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Arnold L. Rheingold
Joshua S. Figueroa
Cecil Dybowski
Peter A. Beckmann

Bryn Mawr College, pbeckman@brynmawr.edu

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Superlattices, polymorphs and solid-state NMR spin–lattice relaxation ($T_1$) measurements of 2,6-di-tert-butylnaphthalene

Arnold L. Rheingold,¹,⁎ Joshua S. Figueroa, Cecil Dybowski and Peter A. Beckmann²

¹ Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA. E-mail: arnrhein@udel.edu
² Department of Physics, Bryn Mawr College, Bryn Mawr, PA 19010, USA

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Two polymorphs of 2,6-di-tert-butylnaphthalene, which differ by a factor of twelve in the number of crystallographically independent tert-butyl group environments, have been characterized by a synergistic combination of low-frequency $^1$H NMR spin–lattice relaxation rate measurements and conventional crystallographic structure determinations.

When molecular materials crystallize, the symmetry-independent portion of the crystal lattice may consist of an ensemble of molecules that collectively form the asymmetric unit. This occurs in about 7–8% of molecular crystals.¹ Most often, the ensemble’s organization has no symmetry relationships among its members, even though order is often created by hydrogen bonds or other weak interactions. However, in cases where the number of independent molecules is greater than two, it often happens that the molecules are arranged in a manner that almost, but not precisely, mimics a periodic translation. When such pseudo-periodic relationships exist among molecules, the diffraction patterns are commonly dominated by a subset of the reflections:² only the very minor differences among molecules contribute to superlattice (actually, the true lattice) reflections. Thus, superlattice reflections may be one to two orders of magnitude weaker than sublattice data and may be undetected during routine data collections.

Failure to recognize the presence of a superlattice results in sublattice dimension, for only a large number of symmetry operations.³ Thus, superlattice reflections may be one to two orders of magnitude weaker than sublattice data and may be undetected during routine data collections.

Our current interest in superlattices was aroused by unusual results obtained in a $^1$H solid-state NMR spin–lattice relaxation⁴ study of 2,6-di-tert-butylnaphthalene (2,6-DTN).¹

A dynamic process producing a local fluctuating magnetic field causes nuclear spin–lattice relaxation. For the molecular solid state, the spin–lattice interactions arise from rotational, and sometimes translational, motions. For molecular solids like 2,6-DTN, the primary process involves alkyl-group reorientation, either the tert-butyl group as a whole, the methyl groups individually, or a synchronized motion of both. Whatever process dominates relaxation in 2,6-DTN, its $C_{3h}$ (2mn) symmetry suggests that the two tert-butyl groups will behave identically. Therefore, it was anticipated that a variable-temperature study of the nuclear spin relaxation rate ($R_1 = 1/T_1$) for 2,6-DTN would have the usual Debye form for a $ln R_1$ vs. $1/T$ plot, as has been recorded previously for several alkyl-substituted aromatics.⁵ Instead, the very complex plots at Larmor frequencies of 8.50 and 22.5 MHz in Fig. 1 (labeled ‘polymorph E’¹) were obtained and found to be a composite of several, partially resolvable Debye relaxation curves.⁶

An X-ray diffraction study was initiated on a crystal of 2,6-DTN grown from ethanol (polymorph E).⁷ Using CCD detection, it was found that the reflection data contained a systematic weakness for $h ≠ 3n$, with the $h = n$ set being approximately 20 times more intense. The unit-cell volume indicated that it contained 12 molecules ($Z = 12$). In the non-centrosymmetric space group, $P2_1$, the only symmetry operation is the $2_1$ screw. There are, therefore, two equivalent positions in the unit cell and the asymmetric unit contains six independent molecules ($Z' = 6$). In the stereoview of the unit cell in Fig. 2(a), the arrangement of molecules appears to be repeated three times along the crystallographic a axis (horizontal), but if viewed from a perpendicular perspective [Fig. 2(b)], the aromatic planes of the three molecules are seen to be twisted by a few degrees along their long axis, one relative to the other. Fig. 2(b) also shows the herring-bone packing pattern formed by the 2,6-DTN molecules. These data for E, although very weak, were sufficient to explain the origin of the unusual relaxation data.

With $Z' = 6$, there are twelve symmetry independent tert-butyl groups and 36 independent methyl groups in E. Each slightly different environment has associated with it a different hindering potential and therefore a different mean reorientation rate. The localized pseudo-symmetry of the lattice suggests that similar environments might group into a smaller number of quasi-environments. The temperature dependence of $ln R_1$ at two Larmor frequencies for E can be fitted to a multiple-environment model, but the complexity of the curve makes a determination of the number of environments impossible. These environmentally sensitive relaxation studies confirm that the true repeat distance along a must be an integral multiple of some sublattice dimension, for only a large number of symmetry independent environments could account for the complex relaxation behavior observed.
We then searched for other polymorphs of 2,6-DTN, assuming that the likelihood was strong that a more symmetrical form existed that would be thermodynamically favored at low temperature. Less symmetrical forms with more degrees of freedom may prevail at higher temperatures due to their higher vibrational entropies, but at lower temperatures denser packing arrangements with greater order commonly prevail.\textsuperscript{7} Crystals from acetone were grown from 18 organic solvents and unit cells were obtained for each. E was recovered unchanged from 17 solvents, but a new polymorph (polymorph A) was obtained from acetone. It is ca. 4% denser, also mononclonic, and crystallizes in the centrosymmetric space group $P2_1/c$ with $Z = 2$ and $Z' = 0.5$. The unit-cell packing diagram for A is shown in Fig. 3. Thus, the asymmetric unit for A is half a molecule on a crystallographic inversion center, which requires all tert-butyl group environments to be chemically and crystallographically identical. As expected, the plot of ln $G$ vs. $1/T$ for A (Fig. 1) is the classical, single-environment Debye curve. When heated, samples of A irreversibly convert to E above 40 °C, no thermal events are seen on slowly lowering the temperature to 20 °C from above the transition temperature. The conversion is accompanied by a small, complex endotherm associated with the enthalpy of the conversion of A to E.

That a single Debye process is observed in A (in marked contrast to E) shows that the motion is characterized by a single thermally activated correlation time $\tau_c$ (and only by a single $\tau_c$). $R_1$ is given by $R_1 = A(\omega^2 + 4/|\omega|)$, where $R(\omega) = 2\tau_c/(1 + \omega^2\tau_c^2)$ for Larmor frequency $\omega/2\pi$. The parameter A can be calculated from the geometry of a tert-butyl group and very reasonable assumptions about the motion.\textsuperscript{3,9} The observation of a single Debye process coupled with the fitted value of A clearly shows that the tert-butyl groups and their methyl groups all reorient at the same rate $\tau_c$, presumably due to some dominating process. The analysis shows, in addition, that there are no further motions on the NMR timescale.

$\Delta^1$C MAS NMR spectra for E and A reveal only small and random chemical shift differences of no more than 1.6 ppm at any site, and only minor differences in line width, despite the averaging of twelve tert-butyl group environments for E. Additionally, both agree closely with high-resolution solution chemical shift data.

Despite an obvious complementary relationship between the static, long-range information (translational order) available from X-ray diffraction data, and the dynamic, short-range information (especially spin–lattice relaxation rates, but also chemical shifts and coupling constants) available from solid-state NMR, surprisingly little effort has been made to exploit these potential synergies.\textsuperscript{10} We have shown in this study of 2,6-DTN that crystallography and $T_1$ measurements can provide information essential to the complete understanding of the other, and that together they provide a very complete picture of both polymeric and superlattice phenomena in these van der Waals molecular solids.

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Notes and references

1. 2,6-DTN was prepared by literature methods and purified by sublimation.

2. $R_1$ rates were measured at 8.50 and 22.5 MHz with Spin-Lock CPMG-2 Solid-State NMR spectrometers, one for each frequency. Measurements used a standard $\pi/2-\tau-\pi/2$ pulse sequence with a recycle delay of at least 87 sec. Temperature was varied by a controlled flow of cold nitrogen gas and measured by a calibrated copper–constantan thermocouple. Low frequencies are required to place the maxima in $R_1$ (corresponding to the motional correlation time being similar to the inverse Larmor frequency) in a convenient temperature region.

3. Crystal data: Siemens P4$_3$/2C, Mo-Kα radiation. E: C$_{18}$H$_{24}$, colorless block, monoclinic, space group $P2_1_2_1_2$ with $Z = 2$ and $Z' = 0.5$. The unit-cell packing diagram for A is shown in Fig. 3. Thus, the asymmetric unit for A is half a molecule on a crystallographic inversion center, which requires all tert-butyl group environments to be chemically and crystallographically identical. As expected, the plot of ln $G$ vs. $1/T$ for A (Fig. 1) is the classical, single-environment Debye curve. When heated, samples of A irreversibly convert to E above 40 °C, no thermal events are seen on slowly lowering the temperature to 20 °C from above the transition temperature. The conversion is accompanied by a small, complex endotherm associated with the enthalpy of the conversion of A to E.


