

# Unprecedented Isomerization of the “Rigid Rod” Organometallic $\{[M(\text{dmb})_2]Y\}_n$ Polymers (M = Ag; dmb = 1,8-diisocyno-*p*-menthane) from “Linear” to “Staircase” to “Ladder”

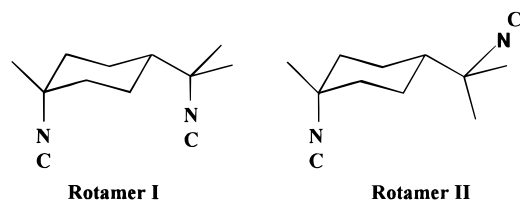
Daniel Fortin, Marc Drouin,<sup>†</sup> and Pierre D. Harvey\*

Département de chimie, Université de Sherbrooke  
Sherbrooke, Québec, Canada J1K 2R1

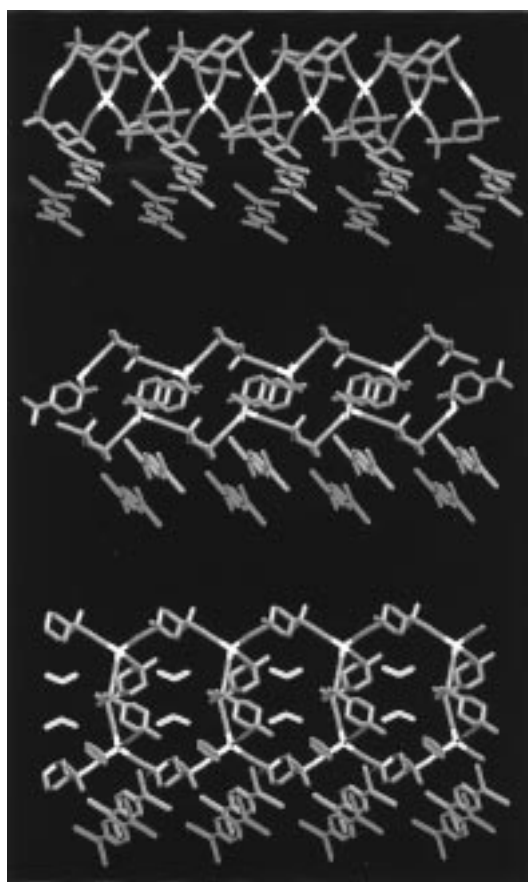
Received November 14, 1997

The design of new polymeric materials based upon organometallic and coordination compounds is becoming a topic of interest.<sup>1</sup> Recently our group reported the preparation and characterization of the first examples of “rigid rod” organometallic polymers using the diisocyanide ligand, dmb, to form the  $\{[M(\text{dmb})_2]Y\}_n$  materials (M = Cu, Ag; Y = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>).<sup>2</sup> The M atoms are tetraordinated by isocyanide groups in a distorted tetrahedral fashion and are doubly bridged by dmb ligands which adopt a conformation where both -N≡C groups point in the same direction (Scheme 1; rotamer I). This conformation dominates the chemistry of bi-, tri-, and polymetallic compounds of dmb.<sup>3</sup> dmb exhibits a C–C single bond allowing rotations which can lead to two types of rotamers (Scheme 1; rotamers I and II). We now wish to report two new structural forms of the  $\{[Ag(\text{dmb})_2]Y\}_n$  polymers that are found in equilibrium at room temperature which can be obtained under certain crystallization conditions. The three conformation isomers are built upon a combination of rotamers I and II.

## Scheme 1



In an attempt to eventually render the recently reported  $\{[Ag(\text{dmb})_2]Y\}_n$  polymers (Y = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>)<sup>2b</sup> electrically conducting, the counterions have been replaced by TCNQ<sup>-</sup> (tetracyanoquinodimethane anion).<sup>4</sup> From either starting material where Y = BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, the metathesis is quantitative,<sup>5</sup> and the identity of the polymer has been confirmed from X-ray crystallography (Figure 1). The material crystallizes as long green needles, and the structure consists of the same “rigid



**Figure 1.** Color sticks drawing showing compounds **1** (top, linear polymer), **2** (middle, staircase), and **3** (bottom, ladder polymer). The H-atoms are not shown for clarity. Compound **3** has a benzene and two dichloromethanes molecules trapped within the large holes of the backbone. Code: TCNQ<sup>-</sup>, blue and red; dmb, green; CH<sub>2</sub>Cl<sub>2</sub>, yellow; benzene, purple; and Ag<sup>+</sup>, white. Please note that only the solvation molecules of the ladder polymer are shown because of their role in trapping the structure. The linear polymer has CH<sub>2</sub>Cl<sub>2</sub> molecules too, but they are not shown.

rod” polymer,<sup>2</sup> where the dmb ligand is found as rotamer I. The Ag···Ag separation (5.065(3) Å) and Ag<sub>3</sub> angle (≈140.0°) are normal for this type of polymer.<sup>2</sup> This structure will be referred

(5) (a)  $\{[Ag(\text{dmb})_2]TCNQ\}_n$  (linear). In 100 mL of acetonitrile was added 1.000 g of  $\{[Ag(\text{dmb})_2]ClO_4\}_n$  or 0.978 g  $\{[Ag(\text{dmb})_2]BF_4\}_n$  (i.e., 1.701 mmol), prior to adding 50 mL of water. When the solution became clear, 0.4 g (1.894 mmol) of LiTCNQ was added, and the solution was stirred for 5 h. The solution was then evaporated until a blue-green precipitate was formed under vacuum. The product was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and extracted with water until the aqueous phase was no longer blue. The CH<sub>2</sub>Cl<sub>2</sub> solution was dried with K<sub>2</sub>CO<sub>3</sub>, filtered, and evaporated. The dark green material afforded a yield of 95%. *T*<sub>m</sub> 181 °C. *T*<sub>d</sub> 203 °C. IR (KBr pellet) 2154 (ν(NC)), 2179 cm<sup>-1</sup> (ν(CN)). <sup>1</sup>H NMR CD<sub>2</sub>Cl<sub>2</sub> 1.12–1.18 ppm (br; 18H) dmb, 1.8–2.4 ppm (br.; 4H) TCNQ<sup>-</sup>. IR spectra showed no evidence for residual BF<sub>4</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> anions. Crystals suitable for X-ray crystallography were obtained from vapor diffusion of diethyl ether in CH<sub>2</sub>Cl<sub>2</sub> solutions and permitted formal identification of the material. Details for the crystallography section is provided in the Supporting Information. (b) For all compounds, the data were collected on an Enraf-Nonius CAD4 automatic diffractometer using monochromated radiation (Cu Kα 1.54184 Å). The DIFRAC program was used for indexing, centering, and data collection. The structures were solved by the application of direct methods using the SOLVER program and refined by least-squares using the LSTSQ program or SHELXL-97, both from NRCVAX.<sup>5c,d</sup> The atomic scattering factors in stored NRCVAX are from Cromer & Waber (International Tables for X-ray Crystallography, Vol. IV). The ORTEP<sup>5e</sup> diagrams were generated from NRCVAX. (c) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. J. Appl. Crystallogr. **1989**, 22, 384. (d) Sheldrick, G. SHELXL-97 Institut Anorg. Chemie, Tammanstr. 4, D37077, Göttingen, Germany, 1997. (e) Johnson, C. K. ORTEP-A Fortran Thermal Ellipsoid Plot Program; Technical Report ORNL-5138, Oak Ridge, TN, 1976.

\* To whom correspondence should be addressed.

<sup>†</sup> Present address: Laboratoire de chimie structurale.

(1) For examples, see: (a) Coat, F.; Lapinte, C. *Organometallics* **1996**, 15, 477. (b) Whang, D.; Jeon, Y.-M.; Heo, J.; Kin, K. *J. Am. Chem. Soc.* **1996**, 118, 11333. Goldberg, N.; Tang, H.; Kroohs, N.; Hoffmann, R. *J. Am. Chem. Soc.* **1996**, 118, 10294. (c) Sponsler, M. B. *Organometallics* **1995**, 14, 1920. (d) Houlton, A.; Mingsos, D. M. P.; Murphy, D. M.; Williams, D. J.; Phang, L. T.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1993**, 3629. (e) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, 113, 703. (f) Pollagi, T. P.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1994**, 116, 6051. (g) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, 115, 1159. (h) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, 114, 6246. (i) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, 113, 4044.

(2) (a) Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1992**, 31, 3688. (b) Fortin, D.; Drouin, M.; Turcotte, M.; Harvey, P. D. *J. Am. Chem. Soc.* **1997**, 119, 531.

(3) (a) A complete bibliography on the dmb complexes is provided in the Supporting Information (15 references). (b) Xiao, H.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3699.

(4) Graja, A. *Low-Dimensional Organic Conductors*; World Scientific: Singapore, 1992.

to as a "linear" polymer. The counter  $\text{TCNQ}^-$  anions stack in a dimeric fashion (interplanar distance = 3.346(7) Å). According to osmometry, the molecular weights ( $M_n < 10\,000$ ) still indicate that these materials are oligomeric in nature.<sup>6</sup>

After weeks in the solution coloration slowly and unexpectedly changes from green to an orange-green. New crystals suitable for X-ray studies were obtained. Among the crystals, two shapes were observed: (1) long green needles which remain green upon crushing and (2) green parallelepipeds which turn orange upon crushing.<sup>7</sup> By comparing the relative number of crystals for both shapes, the parallelepiped crystals appear to be the major product. When parallelepiped crystals are selectively collected and redissolved in solutions, with time (weeks). New crystals were again grown, and both needles and parallelepipeds were again obtained. The unit cell data of the long needles readily identified the product as the "linear" polymer. This observation clearly indicates the presence of an equilibrium in solutions. The X-ray structure determination of the parallelepiped crystals reveals a completely new polymeric form, where the dmb's adopt both rotameric forms (I and II) as shown in Figure 1. The polymer exhibits a "staircase" structure where  $\text{Ag}_2(\text{dmb})_2^{2+}$  units are using two rotamer I dmb's (step shape) and are doubly bridged by two rotamer II dmb's. The Ag atoms are still tetraordinated in a distorted tetrahedral fashion ( $d(\text{Ag}\cdots\text{Ag}) = 5.464(2)$  Å for rotamer I; 10.169(2) Å for rotamer II). The bite distance obtained for rotamer I is the longest one ever reported.<sup>3</sup> The interplanar distance in the  $(\text{TCNQ}^-)_2$  species is 3.436(6) Å.

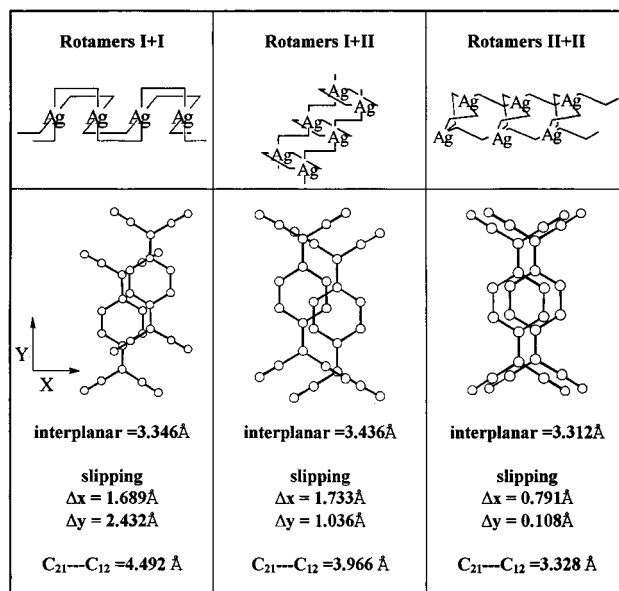
In an attempt to elucidate the isomerization mechanism, by crystallizing an intermediate (like short oligomers or unsaturated species), the crystallization system was changed from diethyl ether/ $\text{CH}_2\text{Cl}_2$  to benzene/ $\text{CH}_2\text{Cl}_2$  using the linear polymer as a starting material. After several days, bluish cubic crystals were obtained as a sole product and were analyzed by X-ray crystallography.<sup>8</sup> A new polymeric isomer was obtained where all dmb's adopted the rotameric form II (Figure 1). The Ag metals were again tetrahedral ( $d(\text{Ag}\cdots\text{Ag}) = 9.340(3)$  Å, 10.511(3) Å), and

(6) The ion-pairing effect has been ignored in the osmometric measurements ( $M_w < 10\,000$ ). However light scattering measurements on the starting materials established the same conclusion (ref 2b). Further for the  $\{[\text{Ag}(\text{dmb})_2]\text{Y}\}_n$  materials ( $\text{Y} = \text{PF}_6^-, \text{BF}_4^-, \text{ClO}_4^-, \text{NO}_3^-, \text{CH}_3\text{CO}_2^-$ ), preliminary results on  $T_1$  measurements (see ref 2b, footnote 37) established the oligomeric nature of the polymers ( $5 < n < 28$   $\text{M}(\text{dmb})_2$  units). A full account of these results will be published in due course (Turcotte, M.; Drouin, M.; Harvey, P. D.). For the  $\text{TCNQ}^-$  species, the unpaired electron on the anion precludes such studies since  $T_1$  here is dominated by paramagnetic relaxations.

(7)  $\{[\text{Ag}(\text{dmb})_2]\text{TCNQ}\}_n$  (staircase). About 50 single crystals of the linear polymer (compound 1) with  $\sim 0.2 \times 0.2 \times 0.2$  mm dimensions were collected and dissolved in  $\sim 1$  mL of  $\text{CH}_2\text{Cl}_2$ . Single crystals were grown from slow vapor diffusion of diethyl ether. Green parallelepiped crystals were obtained along with long green crystals in a 70/30 relative ratio (staircase/linear).  $T_m$  141 °C. IR (KBr pellet) 2149 ( $\nu(\text{NC})$ ), 2178  $\text{cm}^{-1}$  ( $\nu(\text{CN})$ ).  $^1\text{H NMR}$   $\text{CD}_2\text{Cl}_2$  1.12–1.18 ppm (br; 18H) dmb, 1.8–2.4 ppm (br; 4H)  $\text{TCNQ}^-$ . Details for the crystallography section is provided in the Supporting Information.

(8)  $\{[\text{Ag}(\text{dmb})_2]\text{TCNQ}\}_n$  (ladder). About 0.01 g of compound 1 (linear polymer) was dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  and recrystallized from slow diffusion of benzene. Only blue crystals were obtained.  $T_m$  185.5 °C. IR (KBr pellet) 2153 ( $\nu(\text{NC})$ ), 2177  $\text{cm}^{-1}$  ( $\nu(\text{CN})$ ).  $^1\text{H NMR}$   $\text{CD}_2\text{Cl}_2$  1.12–1.18 ppm (br; 18H) dmb, 1.8–2.4 ppm (br; 4H)  $\text{TCNQ}^-$ . Details concerning the crystallography section is provided in the Supporting Information.

Scheme 2



the  $\text{TCNQ}^-$ 's were still dimerized (interplanar distance = 3.312-(6) Å). The macro structure was also linear and will be called "ladder". One question that arises is "why was this form not observed in the diethyl ether/ $\text{CH}_2\text{Cl}_2$  solvent system?" The answer is found in the structure of the new ladder polymer. Large cycles are formed within the backbone of the polymer where  $\text{CH}_2\text{Cl}_2$  molecules are trapped. A benzene is also engaged and lock the dmb rotamer II conformation which renders the isomerization mechanism irreversible in this solvent system. Scheme 2 provides a structural comparison of the three polymers.

Only rotamer I was observed previously in the polymers, and further works on the kinetic and mechanistic aspects of this isomerization are in progress. Also, the doping of these new materials with neutral  $\text{TCNQ}$  and other electron acceptors for conductivity and photoconductivity applications will be reported in due course.

**Acknowledgment.** This research was supported by NSERC (Natural Sciences and Engineering Research Council) and FCAR (Fonds Concerté pour l'Avancement de la Recherche).

**Supporting Information Available:** Tables containing crystal data and details of the structure determination, final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms, hydrogen atom positions and isotropic thermal parameters, (an)isotropic thermal parameters, bond distances, bond angles, and torsion angles, drawings showing atom numberings, and drawings showing segments of the polymers literature comparison of the dmb complexes (27 entries), table giving a comparison of colors, crystals shapes, and melting points of the three polymers (49 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA973902H