

Study of the reactivity of 1,1'-dimethylbistetrazole towards catalytic hydrogenation and chemical reduction: investigation of the tetrazole-reduced compounds formed

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Abstract

Investigating the possibility of a straightforward formation of tetrazoline and/or tetrazolidine structures, the reactivity of a tetrazole derivative towards reducing conditions has been studied. The catalytic hydrogenation of 1,1'-dimethylbistetrazole (DMBT) was carried out using various catalysts (Pd/C, Pt/C, Rh/C, Pd/Pt/C, Lindlar, PtO₂ and Raney Ni) over a wide range of hydrogen pressure (35 to 150 bars) and a temperature range from 20 to 60°C. This exhaustive study enabled to find the optimal conditions for DMBT hydrogenation and to suggest a plausible reaction mechanism. The chemical reduction of DMBT was conducted using several hydrides (BH₃, NaBH₄, DIBAL and LiAlH₄). The reduction products were identified subsequently to conditions optimizing. The suggested reaction mechanism, featuring a retro-[3+2]-cycloaddition, was validated by both experimental and theoretical approaches.

Results and Discussion

Chemical Reduction

Study of the DMBT/LAH reaction

Crudes A, B and C were characterized by ^1H and ^{13}C NMR, IR and MS (CI). The combination of the results of these various analyses enabled us to postulate the structures of the reduction products as being: 1-methyl-5-(N-methyl-methanamino)-tetrazole (MMMAT) and N,N'-dimethylethylenediamine (DMEDA) as well as remaining DMBT (Figure S1).

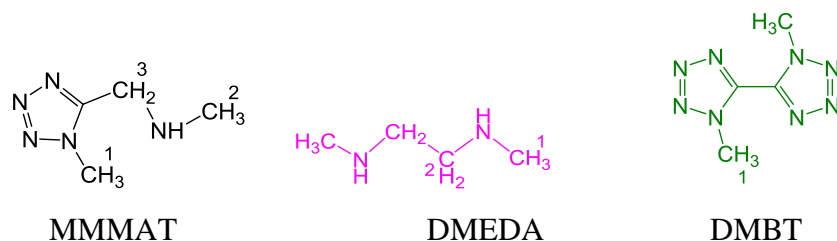
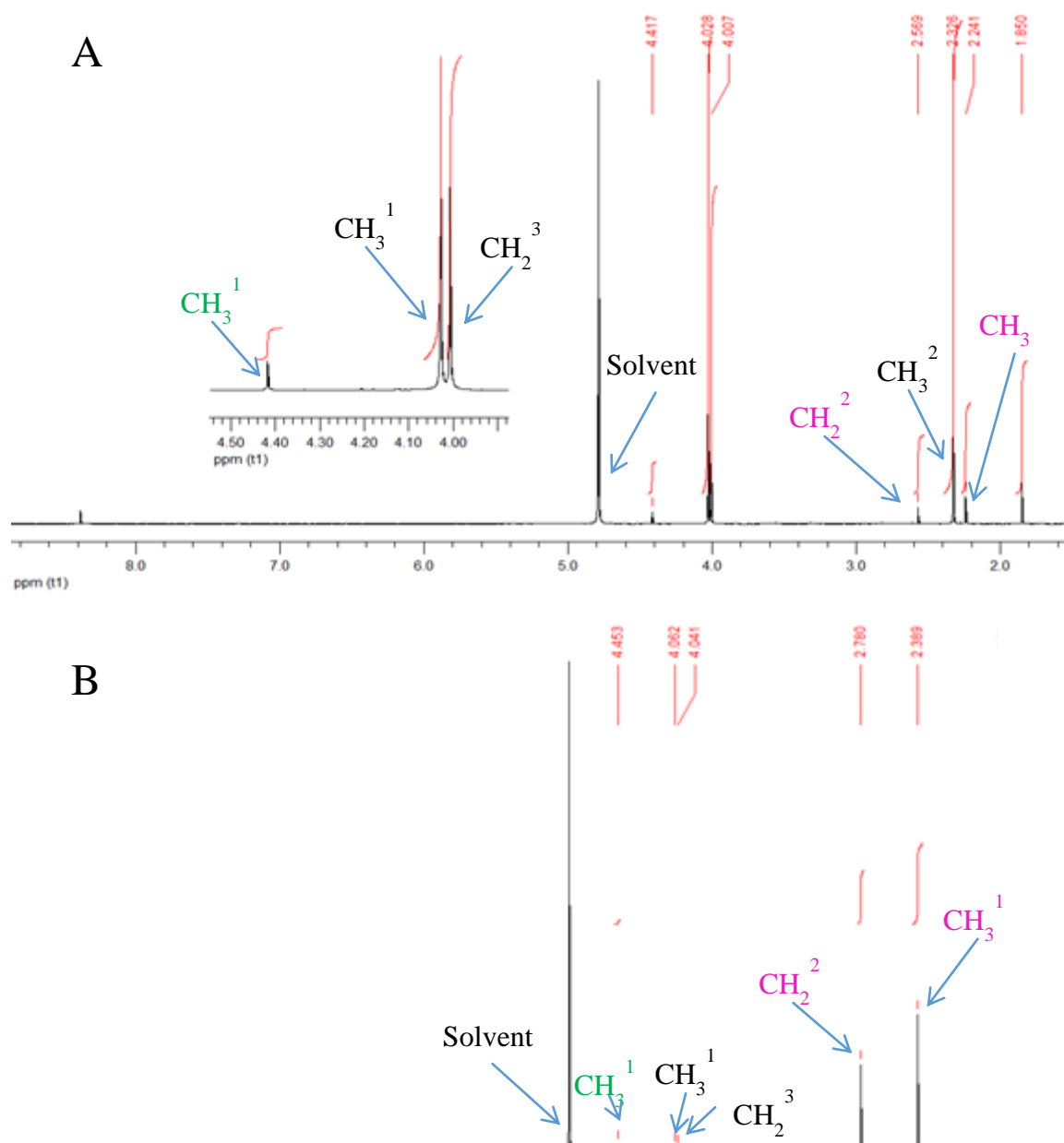


Figure S1. Plausible structures of the DMBT reduction products.

The proportions of these products and DMBT vary according to the work-up conditions (Figure S2):



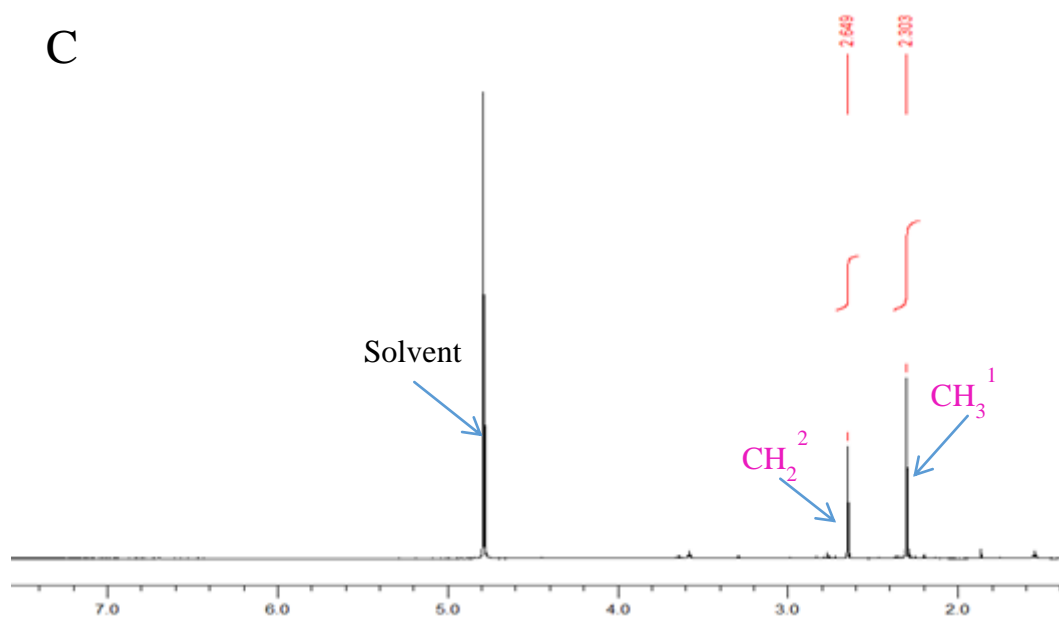


Figure S2. ^1H NMR spectra (400 MHz) of crudes A, B and C in D_2O .

Based on the integration of the NMR signals and taking the CH_3^1 signal as a reference, it is possible to estimate the proportion of the reduction products as follows: 80% MMMAT, 5% DMBT and 15% DMEDA in A; 89% DMEDA, 5% DMBT and 6% MMMAT in B; 0% MMMAT, 0% DMBT and 100% DMEDA in C.

IR spectra of A and DMBT are given below to support these results. In the IR spectrum of A, one can also observe the band at 2053 cm^{-1} corresponding to azido group.

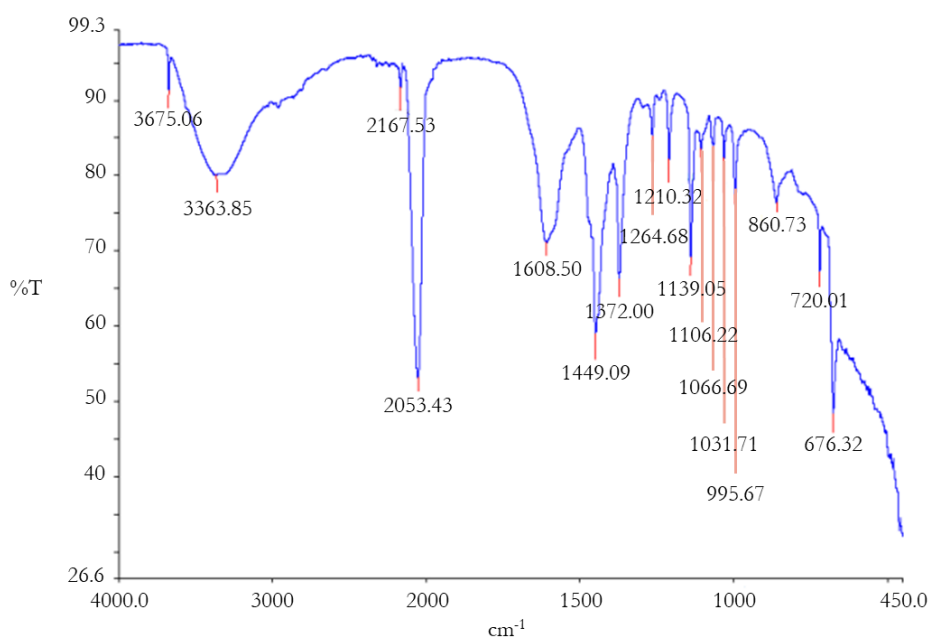


Figure S3. IR spectrum of crude A.

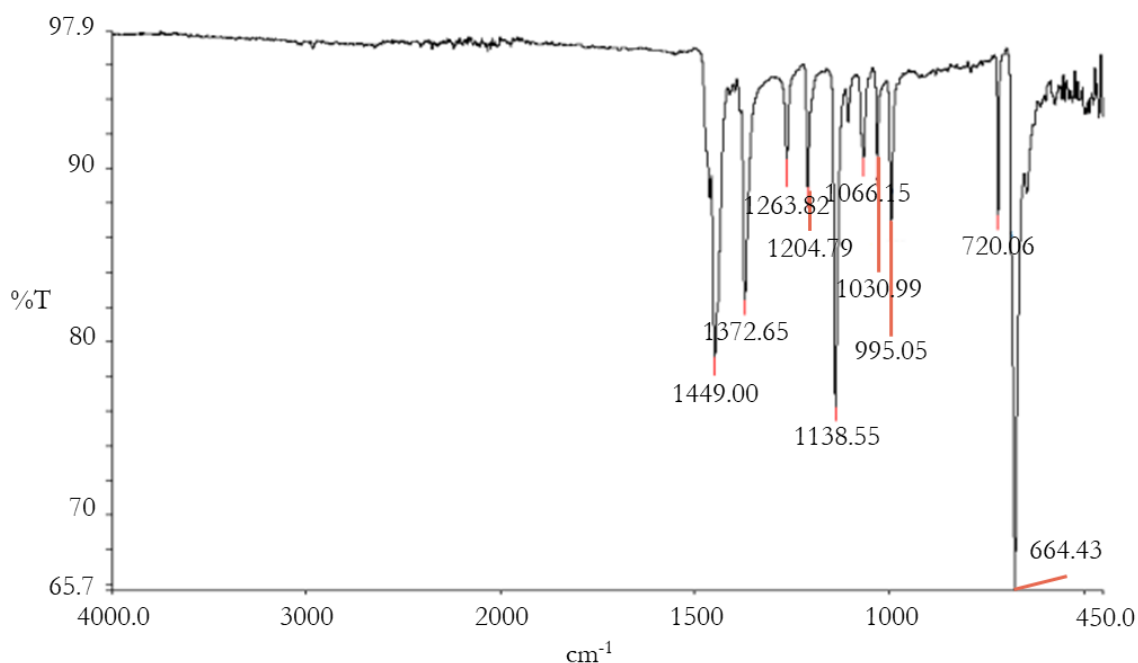
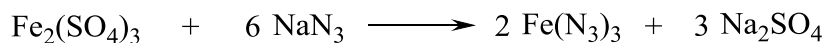


Figure S4. IR spectrum of DMBT.

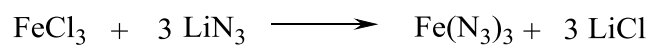
Experimental validation of the retro-[3+2]-cycloaddition

In order to confirm the formation of N_3^- ions during the reaction, a colorimetric detection method described in the literature [ref] was applied. When dry sodium azide is added to a suspension of iron (III) sulfate in methanol, the solution instantly turns red due to the formation of $\text{Fe}(\text{N}_3)_3$, which precipitates as a brownish solid (Scheme S1).



Scheme S1. Literature described formation of iron (III) azide.[ref]

In order to highlight the presence of azide anion in the reaction medium of C, we have followed the same procedure: We prepared a solution of iron (III) chloride in methanol and a solution of crude C in methanol (Figure S5) and we added the latter to the first. The obtained solution turns quickly bright red, and a brown solid is formed thereafter (Figure S6), indicating the formation of the $\text{Fe}(\text{N}_3)_3$ species, according to the following reaction (Scheme S2):



Scheme S2. Reaction of formation of $\text{Fe(N}_3)_3$ highlighting the presence of azide anion as a result of DMBT reduction by LAH.



Figure S5. FeCl_3 solution in methanol (left) and Crude C solution in methanol (right).



Figure S6. Mixture of both FeCl_3 and C solutions (left) and same mixture evolution after stirring (right).

Reference

Fair HD, Walker RF (1977) In: Plenum Press New York and London (ed) Energetic Materials (vol 1): Physics and Chemistry of the Inorganic Azides.