Nitrosoanisoles. Sensitive indicators of dimerisation criteria for *C*-nitrosoarenes

Brian G. Gowenlock, Mark J. Maidment, Keith G. Orrell,* Ivan Prokeš and John R. Roberts

School of Chemistry, The University, Exeter, UK EX4 4QD. E-mail: K.G.Orrell@exeter.ac.uk

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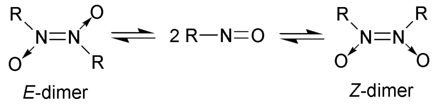
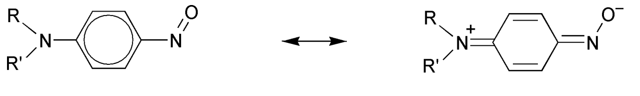
A series of mono- and di-methyl substituted *p*-nitrosoanisoles was synthesised either by direct nitrosation of the anisoles with $NO^+HSO_4^-$ or by mild oxidation (H_2O_2–Mo catalyst) of the appropriate amines. The nature of these compounds in solution was established by ^1H and ^{13}C NMR spectroscopy. Variable temperature ^1H dynamic NMR studies provided thermodynamic data for the cases of dimer–monomer solution equilibria, and $\Delta G^‡$ data for the restricted rotation of the N=O group in the monomers. Magnitudes of $\Delta G^‡$ were in the range 28–41 kJ mol^{-1} and were shown to be sensitive predictors of self-dimerisation tendencies of these compounds. This activation parameter, together with the $^{14,15}N$ and ^{17}O chemical shifts of the N=O group, was shown to be a reliable predictor of self-dimerisation of nitroso compounds in general. The N=O bond length and the wavenumber of the IR-active N=O stretching mode were found to be somewhat less reliable predictors of this behaviour.

Previous studies[1–7] of temperature dependent NMR spectra of a variety of substituted nitrosobenzenes have provided detailed insight into several features of structural interest. The equilibria between the isomeric pair of dimeric nitroso compounds and the monomer (Scheme 1) are a common feature of most of these studies. There is, however, a particular family of 4-substituted nitrosobenzenes† for which there is no evidence for the formation of either dimer whether in the solid state or in solution at temperatures as low as −100 °C. We conclude therefore that for this family, where the 4-substituent is NRR′ (R = R′ = Me, Et; R = Me, R′ = H), dimerisation cannot occur. The accepted explanation of this is that internal charge-transfer from the strong π-electron donating amino group to the strong π-electron accepting nitroso group through the transmitting aromatic ring (Scheme 2) is responsible for this behaviour.



Scheme 1

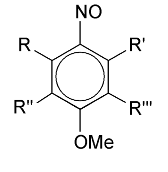


i

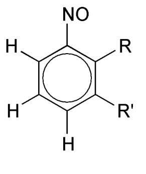
Scheme 2

It has long been established that the consequence of flanking the nitroso group in nitrosobenzene by 2,6-substituents such as methyl or chlorine is an increased stabilisation of the *E*-dimer with respect to the monomer. Thus, at room temperature the equilibrium between the *E*-dimer of 2,4,6-trimethylnitrosobenzene and its monomer is readily studied by the concentration variation of the absorbance of the visible absorption maximum at 790 nm in chloroform, whereas there is no such variation for 4-methylnitrosobenzene which is present solely as monomer. This steric effect of the flanking methyl groups is insufficient to overcome the internal donor–acceptor charge-transfer interaction between the –NRR′ and –N=O groups in structure (**i**) (Scheme 2), causing such 4-(alkylamino)nitrosobenzenes to be monomeric whether in the solid state or in solution. A contrast is provided by the methoxy group, itself a strong π-electron donor, but less so than the dialkylamino group. We have shown that 4-methoxynitrosobenzene (*p*-nitrosoanisole), a monomer in the solid state,[8] remains monomeric in CD_2Cl_2 solution at temperatures down to *ca.* −100 °C. On the other hand, both 2,6-dimethyl-4-methoxynitrosobenzene[9] and 2,6-dichloro-4-methoxynitrosobenzene[10,11] are dimeric in the solid state but dimer–monomer equilibria are established in benzene solution[10] at 25 °C. It is apparent that in these cases the combined steric effect of the 2- and 6-substituents is of very similar magnitude to the charge-transfer effect.

Most other substituted 4-nitrosoanisoles are monomeric solids[12–16] but there are two examples where both a blue monomer and a colourless dimer have been isolated[13] and one where the colourless dimer alone has been formed.[15] In the first two of these examples the methoxy group is flanked by a single $COCH_3$ or CO_2CH_3 group whereas in the other example the nitroso group is flanked by a single CO_2CH_3 group. The presence or absence of dimers can best be shown by low temperature solution-state ^1H NMR spectra. This paper reports on such studies for a series of methyl derivatives of *p*-nitrosoanisoles and for *o*- and *m*-nitrosoanisole.



R	R'	R''	R'''	
H	H	H	H	**1**
Me	Me	H	H	**2**
H	Me	H	H	**3**
H	H	Me	Me	**4**
H	H	H	Me	**5**



R	R'	
OMe	H	**6**
H	OMe	**7**
H	H	**8**

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† As this work focuses on the nitroso group the ring numbering is based on the N=O group being attached to C-1.

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Table 1 Reaction conditions for direct nitrosation of anisole and methyl-substituted anisoles

Starting material	Temp./°C	Reaction time/min	Product[a]	Colour	Yield (%)
Methoxybenzene	25	2	4-Methoxynitrosobenzene	Blue–green	17
3,5-Dimethylmethoxybenzene	0	5	2,6-Dimethyl-4-methoxynitrosobenzene	Off-white	86
3-Methylmethoxybenzene	0	4	2-Methyl-4-methoxynitrosobenzene	Green	71
2,6-Dimethylmethoxybenzene	0	4	3,5-Dimethyl-4-methoxynitrosobenzene	Turquoise	65
2-Methylmethoxybenzene	0	4	3-Methyl-4-methoxynitrosobenzene	Blue–green	91
3,5-Dichloromethoxybenzene	25	30	—	—	~0

[a] Ring numbering based on N=O being attached to C-1.

These studies were initiated in order to elucidate the character of the interactions between the flanking substituents and the nitroso and methoxy groups, and their relationship to the fundamental question[17] 'Why do nitroso compounds dimerise?'

Experimental

Synthesis of compounds

4-Methoxynitrosobenzene (*p*-nitrosoanisole) (**1**), and its methyl derivatives, namely 2,6-dimethyl- (**2**), 2-methyl- (**3**), 3,5-dimethyl- (**4**) and 3-methyl- (**5**), were prepared by direct nitrosation of the appropriate anisole using 40% nitrosyl sulfuric acid in admixture with ethanoic and sulfuric acids, exactly as described by Atherton, Moodie and Noble,[18] except that in the present work nitrogen gas was used throughout the reaction periods. Reaction conditions (times and temperatures) were critical and are given in Table 1. Yields were high and nitrosation occurred solely at the ring position *para* to the methoxy group. The preparation of 2-6-dimethyl-4-methoxynitrosobenzene (below) illustrates the general synthetic procedure.

Synthesis of 2,6-dimethyl-4-methoxynitrosobenzene (2)

50 cm^3 of a mixture of glacial ethanoic acid (50.0 g, Aristar Grade BDH), nitrosyl sulfuric acid (40 wt% solution in sulfuric acid) (7.4 g) and sulfuric acid (23.0 g) were placed in a two-necked 250 cm^3 round-bottomed flask. The mixture was cooled in ice–salt and flushed with nitrogen for 30 minutes until the solution temperature was 0 °C. 3,5-Dimethylmethoxybenzene (1.13 g, 8.0 mmol) was added by injection and the mixture stirred for 5 min before being quenched in saturated sodium hydrogen carbonate solution (1000 cm^3). It was then extracted into dichloromethane (3 × 150 cm^3) and the solvent removed using a rotary evaporator. The crude material was purified by flash chromatography over silica (dichloromethane–hexane, 1 : 4) and the blue–green fraction collected. The solvents were evaporated off using a rotary evaporator to yield 2,6-dimethyl-4-methoxynitrosobenzene as an off-white solid at room temperature. Yield (1.04 g, 86%), mp 122–123 °C (lit. 122 °C,[9] 121–122 °C[16]).

An attempt to make 2,6-dichloro-4-methoxynitrosobenzene by the same route was unsuccessful (see Table 1), presumably as a result of the electron-withdrawing nature of the chlorines deactivating the aromatic ring.

2-Methoxynitrosobenzene (*o*-nitrosoanisole) (**6**) and 3-methoxynitrosobenzene (*m*-nitrosoanisole) (**7**) were prepared by mild oxidation of the appropriate amine using hydrogen peroxide and a molybdenum catalyst, following the method of Porta *et al.*[19]

Spectroscopic methods

Infrared spectra were recorded on compounds **2** to **7** as KBr discs using Nicolet Magna or Avatar 360 FT spectrometers.

NMR spectra were recorded on solutions of compounds **2** to **7** in $CDCl_3$ (for ambient temperature studies) and CD_2Cl_2 (for low temperature studies) using a Bruker Avance DRX 400 spectrometer operating at 400 MHz for ^1H spectra and 100.58 MHz for ^{13}C spectra. The natural abundance ^{17}O spectrum of **1** was recorded as a neat liquid at 54.25 MHz using 5% C_6D_6 as a lock material. The natural abundance ^{15}N spectrum of **2** was recorded as a concentrated solution in $CDCl_3$ at 40.53 MHz using the Bruker program zg30 and collecting 2048 pulses. The Bruker B-VT-2000 unit was used to vary the NMR probe temperatures during low temperature runs, care being taken to ensure good temperature stability before any spectra were recorded. Calculations of thermodynamic parameters for the dissociation equilibria of the *C*-nitroso dimers were based on accurate integrations of appropriate pairs of NMR signals arising from solutions of known molar concentration. Kinetic data for the nitroso-group rotations were based on either bandshape analyses using the authors' version of the DNMR3 program[20] or on band coalescence measurements,[21] allowance being made for exchange between different site populations.

Results

IR spectra

Compounds **2**, **6** and **7** were colourless crystalline materials, like nitrosobenzene, **8**, indicative of dimeric compounds.[22] The remaining compounds, **1**, **3**, **4** and **5**, were isolated as blue–green crystals, indicating primarily monomeric species.[22] IR spectra of all the methyl-substituted nitrosoanisoles were recorded as KBr discs to establish the more precise solid-state nature of these *C*-nitroso compounds.

NMR spectra

^1H NMR spectra of compounds **1**–**8** were undertaken at temperatures between ambient and *ca.* −100 °C to study the dimer–monomer dissociation equilibria and to measure the activation energy associated with the restricted rotation of the N=O group in the monomer species.

^1H NMR chemical shifts are reported (Table 2) at below-ambient temperatures where rates of exchange between dimer and monomer species and rates of N=O group rotation in the monomers are both slow on the NMR timescale. The aromatic hydrogen signals of the dimers remain sharp at all temperatures whereas those of the monomers, particularly those of hydrogens adjacent to the N=O group in the 2- and 6-positions, are greatly affected by the rate of N=O group rotation such that, on decreasing temperature, they broaden considerably, even to the extent of vanishing for a short range of temperature, and then reappear as pairs of signals in the ranges δ = 9.2–9.5 and δ = 6.2–6.5. Such extremely large chemical shift differences are the result of the very large magnetic anisotropy of the N=O group. This is illustrated by the double cone shielding/deshielding diagram[5] (Fig. 1) which identifies shielding of the aromatic hydrogen signals *syn* to the N=O and deshielding of those *anti* to N=O.

The ^{13}C chemical shift data for compounds **1**–**5** and **8** are given in Table 3. Monomer and dimer species are readily distinguished by their C-1 shifts as previously reported.[23,24]

Table 2 ^{1}H NMR chemical shift data^{a} for compounds **1**–**8** in the slow exchange limit

Compound	Solvent	Temp./K	Species	δ_2	δ_3	δ_4	δ_5	δ_6
1	$CDCl_3$	213	M	6.54^{b}	6.84^{b}	3.86^{b,c}	7.26^{b}	9.34^{b}
2	CD_2Cl_2	173	M	~2.1^{d}	~6.6^{d}	3.86	~6.6^{d}	~3.1^{d}
			Z-D	2.30	6.65	3.76	6.65	2.30
			E-D	2.05	6.43	3.67	6.43	2.05
3	CD_2Cl_2	173	M (*anti*, 90%)	3.14	6.76	3.77	6.45	6.15
			M (*syn*, 10%)	2.35	?	?	?	9.23
4	CD_2Cl_2	173	M	6.07	2.16	3.71	2.47	9.08
			Z-D?	7.87	2.26	3.66	2.59	7.87
			E-D?	6.96	2.11	3.54	2.11	6.96
5	CD_2Cl_2	183	M (*syn*, 75%)	6.33	2.05	3.92	7.13	9.13
			M (*anti*, 25%)	9.08	2.34	3.85	6.71	6.34
6	CD_2Cl_2	273	M (*anti*, ~100%)	4.27	7.40	7.72	6.87	6.25
		273	*Z*-D	3.81	7.48	7.34	6.92	6.78
		213	*E*-D?	3.80	?	?	?	?
7	CD_2Cl_2	163	M (*syn*, 84%)	5.77	3.67	7.31	7.77	9.07
			M (*anti*, 16%)	~9.0^{e}	3.98^{f}	~7.3	~7.8	5.88
		243	*Z*-D	6.96	3.73	6.89	7.22	6.93
8	CD_2Cl_2	173	M	6.28^{b}	7.35^{b}	7.76^{b}	7.90^{b}	9.52^{b}

[a] Relative to Me_4Si ($\delta = 0$). [b] Ref. 5. [c] At 303 K. [d] Bands very broad ($\Delta\nu_{1/2}$ ~100 Hz) due to effects of N=O rotation. [e] Partially obscured by band at $\delta = 9.07$. [f] Broad band ($\Delta\nu_{1/2} \approx 30$ Hz) due to effects of N=O rotation.

Table 3 ^{13}C NMR chemical shifts^{a} of compounds **1**–**5** and **8**

Compound	Solvent	Temp./K	Species	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
1	$CDCl_3$	303	M	165.57^{b,c}	124.56^{c,d}	113.81^{c}	55.94 (Me)^{c} 163.92 (qtC)^{b,c}	113.81^{c}	124.56^{c,d}
2	$CDCl_3$	303	M	164.33^{b}	20.29 (Me) 137.23 (qtC)	114.39	55.70 (Me) 163.37 (qtC)^{b}	114.39	20.29 (Me) 137.23 (qtC)
			Z-D	152.26	18.99 (Me) 134.47 (qtC)	114.09	55.45 (Me) 160.41 (qtC)	114.09	18.99 (Me) 134.47 (qtC)
3	$CDCl_3$	303	M	166.12	17.63 (Me) 146.44 (qtC)	111.97^{b}	55.83 (Me) 163.38 (qtC)	111.03^{b}	115.24
4	$CDCl_3$	303	M	163.89^{b}	122.57	16.36 (Me) 132.06 (qtC)	59.76 (Me) 163.59 (qtC)^{b}	16.36 (Me) 132.06 (qtC)	122.57
			?^{e}	132.31	124.24	18.44 (Me) 126.33 (qtC)	58.48 (Me) 162.40 (qtC)	18.44 (Me) 126.33 (qtC)	124.24
5	$CDCl_3$	303	M	164.14^{b}	~127^{d}	16.24 (Me) 127.52 (qtC)	56.07 (Me)^{b} 163.79 (qtC)^{b}	109.14	~121^{d}
8	$CDCl_3$	263	M	165.67^{f}	120.99^{f}	129.38^{f}	136.00^{f}	129.38^{f}	120.99^{f}
			Z-D	143.11^{f}	124.42^{f}	129.55^{f}	130.99^{f}	129.55^{f}	124.42^{f}
			E-D	142.26^{f}	123.63^{f}	128.98^{f}	131.32^{f}	128.98^{f}	123.63^{f}

[a] Relative to Me_4Si ($\delta = 0$). [b] Assignments could possibly be interchanged. [c] Ref. 16. [d] Bands broadened due to effect of N=O rotation. [e] Identification of species uncertain. [f] Ref. 1.

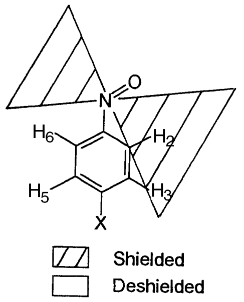


Fig. 1 Shielding/deshielding magnetic anisotropy of the nitroso group.

In the present compounds C-1 shifts for nitroso monomers are in the range δ = 164–166 and for dimers in the range δ = 142–152.

Particular NMR characteristics of the individual compounds will now be summarised.

4-Methoxynitrosobenzene (1). In previous studies[5,6] this compound was shown to exist solely as a monomer at all temperatures. However, a close examination of the ^{1}H spectrum of a concentrated solution of **1** in $CDCl_3$ in conjunction with a 'cross-dimerisation' experiment (see later) identified a weak set of signals thought to be due to an azodioxy species. Cooling a CD_2Cl_2 solution of **1** in the earlier work[5,6] allowed measurement of the activation energy for the N=O rotation in the monomer.

2,6-Dimethyl-4-methoxynitrosobenzene (2). Dissolution of this solid-state dimer in CD_2Cl_2 solution afforded a dimer–monomer equilibrium which was studied in the temperature range 20 to −100 °C. At 20 °C the spectrum consisted of signals due to the monomer plus a weaker set due to the *Z*-dimer. On cooling the latter increased in intensity at the expense of the monomer signals and, below 0 °C, a third set of signals appeared that was attributed to the *E*-dimer. Both sets of dimer signals increased with decreasing temperature and below −80 °C the monomer aromatic and methyl signals broadened as a result of the slowing of the N=O group rotation. At −100 °C the methyl signal had split into two broad bands, enabling an estimate to be made of the energy barrier of the rotation process. Typical spectra of the aromatic signals at different temperatures are shown in Fig. 2. Accurate integrations of the relative signal intensities at different temperatures enabled thermodynamic parameters for the dissociation equilibria to be evaluated.

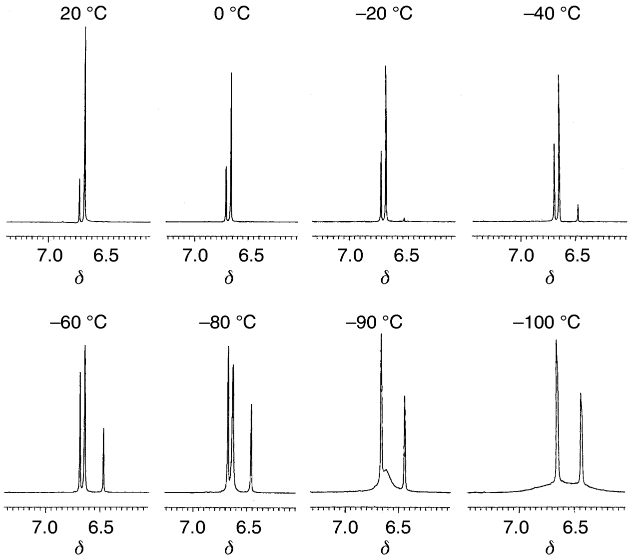


Fig. 2 Variable temperature ^{1}H NMR spectra of the aromatic signals of 2,6-dimethyl-4-methoxynitrosobenzene (**2**) in CD_2Cl_2 showing the formation of *Z*- and *E*-dimers on cooling. At temperatures below −80 °C the monomer signal broadens as a result of the slowing up of the N=O rotation.

4-Methoxynitrosobenzene (1) + 2,6-dimethyl-4-methoxynitrosobenzene (2). The room temperature spectra of **1** and **2**, both in $CDCl_3$, were compared carefully with the spectrum of an equimolar mixture of the two compounds in order to investigate whether any cross-dimerisation had occurred between the two compounds. Additional weak signals were detected at δ = 8.13 (doublet), 6.75 (doublet), 6.49 (singlet), 3.76 (singlet), 3.75 (singlet), 2.28 (singlet) and 2.22 (singlet), six of which were attributed to the mixed dimer species, presumably the *Z*-dimer. (One of the signals at 2.28 or 2.22 was surplus to requirements and its origin was unknown.) This indicates that there is a very slight tendency of **1** to cross-dimerise as well as to self-dimerise.

2-Methyl-4-methoxynitrosobenzene (3). This compound remained monomeric at all temperatures. Cooling to *ca.* −100 °C arrested the N=O group rotation, causing a very large splitting of the 6-position hydrogen signal ($\Delta\delta$ = 3.1) and a smaller splitting ($\Delta\delta$ = 0.8) of the methyl signal into pairs of very unequal intensity signals. This is the result of the very unequal populations of the two rotamers, with the one with N=O being oriented *anti* to the flanking methyl group being highly preferred, leading to a population ratio at −100 °C of 90% *anti*, 10% *syn*.

3,5-Dimethyl-4-methoxynitrosobenzene (4). This monomeric solid gave a strong set of signals in solution due to the monomeric species. A weaker set of signals was also observed at room temperature followed by a second weak set of signals at temperatures below about −20 °C. These signals were initially identified as the *Z*- and *E*-azodioxy dimers respectively. However, their relative intensities did not increase with decreasing temperature as is usual in dissociation equilibria of this type.[6] This may be the result of the appreciably lower solubility of the dimer species at lower temperatures or the extra signals being due to other unidentified solution species. In either case it was not possible to calculate meaningful thermodynamic parameters for the dimer–monomer dissociation equilibria. The restricted N=O rotation in the monomer was reflected in a large splitting of the 2- and 6-hydrogen signals ($\Delta\delta$ = 3.0) and a smaller splitting of the 3- and 5-methyl signals ($\Delta\delta$ = 0.3) at temperatures at or below −90 °C.

3-Methyl-4-methoxynitrosobenzene (5). This compound also was purely monomeric in CD_2Cl_2 solution at all temperatures, and the changes observed were the result of the slowed rates of N=O rotation on lowering the temperature. The changes in the aromatic, methoxy and methyl signals are shown in Fig. 3(a), (b) and (c) respectively. These clearly illustrate the 'freezing out' of the two non-equivalent rotamers at low temperature, the chemical shifts clearly indicating that the more abundant rotamer (75% abundance) has the N=O group oriented *syn* to the 3-methyl substituent in accordance with previous work.[5]

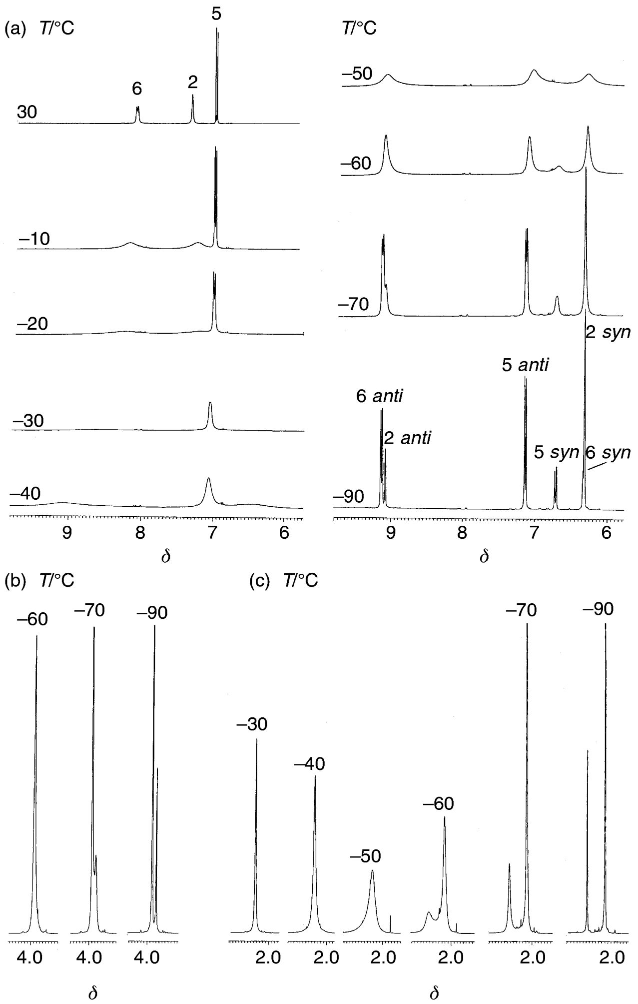


Fig. 3 Variable temperature ^{1}H NMR spectra of 3-methyl-4-methoxynitrosobenzene (**5**) in CD_2Cl_2 showing the effects of 'freezing out' the N=O rotation on (a) the aromatic signals, (b) the methoxy signals and (c) the methyl signals.

2-Methoxynitrosobenzene (6). The colourless crystals of this compound dissolved in CD_2Cl_2 solution to give ^{1}H NMR signals purely due to the monomer, but on cooling to 0 °C evidence of *Z*-dimer signals appeared and these steadily increased in intensity on cooling. At temperatures below *ca.* −20 °C there was some evidence, primarily in the methoxy region (Table 2), of the presence of the *E*-dimer but its signals did not increase greatly on further cooling.

The monomer signals did not change with temperature, implying that only a single N=O rotamer exists, presumably that with the N=O group oriented *anti* with respect to the methoxy group.

3-Methoxynitrosobenzene (7). This compound behaved similarly to **6** with the solid dimer being fully dissociated at room temperature giving monomer signals only. On cooling a solution of **7** signals due to the *Z*-dimer appeared as in the case of compound **6**. When the temperature fell below

Table 4 Thermodynamic data for the dimer dissociation equilibria of *C*-nitrosoanisoles

Compound	Equilibrium	ΔH^0/kJ mol^{-1}	ΔS^0/J K^{-1} mol^{-1}	$\Delta G^{0\,a}$/kJ mol^{-1}
1	Monomer only	—	—	—
2	*Z*-D⟶2M	49.5 ± 1.4	186 ± 5	−6.0 ± 0.1
	E-D⟶2M	36.9 ± 2.5	168 ± 7	−13.2 ± 0.8
3	Monomer only	—	—	—
4	*Z*-D⟶2M	?	?	?
	E-D⟶2M	?	?	?
5	Monomer only	—	—	—
6	*Z*-D⟶2M	44.8 ± 2.4	180 ± 9	−8.9 ± 5.1
7	*Z*-D⟶2M	38.4 ± 1.3	173 ± 5	−13.2 ± 2.8
8	*Z*-D⟶2M	55.4 ± 1.7[b]	213 ± 7[b]	−8.1 ± 0.3[b]
	E-D⟶2M	42.5 ± 1.2[b]	179 ± 5[b]	−10.9 ± 0.3[b]

[a] Measured at 298.15 K. [b] Ref. 1.

ca. −60 °C the monomer signals of the 2- and 6-position hydrogens broadened as a result of the N=O rotation and, at −110 °C, split in a manner similar to the corresponding signals of **5**, the *syn* : *anti* rotamer ratio being 84% : 16% at −110 °C.

Nitrosobenzene (8). This compound has been much studied by NMR spectroscopy previously[6] and is known to exist in solution as both types of dimers (but predominantly the *Z*-isomer) in equilibria with the monomeric form. At low temperatures the N=O rotation of the monomers becomes slow and chemical shift distinction arises between the 2- and 6-position hydrogens and between the 3- and 5-position hydrogens. The second-order spectra have been analysed previously,[5] and the ^{1}H shifts reported (Table 2). ^{1}H shifts of the dimers have not been measured as these species are more usefully characterised by their ^{13}C shifts (Table 3).

Thermodynamic data for dimer–monomer dissociations. Monomer–dimer equilibria in CD_2Cl_2 solutions were clearly established in the cases of compounds **2**, **6** and **7**, and from accurate measurements of relative populations of *Z*- and *E*-dimers co-existing with monomer in the temperature range ambient to *ca.* −40 °C, equilibrium constants K^0 for the dissociations of either or both dimers were calculated. Temperature dependences of K^0 yielded thermodynamic parameters ΔH^0, ΔS^0 and ΔG^0(298.15 K) for these equilibria (Table 4). It should be noted that the solid dimer of **2** as prepared here and elsewhere[9b,16] at room temperature is the *E*-dimer whereas in solution at low temperatures the *Z*-dimer predominates. Compound **4**, the 3,5-dimethyl derivative, was problematical in that two sets of weak signals, originally attributed to the two isomeric dimers, did not change their intensity with temperature. This led to unrealistic magnitudes of thermodynamic parameters so it was concluded that either true monomer–dimer equilibria were not established or the species were of a different chemical nature.

The results in Table 4 for compounds **2**, **6**, **7** and **8** reflect the fact that at ambient temperatures only monomeric species existed in solution, but, on cooling, *Z*-dimer signals appeared with increasing intensity. In the cases of **2** and **8** *E*-dimer signals also appeared but these remained relatively weak and their temperature dependences were less than those of the *Z*-dimer signals. This is reflected in the relative magnitudes of the ΔH^0 values for the *Z*- and *E*-dimers of the same compound. All ΔH^0 values are positive, indicating the endothermic nature of the dissociation process and the stabilisation of the dimer species at lower temperatures. All ΔS^0 values are large and positive, as expected for dissociation processes, and ΔG^0 values are relatively small and negative, reflecting the tendency for solution dissociation at 298.15 K. All these values are in agreement with a more extensive set of values compiled for other aromatic nitroso compounds.[6]

Activation energies for nitroso-group rotation in nitrosoanisole monomers

The results of dynamic NMR studies on the monomers of compounds **1**–**8** are listed in Table 5. Only free energies of activation are quoted as these are relatively insensitive to systematic errors. Where the pairs of monomers are chemically distinct $\Delta G^‡$ values for interconversion in both directions are given. Magnitudes are in the approximate range 28–43 kJ mol^{-1}. Comparisons between certain pairs of compounds reveal a number of significant trends as follows.

(i) **1** ⟶ **2**, $\Delta\Delta G^‡ = -9.3$ kJ mol^{-1}. This represents the lowering of the energy barrier by methyl groups flanking the NO group. This can be envisaged as either an electronic effect or a steric effect whereby the NO group is forced somewhat out of the ring plane and towards the orthogonal transition state geometry, thus reducing the rotation energy barrier.

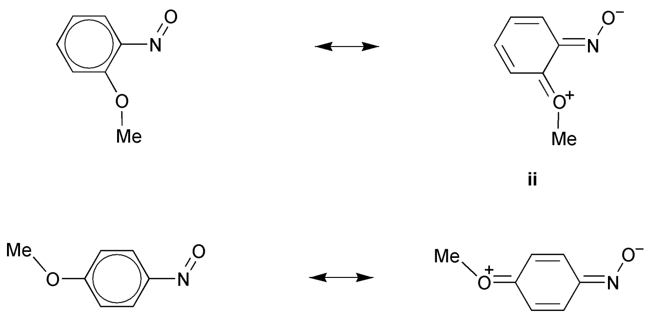
(ii) **1** ⟶ **3**, $\Delta\Delta G^‡ = -8.6$ or -2.0 kJ mol^{-1}. The average of these represents the effect of one methyl group flanking the nitroso group.

(iii) **1** ⟶ **4**, $\Delta\Delta G^‡ = -3.4$ kJ mol^{-1}. This energy change represents either the electronic effect of two methyls *meta* to the NO group or the electronic/steric effect(s) of two methyls flanking the OMe group. The steric effect can be rationalised in terms of the methoxy function being forced slightly out of the aromatic ring plane, thereby making it a slightly less effective π-electron donor.

(iv) **1** ⟶ **5**, $\Delta\Delta G^‡ = +2.3$ or $+0.8$ kJ mol^{-1}. This is the effect of a single *meta* methyl or a single OMe flanking methyl, and the effect on the NO function is very slight.

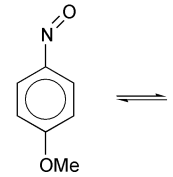
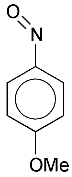
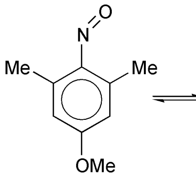
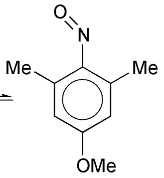
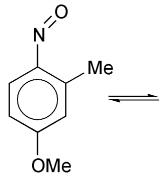
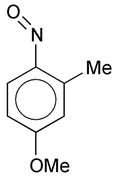
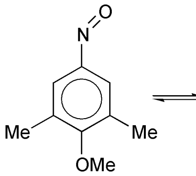
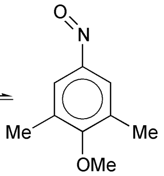
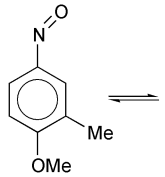
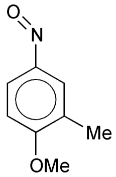
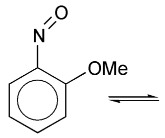
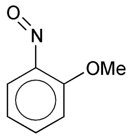
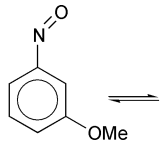
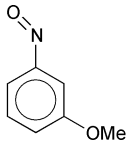
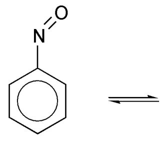
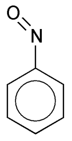
(v) **1** ⟶ **6**, $\Delta\Delta G^‡$ not known, since $\Delta G^‡$ could not be measured for **6** as only a single rotamer was present. A raising of the N=O rotation barrier is, however, predicted theoretically on account of the likely contribution of the quinonoid structure **(ii)**, Scheme 3.

(vi) **8** ⟶ **1**, $\Delta\Delta G^‡ = +6.7$ kJ mol^{-1}. This represents quantitatively the effect of the π-electron donating OMe in the *para*



Scheme 3

Table 5 Activation free energies for nitroso-group rotation in monomers of *C*-nitrosoanisoles

No.	Compound (a)	Compound (b)	Conversion	NMR method[a]	Temp./K	$\Delta G^{\ddagger b}$/kJ mol^{-1}
1			(a)⟶(b) (b)⟶(a)	BSA	298.15	41.0 ± 0.3[c] 41.0 ± 0.3[c]
2			(a)⟶(b) (b)⟶(a)	BCM	173	31.7 ± 0.5 31.7 ± 0.5
3	 minor	 major	(a)⟶(b) (b)⟶(a)	BCM	203	32.4 ± 0.5 39.0 ± 0.5
4			(a)⟶(b) (b)⟶(a)	BCM	213	37.6 ± 0.5 37.6 ± 0.5
5	 major	 minor	(a)⟶(b) (b)⟶(a)	BCM	243	43.3 ± 0.5 41.8 ± 0.5
6			Only (b) present	—	—	—
7	 major	 minor	(a)⟶(b) (b)⟶(a)	BCM	163	30.9 ± 0.7 28.3 ± 0.7
8			(a)⟶(b) (b)⟶(a)	BSA	298.15	34.3 ± 0.2[c] 34.3 ± 0.2[c]

[a] BSA = bandshape analysis; BCM = band coalescence method. [b] Calculated at temperature given. [c] Ref. 6.

position to NO promoting the quinonoid form of the structure (structure (**iii**), Scheme 3), and raising the energy barrier to NO rotation. It should be noted that this barrier is raised to ~21 kJ mol^{-1} when the exceptionally strong electron-donating NMe_2 group occupies the *para* position relative to NO.[3]

(vii) **8** ⟶ **7**, $\Delta\Delta G^{\ddagger} = -3.4$ or -6.0 kJ mol^{-1}. The mean of these values represents the effect of a methoxy group located *meta* to the NO group. No quinonoid form of structure is possible here and so the energy barrier to NO rotation is not raised, but apparently reduced slightly.

Table 6 The relationship between free energies of activation for NO rotation in monomers of *C*-nitrosoanisoles and self-dimerisation tendencies

Compound	$\Delta G^{\ddagger}_{\text{major}\longrightarrow\text{minor}}$/kJ mol^{-1}	$CDCl_3$ or CD_2Cl_2 solution[a]	Solid[a]
5	43.3	M	M
1	41.0	M	M
3	39.0	M	M
4	37.6	M + D[b]	M
8	34.3	M + D[c]	*Z*-D
2	31.7	M + D[c]	*E*-D
7	30.9	M + D[d]	*Z*-D
6	?[e]	M + D[c]	*Z*-D

[a] M = monomer, D = dimer. [b] Trace only of possible dimer. [c] *Z*-D + trace *E*-D. [d] *Z*-D only. [e] Not known since only one rotamer type present.

Table 7 ^{14,15}N and ^{17}O NMR chemical shift data[25] for nitroso compounds

Compound	Self-dimerisation?	$\delta(^{14,15}\text{N})$[a]	$\delta(^{17}\text{O})$[b]	Reference
^{t}BuNO	Yes	590	1538	
$PhCO_2(CMe_2)_2NO$	Yes?	568		26
2-MeC_6H_4NO	Yes	543	1543	
		537		29
PhNO	Yes	530	1533	
		533	1534	27 (^{17}O), 28 (^{15}N)
		519		1
		525		29
C_6F_5NO	Yes	513		28
2,6-Me_2-4-$MeOC_6H_2NO$ (**2**)	Yes	510		This work
4-$MeOC_6H_4NO$ (**1**)	No?	485	1398	This work (^{17}O), 29 (^{14}N)
2-NHMe-3,5-$(NO_2)_2C_6H_2NO$	No	485		30
2-NH_2-3,5-$(NO_2)_2C_6H_2NO$	No	474		31
RSNO	No	452	1300	
$CF_2ClCFClNO$	No	428		26
4-$Me_2NC_6H_4NO$	No	386	1265	
ClNO	No	222	915	
RONO	No	190	800	
R_2NNO	No	155	670	
O^-NO	No	229	650	
NO^+	No	−3	474	

[a] Relative to external $MeNO_2$. Unless stated otherwise, data from Dahn *et al.*[25] [b] Relative to external H_2O. Unless stated otherwise, data from Dahn *et al.*[25]

It is clear from these comparisons that the $\Delta G^{\ddagger}$ parameter for nitroso group rotation in monomers of nitrosoarenes is a very sensitive indicator of the electronic nature of the NO group that in turn determines the tendencies of such compounds to self-dimerisation. This point is made more explicitly by examining the data in Table 6 where the $\Delta G^{\ddagger}$ values for major ⟶ minor rotamer interversions are listed in decreasing order of magnitude for compounds **1**–**8**. Compounds **1**, **3** and **5** are monomeric in both solid and solution phases whereas compounds **2**, **6**, **7** and **8** are solid-state dimers but in solution the dimers coexist with monomers. Compound **4** (3,5-dimethyl-4-methoxynitrosobenzene) is monomeric in the solid but shows possible evidence of some very slight dimer formation in solution, although true equilibrium conditions do not seem to be established (see earlier). From the $\Delta G^{\ddagger}$ data it would appear that all compounds with nitroso group rotational free energies >38 kJ mol^{-1} show no tendency to self-dimerisation under any conditions, whereas those compounds with values <38 kJ mol^{-1} do exist as self-association dimers in the solid and as monomer–dimer equilibria in solution. Compound **4** is at the critical interface between these two types of property and behaves rather abnormally as a result.

Discussion

We have shown that the $\Delta G^{\ddagger}$ values for N=O rotation are very sensitive indicators of self-dimerisation tendencies in nitrosoanisoles. We further suggest that this correlation may be extended to other aromatic *C*-nitroso compounds with π-electron donating groups such as –NRR′ and π-electron acceptors such as halogens. The $\Delta G^{\ddagger}$ parameter is clearly a sensitive probe of the electronic character of the C–N=O moiety for nitrosoarenes, but alternative NMR probes of this character are the ^{14,15}N and ^{17}O chemical shifts, as suggested by Dahn *et al.*[25] These latter parameters have the added advantage that they can be applied to nitrosoalkanes as well as to nitrosoarenes. They have been measured for a wide range of nitroso compounds and are listed in Table 7. It will be seen immediately that compounds with $\delta(^{14,15}\text{N})$ values ≥510 have strong self-dimerisation tendencies whereas those with values <485 do not dimerise, with the dividing line between these two properties lying between the *para* nitrosoanisoles **2** and **1**. Rather fewer $\delta(^{17}\text{O})$ values of nitroso groups have been measured but the data in Table 7 show that self-dimerising compounds have $\delta(^{17}\text{O})$ values ≥1533, whereas those that remain monomeric have values <*ca.* 1400. It has been demonstrated[25] that there is a strong linear correlation between $\delta(^{17}\text{O})$ and $\delta(^{14,15}\text{N})$ values in NO-containing compounds. The dividing line between the property of self-dimerisation and its absence is therefore to be attributed to the extent of deshielding of the NO group. In those 4-substituted nitrosobenzenes where dimerisation does not occur internal partial charge transfer from the strong donor groups to the nitroso group (see Schemes 2 and 3) is responsible for increased shielding of the N and O atoms. Analogous partial charge transfers occur in perhalogenonitroso alkanes such as $CF_2ClCFClNO$, again leading to increased shielding of the N and O atoms (Table 7).

Earlier discussion of the factors affecting dimerisation

Table 8 Criteria relating to dimerisation/non-dimerisation tendencies of *C*-nitroso compounds

Parameter	Dimerisation	No dimerisation
$\delta(^{17}O)^a$	1533↑	1398↓
$\delta(^{14,15}N)^b$	510↑	485↓
$\Delta G^{\ddagger c}$/kJ mol^{-1}	38↓	38↑
$\tilde{\nu}_{(NO\ st)}{}^d$/cm^{-1}	1480–1590	1480↓^{e} or 1590↑^{f} (1480–1440) or (1590–1625)
$r_{NO}{}^g$/Å	1.230–1.192	1.25↑^{e} or 1.19↓^{f} (1.25–1.27) or (1.19–1.17)

[a] NMR shifts relative to external H_2O. [b] NMR shifts relative to external $MeNO_2$. [c] Free energy of activation (at 298.15 K) for rotation of NO group in monomer. [d] Wavenumber of NO stretching vibration. [e] Nitrosoanilines. [f] Perhalogenated NO compounds. [g] NO bond length.

tendencies of nitroso compounds[4] has centred on the lengths of N=O bonds in the monomers and their associated IR-active stretching wavenumbers. The relationship between these two parameters has been established by Cameron, Gowenlock and Vasapollo.[32] Literature data indicate that dimerisation occurs within the N=O stretching wavenumber 'window' of 1480–1590 cm^{-1}, which corresponds to N=O bond lengths in the range 1.230–1.192 Å, Table 8. Nitrosoanilines possess $\tilde{\nu}$ (N=O) values <1480 cm^{-1} (1480–1440 cm^{-1}) corresponding to bond lengths of 1.25–1.27 Å, whereas perhalogenated nitroso compounds have $\tilde{\nu}$ (N=O) values >1590 cm^{-1} (1590–1625 cm^{-1}) which correspond to bond lengths of 1.19–1.17 Å, and neither class of compounds dimerises.

This 'dimerisation window' predicts that 4-methoxynitrosobenzene, **1**, will dimerise since the molecule possesses an N=O bond length of 1.228 Å and a $\tilde{\nu}$ (N=O) value variously reported as 1497,[33] 1508,[9b] 1502[8] and 1504[16] cm^{-1}. Prior to this work there was no evidence of any such dimerisation. However, our examination (earlier) of the ^{1}H NMR spectrum of a concentrated solution of **1** in $CDCl_3$ (see earlier) did show very weak signals attributed to the *Z*-dimer of **1**, so the prediction is verified. Nevertheless, N=O bond lengths and $\tilde{\nu}$ (N=O) values appear to be less reliable indicators of the behaviour of borderline compounds such as nitrosoanisoles, as illustrated by the fact that compound **2** is a solid-state dimer but is reported[9b] to have a $\tilde{\nu}$ (N=O) value of 1492 cm^{-1} for its monomeric form in solution, whereas compounds **3**, **4** and **5** are solid-state monomers with $\tilde{\nu}$ (N=O) of 1493, 1483 and 1488 cm^{-1} respectively.[16] We are therefore strongly inclined to the view that self-dimerisation tendencies of N=O compounds are best defined in terms of the NMR-based parameters ^{14,15}N and ^{17}O chemical shifts and the activation parameter $\Delta G^{\ddagger}$ for N=O rotation in the monomeric species.

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