DYNAMIC EFFECTS IN SINGLE CRYSTAL OF 9,10-DIMETHYLTRIPTYCENE-D$_{12}$ ON BASIS OF PROTON NMR SPECTRA

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Single-crystal and powder X-ray diffraction studies of 9,10-dimethyltriptycene (1) and its d$_{12}$-isotopomer deuterated in the aromatic positions (1a), made lately by us and other authors, consistently delivered undistorted R-3c structure of the material.$^{1}$ In this structure, all methyl groups in the crystal occur in closely spaced pairs in a staggered conformation, with different pairs being both structurally and magnetically equivalent (see Scheme 1). On the other hand, the once obtained $^1$H wide line NMR spectra of polycrystalline 1a were inconsistent with the above structure.$^{1}$ The presently reported $^1$H spectra of a single crystal of 1a also reveal severe inconsistency with the R-3c structure determined for the same crystal from X-ray diffraction data. These NMR and X-ray data were both collected below 135 K where the methyl group dynamics are completely frozen on the NMR timescale. Apart from that shown in Scheme 1, the NMR spectra reveal another sharply defined environment of the methyl groups, involving as much as about 20 per cent of the latter. In this environment, the methyl groups apparently have the same orientations as in the pairs but suffer no dipole-dipole couplings to outer protons. The spectrum at 131 K is shown in Fig. 1, together with the theoretical fit. The theoretical component spectra corresponding to the two environments are also shown. The observed effects can tentatively be explained as follows: (i) in crystals of 1a point vacancies cause their nearest surroundings to form mesoscopic domains only slightly differing from the ordered R-3c phase; (ii) as such, these domains are practically invisible in the X-ray diffraction patterns; (iii) within the domains, the vacancies undergo rapid diffusion by purely translational jumps of the molecules of 1; (iv) in this way, the dipolar spin-spin couplings between the paired methyl groups are lost in a similar way as is the loss of J-couplings between rapidly dissociating and recombining fragments of molecules in solution. A precise definition of the domains mentioned under (i) is still to be elaborated. The dynamic disorder of this type is unusual because of its persistence down to relatively low temperatures.

Fig. 1. $^1$H NMR spectrum of single crystal of 1a at 131 K (black), with the methyl groups’ axes parallel to the magnetic field. The theoretical best fit spectrum and the component theoretical spectra of the ordered and dynamically disordered domains are depicted in red, blue, and green, respectively. The ratio of the intensities of the green and blue spectra is 0.220.
Actually, below 90 K the spectra do start to broaden and change shape but in a way that cannot be unambiguously interpreted in terms of gradual freezing of the considered dynamic disorder.

A distinctive feature of the proposed mechanism of the disorder is that the two types of methyl groups should experience essentially the same environment on the average. In one environment, the two given groups remain permanently in contact while in the other such close contacts are being constantly disrupted to be immediately restored, but with one partner changed.

Above 160 K, effects of thermally activated dynamics of the methyl groups in 1a are evidenced in the spectra. A series of variable temperature spectra of 1a documenting these effects were measured for the orientation where the threefold axes of the methyl groups are directed at right angle to the external field. The spectra are shown in Fig. 2. They could be perfectly fitted with the damped quantum rotation (DQR) model\(^1\) with the additional assumption that the dynamic properties of the isolated methyl groups and those coming in coupled pairs are identical. The conventional fits shown in the right panel of Fig. 2 are evidently defective in the region of slow and moderate exchange.

![Fig. 2](image)

Fig. 2. Variable temperature spectra of oriented single crystal of 1a (black lines) superposed with theoretical best fit spectra calculated with the DQR model (red lines, left panel) and the conventional random jump model (blue lines, right panel). The green line depicts the best fit spectrum to the experimental pattern measured at temperature where the methyl group dynamics are frozen. The threefold axes of the methyl groups are oriented at right angle to the external field. All calculations were performed under assumption that the ratio of the fractions of the isolated and pairwise coupled methyl groups is 0.220, i.e., the same as determined at 131 K.

The perfect character of the DQR fits obtained for experimental spectra from an extended temperature range provides one more corroboration of the postulated mechanism of the dynamic disorder. If the methyl groups resided in two basically different environments, it would be unlikely for them to share the same dynamic parameters controlling their hindered rotation.
