Magnetic Properties of Amorphous-like Carbons Prepared from Tetraaza Compounds by the Chemical Vapour Deposition (CVD) Method

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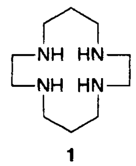
An apparent saturation magnetization (M_s) of the title carbons prepared from 1,5,8,12-tetraazadodecane was found to be 2–3 times larger than those previously reported (2.56 emu g^{-1}; 0.005 μ_B per carbon atom); the M_s value is dependent on the ratio of hydrogen to carbon in the starting materials, particularly for H/C > *ca.* 2.

There has been recent interest in the synthesis of carbon-based compounds exhibiting a spontaneous magnetization at room temperature.[1–4] Our approach uses organic monomers as starting material,[4] and we have now discovered a novel carbonaceous magnetic material prepared from tetraaza compounds with an apparent saturation magnetization higher than those previously reported.[2–4]

The carbonaceous sample (aza-carbon) was prepared from the commercially available tetraaza-compound **1** or **2** according to the procedure described previously.[4] The aza-compound was placed in a quartz tube, which was evacuated overnight. The tube was then heated at 950 °C and the monomer rapidly pyrolysed. The reaction time was 30 min. The tube was cooled and the resulting aza-carbon products were removed.

X-Ray diffraction, laser-Raman and electron diffraction analysis of the aza-carbon showed no distinct crystalline phase, indicating an amorphous-like structure.



1

$H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$

2

The magnetic and ESR properties of the aza-carbon were examined and the reproducibility of data was good. The room temperature magnetization was recorded on a vibrating

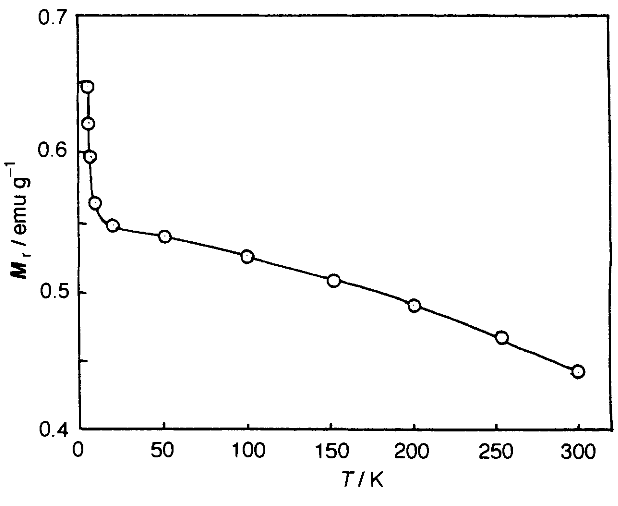


Fig. 1 Temperature dependence of the remnant (M_r) magnetization of the aza-carbon **1**. 1 emu = 10^3 A m^{-1}.

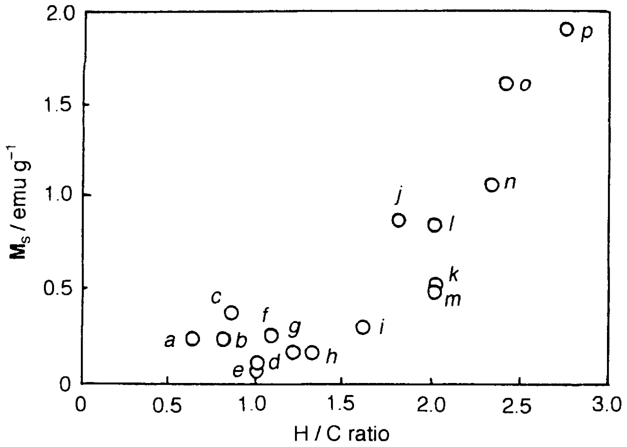


Fig. 2 The effect of H/C ratio of the M_s value at room temperature. *a*: pyrene, *b*: *trans*-1,2-di(thienyl)ethylene, *c*: triphenylmethane, *d*: paracyclophane, *e*: phenol, *f*: tetrahydrocarbazole, *g*: dibenzo-18-crown-6, *h*: octahydroacridine, *i*: adamantane, *j*: tricyclohexylmethanol, *k*: cyclododecanol, *l*: cyclododecane, *m*: cyclopentadecane, *n*: n-hexane, *o*: 1,4,8,11-tetraazacyclotetradecane, *p*: 1,5,8,12-tetraazadodecane.

sample magnetometer (VSM), while the temperature dependence of the magnetization was measured using the SQUID method. The field-dependence of the magnetization (***M***) of the aza-carbon **2** which was prepared from 1,5,8,12-tetraazadodecane exhibited an apparent hysteresis at room temperature; the saturation magnetization (M_s) was found to be *ca.* 1.92 emu g^{-1}, *ca.* 2–3 times those of carbon samples from adamantane[2] and cyclododecane.[4] The M_s value increased with decreasing temperature, reaching 2.56 emu g^{-1} at 4.3 K (0.005 μ_B per carbon atom). The observed M_s value corresponds to *ca.* 0.5% of the value expected by assuming that each carbon atom of the sample has a spin of a ferromagnetic unpaired electron. The remnant magnetization in a magnetic field of 50 G (1 G = 10^{-4} T) decreased with increasing temperature but it is retained even at 300 K (Fig. 1). The ESR spectra of the aza-carbon **1** showed two characteristic signals at 300 K; one is a broad, poorly resolved line over the range 1000–6000 G and the other is relatively sharp (g = 2.0013, ΔH_{pp} = 6.1 G).

It is still not clear why these aza-compounds are favourable as starting materials. However, it seems likely that atomic hydrogen generated from the aza-compounds could play an important role in the predominant formation of amorphous-like carbons rather than graphite under our pyrolysis conditions.[5,6] The M_s value does in fact depend on the hydrogen/carbon (H/C) ratio of the starting materials, particularly for ratios above *ca.* 2, as shown in Fig. 2, where the M_s value is plotted as a function of the H/C ratio. Also the carbon product (carbon A) prepared by pyrolysis of pyrene (H/C = 0.625; 2.47 mmol) under hydrogen (1.1 mmol) instead of vacuum conditions was found to have an M_s value of 0.33 emu g^{-1}, higher than that of the carbon (B; 0.24 emu g^{-1}; Fig. 2*a*) prepared without hydrogen. The XRD intensity† of carbon A was lower than that of carbon B. The aza-compounds having a high H/C ratio may favour an amorphous-like carbon phase, leading to an improvement in the magnetic properties.[7] Further study is in progress to elucidate the role of hydrogen.

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† A distinct broad profile of the X-ray diffraction line near 2θ = 25° (d = 3.48 Å) was observed for the carbon obtained from pyrene, in comparison with those from the aza-compounds.