

# Structural investigations of *C*-nitrosobenzenes. Part 1. Solution state <sup>1</sup>H NMR studies

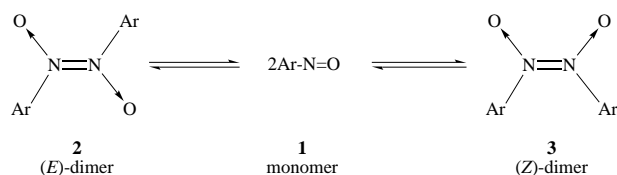


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Ambient and low temperature <sup>1</sup>H NMR spectra of a wide range of 3- and 4-monosubstituted, and some di- and tri-substituted *C*-nitrosobenzenes have enabled –N=O substituent constants for the static and rotating ring molecules to be calculated. This has provided information on the shielding anisotropy of the N=O group which in turn leads to the firm identification of the monomeric and dimeric solution species. In all cases lowering the solution temperature enhances the relative populations of dimers to monomers, with the (*Z*)-azodioxy dimer being preferred over the (*E*)-form, irrespective of the nature of the solid state dimeric structure.

The chemistry of *C*-nitrosobenzene has been studied from 1874 onwards and a wide range of mono-, di- and tri-substituted derivatives have been prepared. The majority of these are isolated as colourless solids although some are obtained as blue crystals. Although it was soon recognised that the colourless solids were dimeric and the blue solids monomeric, it was only when detailed IR spectroscopic studies were made that the existence of two different dimeric forms of *C*-nitrosoarenes was established.<sup>1,2</sup> Thus the structural chemistry of substituted nitrosobenzenes must be discussed in terms of three distinct molecular forms, the monomer **1**, the (*E*)-dimer **2**, and the (*Z*)-dimer **3**. The interrelationship of the three



structures is illustrated in Scheme 1. By the use of a variety of organic solvents and a range of temperatures and concentrations it is therefore possible in principle to study the factors which are responsible for the varying proportions of the three molecular forms by <sup>1</sup>H or <sup>13</sup>C NMR spectroscopy. The earliest studies of these systems used electronic absorption spectroscopy but the much greater sensitivity of <sup>1</sup>H NMR spectroscopy permits studies of a wider ranging character.<sup>3-5</sup> Recently we have shown that crystalline 4-iodonitrosobenzene can be prepared both as **1** and **2** whereas in solution at low temperatures the presence of **1**, **2** and **3** is established, with **3** predominating.<sup>6</sup> Most earlier work had implied that only **1** was isolated in the solid state. We have therefore decided to extend these studies in order to clarify further the reasons for dimer formation and the relative stabilities of the three molecular forms in solution over a wide range of temperatures. The choice of substituted nitrosobenzenes for study here has been made on the basis of published information concerning the nature of the solids obtained by standard synthetic methods coupled with the possibility of comparison of the same substituent in the 3- and 4- position. This paper provides definitive <sup>1</sup>H NMR characterisation of the solution species of a wide range of *C*-nitrosoarenes. Table 1 lists the chosen compounds together with a summary of their methods of preparation and their solid state structural identifications.

**Table 1** Summary of *C*-nitrosoarenes studied previously

Substituent	Solid state structures identified <sup>a</sup>	References (IR*, X-ray <sup>+</sup> )	Preparative method <sup>b</sup>
4-F	( <i>E</i> )-D	2*	I
4-Cl	( <i>E</i> )-D	2*, 7*	I
4-Br	( <i>E</i> )-D, M	2*, 8*, 9*, 10 <sup>+</sup>	I
4-I	( <i>E</i> )-D, M	1*, 7*, 6 <sup>+</sup> , 11 <sup>+</sup>	I
4-Me	( <i>E</i> )-D	2*, 9*	I, II
4-OMe	( <i>E</i> )-D?, M	1*, 2*, 7*, 12*, 13 <sup>+</sup>	II
3-F	( <i>Z</i> )-D	14*	I
3-Cl	( <i>E</i> )-D, ( <i>Z</i> )-D	14*	I
3-Br	( <i>E</i> )-D, ( <i>Z</i> )-D	14*	I
3-I	( <i>E</i> )-D, ( <i>Z</i> )-D	3*, 14*	I
3-Me	( <i>Z</i> )-D	14*	I
3-CH=CHCO <sub>2</sub> Et	( <i>E</i> )-D, M	14*, 15 <sup>+</sup>	I
3,4-diMe	M	14*	I
3,5-diMe	( <i>Z</i> )-D	14*	I
2,4,5-triMe	( <i>E</i> )-D, M	7*, 9*, 12* 14*	II
3-CO <sub>2</sub> H-4-OH	M	16 <sup>+</sup>	III

<sup>a</sup> M = monomer and D = dimer. <sup>b</sup> Synthetic route I, –NO<sub>2</sub>→–NHOH→–NO; II, –NH<sub>2</sub>→–NO; III, direct nitrosation.

## Experimental

### NMR method

All variable temperature solution state spectra were recorded on a Bruker AM250, a Bruker AC300 or Bruker Avance DRX 400 spectrometer, using standard B-VT 1000 or B-VT 2000 variable temperature units. The <sup>1</sup>H spectra were recorded at 250.13, 300.13 and 400.13 MHz, the <sup>13</sup>C spectra at 62.90, 75.47 and 100.62 MHz and the <sup>19</sup>F spectra at 235.32, 282.36 and 376.44 MHz. The <sup>1</sup>H and <sup>13</sup>C shifts are relative to TMS; <sup>19</sup>F shifts are relative to C<sub>6</sub>F<sub>6</sub>. NMR probe temperatures, based on calibration against a Comark digital thermometer are accurate to ca. ±1 °C. Spectra were recorded as solutions in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub>, unless stated otherwise. NMR bands were analysed using a version of the DNMR3 program.<sup>17</sup> The computer simulated spectra were compared visually with those experimentally obtained and the 'best-fit' rate constants were used to calculate the activation parameters from a least squares fitting in Eyring plots, using the THERMO program.<sup>18</sup> The errors quoted are based on the goodness-of-fit of this plot.

### Preparations of nitrosobenzenes

Nitrosobenzene was a commercial product (Aldrich). 2,4,5-Trimethylnitrosobenzene was donated by Professor B. G. Gowenlock and Dr M. Cameron. 4-Chloronitrosobenzene was prepared by Professor W. Lüttke.

**Preparation of 3-substituted nitrosobenzenes.** The substituted nitrobenzene (0.027 mol), ammonium chloride (2.0 g, 0.037 mol) and zinc powder (5.0 g) were added to ethanol (40 cm<sup>3</sup>) and water (12 cm<sup>3</sup>) with stirring. The suspension was then refluxed until the colour of the zinc powder turned white (showing the formation of zinc oxide). The solution was then filtered and added to an iron(III) chloride solution (3.0 g FeCl<sub>3</sub> in 150 cm<sup>3</sup> of ice-water) and stirred for 5 min. The solid which formed was separated, washed with water and then dried overnight. The product was then purified by vacuum sublimation, the crude mixture being kept at 30–40 °C below the melting point of the desired product to reduce the subliming of impurities. Ethyl (*E*)-3-nitrosocinnamate was separated by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>). The samples were recrystallised from CH<sub>2</sub>Cl<sub>2</sub> at –28 °C. 3-F, mp 59–60 °C (lit., 54–55 °C);<sup>19</sup> 3-Cl, mp 71–72 (lit., 72 °C);<sup>20</sup> 3-Br, mp 76–77 °C (lit., 78 °C);<sup>20</sup> 3-I, mp 76–77 °C (lit., 77 °C);<sup>21</sup> 3-Me, mp 52–54 °C (lit., 53 °C).<sup>22</sup>

**Preparation of 4-substituted and alkyl-disubstituted nitrosobenzenes.** The appropriate substituted nitrobenzene (0.027 mol), ammonium chloride (2.0 g, 0.037 mol) and zinc powder (5.0 g) were added to acetone (20 cm<sup>3</sup>) and cooled in an ice bath. Water was added very slowly dropwise with stirring, making sure the temperature remained below 10 °C. This was continued until the majority of the zinc powder had turned white. The mixture was then poured on ice-water (200 cm<sup>3</sup>) and filtered. Iron(III) chloride solution (3.0 g FeCl<sub>3</sub> in 10 cm<sup>3</sup> water) was added to the filtrate with stirring. After 5 min the precipitate formed was filtered off, dried and sublimed under vacuum as in the previous procedure. 4-F, mp 40–41 °C (lit., 39 °C);<sup>23</sup> 4-Br, mp 94–95 °C (lit., 94 °C);<sup>24</sup> 4-I, mp 102–103 °C (lit., 104 °C);<sup>24</sup> 4-Me, mp 46–47 °C (lit., 48.5 °C);<sup>22</sup> 3,4-diMe, mp 43–44 °C (lit., 44–45 °C);<sup>25</sup> 3,5-diMe, mp 58–59 °C (lit., 59 °C).<sup>14</sup>

## Results and discussion

There does not appear to have been any systematic study of the <sup>1</sup>H NMR properties of 3-substituted nitrosobenzenes. This

**Table 2** <sup>1</sup>H NMR spectral parameters for several 4-substituted nitrosobenzenes

4-X	$\delta^a$		$J/\text{Hz}^a$					
	2,6	3,5	2,3	2,5	2,6	3,5	3,6	5,6
H <sup>b</sup>	7.90	7.65	7.91	0.56	1.97	1.35	0.56	7.91
F <sup>c</sup>	7.96	7.30	8.88	0.16	2.62	2.34	0.16	8.88
Cl	7.86	7.63	8.63	0.12	2.19	2.19	0.12	8.63
Br	7.77	7.81	8.54	0.38	2.27	2.17	0.38	8.54
I	7.60	8.03	7.91	0.06	1.35	1.97	0.06	7.91
Me <sup>d</sup>	7.80	7.41	7.25					7.25
OMe <sup>e</sup>	7.90	7.03	9.10					9.10

<sup>a</sup> For CD<sub>2</sub>Cl<sub>2</sub> solution unless stated otherwise. <sup>b</sup> Assignments based on those of Castellano.<sup>29</sup>  $\delta(\text{H4}) = 7.74$ ;  $J_{\text{HH}}/\text{Hz}$  values,  $J_{24} = 1.28 = J_{46}$ ,  $J_{34} = 7.41 = J_{45}$ ,  $\delta(\text{F}) = 61.67$ ;  $J_{\text{HF}}/\text{Hz}$  values,  $J_{2\text{F}} = 5.20 = J_{6\text{F}}$ ,  $J_{3\text{F}} = 8.15 = J_{5\text{F}}$ . <sup>c</sup>  $\delta(\text{CH}_3) = 2.43$ . <sup>d</sup> For CDCl<sub>3</sub> solution,  $\delta(\text{OCH}_3) = 3.95$ .

**Table 4** Spectral parameters for 3-substituted nitrosobenzenes

X	$\delta^a$				$J/\text{Hz}^a$					
	2	4	5	6	24	25	26	45	46	56
F <sup>b</sup>	7.16	7.44	7.70	8.15	2.60	~0	1.71	8.05	1.01	7.92
Cl	7.63	7.67	7.63	8.05	1.85	~0	1.62	7.87	1.27	8.05
Br	7.77	7.84	7.57	8.10	1.91	~0	1.77	7.91	1.08	7.88
I	7.99	8.11	7.42	8.03	1.73	~0	1.70	7.86	1.12	7.80
Me <sup>c</sup>	7.63	7.53	7.50	7.77	1.79	~0	1.79	7.42	1.79	7.42
CH=CH-CO <sub>2</sub> Et <sup>d</sup>	8.05	7.84	7.64	7.84				7.74		7.74

<sup>a</sup> As CDCl<sub>3</sub> solutions. <sup>b</sup>  $\delta(\text{F}) = 61.67$ ;  $J_{\text{HF}}/\text{Hz}$  values,  $J_{2\text{F}} = 5.20 = J_{6\text{F}}$ ,  $J_{3\text{F}} = 8.15 = J_{5\text{F}}$ . <sup>c</sup>  $\delta(\text{CH}_3) = 2.50$ . <sup>d</sup>  $\delta(\alpha\text{H}) = 7.78$ ,  $\delta(\beta\text{H}) = 6.58$ ,  $J_{\alpha\beta} = 16.04$ ,  $\delta(\text{CH}_2) = 4.30$ ,  $\delta(\text{CH}_3) = 1.36$ ,  $J = 7.13$  Hz.

contrasts with the case of the 4-substituted nitrosobenzenes where the substituent is NH<sub>2</sub>, NHR and NR<sub>2</sub> (R = alkyl or aryl) for which we have extended the range of studies<sup>26</sup> at a much higher spectral resolution than was previously employed. An early report<sup>27</sup> of temperature dependent <sup>1</sup>H NMR spectra of such nitrosoanilines also gave details for the 4-substituted compounds where the substituents are OMe, OEt, CO<sub>2</sub>Et, NO<sub>2</sub>, Cl and Me. This previous work also reports the presence at low temperatures in [<sup>2</sup>H<sub>6</sub>]acetone of an unidentified dimeric form for the last four of these substituted compounds. We now report both ambient and low temperature NMR spectra of several 3-, 4-, and di- and tri-substituted nitrosobenzenes.

### Ambient temperature NMR spectra

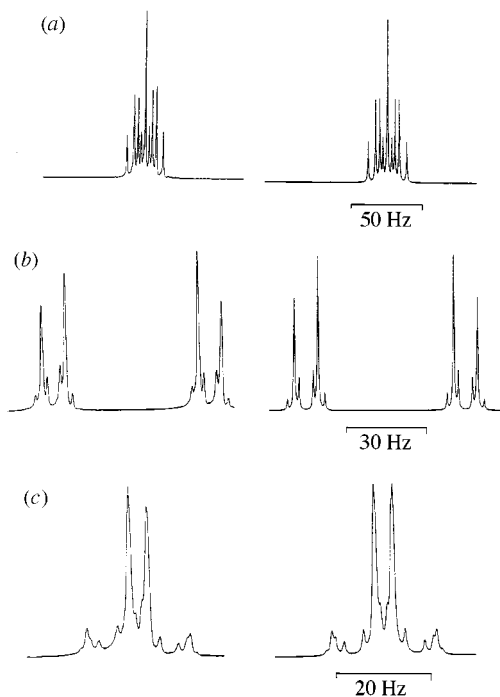
**4-Substituted nitrosobenzenes.** The <sup>1</sup>H NMR parameters for six such compounds in solution at 303 K are given in Table 2. There was no evidence of any dimers present in solution. The spectra were analysed as 4-spin AA'BB' systems (or 5-spin AA'BB'X systems when X = <sup>19</sup>F) using the LAOCOON program.<sup>28</sup> Second order features were very evident particularly for the 4-Br compound. In all cases the spectra showed that the N=O group was either approaching or at the fast rotation limit of the NMR timescale. Signal assignments were made by taking account of the substituent constants for C<sub>6</sub>H<sub>5</sub>R compounds (Table 3), and following the spectral changes on cooling the solutions (see later). It will be observed that in the halogen series there is a switch-over in relative shifts of the 2,6- and 3,5-hydrogens as the halogen becomes less electronegative. The <sup>1</sup>H spectra of the 4-Cl and 4-Br compounds and the <sup>19</sup>F spectrum of the 4-F compound are shown in Fig. 1 with their computer simulations.

**3-Substituted nitrosobenzenes.** The <sup>1</sup>H NMR spectral parameters for seven such compounds are given in Table 4. Note that for the hydrogens *ortho* to N=O, 6-H is invariably more deshielded than the 2-H. This effect can be quantified by calculating the substituent constants for the N=O group,  $S_{\text{NO}}$  (Table 5). Magnitudes of this parameter were obtained by comparing

**Table 3** Substituent constants for shielding of several groups, taken from the spectra of R-C<sub>6</sub>H<sub>5</sub> compounds<sup>30</sup>

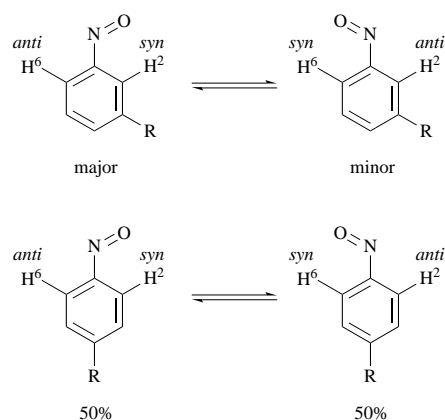
R	$S/\text{ppm}^a$		
	2,6	3,5	4
NO	0.54	0.28	0.34
F	-0.30	-0.03	-0.24
Cl	0.00	-0.07	-0.13
Br	0.16	-0.12	-0.07
I	0.37	-0.24	-0.02
CH <sub>3</sub>	-0.21	-0.13	-0.22
OCH <sub>3</sub>	-0.58	-0.09	-0.48
NMe <sub>2</sub>	-0.79	-0.30	-0.71
NEt <sub>2</sub>	-0.93	-0.17	-0.85
( <i>E</i> )-N <sub>2</sub> O <sub>2</sub> R <sup>b</sup>	0.51	0.18	0.48
( <i>Z</i> )-N <sub>2</sub> O <sub>2</sub> R <sup>b</sup>	0.00	-0.03	0.00

<sup>a</sup> Using  $\delta_{\text{H}}(\text{C}_6\text{H}_6) = 7.38$ . <sup>b</sup> See text.



**Fig. 1** (a) 235.3 MHz  $^{19}\text{F}$  NMR spectrum of *p*-fluoronitrosobenzene in  $\text{CD}_2\text{Cl}_2$ . (b) 250 MHz  $^1\text{H}$  NMR spectra *p*-chloronitrosobenzene and (c) *p*-bromonitrosobenzene, both in  $\text{CD}_2\text{Cl}_2$ . Computer simulations (LAOCOON program) of all three spectra are shown alongside.

the experimental chemical shifts of these ring hydrogens with the base value shift for benzene (measured as  $\delta = 7.38$  †), after allowing for the 3-substituent shifts. The  $S_{\text{NO}}$  values show strong deshielding of the 6-position of the ring. Remembering that the  $\text{N}=\text{O}$  group is rapidly rotating at ambient temperature, this result suggests that the rotamer where the 6-H is in the deshielding zone (*i.e.* in the *anti* position) is preferred over that where 6-H is in a shielding zone (*i.e.* *syn* to  $\text{N}=\text{O}$ ) (Scheme 2).



**Scheme 2**

This agrees with the crystal structure of ethyl (*E*)-3-nitrosocinnamate<sup>15</sup> and the low temperature NMR studies of the 3-Me and 3-I compounds (see later).

**Di- and tri-substituted nitrosobenzenes.**  $^1\text{H}$  NMR chemical shift data for a number of such compounds are reported in Table 6.

#### Low temperature NMR spectra

**4-Substituted nitrosobenzenes.** On cooling  $\text{CD}_2\text{Cl}_2$  solutions of these compounds, the rotation of the nitroso group became slow on the  $^1\text{H}$  NMR timescale leading to distinct chemical

**Table 5** Calculated substituent constants for the nitroso group in 3-substituted nitrosobenzenes at 303 K<sup>a</sup>

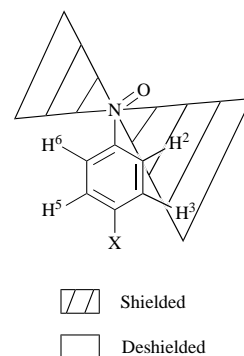
3-Substituent	$S_{\text{NO}}/\text{ppm}$			
	2	4	5	6
F	0.08	0.36	0.35	1.01
Cl	0.25	0.29	0.32	0.80
Br	0.23	0.30	0.31	0.79
I	0.24	0.36	0.28	0.67
Me	0.46	0.36	0.25	0.61
CH=CH-CO <sub>2</sub> Et	0.50	0.29	0.21	0.48
H	0.54	0.34	0.28	0.54

<sup>a</sup> For the benzene  $^1\text{H}$  NMR signal at  $\delta = 7.38$ .

**Table 6** Chemical shifts for selected di- and tri-substituted nitrosobenzenes

Substituents	$\delta^a$				
	2	3	4	5	6
3,4-Dimethyl <sup>b</sup>	7.60	2.38 <sup>c</sup>	2.34 <sup>c</sup>	7.38	7.70
3,5-Dimethyl <sup>d</sup>	7.51	2.46 <sup>c</sup>	7.40	2.46 <sup>c</sup>	7.51
2,4,5-Trimethyl <sup>e</sup>	3.24 <sup>c</sup>	7.28	2.31 <sup>c</sup>	2.21 <sup>c</sup>	6.17
3-CO <sub>2</sub> H-4-OH <sup>f</sup>	8.83	—	—	7.15	7.76

<sup>a</sup>  $\text{CD}_2\text{Cl}_2$  solutions. <sup>b</sup>  $J_{\text{HH}}/\text{Hz}$  values,  $J_{56} = 8.00$ ,  $J_{26} = 1.69$ . <sup>c</sup>  $\delta(\text{CH}_3)$ . <sup>d</sup> Couplings obscured by broadening. <sup>e</sup> No coupling observed. <sup>f</sup>  $J_{\text{HH}}/\text{Hz}$  values,  $J_{26} = 2.41$ ,  $J_{56} = 9.05$ ,  $J_{25} \sim 0$ .



**Fig. 2** Shielding/deshielding magnetic anisotropy of the nitroso group

shifts of all four aromatic ring hydrogens, the chemical shift distinction between the 2-H and 6-H hydrogens being exceptionally large ( $\Delta\delta > 3.0$  in most cases) (Table 7). The substituent constants  $S_{\text{NO}}$  of the static nitroso group were calculated as previously after allowing for the X-substituent effect. These  $S_{\text{NO}}$  values (Table 8) show that 6-H is strongly deshielded, 2-H is strongly shielded, 5-H is significantly deshielded and 3-H is negligibly affected. This is compatible with a double cone shielding/deshielding diagram as shown (Fig. 2). The data also show that these shielding/deshielding effects steadily diminish as the X substituents change from being weak electron acceptors (*viz.* X = halogens) to strong electron donors (*viz.* X =  $\text{NMe}_2$ ,  $\text{NEt}_2$ ). Note that these results are at variance with the earlier chemical shift assignments of Calder and Garratt<sup>27</sup> who, for the compounds 4-X- $\text{C}_6\text{H}_4\text{NO}$ , where X =  $\text{NEt}_2$ ,  $\text{NHMe}$  and  $\text{OMe}$ , suggested that the *ortho*-hydrogen *syn* to the static nitroso group was relatively deshielded compared to the *ortho*-hydrogen *anti* to  $-\text{N}=\text{O}$ .

Our proposed double cone shielding/deshielding diagram (Fig. 2) also applies to methyl groups in the 2- and 6-positions of the ring, as evidenced by the compounds 2-Me-4- $\text{NMe}_2$ -nitrosobenzene and 6-Me-4- $\text{NMe}_2$ -nitrosobenzene which are individually detected in solution at low temperatures.<sup>26</sup>

**3-Substituted nitrosobenzenes.** The low temperature  $^1\text{H}$  NMR spectra of 3-methyl- and 3-iodo-nitrosobenzenes revealed slight

† In  $\text{CD}_2\text{Cl}_2$  solution at 303 K.

**Table 7** Chemical shifts for the aromatic protons of 4-substituted nitrosobenzenes in the slow exchange limit

X	$\delta_{\text{H}}^a$				Ref.
	2	3	5	6	
H	6.28	7.35	7.90	9.52	14
F	6.40	7.05	7.56	9.52	14
Cl	6.26	7.31	7.88	9.46	14
Br	6.18	7.56	8.00	9.39	14
I	6.00	7.76	8.30	9.22	14
Me	6.26	7.15	7.68	9.34	14
OMe <sup>b</sup>	6.54	6.84	7.26	9.34	14
N(H)Me <sup>c</sup>	(Major) <sup>d</sup> ~6.6	~6.6	6.85	8.94	29
	(Minor) <sup>d</sup> ~6.6	~6.6	6.95	8.83	29
NMe <sub>2</sub> <sup>b</sup>	6.60	6.69	6.98	8.91	29
NEt <sub>2</sub> <sup>b</sup>	6.79	6.51	6.80	8.82	29
2-Me-4-NMe <sub>2</sub> <sup>b</sup>	(Major) <sup>e</sup> 3.18 <sup>f</sup>	6.47	6.32	6.63	29
	(Minor) <sup>e</sup> 2.23 <sup>f</sup>	?	?	8.85	29
2,6-Me <sub>2</sub> -4-NMe <sub>2</sub> <sup>b</sup>	2.21 <sup>g</sup>	6.01	6.52	3.04 <sup>g</sup>	29

<sup>a</sup> For CD<sub>2</sub>Cl<sub>2</sub> solutions, unless stated otherwise, measured at -100 °C. <sup>b</sup> CDCl<sub>3</sub> solution, measured at -60 °C. <sup>c</sup> Acetone solution, measured at -90 °C. <sup>d</sup> Rotameric forms. <sup>e</sup> Rotameric forms. <sup>f</sup>  $\delta(\text{CH}_3)$ ;  $\delta(\text{N}-\text{CH}_3) = 3.08$ . <sup>g</sup>  $\delta(\text{CH}_3)$ ;  $\delta(\text{N}-\text{CH}_3) = 3.19$ .

**Table 8** Substituent constants calculated for the static nitroso group for various 4-substituted nitrosobenzenes

X	$S_{\text{NO}}/\text{ppm}$			
	2	3	5	6
H	-1.10	-0.03	+0.52	+2.14
I	-1.14	+0.01	+0.55	+2.08
OMe	-0.75	+0.04	+0.46	+2.05
NMe <sub>2</sub>	-0.48	+0.10	+0.39	+1.83
NEt <sub>2</sub>	-0.42	+0.06	+0.35	+1.61

**Table 9** 'Static' chemical shifts for 3-methyl- and 3-iodo-nitrosobenzene

3-Substituent	Relative population	$\delta_{\text{H}}^a$			
		2	4	5	6
Me <sup>b</sup>	0.555	~6.07	7.61	~7.76	~9.27
	0.445	~9.27	7.61	~7.19	~6.07
I <sup>c</sup>	0.570	~7.63	8.00	~7.59	~9.46
	0.430	~9.66	8.00	~6.90	~7.63

<sup>a</sup> All signals were broad, except for 4-H. <sup>b</sup> For a CD<sub>2</sub>Cl<sub>2</sub> solution at -115 °C. <sup>c</sup> For a C<sub>2</sub>D<sub>5</sub>OD solution at -110 °C.

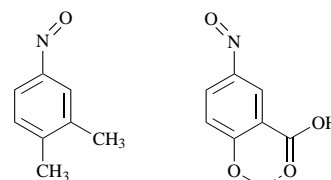
population differences for the two non-equivalent rotamers, the rotamer with the 3-substituent in the *syn* position with respect to the static -N=O group being slightly favoured (Table 9, Scheme 2). In these two cases, the spectra still showed some exchange broadening due to the -N=O rotation even at -110 °C, the lowest temperature attained. A referee has suggested that the main factor determining rotamer populations may be intramolecular van der Waals steric attraction between the nitroso group and the 3-substituents.<sup>31</sup>

**Di- and tri-substituted nitrosobenzenes.** <sup>1</sup>H spectra of these compounds with static -N=O groups were achieved by cooling to *ca.* -105 °C except in the case of 2,4,5-trimethylnitrosobenzene where the methyl in the 2-position reduces the barrier to rotation significantly and this compound remained in the fast rotation regime even at -105 °C. The chemical shifts (Table 10) indicate that the rotamer with the 3-methyl *syn* to -N=O is favoured, whereas in the case of 5-nitrososalicylic acid (*viz.* 3-CO<sub>2</sub>H-4-OH-nitrosobenzene) the opposite rotamer is favoured (Fig. 3). This is in accordance with the crystal structure of this compound.<sup>16</sup> This results in the -N=O group being *trans* to the 4-OH group which is held by hydrogen bonding with the carboxylic acid carbonyl function.

**Table 10** 'Static' <sup>1</sup>H NMR chemical shifts for di- and tri-substituted nitrosobenzenes

Substituent groups	$\delta_{\text{H}}^a$				
	2	3	4	5	6
3,4-Dimethyl <sup>b</sup>	6.08	2.11 <sup>c</sup>	2.22 <sup>c</sup>	7.58	9.12
3,4-Dimethyl <sup>d</sup>	9.14	2.42 <sup>c</sup>	2.22 <sup>c</sup>	7.05	6.06
3,5-Dimethyl	5.88	2.40 <sup>c</sup>	7.37	2.40 <sup>c</sup>	9.04
2,4,5-Trimethyl	3.25 <sup>c</sup>	7.31	2.25 <sup>c</sup>	2.15 <sup>c</sup>	5.93
3-CO <sub>2</sub> H-4-OH <sup>b</sup>	~9.74	12.80 <sup>e</sup>		7.04	~6.80
3-CO <sub>2</sub> H-4-OH <sup>d</sup>	~6.80	12.60 <sup>e</sup>		7.50	~9.74

<sup>a</sup> Measured at -105 °C, except for 2,4,5-trimethylnitrosobenzene (measured at -80 °C). <sup>b</sup> Major rotamer. <sup>c</sup> (CH<sub>3</sub>). <sup>d</sup> Minor rotamer. <sup>e</sup>  $\delta(\text{CO}_2\text{H})$ .

**Fig. 3** Preferred rotamers for 3,4-dimethylnitrosobenzene and 5-nitrososalicylic acid

**Azodioxy dimers of substituted nitrosobenzenes.** On cooling solutions of nitrosobenzenes, the <sup>1</sup>H NMR spectra showed changes not only due to the restricted rotation of the nitroso group in the monomeric species but also due to the formation of one or both azodioxy dimers (except for 4-methoxynitrosobenzene where the electron-donating tendency of the MeO group prevents dimer formation) (Table 11). Where both (*Z*)- and (*E*)-dimers were detected, the (*Z*)-form was always considerably more abundant, irrespective of the nature of the solid dimer. The attribution of the major solution dimer to the (*Z*)-form was based on a previous study<sup>32</sup> of dimers of 4-methylnitrosobenzene where the solid dimer [the (*E*)-dimer] was dissolved at 193 K. At this temperature dissociation to the monomer is negligibly slow and the (*E*)-dimer signals were unambiguously assigned. On warming the solution the monomer-dimer equilibrium was established and the additional signals due to the (*Z*)-dimer were assigned. The results of this study enabled the substituent constants for the two -N<sub>2</sub>O<sub>2</sub>C<sub>6</sub>H<sub>5-n</sub>X<sub>n</sub> groups to be calculated (see Table 3).

It will be seen that shielding/deshielding of aromatic hydrogens due to (*Z*)-N<sub>2</sub>O<sub>2</sub>C<sub>6</sub>H<sub>5-n</sub>X<sub>n</sub> is virtually negligible whereas shielding due to (*E*)-N<sub>2</sub>O<sub>2</sub>C<sub>6</sub>H<sub>5-n</sub>X<sub>n</sub> is substantial, particularly

**Table 11** Experimental  $^1\text{H}$  NMR chemical shifts for (*Z*)-dimers of nitrosobenzenes

Substituent(s)	$\delta_{\text{H}}^a$				
	2	3	4	5	6
None <sup>b</sup>		7.3–7.4	Complex multiplet		
4-F <sup>b</sup>	7.32	7.03	55.00 <sup>c</sup>	7.03	7.32
4-Cl <sup>b</sup>	7.26	7.33		7.33	7.26
4-Br <sup>b</sup>	7.20	7.48		7.48	7.20
4-I <sup>b</sup>	7.11	7.71		7.71	7.11
4-Me <sup>b</sup>	7.22	7.13		7.13	7.22
3-F <sup>d</sup>	7.22	56.40 <sup>c</sup>	7.15	7.37	7.22
3-Cl <sup>d</sup>	7.55		7.42	7.32	7.16
3-Br <sup>d</sup>	7.71		7.50	7.24	7.18
3-I <sup>d</sup>	7.90		7.74	7.07	7.17
3-Me <sup>d</sup>	7.24	2.27 <sup>e</sup>	7.16	7.13	6.99
3-Cinnamate <sup>d</sup>	7.60	<i>f</i>	7.29	7.38	7.58
3,4-Dimethyl <sup>g</sup>	7.21	2.20 <sup>e</sup>	2.20 <sup>e</sup>	7.00	6.91
3,5-Dimethyl <sup>b</sup>	6.93	2.21 <sup>e</sup>	6.96	2.21 <sup>e</sup>	6.93
2,4,5-Trimethyl <sup>b,h</sup>	2.03 <sup>e</sup>	6.97	2.13 <sup>e</sup>	2.34 <sup>e</sup>	6.77
2,4,5-Trimethyl <sup>b,i</sup>	2.34 <sup>e</sup>	6.91	2.13 <sup>e</sup>	2.34 <sup>e</sup>	7.05

<sup>a</sup> For  $\text{CD}_2\text{Cl}_2$  solutions unless stated otherwise. <sup>b</sup> Measured at  $-90^\circ\text{C}$ . The differences in the coupling constants between the monomer and the (*Z*)-dimer were negligible. <sup>c</sup>  $^{19}\text{F}$  shift relative to  $\text{C}_6\text{F}_6$ . <sup>d</sup>  $\text{CDCl}_3$  solutions, measured at  $-60^\circ\text{C}$ . The differences in the coupling constants between the monomer and the (*Z*)-dimer were negligible. <sup>e</sup>  $\delta(\text{CH}_3)$ . <sup>f</sup>  $\delta(\alpha\text{-H}) = 7.53$ ,  $\delta(\beta\text{-H}) = 6.40$ ,  $J_{\alpha\beta} = 16.06$  Hz.  $\delta(\text{CH}_2) = 4.23$ ,  $\delta(\text{CH}_3) = 1.32$ ,  $J = 7.12$  Hz. <sup>g</sup> Measured at  $-30^\circ\text{C}$ .  $J_{\text{HH}}/\text{Hz}$  values,  $J_{56} = 8.12$ ,  $J_{26} = 2.20$ . <sup>h</sup> Major rotamer. <sup>i</sup> Minor rotamer.

**Table 12** Spectral parameters for the (*E*)-dimers of nitrosobenzenes

Substituent(s)	$\delta_{\text{H}}^a$				
	2	3	4	5	6
None	7.89	7.56	7.86	7.56	7.89
4-Cl	7.86	7.51	—	7.51	7.86
4-Br	7.78	7.66	—	7.66	7.78
4-I	7.69	7.87	—	7.87	7.69
3-F	?	54.51 <sup>b</sup>	7.30	7.56	?
3-Cl	7.78	—	7.52	7.85 <sup>c</sup>	7.95 <sup>c</sup>
3-Br	7.86	—	?	7.51	7.86
3-I	8.10	—	?	7.46	7.88
3-Me	8.23	2.41 <sup>d</sup>	7.92	7.31	7.88

<sup>a</sup> Measured at  $-90^\circ\text{C}$  for the 4-substituted compounds and at  $-50^\circ\text{C}$  for the 3-substituted compounds. <sup>b</sup>  $^{19}\text{F}$  shift relative to  $\text{C}_6\text{F}_6$ . <sup>c</sup> Assignments could be interchanged. <sup>d</sup>  $\delta(\text{CH}_3)$ .

for *ortho* and *para* hydrogens. This causes the signals for the (*Z*)-dimer to occur to lower frequencies of the corresponding signals for the monomer and (*E*)-dimer.

In all cases except that of 2,4,5-trimethylnitrosobenzene, ring rotation remained rapid even at the lowest temperatures studied ( $\sim -90^\circ\text{C}$ ). In the case of 2,4,5-trimethylnitrosobenzene two distinct rotamers were detected, presumably due to the steric hindrance of the 2-methyl substituent.

(*E*)-dimer concentrations were always low and their  $^1\text{H}$  NMR shift parameters (Table 12) were detected in a more limited set of compounds. Comparison of these data with the data for the corresponding monomers (Tables 2 and 4) reveals some similarity in shift values.

## Conclusions

A detailed analysis of the ambient and low temperature  $^1\text{H}$  NMR spectra of a wide range of 3- and 4-monosubstituted and some di- and tri-substituted *C*-nitrosobenzenes has established the nature of the shielding anisotropy of the  $\text{N}=\text{O}$  group. At low temperatures where the  $\text{N}=\text{O}$  group rotation is arrested on the NMR timescale, *ortho* hydrogens *syn* to the  $\text{N}=\text{O}$  are strongly shielded whereas those *anti* to the  $\text{N}=\text{O}$  are strongly deshielded. The effects on the *meta* hydrogens are much less pronounced.

At ambient temperatures the main solution species are monomers irrespective of the nature of the solid-state form of the nitroso compound. On cooling solutions of these compounds monomer–dimer equilibria are established with the (*Z*)-azodioxy dimer always greatly preferred over the (*E*)-dimer, again irrespective of the preferred solid state form. For example, in the cases of nitrosobenzene itself and 4-chloro-nitrosobenzene, the (*Z*)-dimers are greatly preferred over the (*E*)-dimers in solution despite the fact that nitrosobenzene exists as a solid-state (*Z*)-dimer and 4-chloronitrosobenzene as a solid-state (*E*)-dimer.<sup>14</sup>

Later parts of this work will discuss the kinetics of these monomer–dimer equilibria and the kinetics of the  $\text{N}=\text{O}$  group rotations in the nitroso monomers.

## Acknowledgements

D. A. F. thanks the University of Exeter for a research scholarship.

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Paper 7/03760K

Received 30th May 1997

Accepted 23rd July 1997