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4-Iodonitrosobenzene. Structural and spectroscopic studies of the monomeric solid and of previously unreported dimers

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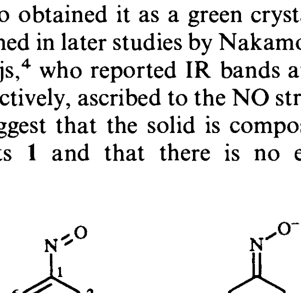
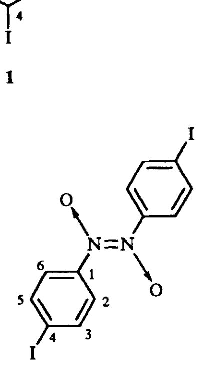
4-Iodonitrosobenzene has been isolated as the (*E*)-azodioxy dimer for the first time. Its solid-state structure has been identified by X-ray crystallography and characterised by IR, MS and ^{13}C NMR techniques. In $CDCl_3$ or CD_2Cl_2 solution dynamic equilibria exist between monomeric 4-iodonitrosobenzene and its (*Z*)- and (*E*)-azodioxy dimers. Thermodynamic data (ΔG°, ΔH° and ΔS°) for these equilibria have been calculated from low temperature ^1H NMR spectra. Criteria for the dimerisation tendencies of all types of *C*-nitroso compounds are proposed.

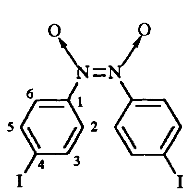
4-Iodonitrosobenzene was first synthesised 100 years ago by Bamberger[1] who obtained it as a green crystalline solid. This was fully confirmed in later studies by Nakamoto and Rundle,[2] Lüttke[3] and Mijs,[4] who reported IR bands at 1485, 1488 and 1490 cm^{-1}, respectively, ascribed to the NO stretching mode.[3,4] The IR data suggest that the solid is composed solely of the monomeric units **1** and that there is no evidence for the formation of either of the two possible azodioxy dimers **2**, **3** due to the absence of the characteristic bands associated with the *E*-and *Z*-N_2O_2 units. In 1957 a two-dimensional X-ray crystallographic study was carried out[5] and this gave r_{CN} = 1.28 Å, r_{NO} = 1.24 Å and $\widehat{CNO}$ = 125 ° On this basis Webster suggested that there was a pronounced contribution from a dipolar quinonoid canonical structure (**1a**) and that, in conformity with the same explanation for the analogous 4-dimethylaminonitrosobenzene, dimerisation would not be possible. There are possible objections to this suggestion in that the dipole moment of 4-iodonitrosobenzene (2.16 D) was much closer to the vector sum of the group moments than was the case for the dimethylaminonitrosobenzene and that the vector sum differences for the 4-chloro- and 4-bromo-nitrosobenzenes are only slightly smaller than for the 4-iodo-compound.[6] There is, however, one piece of structural evidence that casts considerable doubt upon the bond lengths and angle obtained in the two dimensional study. Miao and Prout are quoted in a reference within a paper by Miao *et al.*[7] as having established the following values in a three dimensional X-ray investigation, r_{CN} = 1.43 Å, r_{NO} = 1.21 Å, and $\widehat{CNO}$ = 113.2°. These values imply that there is little evidence for the hypothesis of a quinonoid canonical structure being responsible for the absence of the dimer formation, and are also very much in accord with those established for other monomeric C-nitroso compounds which do have the ability to engage in dimerisation. An early report[8] stated that gentle sublimation of 4-iodonitrosobenzene between two watch glasses led to the formation of almost colourless flakes tinged with a green colour. This would be compatible with dimer formation in company with a small amount of monomer. In view of the success of low temperature ^1H NMR studies of various nitrosobenzenes in demonstrating the existence of both dimeric forms in equilibrium with the monomer,[9–11] it was recognised that the possibility of the participation of such equilibria for 4-iodonitrosobenzene could readily be established.



1 **1a**



E - dimer
2



Z - dimer
3

A study[12] of the temperature variation of the absorbance of the n–π*(N) transition at 750 nm for both 4-iodo- and 4-bromo-nitrosobenzenes suggested that their benzene solutions contained only monomeric species at 20 °C. It is noteworthy that measurements at lower temperatures do not appear to have been made. It may also be noted that Nakamoto and Rundle[2] state that for these two examples 'the actual change in stability of monomer and dimer in the two cases must be relatively small, but it is not unique to find small differences of this sort to alter structure in the crystalline state'. These authors demonstrated that, by modifying the crystallisation conditions, 4-bromo-nitrosobenzene could be obtained as the pure dimer, a mixture of the dimer and monomer, and finally as a green monomeric crystal.

These considerations prompted a detailed reinvestigation of the structural properties of 4-iodonitrosobenzene.

Experimental

Compounds

4-Iodonitrosobenzene was prepared by reduction of 4-iodonitrobenzene with zinc and ammonium chloride to the hydroxylamine derivative followed by mild oxidation, according to a standard procedure.[11] It was purified by vacuum sublimation, the crude product being heated to 60 °C whence the product was collected on a water-cooled finger to yield bright green crystals of the monomer, mp 103.7–104.7 °C (lit.,[13] 103.5–104.5 °C). These crystals were dissolved in dichloromethane to form a solution of concentration 0.25–0.3 mol dm^{-3} and left overnight in the freezer to yield bright yellow crystals of the azodioxy dimer, shown subsequently to be the *E* dimer. These crystals on heating reverted to the green crystals of the monomer which melted at the same temperature as previously.

Physical methods

IR spectra were recorded as KBr discs on a Nicolet Magna 550 FT-IR spectrometer equipped with a CsI beam splitter operating in the range 4000–200 cm^{-1}. Spectral expansions were obtained in the range 1700–600 cm^{-1}. Electron-impact mass spectra were obtained on a Kratos Profile spectrometer with an electron beam energy of 70 eV and a probe temperature of 150 °C.

Solid-state ^{13}C CP/MAS NMR spectra were recorded at 75.42 MHz on a Varian VXR-300 NMR spectrometer at the University of Durham Industrial Research Laboratories. Spectra of the monomeric and dimeric compounds were recorded in the temperature range 193–293 K.

The non-quaternary suppression (NQS) technique was applied to the room temperature spectra and the total sideband suppression (TOSS) method applied to the 273 K spectrum of the monomer. For all spectra of both compounds, the following conditions were used: acquisition time 203 ms, relaxation delay 30.0 s, CP contact time 5 ms. Gaussian broadening of 0.008 s was applied to all spectral lines. Solution-state ^{13}C-{^1H} NMR spectra were recorded on $CDCl_3$ solutions of the title compound at 73.5 MHz on a Bruker AC-F300 spectrometer. Solution state ^1H NMR spectra were recorded on $CDCl_3$ or CD_2Cl_2 solutions of the title compound at 250.13 or 300.13 MHz on Bruker AM250 or AC-F300 spectrometers, both equipped with standard B-VT-1000 variable temperature units. Probe temperatures were accurate to ± 1 °C.

X-Ray crystal structure of $(4\text{-}IC_6H_4NO)_2$

Yellow crystals of (*E*)-azodioxy-4-iodobenzene (size 0.24 × 0.16 × 0.18 mm) were obtained as described above and examined in Lindemann capillaries.

Crystal data. $C_{12}H_8I_2N_2O_2$. M = 466.00, monoclinic, space group $P2_1/c$, a = 13.488(4), b = 4.0262(8), c = 12.747(2) Å, U = 666.5(2) Å^3, Z = 2, D_c = 2.322 Mg m^{-3}, $F(000)$ = 432, Mo-Kα radiation (λ = 0.710 69 Å), μ = 4.713 mm^{-1}.

Data collection and processing. Data were collected on a FAST TV area detector diffractometer situated at the window of a rotating anode generator operating at 50 kV, 55 mA with a molybdenum anode as described elsewhere.[14] A total of 2624 reflections were collected in a range $3.14° \leq \theta \leq 24.88°$ giving 1017 independent reflections [R(int) = 0.0471]. The data were corrected for absorption effects.[15]

Solution and refinement. The structure was solved by standard Patterson methods. Full matrix least squares refinements based on $F_0{}^2$ were performed with non-hydrogen atoms assigned anisotropic thermal parameters. Hydrogen atoms were assigned isotropic thermal parameters. The final R_1 and wR_2 values for data with $I > 2\sigma(I)$ were 0.0335 and 0.0852, respectively. Corresponding values for all data were 0.0351 and 0.0856, respectively. The goodness-of-fit based on $F_0{}^2$ was 1.108.

The final difference Fourier map had peak maxima and minima at 2.637 and −0.849 e Å^3, without any stereochemical differences. Literature programs were used for the solution and refinement of the structure.[16,17] Additional material has been deposited at the Cambridge Crystallographic Data Centre and comprises atomic coordinates and anisotropic displacement parameters.†

Table 1 IR data (ν/cm^{-1}) for the monomeric and dimeric forms of 4-iodonitrosobenzene and of 4-bromonitrosobenzene dimer

$(4\text{-}IC_6H_4NO)_2$	$(4\text{-}BrC_6H_4NO)_2$[a,b]	$4\text{-}IC_6H_4NO$	Assignment[a,b]
1572m	1575w, 1555w	1580s, 1573s	
		1484vs	ω N=O
1472s	1479m, 1455w	1441s	
1393s	1402m	1392s	
1296w	1316vw	1314m	
1285s	1287s	1281m	
1259vs	1259vs		ω_{as} ONNO
1185w, 1159w	1182m, 1157m	1186s	
1107w, 1096w	1112m,sh, 1102m	1116vs	
	1079w		
1052m	1066m	1047s	
1006s	1012m	1007m	
	997w	967w	
936w	938w		
854s	857s	825vs	ω CN
818m	822m		
803s	808m		
703w	712m	688w	
648w	657m		
625w	627m		
524m	530s		
	494m		
418m	428s	474m	δ CNO

[a] Ref. 40. [b] m = Medium, s = strong, w = weak, v = very, sh = shoulder; ω = stretching, δ = deformation. Unassigned bands are due to aromatic rings.

Results

IR Spectra

IR spectroscopy has been much used for distinguishing between the –N=O groups of monomeric C-nitroso compounds and the *Z*- and *E*- $-N_2O_2-$ groups of the corresponding dimers. FT-IR spectra of the two solid-state forms of 4-iodonitrosobenzene were therefore recorded and their bands assigned as far as possible following the earlier work of Lüttke on the monomer of the title compound[3] and of Mijs on the dimer of 4-bromonitrosobenzene[4] (Table 1). The spectra are strikingly different (Fig. 1). The yellow compound is characterised by a strong IR band at 1259 cm^{-1} which is attributed to the antisymmetric ONNO stretch of the *E*-N_2O_2 moiety. The *Z*-dimer would have exhibited two bands in the region of 1350–1400 cm^{-1} due to both symmetric and antisymmetric ONNO stretching modes. The former, however, is IR inactive in the *E*-species. The N=O stretch in the green monomer is at 1484 cm^{-1} [Fig. 1(*a*)] compared to earlier reported values of 1485 cm^{-1} (KBr disc),[2] 1488 cm^{-1} (solution)[3] and 1490 cm^{-1} (solution).[4] These considerably higher values compared to the dimer arise from the greater degree of double bond character of the NO bond in the monomer. The other diagnostic bands are the CN stretch and CNO deformation. The CN stretch occurs at 854 cm^{-1} in the dimer compared to 825 cm^{-1} in the monomer. Earlier values[2–4] for the monomer range from 830 to 812 cm^{-1} and are solvent dependent. The CNO deformation occurs at 418 cm^{-1} in the dimer and at 474 cm^{-1} in the monomer, the lower dimer value reflecting the essentially single bond nature of the

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† For details of the CCDC deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.

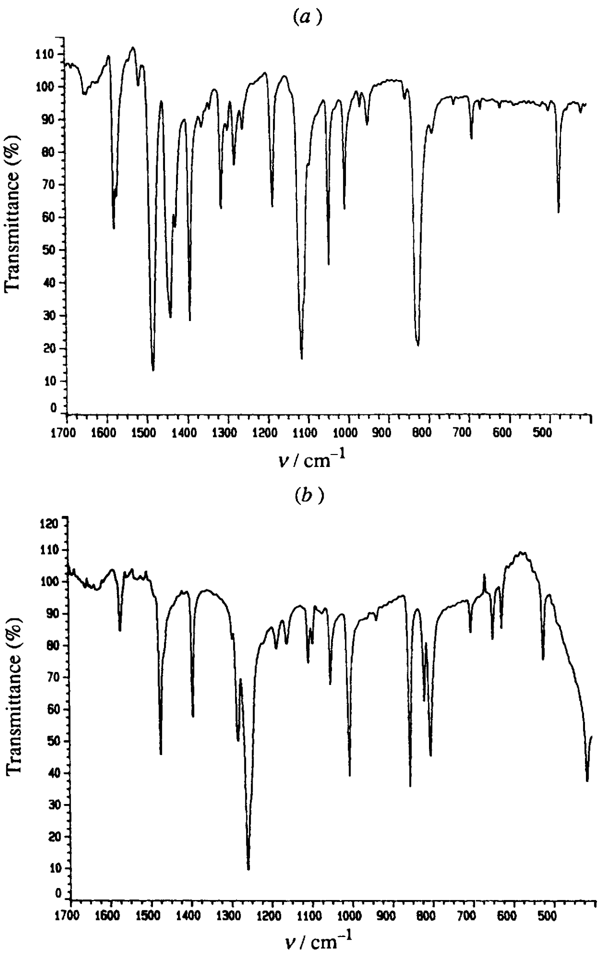

Fig. 1 FT-IR spectra of 4-iodonitrosobenzene monomer (*a*) and the (*E*)-azodioxy dimer (*b*)

CNO moiety in this species. The majority of the other IR bands listed (Table 1) are associated with CC stretches and both in-plane and out-of-plane C–H bending of the aromatic ring. They do not change significantly with the degree of association of the title compound.

Mass spectra

Both precision and nominal mass measurements were made on the yellow dimer using a probe temperature of 150 °C. Using perfluorokerosene as the peak matching reference, a precise mass, *m*/*z*, of 465.86717 was found, which corresponds to $C_{12}H_8I_2N_2O_2$ (M^+), with a deviation of −0.7 ppm, and a mass of 449.87321 which matches for $C_{12}H_8I_2N_2O$ $(M - O)^+$, with a deviation of 1.3 ppm. The nominal mass data were as follows: *m*/*z* 466 (M^+, 0.2%), 451 (M − 17, 0.5), 450 (M − O, 3.6), 434 (M − O_2, 0.8), 254 (M − 212, 19.6), 233 (M − IC_6H_4NO, 20.8), 219 (M − 247, 16.0), 203 (M − $IC_6H_4N_2O_2$, 26.1) and 128 (M − 338, 100%). The peaks at 128 and 254 are probably due to atomic and molecular iodine respectively.

The above results confirm conclusively the presence of the dimeric form of 4-iodonitrosobenzene even in the vapour phase, and show a fragmentation pattern associated with the consecutive loss of oxygen atoms and scission of the N=N bond of the azodioxy group.

Crystal structure

A view of the structure of $(4\text{-}IC_6H_4NO)_2$ with its atom labelling is shown in Fig. 2. The *E* arrangement of the ONNO group is clearly displayed. The bond lengths and angles are listed in Table 2. From this Table the following values should be noted, r_{CN} = 1.467(6) Å, r_{NO} = 1.279(5) Å, r_{NN} = 1.316(7) Å, and $C\hat{N}O$ = 120.3(4)°, which should be compared with values of r_{CN} = 1.43 Å, r_{NO} = 1.21 Å and $C\hat{N}O$ = 113.2°, cited previously[7] for monomeric $4\text{-}IC_6H_4NO$. The similarity of the r_{CN} values implies essentially single bond character of the CN bond in both monomer and dimer. The appreciably longer r_{NO} bond in the dimer reflects the essentially single bond character of the N→O bond as opposed to the double bond character of –N=O in the monomer. The NN bond length (above) falls within the quoted range 1.304–1.329 Å for (*E*)-azodioxy dimers,[18] and represents a high degree of double bond character. The CN bond length is very close to those obtained for other dimeric substituted nitrosobenzenes (1.467, 1.460 Å).[18] Dihedral angle calculations (see additional deposited data) show the aromatic rings to be twisted such that the angle between the phenyl and N_2O_2 planes is 61.4(3)°. This leads to non-bonded distances between *ortho* ring hydrogens and *cis*-oxygen atoms of 2.82 Å for H(2) ··· O(1′) [or H(2′) ··· O(1)] and 2.83 Å for H(6) ··· O(1) [or H(6′) ··· O(1′)]. These almost equal non-bonded distances are a consequence of the relative twisting of the aromatic rings which must stabilise the ground state structure. This high degree of twist between the aromatic rings and the N_2O_2 plane may be compared with a much earlier crystal structure determination of $(4\text{-}BrC_6H_4NO)_2$ where the (*E*)-azodioxy structure was said to be associated with tilting of the rings from the N_2O_2 plane,[19] but accurate estimation of the degree of tilt was not possible at that time and must await a full three-dimensional crystal structure determination.

Table 2 Bond lengths (A) and angles (°) for $C_{12}H_8I_2N_2O_2$

I(1)–C(4)	2.118(5)	N(1)–O(1)	1.279(5)
N(1)–N(1′)[a]	1.316(7)	N(1)–C(1)	1.467(6)
C(1)–C(6)	1.370(7)	C(1)–C(2)	1.392(7)
C(2)–C(3)	1.401(7)	C(3)–C(4)	1.387(6)
C(4)–C(5)	1.395(7)	C(5)–C(6)	1.397(8)
O(1)–N(1)–N(1′)[a]	121.6(5)	O(1)–N(1)–C(1)	120.3(4)
N(1′)[a]–N(1)–C(1)	118.0(5)	C(6)–C(1)–C(2)	122.0(4)
C(6)–C(1)–N(1)	117.5(4)	C(2)–C(1)–N(1)	120.3(4)
C(1)–C(2)–C(3)	118.7(4)	C(4)–C(3)–C(2)	119.1(4)
C(3)–C(4)–C(5)	121.8(4)	C(3)–C(4)–I(1)	119.4(3)
C(5)–C(4)–I(1)	118.9(4)	C(4)–C(5)–C(6)	118.6(5)
C(1)–C(6)–C(5)	119.7(5)		

[a] The primed atom belongs to one and the same molecule and is related to the unprimed one by the centre of symmetry at (1/2,0,0).

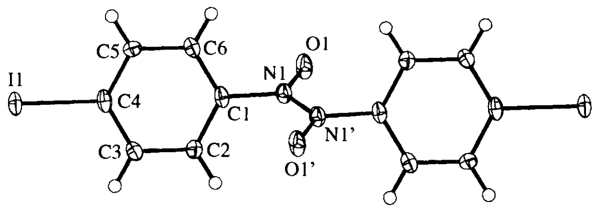

Fig. 2 X-ray structure of (*E*)-4-iodonitrosobenzene dimer showing the atom labelling in the asymmetric unit

NMR spectra

(*i*) **Solid-state ^{13}C spectra.** CP/MAS spectra of both the monomer (**1**) and *E*-dimer (**2**) of 4-iodonitrosobenzene were obtained. Spectra of **1** were recorded over a temperature range of 293–193 K (Table 3). The order of ^{13}C shifts was $C^1 > C^{3,5} > C^{2,6}$ with C^4 being undetected at all temperatures. This signal is expected at *ca.* δ = 105 but its absence in the CP/MAS spectrum is not wholly unexpected and is attributed to the strong dipolar coupling with the quadrupolar ^{127}I ($I = \frac{5}{2}$) nucleus. This coupling is not fully removed by magic-angle spinning which may account for the unobservedly broad signal here.[20] On cooling the solid monomer (**1**) its C^1 and $C^{3,5}$ NMR signals are essentially unchanged, whereas the $C^{2,6}$ signal

Table 3 ^{13}C NMR chemical shift data[a] for 4-iodonitrosobenzene monomer (**1**) and *E*-dimer (**2**)

	(**1**) Solid						(**1**) Solution[b]	(**2**) Solid
T/K =	293	273	243	223	203	193	303	223
C^1	163.9	163.8	163.3	163.3	163.0	162.9	164.2	141.3
$C^{2,6}$	123.7	123.7	~125[c]	~140[d]	138.9[d]	139.1[d]	121.8	126.0
				~110[e]	107.6[e]	107.3[e]		
$C^{3,5}$	138.5	138.4	138.2	138.2	138.9	139.1	138.7	138.0
C^4	?	?	?	?	?	?	105.4	?

[a] Relative to Me_4Si ($\delta = 0$). [b] $CDCl_3$ solvent. [c] Very broad. [d] C^6. [e] C^2.

Table 4 ^1H and ^{13}C data[a] for $CDCl_3$ solutions of 4-iodonitrosobenzene at 223 K

	Monomer (**1**)		*E*-dimer (**2**)		*Z*-dimer (**3**)	
Nucleus	^{13}C	^1H[b]	^{13}C	^1H	^{13}C	^1H[c]
C^1	164.0	—	141.5?	—	142.3	—
$CH^{2,6}$	~122[d]	7.63[d]	125.4	7.69	125.8	7.11
$CH^{3,5}$	139.0	8.03	138.2	7.87	138.8	7.71
C^4	106.9	—	98.5	—	98.5	—

[a] Chemical shifts rel. to Me_4Si ($\delta = 0$). [b] J_{HH}/Hz values: $J_{23} = 8.52$, $J_{25} = 0.13$, $J_{26} = 1.98$, $J_{35} = 1.98$. [c] J_{HH}/Hz values: $J_{23} = 8.65$, $J_{25} = 0.13$, $J_{26} = 2.24$, $J_{35} = 2.24$. [d] Broad due to effects of restricted NO rotation.

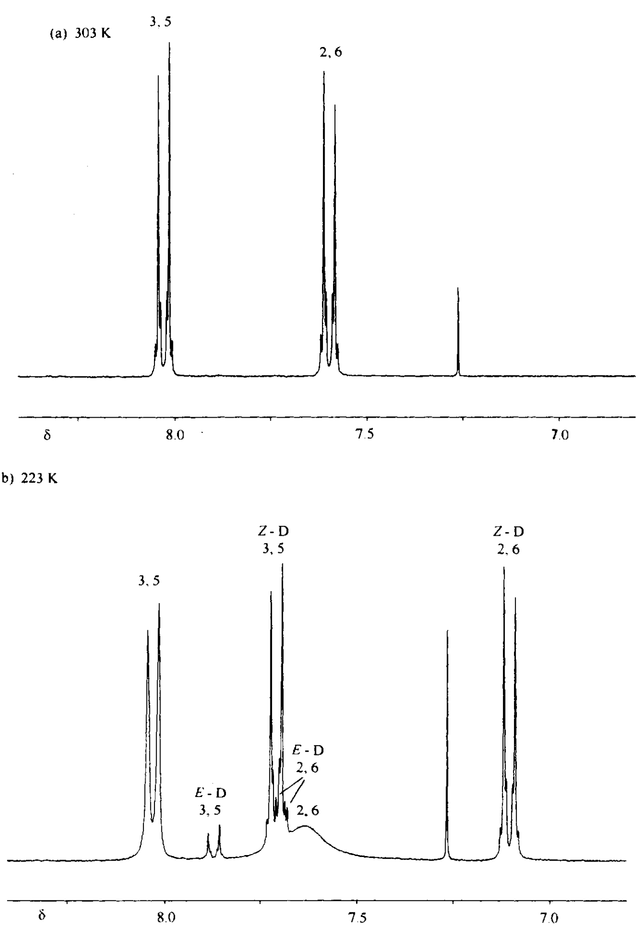

Fig. 3 300 MHz ^1H NMR spectra of a $CDCl_3$ solution of 4-iodonitrosobenzene (*a*) at 303 K showing monomer signals only and (*b*) at 223 K showing signals due to monomer and both *E* and *Z* azodioxy dimers

broadens considerably below 273 K, and then reappears at *ca.* 203 K as two signals, one at *ca.* $\delta = 107$ and the other at $\delta = 139$, which overlaps fortuitously with the $C^{3,5}$ signal. This change is attributed to a slowing down of the rate of rotation of the –N=O group to such an extent that the C^2 and C^6 carbon environments become distinguishable. From the observed bandshape changes an estimated $\Delta G^{\ddagger}$ value of *ca.* 42 kJ mol^{-1} was obtained for the N=O rotation barrier. This compares with 34.3 ± 0.4 kJ mol^{-1} from CD_2Cl_2 solution studies.[21] This is the second recent observation of N=O group rotation in solid C-nitroso compounds, the first being for *p*-nitroso-N,N-dimethylaniline,[22] and suggests widespread occurrence of the phenomenon in the solid state.

The CP/MAS spectrum of the *E*-dimer (**2**) was also recorded at temperatures between ambient and 193 K but, as the spectra were essentially unchanged, only the shift data at 293 K are quoted (Table 4). The spectrum of **2** differs from that of the monomer **1** primarily in the C^1 chemical shift.[23,24] The value of $\delta = 141.5$ compares with $\delta = 164.8$ in the monomer and reflects the very different electronic influences of the N_2O_2 and NO groups on the phenyl rings in the dimer and monomer respectively. In the monomer the significantly higher frequency shift reflects the π-electron acceptor nature of the –N=O group, whereas in the dimer the N_2O_2 group has a much weaker electronic influence on the aromatic C^1 position.

***(ii)* Solution phase ^{13}C and ^1H spectra.** ^{13}C NMR spectra of a $CDCl_3$ solution at ambient temperature of either the monomer (**1**) or the *E*-dimer (**2**) gave a set of signals (Table 3) indicative of the monomer only. However, on cooling this solution to *ca.* 233 K additional signals appeared at chemical shift positions which were attributed to the *E*- and *Z*-dimers (Table 4). The less intense set had shift values very close to those of the CP/MAS spectrum of the solid *E*-dimer. It thus appears that on lowering the solution temperature, the dynamic equilibria involving the monomer and both dimer species shift in favour of the dimers with the *Z*-form being favoured over the *E*-form at all measured temperatures. This is in stark contrast to the *E*-form being the exclusively preferred dimer in the solid state.

Hydrogen-1 NMR studies confirmed further the existence of the *Z*-dimer at low solution temperatures. Spectra of the title compound in $CDCl_3$ solution at 303 and 223 K are shown in Fig. 3. At room temperature, only the monomer signals are clearly visible, but, on cooling, additional signals appear with increasing relative intensity and are assigned as shown (Table 4). From other ^1H NMR studies of all the 4-halogenonitrosobenzene substituent constants for the –N=O, Z-N_2O_2 and E-N_2O_2 groups have been evaluated and allow reliable assignments to be made of all ring hydrogens in *ortho* and *meta* positions to these groups. Using this method, the *Z*-dimer was confirmed as being the more favoured solution dimer for 4-iodonitrosobenzene, and indeed for all other 4-halogenonitrosobenzenes at temperatures below *ca.* 273 K. It is characterised by its

Table 5 Thermodynamic data for the 4-iodonitrosobenzene and nitrosobenzene dimer–monomer equilibria

Compound	Equilibrium	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	$\Delta G^{\circ\,a}$/kJ mol^{-1}	Ref.
IC_6H_4NO	*b*	49.0 ± 0.6	211 ± 3	−14.1 ± 0.1	This work
IC_6H_4NO	*c*	30.4 ± 2.2	141 ± 9	−11.5 ± 0.5	This work
C_6H_5NO	*b*	55.4 ± 1.7	213 ± 7	− 8.1 ± 0.3	9
C_6H_5NO	*c*	42.5 ± 1.2	179 ± 5	−10.9 ± 0.3	9

[a] At 298.15 K. [b] *Z*-dimer $\rightleftharpoons$ 2 monomer. [c] *E*-dimer $\rightleftharpoons$ 2 monomer.

significantly lower frequency ^1H shifts compared to the monomer and *E*-dimer species.

The room temperature ^1H spectrum consists of an AA′XX′ spectrum from the four aromatic hydrogens of the monomer. This spectrum was analysed iteratively, using the LAOCOON program,[25] and the final parameters are given in Table 4. A similar calculation was made on the strong AA′XX spectrum of the *Z*-dimer at a temperature of 223 K. The four-bond *meta* H–H spin–spin coupling constants are significantly larger for the *Z*-dimer reflecting the rather different electronic influences of the -N=O and *Z*-N_2O_2 groups on the C^1 and C^4 positions. The other *J* couplings are of rather similar magnitude for both species.

The ^1H spectrum at 223 K also showed weaker signals due to the *E*-dimer, in this case the internal chemical shift between the A and X hydrogens being significantly smaller with the lower frequency component of the spectrum partially overlapping the high frequency multiplet of the *Z*-dimer. The other notable feature of this spectrum is the broadened nature of the monomer 2,6-hydrogen signal. This is caused by a slowing of the -N=O group rotation, details of which will be reported elsewhere.[21] The dynamic equilibria between monomer and both dimer species were studied by recording ^1H spectra at five temperatures in the range 223–253 K. From the temperature dependencies of the relative populations of the three species, equilibrium constants for the equilibria, *Z*-dimer $\rightleftharpoons$ 2 monomer, and *E*-dimer $\rightleftharpoons$ 2 monomer, were calculated and thence the thermodynamic parameters ΔH°, ΔS° and ΔG° (298.15 K) (Table 5). The negative ΔG° (298.15 K) values indicate that the monomeric structure is thermodynamically favoured at room temperature. The sizeably positive ΔH° values for both equilibria reflect the breaking of the N–N bonds of the *Z*- and *E*-dimers, whereas the positive ΔS° values may be related to the increased translational and rotational degrees of freedom associated with the monomer pairs as compared with either type of dimer. However, it can be inferred from these thermodynamic data that the *Z*- and *E*-dimers will be more favoured compared to the monomer compound at temperatures below *ca.* 230 and 215 K, respectively. These values are very comparable to those of nitrosobenzene itself, implying very similar solution behaviour of the two compounds, in contrast to the solid-state behaviour where only the *Z*-dimer of nitrosobenzene has ever been isolated.[26]

Discussion

These new observations on 4-iodonitrosobenzene in both solid and dissolved states call for a reassessment of the factors that govern the relative stability of the three forms of nitrosoarenes.

The interrelationships between the three molecular forms are illustrated in Scheme 1, where it is assumed that no chemical changes take place between the three possible solid forms.

Prior to the application of high resolution ^1H NMR spectroscopy to such systems the only available evidence for participation of the different molecular forms was obtained from electronic absorption and IR spectroscopies and there was little evidence available from these sources for the presence of both of the isomeric azodioxy compounds. Our earlier studies demonstrate that for nitrosobenzene all three forms are present in solution over the temperature range 20 to −50 °C the (*Z*)-azodioxy dimer being the predominant species below −20 °C and the (*E*)-azodioxy dimer being present only in small quantities[9] whereas when there are 2,6-dimethyl substituents the *E*-isomer is favoured over the *Z*-species.[10,11] For 3,5-dimethyl substitution, however, the *Z*-species appears to be favoured. Evidence for the preferred formation of the *Z*-species from the monomer at low temperatures has long been established for nitrosoalkanes.[27,28] In these previous studies thermodynamic data for both equilibria and for kinetic processes were obtained.

$$\begin{tikzcd}
Z\text{-D} \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon] & 2\text{M} \arrow[l, shift left, harpoon] \arrow[r, shift left, harpoon] \arrow[d, shift left, harpoon] & E\text{-D} \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon] & \text{solution} \\
Z\text{-D} \arrow[u, shift left, harpoon] & 2\text{M} \arrow[u, shift left, harpoon] & E\text{-D} \arrow[u, shift left, harpoon] & \text{solid}
\end{tikzcd}$$

Scheme 1

We turn now to the application of Scheme 1 to preparative and recrystallisation studies of aromatic *C*-nitroso compounds. The majority of these compounds are obtained as the *E*-dimers from the general preparative routes of either mild oxidation of the amine or reduction of the nitro compound to the *N*-arylhydroxylamine followed by oxidation.[29] The preparations are usually carried out in aqueous ethanol and recrystallisations are from ethanol. In applying Scheme 1 it is noted that the preparative step produces the monomer and that therefore the resultant product is dependent upon (*a*) temperature, (*b*) monomer concentration, (*c*) solvent character and (*d*) relative solution solubilities of the three compounds. It has usually been assumed that the *E*-dimer is the thermodynamically most stable form at room temperature[30] and that, where the nitrosocompound has been isolated as the solid monomer, dimer formation cannot take place. There is evidence however that some nitrosoarenes can exist in two solid forms but the formation of all three solids is as yet unknown. It is clear from the present studies that 4-iodonitrosobenzene, hitherto presumed to be formed only as the monomeric solid, can also exist as the solid *E*-dimer and be detected as the *Z*-dimer in solution at temperatures below ~ 0 °C. It has long been known[8] that 2,4,5-trimethylnitrosobenzene can be isolated as a colourless dimer (Mijs[4] showed this to be the *E*-form) and as a green monomeric solid metastable at room temperature (but stable indefinitely at −10 °C[31]). Also, pentafluoronitrosobenzene crystallises as a mixture of the monomer and *Z*-dimer.[32] We have recently shown[33] that 3-iodonitrosobenzene, which has been isolated as the solid *Z*-dimer,[4] can also be transformed into the solid *E*-dimer. These observations, coupled with the NMR evidence for the existence in solution of *Z*-dimers for nitrosocompounds previously known only as the *E*-dimers or as the solid monomers suggest that a reappraisal of the understanding of the relative stability of the three forms of nitrosoarenes should be made. In particular, it is suggested that future studies should concentrate upon the variation of the isolation and recrystallisation techniques, in particular the use of different solvents and also of subliming, *via* the gaseous monomer, followed by trapping at low temperature and subsequent slow warming to allow dimerisation to occur. This could well lead to a greater number of examples of nitrosocompounds which can exist in more than one solid form.

The dimerisation of *C*-nitroso compounds has long been known as a feature which distinguishes them from other compounds containing the –N=O group, namely compounds such as X–N=O (where X = halogen, RO, RS or R_2N) which are formed only as the monomer. In that sense the dimerisation of *C*-nitroso compounds has been viewed as an unusual feature. There are, however, some *C*-nitroso compounds which apparently do not dimerise under any experimental conditions including low temperatures, variation of solvent and increased concentration. Attention was drawn to such many years ago[30,34] and examples are to be found in the following: CF_3NO, CCl_3NO, RCF_2NO, RR′CFNO, $RCCl_2NO$ and $R_2NC_6H_4NO$. In the halogenated nitroso compounds there is a contribution from ionic structures such as $CF_3{}^-NO^+$ leading to a shortening of the NO bond[35,36] to 1.171 and 1.198 Å, whereas in the nitrosoanilines the NO bond is lengthened due to participation of the quinonoid structure akin to **1a**[37] giving a value in the range 1.25–1.27 Å. The *C*-nitroso compounds which readily dimerise have NO bond lengths which lie within these extremes of 1.17–1.27 Å, *e.g.* nitrosomethane where this bond length is 1.211 Å.[38] We suggest that the dimerisation of a *C*-nitroso compound is dependent upon the NO bond length, which is itself a function of the electronic character of the nitrogen atom. A further indication of the NO bond length is provided by the IR-active NO stretching wavenumber, relationships between the two parameters having been proposed by Lüttke,[3] Talberg[37] and Cameron, Gowenlock and Vasapollo.[39] Much more data are available of NO stretching wavenumbers than of the NO bond lengths and consequently it is possible to use the wavenumber value as a convenient surrogate for the bond length. An early attempt to discuss dimerisation on this basis was made by Lüttke.[40] Some of his suggestions concerning non-dimerising nitroso compounds can be modified on the basis of later studies such as this for 4-iodonitrosobenzene and of others for *gem*-chloronitroso compounds. NO-containing compounds that do not dimerise include the nitrosyl halides and alkyl nitrites. The NO wavenumbers for the latter are 1610–1625 cm^{-1} (*cis*-rotational isomer) and 1650–1685 cm^{-1} (*trans*-rotational isomer). Non-dimerising *C*-nitroso compounds are trichloronitrosomethane and trifluoronitrosomethane (1621 and 1595 cm^{-1}, respectively). Compounds of the type $(CH_3)_2CXNO$ which can form dimers include X = Cl (1587 cm^{-1}), NO_2 (1585 cm^{-1}), CN (1570 cm^{-1}), CH_3 (1546 cm^{-1}) and $COCH_3$ (1539 cm^{-1}). The upper NO wavenumber limit for dimerisation is therefore about 1590 cm^{-1}. At the other end of the scale is *p*-nitrosodimethylaniline (1363 cm^{-1}),[41] and all dialkylnitrosamines (1440–1480 cm^{-1}). The dimerising substituted *C*-nitrosobenzenes have their NO stretching wavenumbers in the range 1511–1480 cm^{-1}, the lowest values being for 4-iodonitrosobenzene (1484 cm^{-1}) and ethyl *m*-nitroso-*E*-cinnamate (1480 cm^{-1}).[42] Whereas previously this compound had been known only as a monomer, recent studies of our own[21] have shown that dimerisation does occur in $CDCl_3$ solution at low temperatures. The compound thus represents a very borderline example of potential dimerisation. We therefore set the lower NO wavenumber limit for dimerisation at 1480 cm^{-1}. This 'dimerisation window' of 1590–1480 cm^{-1} corresponds approximately to the range 1.192–1.230 Å for NO bond lengths using the relationship given by Cameron, Gowenlock and Vasapollo.[39] The boundaries are not completely exact given that the NO lengths used in establishing the relationship include X-ray crystallographic data for solids, and electron diffraction and microwave data for gaseous nitroso compounds, but the overall correlation of an NO wavenumber/bond length window for dimerisation of XNO compounds gives rise to the following considerations.

We have presented evidence for the close similarity in the molecular dimensions of the (E)-$C_2N_2O_2$ structure in a wide variety of dimers,[18] there being, for example, no correlation between the NN bond length and the ease of dissociation to the monomer. We therefore suggest that the differences in dimer stabilities relative to the monomer are to be found in small but significant differences in monomer structures as evidenced primarily in the NO bond lengths of the respective monomers. Several studies have been made of the kinetics of dissociation of *E*-dimers in organic solvents, the smallest rate constant at 25 °C for the dissociation reaction (1) being found when R = CH_3

$$(E)\text{-}(RNO)_2 \longrightarrow 2RNO \qquad (1)$$

and this monomer possesses an NO bond length and stretching wavenumber that are found almost in the centre of the two 'dimerisation windows' described above. Other relatively stable *E*-dimers are R = $(CH_3)_2C{\cdot}COCH_3$ and R = cyclo-C_6H_{11}. In general, the *E*-dimeric nitrosoalkanes are less ready to dissociate than 3- or 4-substituted nitrosobenzenes. It is implicit in this approach that the molecule HNO should undergo dimerisation and two recent theoretical studies have also come to this conclusion.[43,44]

It should be noted that the majority of nitrosoalkenes do not dimerise, the main exception to this being the ω-nitrosostyrenes studied by Pritzkow and co-workers.[45] A summary of the properties of nitrosoalkenes[46] gives values for the stretching wavenumbers of a range of nitrosoalkenes lying within the range 1420–1485 cm^{-1}, most of which values lie outside the proposed dimerisation window and are therefore compatible with the absence of any dimerisation. Nitrosoarenes which are unable to self-dimerise due to steric hindrance but which can cross-dimerise with other *C*-nitroso compounds should possess NO stretching wavenumbers within the dimerisation window range. An example is provided by 2,6-di-*tert*-butylnitrosobenzene for which the NO stretching mode is at 1502 cm^{-1}.

In conclusion, it would appear that the criterion for dimerisation of *C*-nitroso compounds, namely that the NO group of the monomer exhibits a stretching mode in the IR range 1590–1480 cm^{-1}, is wholly reliable for all such compounds in which there are no particular steric restraints. Where there are such restraints, the above criterion will apply to potential cross-dimerisation.

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