

# Structural Investigations of C-Nitrosobenzenes. Part 3.<sup>1</sup> Solid-state and Solution <sup>13</sup>C NMR Studies, and Crystal Structure of *E*-(4-ClC<sub>6</sub>H<sub>4</sub>NO)<sub>2</sub>

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J. Chem. Research (S),

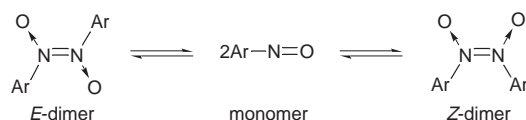
1999, 202–203

J. Chem. Research (M),

1999, 1115–1134

Solid-state and solution <sup>13</sup>C NMR data for the monomers and dimers of 3- and 4-substituted nitrosobenzenes, and the crystal structure of *E*-(4-ClC<sub>6</sub>H<sub>4</sub>NO)<sub>2</sub> are reported.

Earlier parts of this work<sup>1,2</sup> demonstrated the insight achieved by <sup>1</sup>H NMR studies on the structural behaviour of C-nitrosobenzene derivatives in organic solvents. Most of these compounds exist in solution as equilibrium mixtures of the monomer with one or both dimers (Scheme 1). Such equilibria usually favour the monomeric species at ambient temperatures, but dimer formation is enhanced on lowering the temperature, with the *Z*-form always favoured over the *E*-form. In order to gain further insight into the differing solid- and solution-state properties of these compounds <sup>13</sup>C NMR spectroscopy has now been employed.



**Scheme 1**

<sup>13</sup>C NMR chemical shifts of six solid-state dimeric halonitrosobenzenes are given in Table 1. The designated structural forms are based on IR data<sup>7,8</sup> or crystal structures.<sup>9,10</sup> The C<sup>1</sup> shifts fall within the range  $\delta$  139–146 and such magnitudes characterise aromatic azodioxy dimers<sup>11,12</sup> as opposed to nitroso monomers. The <sup>13</sup>C CP MAS spectra exhibited novel features arising from the quadrupolar effects of the halogen nuclei being transferred to the *ipso* <sup>13</sup>C nuclei.<sup>14</sup> These have been discussed in terms of current NMR theory for *I* = 3/2 nuclei (*viz.* <sup>35</sup>Cl/<sup>37</sup>Cl, <sup>79</sup>Br/<sup>81</sup>Br).<sup>19</sup>

**Table 1** <sup>13</sup>C NMR chemical shifts for several solid-state dimeric halonitrosobenzenes.

Compound	$\delta_c$					
	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>
<i>E</i> -(4-ClC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	139.8	129.2 <sup>a</sup>	127.7	131.7 <sup>b</sup> ~140 <sup>b</sup>	127.7	125.1 <sup>a</sup>
<i>E</i> -(4-IC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	141.5	126.0	137.6 <sup>c</sup>	?	137.6 <sup>c</sup>	126.0
<i>Z</i> -(3-FC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	145.5	114.2	162.5 <sup>d</sup>	121.3	130.6	121.3
<i>E</i> -(3-ClC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	142.3	124.7	136.2 <sup>b?</sup>	130.3	130.3	124.7
<i>E</i> -(3-BrC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	141.6	124.2	<sup>e</sup>	130.5	130.5	124.2
<i>E</i> -(3-IC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub>	142.2	132.1 <sup>c</sup>	70–115 <sup>c</sup>	140.4 <sup>c</sup>	132.1	125.1

<sup>a</sup> These assignments may be reversed. <sup>b</sup> A broad symmetric doublet (see text). The high frequency component partially overlaps the C<sup>1</sup> signal. <sup>c</sup> Broad due to large dipolar interaction with <sup>127</sup>I (*I* = 5/2). <sup>d</sup> Broad due to partially resolved <sup>1</sup>J<sub>CF</sub> coupling. <sup>e</sup> Split by <sup>79,81</sup>Br (*I* = 3/2) into four peaks at  $\delta$  103.7, 113.7, 121.3 and 148.0.

The residual dipolar splittings of the *ipso* <sup>13</sup>C signals tended to be rather indistinct, particularly in the case of the iodo derivatives which contain <sup>127</sup>I as an *I* = 5/2 nucleus.

Solution-state <sup>13</sup>C NMR spectra provided chemical shift data for the monomeric species (Table 3) which are distinctly different from those of the dimers, whereas shifts for the dimers are comparable, to within a few ppm, of the CP MAS solid-state values. It should be noted that all C<sup>1</sup> shifts in Table 3 fall within the range  $\delta$  164.2–165.7, in agreement with previous data on *para*-substituted nitrosobenzenes.<sup>28</sup>

**Crystal Structure of (4-ClC<sub>6</sub>H<sub>4</sub>NO)<sub>2</sub>.**—The X-ray structure was obtained with a FAST TV area detector diffractometer; radiation: Mo-K $\alpha$ ,  $\lambda$  = 0.71069 Å,  $\mu$  = 0.549 mm<sup>−1</sup>. Crystal data: C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, *M* = 283.10, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 11.7290(10), *b* = 3.7320(2), *c* = 13.946(3) Å, *U* = 583.84(14) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.610 Mg m<sup>−3</sup>, *F*(000) = 288. A total of 2025 reflections were collected in the range 1.82 ≤  $\theta$  ≤ 25.02° giving 830 independent reflections (*R*<sub>int</sub> = 0.0619). Full matrix least squares refinements based on *F*<sup>2</sup> were performed on all non-hydrogen atoms. Final *R*<sub>1</sub> and *wR*<sub>2</sub> values for data with *I* > 2 $\sigma$ (*I*) were 0.0484 and 0.1202 respectively.

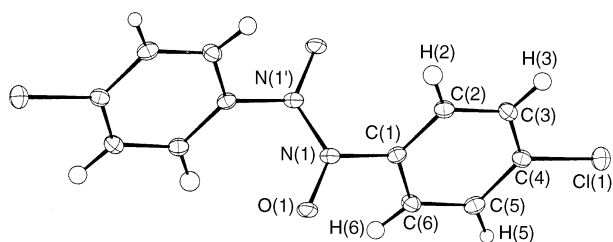
The labelled structure is depicted in Fig 2. The *E* arrangement of the ONNO group is immediately evident. The most pertinent bond lengths and angles are *r*<sub>CN</sub> = 1.453(4) Å, *r*<sub>NO</sub> = 1.265(3) Å, *r*<sub>NN</sub> = 1.318(5) Å,  $\theta_{\text{CNN}}$  = 118.5(3)°,  $\theta_{\text{CNO}}$  = 119.7(2)° and  $\theta_{\text{NNO}}$  = 121.8(3)°. These parameters are very similar to the corresponding values in other *E*-azodioxy aromatic dimers for which crystal structures have been obtained.<sup>10,31,32</sup> The NN bond lengths fall within the narrow range 1.31–1.32 Å, indicating appreciable  $\pi$ -electron character. Dihedral angle calculations show that the central azodioxy moiety deviates somewhat from planarity with torsional angles between the ONNO group and the aromatic rings of 51.6 and 56.6°

**Table 3** <sup>13</sup>C NMR chemical shifts for several nitrosobenzene monomers, RC<sub>6</sub>H<sub>4</sub>NO, in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solution

R	$\delta_c$ /ppm					
	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>
H <sup>25</sup>	165.7	121.0	129.4	136.0	129.4	121.0
3-Me <sup>a</sup>	166.3	120.9	139.4	136.2	129.1	119.0
3- <i>E</i> -C <sub>2</sub> H <sub>2</sub> CO <sub>2</sub> Et <sup>b</sup>	165.3	120.1	136.0	134.2	129.9	121.7
3-F <sup>c</sup>	165.8	103.6	163.2	122.1	131.1	120.9
	(4.8)	(22.6)	(251.8)	(22.4)	(7.7)	(2.7)
3-Br	165.1	121.8	123.8	137.8	131.0	121.7
4-Cl <sup>12</sup>	164.8	122.8	130.6	142.7	130.6	122.8
4-I	164.2	121.8	138.7	105.4	138.7	121.8

<sup>a</sup>  $\delta$ (CH<sub>3</sub>) = 21.1. <sup>b</sup>  $\delta$ ( $\alpha$ CH) = 142.4,  $\delta$ ( $\beta$ CH) = 121.0,  $\delta$ (CO<sub>2</sub>) = 166.3,  $\delta$ (CH<sub>2</sub>) = 60.8 and  $\delta$ (CH<sub>3</sub>) = 14.3 from the results of a HMQC experiment. <sup>c</sup> *J*<sub>CF</sub>/Hz values given in parentheses.

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**Fig 2** A view of the crystal structure of *E*-(4-ClC<sub>6</sub>H<sub>4</sub>NO)<sub>2</sub> showing the atom labelling

We thank the University of Exeter for a research scholarship (for D. A. F), and the EPSRC for use of both the solid-state NMR service at the University of Durham Industrial Research Laboratories and the X-ray crystallographic service at the University of Wales, Cardiff.

Techniques: <sup>13</sup>C solid- and solution-state NMR, IR, X-ray crystallography

References: 32

Figures: 2

Table 2: <sup>13</sup>C NMR substituent constants

Tables 4,5: <sup>13</sup>C NMR chemical shifts of *E*- and *Z*-dimers of nitrosobenzenes in solution

Tables 6–10: X-ray crystal structure data of *E*-(4-ClC<sub>6</sub>H<sub>4</sub>NO)<sub>2</sub>

Table 11: Crystal data for various aromatic *E*-(RNO)<sub>2</sub> compounds

Received and Accepted, 17th December 1998  
Paper E/8/09836K

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