Preparation of Highly Conducting Compounds by the Room Temperature Solid State Reaction of S_4N_4 with Halogens

By G. BRYAN STREET,* ROBERT L. BINGHAM, JOHN I. CROWLEY, and JAN KUYPER
(*IBM Research Laboratory, 5600 Cottle Road, San Jose, California* 95193)

Summary S_4N_4 has been converted into highly conducting solids by treatment with Br_2, ICl, IBr, and I_2.

RECENTLY we reported that the room temperature conductivity of crystals and films of $(SN)_x$ is increased by an order of magnitude on reaction with bromine.[1,2] This observation encouraged us to investigate the reaction of halogens with other sulphur–nitrogen compounds. In this note we report preliminary results on the solid state bromination of the insulator S_4N_4 ($\sigma = 10^{-14}\ \Omega^{-1}\ cm^{-1}$ at 25 °C) which leads to a highly conducting material with composition $(SNBr_{0\cdot4})_x$, and with physical and spectral properties remarkably similar to those of $(SN)_x$ brominated under similar conditions. Treatment of crystals of S_4N_4 with bromine vapour resulted in a rapid surface reaction followed by extensive exfoliation and volume expansion of the crystals. This bromination, like that of $(SN)_x$, is slightly exothermic and eventually destroys the original crystal habit giving a black material which after evacuation of free bromine at room temperature and 10^{-5} Torr had a composition $(SNBr_{0\cdot4})_x$. This composition will be referred to as brominated S_4N_4 and the identical composition obtained by bromination of $(SN)_x$ will be referred to as brominated $(SN)_x$. The i.r. spectra of brominated S_4N_4 (films) coincide closely with that of $(SN)_x$ and brominated $(SN)_x$ (1000, 810, 690, and 620 cm^{-1}); the four intense bands associated with S_4N_4 are absent (930, 700, 558, and 345 cm^{-1}). The products of bromination of both S_4N_4 and $(SN)_x$ show Raman peaks at 154 and 230 cm^{-1} attributed to weakly bonded Br_2 or 'Br_3^-'. *X*-Ray power diffraction data of the poorly crystalline brominated S_4N_4 exhibit one strong peak corresponding to the $\bar{1}02$ peak of brominated $(SN)_x$. The density of the two materials is the same within experimental error (2·65 g ml^{-1}). On heating, both materials behave similarly, losing bromine relatively slowly below 100 °C but decomposing rapidly and exothermically at 165 °C. Heating the brominated S_4N_4 at 80 °C for 18 h under reduced pressure (10^{-5} Torr) with continuous pumping leads to conducting films and a copper-bronze coloured residue of composition $SNBr_{0\cdot07}$, whereas heating the brominated $(SN)_x$ under similar conditions at 135 °C gives a similar coloured conducting compound $(SNBr_{0\cdot04})_x$. These data strongly suggest that brominated S_4N_4 is structurally very similar to brominated $(SN)_x$. Since polymeric SN-chains are still present in the latter compound, we infer that in the presence of bromine S_4N_4 undergoes a solid state polymerization with simultaneous incorporation of bromine. This represents the first report of a direct room temperature polymerization of S_4N_4. However, bromination of S_4N_4 in solution has been reported[3] to give $(SNBr)_x$, but the composition[4] of these bronze and, in our experience, non-conducting crystals, is not certain. The room temperature electrical conductivity of a compressed (350 atm) pellet of brominated S_4N_4 is 32 $\Omega^{-1}\ cm^{-1}$, which is similar in magnitude to that measured for $(SN)_x$ under similar circumstances.[5]

We have also observed that S_4N_4 reacts readily with ICl and IBr at room temperature to give conducting solids *e.g.*, the corresponding iodine monochloride derivative has a room temperature pellet conductivity of 50 $\Omega^{-1}\ cm^{-1}$. Iodine does not react with either $(SN)_x$ or S_4N_4 at room temperature. However, at higher temperature (*ca.* 125 °C)

it reacts with both materials to give conducting solids. All these materials are air sensitive, their surfaces slowly deteriorating over a period of several days.

We thank the office of Naval Research for partial support of this work.

(*Received*, 13*th April* 1977; *Com.* 359.)

[1] G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J.C.S. Chem. Comm.*, 1977, 407.
[2] W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, and G. B. Street, *Phys. Rev. Letters*, 1977, **38**, 1305.
[3] A. Clever and W. Muthmann, *Ber.*, 1896, **29**, 340.
[4] H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.
[5] M. Goehring, *Quart. Rev.*, 1956, **10**, 437.