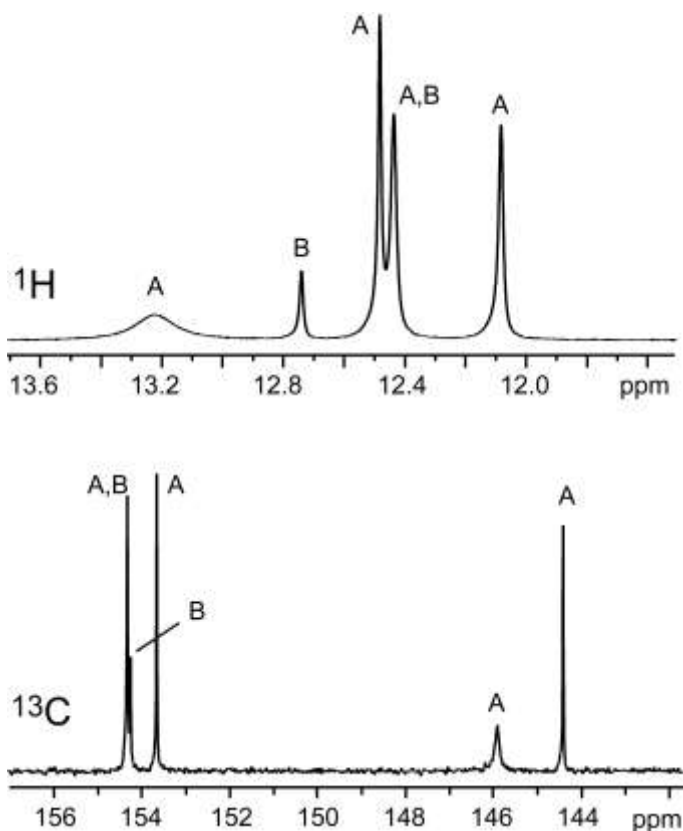


SUPPLEMENTARY INFORMATION

Electrochemical reduction of nitroazoles in aqueous media as an approach to the synthesis of new green energetic materials

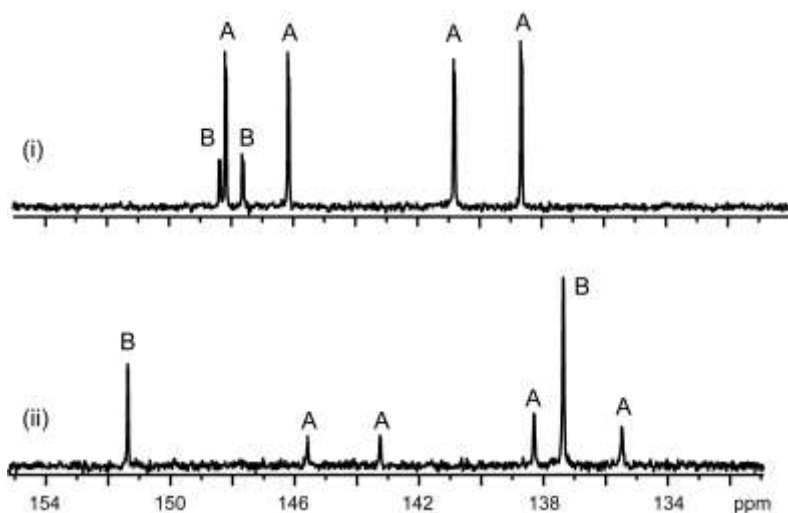
Lynne Wallace, Christie J. Underwood, Anthony I. Day and Damian P. Buck

Figure SI-1. ^1H (upper panel) and ^{13}C (lower panel) spectra of NTO solid reduction products in DMSO- d_6 . A = peaks due to AZTO, B = peaks due to azoTO.



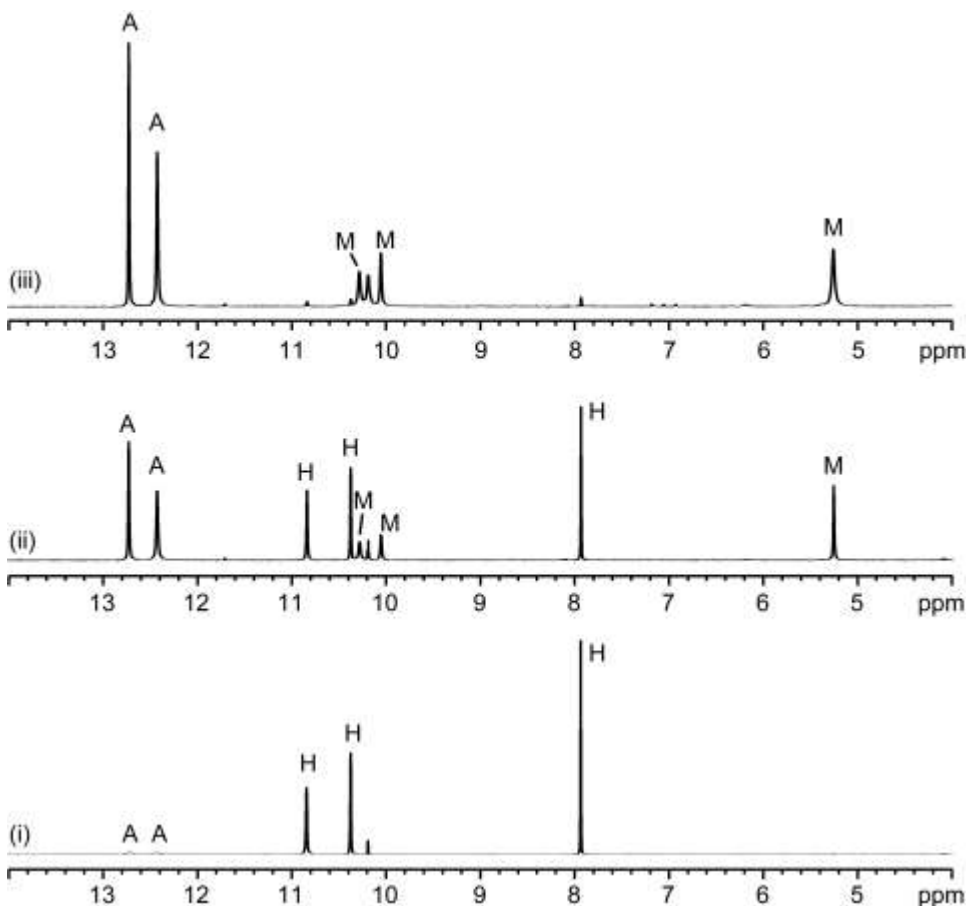
The ^1H NMR spectrum of the precipitate from NTO reduction (DMSO- d_6) showed 5 peaks, 4 corresponding to AZTO and one additional peak at 12.74 ppm due to azoTO (Figure SI-1, upper panel). The other azoTO peak occurs at 12.44 ppm, coincident with the 12.44 ppm AZTO peak. All peaks are broad, as expected for N-H protons, particularly the AZTO peak at 13.2 ppm. The initial ^{13}C spectrum in DMSO (Figure SI-1, lower panel) also showed 5 peaks, 2 of which were very close, and one of which was quite broad. Present work has found that there are actually 6 peaks in most ^{13}C spectra of the NTO product in DMSO (see Section 2, Experimental), but the chemical shifts are so close that they are not always resolved. Possibly the water content affects the chemical shift slightly.

Figure SI-2. ^{13}C spectra in D_2SO_4 of (i) NTO solid reduction products and (ii) NTr solid reduction products. A = peaks for azoxy component, B = peaks for azo component.



In the ^{13}C spectrum of the NTO product mixture in D_2SO_4 (Figure 2(i)), the 4 peaks for the major product (AZTO) and the 2 peaks for the minor product (azoTO) are clearly seen. The solid product mixture from NTr reduction also displays 6 peaks in the ^{13}C spectrum in D_2SO_4 (Figure 2(ii)), but in this case the intensities are reversed: the major product shows 2 peaks and the minor product 4 peaks. This is confirmed by the ^1H spectrum of the same sample, which shows one strong CH peak and 2 smaller CH peaks of approximately equal intensity. The results indicate that the NTr precipitate, like that of NTO, is composed of azo- and azoxy species. An authentic sample of azotriazole was prepared by a chemical method¹ to allow comparison of data. Peaks in the ^{13}C and ^1H spectra of the authentic sample in D_2SO_4 corresponded to those of the symmetric product (B) from NTr, and confirmed azotriazole as the major component in the electrochemical reduction. The microanalysis and IR spectra confirm this identification.

Figure SI-3. Effect of heating on the ^1H NMR spectrum of the reduction product of AZTO in DMSO- d_6 . The lowest panel (i) shows the spectrum prior to heating, and the upper two panels show the effect of heating for (ii) 2 and (iii) 4.5 minutes respectively, at ca. 120°C. The spectra are not scaled relative to one another.



Peaks at 10.85 and 10.38 are assigned to NH protons in the triazolone ring, and the peak at 7.95 to the NH protons of the hydrazine bridge. Peaks due to hydrazotriazolone (labelled H) decrease, while peaks due to azoTO (labelled A) and ATO (labelled M) increase. There is also a small peak seen at 10.2 ppm, due to an unknown species. In the initial spectrum, azotriazolone comprises 15% by mole. In the final spectrum (iii), the azo:amine ratio of 1.3:1 is much higher than expected from disproportionation alone

(allowing for azoTO present initially, the ratio should be 1:1.44), indicating that some oxidation of hydrazoTO to azoTO has also occurred. This is also supported by the unpleasant smell of dimethylsulfide (formed on reduction of DMSO) from the NMR tube after strong heating. Competing decomposition is also evidenced by the appearance of a small ammonium ion multiplet in spectrum (iii) at around 7ppm. These competing mechanisms do not occur to a significant extent in the bulk electrochemical cell.

References

1. R. Sivabalan , M. Anniyappan, S.J. Pawar, M.B. Talawar, G.M. Gore, S. Venugopalan and B.R. Gandhe, *J. Hazard. Mater.* 2006, **A137**, 672–680.