80.1%, T_3 11.0%, 7-DHC 0.1%, L_3 8.7%).

Thus by two-stage photolysis using narrow spectral width laser sources it is possible to greatly reduce or eliminate competing photoreactions leading to photoequilibria of complex composition and to have *high conversion* of 7-DHC (>90%) to P_3 with very low final yields of T_3 and L_3.

Acknowledgment. We wish to express our thanks to Drs. N. Thompson and K. Pfoertner for their helpful suggestions. Samples of tachysterol$_3$ 4-methyl-3,5-dinitrobenzoate, lumisterol$_3$, and lumisterol$_2$ were generous gifts of Dr. K. Pfoertner (Hoffmann-La Roche & Co. Ltd., Basel, C.H.) and Dr. M. P. Rappoldt (Duphar Co., Weesp, N.L.).

Spinning Near the Magic Angle: A Means of Obtaining First-Order Dipolar NMR Spectra of Molecules Dissolved in Nematic Liquid Crystals

Jacques Courtieu,† D. W. Alderman, and David M. Grant*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received August 6, 1981

Chemical applications of the dipolar NMR spectra obtained from molecules dissolved in nematic crystals are limited by the difficulty of solving the complicated multispin second-order patterns which arise from the large values of the partially averaged dipolar interactions. As a consequence the only spectra which have been interpreted have been those from molecules either with a small number of resonating nuclei or with high symmetry. Large or nonsymmetrical molecules have not been successfully studied with this otherwise powerful method of determining the molecular geometry.

This communication reports a technique which obtains first-order spectra from such systems by reducing the averaged dipole coupling by any factor up to 100. Such reduction is accomplished by making the angle α between the nematic director and the magnetic field any value between 0° and the magic angle, 54.73°, at which point the averaged dipole interaction is null. This is accomplished by spinning the sample at a moderate speed (ca. 50 Hz) about an axis which makes an angle less than the magic angle with the magnetic field. The director aligns along the spinning axis instead of along the magnetic field if the rate of spinning exceeds the rate of director reorientation. Large reductions in the dipole interaction are obtained as α approaches the magic angle. When the director of the liquid crystal is aligned at an angle α with the magnetic field all the tensor contributions (e.g., the dipole-dipole interaction, the chemical shift anisotropy, the anisotropy of the scalar spin-spin coupling, and the quadrupolar coupling for nuclei with spins greater than $^1/_2$) in the Hamiltonian are reduced[1,2] by a factor $R = (1/2)(3\cos^2\alpha - 1)$.

Previous attempts to orient the director of a nematic liquid crystal at a variable angle from the magnetic field have not successfully approached the magic angle. The use of electric fields[3,4] apparently presents serious technical problems which have limited their utility to values of α near 0 and 90°. Spinning the sample below a critical rotation rate around an axis perpendicular to the magnetic field has also been used to change the director orientation[5,6] from 0 to 45° from the magnetic field,[2] thus missing the magic angle by almost 10°. Furthermore, at rotation speeds which should produce angles larger than 30°, the director is distributed in such a way that the line widths become large. All previous work on rotating liquid crystals has used two particular orientations of the spinning axis relative to the field, viz, 90° in classical electromagnets and 0° in superconducting magnets. Thus, the very interesting region about the magic angle and between these two limiting cases has been neglected.

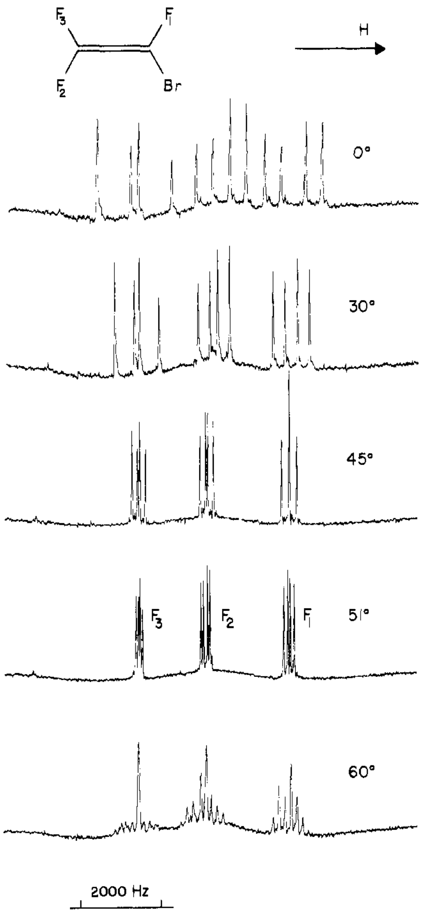

Figure 1. ^{19}F spectra of $CF_2{=}CFBr$ in liquid crystal as a function of the angle between the axis of rotation and the magnetic field. Spinning rate 70 rps.

For this work a spinner has been constructed for 10-mm NMR tubes with a length of 23 mm. The sample spins at frequencies between 20 and 100 Hz around an axis which is horizontal. The spinning axis may be rotated around the vertical so as to make any angle with the horizontal magnetic field of our wide-gap electromagnet.

Fluorine-19 spectra obtained at 75.25 MHz on trifluorobromoethylene dissolved in the liquid crystal *p*-pentylphenyl 2-chloro-4-(*p*-pentylbenzoyloxy)benzoate are shown in Figure 1. It is quite apparent that a second-order spectrum of the ABC type is obtained when spinning the sample parallel to the field. Upon spinning about an axis which is 3° less than the magic angle, the spectrum is clearly of the AMX type. The couplings are no longer dominated by the large dipolar terms, but they are now comparable with the scalar interactions. Note that resolution increases when the sample is oriented closer to the magic angle. When α is greater than the magic angle, a new pattern is observed. In this situation the director of the liquid crystal no longer reaches a homogeneous steady state but instead distributes in the plane perpendicular to the spinning axis. The result is a frequency modulated spectrum

---

† Permanent address: Laboratoire de Chimie Organique Structurale, Université Paris Sud, 91405 Orsay, France.

(1) Snyder, L. C. *J. Chem. Phys.* **1965**, *43*, 4041.

(2) Emsley, J. W.; Lyndon, J. C. In "NMR Using Liquid Crystal Solvents"; Pergamon Press: Oxford, 1975; Chapter 9.

(3) deGennes, P. G. "The Physics of Liquid Crystals"; Pergamon Press: Oxford, 1974.

(4) Diehl, P.; Khetrapel, C. L.; Kellerhals, H. P.; Lienhard, U.; Niederberger, W. *J. Magn. Reson.* **1969**, *1*, 527.

(5) Carr, S. G.; Luckhurst, G. R.; Poupko, R. and Smith, H. J. *J. Chem. Phys.* **1975**, *7*, 278.

(6) Emsley, J. W.; Lyndon, J. C.; Luckhurst, G. R.; Shaw, D. *Chem. Phys. Lett.* **1973**, *19*, 345.

0002-7863/81/1503-6783$01.25/0

with the spacing between lines equal to twice the spinning frequency.

It must be noted that this technique is very different from the fast magic-angle spinning used in high-resolution NMR spectroscopy in solids. Here the spinning is solely for the purpose of orienting the nematic director and need only be rapid compared with the rate of director relaxation. The very rapid tumbling motions within the liquid crystal are sufficient to time average the residual dipolar interactions which depend only on the angle α between the director and the magnetic field as specified by the $3\cos^2\alpha - 1$ dependence from which magic-angle considerations arise.

The above technique will allow study of the geometry of nonsymmetrical molecules or parts of large molecules. This should thus be of great use in chemical-structure elucidation and intramolecular dynamic studies. Further applications of this technique in thermotropic and lyotropic liquid crystal are now under way and will be published along with a detailed analysis of the director dynamics.

Acknowledgment. This work was sponsored by the Public Health Service under Grant GM08521 from the Institute of General Medical Sciences.

Synthetic Model Approach to the Active Site Structure of Cytochrome Oxidase. Novel Porphyrin-Containing Heterobinuclear Fe(III)-Cu(II) Complexes

Maxwell J. Gunter* and Lewis N. Mander

Research School of Chemistry
Australian National University
Canberra, A.C.T. 2600, Australia

Keith S. Murray

Chemistry Department, Monash University
Clayton, Victoria 3168, Australia

Paul E. Clark

Physics Department, Monash University
Clayton, Victoria 3168, Australia

Received May 20, 1981
Revised Manuscript Received August 31, 1981

The active site structure and related function of cytochrome *c* oxidase still remains one of the most enigmatic and controversial problems in biophysical chemistry.[1] This is despite extensive application of a wide variety of physical techniques over almost half a century since Warburg's discovery of this very important enzyme. We,[2] and several other groups,[3-7] have adopted the synthetic model approach in an effort to elucidate at a molecular level the structural requirements which might explain the observed properties of the natural system. Heterobinuclear complexes containing antiferromagnetically coupled Fe(III) and Cu(II) ions generally have been the focus of these model studies, since it seems likely that such a situation exists in the enzyme;[8] proposed bridging groups between the Fe of heme a_3 and Cu_{a_3} have included imidazolate,[9a] oxo,[9b] and thioether (methionine).[9c] An alternative postulate[9d] involving the Fe(IV) and Cu(I) centers to explain the lack of observable ESR signals has recently received some attention.

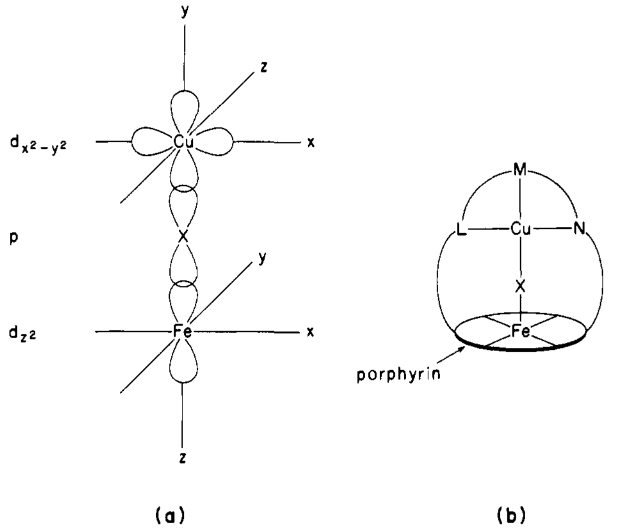

Figure 1. Schematic representation of (a) the orientation of metal atomic orbitals predicted for significant exchange interaction between a single electron in the d_{z^2} orbital of a high-spin Fe(III) ion in a porphyrin with an electron in the singly occupied $d_{x^2-y^2}$ orbital of a Cu(II) ion in a square-planar, square-pyramidal, or tetragonal ligand field, via the p orbitals of a single bridging ligand X. The labeling of the axes around Cu as shown are to indicate the orthogonality of the ligand field of the Cu with respect to Fe and the singly-occupied orbital as $d_{x^2-y^2}$. Alternative labeling of the axes to match those of the Fe requires the appropriate Cu orbital to be designated $d_{x^2-z^2}$. (b) A ligand system which could maximize such orbital overlap.

We[2] have synthesized a model system containing an iron(III) porphyrin with an appended Cu(II)-containing tetrapyridine ligand system with a variety of bridging ligands. However, we have shown recently[10,11] that this system has limited applicability as a model to describe the magnetic properties of the fully oxidized or resting state of the enzyme. The lack of significant antiferromagnetic coupling has been attributed to a mismatch of the appropriate singly occupied atomic orbitals.[10] In the light of these observations, we have synthesized a model system containing an iron(III) porphyrin with an appended Cu(II)-containing ligand system which should allow correct orientation for significant exchange coupling between the two metal centers. We now describe the synthesis and properties of some Fe/Cu heterobinuclear complexes of this system.

In the light of our observations on the previous model system,[2,10,11] we expected that the most effective exchange pathway would result from σ overlap (via the p orbitals of a bridging ligand) of the singly occupied $d_{x^2-y^2}$ Cu(II) orbital in a tetragonal, square-pyramidal, or square-planar ligand field with the d_{z^2} orbital of the high-spin Fe(III) (Figure 1a).[12] This requires a ligand system such as that represented in Figure 1b where the average

---

(1) Recent reviews on the present state of knowledge of cytochrome *c* oxidase include: "Cytochrome Oxidase"; King, T. E., Orii, Y., Chance, B., Okunuki, K., Eds.; Elsevier: New York, 1979. Malstrom, B. G. "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley: New York, 1980; Chapter 5, p 181. Wilson, D. F.; Erecińska, M. in "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. VII, Chapter 1, p 1.

(2) Buckingham, D. A.; Gunter, M. J.; Mander, L. N. *J. Am. Chem. Soc.* **1978**, *100*, 2899. Gunter, M. J.; Mander, L. N.; McLaughlin, G. M.; Murray, K. S.; Berry, K. J.; Clark, P. E.; Buckingham, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1470.

(3) Petty, R. H.; Wilson, L. J. *J. Chem. Soc., Chem. Commun.* **1978**, 483. Petty, R. H.; Welch, B. R.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 611.

(4) Landrum, J. T.; Reed, C. A.; Hatano, K.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3232. Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *Ibid.* **1980**, *102*, 6729.

(5) Okawa, H.; Kanda, W.; Kida, S. *Chem. Lett.* **1980**, 1281.

(6) Jaud, J.; Journaux, Y.; Galy, J.; Kahn, O. *Nouv. J. Chim.* **1980**, *4*, 629.

(7) Chang, C. K. In "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; p 437.

(8) Tweedle, M. F.; Wilson, L. J.; García-Iñiguez, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, *253*, 8065.

(9) (a) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206. (b) Reed, C. A.; Landrum, J. T. *FEBS Lett.* **1979**, *106*, 265. (c) Chance, B.; Powers, L. *Biophys. J.* **1981**, *33*, 95a. Powers, L.; Chance, B.; Ching, U.; Angiolillo, P. *Ibid.* **1981**, *33*, 95a. (d) Seiter, C. H. A.; Angelos, S. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 1806.

(10) Berry, K. J.; Clark, P. E.; Gunter, M. J.; Murray, K. S. *Nouv. J. Chim.* **1980**, *4*, 581.

(11) Gunter, M. J.; Mander, L. N.; Berry, K. J.; Murray, K. S.; Clark, P. E., manuscript in preparation.

(12) The most effective pathways for exchange coupling in terms of orbital symmetry properties has been discussed in detail: Ginsberg, A. P. *Inorg. Chim. Acta. Rev.* **1971**, *5*, 45.

0002-7863/81/1503-6784$01.25/0