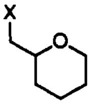
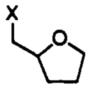
This remarkable selective reactivity and difference in product stability is not unique to **7** and **10**. Iodide **13a** reacted rapidly with **2** to produce the air-stable stibine **13b** (65%). In contrast, iodide **14a** only slowly gave an air-sensitive adduct, presumably **14b**, and this was readily oxidized in air to produce the alcohol **14c** (40–60% overall). This difference in reactivity is underscored by a competition experiment. *Brief reaction of a 1:1 mixture of iodides **13a** and **14a** with **2** gave only the stibine **13b** (60%) and unchanged iodide **14a** (98%).*



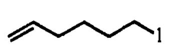
13

a X = I
b X = SbPh$_2$

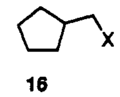


14

a X = I
b X = SbPh$_2$
c X = OH

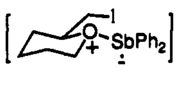


15

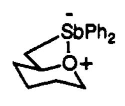


16

a X = I
b X = SbPh$_2$
c X = OH



17



18

These photolytic reactions are certainly radical in nature. The iodide **15**[10] reacted slowly with **2** on irradiation to produce an air-sensitive organoantimony compound, presumably **16b**, and this was easily air oxidized to produce **16c** (59% overall). In the blank experiment, photolysis of **2** and **16a** and air oxidation gave **16c** but at a slower rate. Irradiation of 3α-iodo-5α-cholestane[8,11] slowly gave, via an air-sensitive stibine, 5α-cholestan-3-ol (α:β = 3:4, 10–20%). Generation of 1-adamantyl radicals,[12] in the presence of **2**, gave an air-sensitive antimony derivative, probably (1-adamantyl)diphenylstibine. Again, air oxidation rapidly gave 1-adamantanol (58% overall). Finally, the fact that tetraphenyldistibine (**2**) is an excellent radical trap is underscored by two competition experiments. Generation of 1-adamantyl radicals in the presence of **2** and ethyl acrylate gave only 1-adamantanol (54%) on aerobic workup rather than acrylate-trapped adducts. In the same way, the addition of ethyl acrylate did not divert the conversion of **7** into **8**.

These results are consistent with the operation of a coordinated radical mechanism. The Lewis amphoteric[4] diphenylantimony(II) (**3**) may be coordinated by oxygen as **17** prior to an intramolecular iodine atom transfer via a *trans*-hydrindan-like transition state. Subsequent alkyl radical trapping by **2** should produce **3**, **13b**, and Ph$_2$SbI. In addition, we propose that **13b** may indeed be chelated as **18** and this may account for its air stability. In contrast, the tetrahydrofuranyl analogues of the transition state derived from **17**[13] and **18** would be more strained and therefore of less consequence. Thus, the iodides **10**, **14a**, **16a**, and 3α-iodo-5α-cholestane probably undergo reaction via a slow intermolecular process to give nonchelated, air-sensitive stibines. It is possible that metal centered radical chelation may be involved in the controversial oxygen–carbon bond effects in radical reactions.[14,15] Whatever the mechanistic origin of these unusual effects, highly selective radical transformations of tetraphenyldistibine (**2**) and other Lewis acidic dimetallic systems should find considerable use in synthesis.

Acknowledgment. We thank the National Science Foundation for generous support of our research (CHE-9096322), GD Searle and Company for microanalyses, and the Department of Chemistry at Northwestern University for HRMS data.

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(10) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986; pp 141–150.

(11) Gschwendtner, W.; Schneider, H.-J. *J. Org. Chem.* **1980**, *45*, 3507.

(12) Barton, D. H. R.; Sas, W. *Tetrahedron* **1990**, *46*, 3419.

(13) The efficiency of intramolecular atom transfer reactions depends on the distance between the radical center and the atom undergoing transfer. Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Smith, L. C. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1159. Breslow, R.; Heyer, D. *J. Am. Chem. Soc.* **1982**, *104*, 2045. The Breslow functionalization of steroids is similar to our observations since the process involves the precoordination of a chlorine atom by an aryl iodide group prior to hydrogen atom transfer.

(14) For examples of the acceleration of radical reactions by β-oxygen substituents, see: Barton, D. H. R.; Hartwig, W.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1982**, 447.

(15) Beckwith has disputed the accelerating effects of β-oxygen functionality at least in the reaction of 1,2-dimethoxyethane with the *tert*-butoxy radical; see: Beckwith, A. J.; Brimby, S. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1801.

Crystal Structure of an η^2-Acetonitrile Complex of Tungsten(II): Acetonitrile as a Four-Electron Donor

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Received July 5, 1991

Although coordination of a nitrile to a transition metal through the nitrogen lone pair has been well established,[1] the ability of these ligands to donate through one of their π-orbitals has been demonstrated only recently.[2a–c] Of the few η^2-nitrile complexes which have been structurally characterized, most can be regarded as electronically saturated complexes by considering the nitrile as a two-electron donor. Presently, we report the preparation and characterization of the 16e$^-$ complex [W(bpy)(PMe$_3$)$_2$Cl(η^2-NCCH$_3$)]$^+$, along with structural and spectroscopic evidence for the nitrile ligand acting as a four-electron donor.

The addition of TlPF$_6$ to an acetonitrile solution of W(bpy)(PMe$_3$)$_2$Cl$_2$ produces a deep green material, [**1**]PF$_6$, in 67% yield.[3] In contrast to typical W(II) monomeric complexes, [**1**]$^+$ resists reaction with water or oxygen. Crystals of [**1**]PF$_6$ suitable for X-ray analysis[4] were obtained by allowing the acetone to diffuse from an acetone/water mixture. An ORTEP drawing for [**1**]$^+$ appears in Figure 1 featuring an acetonitrile ligand with C(1)–W (1.998 (5) Å) and N(1)–W (2.008 (4) Å) bonds which are virtually equal. The M–C bond is over 0.25 Å *shorter* than that found in typical W(II)–olefin complexes, yet is quite similar to what is reported for alkynes known to act as four-electron donors.[5] The C(1)–N(1) bond (1.267 (7) Å) has been lengthened by 0.12 Å compared to that of the free ligand,[6] the largest distortion reported to date for a nitrile with such coordination (Table I). Notably, this value is roughly equal to that observed for a *doubly*

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(1) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

(2) (a) Anderson, S. J.; Wells, F. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7*(24), 2615. (b) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650. (c) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2017.

(3) TlPF$_6$ (0.0645 g, 0.185 mmol) was added to W(PMe$_3$)$_2$(bpy)Cl$_2$ (0.104 g, 0.185 mmol) in 5 mL of acetonitrile and stirred at room temperature for 5 h. The solution was filtered through Celite and the acetonitrile removed in vacuo. The resulting solid was dissolved in acetone (3 mL), and upon the slow addition of H$_2$O a precipitate formed, which was filtered and dried in vacuo (0.088 g, 67%).

(4) Crystal data: C$_{18}$H$_{23}$ClF$_6$N$_3$P$_3$W; monoclinic, $P2_1/c$ (No. 14), a = 14.932 (3) Å, b = 10.138 (4) Å, c = 17.271 (4) Å, β = 107.26 (2)°, V = 2497 (2) Å^3, Z = 4. The structure was solved by Patterson and Fourier techniques (TEXSAN 5.0) and refined to R(F) and R_w(F) of 0.026 and 0.039, respectively, by using 3687 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a Rigaku AFC6S diffractometer at −120 °C (Mo Kα radiation, λ = 0.71069 Å).

(5) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956.

(6) Karakida, L.; Fukuyama, T.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 299.

Table I

complex	M–C,[a] Å	M–N,[a] Å	C–N,[a] Å	ΔC–N,[a] Å	N–C–C, deg	ref
$[W(bpy)(PMe_3)_2Cl(CH_3CN)]^+$	2.00	2.01	1.26	0.11	130	
$[Mo(dmpe)_2Cl(CH_3CN)]^+$	1.98	1.96	1.22	0.07	130	2a
$Mo(Cp)_2(CH_3CN)$	2.11	2.22	1.20	0.05	139	2c
$Ir(Cp)(PPh_3)(NCC_6H_4Cl)$	2.10 (2)	2.17 (1)	1.23 (3)	0.08 (3)	136	2b
$Ir(Cp^*)(CO)(NCC_6H_4Cl)$	2.04	2.18	1.21	0.06	141	2b

[a] Reported error less than 0.01 Å unless otherwise noted.

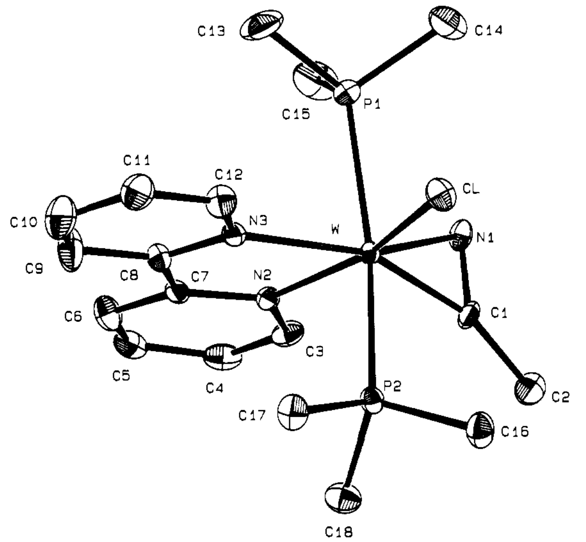

Figure 1. ORTEP drawing for the cation $[W(bpy)(PMe_3)_2Cl(\eta^2\text{-}CH_3CN)]^+$ showing 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): W–N(1), 2.008 (4); W–C(1), 1.998 (5); W–Cl, 2.397 (1); W–P(1), 2.505 (2); W–P(2), 2.476 (1); W–N(2), 2.140 (4); W–N(3), 2.225 (4); C(1)–N(1), 1.267 (7); N(1)–C(1)–C(2), 129.6 (5); W–N(1)–C(1), 71.2 (3).

π-bound nitrile found in an iron–carbonyl cluster[7] and is clear indication of a reduction in bond order as a result of substantial π-interactions. The acetonitrile framework is highly nonlinear (129.6°), characteristic of substantial sp^2 character in the ligand, a feature found in other η^2-nitrile[2a–c] and alkyne complexes.[8] A notable difference is observed for the W–N bond lengths of the bipyridine ligand, the nitrogen trans to the nitrile (N(3)) lying 0.08 Å further from the metal than the nitrogen trans to the chloride (N(2)). Such a discrepancy provides the first direct evidence of a trans influence for an η^2-nitrile.[9] The acetonitrile ligand lies in an eclipsed configuration with the phosphines, such an orientation bringing the C–N bond vector normal to the bipyridine plane. As originally described for alkynes by McDonald[10] and later demonstrated by Templeton et al.[11] specifically for W(II), we suggest that the nitrile ligand is capable of acting simultaneously as a single-faced π-acid (through $\pi_\parallel$) and as a single-faced π-base (through $\pi_\perp$).[12] The orientation adapted by the nitrile allows for maximum overlap of its $\pi_\perp$ orbital with the d_π orbital which is orthogonal to the bipyridine donor and acceptor orbitals.

In Table I, various structural parameters for known η^2-nitriles are summarized. It is noteworthy that for the 16e$^-$ complexes listed (first two entries), where the nitrile can act as a π-donor, the C–N bonds are longer, the nitrile is held closer to the metal, and the nitrile framework is more nonlinear than for the 18e$^-$ species. Perhaps even more significant, the M–N bond for the latter complexes is significantly longer (~0.1 Å) than the M–C bond, whereas the 16e$^-$ complexes are virtually symmetrical in this regard.

An infrared spectrum (KBr) of [**1**]PF$_6$ does not reveal a ν(C–N) absorption in the range of 1610–2500 cm^{-1}, whereas typical η^1-nitrile complexes show C–N stretches in the range of 2200–2300 cm^{-1}.[13] ^{1}H NMR data[14] for [**1**]PF$_6$ recorded at 24 °C show a pseudotriplet corresponding to the trans PMe$_3$ ligands, in addition to bipyridine and acetonitrile resonances. At lower temperatures the rotation rate of the nitrile decreases, and inequivalent phosphine doublets are observed. From coalescence data, the free energy of activation for rotation of the nitrile is determined to be $\Delta G^{\ddagger} = -49.9 \pm 0.5$ kJ/mol at −32 °C, a value similar to that reported for alkyne complexes of W(II).[15] In contrast to the precursor W(bpy)(PMe$_3$)$_2$Cl$_2$, a solution susceptibility analysis (Evans method) in acetone-d_6/cyclohexane confirms that [**1**]PF$_6$ is diamagnetic, as suggested by the ^{1}H NMR spectrum. For η^2-coordinated alkyne complexes, Templeton et al. have reported a correlation between the alkyne ^{13}C chemical shift and the effective number of electrons donated by the alkyne ligand to the metal center:[16] four-electron donors typically show ^{13}C resonances in the range of 190–250 ppm, whereas for two-electron donors, the range drops to 100–120 ppm. The ^{13}C NMR spectrum of [**1**]$^+$ exhibits a triplet (J_{CP} = 52.8 Hz) at 235 ppm, which is assigned to the nitrile carbon. Given the relative proximity of ^{13}C chemical shifts for uncoordinated nitriles (~110 ppm) and alkynes (70–90 ppm), the NMR data reported for [**1**]$^+$ are most consistent with the nitrile serving as a four-electron donor. For comparison, η^1-nitrile complexes typically show ^{13}C resonances similar to that of the uncoordinated ligand.[17]

A cyclic voltammogram of [**1**]PF$_6$ exhibits a reversible II/I couple at −1.62 V (Fc$^+$/Fc), located 0.6 V positive with respect to that of W(bpy)(PMe$_3$)$_2$Cl$_2$,[18] demonstrating the π-acidic nature of the nitrile. In addition, an irreversible II/III oxidation wave and an I/0 reduction wave occur at −0.08 V and −2.21 V, respectively.

In conclusion, the dramatic elongation of the nitrile C–N bond upon coordination, the short metal–nitrile distance, the low-field ^{13}C NMR resonance of this ligand, and the uncharacteristic stability of [**1**]$^+$ in the presence of water, oxygen, or CD$_3$CN[19] together provide strong support for the formulation of acetonitrile as a four-electron donor.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, (PRF 23361-G) and Catalytica (Mountain View, CA) for their generous support of this work.

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(8) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(9) For review of trans influence, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 1199.

(10) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *97*, 1970.

(11) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956.

(12) Keeping with convention, $\pi_\perp$ and $\pi_\parallel$ represent π-orbitals which are perpendicular or parallel, respectively, to the metal–nitrile bond axis.

(13) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; J. Wiley and Sons: New York, 1986.

(14) ^{1}H NMR (24 °C, acetone-d_6): 9.63 (d), 8.78 (d), 8.67 (d), 8.19 (t), 7.68 (t), 7.00 (t), 6.82 (t), 6.46 (d) (bpy, 1 H each); 4.14 (CH$_3$CN, s, 3 H), 1.18 (PMe$_3$, t, 18 H). ^{13}C{^{1}H} NMR (acetone-d_6): 235 (t, J_{CP} = 52.8 Hz, CN), 152.3, 149.3, 148.3, 142.4, 140.4, 138.6, 124.9, 123.7, 122.1, 121.9 (s, bpy), 24.0 (s, MeC), 13.1 (t, J_{CP} = 53.4 Hz, PMe$_3$). Anal. Calcd for $WC_{18}H_{29}N_3P_3ClF_6$: C, 30.29; H, 4.10; N, 5.89. Found: C, 30.30; H, 4.08; N, 5.70.

(15) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

(16) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(17) Armstrong, E. M.; Baker, P. K.; Drew, M. G. B. *Organometallics* **1988**, *7*, 319. Baker, P. K.; Drew, M. G. B.; Flower, K. R. *J. Organomet. Chem.* **1990**, *391*, C12.

(18) Cyclic voltammograms were recorded in *N*,*N*-dimethylacetamide (100 mV s^{-1}/TBAH) for [**1**]PF$_6$ and W(bpy)(PMe$_3$)$_2$Cl$_2$, the latter showing a W(II/I) couple with $E_{1/2} = -2.21$ V (Fc$^+$/Fc).

(19) After 15 h in CD$_3$CN at 53 °C, an NMR spectrum of [**1**]$^+$ shows no detectable substitution. At higher temperatures partial decomposition occurs.

Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles for $[\mathbf{1}]PF_6$ and an ORTEP drawing of the asymmetric part of the unit cell (9 pages); table of observed and calculated structure factors for $[\mathbf{1}]PF_6$ (25 pages). Ordering information is given on any current masthead page.

The Chemical Consequences of Conformational Polymorphism: The Phase-Transition-Dependent Photochemistry of Crystalline 1,14-Cyclohexacosanedione

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It has been recognized for some time that polymorphic crystal modifications of organic compounds differ not only in packing arrangement but also frequently in the *shape* of the constituent molecules as well, a phenomenon that has been termed "conformational polymorphism" by Bernstein.[1] Only rarely, however, have such structural differences been exploited chemically, the idea being that by comparing the solid-state chemistry of conformational polymorphs, one can arrive at an increased understanding of the effects of conformation on chemical reactivity.[2] In the present communication we describe the case of a macrocyclic diketone that exhibits very different photochemical behavior from each of the two well-defined conformational polymorphs (dimorphs) whose structures have been determined by X-ray crystallography. The results are interpreted as arising primarily from the different conformations of the molecules in each dimorph rather than from their different packing arrangements.

As a continuation of our studies on the crystalline-phase photochemistry of macrocyclic "diametric" diketones,[3] we prepared 1,14-cyclohexacosanedione (**1**), the 26-membered ring homolog.[4] Careful recrystallization of this material at room temperature from a mixture of ethyl acetate and petroleum ether leads to clear plates which, upon heating, crack and become opaque at 54 °C and melt at 70 °C. The existence of an endothermic ($\Delta H \approx 6$ KJ/mol) solid–solid-phase transition at 54 °C was confirmed by differential scanning calorimetry. The phase transition is not reversible. When crystals that had been annealed at ca. 60 °C were cooled to room temperature and resubjected to DSC, no phase transition at 54 °C was observed, but melting still occurred at 70 °C. When saturated solutions of **1** were seeded with annealed material, needle-shaped crystals were obtained instead of clear plates; the needles and the annealed samples were identical in all respects (DSC, FTIR, CPMAS ^{13}C NMR, powder pattern) and were clearly different from the plates.

The existence of conformational polymorphism in the plate and needle modifications of compound **1** was confirmed by X-ray crystallography.[5] Stereodiagrams showing the molecular conformations are given in Figure 1. The plates are characterized by a rectangular [3,10,3,10] conformation similar to the [3,5,3,5] conformation adopted by the 16-membered ring diketone.[3] In contrast, the molecules in the needle dimorph have what might be termed a zigzag conformation in which indentations in the methylene chain along one side of the long molecular axis are matched by extrusions on the other.

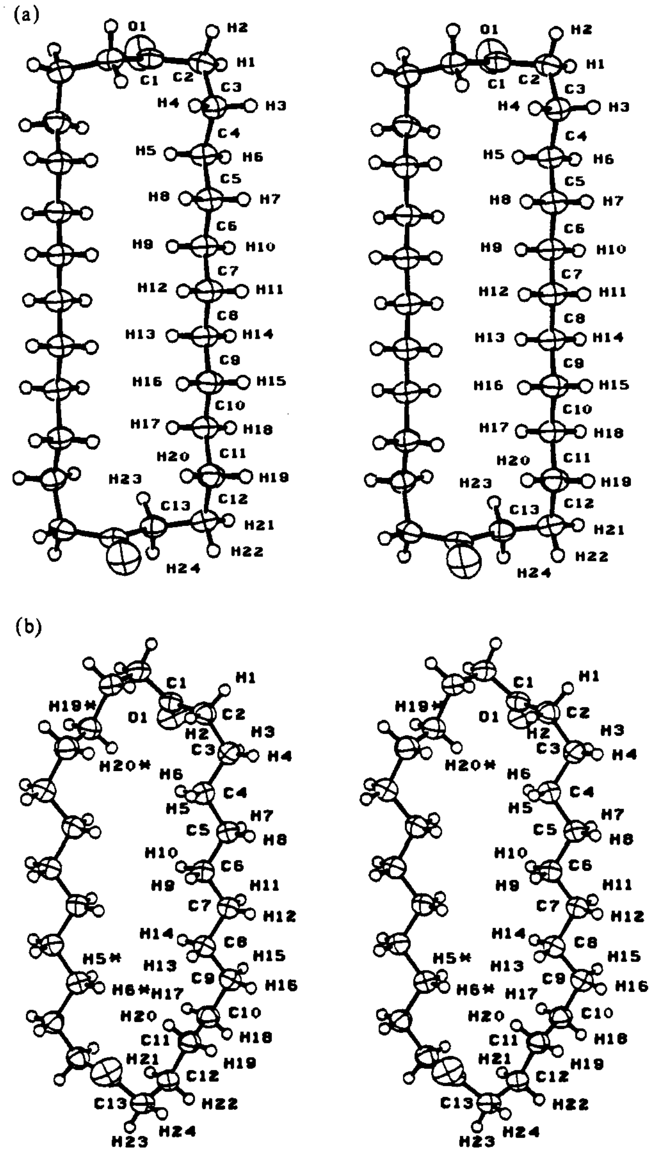
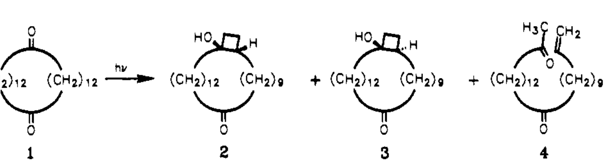


Figure 1. (a) Stereodiagram of the molecular conformation of the $P2_1/n$ (plate) dimorph of diketone **1** and (b) molecular conformation stereodiagram of $P2_1/c$ (needle) dimorph. Owing to a molecular center of symmetry in each case, only half the atoms are numbered.

Scheme I



Compound **1** was photolyzed at room temperature through Pyrex in both of its dimorphic crystal modifications as well as in hexane solution.[6] Fascinatingly, widely divergent results were

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(1) Bernstein, J. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; Chapter 13, pp 471–518.

(2) The only other example of a study of this type of which we are aware is that reported: Evans, S. V.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1986**, *27*, 1419.

(3) Lewis, T. J.; Rettig, S. J.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1990**, *112*, 3679.

(4) Prepared according to the procedure: Blomquist, A. T.; Prager, J.; Wolinsky, J. *J. Am. Chem. Soc.* **1955**, *77*, 1804. Compound **1** was first prepared: Ruzicka, L.; Stoll, M.; Huyser, H. W.; Boekenoogen, H. A. *Helv. Chim. Acta* **1930**, *13*, 1152.

(5) Plates: $P2_1/n$; $a = 5.541$ (2) Å, $b = 28.327$ (2) Å, $c = 8.005$ (2) Å; $\beta = 98.89$ (3)°; $Z = 2$; $R = 3.5\%$. Needles: $P2_1/c$; $a = 8.107$ (2) Å, $b = 5.526$ (1) Å, $c = 28.274$ (3) Å; $\beta = 97.98$ (1)°; $Z = 2$; $R = 3.7\%$. Full details will be published separately.

0002-7863/91/1513-8180$02.50/0