 0.001 to 0.3 mol dm^{-3} in benzene. The changes in absorbance during the reaction were followed spectrophotometrically at λ = 362 nm and 365 nm for the formation of product for all amines in methanol and benzene respectively. The pseudo first order rate constants k_ψ were determined using equation (1).

$$\log (A_\infty - A_t) = -\frac{k_\psi}{2.303} + \log (A_\infty - A_o) \qquad (1)$$

CAUTION: Respirators should be worn. Protective gloves, adequate ventilation, splash resistant goggles, and a pipette filler for the transfer of amine solution must be used when working with the flammable, corrosive, highly irritating and/or toxic amines and solvents.

Results and discussion

A. Structural determination of the reactant and products

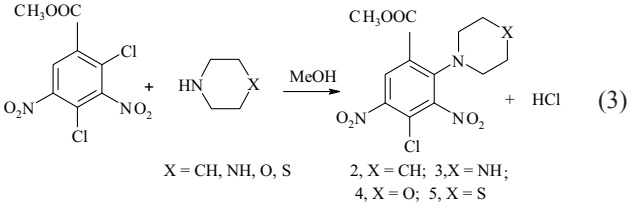
The heating of 2,4-dichlorobenzoic acid with a solution of conc. HNO_3 and conc. H_2SO_4 mixture gave 2,4-dichloro-3,5-dinitrobenzoic acid which is consistent with the elemental analysis and the presence of only one proton at δ 8.76 ppm (see Experimental).

Esterification of the above acid with absolute methanol and a catalytic amount of conc. H_2SO_4 afforded methyl 2,4-dichloro-3,5-dinitrobenzoate **1** as indicated from elemental analysis and the presence of two peaks at δ 8.58 ppm (H-6) and 3.99 ppm (–CH_3 of the ester group).

The reaction of **1** with secondary amines gave the corresponding monoamino derivatives. Elemental analyses indicated that only one chlorine atom is present and that the second one is replaced by the amine. Spectroscopic analyses are used to indicate which chlorine atom (at C–2 or C–4) of **1** is replaced by the amine forming the methyl chloro-amino-3,5-dinitrobenzoate derivatives **2–5**. Whereas ^{1}H NMR and IR spectroscopic data do not indicate which C–2 or C–4 is attacked, the UV bands at λ = 302 and 362 nm for **2–5** are comparable to those of 2,4,6-trinitroaniline.[20] This indicates that the electronic transitions between C(2)–C(3) and C(2)–C(5) take place respectively,[21] *i.e.* electronic transitions between the lone pair on nitrogen at C–2 and the nitro groups at C–3 and C–5, Equation (2).

$$>\overset{+}{N}{=}C(2)-C(3){=}N\overset{-}{O_2} \quad \text{and} \quad >\overset{+}{N}{=}C(2)-C(5){=}N\overset{-}{O_2} \qquad (2)$$

As a result the amino-dechlorination process takes place at C–2 giving methyl 4–chloro–2–(*N*-dialkylamino)-3,5-dinitrobenzoate **2–5**, equation (3):



(3)

This suggestion is based on the lower reactivity at C–4 relative to C–2, which is attributed to the lower electron density at the latter carbon relative to the former one and was confirmed by theoretical calculations of electron densities.[22] In addition, unfavourable congestion[23] is present in the intermediate developed from the attack of amine on C–4.

B. Kinetic studies and rate measurements

In all cases the dependence of rate on amine concentration was studied and the reactions of **1** with piperidine, piperazine, morpholine and thiomorpholine were carried out under pseudo first-order conditions. Spectra at completion of the reactions were identical to those of the corresponding authentic samples of the product dissolved in the reaction medium.

The rate constants k_ψ in methanol and benzene were collected in Tables 1 and 2 respectively. The plots of k_ψ values *vs* amine concentration in each solvent gave straight lines passing through the origin where the slopes are equal to the specific second-order rate constant k_A (R = 0.992–0.999). This indicates that these reactions are not amine catalysed, a behaviour expected when chlorine atom is the leaving group.[11] The k_A values for the reaction of **1** with piperidine, piperazine, morpholine and thiomorpholine at 25°, 30°, 35°, 40° and 45 °C and the corresponding activation parameters in methanol and benzene are given in Tables 1 and 2 respectively. The negative entropy of activation values are consistent with a bimolecular mechanism reported for most nucleophilic aromatic substitutions.[24]

In Scheme 1, the intermediate **Z** resulting from attack at 2-position is not observed meaning that it spontaneously decomposes to substitution products **2–5**. This uncatalysed route is discussed in terms of unimolecular decomposition either by catalysis by solvent molecules in methanol or intramolecular hydrogen-bond transition states **Z–A** and/or **Z–B** in methanol and benzene. *i.e.* hydrogen bonding occurs in intermediate **Z** between the ammonium hydrogen atom and the oxygen of the nitro group or with the carbonyl group oxygen, respectively.

Steps in Scheme 1 can be represented by equation (4):

$$\mathbf{1} + \text{HN}< \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{Z} \xrightarrow{k_2} \text{(2–5)} \qquad (4)$$

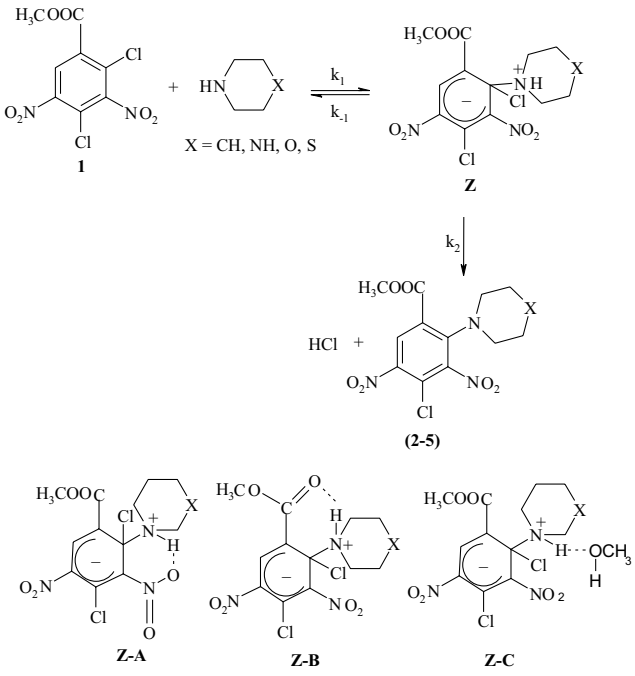
Applying the steady state approximation to the intermediate **Z**, the rate law leads to equation (5)

$$\frac{\text{Rate}}{[\mathbf{1}][\text{amine}]} = k_A = \frac{k_1 k_2}{k_{?1} + k_2} \qquad (5)$$

Since the reaction is not amine-catalysed, $k_2 >> k_{-1}$, then, equation (5) will be reduced to equation (6),

$$k_A = k_1 = \frac{k_{obs}}{[>\text{NH}]} \qquad (6)$$

where k_{obs} is the pseudo first-order rate constant and k_A is the second-order rate constant. This is consistent with the fact that, when chlorine is the nucleofuge and the substrate is highly activated, the formation of zwitterion intermediate **Z**, k_1, is the rate determining step followed by spontaneous decomposition of the intermediate[23-27] to products. This is different from the behaviour observed for the reaction of



Scheme 1

Table 1 Rate constants for the reaction of methyl-2,4-dichloro-3,5-dinitrobenzoate **1** with secondary amine at different temperatures in methanol

t/ °C	25	30	35	40	45	ΔH#/	-ΔS#/
[Amine] M	$k_\psi \times 10^{-4}$, s^{-1}					kJ mol^{-1}	J mol^{-1} K^{-1}
[Piperidine]							
0.03	2.4	3.7	4.8	6.1	7.7		
0.04	3.4	5.1	6.3	7.8	9.5		
0.05	4.4	6.4	7.8	9.5	11.5		
0.06	5.3	7.5	9.3	11.5	14.1		
0.07	6.5	9.3	11.3	13.6	16.3		
10^3 k_2	8.9	12.8	15.8	19.3	23.5	35	167
/l $mol^{-1}s^{-1}$	± 0.2	± 0.2	± 0.1	± 0.1	± 0.3	± 3	± 9
[Piperazine]							
0.10	3.7	4.5	6.2	8.5	11.5		
0.15	5.6	6.5	8.7	11.6	15.2		
0.20	7.4	8.4	11.1	14.6	18.9		
0.25	9.3	11.0	14.6	19.1	24.9		
0.30	11.6	13.2	17.2	22.2	28.5		
10^3 k_2	3.8	4.4	5.8	7.5	9.8	36	172
/l $mol^{-1}s^{-1}$	± 0.1	± 0.1	± 0.1	± 0.1	± 0.2	± 3	± 8
[Morpholine]							
0.34	2.1	3.2	3.9	6.1	7.1		
0.46	2.7	4.0	5.0	7.1	8.8		
0.57	3.6	4.7	6.0	8.7	10.3		
0.69	4.4	5.7	7.6	9.7	12.1		
0.80	4.8	7.0	8.8	11.7	14.3		
10^3 k_2	0.6	0.8	1.1	1.5	1.8	42	165
/l $mol^{-1}s^{-1}$	± 0.0	± 0.0	± 0.0	± 0.1	± 0.1	±2	± 6
[Thiomorpholine]							
0.2	0.6	0.8	1.1	1.4	1.8		
0.3	0.9	1.2	1.6	2.1	2.7		
0.4	1.3	1.7	2.2	2.9	3.8		
0.5	1.5	2.1	2.8	3.8	4.9		
0.6	1.8	2.5	3.3	4.5	5.9		
10^3 k_2	0.3	0.4	0.6	0.7	1.0	44	163
/l $mol^{-1}s^{-1}$	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 3	± 9

methyl 4-methoxy-3,5-dinitrobenzoate with amines in DMSO.[18] We explain the different kinetic behaviour between these reactions on the nature and position of the leaving group with respect to the activating ones as well as the possibility of hydrogen bonding in the developing transition state.

Tables 1 and 2 reveal that k_A values decrease in the following order for the reaction of **1**: piperidine > piperazine > morpholine > thiomorpholine. This order is in harmony with K_B values of amines measured in methanol and benzene[28] and the electron withdrawing effect of the X atom except for thiomorpholine. The rate enhancement observed for the reaction of **1** with piperazine in methanol and benzene compared to thiomorpholine is perhaps attributed to the presence of two nucleophilic centres although the second nitrogen atom in the former amine has a $-I_S$ effect greater than that of the sulfur atom in the latter one.

Actually the rate constants are found to be greater in benzene than in methanol. The major effect should be on the ionic zwitterion **Z,** which one would expect to be better solvated in the more polar solvent, methanol. Hence, k_1 should have a higher value in methanol, which is not the case. However, the amine is surrounded by the methanol molecules through hydrogen bonding inhibiting its nucleophilicity and in turn a lower rate constant is observed.[29]

Alternatively, an explanation for the faster rate constants in benzene may possibly be found in terms of intramolecular hydrogen-bonding as shown in **Z–A** and **Z–B**. It is likely that such hydrogen-bonding exists in benzene while its existence in methanol is doubtful.[30] Thus, in solvents which are good hydrogen-bonding acceptors, such as DMSO and methanol, the N–H hydrogen in the zwitterion **Z–C** is likely to be intermolecularly hydrogen-bonded rather than intramolecularly. The presence of intramolecular H-bonding in benzene may help to stabilise the zwitterion **Z** and lower its energy thus increasing values of k_1. Such intramolecular H-bonding should lower the values of k_2, but if, as in the present work, k_1 is rate-limiting this will not be apparent.

The $\Delta H^{\#}$ values and the absence of amine catalysis in methanol and benzene Tables 1 and 2, indicate a fast proton transfer. While the large negative $\Delta S^{\#}$ in both solvents perhaps suggest hydrogen-bonded cyclic transition states **Z–A** and/or **Z–B**.

Table 2 Rate constants for the reaction of methyl-2,4-dichloro-3,5-dinitrobenzoate **1** with secondary amine at different temperatures in benzene

t/ °C	25	30	35	40	45	ΔH#/	-ΔS#/
[Amine] M	$k_\psi \times 10^{-4}$, s^{-1}					kJ mol^{-1}	J mol^{-1} K^{-1}
[Piperidine]							
0.001	1.8	2.2	2.6	3.2	3.8		
0.002	2.8	3.4	4.2	5.1	6.1		
0.003	3.9	4.9	6.2	7.7	9.5		
0.004	5.0	6.3	7.9	9.9	12.2		
0.005	6.1	7.9	10.2	12.8	15.9		
0.006	7.9	10.0	12.4	15.4	18.1		
10^3 k_2	128.6	163.1	205.0	255.5	309.5	32	153
/l $mol^{-1}s^{-1}$	± 3.2	± 3.3	± 3.0	± 3.4	± 4.6	± 1	± 1
[Piperazine]							
0.002	1.8	2.5	3.1	3.8	4.8		
0.004	2.8	3.9	5.1	6.0	8.0		
0.006	4.0	5.93	6.9	8.6	11.1		
0.008	5.6	8.5	9.8	12.2	14.0		
0.010	6.7	9.3	11.6	14.9	18.0		
0.012	8.7	12.4	14.2	17.7	22.3		
10^3 k_2	70.1	100.5	119.0	149.0	183.5	33	157
/l $mol^{-1}s^{-1}$	± 1.5	± 2.5	± 2.2	± 2.2	± 3.6	± 2	± 8
[Morpholine]							
0.05	2.1	2.8	3.9	4.3	5.1		
0.10	3.5	4.7	6.0	7.4	9.2		
0.15	5.4	7.9	8.9	11.1	13.3		
0.20	7.8	10.6	12.3	14.0	17.0		
0.25	9.5	12.2	14.4	17.8	21.0		
0.30	12.2	16.0	20.5	23.1	28.8		
10^3 k_2	3.9	5.2	6.3	7.6	9.1	34	177
/l $mol^{-1}s^{-1}$	± 0.1	± 0.1	± 0.2	± 0.2	± 0.2	± 4	± 5
[Thiomorpholine]							
0.04	0.4	0.5	-	0.9	1.2		
0.05	0.5	0.7	-	1.1	1.5		
0.06	0.6	0.8	-	1.3	1.7		
0.07	0.7	0.9	-	1.5	1.9		
0.08	0.8	1.1	-	1.8	2.3		
10^3 k_2	1.0	1.3	-	2.2	2.8	38	174
/l $mol^{-1}s^{-1}$	± 0.0	± 0.0		± 0.0	± 0.0	± 1	± 1

The higher ratio $k_{benzene}/k_{methanol}$ value at 25 °C in the case of the reaction of **1** with piperazine (18.5) compared to those with piperidine (14.4), morpholine (6.5) and thiomorpholine (3.3) is presumably due to the presence of two >N–H groups which are solvated by methanol molecules more than the other nucleophiles are in benzene.

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