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^{6}Li,^{6}Li-COSY - A NEW TOOL FOR STRUCTURE DETERMINATIONS OF LITHIUM ORGANIC COMPOUNDS IN SOLUTION

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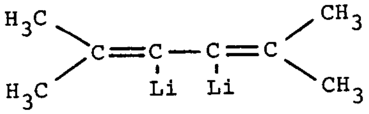
Abstract: A homonuclear ^{6}Li,^{6}Li shift correlation experiment has been successfully performed for 3,4-dilithio-2,5-dimethyl-2,4-hexadiene, thereby providing information about the structure of this compound.

While the majority of homonuclear shift correlation experiments have so far been performed with protons, quite a number of δ,δ spectra for other nuclei exist¹⁾. In most of these cases, however, spin-1/2 nuclei have been correlated and with respect to metal NMR the information about COSY experiments with quadrupolar nuclei is still rather limited. From the theory of homonuclear 2D δ,δ spectroscopy²⁾ it follows that magnetization transfer should be severely hampered in the case of fast relaxing nuclei with small scalar couplings. It is therefore to be expected that COSY experiments for metal nuclei with large quadrupolar moments Q are difficult to perform. On the other hand, successful COSY experiments have been reported for ^{11}B (I = 3/2)³⁾ and more recently for ^{51}V (I = 7/2)⁴⁾. Both nuclei possess sizeable Q-values⁵⁾. Furthermore, a particular attractive feature of the COSY experiment became apparent from these measurements, namely its response to scalar couplings which are not resolved in the 1D spectrum due to line broadening effects. Such a case was recently also reported for a ^{1}H,^{1}H shift correlation of a paramagnetic nickel(0) complex⁶⁾.

With respect to lithium organic compounds, the isotope ^{6}Li (I = 1) has the advantage of a very small quadrupolar moment⁵⁾, in fact the smallest one known, and ^{6}Li NMR is a powerful technique for the investigation of the solution structure of such systems⁷⁾. The possibility to record ^{6}Li,^{6}Li COSY spectra for lithium organic compounds is therefore of general interest and encouraged by the experimental findings discussed above we performed such an experiment with the newly synthezised 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (1)[8].



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In THF-d_8 solution at -70 °C 1 shows two distinct ^{6}Li signals separated by 0.57 ppm which at elevated temperatures broaden and finally coalesce into a single line. At room temperature, only one sharp ^{6}Li signal is observed (Fig. 1). In principle, the two ^{6}Li signals in the slow exchange limit could belong to two non-equivalent lithium sites in one cluster or to two different clusters with one ^{6}Li NMR signal each. A number of observations strongly support the first of these alternatives: (1) The intensities of the two lines in the slow exchange limit are identical; (2) their relative intensity as well as the coalescence behavior of the spectrum is independent of concentration and solvent. However, a more direct proof of the fact that the two signals correspond to non-equivalent ^{6}Li nuclei in the same cluster would be provided by the detection of a scalar ^{6}Li,^{6}Li coupling. Up to now, such couplings have not been observed and due to the low gyromagnetic ratio of ^{6}Li they are expected to be small. In the present case, the lines in the slow exchange limit show no indication of line splitting and from the half width at 193 K (1.5 Hz) an upper limit of 0.5 Hz can be estimated for a possible coupling

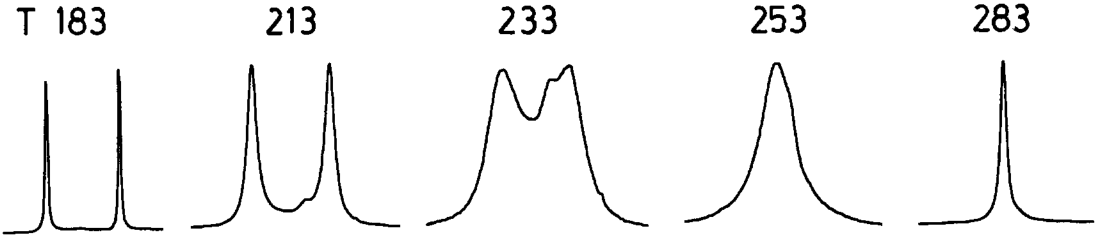

Fig. 1: ^{6}Li-NMR spectrum of 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (1) at various temperatures (°K); small absorptions are due to impurities or minor byproducts.

In order to detect a hidden scalar interaction we performed a COSY-90 experiment using the sequence developed for the enhancement of cross peaks that are due to small coupling constants[2]. As is shown in Fig. 2, cross peaks can indeed be observed, thus establishing a scalar interaction between the ^{6}Li nuclei giving rise to the two signals in the slow exchange limit. The solution structure of 1, therefore, has two non-equivalent lithium sites.

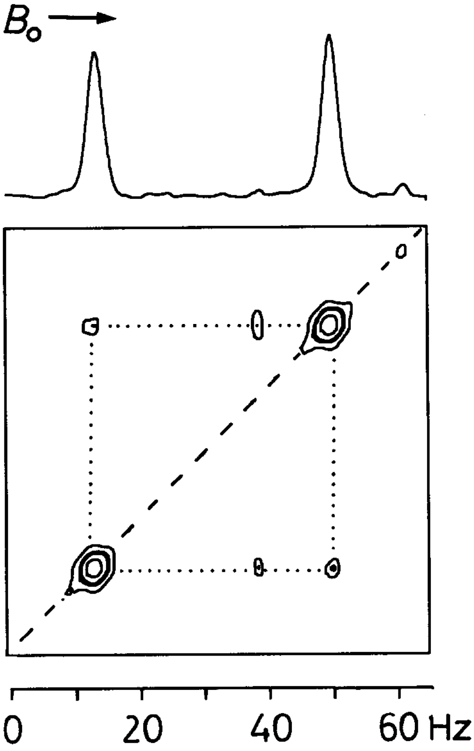

Fig. 2: 58.864 MHz ^{6}Li,^{6}Li COSY-90 spectrum of 1 in THF-d$_8$. Sweep-width 120 Hz, 64 t_1 increments of 8.33 ms, delay Δ for the enhancement of small coupling constants 0.1 s, t_2 1.07 s, relaxation delay 3 s.

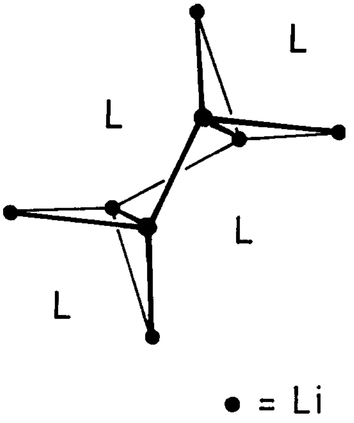

Fig. 3: Structure of 1 in the solid (L = 2,5-dimethyl-2,4-hexadiene-3,4-diyl).

Preliminary results of an X-ray analysis of 1[9] show that it exists in the solid as a cluster with 4 equivalent inner and 4 equivalent outer lithium atoms (Fig. 3). Both sites are non-equivalent and may give rise to scalar spin-spin coupling. Our findings therefore strongly support the conclusion that 1 has the same structure in the solid as well as in solution.

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