

washed with 2% sodium bicarbonate (4 × 40 mL), dried over anhydrous sodium sulfate, and evaporated to dryness on a Rotovap. The resulting crude product was purified by using two preparative TLC plates (20 × 20 cm, 0.5 mm thick), developed with CH<sub>2</sub>Cl<sub>2</sub>-MeOH-CH<sub>3</sub>COOH (100:2:3). Two major yellow bands were separated and rechromatographed on preparative TLC under the same conditions as above to give 30% of a faster moving pigment (7a) and 30% of a slower moving pigment (7b). Each amide was crystallized from dichloromethane-hexane.

**Pigment 7a:** mp 200 °C dec;  $[\alpha]_D^{25} +3400^\circ$  (*c* 2.0 × 10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3342, 3050, 2968, 1675 cm<sup>-1</sup>; UV-visible,  $\epsilon_{220}^{max}$  52000 (CHCl<sub>3</sub>); <sup>1</sup>H NMR (DMSO)  $\delta$  0.87 (d, 6 H, *J* = 6.3 Hz), 1.04 (t, 6 H, *J* = 7.5 Hz), 1.11 (d, 6 H, *J* = 6.9 Hz), 1.73 (s, 6 H), 1.97 (s, 6 H), 2.6-2.1 (m, 10 H) 3.92 (s, 2 H), 4.52 (q, 2 H) 5.94 (s, 2 H), 7.3-7.0 (m, 10 H), 7.87 (s, 2 H), 9.80 (s, 2 H) 10.25 (s, 2 H) ppm; <sup>13</sup>C NMR (DMSO)  $\delta$  8.55 (q), 10.03 (q), 15.32 (q), 17.65 (t), 18.12 (q), 22.55 (q), 24.02 (t), 28.80 (t), 41.40 (d), 47.91 (d), 98.40 (d), 119.24 (s), 122.49 (s), 123.38 (s), 123.41 (s), 126.35 (d), 126.92 (d), 128.24 (s), 128.59 (d), 131.45 (s), 145.07 (s), 147.64 (s), 172.38 (s), 175.17 (s) ppm. Anal.

Calcd for C<sub>51</sub>H<sub>62</sub>N<sub>6</sub>O<sub>4</sub> (823.1): C, 74.74; H, 7.59; N, 10.21. Found: C, 74.65; H, 7.71; N, 10.28.

**Pigment 7b:** mp 210 °C dec;  $[\alpha]_D^{25} -1860^\circ$  (*c* 2.0 × 10<sup>-4</sup> M, CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3338, 3062, 2968, 1672 cm<sup>-1</sup>; UV-visible,  $\epsilon_{223}^{max}$  51000 (CHCl<sub>3</sub>); <sup>1</sup>H NMR (DMSO)  $\delta$  0.92 (t, 6 H, *J* = 6.3 Hz), 1.06 (t, 6 H, *J* = 7.2 Hz), 1.12 (d, 6 H, *J* = 6.6 Hz), 1.76 (s, 6 H), 1.85 (s, 6 H), 2.5-2.0 (m, 10 H), 3.78 (s, 2 H), 4.83 (q, 2 H), 5.89 (s, 2 H), 7.3-6.9 (m, 10 H), 8.00 (s, 2 H), 9.88 (s, 2 H), 10.31 (s, 2 H) ppm; <sup>13</sup>C NMR (DMSO)  $\delta$  8.57 (q), 9.82 (q), 15.29 (q), 17.64 (t), 18.71 (q), 22.13 (q), 24.13 (t), 29.02 (t), 41.96 (d), 47.48 (d), 98.46 (d), 119.42 (s), 122.27 (s), 123.07 (s), 123.73 (s), 126.01 (d), 126.44 (d), 127.66 (s), 128.28 (d), 131.67 (s), 144.60 (s), 147.64 (s), 172.35 (s), 175.38 (s) ppm. Anal. Calcd for C<sub>51</sub>H<sub>62</sub>N<sub>6</sub>O<sub>4</sub> (823.1): C, 74.42; H, 7.59; N, 10.21. Found: C, 74.22; H, 7.72; N, 10.09.

**Acknowledgment.** We thank the National Institutes of Health (Grant HD 17779) for generous support of this work. Y.M.P. was supported by a Jerry and Betty Wilson Graduate Fellowship.

## Communications to the Editor

### Nuclear Magnetic Resonance Crystallography: Molecular Orientational Ordering in Three Forms of Solid Methanol

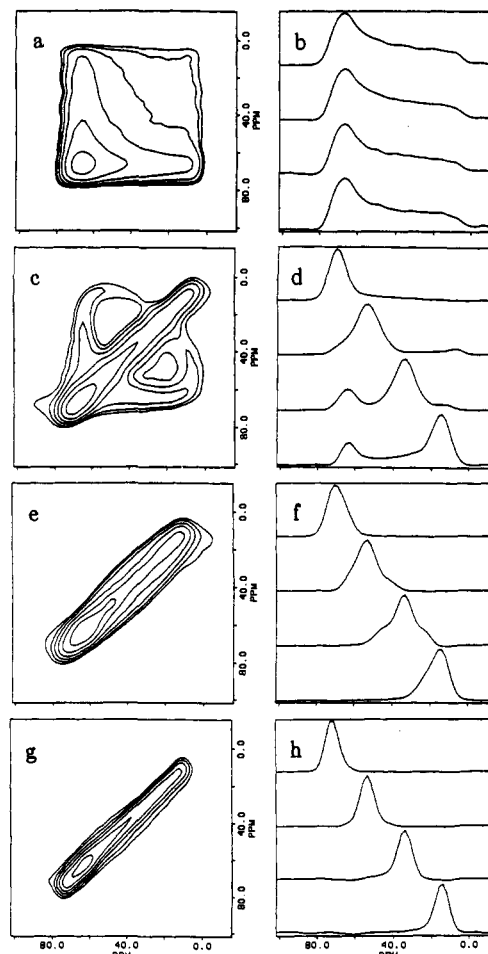
Robert Tycko\* and Gary Dabbagh

AT&T Bell Laboratories  
Murray Hill, New Jersey 07974  
Received December 5, 1990

The arrangement of molecules in crystalline solids is a principal concern of structural chemistry that is usually addressed by diffraction techniques. The applicability of X-ray and neutron diffraction is frequently limited by the need for single crystals of sufficient size and quality. In this communication, using methanol as an interesting example, we demonstrate that information about the relative orientations of nearby molecules in both polycrystalline and noncrystalline solids can be obtained from simple two-dimensional NMR measurements. Our results support one of two proposed crystal structures of  $\alpha$ -methanol, call into question the accepted structure of  $\beta$ -methanol, and indicate the absence of a preferred local structure in methanol glass.

Methanol exists in two crystalline forms at ambient pressure.<sup>1,2</sup> The  $\alpha$  form is stable below 157.4 K; the  $\beta$  form is stable between 157.4 K and the melting point (175.4 K). Methanol glass is formed by cooling the liquid at a rate of approximately 4 K/s, with a glass transition at about 115 K. In 1952, Tauer and Lipscomb proposed crystal structures based on X-ray diffraction measurements on single crystals of  $\beta$ -methanol and imperfect crystals of  $\alpha$ -methanol.<sup>3</sup> For present purposes, the significant feature of the Tauer and Lipscomb structures is the fact that all C-O bonds in the unit cells are either parallel or antiparallel (or nearly so in the  $\alpha$  form). Quite recently, Torrie et al. have proposed a very different structure for  $\alpha$ -methanol, based on neutron diffraction measurements on polycrystalline samples, in which there are four nonparallel C-O bond directions in the unit cell.<sup>4</sup>

The anisotropic chemical shift (CSA) provides information about molecular orientations relative to the external static magnetic field in NMR measurements.<sup>5,6</sup> The methanol <sup>13</sup>C CSA

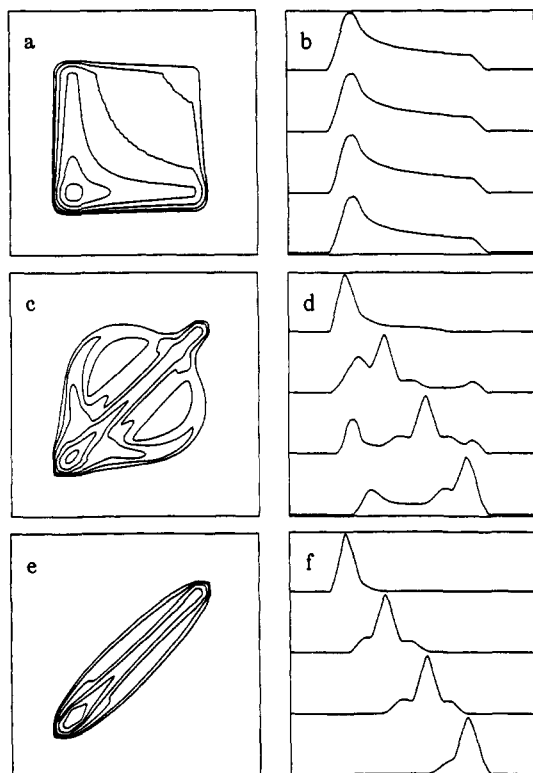


**Figure 1.** Two-dimensional <sup>13</sup>C NMR (100.5 MHz) exchange spectra of solid <sup>13</sup>CH<sub>3</sub>OH: (a,b) glass at 103 K; (c,d)  $\alpha$  form at 133 K; (e,f)  $\beta$  form at 168 K; (g,h)  $\beta$  form at 168 K, 4.5% <sup>13</sup>CH<sub>3</sub>OH/95.5% CH<sub>3</sub>OH. Spectra are represented as contour plots (a, c, e, and g) and as vertical cross sections at 73, 53, 34, and 14 ppm (b, d, f, and h).

tensor is characterized by principal values  $\delta_{11} = 76$  ppm,  $\delta_{22} = 68$  ppm, and  $\delta_{33} = 7$  ppm (relative to TMS). Separated-local-field

(6) Mehring, M. *Principles of High Resolution NMR in Solids*; Springer-Verlag: New York, 1983.

- (1) Parks, G. S. *J. Am. Chem. Soc.* **1925**, *47*, 338-345.
- (2) Kelley, K. K. *J. Am. Chem. Soc.* **1929**, *51*, 180-187.
- (3) Tauer, K. J.; Lipscomb, W. N. *Acta Crystallogr.* **1952**, *5*, 606-612.
- (4) Torrie, B. H.; Weng, S.-X.; Powell, B. M. *Mol. Phys.* **1989**, *67*, 575-581.
- (5) Haeberlen, U. *High Resolution NMR in Solids: Selective Averaging*; Academic Press: New York, 1976.



**Figure 2.** Simulated exchange spectra for  $^{13}\text{CH}_3\text{OH}$  glass with uncorrelated molecular orientations (a,b),  $\alpha$  form proposed by Torrie et al. (c,d), and model " $\beta$ " form with two C-O directions in the unit cell separated by  $12^\circ$  (e,f).

spectra<sup>7,8</sup> indicate that the  $\delta_{33}$  axis lies within less than  $10^\circ$  of the C-O bond direction. Thus, roughly speaking, the  $^{13}\text{C}$  NMR frequency is determined by the angle between the C-O bond and the external field.

Information about molecular orientations *relative to one another* is obtained from two-dimensional NMR exchange<sup>9</sup> experiments on pure  $^{13}\text{CH}_3\text{OH}$ . The pulse sequence is  $90_{\phi_1}-t_1-90_{\phi_2}-\tau-90_{\phi_3}-t_2$ , with phase-cycling of  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  to eliminate artifacts and with proton decoupling during  $t_1$  and  $t_2$ . In effect, the two-dimensional experiment prepares nuclear spin magnetization on a molecule  $M_1$ , measures its NMR frequency  $f_1$  during  $t_1$ , transfers the magnetization to nearby molecules  $M_2$  by spin diffusion during  $\tau$ , and measures their NMR frequencies  $f_2$  during  $t_2$ .<sup>10-13</sup> If  $M_2$  has the same orientation as  $M_1$ , then  $f_1 = f_2$  and the two-dimensional exchange spectrum has intensity only along the diagonal. Otherwise, the spectrum has off-diagonal intensity in a pattern that is determined by the relative orientations of molecules in the unit cell in polycrystalline samples.<sup>10,11</sup>

$^{13}\text{CH}_3\text{OH}$  (dried over  $\text{CaH}_2$ , vacuum distilled) was frozen rapidly to form a glass at 103 K, crystallized into the  $\alpha$  form by warming to 123 K for 15 min, and converted to the  $\beta$  form by warming to 168 K for 1 h. Figure 1 shows the results of two-dimensional experiments with  $\tau = 1$  s on  $^{13}\text{CH}_3\text{OH}$  glass (Figure 1a,b),  $\alpha$ - $^{13}\text{CH}_3\text{OH}$  (Figure 1c,d), and  $\beta$ - $^{13}\text{CH}_3\text{OH}$  (Figure 1e,f), both as contour plots of the two-dimensional spectra and as series of cross sections through the two-dimensional spectra parallel to the  $f_1$  axis. The spectra of  $\alpha$ - $^{13}\text{CH}_3\text{OH}$  have substantial off-di-

agonal intensity, in obvious disagreement with the Tauer and Lipscomb structure. Significant off-diagonal intensity is also apparent in the cross sections for  $\beta$ - $^{13}\text{CH}_3\text{OH}$ , again in disagreement with the Tauer and Lipscomb structure (assuming that  $\delta_{33}$  is along the C-O bond). In parts g and h of Figure 1, the off-diagonal intensity is greatly reduced when spin diffusion is suppressed by diluting  $^{13}\text{CH}_3\text{OH}$  in  $^{12}\text{CH}_3\text{OH}$ , indicating that the off-diagonal intensity does not arise from *slow* molecular reorientations.<sup>14,15</sup> The one-dimensional spectrum of the  $\beta$  form (not shown) does show motional averaging, consistent with *rapid* ( $>10$  kHz) librations of methanol molecules about the O-H bond direction with an amplitude of about  $30^\circ$ .<sup>3,16,17</sup>

Figure 2 shows simulated spectra for a methanol glass in which neighboring molecules have uncorrelated orientations (Figure 2a,b), the  $\alpha$  structure proposed by Torrie et al. (Figure 2c,d), and a model " $\beta$ " structure in which there are two molecular orientations in the unit cell with  $12^\circ$  between the C-O bond directions. The simulations assume complete exchange of magnetization during  $\tau$  and a CSA tensor with  $\delta_{33}$  along the C-O bond and  $\delta_{22}$  perpendicular to the C-O-H plane. The good agreement with experiments indicates that the Torrie et al. structure for  $\alpha$ -methanol is substantially correct, that there are at least two distinct average C-O bond orientations in the  $\beta$ -methanol unit cell, and that there is apparently no preferred local structure in methanol glass<sup>18</sup> (e.g., the glass is not a defective  $\alpha$  form).

(14) Schmidt, C.; Blumich, B.; Spiess, H. W. *J. Magn. Reson.* **1988**, *79*, 269-290.

(15) Blumich, B.; Spiess, H. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1655-1672.

(16) Garg, S. K.; Davidson, D. W. *J. Chem. Phys.* **1973**, *58*, 1898-1904.

(17) Denney, D. J.; Cole, R. H. *J. Chem. Phys.* **1955**, *23*, 1767-1772.

(18) Evidence for subtle short-range orientational correlations in the glass may be contained in the dependence of the two-dimensional spectra on  $\tau$  for  $\tau < 1$  s. We are investigating this possibility. At  $\tau = 1$  s, the spectra of all three solid forms are fully developed, indicating that spin diffusion has occurred over a distance of several intermolecular spacings.

## Electron Propagator Theory of the Ground and Excited States of $\text{CaC}_5\text{H}_5$

J. V. Ortiz

Department of Chemistry, University of New Mexico  
Albuquerque, New Mexico 87131

Received October 9, 1990

Few ligands appear as frequently in contemporary organometallic chemistry as  $\text{C}_5\text{H}_5$  and its derivatives. Several spectroscopic<sup>1-3</sup> and theoretical<sup>4,5</sup> studies have shown that radicals composed of group 2 metal atoms and a single ligand with a positive electron affinity have an unpaired electron localized about the positively charged metal atom, coordinated to the anionic ligand. Ab initio electron propagator calculations<sup>6</sup> on the ground and

(1) Nakagawa, J.; Domaille, P. J.; Steimle, T. C.; Harris, D. O. *J. Mol. Spectrosc.* **1978**, *70*, 374. Dulick, M.; Bernath, P. F.; Field, R. W. *Can. J. Phys.* **1980**, *58*, 703. Bernath, P. F.; Field, R. W. *J. Mol. Spectrosc.* **1980**, *82*, 339.

(2) Wormsbecher, R. F.; Trkula, M.; Martner, C.; Penn, R. E.; Harris, D. O. *J. Mol. Spectrosc.* **1983**, *97*, 29. Hilborn, R. C.; Qingshi, Z.; Harris, D. O. *J. Mol. Spectrosc.* **1983**, *97*, 73. Bernath, P. F.; Kinsey-Nielsen, S. *Chem. Phys. Lett.* **1984**, *105*, 663. Bernath, P. F.; Brazier, C. R. *Astrophys. J.* **1985**, *288*, 373.

(3) Ellingboe, L. C.; Bopeggedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *Chem. Phys. Lett.* **1986**, *126*, 285. Bopeggedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *Chem. Phys. Lett.* **1987**, *136*, 97. Bopeggedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *J. Mol. Spectrosc.* **1988**, *129*, 268. Brazier, C. R.; Bernath, P. F. *J. Chem. Phys.* **1988**, *88*, 2112.

(4) Ortiz, J. V. *J. Chem. Phys.* **1990**, *92*, 6728.

(5) Ortiz, J. V. *Chem. Phys. Lett.* **1990**, *169*, 116.

(6) Linderberg, J.; Öhrn, Y. *Propagators in Quantum Chemistry*; Academic Press: New York, 1973. von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57. Herman, M. F.; Freed, K. F.; Yeager, D. L. *Adv. Chem. Phys.* **1981**, *48*, 1. Öhrn, Y.; Born, G. *Adv. Quantum Chem.* **1981**, *13*, 1. Simons, J. In *Theoretical Chemistry: Advances and Perspectives*; Eyring, H., Ed.; Academic Press: New York, 1978.

(7) Hester, R. K.; Ackerman, J. C.; Neff, B. L.; Waugh, J. S. *Phys. Rev. Lett.* **1976**, *36*, 1081-1083.

(8) Linder, M.; Hohener, A.; Ernst, R. R. *J. Chem. Phys.* **1980**, *73*, 4959-4970.

(9) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546-4553.

(10) Edzes, H. T.; Bernards, J. P. C. *J. Am. Chem. Soc.* **1984**, *106*, 1515-1517.

(11) Henrichs, P. M.; Linder, M. *J. Magn. Reson.* **1984**, *58*, 458-461.

(12) Henrichs, P. M.; Linder, M.; Hewitt, J. M. *J. Chem. Phys.* **1986**, *85*, 7077-7086.

(13) Suter, D.; Ernst, R. R. *Phys. Rev. B* **1985**, *32*, 5608-5627.