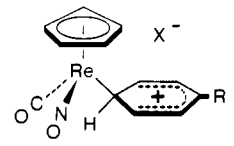

4a R = H, X = BF_4
4b R = CH_3, X = BF_4
4c R = CF_3, X = SO_3F

Protonation of the trifluoromethyl derivatives *m*-**2c** and *p*-**2c** at −78 °C required fluorosulfonic acid.[11] Both isomers afforded the same salt, **3c**, as an intractable oil that could not be isolated in the manner of **3a** and **3b**. Spectra of good quality were nevertheless obtained.[12]

Further evidence consistent with an equilibrium between the η^2-forms **3** and small amounts of the η^1-arenium species **4** is now provided by deprotonation studies. Complexes **3b** and **3c**, as well as **1**,[3] are deprotonated by triethylamine in high yield at −78 °C (the reverse of eq 1). In each case the products of deprotonation are the para and meta aryls, in a ratio dependent upon the ring substituent as summarized in Table I.

A clear trend toward an increased para:meta ratio as the electron-releasing ability of the substituent increases is apparent. Apart from the lack of detectable ortho aryl isomers, this trend parallels the directive effects of electrophilic aromatic substitution and can be similarly explained by familar arguments[13] as to the relative stabilities of the para and meta η^1-arenium cations through which deprotonation of the η^2-arene cations is believed to occur.

These direct observations of η^2-arene complexes add substance to earlier suggestions as to their role as intermediates.[2] Not surprisingly, the properties of the η^2-arene cations differ markedly from those of related η^2-olefin compounds.[14] The present work provides evidence for a mechanism of aromatic carbon–hydrogen activation by $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^+$ that may be common to many cationic, electrophilic metal centers.[2a,b] However, carbon–hydrogen activation by metal centers having different electronic properties will in all likelihood follow different pathways; recent examples of activation by an oxidative-addition process are provided by the relatively electron-rich intermediates $(\eta\text{-}C_5Me_5)Ir(PMe_3)$[15] and $(\eta\text{-}C_5Me_5)Ir(CO)$.[16]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council and the University of Alberta for financial support.

Registry No. 2a, 84081-68-5; **2b** (R = *o*-CH_3), 84081-69-6; **2b** (R = *m*-CH_3), 84081-70-9; **2b** (R = *p*-CH_3), 84081-71-0; **2c** (R = *m*-CH_3), 84081-72-1; **2c** (R = *p*-CH_3), 84081-73-2; **3a**, 84081-75-4; **3b**, 84081-77-6; **3c**, 84081-79-8.

Supplementary Material Available: ^1H NMR spectrum (400 MHz, CD_2Cl_2, −60 °C) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(3,4\text{-}\eta^2\text{-}C_6H_5CH_3)][BF_4]$ (**3b**) (1 page). Ordering information is given on any current masthead page.

(11) The rate of protonation of *m*- and *p*-**2c** by $HBF_4{\cdot}Et_2O$ was significant only above −60 °C, where decomposition was moderately rapid, giving rise to a ^1H NMR signal at δ 5.99, which we tentatively ascribe to $(\eta\text{-}C_5H_5)Re(NO)(CO)(FBF_3)$. This implies displacement of $\eta^2\text{-}C_6H_5CF_3$ by a fluorine-bonded BF_4^- counterion and demonstrates the extraordinary lability of this η^2-arene ligand. Trifluoromethylsulfonic acid protonates **2c** below −60 °C, but above −80 °C the counterion displaces $C_6H_5CF_3$, forming stable $(\eta\text{-}C_5H_5)Re(NO)(CO)(OSO_2CF_3)$, which we have prepared independently and fully characterized.

(12) Data for **3c**: IR (CH_2Cl_2) 2013 (ν_{CO}), 1757 cm^{-1} (ν_{NO}); ^1H NMR (CD_2Cl_2, −78 °C) δ 6.19 (s, 5 H, C_5H_5), 6.74 (t, 1 H), 7.20 (overlapping triplets, 2 H), 7.31 (d, 1 H), 7.53 (d, 1 H).

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(14) The very stable $[(\eta\text{-}C_5H_5)Re(NO)(CO)(1,2\text{-}\eta^2\text{-}C_7H_8)][BF_4]$ shows no evidence for nonrigidity and does not react with PPh_3 at room temperature: Sweet, J. R.; Graham, W. A. G. *J. Organometal. Chem.* **1981**, *217*, C37.

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Protein Structure by Solid-State NMR

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This communication outlines a general approach for determining the structure of proteins and other biopolymers that are part of supramolecular structures that orient in the applied magnetic field of an NMR spectrometer. The method is illustrated with the Trp-26 side chain of the coat protein of fd bacteriophage. Since the protein is part of an infectious virus particle in solution, this is an in vivo structure determination.

This approach exploits the spectral simplifications that accompany macroscopic uniaxial orientation of a polymeric sample parallel to the magnetic field.[1] The angular dependence of nuclear spin interactions described by second-rank tensors is used to determine the orientation of individual sites relative to the axis of orientation. Solid-state NMR studies of oriented and unoriented samples allows geometrical and dynamical parameters[2] to be explicitly separated and analyzed to give an integrated view of protein structure. A variety of biological structures are oriented by strong magnetic fields, including membrane–protein and nucleoprotein complexes;[3] as higher magnetic fields become available and more suitable conditions are developed, it can be anticipated that many interesting systems will be amenable for structural NMR studies. Myoglobin crystals orient in a magnetic field because of the paramagnetic iron in the heme group; this made possible NMR studies of labeled sites in the protein similar to those described here.[4]

The filamentous bacteriophages are nearly ideal systems for these investigations. Their large size (9 nm by 900 nm) is a result of the symmetrical arrangement of 2700 helical coat protein subunits extended along the filament.[5] Almost all of the carbonyl groups of the peptide linkages are parallel to the filament axis, and their total diamagnetic anisotropy results in essentially perfect alignment of the virus particles in the magnetic field.[6] Each coat protein has a single tryptophan residue (Trp-26), which can be labeled with stable isotopes. Previous NMR studies have shown this residue to be immobile on the slowest time scale measured (10^3 Hz) and to have the same environment in all of the coat protein subunits.[2]

The angular dependence of the nuclear spin interactions is directly manifested in solid-state NMR spectra. In unoriented samples, the resonances are powder patterns, while in oriented samples, the resonances are single lines (chemical shift anisotropy) or doublets (quadrupole, dipole) whose frequencies reflect the relative orientation of the spin interaction tensor and the applied magnetic field. The most general case is where the tensor is completely asymmetric, i.e., none of the principal elements have the same magnitude. The nonaxially symmetric $^{15}N_{\epsilon_1}$ chemical shift anisotropy of tryptophan gives the characteristic powder pattern in Figure 1A. The magnitudes of the principal values of the chemical shift tensor are determined from the discontinuities of the powder pattern. The orientations of the principal axes in the molecular frame shown in Figure 1 are based on those found for secondary amines, including histidine,[7] where σ_{33} is along the N–H bond axis and σ_{11} is perpendicular to the plane of the C–N

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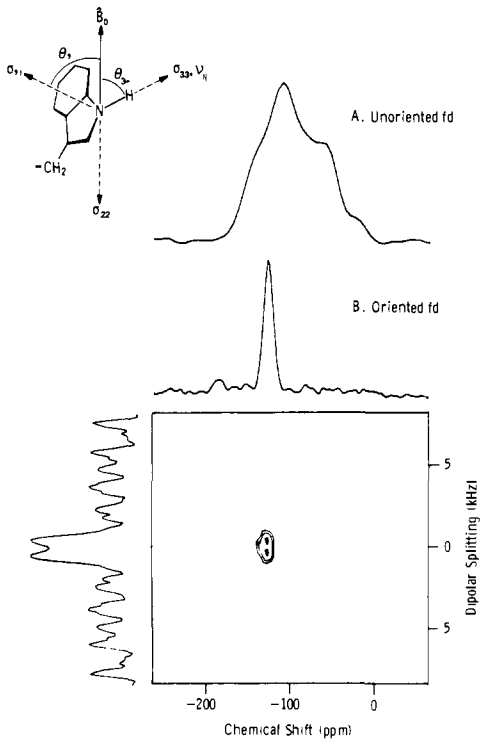

Figure 1. ^{15}N NMR spectra of [$^{15}N_{\epsilon_1}$]Trp-26-labeled fd in solution. These spectra were obtained at 15.2 MHz on a home-built double resonance spectrometer: (A) chemical shift powder pattern for an unoriented sample (150 mg/mL, pH 6; σ_{33} −147 ppm, σ_{22} −108 ppm, σ_{11} −39 ppm); (b) chemical shift spectrum of an oriented sample (45 mg/mL, pH 8). The contour plot represents the data from a two-dimensional separated local field experiment using off-resonance ^1H irradiation to suppress ^1H–^1H interactions;[11] the projection of the dipolar splitting is aligned on the left side with $|\Delta\nu_d|$ = 1.0 kHz when corrected for the experimental scaling factor. The spin-interaction tensors are drawn schematically in the molecular frame of a tryptophan side chain. σ_{ii} are the principal elements of the chemical shift tensor and $\nu_\parallel$ is the component of the dipolar interaction parallel to the N–H bond.

bonds. The ^{15}N–^1H dipolar interaction is axially symmetric about the N–H bond. The magnitude of the interaction can be calculated directly[8] and has been measured for N–H bonds in unoriented fd by using magic angle spinning.[9] In the case of N–H groups, the principal axes of the chemical shift and dipolar tensors are approximately collinear, making determination of angles particularly straightforward.

[$^{15}N_{\epsilon_1}$]Trp-26-labeled fd aligned in the magnetic field gives the single-line spectrum in Figure 1B because all of the Trp rings are related by translation and a simple rotation about the axis of orientation. In general if more than one orientation of a particular label is present, whether due to more than one residue of a type in the protein or different classes of protein subunits, multiple lines will be present in the oriented chemical shift spectrum. Aside from demonstrating that the virus particles are indeed oriented parallel to the applied magnetic field and that the Trp-26 side chains all have the same orientation with respect to the filament axis, very limited structural information is available from the chemical shift frequency because of the complex angular dependence of a nonaxially symmetric tensor.

^{15}N chemical shift and ^{15}N–^1H dipolar measurements must be combined in order to unambiguously determine the orientation of the Trp-26 side chain. The contour plot in Figure 1 presents the results of a two-dimensional ^{15}N–^1H separated local field experiment[10] on the oriented fd sample. The spectral projection showing the dipolar splitting ($\Delta\nu_d$) associated with the chemical

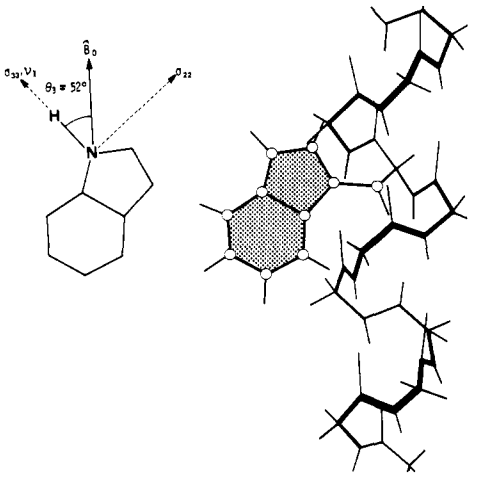

Figure 2. Orientation of Trp-26 of fd coat protein based on the NMR results. The plane of the ring is parallel to the α-helical axis, which is parallel to the filament axis and the applied magnetic field. The N–H bond makes an angle of 52° with respect to the filament axis, as determined by θ_3. The angle θ_1 = 90° with σ_{11} perpendicular to the plane of the paper.

shift frequency is on the left side of the figure. The angle θ_3 between $\nu_\parallel$, which is the component of the dipolar interaction parallel to the N–H bond and B_0, the direction of the applied magnetic field is determined by eq 1. The chemical shift fre-

$$\Delta\nu_d = \nu_\parallel((3\cos^2\theta_3) - 1) \quad (1)$$

quency is a function of both the magnitudes and orientations of the three principal elements of the chemical shift tensor. Two of the direction cosines are sufficient to completely describe the orientation of the spin tensor and therefore the molecular site, relative to the applied field. The dipolar splitting of $|\Delta\nu_d|$ = 1 kHz corresponds to an angle of 52 or 57° between the N–H bond and the applied field. By use of θ_3 = 52° and σ_{obsd} = −128 ppm in the equation (2) that describes the angular dependence of the

$$\sigma_{obsd} = (\sigma_{33} - \sigma_{22})\cos^2\theta_3 + (\sigma_{11} - \sigma_{22})\cos^2\theta_1 + \sigma_{22} \quad (2)$$

chemical shift gives a value for $\cos^2\theta_1 \approx 0$, making θ_1 = 90°. The alternative value of θ_3 = 57° in eq 2 gives a large, negative value for $\cos^2\theta$, which is a physically unreasonable result. The orientation of the Trp-26 side chain relative to the filament axis is completely described by θ_3 = 52° and θ_1 = 90°. The 10 ppm line width of the oriented spectrum can be accounted for by couplings of the $^{15}N_{\epsilon_1}$ to nearby nitrogen and carbon nuclei (~5 ppm) and ±3° of static or dynamic disorder in the orientation of the side chain. This structural determination is precise within several degrees; however, the accuracy depends on chemical shift tensors, which are often found to deviate by 10–15° from bond or symmetry axes as used here. Refinement schemes may be needed to compensate for inexact alignment of tensors. The use of ^2H and ^{13}C labels will allow other interactions and sites to be observed and will increase both the precision and accuracy of the structure determination.

Both X-ray diffraction studies of oriented fibers of fd[5] and solid-state NMR studies of oriented solutions of fd labeled in protein backbone sites[12] indicate that nearly all of the coat protein backbone is in an α helix that is extended parallel to the filament axis of the virion. Figure 2 places the properly oriented Trp-26 side chain on the α-helix backbone oriented parallel to the filament axis and the magnetic field. The plane of the rings is approximately parallel to the axis of the coat protein α helix. The N–H bond is tilted by 52° with respect to this axis.

Acknowledgment. We thank Drs. D. A. Marvin and D. W. Banner of the European Molecular Biology Laboratory, Heidelberg, for showing us how to orient fd in a magnetic field; in

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particular, T.A.C. is grateful for their hospitality during a visit to that laboratory. This research is being supported by a grant from the National Institutes of Health (GM-24266). S.J.O. is a Fellow of the A.P. Sloan Foundation (1980–1982).

Registry No. L-Tryptophan, 73-22-3; nitrogen-15, 14390-96-6.

Book Reviews

Organic Chemistry. Topics in Current Chemistry. Volume 97. Edited by F. L. Boschke. Springer-Verlag Publishers, New York, NY. 1981. 165 pp.

This interesting volume continues the high standards set for this series. The topics covered here are rather special, but they are expertly done and well written. Chapter 1 by H. Schwartz reviews radical eliminations from gaseous cation radicals; it specifically covers reactions in which a hydrogen atom rearrangement occurs within the charge-carrying part of the molecule, a rearrangement that is invisible to many experimental techniques. Chapter 2 covers advances in thiepin chemistry by I. Murata and K. Nakasuji. Thiepins are seven-membered rings containing three double bonds and a sulfur atom (thiacycloheptatrienes) and are mainly of interest as antiaromatic compounds. Chapter 3 by M. Regitz and G. Maas reviews short-lived phosphorus(V) compounds with coordination number 3. Chapter 4 by W. Adam and A. J. Bloodworth treats the chemistry of bicyclic peroxides. The first example of these compounds was synthesized in 1938 by hydrogenation of ascaridole peroxide, but no complete synthesis was published of a bicyclic peroxide until the importance of these compounds in the prostaglandin field was recognized. The prostaglandin endoperoxide, PGH, has a lifetime of just minutes when isolated from natural sources, but endoperoxides should be reasonably stable in organic solvents. Therefore, an important synthetic goal was the synthesis of these materials. A number of people, including one of the authors of this chapter, have had considerable success in this field: the parent ring system has been made, PGG itself has been made, and numerous more stable analogues have been synthesized.

William A. Pryor, *Louisiana State University*

Studies in Environmental Science. Volume II. Atmospheric Chemistry, Fundamental Aspects. By E. Mészáros. Elsevier Scientific Publishing Company, Amsterdam and New York. 1981. 170 pp. $41.50.

Originally written in Hungarian in 1975, this work was revised up to about 1978 and is now being republished in English. The book has five major chapters: atmospheric evolution and major constituents; cycles of trace constituents; the atmospheric aerosol; removal of trace substances from the atmosphere; climatic effects.

It seems that atmospheric chemistry is cursed with a dichotomy of specialization between particle people and gas people. Dr. Mészáros is a particle person and thus is most at home in his discussion of aerosols and removal of trace substances. These chapters alone would make this book a worthy addition to the bookshelf of any specialist in atmospheric chemistry. Of added value are the presence of a good index and reference list, coupled with the author's usually accurate historical introductions to each topic. On the negative side, the organization of the book is much like an early inorganic chemistry textbook—here is one compound...here is another—guaranteed to bore the curious student even if the information contained is as accurate and well-written as that in this book.

It seems to me that there are certain common chemical threads underlying atmospheric chemistry. These are stoichiometry (mass balance and species conservation), thermodyamics, kinetics, and photochemistry. Would that someone would write a student textbook which tied the topic together with these threads into a coherent and digestable picture! Dr. Mészáros' contribution is certainly inadequate as far as the kinetics and photochemistry are concerned. His book is thus a useful specialist's reference but should not be used as student text.

Donald H. Stedman, *University of Michigan*

Heat and Mass Transfer in Metallurgical Systems. Edited by D. B. Spalding (Imperial College of Science and Technology) and N. H. Afgan (International Centre for Heat and Mass Transfer). Hemisphere Publishing Corporation, New York. 1981. x + 758 pp. $99.00.

This proceedings volume contains a large number of papers presented at the 1979 Seminar of the International Centre for Heat and Mass Transfer held in Dubrovnik, Yugoslavia.

The authorship is quite international, respresenting 16 countries. The major subject is heat and mass transfer in metallurgical systems under high temperatures, but quite a few papers have nothing or little to do with heat and mass transfer and some have little relevance to metallurgical systems.

A number of papers deal with very basic topics including sophisticated mathematical techniques, while others present industrial practices and existing methodologies. Subject systems include ferrous production metallurgy, nonferrous processes, fluid dynamics in molten metal systems, solidification, heat treatment, heat transfer in nuclear reactors, turbines and combustors, and corrosion. While a rather wide range of systems is discussed in the volume, the coverage of nonferrous extractive metallurgy is sadly inadequate despite the fact that exciting new smelting processes are coming to maturity. The entire field of hydrometallurgy, in which many interesting mass-transfer problems are encountered, is absent—perhaps by design.

The level of discusison in most papers is quite advanced. Understanding these papers will require substantial amounts of prior knowledge in the specific field including fluid flow, heat and mass transfer, and the mathematical representation of these transport phenomena.

For the readers who are familiar with the subjects and the necessary mathematical techniques, this volume will provide a useful reference as a source of information on recent advances in the state of the art. As far as the readers of *Journal of the American Chemical Society* are concerned, I believe this book would be of interest to only a limited number of those with special interest in the subject area.

H. Y. Sohn, *University of Utah*

Principles of Polymer Morphology. By D. C. Bassett (University of Reading, U.K.). Cambridge University Press, New York. 1981. ix + 251 pp. $55.00 ($19.95 paperback).

The morphology of polymeric solids is a comparatively young science that is just now entering its second quarter-century. The first was characterized by an explosion of data, much of it in the form of micrographs and the postulating of, often contradictory, theories to explain these data. Bassett does an excellent job of selecting and compressing the data, providing a qualitative discussion of its significance and introducing current theories of macromolecular crystallization all in a compact and affordable volume.

A predilection for polyethylene and for the "Bristol" school of thought is both understandable and acknowledged by the author, yet this reader would prefer a more even approach and a definition of those areas that remain controversial. If the book is used in a course on solid-state properties of polymers, it will need to be greatly elaborated upon with more attention to the rationale of particular experiments. Nevertheless, the abundant graphics and clear easily read descriptive material will lead me to recommend this book to my students next year.

William T. Winter, *Polytechnic Institute of New York*