Steric and electronic effects on the mechanism of nucleophilic substitution (S_NAr) reactions of some phenyl 2,4,6-trinitrophenyl ethers with aniline and *N*-methylaniline in acetonitrile and in dimethyl sulfoxide

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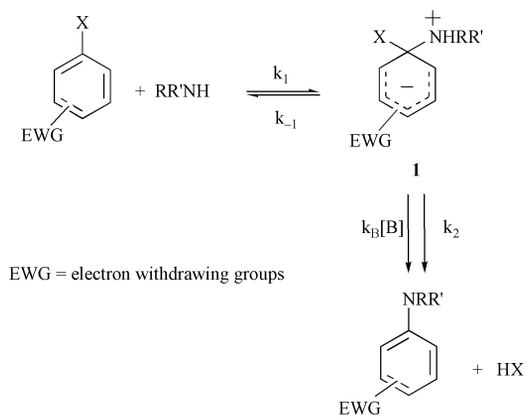
Rate data are reported for the reactions of a series of 3′- and 4′-substituted phenyl 2,4,6-trinitrophenyl ethers, **4**, with aniline in acetonitrile, leading to 2,4,6-trinitrodiphenylamine. The main reaction flux occurs through a base catalysed pathway involving formation of a zwitterionic intermediate, equilibrium constant K_1, and rate-limiting proton transfer to base, rate constant k_{An}. The effects of ring substituents on values of rate and equilibrium constants are discussed. In contrast the corresponding reactions in DMSO involve both uncatalysed and base catalysed pathways. Reactions of **4** with *N*-methylaniline are extremely slow, but values of rate constants for reaction of 4-nitrophenyl 2,4,6-trinitrophenyl ether were measured using ^{1}H NMR spectroscopy. The value of the parameter K_1k_{An} is lowered by a factor of 10^5 for *N*-methylaniline relative to aniline in both acetonitrile and in DMSO. This reduction is attributed to increased steric hindrance both in formation of the intermediate and to proton transfer.

The general mechanism of S_NAr reactions[1,2] when either primary or secondary amines are the nucleophiles is given in Scheme 1. Eqn. (1) is the steady state expression for the



Scheme 1

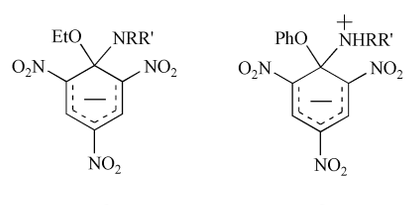
observed second order rate constant, k_A, expressed in terms of the component steps in Scheme 1.

$$k_A = \frac{k_1(k_2 + k_B[B])}{k_{-1} + k_2 + k_B[B]} \quad (1)$$

When $k_{-1} \gg k_2 + k_B[B]$, base catalysis may be observed and there is continued interest in the mechanism of such catalysis[3,4] and in its importance relative to the uncatalysed, k_2, step. The observation of general base catalysis is indicative of rate-limiting proton transfer. This may be from the zwitterionic intermediate, **1**, to base; or, it may involve general acid catalysis of leaving group expulsion from the deprotonated form of **1**. In dimethyl sulfoxide (DMSO) the latter, the SB-GA mechanism, has been shown to apply to substrates, such as alkyl ethers, carrying poor leaving groups.[5–7] However there is good evidence that for substrates carrying good leaving groups, such as phenyl ethers and phenyl sulfides, the rate-limiting proton transfer is from zwitterion to base.[8]

Although acetonitrile has been widely used as a solvent for the examination of base catalysis in substitution reactions, the mechanistic conclusions reached are rather less clear than those relating to those in DMSO as solvent. A general conclusion has been that the susceptibility to base catalysis increases as the polarity of the solvent decreases, and is higher for secondary than for primary amines.[9–11]

There have been few studies involving substitutions in highly activated substrates in acetonitrile. However it is known[12] that reactions of aliphatic amines with ethyl 2,4,6-trinitrophenyl ether yield observable σ-adduct intermediates, **2**, which may be converted by general acid catalysis to substitution products (SB-GA mechanism) while base catalysis in reactions of the corresponding phenyl ether is due to rate-limiting proton transfer from zwitterions, **3**, to base.



We report here kinetic studies of the reactions in acetonitrile of some 3′- and 4′-substituted phenyl 2,4,6-trinitrophenyl ethers, **4**, with aniline catalysed by aniline itself and by DABCO. Our aims were to compare values for the rate constants for the individual steps in the reaction pathway and to determine the electronic effects of substituents in the leaving group on the rate and mechanism of substitution. The results are nicely interpreted by Scheme 2 in which base catalysis is attributed to rate-limiting proton transfer from zwitterionic intermediates, **5**, to base and is followed by rapid expulsion of

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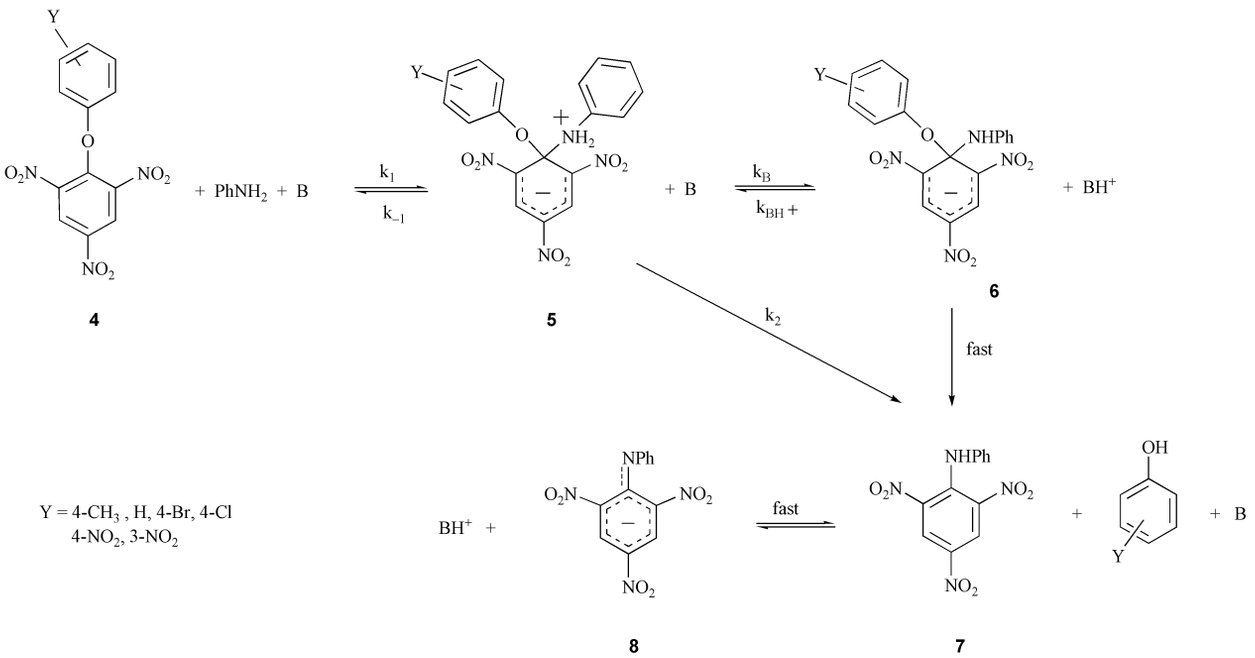
Table 1 Kinetic results for the reactions of **4**, Y-phenyl-2,4,6 trinitrophenyl ethers (Y = CH_3, H, Br, Cl, NO_2) with aniline in acetonitrile at 25 °C

	$k_A/10^{-2}$ dm^3 mol^{-1} s^{-1}					
[Aniline]/mol dm^{-3}	4-CH_3	4-H	4-Br	4-Cl	4-NO_2	3-NO_2
0.01	0.47	0.47	0.83	0.92	0.93	1.10
0.02	0.95	0.93	1.58	1.60	1.98	2.12
0.03	1.42	1.38	2.41	2.55	2.78	3.14
0.04	1.90	1.71	3.10	3.40	3.62	4.06
0.05	2.25	2.22		4.00	4.26	5.00
0.06	2.85		4.40	4.60	5.02	6.10
0.07	3.23		5.02		5.68	
0.08	3.49				6.24	



Scheme 2

phenoxide. In the presence of excess DABCO the diphenylamine product, **7**, may be deprotonated in a rapid equilibrium to give **8**. In the case of 4′-nitrophenyl 2,4,6-trinitrophenyl ether we also report rate measurements, by ^{1}H NMR spectroscopy, for reaction with *N*-methylaniline, a much more sterically demanding nucleophile.

Results and discussion

Reactions with aniline in acetonitrile

The reactions of the diphenyl ethers, **4**, with aniline in acetonitrile proceeded to give 2,4,6-trinitrodiphenylamine, **7**, in quantitative yield in a single stage without the observation of intermediates. UV spectra, λ_{max} = 365 nm, ε = 1.4 × 10^4 dm^3 mol^{-1} cm^{-1}, and ^{1}H NMR spectra at the completion of the reaction were identical to those of an authentic sample of **7** in the reaction medium. The increase in absorbance at 365 nm was used for kinetic measurements; with aniline in large excess of substrate a first-order process was observed whose rate constant, k_{obs}, was evaluated by standard methods.

Division, by the aniline concentration, of values of k_{obs} gave values of the second order rate constant, k_A, and data are collected in Table 1. A typical plot, in this case for the 4-bromophenyl substrate, of k_A *versus* aniline concentration is given in Figure 1. It shows a line with some downward curvature and with an intercept on the *y*-axis indistinguishable from zero. In terms of eqn. (1) the latter indicates that the contribution of k_2, the uncatalysed pathway, is negligible. Hence eqn. (1) reduces to eqn. (2), where k_{An} represents the pathway

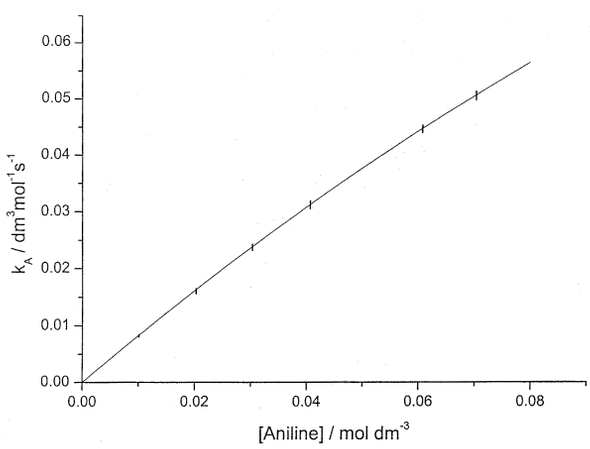


Fig. 1 Plot of k_A *versus* [aniline] in acetonitrile at 25 °C for the reaction of 4-bromophenyl 2,4,6-trinitrophenyl ether. Experimental values are denoted by |, and the curve is generated by k_A = 0.85[aniline]/(1 + 2.6[aniline]).

$$k_A = \frac{k_{obs}}{[\text{aniline}]} = \frac{k_1 k_{An}[\text{aniline}]}{k_{-1} + k_{An}[\text{aniline}]} \quad (2)$$

catalysed by aniline. An equivalent form is eqn. (3).

$$k_A = \frac{K_1 k_{An}[\text{aniline}]}{1 + \dfrac{k_{An}[\text{aniline}]}{k_{-1}}} \quad (3)$$

The data allow the calculation of values of K_1k_{An} with good precision. However the rather small curvature means that there is some uncertainty in the values obtained for the ratio k_{An}/k_{-1}, and hence also in the values calculated for k_1 (= $K_1k_{An}k_{-1}/k_{An}$). Values for these quantities are summarised in Table 4, below.

Confirmation that the reaction is subject to general base catalysis is given by measurements in the presence of added DABCO. Values of K_1k_{DABCO}, where k_{DABCO} represents the rate constant for the DABCO catalysed route, were obtained from the slopes of approximately linear plots of the data in Table 2. Values were alternatively calculated from the intercepts of plots of the data in Table 3, obtained with constant DABCO but varying aniline concentrations.

Reactions with aniline in DMSO

A typical plot of data obtained in DMSO is shown in Figure 2. The sizeable intercept on the *y*-axis represents reaction by an uncatalysed pathway, while the positive slope indicates the presence of a base catalysed route. The data conform to eqn. (1) with the condition $k_{-1} \gg k_2 + k_B[B]$, resulting in eqn. (4).

$$k_A = K_1k_2 + k_1k_{An}[\text{aniline}] \quad (4)$$

Values obtained for K_1k_2, K_1k_{An}, and for K_1k_{DABCO} obtained in the presence of added DABCO, are collected in Table 5.

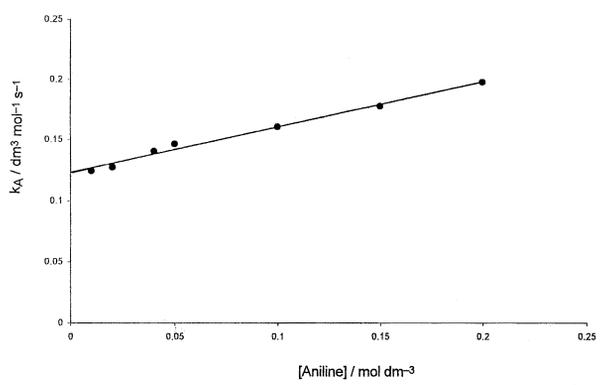


Fig. 2 Plot of k_A *versus* [aniline] in DMSO at 25 °C for the reaction of 4-chlorophenyl 2,4,6-trinitrophenyl ether.

Table 2 Kinetic results for the reactions of **4** with aniline, 0.01 mol dm^{-3}, and various concentrations of DABCO in acetonitrile at 25 °C

	$k_A/10^{-2}$ dm^3 mol^{-1} s^{-1}				
[DABCO]/mol dm^{-3}	4-CH_3	4-H	4-Cl	4-NO_2	3-NO_2
0.01	1.92	1.94	3.19	3.81	4.41
0.02	3.36	3.30	4.90	6.84	6.41
0.03	5.36	5.27	7.61	10.0	9.60
0.04	6.90	6.85	9.79	13.5	12.1
0.05	8.67	8.66	12.7	17.8	15.2
0.06				20.1	20.0

Table 3 Kinetic results for the reaction of **4** with aniline in the presence of DABCO, 0.01 mol dm^{-3}, in acetonitrile at 25 °C

	$k_A/10^{-2}$ dm^3 mol^{-1} s^{-1}				
[Aniline]/mol dm^{-3}	4-CH_3	4-H	4-Cl	4-NO_2	3-NO_2
0.02	2.01	2.09	3.94	5.19	4.61
0.04	3.23	3.27	5.48	6.60	6.80
0.06	3.57	3.73	6.85	8.62	7.93
0.08	4.65	4.61	7.52	9.81	9.70

Base catalysis

The data in Table 4 show that values of k_1, the rate constant for nucleophilic attack by aniline at the 1-position of **4**, are within experimental error independent of the nature of the substituent Y. The value obtained, 0.3 dm^3 mol^{-1} s^{-1}, can be compared[12] with a value of 183 dm^3 mol^{-1} s^{-1} for corresponding attack by *n*-butylamine. The decrease in reactivity of aniline compared to the butylamine is relatively small when considered, Table 6, in relation to the difference in basicity of nearly 8 pK units. This is compatible with an 'early' transition state for nucleophilic attack with relatively little bond formation. The independence of k_1 on the nature of the substituent Y is also in accord with this idea.

The rate constant, k_{An}, represents proton transfer from a zwitterionic intermediate, **5**, to aniline. It has been argued previously[12,15,16] that such trinitro-activated zwitterions are considerably stronger acids than the parent ammonium ion. Hence k_{An} will represent a thermodynamically favourable proton transfer between nitrogen atoms, and its value will depend more on steric constraints than on relative basicities. This is confirmed by the results in Table 4 which give a value for k_{An}/k_{DABCO} of 0.3. Despite the large difference, by 7 pK units, in the basicities of aniline and DABCO their ability to effect the proton transfer from **5** is similar. Since the ratio <1 it is likely that DABCO is rather less sterically demanding than aniline here. In related fashion values of k_{An} are unlikely to depend on the nature of the remote substituent, Y, since this will not affect the steric situation at the reaction centre.

A consequence of this is that changes in value of K_1k_{An} in Table 4 will reflect variations in value of K_1. The general trend is that values of K_1 increase with increasing electron withdrawal by the substituent Y. Since k_1 is independent of Y the changes will result largely from decreases in value of k_{-1} as the stability of **5** increases. The values of k_{An}/k_{-1} in Table 4 similarly reflect variations in values of k_{-1}. The effects are not large, a Hammett plot would give a ρ value of *ca.* 0.5, since the bulk of the negative charge can be delocalised conjugatively into the trinitro-substituted ring.

Values in Table 5 of K_1k_{An} measured in DMSO, similarly show a small dependence on the nature of Y. Interestingly the numerical values of K_1k_{An} are close in the two solvents. However this similarlity is likely to be due to the compensation of large increases in value of K_1 and correspondingly large decreases in value of k_{An} as the solvent is changed from acetonitrile to DMSO. It has been shown previously[12] that values of equilibrium constants for σ-adduct formation are several orders of magnitude higher in DMSO than in acetonitrile. The dominant factor here is likely to be the greater ability of DMSO to solvate charged species.[17,18] However values of k_{An} in related systems are considerably lower in DMSO. It

Table 4 Summary of the rate data for the reaction of **4**, Y-phenyl-2,4,6 trinitrophenyl ethers, with aniline in acetonitrile

Reactant Y	K_1k_{An}/dm^6 mol^{-2} s^{-1}	k_{An}/k_{-1} dm^3 mol^{-1}	k_1/dm^3 mol^{-1} s^{-1}	K_1k_{DABCO}/dm^6 mol^{-2} s^{-1}	k_{An}/k_{DABCO}
4-CH_3	0.48 ± 0.02	1 ± 0.5	0.48 ± 0.20	1.5 ± 0.3	0.32 ± 0.10
H	0.48 ± 0.02	2 ± 1	0.24 ± 0.10	1.6 ± 0.2	0.30 ± 0.05
4-Br	0.85 ± 0.03	2.6 ± 1	0.33 ± 0.10	2.1 ± 0.1	0.40 ± 0.05
4-Cl	0.95 ± 0.03	3.7 ± 1	0.26 ± 0.08	2.7 ± 0.4	0.35 ± 0.10
4-NO_2	1.03 ± 0.03	4 ± 1	0.26 ± 0.08	3.4 ± 0.3	0.30 ± 0.05
3-NO_2	1.13 ± 0.05	3 ± 1	0.38 ± 0.10	3.2 ± 0.4	0.35 ± 0.10

Table 5 Summary of rate data[a] for reaction of **4**, Y-phenyl 2,4,6-trinitrophenyl ethers, with aniline in DMSO

Reactant, Y	$K_1k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}	K_1k_{An}/dm^6 mol^{-2} s^{-1}	K_1k_{DABCO}/dm^6 mol^{-2} s^{-1}	k_{An}/k_{DABCO}	k_{An}/k_2 dm^3 mol^{-1}
4-CH_3[b]	5.5	0.42	1.2	0.35	7.6
H[b]	5.0	0.27	1.6	0.17	5.4
4-Cl[c]	12.3	0.37	1.5	0.25	3.0
4-Br[c]	12.3	0.46	1.9	0.24	3.7
4-CN[d]	22.0	0.35	1.3	0.27	1.6
4-NO_2[b]	32.0	0.65	0.9	0.72	2.0

[a] Values quoted are ±10%. [b] Data from ref. 13. [c] Present work. [d] Data from ref. 14.

Table 6 Comparison of pK_a values

Acid	Acetonitrile	DMSO[c]
Aniline H^+	10.56[a]	3.82
n-Butylamine H^+	18.26[a]	11.12
DABCO H^+	18.29[a]	9.06
2,4,6-Trinitrodiphenylamine	19.97[b]	8.01

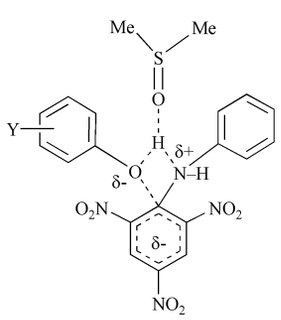
[a] Ref. 21. [b] Current work. [c] Ref. 22.

has been argued[12] that this reflects the excellent hydrogen-bond acceptor properties of DMSO, so that the amino proton to be transferred to base will be strongly associated with the solvent. Before the proton transfer may occur the hydrogen bond to solvent must be broken.

Uncatalysed pathway

The likely mechanism for the k_2 step involves intramolecular proton transfer from nitrogen to oxygen in the zwitterions, **5**, coupled with carbon–oxygen bond breaking.[1,2] The results for DMSO in Table 5 show that values of K_1k_2 are more susceptible than values of K_1k_{An} to changes in the nature of Y. This is compatible with the involvement of the expulsion of phenoxide in the k_2 step, so that values increase as the electron withdrawing capability of Y increases.

In contrast the k_2 step makes a negligible contribution to the reaction flux in acetonitrile, indicating a higher value of the ratio k_{An}/k_2. It is known[12] that values of k_{An} are considerably higher in acetonitrile than in DMSO. The present results show that values of k_2 do not experience a similar solvent dependence. A possible explanation is that the good hydrogen-bonding properties of DMSO allow a solvent assisted pathway with a transition state such as **9**. There is evidence for bifurcated hydrogen bonds in both small molecule crystal structures, and in protein structures.[19,20]



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Ionisation of 2,4,6-trinitrodiphenylamine

Interestingly in the presence of DABCO, a relatively strong base, the reaction product 2,4,6-trinitrodiphenylamine, **7**, is sufficiently acidic to ionise to give **8**, $\lambda_{max} = 440$ nm, $\varepsilon = 2.8 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The UV/visible spectra in Figure 3 show the conversion of **7** to **8** as the concentration of DABCO is increased at constant concentration of DABCO H^+. Measurements of absorbance at 440 nm allowed the calculation of a value of 0.021 ± 0.002 for K_3, the equilibrium constant relating to eqn. (5).

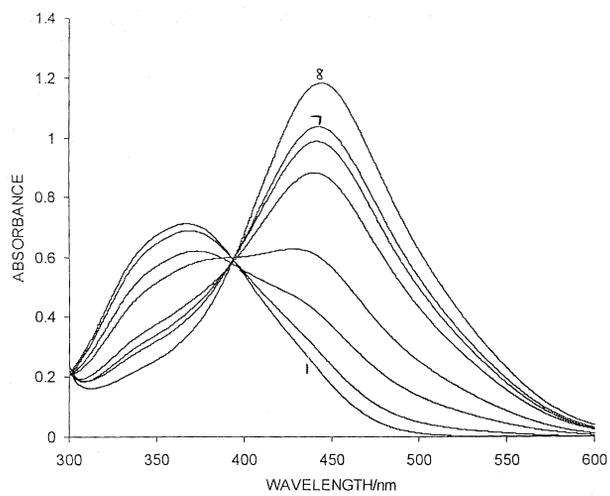


Fig. 3 UV/visible spectra of **7**, 5×10^{-5} mol dm^{-3}, in acetonitrile containing [DABCO H^+], 1.15×10^{-3} mol dm^{-3} and 1–7, [DABCO], 0, 0.005, 0.015, 0.031, 0.069, 0.092 and 0.115 mol dm^{-3}. Spectrum 8 contains [DABCO] 0.096 mol dm^{-3}and zero [DABCO H^+].

$$\mathbf{7} + \text{DABCO} \rightleftharpoons \mathbf{8} + \text{DABCO H}^+ \qquad (5)$$

Hence in acetonitrile the pK_a value of **7** is 1.7 units higher than that of DABCO H^+. The data collected in Table 6 show that in DMSO the order is reversed so that 2,4,6-trinitrodiphenylamine is a stronger acid than DABCO H^+. This reflects the enhanced ability of DMSO, compared to acetonitrile, to solvate the delocalised aromatic anion, **7**, and the DABCO H^+ cation. Hence the equilibrium of eqn. (5) is moved to the right.

Reactions with *N*-methylaniline

Substitutions involving *N*-methylaniline may be considerably slower than the corresponding reactions of aniline. When nucleophilic attack is rate-limiting this is reasonably attributed to the greater steric requirement of the secondary amine. Thus in reaction with 1-chloro-2,4-dinitro-6-X-benzenes in acetonitrile the aniline/*N*-methylaniline reactivity ratio was found[23] to increase from 1.8 to 2×10^4 as the 6-substituent was varied from H to NO_2. Studies of base catalysed reactions have produced conflicting results.[24,25] However reactions of **4**, Y = 4-NO_2 in methanol yielded ratios of 2×10^2 and 3×10^4 respectively for uncatalysed and catalysed pathways.[26]

We found that studies by uv/vis spectroscopy of the reactions of **4**, 5×10^{-5} mol dm^{-3}, with *N*-methylaniline, 0.1 mol dm^{-3}, in acetonitrile were not successful. The reactions were very slow and did not produce the expected product, *N*-methyl-2,4,6-trinitrodiphenylamine, **10**, λ_{max} = 425 nm, $\varepsilon = 6.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}. This may be due to trace quantities of impurities in the solvent or the amine, which had been re-distilled.

However ^{1}H NMR measurements, with higher concentrations of reagents in CD_3CN solvent, were more fruitful and as shown in Figure 4 show the development of bands

Table 7 Kinetics of reaction of 4-nitrophenyl 2,4,6-trinitrophenyl ether, 0.04 mol dm^{-3}, with *N*-methylaniline 0.25 mol dm^{-3} in CD_3CN at 25 °C.

	Relative concentrations[a]		
Time/10^5 s	**A**	**C**	k_{obs}[b]/10^{-6} s^{-1}
0.92	91.4	8.6	1.0
1.74	80.6	19.4	1.2
2.61	73.2	26.8	1.2
3.50	65.4	34.6	1.2
6.05	48.7	51.3	1.2
6.93	45.0	55.0	1.2
9.55	34.3	65.7	1.1
12.2	26.5	73.5	1.1
13.0	24.1	75.9	1.1
14.7	20.5	79.5	1.1

[a] Determined by ^{1}H NMR integration of bands at δ 9.11 due to **A**, 4-nitrophenyl 2,4,6-trinitrophenyl ether, and at δ 8.85 due to **C**, *N*-methyl 2,4,6-trinitrodiphenylamine. [b] Calculated as $(1/t)\ln(100/[\mathbf{A}])$.

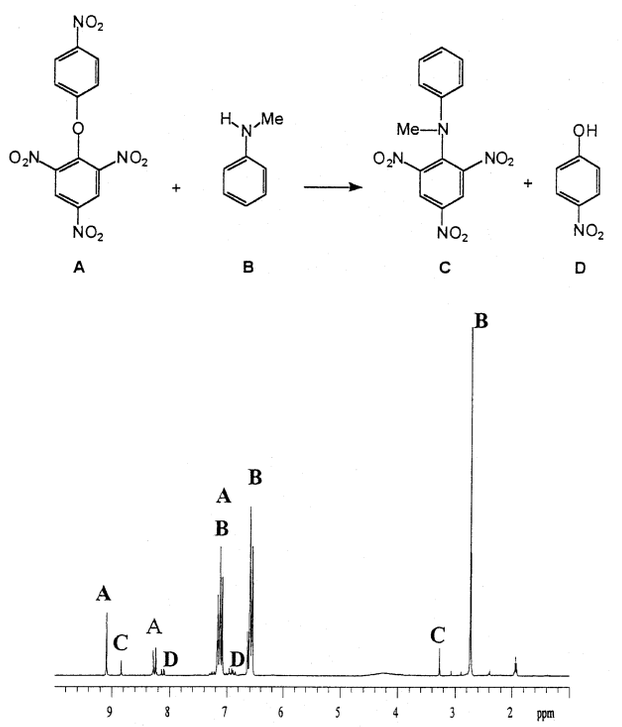


Fig. 4 ^{1}H NMR spectrum of the reaction of 4-nitrophenyl-2,4,6-trinitrophenyl ether, 0.04 mol dm^{-3}, with *N*-methylaniline, 0.25 mol dm^{-3}, in CD_3CN after 48 hours at 25 °C.

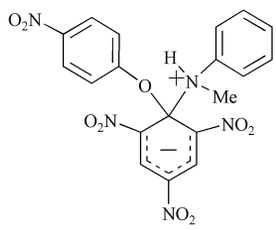
attributable to the expected reaction products. Integration of bands due to reactant and product allowed the calculation of a value for the first order rate constant, k_{obs}. Typical data are in Table 7. Due to the slowness of the reactions which were carried out over several days, measurements were limited to the 4-nitrophenyl derivative.

Values obtained for k_{obs} in CD_3CN were 1.15×10^{-6} s^{-1} and 1.0×10^{-5} s^{-1} when the amine concentrations were 0.25 and 0.85 mol dm^{-3} respectively. The results indicate an approximately squared dependence of k_{obs} on the amine concentration, showing that the base catalysed pathway is dominant. In terms of eqn. (2), the condition $k_{-1} \gg k_B[B]$ applies. Division of k_{obs} by the square of the amine concentration leads to a value for $K_1k_{N\text{–}MeAn}$ of $(1.6 \pm 0.2) \times 10^{-5}$ dm^6 mol^{-2} s^{-1} where $k_{N\text{-}MeAn}$ represents the rate constant for proton transfer from the zwitterionic intermediate, **11**, to *N*-methylaniline. The value, from Table 4, of K_1k_{An} for the corresponding reaction of aniline is 1.03 dm^6 mol^{-2} s^{-1} which is *ca.* 10^5 higher than the value of *N*-methylaniline.

Table 8 Rate data[a] for the reaction of **4**, Y = 4-NO_2 with *N*-methylaniline in [$^2H_6$] DMSO at 25 °C

[*N*-Methylaniline]/ mol dm^{-3}	k_{obs}[b]/10^{-6} s^{-1}	k_A/10^{-6} dm^3 ml^{-1} s^{-1}
0.4	2.7	6.7
0.6	4.7	7.8
0.8	7.8	9.8

[a] Measured by integration of ^{1}H NMR bands, with substrate 0.04 mol dm^{-3}. [b] Values ±10%.



11

The lower value for the secondary amine is likely to be the result of decreases in both K_1 and in k_{An}. In **11** there will be considerable steric crowding at the 1-position resulting in a reduction in the value of K_1. Also it is known[7,12,15] that rate constants for proton transfer in related adducts are drastically reduced by increasing steric hindrance to approach of the reagents. Hence a major factor here is likely to be the much smaller value of $k_{N\text{–}MeAn}$ than of k_{An}.

An additional factor which may contribute[1,2] to lower values of rate constants for proton transfer in reactions of *N*-methylaniline is intramolecular hydrogen bonding in the zwitterion **11** between the N–H proton and an *ortho*-nitro group. The presence of such hydrogen bonding, affecting the proton to be transferred, is often used as an argument to explain differences in reactivity between primary and secondary amines.[1,2] (In the case of primary amines there will always be one non-hydrogen-bonded proton available for transfer.)

Nevertheless comparison of our results for acetonitrile with those obtained in DMSO, detailed below, do not provide evidence for such intramolecular interaction and are better interpreted in terms of steric effects alone.

The data in Table 8 for reaction of **4**, Y = 4-NO_2 with *N*-methylaniline in [$^2H_6$]DMSO show a similar pattern to those obtained with aniline with both uncatalysed and base catalysed pathways contributing to the reaction flux. The results conform to an equation of type 4 with $K_1k_2 = 3 \times 10^{-6}$ dm^3 mol^{-1} s^{-1} and $K_1k_{N\text{–}MeAn} = 9 \times 10^{-6}$ dm^6 mol^{-2} s^{-1}. Comparison with the results in Table 5 for reaction with aniline indicate a factor of *ca.* 10^5 in each of these values.

Interestingly this is exactly the same aniline/*N*-methylaniline reactivity ratio as found in acetonitrile. If intramolecular hydrogen bonding to the *ortho*-nitro group were an important factor in determining the reactivity of **11** then differential effects would be expected between acetonitrile, the less polar solvent where such bonding should be strong, and DMSO, an excellent H-bond acceptor where hydrogen bonding should be to the solvent.[12] In DMSO the weaker intramolecular hydrogen bonding would be expected to lead to a lower value of the aniline/*N*-methylaniline reactivity ratio, which is not observed experimentally. It appears that in this case, at least, where there is severe steric crowding at the reaction centre, steric effects alone, which should not be strongly solvent dependent, can adequately explain the observed reactivity patterns.

Experimental

Diphenyl ethers, **4**, were prepared[13] by the reaction of picryl chloride with one equivalent of base in the presence of an

Table 9 ^{1}H NMR shifts in CD_3CN, and melting points for reactants and products.

Compound	^{1}H NMR Shifts[a]					mp/°C	
	H3,5	H2′	H3′	H4′	Other	Observed	Literature
4, Y = H	9.03	7.00	7.40	7.25	—	151	153[27]
4, Y = 4-Cl	9.02	6.98	7.52	—	—	135	—
4, Y = 4-Br	9.03	6.93	7.52	—	—	141	—
4, Y = 4-Me	8.99	6.82	7.17	—	2.30(Me)	100	103[28]
4, Y = 4-NO_2	9.11	7.15	8.26	—	—	158	157[28]
4, Y = 3-NO_2	9.11	7.81	—	8.05	{7.65(H5′) 7.43(H6′)	172	174[28]
7	8.96	7.15	7.33	7.25	9.96NH	179	178[29]
10	8.85	6.86	7.26	7.00	3.27(Me)	127	108[23]

[a] Compounds **4** are numbered as 4′- and 3′-substituted phenyl 2,4,6-trinitrophenyl ethers. **7** and **10** are 2,4,6-trinitrodiphenylamine, and its *N*-methyl derivative respectively. *ortho*-coupling, *J* 7–8 Hz is observed.

excess of the appropriate phenol in aqueous ethanol. Recrystallisation was from ethanol. 2,4,6-Trinitrodiphenylamine and its *N*-methyl derivative were prepared by reaction of picryl chloride with a four-fold excess of the appropriate amine in ethanol. Recrystallisation was from ethanol. C,H,N analyses of all substrates were in excellent agreement with theoretical values. ^{1}H NMR data and melting points are listed in Table 9. DABCO, acetonitrile and DMSO were the purest available commercial samples; Aniline, and *N*-methylaniline were redistilled before use.

^{1}H NMR spectra were measured with Varian Mercury 200 MHz or Varian Unity 300 MHz instruments. UV/visible spectra and kinetic measurements with aniline were made at 25 °C with a Perkin-Elmer Lambda 2 or a Shimadzu UV PC spectrophotometer. First order rate constants were measured with aniline concentration in large excess of substrate concentration, 5×10^{-5} mol dm^{-3}, and were evaluated using standard methods. Values are precise to ±3%. Kinetic measurements with *N*-methylaniline were made using ^{1}H NMR spectroscopy in deuteriated solvents and are precise to ±10%.

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