Study of the Monomer–Dimer Equilibrium of Nitrosobenzene Using Multinuclear One- and Two-Dimensional NMR Techniques

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The monomer-dimer equilibrium of nitrosobenzene in $CDCl_3$ solution was studied in the temperature range -50 to 30 °C using ¹³C, ¹⁵N and ¹⁷O NMR spectroscopy. Decreasing temperature favours the dimeric azodioxy species, and below *ca* 10 °C both *cis* and *trans* dimers were detected in addition to the monomer. The relative abundance of the *trans* dimer is low ($\leq 6\%$) at all temperatures and this is the first report of its existence in solution. The monomer and dimer species were characterized by their ¹³C and ¹⁵N shifts, and exchange between them was measured quantitatively by ¹³C 2D-EXSY spectra. Exchange occurred exclusively between the *cis*-dimer and monomer and between the *trans*-dimer and monomer, activation energies, $\Delta G^+(298.15 \text{ K})$ being 65.8±0.1 and 70.0±0.3 kJ mol⁻¹, respectively.

KEY WORDS ¹³C, ¹⁵N, ¹⁷O NMR ¹³C 2D-EXSY nitrosobenzene activation energies

INTRODUCTION

Structural interest in C-nitroso compounds has existed for many decades.¹⁻⁴ Aromatic C-nitroso compounds can occur as blue or green monomers (**A**) or colourless azodioxy dimers. Cis and trans dimers (**B**, **C**) can exist,



and both crystalline forms have been isolated in the case of ortho-nitrosotoluene.⁵ Nitrosobenzene, however, exists solely as the crystalline *cis* dimer,⁶ as also does *m*-nitrosotoluene,⁷ whereas *p*-nitrosotoluene⁷ and 2,6dimethylnitrosobenzene⁸ crystallize exclusively in the trans-azodioxy form. In solution, monomer-dimer equilibria are established in most cases, with both cis and *trans* dimers usually co-existing. The reported exceptions are nitrosobenzene and 2,6-dimethylnitrosobenzene, where only single dimer species have been detected to date from ¹H NMR data. In the case of nitrosobenzene the detected dimer in solution has been assumed to be the cis form by analogy with the x-ray data.⁶ Other previous structural studies of nitrosobenzene derivatives have involved the measurement of rates of restricted rotation about the C-N bond (by low-temperature ^{1}H and ^{13}C NMR $^{9-12}$) and rates of exchange between monomers and dimers (by UV-visible spectrophotometry^{7,8}).

We felt there was scope for reinvestigating the solution properties of nitrosobenzene using the latest NMR methods. We have accordingly obtained natural abundance ${}^{13}C$, ${}^{15}N$ and ${}^{17}O$ 1D spectra to provide definitive characterization of the solution species over the low-temperature range -50 to 30 °C, and also applied the recent 2D-EXSY method ${}^{13-15}$ to the ${}^{13}C$ nuclei in these molecules to measure accurately the rates of exchange between the monomer and dimer species.

EXPERIMENTAL

Natural abundance ¹³C, ¹⁵N and ¹⁷O NMR spectra were obtained at frequencies of 62.9, 25.4 and 34.0 MHz, respectively, on a Bruker AM250 spectrometer equipped with an ASPECT 3000 computer. Proton decoupling was employed for the ¹³C and ¹⁵N spectra. Two-dimensional ¹³C EXSY spectra¹⁶ were obtained with the Bruker automation program NOESY, which uses the NOESY pulse sequence D1-90°-D0-90°-PJ-90°-FID. The conditions used in the different experiments are summarized in Table 1. The first experiment, performed at 0 °C, used a spectral width which contained the signals of the ring carbons C-4, C-3,-5 and C-2,-6 for all three solution

Table 1.	Conditions	used	for	¹³ C	2D-	-EXSY	experiments	

Temperature/						
°C	D1ª/s	D9 ^b /s	NS°	TD1 ^d	TD2°	SW ^f /Hz
-10	15	5	32	64	1024	400
0	4	2	48	128	2048	1200
10	5	0.5	112	64	1024	350
20	5	0.2	64	1 28	1024	400

^a Initial relaxation delay.

^b Mixing time, $\tau_{\rm m}$.

° Number of scans per experiment.

^d Number of experiments, NE.

^e Number of words in F_2 dimension.

^f Spectral width.

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species. However, it was found that the exchange information from the C-2,-6 signals was the most accurate, since the signals associated with C-4 and C-3,-5 were less suitably dispersed in position and intensity. Therefore, subsequent 2D experiments were performed using a much smaller spectral width which encompassed only the three signals of the C-2,-6 carbons. The position of the spectral window was carefully adjusted to avoid foldback signals overlapping with the C-2,-6 resonances. The F_1 dimension of the data table contained either 64 or 128 words (NE = TD1), which was then zero-filled to 512 words (1024 words at 0 °C). The F_2 dimension contained 1024 words (2048 words at 0 °C). The choice of mixing time $\tau_{\rm m}$ (D9, Table 1) was made in accordance with the factors discussed previously.¹⁶ The data were processed using Gaussian broadening of 0.5 Hz in both dimensions and calculating magnitude-mode spectra followed by symmetrization about the diagonal. Four 2D-EXSY spectra were recorded in the range -10 to 20 °C. One-dimensional ¹³C-{¹H} spectra were obtained in the temperature range -50 to 30 °C.

The sample of nitrosobenzene was purchased from Aldrich and used without further purification. All NMR spectra were recorded for a CDCl₃ solution of concentration *ca* 2 mol dm⁻³. A small amount of $Cr(acac)_3$ was added to the solution prior to recording the ¹⁵N spectrum, in order to reduce the ¹⁵N relaxation times and so enable a more rapid pulse rate to be employed.

RESULTS AND DISCUSSION

Characterization of solution species

Proton decoupled ¹³C spectra, recorded in the temperature range 30 to -50 °C, revealed very distinct changes arising from the varying proportions of monomer and dimer species present in solution. ${}^{13}C-{}^{1}H$ spectra at 30, -10 and -30 °C are shown in Fig. 1. At the highest temperature, signals due solely to the monomer species are present. On cooling, these signals decrease in relative intensity and two additional sets of signals appear. The more intense set has shifts very similar to those reported earlier¹¹ and is attributed to the cis dimer. The weaker set of signals does not appear to have been previously observed, and is attributed to the trans dimer by virtue of the close similarity of the shifts to the *cis* dimer. This would appear to be the first direct evidence of the trans-azodioxy dimer of nitrosobenzene in solution. This species has been detected previously in the molten state by infrared studies on the crystalline melt when a band at 1260 cm^{-1} was attributed to its presence. However, attempts to isolate it by rapid cooling of the melt were unsuccessful.⁶

The abundance of the *trans* dimer in CDCl₃ solution remains very low ($\leq 6\%$) at all temperatures, whereas the concentration of the *cis* dimer increases on cooling at the expense of the monomer concentration. The ¹³C spectra at -10 and -30 °C (Fig. 1) provide evidence of all three species. Additionally, it should be noted that the C-2,-6 signal of the monomer at -30 °C is very broad owing to the rather slow rate of rotation about the C--N bond.¹¹ The chemical shift assignments are based on the



Figure 1. Variable-temperature ${}^{13}C-\{{}^{1}H\}$ spectra of nitrosobenzene in CDCl₃. Concentration *ca* 2 mol dm⁻³. (a) 30 °C; (b) -10 °C; (c) -30 °C. Assignments are shown; m=monomer; c=*cis* dimer; t=*trans* dimer. Note the broad C-2,-6 monomer signal at -30 °C due to the slow rate of C-N bond rotation.

usual ring labelling of aromatic compounds, namely



The ¹³C shifts at -10 °C are recorded in Table 2. The high-frequency shift of C-1 in the monomer reflects the strong electron-withdrawing nature of the nitroso substituent. The corresponding signals in the dimers occur at *ca* 20 ppm to lower frequency and indicate the different electronic nature of the azodioxy moiety. The order of shifts in the monomer, namely C-1 \gg C-4> C-3,-5> C-2,-6, also occurs for both dimers, the difference being that the C-1-C-4 shift separation is now appreciably smaller. For corresponding carbons in the two dimers the *cis* dimer shifts are greater by 0.6-0.8 ppm, with the exception of C-4, where the *trans* shift exceeds the *cis* shift by 0.3 ppm.

Table 2 also gives the ¹⁵N shifts for the monomer and dimer species. The ¹⁵N spectrum (Fig. 2) recorded at 0 °C with proton decoupling and added $Cr(acac)_3$ was the result of 44×10^3 pulses. There is a dramatic difference in ¹⁵N chemical shifts between monomer and dimer but only a very small difference (*ca* 3 ppm) between *cis* and *trans* dimers. The natural abundance ¹⁷O spectrum acquired from 2.6×10^6 pulses produced

Table 2.	Multinuclear	chemical	shifts	for	nitrosobenzene	in
	CDCl ₂ solution)n				

Nucleus	Label	Monomer	cis Dimer	trans Dimer
	C-1	165.67	143.11	142.26
¹³ C ^a	C-2,-6	120.99	124.42	123.63
	C-3,-5	129.38	129.55	128.98
	C-4	136.00	130.99	131.32
¹⁵ N ^b	N	518.7	-77.1	-80.2
¹⁷ 0 ^c	0	~1524	~1524	~1524

^a Shifts at -10 °C relative to Me₄Si.

^b Shifts at 0 °C relative to MeNO₂.

^c Shift at 0 °C relative to D₂O. Value attributed to all three species.

a single line of width ca 20 ppm, which did not allow distinction between the monomer and dimer species (Table 2). This is surprising, but clearly indicates that the different electronic natures of the monomer and dimer species are mainly centred at the nitrogen atom(s), with only slight differences being transmitted to the peripheral oxygen atom(s).

The large differences in ¹³C C-1 shifts and ¹⁵N shifts for monomer and dimer species reflect the different orientations of the NO group with respect to the benzene ring. The preferred monomer structure is that with the NO group coplanar with the aromatic ring, as is evident from low-temperature NMR studies,¹¹ allowing overlap of nitrogen π -orbitals with the aromatic π -system. In the case of the *cis*-azodioxy dimer the x-ray crystal structure⁶ shows the planes containing the NO groups to be approximately 90° to the adjacent aromatic ring planes. Presumably this will also apply to the *trans* dimer. Thus, conjugation with the ring π -systems will not occur and this is reflected in the large low-frequency shifts of the carbon (C-1) and nitrogen atoms on going from monomer to dimer.

The ¹⁴N shift of nitrosobenzene monomer has been reported earlier.¹⁷ The value of $\delta = 540 \pm 3$ (relative to MeNO₂) for a saturated solution of the compound in diethyl ether is similar to our value. An earlier report of ¹⁴N and ¹⁵N shifts for nitrosobenzene¹⁸ appears to be erroneous. There do not appear to have been any previous reports of the nitrogen shifts for the nitrosobenzene dimers.

The low-frequency shifts of the nitrogen and carbon (C-1) atoms on going from monomer to dimers illustrates the common parallelism of carbon and nitrogen shifts.¹⁹ The higher frequency value for the monomer may be related to the small frontier orbital separation ΔE (HOMO-LUMO) associated with the $n \rightarrow \pi^*$ electron circulation, which enhances the paramagnetic shielding term. In the nitrosobenzene dimers there are no low-lying singlet states. The effective excitation energy term ΔE (HOMO-LUMO) therefore increases, the $n \rightarrow \pi^*$ absorption moves into the UV range with $\lambda_{max} \approx 300$ nm, and the nitrogen shift shows a large decrease (*ca* 600 ppm). Such a δ/λ correlation has been discussed by Mason¹⁹ for -N=O and -N=Ngroups, and appears to be even more strikingly apparent for -N=O and -(O)N=N(O)- groups.

The very small ¹⁵N chemical shift distinction of the cis and trans dimers ($\Delta \delta \approx 3$ ppm) implies very weak electronic interaction between the two -NO moieties.

Monomer-dimer equilibrium

The relative populations of all three solution species were measured from the ¹³C signal intensities in the temperature range -50 to 30 °C, and the values are listed in Table 3. From their temperature dependencies, equilibrium constants, K^{\ominus} , were calculated for the equilibria

$$cis$$
 (PhNO)₂ \rightleftharpoons 2PhNO (1)

trans
$$(PhNO)_2 \rightleftharpoons 2PhNO$$
 (2)

•Plots of ln K^{\ominus} versus T^{-1} enabled ΔH^{\ominus} and ΔS^{\ominus} values to be calculated, from which ΔG^{\ominus} (298.15 K) values were deduced (Table 4).

The sizeably positive ΔH^{\ominus} values for equilibrium (1) show that the *cis* dimer is the thermodynamically preferred species both in CDCl₃ solution and in the solid state. The large positive ΔS^{\ominus} values for both equilibria (1) and (2) are typical of dimer-monomer dissociation equilibria. These large entropy terms cause the Gibbs



Figure 2. Natural abundance ¹⁵N spectrum of nitrosobenzene in CDCl₃ containing a small amount of Cr(acac)₃. Temperature, 0 °C; acquisition time, 1.3 s; number of pulses, 44.5 × 10³.

(2)

Table 3. Nitrosobenzene monomer-dimer equilibrium

	Populations/% ^a				
Temperature/°C	Monomer	<i>cis</i> Dimer	trans Dimer		
-50	9.5	84.3	6.2		
40	12.6	81.3	6.1		
-30	22.0	72.8	5.2		
-20	33.0	61.2	5.8		
-10	52.6	41.4	6.0		
0	68.0	27.0	5.0		
10	80.1	15.8	4.1		
20	88.8	8.5	2.7		
30	95.4	4.6			

Table 4.	Grou mon	ınd-state omer–dime	therm er equi	odynamic librium ^a	data	for	PhNO
Equilibriu	ım	∆ <i>H</i> [⊕] /kJ mol	r-1 4	∆ <i>S</i> ⊖∕JK ^{−1} mol [−]	¹ ∆ <i>G</i> ⊖(298.15 K)/kJ mol ⁻¹
(1)		55.4 ± 1^{-5}	7	213 + 7		-81-	+03

^a Errors are based on least-squares fittings using the population data in Table 3.

 179 ± 5

 42.5 ± 1.2

 -10.9 ± 0.3

function changes, ΔG^{\ominus} , to vary significantly with temperature. For example, while ΔG^{\ominus} (298.15 K) is -8.1 kJ mol⁻¹, at -40 °C (233 K) the ΔG^{\ominus} value is 5.8 kJ mol⁻¹, which compares with a previous estimate¹¹ of 4.2 kJ mol⁻¹.

Since $\Delta S^{\ominus}(1) - \Delta S^{\ominus}(2) = S^{\ominus}[trans-(PhNO)_2] - S^{\ominus}[cis-(PhNO)_2]$, it follows from the data in Table 4 that the difference in standard entropies of the *cis* and *trans* dimers is *ca* $34 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$ with the *trans* species having the larger value. This is thought to be primarily a consequence of the greater rotational contribution to the partition function for the *trans* species than for the *cis* species. In the *cis* dimer there is likely



Figure 3. Carbon-13 2D-EXSY spectrum of nitrosobenzene in $CDCI_3$ at 10 °C showing the C-2,-6 carbon region only. Assignments are given; m=monomer; c=*cis* dimer; t=*trans* dimer; f=fold-back signal.

Table 5.	First-order rate data	for the nitrosobenzene	monomer-
	dimer system ^a		

	Rate constant, k/s^{-1}					
Temperature/°C	<i>cis</i> Dimer → monomer	trans Dimer → monomer	<i>trans- → cis</i> -Dimer			
-10	0.14 ± 0.01	0.021 ± 0.02	0.001 ± 0.02			
0	0.61 ± 0.04	$\textbf{0.082} \pm \textbf{0.05}$	0.076 ± 0.07			
10	2.67 ± 0.25	$\textbf{0.40} \pm \textbf{0.18}$	0.10 ± 0.2			
20	9.63 ± 1.1	1.91 ± 1.0	-0.2 ± 1.5			
^a Rate constan	t uncertainties co	mputed as describe	ed in Ref. 16.			

to be greater restriction to rotation of the aromatic rings about the C—N bonds. Indirect evidence for this may be obtained by comparing the internal rotational characteristics of the *cis* and *trans* dimers of *o*-nitrosotoluene. The *ortho*-methyl group clearly causes greater restriction to ring rotation in the *cis* dimer than in the *trans* dimer, since at low temperatures the rotation becomes slow on the ¹H NMR time scale in the *cis* but not in the *trans* species.

Monomer-dimer exchange

Carbon-13 two-dimensional NMR exchange spectroscopy (2D-EXSY) was used to identify any slow rates of exchange between the nitrosobenzene monomer and dimer species in the temperature range -10 to 20 °C. The first spectrum was obtained at 0 °C and contained all the ring carbon signals of the monomer and dimer species. Many cross-peaks were observed, indicating appreciable magnetization transfer due to chemical exchange. In order to examine this exchange more precisely, the ¹³C spectral window was reduced to include only the C-2,-6 carbon signals of all three solution species. The spectrum recorded at 10 °C is shown in Fig. 3. Cross-peaks are visible between all species. This, however, does not necessarily imply that all rates in the exchange network are non-zero. Second-order crosspeaks can occur if the mixing time, τ_m , is too long for particular pathways.^{16,20} Analysis of the signal intensity data was performed using the computer program D2DNMR¹⁶ and rate constant uncertainties were obtained from estimates of signal integration errors using standard error propagation analysis.¹⁶ The values for the three independent rate constants are given in

Table 6. Activation energy data for nitrosobenzene monomerdimer exchange^a

Parameter	<i>cis</i> -Dimer→monomer	<i>trans</i> -Dimer → monome
$E_{\rm a}/\rm kJmol^{-1}$	$90.8\pm1.0^{\texttt{b}}$	$\textbf{96.7} \pm \textbf{4.4}$
$\log(A/s^{-1})$	17.17 ± 0.18°	17.47 ± 0.83
$\Delta H^{+}/kJ \text{ mol}^{-1}$	88.5 ± 1.0	94.4 ± 4.4
$\Delta S^{+}/J \mathrm{K}^{-1} \mathrm{mol}^{-1}$	76.1 ± 3.4^{d}	81.9 ± 15.8
ΔG^{+} (298.15 K)/kJ mol ⁻¹	65.8 ± 0.1	$\textbf{70.0} \pm \textbf{0.3}$

^a Uncertainties based on least-squares fittings of Arrhenius and Eyring plots. If rate constant uncertainties (Table 5) are propagated through the calculations, the errors in columns 2 and 3 should be increased by factors of 4 and 8, respectively.

^b 85 ± 4 kJ mol⁻¹ (Ref. 7).

° 16.1 (Ref. 7).

^d 58 J K⁻¹ mol⁻¹ (Ref. 7).

Table 5. It will be noted that the rate of direct *cis-trans* dimer exchange is zero within the error limits of the experiments. Such a result is not surprising, as it implies the absence of any detectable internal rotation about the N=N bond in the nitrosobenzene dimers. Instead, *cis-trans* dimer exchange occurs exclusively via the monomer. This finding is compatible with the fact that *trans-cis* interconversion of azobenzene does not proceed at an NMR-measurable rate. It can only be induced by UV-visible photochemical irradiation.²¹

Activation parameters based on the Arrhenius and Eyring rate theories were computed for the *cis*-dimer \rightarrow monomer and *trans*-dimer \rightarrow monomer pathways and are presented in Table 6. The *trans*-dimer \rightarrow monomer data have not been reported previously by any method, since the *trans* dimer was thought not to exist in solution. A limited amount of data based on UV absorption studies has previously been reported⁷ for the *cis*-dimer \rightarrow monomer dissociation, and comparisons are included in Table 6. The agreement is modest but the present NMR-derived values are considered appreciably more accurate since they are based on a wider temperature range and because the NMR method does not suffer from the resolution limitations of the UV method.

A reaction profile which combines the activation enthalpy changes with the ground state enthalpy differences for the three species is shown in Fig. 4. This summarizes the findings of this NMR study, namely that (i) at low CDCl₃ solution temperatures nitrosobenzene molecules are predominantly dimerized, with the *cis* dimer being more favoured, (ii) at ambient solution temperatures the species are mainly monomeric, (iii) exchange between *cis*- and *trans*-azodioxy dimers is



Figure 4. Enthalpy profile for the nitrosobenzene-CDCl₃ system.

relatively slow and occurs exclusively via the monomer species and (iv) the dissociation pathway cis-dimer \rightarrow monomer is more favoured by $ca \ 6 \ \text{kJ mol}^{-1}$.

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