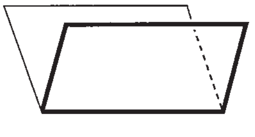
Novel π-Conjugated Cyclophanes: Magazine Rack Molecules

Akihiro Orita, Lasheng Jiang, Madoka Tsuruta, and Junzo Otera*
Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005

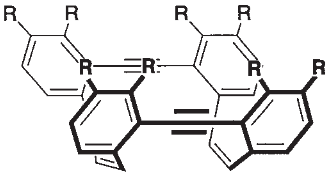
(Received October 31, 2001; CL-011086)

Synthesis of cyclophanes having alternating arylene-ethynylene as well as-ethenylene arrays is described. It is disclosed that these compounds are chiral on the basis of X-ray analysis and fluxional in solution on the basis of NMR spectra.

The construction of cyclic π-conjugated array is one of the challenging topics.[1] Above all, topologically interesting π-conjugated molecules are attracting considerable attention from the viewpoint of their structural and electronic properties[2] as well as host/guest interaction.[3] Therefore, a variety of π-conjugated cyclophanes bearing iterative arylene-ethynylene[4] or -ethenylene[5] moieties have been synthesized so far. As part of our project to explore π-conjugated cyclophanes bearing unique structural features, we have tackled the synthesis of cyclophanes **1** since these compounds were expected to adopt a magazine rack-like structure on the basis of molecular modeling.



"magazine rack"



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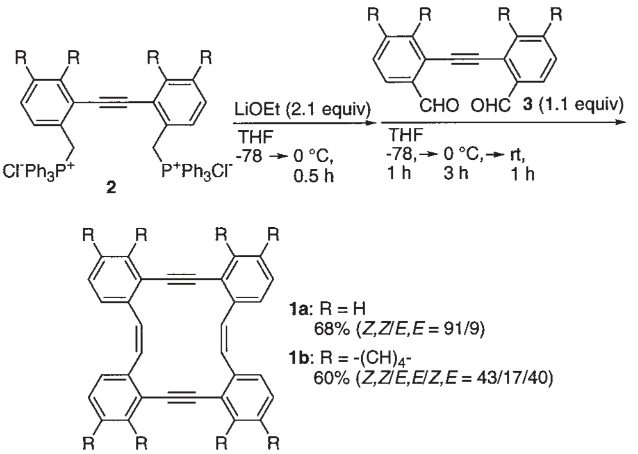
The desired compounds **1** were readily synthesized by Wittig reaction between **2** and **3** (Scheme 1).[6]



Scheme 1.

With LiOEt (2.1 equiv) in THF, Wittig olefination of **2a**, with dialdehyde **3a** (1.1 equiv) proceeded quite smoothly to furnish **1a** in a pure form (68%, $Z,Z/E,E = 91/9$). Recrystallization from EtOAc/hexane furnished pure crystals of (Z,Z)-**1a**, which was subjected to X-ray analysis (Figure 1).[7]

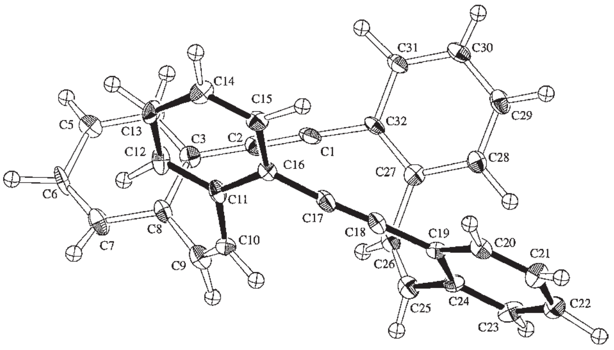


Figure 1. The ORTEP view of (Z,Z)-**1a** (thermal ellipsoids for 50% probability). Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.212(8), C(17)-C(18) 1.200(8), C(3)-C(8)-C(9)-C(10) 68.2(8), C(9)-C(10)-C(11)-C(12) 34.0(9), C(15)-C(16)-C(19)C(20) 23.0.

Naphthylene analog **1b** was obtained similarly in 60% yield ($Z,Z/E,E/Z,E = 43/17/40$). Although attempted isomerization of (E,E) and (Z,E) isomers to (Z,Z) by UV irradiation[8] or thiol/AIBN catalysis[9] was not successful, recrystallization from AcOEt/hexane furnished single crystals of pure (Z,Z) isomer which were suitable for X-ray analysis (Figure 2).[10]

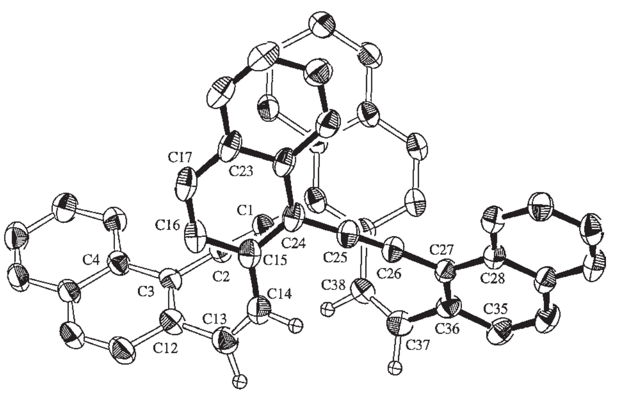


Figure 2. The ORTEP view of (Z,Z)-**1b** (thermal ellipsoids for 50% probability). Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.207(4), C(25)-C(26) 1.199(4), C(3)-C(12)-C(13)-C(14) 52.4(5), C(13)-C(14)-C(15)-C(16) 34.5(5), C(23)-C(24)-C(27)-C(28) 41.6. Several hydrogens are omitted for clarity.

X-ray analyses revealed both cyclophanes **1a** and **1b** adopt the magazine rack motif as expected, yet, surprisingly, dihedral angles of arylenes connected by the ethynylene unit are 23.0 ° and 41.6 °, respectively, indicating that the structure is distorted from the symmetrical one. As a consequence, the compounds are chiral and the (M)- and (P)-isomers are packed alternatively in the crystal as depicted schematically in Figure 3.

On the other hand, NMR spectra of **1a** and **1b** showed totally symmetric patterns at rt. Upon lowering the temperature, signals

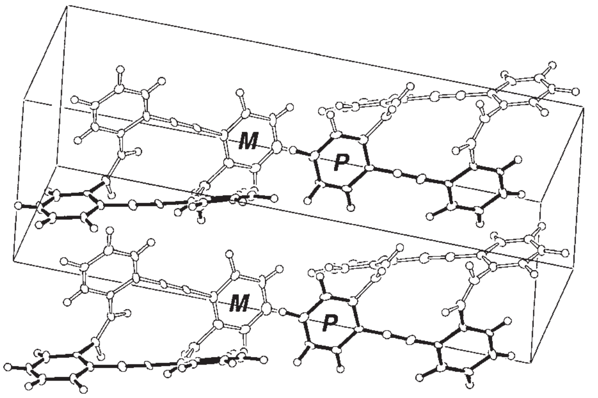


Figure 3. Partial view of (*Z*,*Z*)-**1a** in the crystal.

experienced broadening to some extent although no splitting was observed even at −80 °C.[11] This phenomenon may possibly be explained in terms of the rapid fluxional conformational change in solution between the enantiomeric species which innately should give rise to unsymmetrical patterns.[12]

In summary, we have succeeded in the syntheses of cyclophanes with a magazine rack motif which is distorted into chiral conformations in the solid state. In solution, these molecules are quite fluxional even at low temperature.

This work was partially supported by a Grant-in-Aid for Science Research (No. 12750752) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

This paper is dedicated to Prof. Teruaki Mukaiyama on the occasion of his 75th birthday.

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6 Preparation of **2** and **3**: 2,2′-Dibromo-1,1′-diphenylacetylene was prepared from 2-bromobenzyl sulfone and 2-bromobenzaldehyde according to our method.[13] The treatment of dibromide with BuLi and DMF in THF afforded dialdehyde **3a** in 79% yield. Reduction of **3a** with $LiAlH_4$ and the following chlorination of crude product by NCS/PPh_3 provided dichloride in 82% yield. The reaction of dichloride with PPh_3 (4 equiv) gave **2a** in 87% yield. Naphthylene analogue **3b** was prepared by conventional methods: Sonogashira coupling[14] of 1-bromo-2-formylnaphthalene with trimethylsilyl acetylene, deprotection and coupling with another bromoaldehyde. Dialdehyde **3b** was transformed to **2b** analogously.

7 (*Z*,*Z*)-**1a**: ^{1}H NMR ($CDCl_3$) δ 6.90 (s, 4H), 7.06–7.09 (m, 4H), 7.11–7.15 (m, 8H), 7.21–7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 92.3, 122.6, 126.7, 127.6, 128.6, 131.2, 131.8, 140.3. The crystal data are as follows; $C_{32}H_{20}$, FW = 404.51, Monoclinic, Space Group $P2_1$ (#4), $a = 8.038(2)$, $b = 11.138(5)$, $c = 24.128(4)$, $\beta = 94.28(2)^\circ$, $D_{calc} = 1.25\,g\,cm^{-3}$, $V = 2154.0(9)\,Å^3$, $Z = 4$, $R = 0.039$, $R_w = 0.051$ for 3931 reflections with $I > 3\sigma(I)$ and 738 variable parameters.

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10 (*Z*,*Z*)-**1b**: ^{1}H NMR (CD_2Cl_2) δ 7.12 (t, J = 7.5 Hz, 4H), 7.20 (s, 4H), 7.26 (d, J = 8.5 Hz, 4H), 7.33 (t, J = 7.5 Hz, 4H), 7.61 (d, J = 8.5 Hz, 4H), 7.72 (d, J = 8.5 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 96.8, 119.5, 125.8, 125.9, 126.2, 126.5, 127.7, 132.0, 132.3, 133.3, 139.2. The crystal data are as follows; $C_{48}H_{28}$, FW = 604.75, Monoclinic, Space Group $P2_1$ (#4), $a = 9.417(1)$, $b = 14.999(3)$, $c = 23.142(3)$, $\beta = 98.50(1)^\circ$, $D_{calc} = 1.24\,g\,cm^{-3}$, $V = 3232.9(3)\,Å^3$, $Z = 4$, $R = 0.034$, $R_w = 0.033$ for 5434 reflections with $I > 3\sigma(I)$ and 1089 variable parameters.

11 Further decreasing the temperature caused precipitation due to relatively low solubility of **1b**.

12 PM3 calculations suggested that the distorted structure is the most stable conformation of **1a** and the interchange barrier between (*P*)- and (*M*)-**1a** was estimated less than 5 kcal/mol: MOPAC 2000; Fujitsu Ltd.: Tokyo, Japan.

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