Final Report to BES-DOE
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CARBON-13 NMR OR SOLID STATE HYDROCARBONS AND RELATED
SUBSTANCES

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Bonding in Various Ionic Forms of Tetracyanoethylene (TCNE).

An initial investigation of several ionic crystalline systems of TCNE explores a comparison of various reduction states of this species. We have measured the chemical shift tensors of neutral TCNE, TCNE^{-1} , and TCNE^{-2} (see list of recent publications at the end of this report). Of particular interest is the radical anion, TCNE^{-1} . The ESR data on this salt sample reveal that the radical is present at about 0.5% w/w. The rest of the sample forms an unusual dimer in which carbons from the two monomers have paired. Carbon-carbon bonding well understood enabling computational studies of the structure, conformation, bonding, and spectroscopic (*e. g.*, IR, UV-vis, NMR) features of a myriad of organic and biochemical compounds. The longest known typical C–C bond is the 1.54 Å bond found in diamond, although elongated $\text{sp}^3\text{-sp}^3$ bonds as long as 1.83 Å for *o*-(PhSC)₂B₁₀H₁₀ have been reported.¹ The recent report of 2.90 Å four-centered C–C bonding scheme as observed in thirteen structures of singlet $\pi\text{-}[\text{TCNE}]_2^{-2}$ established a new bonding paradigm that expands our understanding of C–C bonding.² $\pi\text{-}[\text{TCNE}]_2^{-2}$ arises from the overlap of the SOMO's of two doublet $[\text{TCNE}]^{\bullet-}$ s forming $^1\text{A}_{1g}$ ($\text{b}_{2u}^2\text{b}_{1g}^0$) $\pi\text{-}[\text{TCNE}]_2^{-2}$ with the HOMO being a single 2-electron bond delocalized over four C atoms. As a consequence of the four carbon C–C bonding arrangement new IR and UV-vis absorptions are observed for $[\text{TCNE}]_2^{-2}$, which are not present for the $[\text{TCNE}]^{\bullet-}$ monomer. The presence of an NMR signal supports the existence of a diamagnetic species, in contrast to the expectation for doublet $[\text{TCNE}]^{\bullet-}$, which would exhibit very strong coupling between the free electrons and the carbon nuclei broadening any signal to the point of invisibility. Unlike the isotropic chemical shift, δ , the chemical shift tensor reveals information about the three-dimensional structure of the observed nucleus, enabling a more detailed probe of molecular structure. The study of these species is more difficult than most samples typically studied in this laboratory, as these air sensitive samples requires special preparation and handling methodologies. On the other hand, the presence of a residual radical species does introduce a desirable side effect, *i.e.*, the shortening of the T_1 s in the sample, thereby enabling much faster signal acquisition.

**Enhancing Structure Determination from Powder Diffraction Patterns
with Solid-State NMR Data.**

Despite significant advances in structural determination from powder diffraction data, difficult samples are commonly encountered. By all odds high-energy photon beams provide the most sensitive and best resolution of diffraction methods presently available. The relatively

¹ Llop, J.; Vinas, C.; Oliva, J. M.; Teixidor, F.; Flores, M. A.; Kivekas, R.; Sillanpaa, R. *J. Organomet. Chem.* **2002**, 657, 232-238.

² Del Sesto, R. E.; Miller, J. S.; Novoa, J. J.; Lafuente, P. *Chem. Eur. J.* **2002**, 8, 4894-4908.

large molecular weight natural products clearly require this optimal resolution and the synergistic information that can be obtained from solid-state NMR. Independent structural information from solid-state NMR analysis has shown capability of significantly assisting these powder analyses. We have collected high-resolution powder diffraction data on samples for which good solid-state NMR data already exists to explore the enhancements possible from the combination of the two methods.

Structural characterization from powder diffraction data has improved to the point that many materials, even of relatively large MW, can now be characterized using this approach. However, in spite of the advances made significant challenges remain. For example, samples containing mixtures of polymorphs, those containing more than one molecule per asymmetric unit and molecules with a large number of conformational degrees of freedom are still difficult to characterize solely from powder diffraction data. Recent advances in solid-state NMR now allow many of these additional structural facts to be rapidly obtained, providing the required information to assist analysis of powder diffraction data. The combination of both methods thus offers a powerful new approach to structure determination. We have shown powder structure determination of mixtures of polymorphs previously identified by solid-state NMR methods.

Using a combination of solid-state NMR and the APS synchrotron data provides relative polymorphic concentrations required to separate the diffraction response of two interspersed crystal lattices. Some of our most recent results confirm, in a large measure, the continuation of present efforts with major emphasis placed on recently developed theoretical and experimental techniques. Synergism with applied efforts is established by our participation in the DOE/ASCI alliance program that continues to employ theory and experimental methods developed largely with DOE/BES support. The extension of our ^{13}C NMR efforts into the ^{15}N NMR field is evolutionary in character and fits nicely into this grant. Spectroscopic developments in our laboratory include a solid-state **INADEQUATE** method and an intense **FIREMAT** variant of a single crystal experiment that has high promise for smaller single crystals. We also report on a very promising x-ray method with which **REITVELD** analysis complements our NMR efforts.

These approaches are especially fruitful in powder samples when complete crystallographic data are not presently available from single crystals. The appearance of impurities, mixed crystals, polymorphs, and multiple molecules per asymmetric unit are readily characterized by solid-state NMR, whereas it is difficult to determine this information directly from micro-crystalline powder diffraction data, especially on materials of unknown structure. Furthermore, chemical shift tensors provide reasonably good estimates of an initial set of vicinal angles that speeds up the data reduction of powder diffraction histograms from several months to merely hours in relatively large molecules that presently are too large to do the analysis without good initial estimates of the conformational angles. There is also some evidence that the chemical shift tensors give a more sensitive estimate of bond distances between directly bonded atoms. The mutual verification of the solid state NMR and diffraction data from the Sector 1 beam line at the Advanced Photon Source (APS) at Argonne exhibits the synergism between the two techniques, and exhibits the success one can have on molecules in the 500 to 2000 Dalton range.

These diffraction data provide structural verification of new NMR results on conformation and local molecular structure. Further, good diffraction data is much more sensitive to long-range crystal packing order. Such information is needed from quality diffraction data to calculate the long-range electric field forces necessary for accurately modeling chemical shift tensor results available from solid-state NMR spectra. NMR results, at this point in time, are

insufficient to obtain lattice types, unit cell dimensions and angles. Only APS diffraction data appear to have adequate resolution to deal with the molecular weights encountered in the typical natural products in our work.

Previously Unreported Publications

Solid-State NMR Spectra and Long Intradimer Bonds in the $-\text{[TCNE]}-2$ Dianion, Mark Strohmeier, Dewey H. Barich, David M. Grant, Joel S. Miller, Ronald J. Pugmire, and Jack Simons, *J. Phys. Chem. A*, **2006**, *110*(25), 7962-7969.

The Structure of Fractionally Charged Tetracyanobenzenes- Present in $[\text{TCNB}]^{-2}$, Joshua D. Bagnato, William W. Shum, Mark Strohmeier, David M. Grant, Atta M. Arif, and Joel S. Miller, *Angew. Chem. Int. Ed.*, **2006**, *45*, 5322-5326.

^{15}N NMR Chemical Shift Tensors of Substituted Hexaazaisowurtzitanes: The Intermediates in the Synthesis of CL-20, Jacalyn S. Clawson, Karen L. Anderson, Ronald J. Pugmire, and David M. Grant. *J. Phys. Chem. A*, **2004**, *108*, 2638-2644.

A new sensitive isotropic-anisotropic separation experiment--SPEED MAS, Mark Strohmeier, and David M. Grant, *J. Mag. Res.*, **2004**, *168*, 296-306.