A Photoelectron/Photoionisation and *ab initio* Study of the S_3N_3 Radical produced by Vaporisation of $(SN)_x$

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The previously unknown S_3N_3 radical is the major species produced by vaporisation of the $(SN)_x$ polymer; the electronic and geometric structures are studied by means of u.v. photoelectron spectroscopy and electronic structure calculations.

The vaporisation of the unusual $(SN)_x$ polymer, with its anisotropic three-dimensional metallic properties and low temperature superconductivity,[1] is of considerable interest since the gaseous products are known to recondense back to the polymer[2,3] and are therefore of some relevance to the polymerisation process. Such gaseous species have been probed previously by mass spectroscopic methods leading to the conclusion that a 'linear bent' $(SN)_4$ unit is the dominant gas phase species.[4—6]

In Figure 1 we show the He I photoelectron (P.E.) spectrum of $(SN)_x$ vaporised at ~140 °C, and in Figure 2, the corresponding photoionisation mass spectrum (P.I.M.S.) recorded on a P.E./P.I.M. spectrometer specifically designed to study transient–reactive species.[7] Apart from N_2, this completely new P.E. spectrum represents one molecular species, and the P.I.M.S. indicates, particularly with the filtered HL_α light source (10.2 eV), a dominant $S_3N_3^+$ ion, with no evidence for an SN^+ fragment. We emphasise that the P.I.M.S. appears only at a vaporisation temperature of 130—150 °C, at low pressure, (*ca.* 3×10^{-6} Torr in the analyser region), and with fast pumping. Under less stringent conditions, or indeed in a commercial photoelectron spectrometer, the main product is the well known S_2N_2 molecule,[8,9] together with traces of S_4N_4[9] and S_4N_2,[10] detected by their characteristic P.E./P.I.M. spectra.

Although, in principle, an $(SN)_4^+$ parent ion could be unstable and therefore not observed, we believe, contrary to the early work,[4—6] that an S_3N_3 neutral species is the dominant product under the conditions of our experiment. Our lowest ionising energy (10.2 eV) is well below that used in the electron impact work and yet we have no evidence for $(SN)_4^+$. In the early work, S_8^+, and $S_4N_4^+$ impurities were observed, and indeed, under certain conditions we also can see $S_4N_4^+$ and $S_4N_2^+$ (*vide supra*). The species shown in Figure 1 yields back the polymer upon condensation, and when revaporised shows the presence of S_4N_4, S_4N_2, and S_2N_2, in addition to S_3N_3. This has led to considerable confusion,

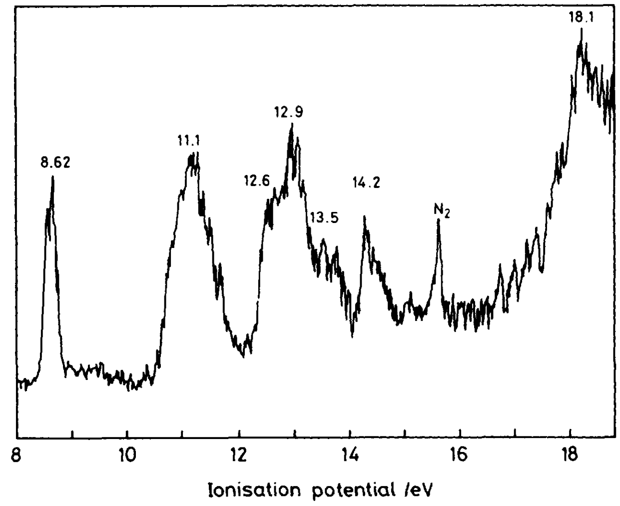

Figure 1. The He I photoelectron (P.E.) spectrum of the vaporisation products of $(SN)_x$ at 140 °C. Numbers refer to ionisation potentials (in eV) at the band maxima or estimated shoulders.

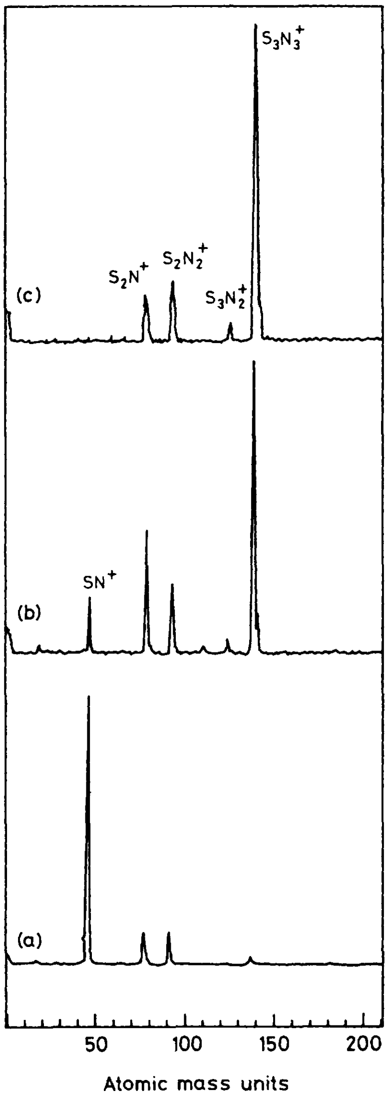

Figure 2. Photoionisation mass spectra (P.I.M.S.) of the species in Figure 1 at different light source energies: (a) He I, 21.2 eV; (b) $HL_{\alpha,\beta,\gamma}$, 10.2—13.6 eV; (c) HL_α (filtered with LiF), 10.2 eV.

especially in the previous field ionisation and field desorption experiments.[5,6] Also the appearance potentials (A.P.s) determined previously[4,6] for $S_2N_2^+$ and $S_4N_4^+$ from the corresponding neutrals are ~1.1 eV too high when compared with the P.E. results.[8,9] This implies that the A.P. observed[4,6] for $S_3N_3^+$ from $(SN)_x$ (9.5 eV) is probably too high, and possibly as low as 8.4 eV. This is close to the first ionisation potential (I.P.) in Figure 1 (8.62 eV), and implies that $S_3N_3^+$ arises from direct ionisation rather than fragmentation. We note also that the *same* spectrum can be obtained by pyrolysis of S_4N_4 over silver or glass wool at 275 °C, although the yields are poorer (S_2N_2, S_4N_2, and S_4N_4 are also produced). This concurs with more recent mass spectroscopic work on similar pyrolyses where the presence of S_3N_3 [and *not* the 'linear bent' $(SN)_4$] was suggested.[11]

The P.E. spectrum of Figure 1 is clearly not that of an open 'linear bent' $(SN)_4$ species which would have a much more complicated spectrum (see *e.g.* the calculations of refs. 12—14). The small vaporisation coefficient and magnitude of the heat of vaporisation of $(SN)_x$,[15] the molecular beam electric resonance study of $(SN)_x$ vapours,[16] and the known structure for the S_3N_3 anion,[17] all point to a ring structure for S_3N_3 with little or no dipole moment. On this basis we have optimised ring structures for the 9π S_3N_3 radical and the 8π cations (C_s, C_{2v}, and D_{3h}) using *ab initio* methods akin to those successfully used for the structure of S_4N_2.[18] An initial C_s (non-planar) structure for the radical became C_{2v} (planar), and then gave the lowest energy structure as D_{3h} with SN = 1.645 Å, $\angle$NSN = 113.0°, and $\angle$SNS = 127.1°. The triplet and singlet cations retained similar D_{3h} geometries with identical NS bond lengths (1.645 Å) and NSN and SNS angles of 110.0 and 130.0° respectively. These structures seem quite reasonable in the light of the S_3N_3 anion structure.[17]

Configuration interaction (C.I.) calculations were then performed in a double zeta basis[10] for a variety of electronic states, and indicated Jahn–Teller distortion towards C_{2v} for the radical and triplet/singlet cations. The ground state cation $^3A_2'$ was preferred to $^1A_1'$ by 1.12 eV.

The calculated P.E. spectrum shows a considerable number of singlet and triplet states together with many states involving shake up; the overall distribution gives a reasonable correspondence with the experimental spectrum particularly for the more intense triplet states. All the main I.P.s up to about 15 eV can be explained in terms of one-electron processes from the highest group of orbitals which are 3e″ (HOMO), 4e′, 2e″, 3e′, and $1a_2''$. The more intense triplet states are grouped as follows: 8.6 eV ($^3A_2'$), 10.5—12 eV ($^3A_1'' + {}^3E'' + {}^3A_2'' + {}^3A_2'$), *ca.* 13 eV ($^3A_1' + {}^3A_2' + {}^3A_1'' + {}^3A_2''$), and 14.2 eV ($^3E''$). Full details will be published elsewhere,[19] as will the particularly germane question of the mechanism of vaporisation and the recondensation of the S_3N_3 species back to $(SN)_x$.

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