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THE TEMPERATURE VARIABLE NMR SPECTRA OF *p*-SUBSTITUTED NITROSOBENZENES

A CORRELATION OF THE ENERGY BARRIER TO RESTRICTED ROTATION WITH HAMMETT FUNCTIONS

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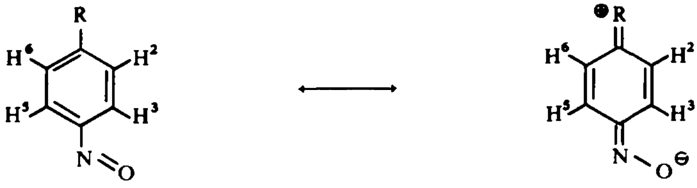
Abstract—The thermal dependence of the NMR spectra of 14 *p*-substituted nitrosobenzenes is described. The barriers to restricted rotation have been calculated, and an attempt to correlate these with Hammett σ functions has been made. The presence of conformational rotamers in those systems having unsymmetrical *p*-substituents is discussed.

THE energy barrier to rotation around the single C—N bond of nitrosobenzenes (**1**) is known to be in the range accessible to study by NMR techniques.[1] The restriction to rotation arises from the partial double bond character of the C—N bond, for which the canonical structure **2** is the major contributor.

The Hammett substituent constant, σ, measures the ability of the substituent to change the electron density at the reacting centre,[2,3] and a correlation between the temperature of coalescence, T_c, or the barrier to rotation, $\Delta G^‡$, with σ might be expected. The temperature dependence of the NMR spectra of a series of *p*-substituted nitrosobenzenes was investigated, and $\Delta G^‡$ was obtained by the method of Gutowsky and Holm.[4]



1 **2**

RESULTS

NMR spectra

The NMR spectra of *p*-nitrosoaniline and N-substituted *p*-nitrosoanilines, and of *p*-nitrosophenol and O-substituted *p*-nitrosophenols are shown in Table 1 and Figs 1 to 5.

In the low temperature spectrum of *p*-nitroso-N-phenylaniline (**3**: R^1 = Ph, R^2 = H), the assignment of the multiplet at τ 2·84 to H^2 is based on the chemical

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TABLE 1

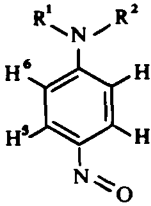
Compound	T °C	NMR spectrum (τ)* (100 MHz)	T °C	NMR spectrum (τ)* (100 MHz)
p-Nitrosoaniline	+30	2·36 (bb, H^3, H^5), 3·26 (d, H^2, H^6) 3·68 (bm, $N\underline{H}_2$)	−80	1·02 (d, H^3, 9 Hz), 2·70 (m, $N\underline{H}_2$), 2·98 (d, H^2, 9 Hz), 3·34 (s, H^5, H^6)
p-Nitroso-N,N-diethyl aniline (3: $R^1 = R^2 =$ Et)	+20	2·3 (bb, H^3, H^5), 3·18 (d, H^2, H^6)	−50	1·08 (dd, H^3, 9·2 Hz), 2·98 (dd, H^2, 9,2 Hz), 3·33 (m, H^5, H^6)
p-Nitroso-N-ethylaniline (3: R^1 = Et, R^2 = H)	+30	2·30 (bb, H^3, H^5), 3·28 (d, H^2, H^6) 3·28 (bb, $N\underline{H}$), 6·64 (m, $C\underline{H}_2$), 8·70 (t, $C\underline{H}_3$, 7 Hz)	−65	1·13 (dd, H^3), 2·59 ($N\underline{H}$), 3·11 (dd, H^2) 3·43 (s, H^5, H^6), 6·71 (bm, $C\underline{H}_2$), 8·77 (m, $C\underline{H}_3$)
p-Nitroso-N-methyl aniline (3: R^1 = Me, R^2 = H)	+30	2·28 (bb, H^3, H^5), 3·28 (d, H^2, H^6) 3·28 (bb, $N\underline{H}$), 7·04 (d, $C\underline{H}_3$)	−70	1·08 (dd, H^3), 2·36 (bb, $N\underline{H}$) 3·10 (dd, H^2), 3·30 (H^5, H^6), 7·05 (bb, $C\underline{H}_3$)
p-Nitroso-N-phenyl aniline (3: R^1 = Ph, R^2 = H)	+30	2·27 (d, H^3, H^5), 2·69 (m, $C_6\underline{H}_5$—$N\underline{H}$), 2·91 (d, H^2, H^6)	−65	0·62 (bb, NH), 0·94 (dd, H^3, 9, 2 Hz), 2·64 (m, $C_6\underline{H}_5$), 2·84 (m, H^2)
p-Nitrosophenol (4: R = H)	0	2·37 (d, H^3, H^5, 10 Hz), 3·41 (d, H^2, H^6, 10 Hz)	−80	low field band has almost disappeared.
Sodium *p*-nitrosophenate (4; R = Na)†	+90	2·34 (bb, H^3, H^5), 3·54 (d, H^2, H^6, 9·5 Hz)	+35	2·08 (dd, H^5, 9·5, 2·5 Hz), 2·72 (dd, H^3, 9·5, 2·5 Hz), 3·60 (m, H^2, H^6)
p-Nitrosophenotole (4: R = Et)	+30	2·12 (d, H^3, H^5, 9 Hz), 2·86 (d, H^2, H^6, 9 Hz), 5·74 (q, $C\underline{H}_2$), 8·54 (t, $C\underline{H}_3$)	−75	0·54 (bd, H^3, 9 Hz), 2·58 (bd, H^2, 9 Hz), 3·06 (bd, H^6, 9Hz), 3·52 (bd, H^5, 9 Hz), 5·81 (q, $C\underline{H}_2$), 8·60 (t, $C\underline{H}_3$)
p-Nitrosoanisole (4: R = Me)	+30	2·12 (d, H^3, H^5, 9 Hz), 2·87 (d, H^2, H^6, 9 Hz) 6·14 (s, $C\underline{H}_3$)	−80	0·52 (d, H^3, 9 Hz), 2·52 (d, H^2, 9 Hz), 3·02 (d, H^6, 9 Hz), 3·51 (d, H^5, 9 Hz) 6·02 (s, $C\underline{H}_3$)

* all spectra were taken as 5% w/v solutions in perdeuterioacetone unless stated otherwise.

† spectrum taken in D_2O.

bb = broad band, d = doublet, dd = double doublet, s = singlet, m = multiplet, q = quartet, t = triplet, bd = broad doublet.

shift, and the apparent major coupling of the double doublets at τ 3·08 and τ 3·52. The assignment of the bands at τ 3·08 and τ 3·52 to the H^6 and H^5 protons respectively, was made by calculating the average position of these bands with the signals for H^2 and H^3, and then comparing these values with the actual positions of the average values known from the spectra taken at higher temperatures. Similar assignments were made for the H^5 and H^6 protons of *p*-nitrosoanisole (**4**: R = Me) and *p*-nitrosophenetole (**4**: R = Et).



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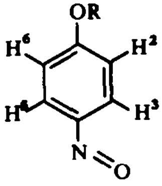

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The assignments of the protons of the sodium salt of *p*-nitrosophenol (**4**: R = Na) are based on those of Norris and Sternhell.[1e]

p-*Nitrosotoluene.* The NMR spectrum of *p*-nitrosotoluene (**1**: R = Me) at −20° showed a doublet at τ 2·15 (H^3, H^5, $J = 8$ Hz), a doublet at τ 2·46 (H^2, H^6, $J = 8$ Hz) and a singlet at τ 7·54 (Me). On cooling, the τ 2·15 doublet broadened and finally disappeared at −80°, when the doublet at τ 2·43 had considerably broadened. A low intensity doublet at τ 1·78 and a multiplet at τ 2·70 in the cold spectrum are visible, probably due to dimer formation.

Nitrosobenzene, ethyl p-*nitrosobenzoate,* p-*nitrosonitrobenzene and* p-*nitrosochlorobenzene.* In all of these cases the coalescence point could not be determined due to difficulties of solubility and dimerization.

In nitrosobenzene, the complex multiplet at τ 2·14 observed in the spectrum at 0° on cooling broadens and then splits into three multiplets at −65°.

The spectrum of ethyl *p*-nitrosobenzoate (**1**; R = CO_2Et) at +30° (Fig. 6), taken as a 2% w/v solution in acetone-d_6, shows a doublet at τ 1·62 (H^3, H^5, $J = 9$ Hz), a doublet at τ 1·98 (H^2, H^6, $J = 9$ Hz), a quartet at τ 5·56 ($O{-}CH_2{-}$) and a triplet at τ 8·57 (Me). On cooling little change occurs in the spectrum until at −30° two new sets of doublets begin to appear at ca. τ 1·85 and τ 2·22. At −65°, the spectrum shows a doublet at τ 1·58 ($J = 8$ Hz), a multiplet at τ 1·88 consisting of two overlapping doublets, a doublet at τ 2·16 ($J = 9$ Hz), two overlapping quartets at τ 5·66, and two overlapping triplets at τ 8·64. The temperature dependence of the spectrum of *p*-nitrosonitrobenzene (**1**: R = NO_2) as a 2% w/v solution in acetone-d_6 is similar to that of ethyl *p*-nitrosobenzoate. At +30°, the spectrum shows a doublet at τ 1·38 (H^3, H^5, $J = 9$ Hz) and a doublet at τ 1·83 (H^2, H^6, $J = 9$ Hz). At −70°, the spectrum shows two sets of doublets at τ 1·28 and τ 1·69 ($J = 9$ Hz) and at τ 1·56 and τ 1·92 ($J = 9$ Hz), of which the latter pair are more intense.

The NMR spectrum of a 2% w/v solution of *p*-nitrosochlorobenzene in acetone-d_6 (**1**: R = Cl) at +10° shows two doublets at τ 2·02 ($J = 9$ Hz) and τ 2·21 ($J = 9$ Hz). On cooling to −50°, new peaks become apparent at higher field than the original doublets, and at −65° the spectrum consists of the original pair of doublets superimposed on a pair of doublets at higher field (τ 2·26, τ 2·45). At −80°, the lowest

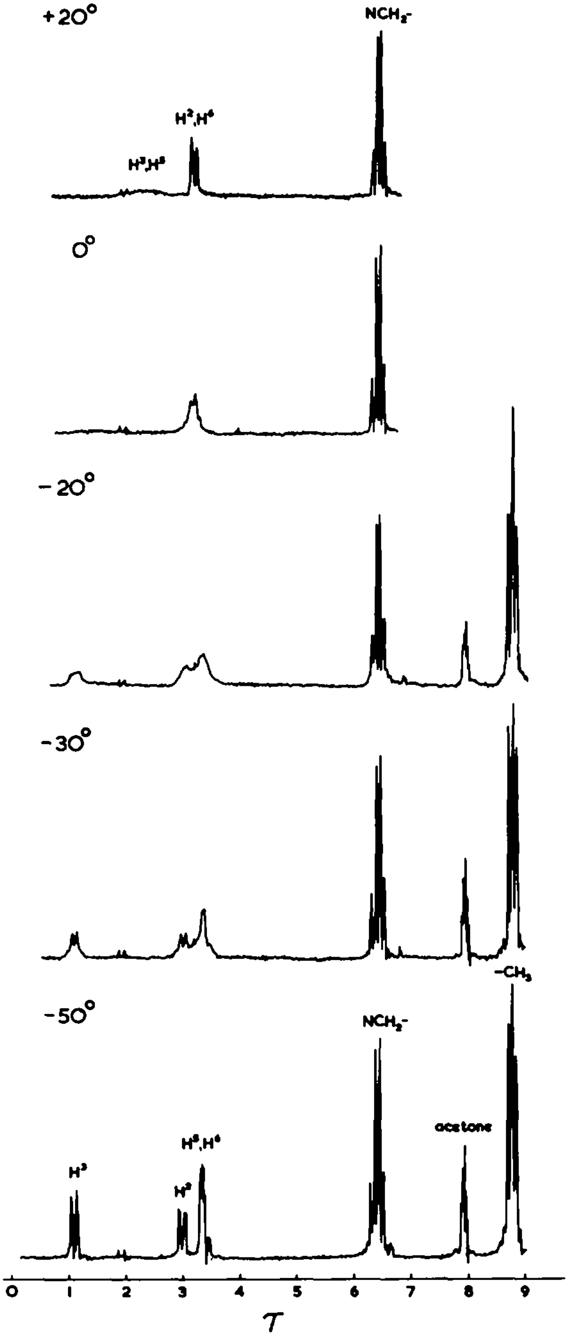


FIG. 1 NMR spectrum of *p*-nitroso-N,N-diethylaniline (3: $R_1 = R_2 = Et$) as a 5% w/v solution in acetone-d_6, taken at various temps at 100 MHz.

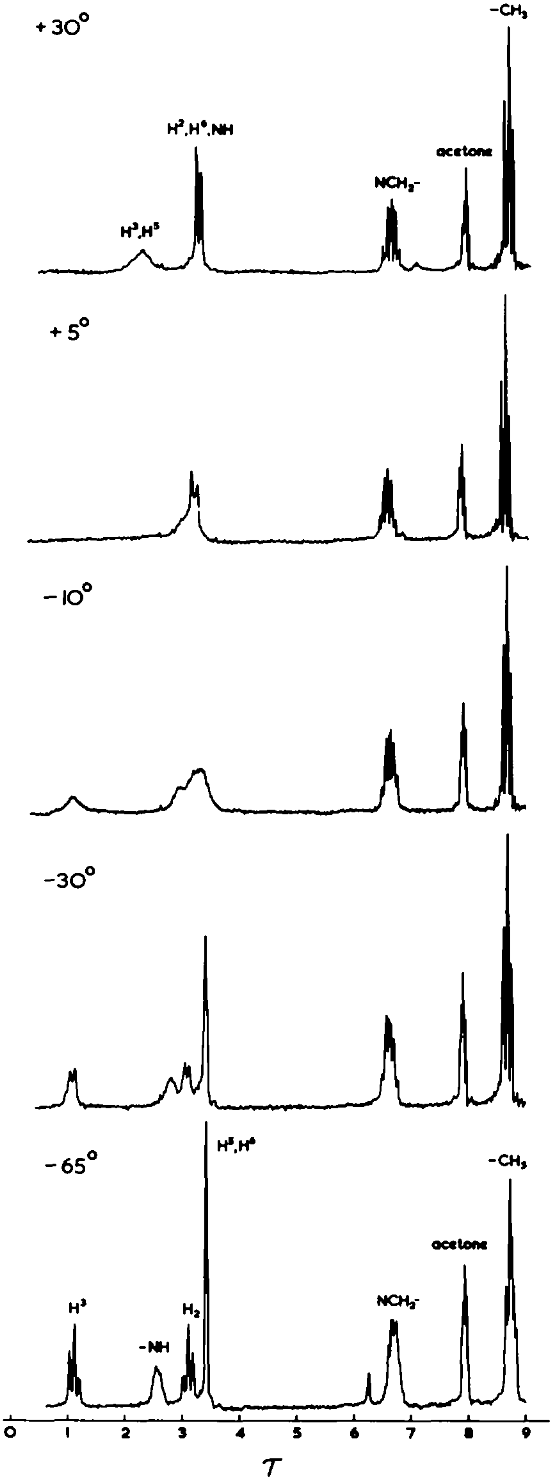


FIG. 2 NMR spectrum of *p*-nitroso-N-ethylaniline (3: R_1 = Et, R_2 = H) as a 5% w/v solution in acetone-d_6 taken at various temps at 100 MHz.

field doublet at τ 1·98 has lost its fine structure, while the remainder of the spectrum remains relatively sharp.

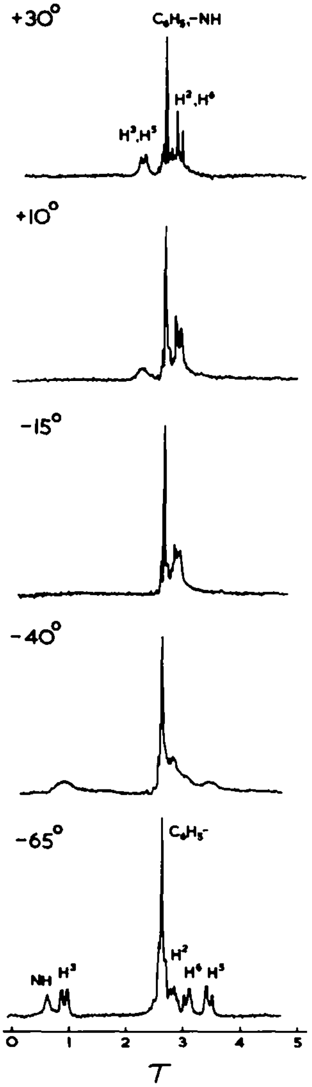


Fig. 3 NMR spectrum of *p*-nitroso-N-phenylaniline (3: R_1 = Ph, R_2 = H) as a 5% w/v solution in acetone-d_6, taken at various temps at 100 MHz.

Rotational barriers. The rate of exchange, k^1, at the temperature of coalescence, T_c, was calculated by the method of Gutowsky and Holm,[4] using Eq. 1, where $\Delta\nu$ is the frequency separation of the resolved signals at low temperature. The values of

$\Delta G^{\ddagger}$ were derived from the Eyring Eq. 2,[5] a unit transmission coefficient (K) being assumed. Eq. 2 was transformed to Eq. 3 for the purpose of calculation.

$$k^1 = \frac{\pi \Delta v}{\sqrt{2}} \tag{1}$$

$$k^1 = K\frac{kT}{h}\exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \tag{2}$$

$$\Delta G^{\ddagger} = 2{\cdot}303\, RT_c\,(10{\cdot}319 - \log_{10} k^1 + \log_{10} T_c) \tag{3}$$

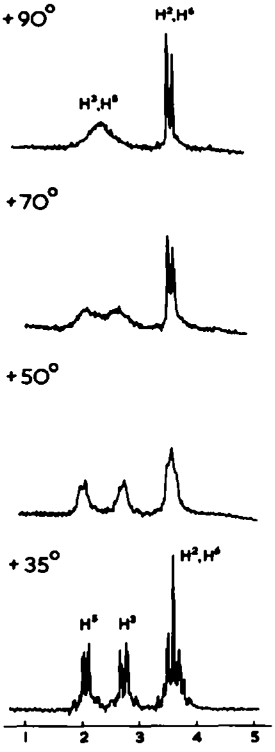


FIG. 4 NMR spectrum of the sodium salt of *p*-nitrosophenol (4: R = Na) as a solution in D_2O, taken at various temps at 100 MHz.

The calculated values of k^1 and $\Delta G^{\ddagger}$ are reported in Table 2. Plots of T_c and $\Delta G^{\ddagger}$ against σ are shown graphically.

The relationship between T_c and σ can only be approximate, since the value of T_c also depends on non-thermodynamic parameters. Also the relationship between $\Delta G^{\ddagger}$ and σ only holds exactly if $\Delta S^{\ddagger} = 0$. However, the errors arising from these factors are likely to be similar for each compound in the series, and compared with the errors involved in deriving parameters from the coalescent temperature they can be neglected.

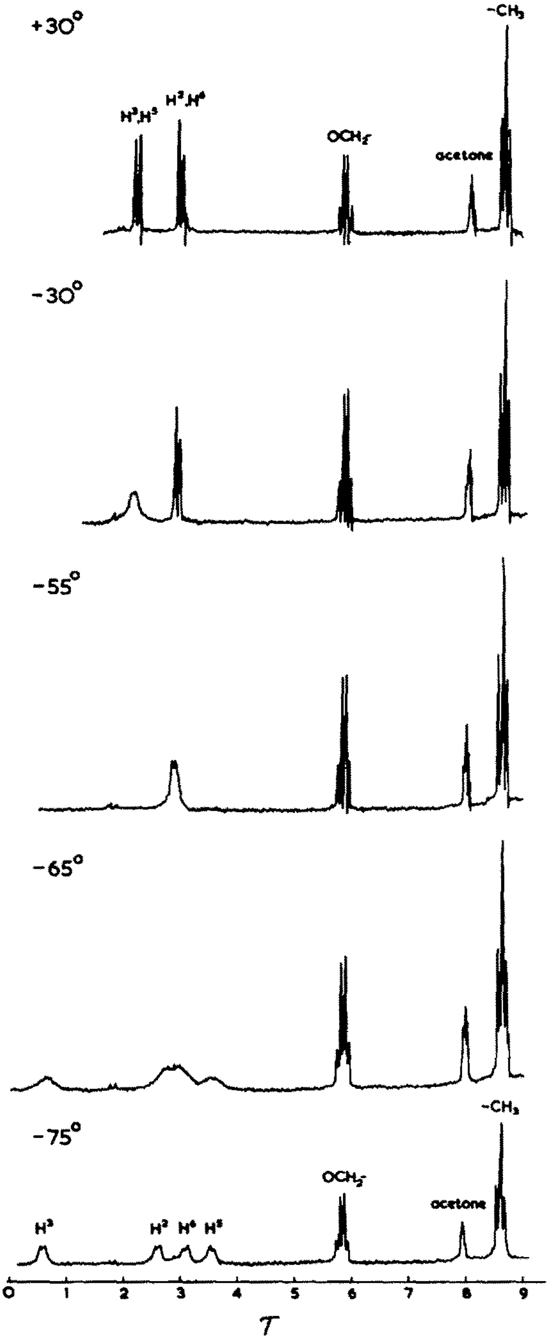
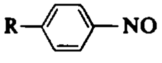


FIG. 5 NMR spectrum of *p*-nitrosophenetole (4: R = Et) as a 5% w/v soln in acetone-d_6, taken at various temps at 100 MHz.

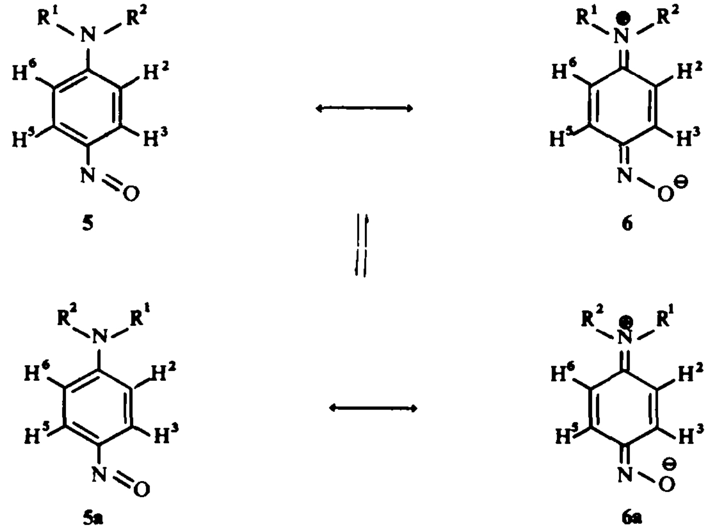
TABLE 2

	T_c °K[a] ±3°	Δν 3,5 Hz	k^1 sec^{-1}	ΔG‡ kcal/mole	σ[d]
R =					
Me	ca. 193	—	—	—	−0·170
OEt	221	298	662	10·0	−0·250
OMe	220	301	669	9·9	−0·268
OH	ca. 193	—	—	—	−0·357
NMe_2	270	232	515	12·4	−0·600
NEt_2	277	226	502	12·8	—
NHMe[b]	270	232	515	12·4	−0·592
NHEt[b]	278	230	511	12·8	—
NHPh	257	256	569	11·7	—
NH_2	269	230	511	12·4	−0·660
ONa[c]	353	67	149	17·3	−1·00[e]

[a] Coalescence temperature of H^3, H^5; [b] The presence of unequal proportions of two rotational isomers has been ignored for the purpose of calculation; [c] Spectrum taken in D_2O; [d] Values from Ref 3; [e] Values from Ref 2.

DISCUSSION

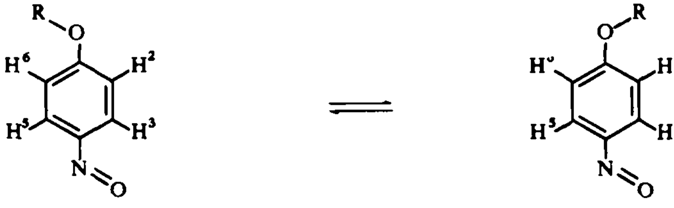
The NMR spectra of the N,N-dialkyl nitrosoanilines show clearly temperature dependent effects expected for restricted rotation around the nitroso C—N bond. At low temperatures the H^3 and H^5 protons are non-equivalent, and the H^3 proton appears at lower field.[1a–c] The restriction of rotation around the C—N aniline bond in these compounds does not have any effect on the spectrum. However, in the mono N-alkyl nitrosoanilines **5** (R^1 = alkyl, R^2 = H) the possibility of rotational isomerism occurs due to the unsymmetrical substituent (**6**, **6a**). The NMR spectrum at low



temperatures of both *p*-nitroso-N-methylaniline (5: R^1 = Me, R^2 = H) and *p*-nitroso-N-ethylaniline (5: R^1 = Et, R^2 = H) reveals the presence of this type of isomerism in these compounds. The low field superimposed doublets in the NMR spectrum at low temperatures of *p*-nitroso-N-ethylaniline (Fig. 2) at τ 1·13 are assigned to the H^3 proton in the two conformational forms **6** and **6a**, and the superimposed doublets at τ 3·11 to the H^2 proton in these conformers. A similar explanation holds for the low temperature spectra of *p*-nitroso-N-methylaniline. The ratio of the conformers was determined from the integrated area of the inner peaks of the doublets, and is approximately 3 : 1, considering a simple first order analysis. It appears probable that the "transoid" form **6** predominates, as dipole interactions are minimised in this structure.

The NMR spectrum at low temperatures (Fig. 3) of *p*-nitroso-N-phenylaniline (5: R_1 = Ph, R_2 = H) indicates that only *one* of the two possible conformational isomers occurs, and this is probably the transoid form.

The possibility of rotational isomerism also occurs in *p*-nitroanisole (7: R = Me) and *p*-nitrosophenetole (7: R = Et). The NMR spectra at low temperatures of these compounds (see for example Fig. 5) indicates that only *one* of these rotamers occurs.*



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In the calculation of exchange rates the equation of Gutowsky and Holm was used in its simplified form, which holds for *two* states having equal populations and lifetimes, and in which the signal width is small in comparison to the signal separation. The only compounds for which this does not apply in the present work are the *p*-nitroso-N-alkyl anilines (5: R^1 = Me, R^2 = H; R^1 = Et, R^2 = H), for which there are two pairs of possible states that do not have equal populations. However, the energy differences between the rotational conformers is small, and it appears unlikely from the work of Bovey *et al.*[6] that large errors will result from not taking these factors into account.

The value of T_c for *p*-nitrosophenol (7: R = H) appears to be lower than that expected from the value of σ. *p*-Nitrosophenol is reported to exist in acetone mainly (70Π,[7] 75Π[1f]) as the tautomer, benzoquinone monoxime, the two forms being in rapid equilibrium.[1e] In dioxane containing 0·5% water, the spectrum was reported to be temperature dependent,[1e] changing from an ABMX to an AA′BB′ pattern on going from 283°K to 393°K. This change was attributed to a change in the rate of rotation around the C—N bond in the monoxime form. The T_c observed at 193°K may be due to the same phenomena, the process occurring at a lower temperature with the more polar solvent. The spectrum of the *p*-nitrosophenolate anion (9) has been interpreted

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* It is possible that the appearance of only one rotamer is due to the occurrence of a rapid lone pair inversion in the oxime form.

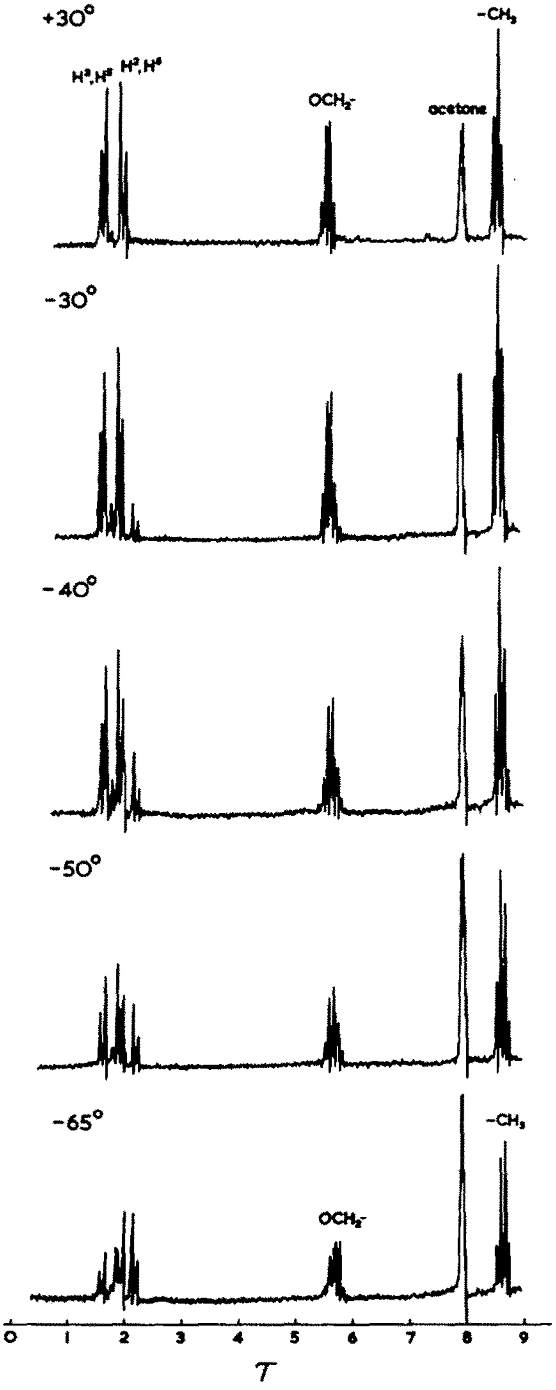


FIG. 6 NMR spectrum of ethyl *p*-nitrosobenzoate (1: $R = CO_2Et$) as a 2% w/v soln in acetone-d_6, taken at various temps at 100 MHz.

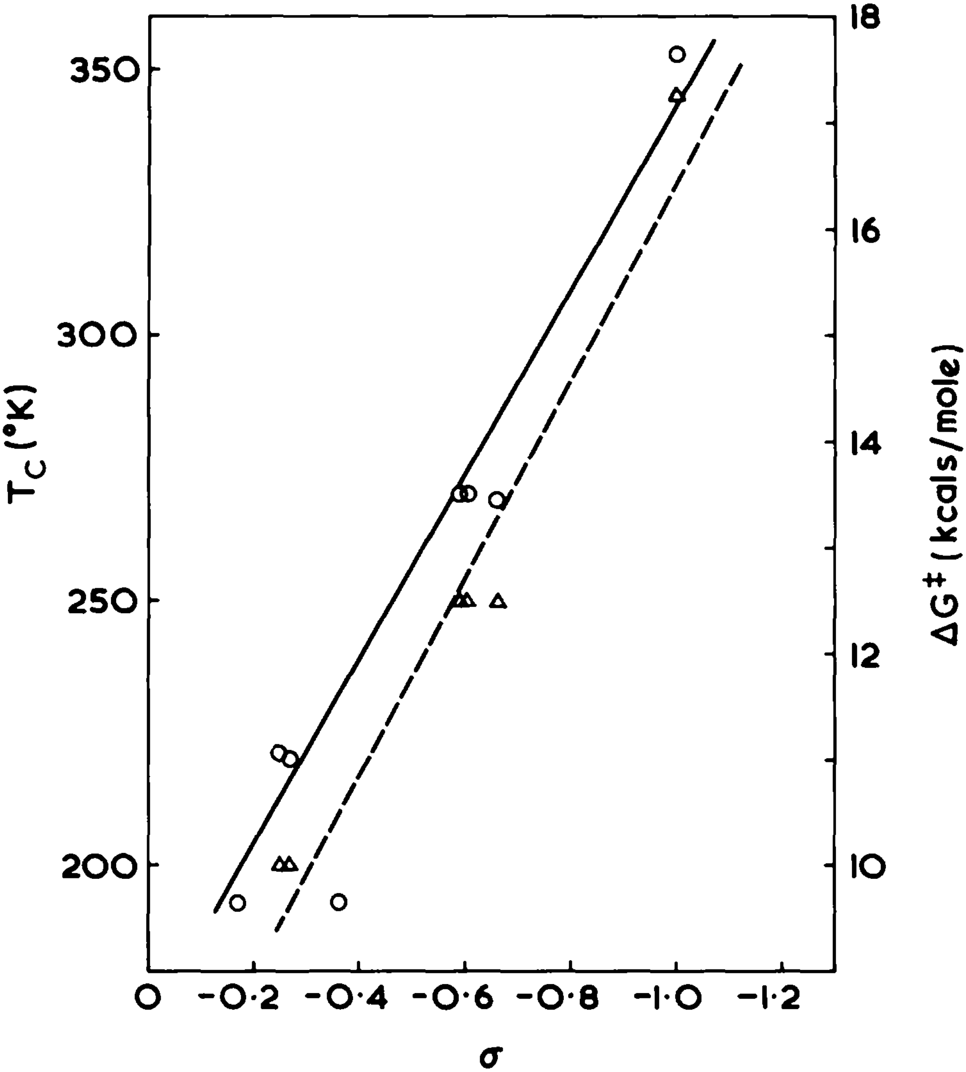
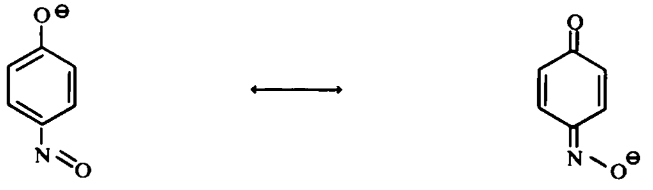


FIG. 7 Plots of coalescence temp (T_c °K) vs σ (circles and solid line), and $\Delta G^‡$ (kcal/mole) vs σ (triangles and broken line).

to suggest that the negative charge is mainly located on the oxime oxygen (**10**).[1e] However, unlike the nitrosophenol-benzoquinone monoxime tautomerism, which involves proton transfer, the phenolate and monoxime anions are canonical resonance forms of the same structure, the monoxime form corresponding to **2**, which we have invoked for restriction around the C—N bond. Comparison of the values for the phenolate anion, and the rotational barriers for the benzoquinone monoxime and *p*-nitrosophenol tautomers, suggests that the contribution of **10** to the overall reasonance structure is that expected for a *p*-substituent with a σ value of −1·0.

The range of Hammett σ values over which the coalescence of the spectra could be observed was small. Attempts to extend the range with electron withdrawing substituents were frustrated by solubility difficulties at low temperatures, and the problem of the formation of dimers.[8] The appearance of the new bands in the spectra of ethyl *p*-nitrosobenzoate, *p*-nitrosobenzene and *p*-nitrosochlorobenzene at low temperature is attributed to the presence of dimers.



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However, over the accessible temperature range approximately linear plots of either T_c or $\Delta G^{\ddagger}$ against σ were obtained. The amount of double bond character of the C—N nitroso bond shows a clear dependence on the electron availability in the benzene ring. With *p*-substituted electron withdrawing groups the possibility occurs that the nitroso group will donate, rather than accept, electrons.* We were, however, using the present experimental methods, unable to detect any restriction of rotation arising from this effect.

EXPERIMENTAL

The *p*-nitroso compounds were obtained commercially or were prepared by standard lit methods.[8–10] All compounds were recrystallized to constant m.p., and the NMR spectra indicated less than 5% impurity. A number of the nitroso compounds are unstable, and in these cases the compounds were recrystallized immediately before taking the spectra. The sample of *p*-nitrosoanisole, after low temp recrystallization from ether, had m.p. 20–21°.[11] *p*-Nitrosonitrobenzene could only be obtained in low yield by the method of Hamberger and Hübner.[12]

NMR spectra were taken on a Varian HA-100 MHz spectrometer with a variable temp probe. The probe temp was calibrated over the range $+40 - 80°$ using a MeOH sample. At the coalescence temp the sample temp was remeasured by this method. The coalescence temps have an error of $\pm 3°$. TMS was used as an internal standard, but all chemical shifts were measured on calibrated paper from the residual acetone peaks, assumed to be τ 7·95. The initial calibration was checked by a frequency counter (Advance time counter Type T.C. 2A).

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