Rapid Scan Ultraviolet Spectroscopy of the Formation of 1,1- and 1,3-Complexes. Reaction of 1-Methoxy-2,6-dinitro-4-trifluoromethylbenzene with Piperidine, Pyrrolidine, and n-Butylamine in Dimethyl Sulphoxide

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Rapid scan u.v. spectra for the reactions of 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene with piperidine, pyrrolidine, and n-butylamine in dimethyl sulphoxide have been observed. The formation not only of 1,1-complexes but also of 1,3-complexes has been confirmed. Equilibrium constants for the formation of the 1,1- and 1,3-complexes have been determined and compared with data for the related systems.

In flow n.m.r. spectroscopy of the reaction of 2,4,6-trinitroanisole with n-butylamine in methanolic dimethyl sulphoxide (DMSO) Fyfe *et al.* have confirmed that the intermediate 1,1-complex (**1**; OAlk = OMe, NR^1R^2 = NHBu) appeared transiently on the reaction pathway and suggested that the 1,3-complex (**2**; OAlk = OMe, NR^1R^2 = NHBu) is formed in the initial stages of the reaction.[1] Kinetic studies of the reactions of 2,4,6-trinitrophenetole with aliphatic amines[2] and 2,4,6-trinitroanisole with n-butylamine[3] in DMSO have recently confirmed the rapid formation of the 1,3-complex (**2**) followed by the appearance of the intermediate 1,1-complex (**1**).

We have previously observed the absorption spectra of the intermediate complex (**3**) in the reactions of 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene with piperidine and n-butylamine in DMSO and reported kinetic data for the formation[4,5] and decomposition[5] of (**3**).

In this paper we report rapid scan u.v. spectroscopic studies of the reactions of 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene (**4**) with piperidine, pyrrolidine, and n-butylamine in DMSO.

Results

Rapid Scan U.v. Spectroscopy.—Initially we tried to observe spectra for the reaction of (**4**) with sodium methoxide in methanolic DMSO. Curves (a) and (b) in Figure 1 are the spectra observed 42 ms and 150 s after mixing, respectively. The absorption with $\lambda_{max.}$ 463 and 358 nm, which appeared at the initial stage, is attributed to the 1,3-complex (**6**).[6] The final spectrum (b) with $\lambda_{max.}$ 545 and 350 nm is due to the 1,1-complex (**5**).[6,7]

Curves (c) and (d) are the rapid scan u.v. spectra observed 0.6 and 40 s after mixing of (**4**) with piperidine in DMSO, respectively. It is revealed that two coloured species appeared with $\lambda_{max.}$ 558 and 480 nm in the visible region. The first coloured species, having a band 480 nm, appeared predominantly in the initial stage and the second coloured species, with $\lambda_{max.}$ 558 nm, was predominant in the final stage. Some of the first coloured species was present at equilibrium.

From comparison with curves (a) and (b), the absorption band at $\lambda_{max.}$ 480 nm is assigned to (**8a**) and that at $\lambda_{max.}$ 558 nm to (**7a**).

The spectral behaviour of the reaction of (**4**) with pyrrolidine is similar to the (**4**)–piperidine system: (**7b**), $\lambda_{max.}$ 559 nm; (**8b**), $\lambda_{max.}$ 480 nm.

Complexes (**7c**) and (**8c**) from (**4**) and n-butylamine have their absorption bands at $\lambda_{max.}$ 566 and 490 nm in the visible region, respectively.

Equilibrium Constants. Reaction of (**4**) *with Piperidine.*—Equilibrium measurements were made in the presence of piperidine in large excess of (**4**) at fixed concentration of piperidine hydrochloride. Under these conditions, the appearance of the absorption at 480 nm was more rapid by two-fold than that at 558 nm and distinct equilibrium absorbances at 480 and 558 nm could be obtained. Data are listed in Table 1.

As some of the 1,3-complex (**8a**) as well as the 1,1-complex (**7a**) is present at equilibrium, equation (i) can be written.

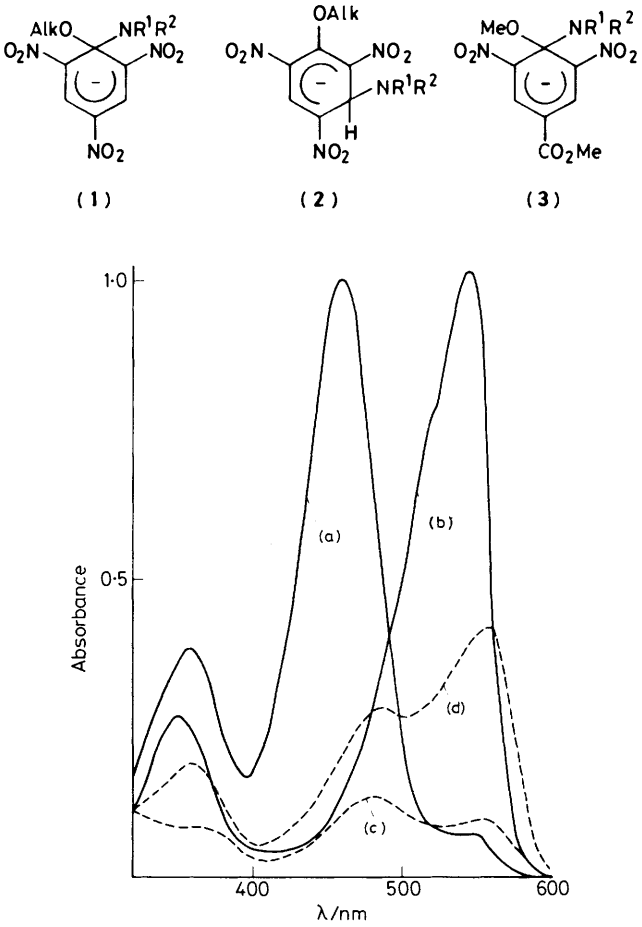
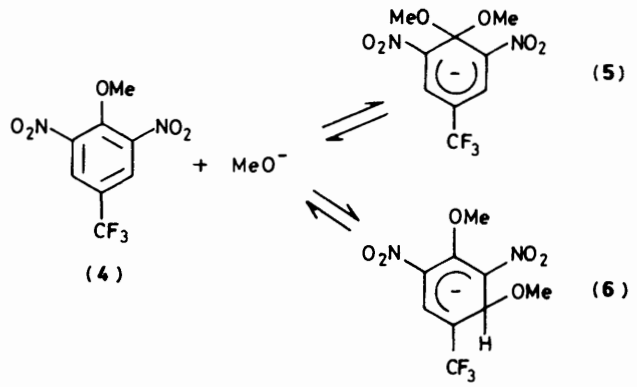


Figure 1. U.v. spectra for reaction of (**4**) (4.0×10^{-5}M) with sodium methoxide (0.012M) in methanolic DMSO (0.8% methanol by volume): (a) and (b), 42 ms (sweep time = 20 ms) and 150 s after mixing respectively; spectra for reaction of (**4**) (4.0×10^{-5}M) with piperidine (0.20M) in DMSO: (c) and (d), 0.6 and 40 s (sweep time = 100 ms) after mixing respectively

Table 1. Equilibrium data of 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene with piperidine in DMSO at 25 °C[a]

[piperidine]/M	A_{558}[b]	A_{480}	$A_{480.1}$[c]	$A_{480.3}$[d]	$K_{c.3}$/l mol^{-1}[e]
0.050	0.0105				
0.074	0.023	0.0116	0.0037	0.0079	0.0048
0.100	0.044	0.022	0.0070	0.0150	0.0051
0.119	0.057	0.032	0.0091	0.023	0.0056
0.149	0.088	0.050	0.0141	0.036	0.0057
0.20	0.0146	0.080	0.023	0.057	0.0052
				mean	0.0053

[a] $[(4)]_0$ = 6.0 × 10^{-5}M; [piperidine hydrochloride] = 0.0050M. [b] Absorbance of 1,1-complex at 558 nm. [c] Absorbance of 1,1-complex at 480 nm. [d] Absorbance of 1,3-complex at 480 nm. [e] Calculated using equation (iii).



Equilibrium constants $K_{c.1}$ and $K_{c.3}$ are defined by equations (ii) and (iii) respectively, where $[(4)]_0$ designates the stoicheiometric concentration of (4).

$$(4) + 2\,NR^1R^2H \rightleftharpoons (7) + NR^1R^2H_2^+ \rightleftharpoons (8) + NR^1R^2H_2^+ \quad \text{(i)}$$

$$K_{c.1} = \frac{[(7)][NR^1R^2H_2^+]}{\{[(4)]_0 - [(7)] - [(8^2)]\}[NR^1R^2H]^2} \quad \text{(ii)}$$

$$K_{c.3} = \frac{[(8)][NR^1R^2H_2^+]}{\{[(4)]_0 - [(7)] - [(8)]\}[NR^1R^2H]^2} \quad \text{(iii)}$$

Under our conditions, $[(4)]_0 - [(7)]$ is much larger than [(8)]* and so equation (ii) is reduced to (iv). A Benesi–

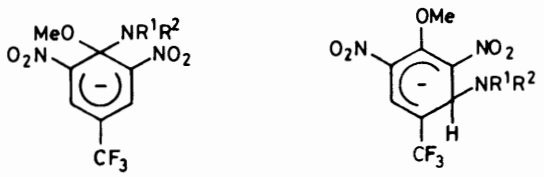
$$K_{c.1} = \frac{[(7)][NR^1R^2H_2^+]}{\{[(4)]_0 - [(7)]\}[NR^1R^2H]^2} \quad \text{(iv)}$$

Hildebrand-type equation (v) is derived,[4] where A and ε are the equilibrium absorbance and molar extinction coefficient, respectively.

$$\frac{[(4)]_0}{A} = \frac{[NR^1R^2H_2^+]}{K_{c.1}\varepsilon[NR^1R^2H]^2} + \frac{1}{\varepsilon} \quad \text{(v)}$$

A plot of $[(4)]_0/A_{558}$ *versus* $[NR^1R^2H]^{-2}$ (Figure 2) is linear a slope of 1.42 × 10^{-5} mol^3 l^{-3}. The straight line passes near the origin. Therefore ε_{558} cannot be determined precisely.

The molar extinction coefficient in methanolic DMSO for (5), which has the same electronic structure as (7), has been



a; NR^1R^2H = piperidine
b; NR^1R^2H = pyrrolidine
c; NR^1R^2H = n-butylamine

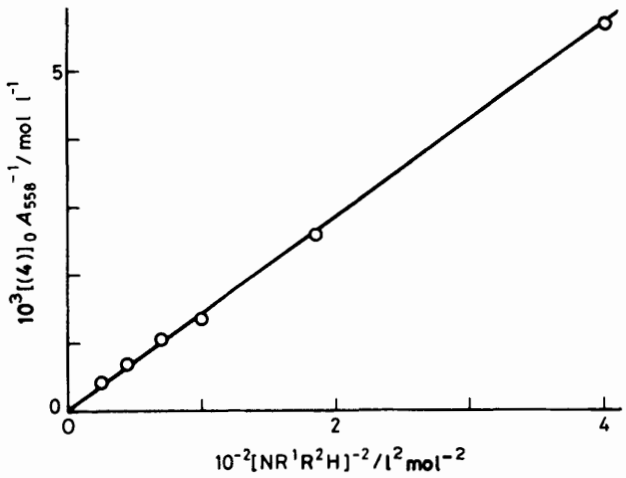
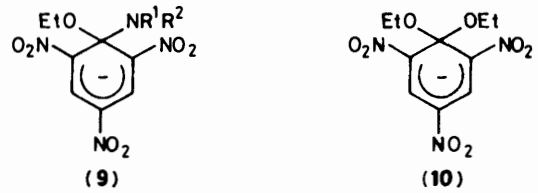


Figure 2. A plot of $[(4)]_0A_{558}^{-1}$ *versus* $[NR^1R^2H]^{-2}$



reported: $\varepsilon_{max(545)}$† 27 800 l mol^{-1} cm^{-1}.[8] There is evidence that adducts formed by attack of alkoxide ions or amines at similarly activated ring positions have rather similar extinction coefficients; an extinction coefficient of *ca.* 25 000 l mol^{-1} cm^{-1} for (9)[2] is close to the value of 25 000 l mol^{-1} cm^{-1} for the diethoxy adduct (10).[9] Thus, assuming that $\varepsilon_{max(558)}$ for (7a) is taken to be 27 800 l mol^{-1} cm^{-1},‡ $K_{c.1}$ is determined to be 0.013 l mol^{-1}.

The apparent absorbance at 480 nm, A_{480}, is made up by the superposition of $A_{480.1}$ and $A_{480.3}$ where $A_{480.1}$ and $A_{480.3}$ represent the absorbance of (7a) and (8a) at 480 nm, respectively. We need to obtain $A_{480.3}$ separately. The ratio of $\varepsilon_{467}/\varepsilon_{max(545)}$ for the absorption of (5) is 0.16. We assume that the bandshape of (7a) is the same as that of (5) and that the absorption of (7a) has the value $\varepsilon_{480}/\varepsilon_{max(558)}$ 0.16. Multiply A_{558} by 0.16 and $A_{480.1}$ is obtained. From $A_{480} = A_{480.1} + A_{480.3}$, $A_{480.3}$ is determined. $\varepsilon_{max(465)}$ 25 600 l mol^{-1} cm^{-1} for (6)

* The estimated ratio of $\{[(4)]_0 - [(7)]\}/[(8)]$ is 26—191 in the range of 0.20—0.074M of piperidine concentration.

† $\varepsilon_{max(545)}$ symbolises the molar extinction coefficient of the absorption maximum at 545 nm.

‡ We thank a referee for this estimate of the extinction coefficient.

Table 2. Equilibrium data of 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene with pyrrolidine in DMSO at 25 °C[a]

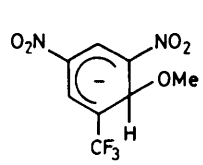
[pyrrolidine]/M	A_{559}[b]	A_{480}	$A_{480.1}$	$A_{480.3}$[c]	$K_{c.3}$/l mol^{-1}[d]
0.040	0.044	0.0145	0.0066	0.0079	0.0167
0.050	0.068	0.021	0.0102	0.0108	0.0147
0.060	0.092	0.029	0.0138	0.0152	0.0146
0.070	0.114	0.038	0.0171	0.021	0.0152
0.080	0.150	0.048	0.023	0.025	0.0143
				mean	0.0151

[a] $[(4)]_0$ = 6.0 × 10^{-5}M; [pyrrolidine hydrochloride] = 0.0050M. [b] Absorbance of 1,1-complex at 559 nm. [c] Absorbance of 1,3-complex at 480 nm. [d] Calculated using equation (iii).

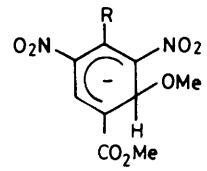
Table 3. Equilibrium data of 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene with n-butylamine in DMSO at 25 °C[a]

[n-butylamine]/M	A_{566}[b]
0.040	0.066
0.050	0.116
0.060	0.128
0.100	0.22

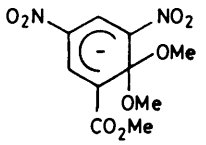
[a] $[(4)]_0$ = 6.0 × 10^{-5}M; [n-butylamine hydrochloride] = 0.0050M. [b] Absorbance of 1,1-complex at 566 nm.



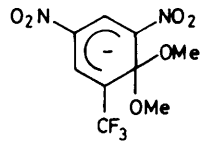
(11)



(12)
a; R = H
b; R = OMe



(13)



(14)

4, this order is similar to that for the formation of an intermediate complex of 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene[4,5,10] and 1-ethoxy-2,4-dinitronaphthalene.[11,12] On the other hand, for attack at the 3-position $K_{c.3}$ values are in the

Table 4. Summary of equilibrium constants at 25 °C.

		n-Butylamine	Pyrrolidine	Piperidine
	(4)	0.15	0.089	0.013
$K_{c.1}$/l mol^{-1}	1-Methoxy-2,6-dinitro-4-methoxycarbonylbenzene	1.32[a]	0.44[b]	0.083[c]
	1-Ethoxy-2,4-dinitronaphthalene	540[d]	3.44[e]	1.55[e]
	(4)	Very low[f]	0.015	0.005
$K_{c.3}$/l mol^{-1}	1,3,5-Trinitrobenzene[g]	1 000	3 500	2 140
	2,4,6-Trinitrobenzyl chloride[h]	73	240	93
	2,2',4,4',6,6'-Hexanitrobibenzyl[i]	25	79	26

[a] From ref. 5. [b] From ref. 10. [c] From ref. 4. [d] From ref. 11. [e] From ref. 12. [f] In the presence of n-butylamine hydrochloride the stability is so low that no complex is formed. [g] From refs. 13 and 14. [h] From ref. 15*a*. [i] From ref. 15*b*.

has been reported in methanolic DMSO.[8] Again, assuming that $\varepsilon_{max(480)}$ for (**8a**) is 25 600 l mol^{-1} cm^{-1}, $K_{c.3}$ is calculated at a given concentration of piperidine using equation (iii). The mean value of $K_{c.3}$ thus obtained is 0.005 l mol^{-1}.

Equilibrium Constants. Reactions of (4) *with Pyrrolidine and n-Butylamine.*—In the (**4**)–pyrrolidine system, distinct equilibrium absorbances at 480 and 559 nm could be obtained and are given in Table 2. Taking $\varepsilon_{max(559)}$ for (**7b**) and $\varepsilon_{max(480)}$ for (**8b**) to be 27 800 and 25 600 l mol^{-1} cm^{-1}, $K_{c.1}$ and $K_{c.3}$ are determined to be 0.089 and 0.015 l mol^{-1}, respectively.

In the (**4**)–n-butylamine system, (**8c**), which was formed in the absence of n-butylamine hydrochloride, did not appear in the presence of the amine salt. The equilibrium absorbance of (**7c**) is given in Table 3. Taking $\varepsilon_{max(566)}$ to be 27 800 l mol^{-1} cm^{-1}, $K_{c.1}$ is determined to be 0.15 l mol^{-1}.

The equilibrium constants are summarised in Table 4 together with data for the related compounds.

Discussion

For attack at the 1-position $K_{c.1}$ values decrease in the order of n-butylamine > pyrrolidine > piperidine. As shown in Table order pyrrolidine > piperidine > n-butylamine. This remarkable change in relative stability may be rationalised as follows.

The normal stability order for amine adducts observed when attack occurs at an unsubstituted ring position is pyrrolidine > piperidine > n-butylamine; examples[13–15] are given in Table 4. This order is expected to apply when steric effects are not too important as observed in the present case for attack at the 3-position. The view[2,15] has been expressed that 1,1-adducts may be destabilised by unfavourable steric interactions when reaction involves bulky amines. Thus with the secondary amines structures (**7a** and **b**) are likely to be destabilised by the proximity of bulky groups at the 1-position. This factor will reduce the values for $K_{c.1}$ for reaction with piperidine and pyrrolidine so that the highest stability is observed for the adduct with n-butylamine.*

The value of $K_{c.1}$ in the (**4**)–amine system is several times smaller than the corresponding one for the 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene–amine system. This is quite analogous to the fact that the K value (2 l mol^{-1}) for (**5**) in methanol is smaller by three-fold than that (6 l mol^{-1}) for the

* We thank a referee for this explanation.

corresponding complex of 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene in the same solvent.[7] This reflects the electron-withdrawing ability of CF_3 and CO_2Me at the *para* position.

In the present case, (**4**) reacts with each amine to form a 1,3-complex. On the other hand, the formation of a 1,3-complex has never been observed in the reactions of 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene with the three amines.[4,5,10] However, (**12b**) with NO_2 and CO_2Me groups *ortho* to the sp^3 ring carbon as well as (**6**) with *o*-NO_2 and *o*-CF_3 has been observed.[6] Formation not only of (**11**) but (**12a**) has been reported, although the stability (K 0.006 l mol^{-1}) of (**12a**) in methanol is somewhat less than that (K 0.012 l mol^{-1}) of (**11**).[16] (**13**) (K 10 l mol^{-1}) and (**14**) (K 14 l mol^{-1}) have been also observed.[7,17]

It is likely that the bulky CO_2Me group at the C-4 position together with NO_2 at C-2 prevent the amines from attacking 1-methoxy-2,6-dinitro-4-methoxycarbonylbenzene at C-3. It seems that the amines are not so hindered by CF_3 at C-4 from attacking 1-methoxy-2,6-dinitro-4-trifluoromethylbenzene (**4**) at C-3. MeO^- is not so bulky, compared with the amines used, so that (**12b**) having *o*-NO_2 and *o*-CO_2Me as well as (**6**) is formed.

Experimental

Materials.—1-Methoxy-2,6-dinitro-4-trifluoromethylbenzene was synthesised by nucleophilic substitution of 1-chloro-2,6-dinitro-4-trifluoromethylbenzene with sodium methoxide and purified by recrystallisation from methanol. The required compound was indicated by elemental analysis (Found: C, 36.4; H, 1.9; N; 10.5. Calc. for $C_8H_5F_3N_2O_5$: C, 36.1; H, 1.9; N, 10.5%) and ^{1}H n.m.r. measurements. Pyrrolidine was refluxed over sodium and distilled. Pyrrolidine hydrochloride was prepared from pyrrolidine and concentrated hydrochloric acid and purified by repeated recrystallisation.[12] DMSO, piperidine, n-butylamine, piperidine hydrochloride, n-butylamine hydrochloride, and sodium methoxide solution were prepared as described previously.[4,5,18]

Measurements.—Rapid scan u.v. spectra at various stages of the reaction were measured with a Union RA 415 rapid scan spectrophotometer. This was equipped with an automatically controlled mixing cell. A mixing cell having the path length of 1 cm was controlled by a thermocirculater. The sweep time could be taken to be 4, 10, 20, 40, 100, and 200 ms.

Absorption spectra were recorded on a Hitachi 340 spectrophotometer.

Acknowledgements

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