Properties and Spectroscopic Studies of Polymeric Dinitrosobenzenes

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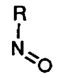
Spectroscopic studies of the polymeric 1,4- and 1,3-dinitrosobenzenes show that the solid polymers are long chain and based upon the *trans* N_2O_2 group. The 'ageing' phenomenon reported elsewhere is not accompanied by any structural change that is detectable by the techniques employed. The importance of the solid state for stabilisation of the polymers is emphasised and it is shown that depolymerisation to the monomer (disubstituted benzenes containing two monomeric N=O groups) occurs on heating and on vaporisation.

C-Nitroso compounds can exist in the monomeric form **1** and in the *cis* and *trans* dimeric forms[1] **2** and **3**, respectively. The monomers are green–blue in colour and the dimers are colourless. The relative stabilities of the three forms are dependent upon the structure of R, the physical state, the temperature and, where appropriate, the solvent properties. In contrast to extensive investigations into the molecules containing one nitroso group (**1**) and the dimers thereof (**2** and **3**) relatively little attention has been directed to the chemistry of molecules containing two independent monomeric nitroso groups, both of which are in principle available to engage in formation of separate dimeric N_2O_2 groups. There is little, if any, experimental evidence for dinitrosoalkanes but it is well known[2–4] that 1,4-dichloro-1,4-dinitrosocyclohexane can exist both as a stable *trans* compound with two monomeric N=O groups (**4**) and as an internal *cis* dimer (**5**).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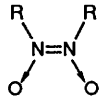
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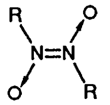
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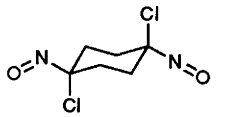
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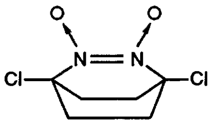
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Dinitrosobenzenes have been known for over a hundred years.[5] The *ortho*-isomer has only a transient existence as an intermediate in the thermal decomposition[6] of the more stable benzofuroxan. *m*- and *p*-Dinitrosobenzene, on the other hand, have long been known to polymerise, presumably by the formation of dimeric N_2O_2 functions linking different monomer units. IR spectroscopy[3,7] of these two polymers implies that only the *trans* dimeric N_2O_2 group is present; for the *m*-dinitrosobenzene polymer, IR implies it is possible that the monomeric NO group is also present. Although there is an extensive patent literature concerning the industrial applications of polymeric dinitrosobenzenes structural information is limited to the IR data. Oligomeric dinitrosocyclohexanes have been prepared by Donaruma *et al.*[8,9] and degrees of oligomerisation of two,[8] ten,[9] and 87[9] have been obtained.

^{13}C NMR spectroscopy has yielded interesting structural information for *C*-nitrosocompounds[10–14] and the large difference (> 20 ppm) between the resonances for *C*-NO and *C*-N_2O_2-*C* clearly permits an estimate to be made for any participation of monomeric NO end groups in the solid polymers. The small, but easily distinguishable difference between the ^{13}C NMR spectra of *cis* and *trans* dimers[13,15] formed from the same monomers implies also that it will prove possible to show whether one or both N_2O_2 groups participate in the polymer structures.

Experimental

Polymeric 1,4-dinitrosobenzene was prepared by the direct chlorination of *p*-benzoquinone dioxime using the method of Khishchenko *et al.*[16] This method was found to give better yields of pure material than the conjugate oxidation method of Ermakov and Komkova.[17] The previously noted[18] low solubility of the product in most organic solvents led us to adopt a vacuum sublimation technique. The polymeric solid was filtered off from the reaction mixture, washed with hot water, dilute sodium hydroxide, water and finally acetone and then dried and powdered. It was then vacuum sublimed at 10^{-3} mmHg, from a temperature of 50–80 °C to a solid CO_2-cooled thimble (Bartusch[19] used 12 mmHg from a temperature of 130–150 °C to a water-cooled thimble). Sublimation occurred readily at 60 °C giving a green powdery solid under vacuum at -78 °C. Admission of air led to a slight yellowing of the solid. Slow warming of the sublimate to room temperature gave a yellow solid at about 0 °C. The early literature[5,18–20] indicates that the m.p. of the polymeric solid is a function of heating rate. Consequently thermogravimetric analysis was carried out under nitrogen, heating rate 20 °C min^{-1} using a Perkin-Elmer TGS-2. Weight loss began at 100 °C and was rapid between 120 and 140 °C, the material changing colour to bright green. DSC analysis was carried out at the same heating rate and an exothermic process accompanied the formation of a bright green colour in the region 130–140 °C. Polymeric 1,3-dinitrosobenzene, prepared by the method of Alway and Gortner,[21] was provided by Professor W. Lüttke. It was purified by vacuum sublimation under similar conditions to those used for the 1,4-analogue. The sublimate was a yellow–green solid at -78 °C which turned yellow brown at about 0 °C when allowed to warm. Thermogravimetric analysis (conditions as above) gave a weight loss beginning at 95 °C with rapid loss between 120 and 140 °C in an exothermic process accompanied by the formation of a bright green colour. IR spectra were measured using KBr discs the major bands being ν/cm^{-1} 1481, 1411, 1304, 1265, 1100, 1010, 860 and 780 (1,4-); and 1640, 1620, 1442, 1350, 1270, 880 and 805 (1,3-).

Laser Raman spectra were obtained at the University of Glasgow using both 457.0 and 488.0 nm excitation and absorption bands at 1129, 1270, 1314, 1388, 1396, 1441 and 1590 cm^{-1} were observed for the 1,4-compound. Mass spectra were measured at 70 eV and a source temperature of 100 °C using a solid sample. The eight most prominent peaks were: *m*/*z* 136

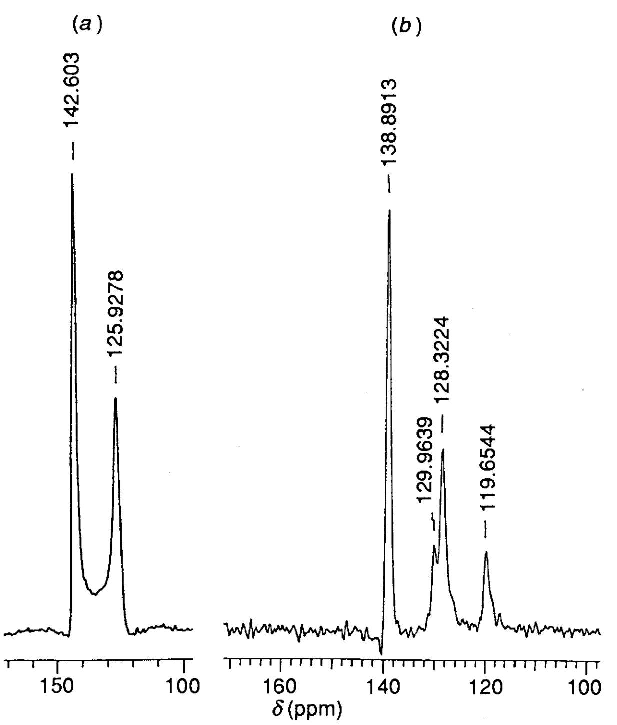


Fig. 1 CP MAS ^{13}C NMR spectra of (*a*) polymeric 1,4-dinitrosobenzene and (*b*) polymeric 1,3-dinitrosobenzene

(100), 106 (99.3), 77 (19.8), 76 (99.7), 75 (31.7), 74 (38.7), 50 (98.8) and 30 (78.8) (1,4-); and 136 (63.1), 106 (23.8), 76 (100), 75 (16.4), 74 (18.1), 51 (33.8), 50 (56.0) and 28 (37.9 (1,3-). Of the remaining 18 smaller peaks for each compound 14 were common.

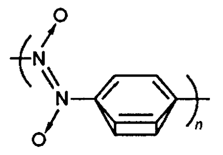
Natural abundance solid state ^{13}C NMR spectra, CP–MAS with proton decoupling, were measured at the University of Durham, Industrial Research Laboratories. δ_C (ppm) 142.6 [q, C(1,4)] and 125.9 [nq, C(2,3,5,6)] (1,4-); 138.9 [q, C(1,3)], 130.0 [nq, C(5)], 128.3 [nq, C(4,6)] and 119.7 [nq, C(2)] (1,3-).

Discussion

Attention is directed first to the ^{13}C NMR spectra (Fig. 1). For the 1,4-compound only two resonances, one quaternary and one non-quaternary, are observed. It is evident that there is no indication of any resonance in the 155–168 ppm range where an aromatic C–NO resonance would appear. This result is consistent either with a linear polymer or with a cyclic polymeric structure in which no monomeric nitroso end groups participate. An oligomer is excluded. It is also evident that only one N_2O_2 isomer is present. Both the scientific and the patent literature suggest that the properties of this polymer vary with age and it seemed possible that this reflected structural change *e.g.* isomerism of N_2O_2, or greater degree of polymerisation. Samples that varied in age from a few hours to four years showed no difference in their solid state ^{13}C NMR spectra and consequently it appears from this relative test that ageing involves no structural change. The IR spectrum demonstrates the absence of the characteristic doublet[3,22] of the *cis*-N_2O_2 group at 1350–1400 cm^{-1} and also the absorption band at 1495–1515 cm^{-1} characteristic of an aromatic N=O stretch.[2] Consequently it is suggested that only the *trans*-N_2O_2 group is present. Further support for this is provided by the fact that the strongest IR absorption is found at 1265 cm^{-1} and this is in accord with the *trans* dimers[3] of *para*-substituted nitrosobenzenes for which ν_{as}(NO) falls in the range 1248–1285 cm^{-1}. Our IR spectrum is in reasonable agreement with the published data[7] except for the fact that we find no absorption in the region 1500–1700 cm^{-1}. Comparison with the IR spectrum of *p*-benzoquinonedioxime suggests that the purification techniques adopted by Boyer *et al.*[7] failed completely to remove this starting material from the product.

It has been demonstrated[23] that the N=N bond length in *trans* dimeric nitroso compounds is virtually constant and that for six *trans* dimeric *para*-substituted nitrosobenzenes the N=N stretching frequency which is Raman but not IR active lies in the range[24] 1436–1447 cm^{-1}. For five different ω-dimeric nitrosostyrenes we find[15] the N=N stretching frequency to lie in the range 1431–1440 cm^{-1} and for *trans* dimeric nitrosomethane the value[25] is 1417 cm^{-1}. It seems probable that the observed Raman absorption at 1441 cm^{-1} (absent in the IR) corresponds to the N=N stretch in the polymer.

We therefore suggest that the most probable structure of the 1,4-compound is **6** and that the material is a polymer *i.e.* the monomeric N=O end group is not detected. It appears that there would be considerable difficulty in constructing a cyclic polymeric structure with the N_2O_2 group displaying the *trans*-configuration throughout and we therefore exclude this from further consideration.



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The 1,3-compound is similar to the 1,4-compound in that the ^{13}C NMR spectrum demonstrates the absence of absorption in the 155–168 ppm region and thus the virtual absence of the monomeric N=O group. The spectrum shows one quaternary and three non-quaternary resonances as would be expected for a polymer containing only one of the two isomeric N_2O_2 groups [see (Fig. 1(*b*)]. If it is assumed that the substituent chemical shifts (SCS) of the N_2O_2 groups (based upon 128.5 ppm for benzene) are additive than we obtain the following SCS values for the *trans* N_2O_2 group: *ipso*, +9.65, *o* −4.4, *m* +0.75 and *p* +4.2 ppm. These values may be used to predict resonances of 142.35 [C(1,4)] and 124.85 [C(2,3,5,6)] ppm for the 1,4-compound, both of which are close to the observed values (142.6 and 125.9 ppm).

The IR data for the 1,3-compound purified by vacuum sublimation give strong absorption at 1270 and 805 cm^{-1} (1272,[3] 1282–74,[7] 808[3] and 812[7] cm^{-1}) and show the absence of the characteristic *cis*-N_2O_2 doublet. We therefore consider this polymer to have the repeating *trans* dimeric N_2O_2 unit and for the degree of polymerisation to be high such that the monomeric NO end group is unable to be detected by solid state ^{13}C NMR spectroscopy.

Before discussing the TGA, DSC and MS data for the two polymers it is appropriate to consider the behaviour of nitrosobenzene and of *meta*- and *para*-substituted nitrosobenzenes in the solid and gaseous states and in solution. Orrell's studies[13,14] make it plain that at room temperature both dimers of nitrosobenzene are thermodynamically unstable in solution with respect to the monomer and that, although there is a significant activation enthalpy for the dissociation reaction, the high positive entropy of activation leads to very fast dissociation at room temperature. In the gas phase at these temperatures there is a similar feature in that all spectroscopic evidence leads to the detection of only the monomer of nitrosobenzene. Consequently it is evident that it is only in the solid state that the dimeric forms are stable. Dimers that are substituted in the *meta*- and *para*-positions display the same behaviour. There are, of course, extra steric features to be considered for the *ortho*-substituted and 2,6-disubstituted nitrosobenzenes. This importance of the solid state can therefore be expected to be repetated for the *m*- and *p*-dinitrosobenzene polymers. For a variety of solutions of *p*-dinitrosobenzene Donaruma reported[8,26] the absence of evidence for species which were not monomeric. This is explicable on the basis that, in the absence of the stabilisation afforded by the solid state, the polymer is thermodynamically unstable with respect to the monomer and that the dissociation reaction is very rapid. On heating the polymers, both TGA and DSC show that depolymerisation begins to occur below 100 °C and that this is more rapid as the temperature increases. In particular the DSC traces show that exothermic changes occur for both polymers in the neighbourhood of 130° (*p*), 125 °C (*m*). This is compatible with the proposal that the solid polymer is dissociating rapidly to the liquid or gaseous dimonomer and that the latter is thermodynamically more stable than the polymer in the absence of the solid lattice effect. The mass spectroscopic data also show that there is no evidence at 100 °C for any structural units greater in size than the monomeric one ($m/z = 136$).

The preparation of the solid polymer is of interest in that the mechanism of polymerisation is dependent upon the formation of *trans* dimeric N_2O_2 groups from two monomeric NO groups. This reaction, which is dependent upon electronic rearrangement at the nitrogen atoms,[1,27,28] is of fundamental interest. In contrast to most other types of polymerisation processes which are either free radical or ionic in character, the polymerisation of dinitrosocompounds is both non-radical and non-ionic. It appears that the very small number of monomeric NO end groups (too small to be detected by ^{13}C NMR or IR spectroscopy) could be available to act as 'living' polymer ends. Presumably copolymerisation of different dinitrosocompounds (whether random or block) would also be possible. It also appears possible that the ageing effect noted in the literature for 1,4-dinitrosobenzene polymers is compatible with further polymerisation in the solid state. Such a reaction would lead to no discernible difference in the ^{13}C NMR spectrum provided that the initial degree of polymerisation was high.

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