Structural investigations of *C*-nitrosobenzenes. Part 2.[1] NMR studies of monomer–dimer equilibria including restricted nitroso group rotation in monomers

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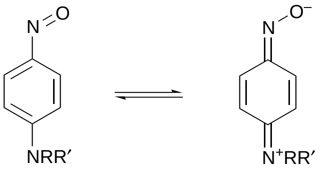
Energy barriers associated with rotation of nitroso groups in monomeric nitrosobenzene and eleven monomeric substituted nitrosobenzenes in solution have been measured by total ^{1}H NMR bandshape analysis. $\Delta G^\ddagger$ (298.15 K) values for the rotations are in the range 31–41 kJ mol^{-1}. The values for 4-substituted compounds correlate well with the Hammett $\sigma_p{}^+$ parameter for the substituent. The experimental energy barrier for nitrosobenzene is compared with theoretical calculations. Monomer–dimer equilibria of these compounds in solution have been investigated, with $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ data calculated for the dissociation of both *Z*- and *E*- azodioxy dimers to monomers. Kinetic data, based on time-dependent and two-dimensional exchange spectroscopy (2D-EXSY) NMR measurements, have been obtained for the dissociation of 3-methylnitrosobenzene and 3,5-dimethylnitrosobenzene dimers. Energy profiles for the ground and transition states of both dimers and monomers (including exchange between both their rotameric forms) are discussed.

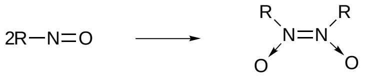
The structural properties of substituted *C*-nitrosobenzenes are of considerable interest as they are unpredictably varied. In the first paper of this series[1] we calculated −N=O substituent constants for a wide range of substituted nitrosobenzenes from ambient and low temperature ^{1}H NMR spectra, thereby making it possible firmly to identify the monomeric and the two dimeric solution species. Earlier studies by ourselves[2] and others[3–8] demonstrated that the various *N*-substituted 4-nitrosoanilines **1** (Scheme 1), which do not form dimers under any conditions of concentration and temperature, have much higher energy barriers to rotation for the −N=O group than other 4-substituted nitrosobenzenes. Such energy barriers to free rotation of the nitroso group are associated with the contribution of the quinonoid canonical state **2** (Scheme 1) to the structure of the nitrosoaniline.



1 **2**

Scheme 1

π-Electron donor 4-substituents other than NRR′, such as OR, have rather lower donor character and therefore may be expected to contribute little quinonoid character and thus induce much lower partial double bond character to the C–NO bond. On the other hand most other 4-substituents, whether of weak π-electron donor or π-electron acceptor character, result in substituted 4-nitrosobenzenes which form both *E*- and *Z*-dimers. Such observations therefore suggest that there may be a connection between the rotational energy barrier for the NO group and the reaction pathways for the two possible dimerisation reactions (1) and (2). In a recent paper[9] we related the possibility of dimerisation of a *C*-nitroso compound to the wavenumber of the NO stretching vibration in the IR spectrum of its monomeric form, and on this basis were able to predict that 4-iodonitrosobenzene should dimerise. This prediction gained support from the subsequent preparation of the *E*-dimer of this compound.[9]



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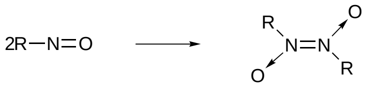


(2)

In order to explore further this possible connection between dimerisation tendencies of *C*-nitroso compounds and −N=O group behaviour it was decided to carry out accurate measurements of the rotational energy barriers of the NO group in the monomers and of the activation parameters for the monomer–dimer exchanges for a variety of 3- and 4-monosubstituted nitrosobenzenes, together with a few di- and tri-substituted nitrosobenzenes. Substituents were chosen with weak π-electron donor or π-electron acceptor properties, in order that the monomer–dimer equilibria could be readily studied. Such systems have a disadvantage in that the NO rotational energy barriers in these monomers are relatively low, placing considerable demands on the low temperature dynamic NMR studies. In most cases, however, including that of nitrosobenzene itself, total NMR bandshape analysis was possible and yielded reliable rotational energy data.

Experimental

The nitrosobenzenes were prepared as described in Part 1.[1] NMR studies were performed on Bruker equipment (Bruker AM250, AC300 or Avance DRX 400 spectrometers), using standard variable temperature units (B-VT 1000 or B-VT 2000). The calibration of these units was checked periodically against a Comark digital thermometer and temperatures are considered accurate to ±1 °C. The ^{1}H NMR spectra were recorded at 250.13, 300.13 or 400.13 MHz. Spectra were recorded as solutions in $CDCl_3$ or CD_2Cl_2. NMR bandshapes were analysed using the authors' version of the DNMR3 program.[10] Computer simulated spectra were compared visually with those obtained experimentally, and the 'best-fit' rate constants were used to calculate the activation parameters from a least-squares fitting of Eyring plots using the THERMO program.[11] The errors quoted are based on the goodness-of-fit of such plots. The 2D-EXSY NMR spectra were obtained using the Bruker automation program NOESYPH. The sizes of the frequency domains *F*1 and *F*2 were 512 words. Data processing incorporated an exponential window function with a line broadening of 0.5 Hz in both frequency domains. Intensities of diagonal and cross peaks were measured accurately by appropriate row integration. Rate data were computed using the authors' D2DNMR program.[12]

Results and discussion

Restricted nitroso group rotation in monomers

The effects of restricted rotation of the −N=O group on the NMR spectra of nitrosobenzenes have been known for many years. Most previous studies[3–8] have been directed towards compounds where the energy barriers are relatively high, with most of these studies based on the approximate band coalescence method. We now report results based on total bandshape analysis of the aromatic ^{1}H NMR signals measured over wide temperature ranges which provide more accurate rotational energy data. It was necessary, in most cases, to measure spectra down to the low temperature limit of the solvent (*i.e.* 173 K for CD_2Cl_2) in order to obtain 'static' spectra, since the −N=O groups were relatively unhindered in the nitrosobenzenes chosen.

For the 4-substituted nitrosobenzenes bandshapes were computed on the basis of exchanging ABCD $\rightleftharpoons$ BADC systems (where A,B = 2,6 hydrogens and C,D = 3,5 hydrogens) (Scheme 2). Nitrosobenzene itself constitutes an exchanging 5-spin system, but this was too large to be handled by the DNMR3 program.[10] The 4-H signal was therefore ignored and fittings were applied only to 2,6-H signals, which showed no scalar coupling to 4-H. For most compounds exchange-broadened spectra at seven or eight temperatures were fitted. The exception to this was 4-bromonitrosobenzene where special problems of signal overlap restricted fittings to only four temperatures. Often fittings of spectra near or at coalescence proved to be difficult, particularly for the 2- and 6-H signals, which were very widely spaced in the static temperature regime. At coalescence their signals were often unobservedly broad. However, their spectra in general displayed dynamic broadening over wide temperature ranges, thus aiding the DNMR analysis. Bandshape fittings were hampered somewhat by the signals of the *E* and *Z* dimers which overlapped the broader monomer signals in many cases. The ^{1}H NMR spectra of 4-chloronitrosobenzene, measured in the temperature range 168–243 K (Fig. 1), illustrate many of the analytical difficulties referred to. The effects of restricted rotation in the 3-, and 3,4-substituted nitrosobenzenes were slightly more involved as the −N=O group rotation exchanged chemically different species with different solution populations. It has been shown in the earlier part of this work[1] that the more abundant rotamer was the one having the 3-substituent *syn* to the −N=O group (Scheme 2).

Activation energies for the nitroso group rotation based on the Eyring rate theory are given in Table 1, with previously reported[2] values for some 4-nitrosoanilines included for comparison purposes. $\Delta S^{\ddagger}$ parameters are relatively small, as expected for intramolecular rearrangements, causing $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ values to be very similar. $\Delta G^{\ddagger}$ values have the lowest associated uncertainties and thus are most meaningful for comparison purposes. Magnitudes of $\Delta G^{\ddagger}$ lie in the range 31–41 kJ mol^{-1}, the value for nitrosobenzene itself being 34.3 ± 0.2 kJ mol^{-1}. This value is considered more accurate than the previous values of 32.2 ± 1.7[6] and 31.8 ± 0.4,[13] which were based on very approximate ^{13}C NMR studies. It should, however, be noted that these $\Delta G^{\ddagger}$ values for nitrosobenzene refer to different solvent systems, namely, CD_2Cl_2 (present work), $(CD_3)_2CO$[6] and Me_2O,[13] so any slight solvent influence on the N=O rotational energy barrier should not be ignored. Examination of Table 1 shows that substituents in the 3- and/or 5-position of the ring produce a slight lowering effect on the barriers to rotation, but the effect is small. Substituents in the 4-position of the ring can affect the N=O rotation energies more greatly depending on their electronic character. 4-Halogen derivatives have rotation energies clustered around that of nitrosobenzene itself, indicating very weak π-electron acceptor/

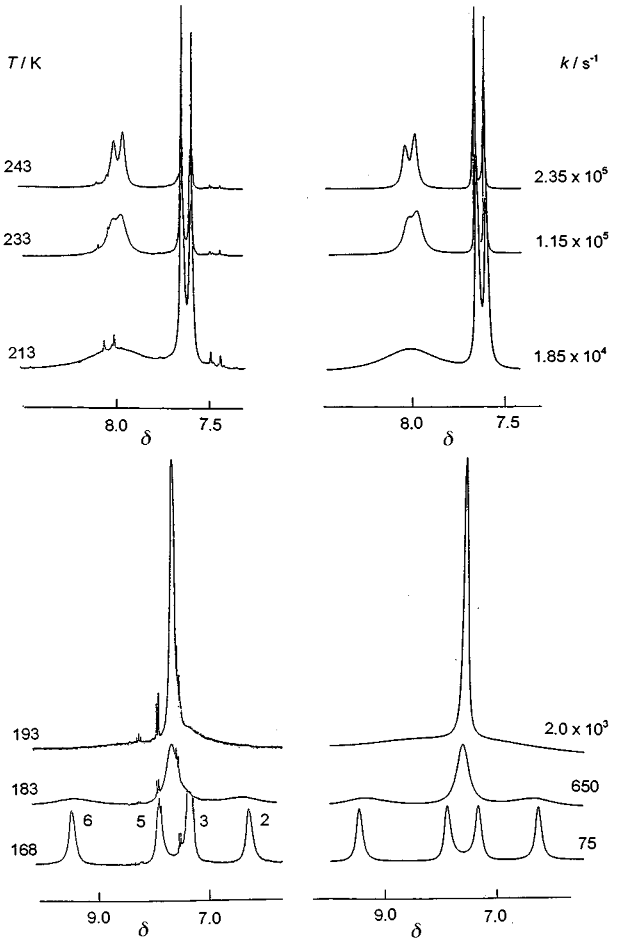
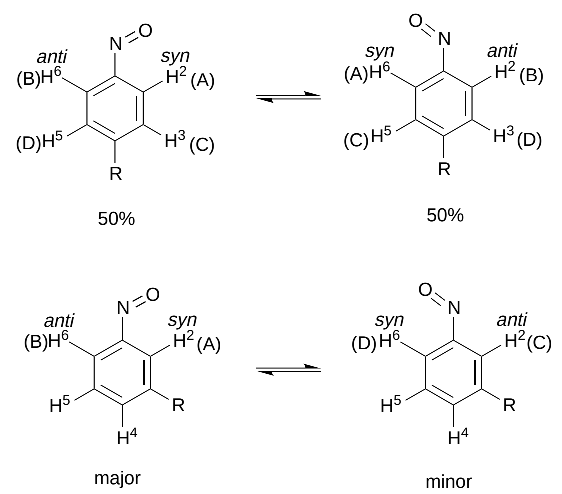


Fig. 1 250 MHz ^{1}H NMR spectra of 4-chloronitrosobenzene in CD_2Cl_2 recorded at variable temperatures, showing the effects of restricted rotation of the −N=O group. Note the change of frequency scale for the two temperature ranges. The weak additional signals in the spectra near δ 7.5 and δ 8.0 are due to the *E* dimer species. Computer simulated spectra with the best-fit rate constants are shown alongside the experimental spectra.



Scheme 2

Table 1 Activation parameters for C–NO rotation in nitrosobenzenes

Substituents	Solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kJ mol$^{-1\,a}$
None	CD_2Cl_2	32.3 ± 0.3	−7 ± 1	34.3 ± 0.2
3-I[b]	CD_3CD_2OD	26.5 ± 0.9	−24 ± 6	33.6 ± 0.7
c	CD_3CD_2OD	26.1 ± 0.9	−24 ± 6	33.1 ± 0.7
3-Me[b]	CD_2Cl_2	34.3 ± 0.4	9 ± 2	31.6 ± 0.3
c	CD_2Cl_2	34.0 ± 0.4	9 ± 2	31.3 ± 0.3
4-F	CD_2Cl_2	35.1 ± 0.4	−2 ± 2	35.6 ± 0.2
4-Cl	CD_2Cl_2	35.0 ± 0.2	4 ± 1	33.9 ± 0.1[d]
4-Br	CD_2Cl_2	34.3 ± 0.9	1 ± 5	34.0 ± 0.4
4-I	CD_2Cl_2	33.7 ± 0.8	−2 ± 4	34.2 ± 0.4
4-Me	CD_2Cl_2	39.2 ± 1.0	12 ± 5	35.7 ± 0.4[e]
4-MeO	$CDCl_3$	52.6 ± 1.0	39 ± 5	41.0 ± 0.3[f]
3,4-Me_2[b]	CD_2Cl_2	40.0 ± 0.6	16 ± 4	35.1 ± 0.4
c	CD_2Cl_2	39.4 ± 0.3	16 ± 4	34.5 ± 0.4
3,5-Me_2	CD_2Cl_2	35.8 ± 0.3	13 ± 2	32.0 ± 0.2
3-CO_2H-4-OH[4]	$(CD_3)_2CO$	41.2 ± 0.6	0 ± 3	41.1 ± 0.2
c	$(CD_3)_2CO$	39.4 ± 0.6	0 ± 3	39.3 ± 0.2
4-NMe_2	$CDCl_3$	60.3 ± 0.3	25 ± 1	52.8 ± 0.1[g]
4-NEt_2	$CDCl_3$	73.2 ± 1.7	61 ± 6	54.9 ± 0.1[h]
4-NEt_2	CD_3OD	52.2 ± 0.4	−16 ± 1	57.0 ± 0.1[h]
2-Me-4-NMe_2[b]	$CDCl_3$	57.2 ± 1.8	14 ± 7	52.9 ± 0.3[h]
c	$CDCl_3$	50.6 ± 1.8	14 ± 7	46.2 ± 0.3[h]
2,6-Me_2-4-NMe_2	$CDCl_3$	70.3 ± 1.7	107 ± 7	38.3 ± 0.5[h]

[a] Measured at 298.15 K. [b] Major→minor rotamer. [c] Minor→major rotamer. [d] 31.4 ± 1.7 (ref. 6). [e] 34.3 ± 1.7 (ref. 6). [f] 43.1 ± 1.7 (ref. 6), 41.4 ± 0.2 (ref. 3). [g] Ref. 15. [h] Ref. 2.

Table 2 Calculated values of $\Delta G^{\ddagger}$ for the restricted rotation in 4-substituted nitrosobenzene and values of σ_p^+ for the substituent groups

4-Substituent	$\Delta G^{\ddagger}$ (298.15 K)/kJ mol^{-1}	σ_p^+
NEt_2	57.0 ± 0.1, 54.9 ± 0.1[a]	−2.07
NHMe	54.2 ± 0.8, 53.2 ± 0.8[a]	−1.81
NMe_2	52.8 ± 0.1[b]	−1.70
OMe	41.0 ± 0.3	−0.78
Me	35.7 ± 0.4	−0.31
F	35.6 ± 0.2	−0.07
H	34.3 ± 0.4	0.00
Cl	33.9 ± 0.1	0.11
I	34.2 ± 0.4	0.14
Br	34.0 ± 0.4	0.15

[a] Ref. 2. [b] Ref. 15.

donor properties of halogens. 4-Methoxynitrosobenzene (4-nitrosoanisole) has a significantly higher N=O rotation barrier, in keeping with the stronger π-electron donating nature of the OMe group.

In much earlier work Calder and Garrett[3] attempted to show a correlation of their $\Delta G^{\ddagger}$ values for N=O rotation with Hammett σ values for 4-substituents. However, due to instrumental and experimental limitations, their correlation was restricted to a narrow range of compounds. Our present study allows a much more extensive correlation to be made. Our $\Delta G^{\ddagger}$ values have been correlated with the Hammett σ_p^+ parameter[14] of the substituent (Table 2). This parameter was felt to be a better measure of the resonance interaction of the substituent with the *p*-nitroso group. Values of this parameter vary from strongly negative (for strong π-electron donors) to positive (for π-electron acceptors). The graph of $\Delta G^{\ddagger}$ values *versus* σ_p^+ for ten compounds is shown in Fig. 2. It includes pairs of $\Delta G^{\ddagger}$ values for 4-nitroso-*N*,*N*-diethylaniline (for two different solvents) and 4-nitroso-*N*-methylaniline (for both major→minor and minor→major rotamer changes).[2] A good correlation was achieved, the best fit equation being $\Delta G^{\ddagger} = -10.34\ \sigma_p^+ + 34.59$, with a goodness-of-fit value of −0.994.

Theoretical calculations of nitroso group rotation barrier

Having obtained the first accurate experimental value of the energy barrier to −N=O rotation in nitrosobenzene, it was of considerable interest to compare this with theoretical predictions. Accordingly, an *ab initio* calculation was performed[15] on nitrosobenzene using the GAMESS program[16] with complete geometry optimizations being carried out at the 6-31G* level. Such an approach has been shown to provide reliable results for the structures of many neutral molecules.[17] The ground state geometry was optimised in C_1 symmetry, and the transition state geometry in C_s symmetry, it being assumed that the N=O and the C_1 and C_4 atoms are co-planar. Optimised ground state and transition state geometries are given in Table 3, with corresponding values from previous work[18,19] shown for comparison. The three sets of figures are in good agreement both with each other and with the CN and NO bond lengths and the CNO bond angle obtained from the crystal structure of 4-iodonitrosobenzene monomer.[9] Total energies for both ground and transition states of nitrosobenzene, and hence the rotational barrier energies, are given in Table 4. It is clear that, as the basis functions used in the calculations become more extensive and sophisticated, the estimated rotational barrier energies fall within a range 31–42 kJ mol^{-1}. This is *not* consistent with the experimental value of 23.9 ± 4.2 kJ mol^{-1} based on microwave spectroscopy,[23] but does agree well with the present experimental value based on total NMR bandshape analysis, namely $\Delta H^{\ddagger}$ = 32.3 ± 0.3 kJ mol^{-1} (Table 1). As this value is

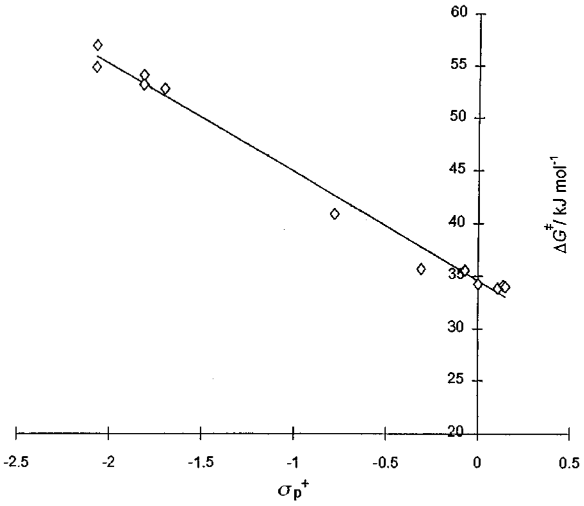


Fig. 2 Graph of $\Delta G^{\ddagger}$ values for nitroso group rotation against the Hammett σ_p^+ for the 4-position substituents

Table 3 Calculated ground state and transition state geometries for nitrosobenzene

	Distances/Å				Angles (°)		
	this work	ref. 18	ref. 19		this work	ref. 18	ref. 19
Ground state							
C_1–N	1.433	1.441	1.443	C_1–C_2–C_3	119.0	119	118.6
C_1–C_2[a]	1.391	1.385	1.400	C_2–C_3–C_4	120.1		120.3
C_2–C_3	1.380	1.379	1.391	C_3–C_4–C_5	120.6	120	120.0
C_3–C_4	1.392	1.389	1.402	C_4–C_5–C_6	119.5	120	119.8
C_4–C_5	1.384	1.384	1.397	C_5–C_6–C_1	119.6		119.2
C_5–C_6	1.383	1.383	1.395	C_6–C_1–C_2	121.2		121.3
C_6–C_1	1.383	1.380	1.397	N–C_1–C_2	123.4	123	124.1
N–O	1.181	1.223	1.245	C_1–N–O	115.5	115	114.1
C–H	1.073–1.075	1.069–1.072					
Transition state							
C_1–N	1.452		1.462	C_1–C_2–C_3	119.0		118.7
C_1–C_2	1.382		1.396	C_2–C_3–C_4	120.3		120.3
C_2–C_3	1.385		1.396	C_3–C_4–C_5	120.0		120.0
C_3–C_4	1.386		1.397	C_6–C_1–C_2	121.5		121.9
N–O	1.177		1.243	N–C_1–C_2	119.2		119.0
C–H	1.075			C_1–N–O	113.6		111.3

[a] C_2 is *cis* with respect to the N=O bond.

Table 4 Calculated energy data for nitrosobenzene

Basis	State	Energy/hartree	Rel. energy/kJ mol^{-1}	Ref.
6-31G*	ground	−359.346 453	0.0	15
	transition	−359.333 160	34.9	
STO-3G	ground	−345.815 88	0.0	20
	transition	−354.808 16	20.3	
STO-3G	ground	−345.816 52	0.0	21
	transition	−354.807 76	23.0	
STO-3G//STO-3G	ground	−354.827 46	0.0	21
	transition	−354.820 36	18.7	
3-21G	ground	−357.315 08	0.0	21
	transition	−357.297 76	45.5	
3-21G//3-21G	ground	−357.317 52	0.0	21
	transition	−357.301 72	41.5	
4-31G	ground	−358.809 97	0.0	21
	transition	−358.793 40	43.5	
HF/6-311G**//MP2/6-31G*	ground	−359.417 852	0.0	19
	transition	−359.404 202	35.8	
MP2/6-311G**//MP2/6-31G*	ground	−360.604 674	0.0	19
	transition	−360.592 702	31.4	
6-31G	ground	−359.195 236	0.0	22
	transition	−359.179 355	41.7	

based on a dissolved phase study, it would appear that any solvent influence on nitrosobenzene molecules is very slight. Furthermore, the barrier to rotation shows only a very slight increase on going from the dissolved to the solid-state phases, *e.g.* $4\text{-}IC_6H_4NO$[9] and $4\text{-}Me_2NC_6H_4NO$.[2]

Monomer–dimer equilibria—thermodynamic studies

Monomer–dimer equilibria are established for many nitrosobenzenes dissolved in organic solvents, with both *Z* and *E* dimers usually co-existing.[24] NMR techniques have been successfully used previously to study the equilibria of several systems including mixed dimer systems.[25–27] This earlier work has now been extended to the present nitrosobenzene derivatives. From the relative populations of all three solution species at several temperatures in the range 303 to 213 K, equilibrium constants, $K^\ominus$, for the dissociations of both types of dimers have been calculated. Temperature dependences of $K^\ominus$ have yielded the thermodynamic parameters $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ (298.15 K) for these equilibria. Results are tabulated in Table 5. In general the ^1H NMR spectra revealed that, at ambient temperatures, only monomeric species existed in solution, but on cooling two additional sets of signals due to the *E* and *Z* dimers appeared. The abundance of the *E* dimer remained relatively low at all temperatures ($\leqslant 6\%$) whereas the concentration of the *Z* dimer increased on cooling at the expense of the monomer concentration. This can be seen clearly in the case of ethyl 3-nitrosocinnamate in CD_2Cl_2 solution where the relative abundances of species have been monitored *via* the β-hydrogen of the $-CH{=}CHCO_2Et$ group (Fig. 3). These observations represent the first recorded examples of dimer formation of this nitroso compound. We also found that crystallisation of a solution of the monomer in CH_2Cl_2 at −28 °C produced a colourless dimer shown by IR spectroscopy to be the *E* dimer. The solid monomer could also be obtained by column chromatographic separation from a solution of the monomer. It should be noted that Talberg[28] prepared two crystalline forms of the monomer and showed that dealkylation led to colourless crystals of a dimer of 3-nitrosocinnamic acid.

Similarly, the occurrence of the *Z* dimer of 3,4-dimethylnitrosobenzene in solution is the first recorded example of the existence of any dimeric form of this compound, all reported preparations to date, including ours, yielding only the monomer.[29]

The 3-halogeno- and 3-methyl-nitrosobenzenes all show the formation of both *Z* and *E* dimers at low temperatures in solution. Of these compounds we have isolated the fluoro and

Table 5 Ground state thermodynamic data for the dimer–monomer equilibria of aromatic nitroso compounds

Compound	$\Delta H^\ominus$/kJ mol^{-1}	$\Delta S^\ominus$/J K^{-1} mol^{-1}	$\Delta G^\ominus$ (298.15 K)/kJ mol^{-1}
Z-(RNO)$_2 \rightleftharpoons$ 2RNO			
Nitrosobenzene	55.5 ± 1.7[a]	219 ± 7[a]	−9.8 ± 0.3[a]
3-Fluoronitrosobenzene	38.4 ± 1.9	169 ± 8	−12.0 ± 0.5
3-Chloronitrosobenzene	47.4 ± 1.5	205 ± 7	−13.7 ± 0.4
3-Bromonitrosobenzene	40.6 ± 1.1	176 ± 5	−11.9 ± 0.3
3-Iodonitrosobenzene	48.1 ± 1.3	206 ± 6	−13.4 ± 0.4
3-Methylnitrosobenzene	46.3 ± 0.5	189 ± 2	−10.2 ± 0.1
Ethyl 3-nitrosocinnamate	50.0 ± 1.0	209 ± 4	−12.4 ± 0.3
4-Iodonitrosobenzene	49.0 ± 0.6	211 ± 32	−14.1 ± 0.1
3,4-Dimethylnitrosobenzene	49.7 ± 0.9	209 ± 4	−12.8 ± 0.2
3,5-Dimethylnitrosobenzene	53.4 ± 3.8	215 ± 14	−10.7 ± 0.4
E-(RNO)$_2 \rightleftharpoons$ 2RNO			
Nitrosobenzene	42.5 ± 1.2[a]	185 ± 5[a]	−12.6 ± 0.2[a]
3-Fluoronitrosobenzene	27.8 ± 1.0	134 ± 4	−12.0 ± 0.3
3-Chloronitrosobenzene	26.3 ± 1.6	123 ± 7	−10.5 ± 0.4
3-Bromonitrosobenzene	24.8 ± 3.9	116 ± 17	−9.6 ± 1.1
3-Iodonitrosobenzene	35.7 ± 2.7	161 ± 11	−12.6 ± 0.8
3-Methylnitrosobenzene	29.5 ± 0.9	135 ± 4	−10.9 ± 0.2
Ethyl 3-nitrosocinnamate	31.4 ± 4.1	138 ± 17	−9.8 ± 1.1
4-Iodonitrosobenzene	30.4 ± 2.2	131 ± 9	−11.5 ± 0.5

[a] Calculated from the intensities given in ref. 25.

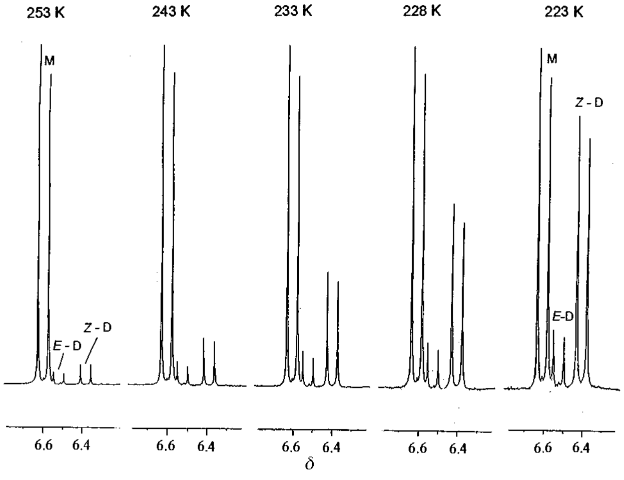


Fig. 3 The changes in the β-H signal in the 250 MHz ^{1}H NMR spectra of ethyl 3-nitrosocinnamate in CD$_2$Cl$_2$ showing the effects of temperature on the monomer–dimer equilibrium

methyl compounds in the solid state solely as Z dimers, whereas for the chloro, bromo and iodo compounds crystallisation from CH$_2$Cl$_2$ at −28 °C gives the E dimer and from ethanol at room temperature a mixture of Z and E forms. Our earlier NMR studies[9] have demonstrated that the 4-iodo compound can exist in both Z and E dimeric forms in solution at low temperatures although only the E dimer has been isolated in the solid state.

It can be seen from Table 5 that all $\Delta H^\ominus$ values for the dissociations are positive, with those for Z dimer dissociations being greater than those for corresponding E dimer dissociations. Ring substituents appear to lower the $\Delta H^\ominus$ values for the equilibria. All $\Delta S^\ominus$ values are large and positive as expected for dissociation processes, those for Z dimer dissociations being greater than those for E dimer dissociations. This may reflect the greater increase in rotational degrees of freedom on going from the somewhat rotationally restricted Z dimer structure to the monomer structure, compared to the E dimer to monomer change where rotations about most bonds in the E dimer will be fairly unrestricted. Support for this argument comes from the observation that, in the dimers of 2-methylnitrosobenzene[30] and 2,4,5-trimethylnitrosobenzene,[31] there is such a degree of restriction to rotation about the C–N bonds that two distinct rotamers of the Z dimer are detected in low temperature spectra. These have previously been described[30] as Z,E and Z,Z dimers, where the second label refers to the relative positioning of the 2-methyl groups. The Z,E dimers are more favoured in solution and the following rotational energy barriers, $\Delta G^\ddagger$, have been calculated for $Z,E \rightarrow Z,Z$ exchanges: 43.7 ± 0.1 kJ mol^{-1} for 2-methylnitrosobenzene[30] and 55.8 ± 0.1 kJ mol^{-1} for 2,4,5-trimethylnitrosobenzene.[31]

Monomer–dimer equilibria—kinetic studies

The compounds 3-methylnitrosobenzene and 3,5-dimethylnitrosobenzene were chosen for studying rates of Z dimer dissociations. E dimer concentrations were too low for reliable dissociation rates to be measured. At temperatures in the range 263–303 K rates of dissociation are quite well-suited to 2D-EXSY NMR experiments, despite rather low dimer concentrations. At temperatures below *ca.* 263 K, the equilibrium state is only slowly established, and time-dependent (TD) NMR studies were performed. These involved dissolving a known amount of the nitroso compound in CDCl$_3$, warming to *ca.* 333 K to produce a solution of exclusively monomeric species and then placing the sample in the NMR spectrometer probe which was already at the chosen temperature. When thermal equilibrium was established, the relative amounts of monomer and dimer signals were measured at regular time intervals (typically 1 s or more, depending on the probe temperature) for about 10–15 seconds. Assuming the relative intensities of the signals are directly proportional to the relative concentrations of monomer and dimer, rate constants for the Z dimer→monomer conversions were calculated using the kinetic treatment previously described.[26] In the case of 3-methylnitrosobenzene, dissociation rate data were measured at 223, 228 and 238 K using this time-dependent NMR method, and at 263 and 268 K using the 2D-EXSY NMR method. For 3,5-dimethylnitrosobenzene rate data were measured for temperatures of 263, 268 and 273 K by the 2D-EXSY method and these were combined with earlier reported values[26] for temperatures of 233, 243, 253 and 283 K. The results for both compounds are collected in Table 6. The rates obtained were used to calculate Eyring activation parameters for the Z dimer dissociation (Table 7). The values in Table 7 indicate that successive addition of methyl groups into the 3- and 5-positions of the ring causes a small step-wise increase in the Gibbs free energy of activation. The trends in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are unclear, with the values for 3-methylnitrosobenzene being rather out of line.

Knowing the relative energies (enthalpies) of the ground states of the Z dimer, E dimer and monomer from the earlier

Table 6 Rates of Z dimer→monomer dissociation for 3-methyl- and 3,5-dimethyl-nitrosobenzene

3-Methylnitrosobenzene				3,5-Dimethylnitrosobenzene		
T/K	[Monomer] : [dimer]	k^a/s^{-1}	Method	T/K	k/s^{-1}	Method
223	68:32	2.2×10^{-4}	TD-NMR	233	1.6×10^{-4}	TD-NMR[b]
228	67:33	5.2×10^{-4}	TD-NMR	243	3.8×10^{-4c}	TD-NMR[b]
238	77:23	3.3×10^{-3}	TD-NMR	253	6.0×10^{-3}	TD-NMR[b]
263	84:16	0.16	2D-EXSY	263	2.7×10^{-2}	2D-EXSY
268	88:12	0.25	2D-EXSY	268	6.5×10^{-2}	2D-EXSY
				273	0.23	2D-EXSY
				283	0.59	2D-EXSY[b]

[a] Rate constants forZ dimer→2 monomer. [b] Data from ref. 26. [c] Value anomalously low and not used in the Eyring plot.

Table 7 Activation parameters for the dissociation of Z dimeric aromatic nitroso compounds in $CDCl_3$ solution

Compound	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$ (298.15 K)/kJ mol^{-1}
Nitrosobenzene[a]	88.5 ± 1.0	76 ± 3	65.8 ± 0.1
3-Methylnitrosobenzene	77.1 ± 1.0	33 ± 4	67.2 ± 0.2
3,5-Dimethylnitrosobenzene	89.6 ± 2.7	69 ± 10	69.2 ± 0.5

[a] From ref. 25.

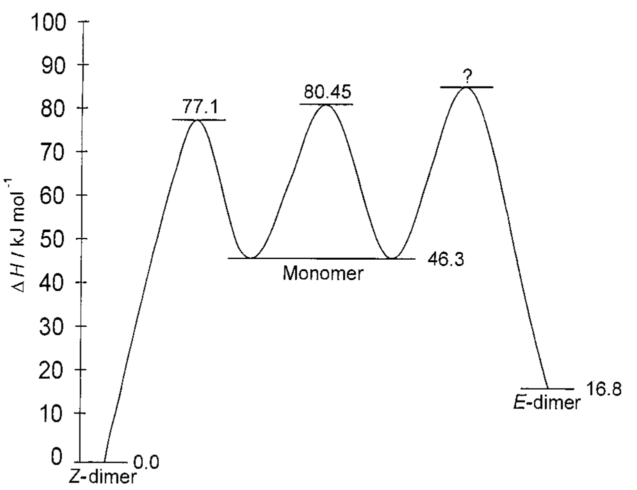


Fig. 4 Enthalpy-change profile for 3-methylnitrosobenzene showing the ground and transition states associated both with its monomer–dimer equilibrium and with restricted −N=O rotation in the monomer

equilibrium studies, and knowing the energies of the transition states associated both with Z dimer dissociation and N=O group rotation in the monomer, it is possible to construct an energy (enthalpy) profile which relates all these parameters. The enthalpy profile for 3-methylnitrosobenzene is chosen as an example (Fig. 4), and includes the activation energy for N=O rotation in the monomeric species. It is noteworthy that the magnitudes of $\Delta H^‡$ (monomer→Z dimer) and $\Delta H^‡$ (NO rotation in monomer) are very comparable in magnitude. This similarity also applies to the other two compounds studied (Table 8).

It is not known whether this similarity in $\Delta H^‡$ values is real or coincidental, as the three compounds studied are very similar in chemical nature. The choice of suitable compounds is limited by solubility restrictions at the low temperatures at which 2D-EXSY and time-dependent NMR studies had to be carried out. For the compounds studied the ring substituent effects are either absent or very weak. It is of importance to know whether this parallelism in $\Delta H^‡$ values is seen in compounds with strong π-electron donor or acceptor substituents, particularly in the 4-position. This uncertainty is highlighted by the case of 4-nitrosoanilines where the barrier to N=O group rotation is high (due to considerable contribution of the quinonoid structural form) and there is no tendency towards self-dimer formation. (It should be noted that there is a very slight tendency towards mixed dimer formation in the case of 4-nitroso-*N*,*N*-dimethylaniline with 2,4,6-trimethylnitrosobenzene.[31])

Table 8 Activation parameters for monomer association to the Z dimer and for N=O rotation

Compound	$\Delta H^‡$/kJ mol^{-1}	$\Delta H^‡$(NO rotation)/ kJ mol^{-1}
Nitrosobenzene	33.0 ± 1.7	32.3 ± 0.3
3-Methylnitrosobenzene	30.8 ± 0.5	34.3 ± 0.4, 34.0 ± 0.4
3,5-Dimethylnitrosobenzene	36.2 ± 3.8	35.8 ± 0.3

It is tempting to suggest that there is a connection between these two ΔH parameters, since the activation enthalpy for restricted N=O rotation in the monomer is the enthalpy required to achieve an N=O group orthogonal to the aromatic ring. In the ground state structure of a Z dimer the phenyl rings are twisted by *ca.* 70° from the plane containing the azodioxy group. Thus, some considerable rotation of the phenyl rings is essential for Z dimer formation. The case of E dimer formation is less clear as the transition state for this dimerisation process could be measured only in the case of nitrosobenzene itself, where $\Delta H^‡$ (monomer→E dimer) is *ca.* 20 kJ mol^{-1} higher than $\Delta H^‡$ (NO rotation in monomer). An additional concern in relating these two $\Delta H^‡$ parameters is that restricted N=O rotation is a first-order kinetic process whereas the association of pairs of monomer molecules to form dimers is kinetically second-order. We nevertheless feel that a possible connection between these two processes is worthy of further investigation.

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