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Synthesis and Characterization of Novel Stilbenophanes: the Smallest Members of this Class of Compounds

HOSSEIN REZA DARABI*, ALI REZA MOHEBBI and MOHAMMAD BOLOURTCHIAN

Chemistry and Chemical Engineering Research Center of Iran (CCERCI), P.O. Box 14335-186, Tehran, Iran

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The synthesis, properties and energy-optimized structure of stilbenophanes **1a–3a** are reported. ^1H NMR spectroscopy of **1a** shows it contains vinylic protons (unlike larger stilbenophanes), which appear as two doublets showing its unexpected configuration. Protons of the methylene bridge of **1b** are also observed at different chemical shift, showing that they are diastereomeric protons. It is also found that the stereochemical outcome of the intramolecular McMurry reaction is strongly influenced by the length of the alkyl bridge.

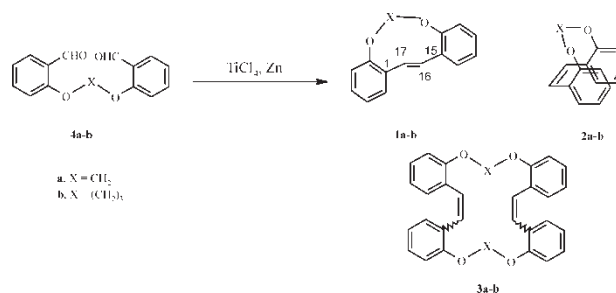
Keywords: Stilbenophane; Cyclization; McMurry reaction; *Ab initio*

The design and synthesis of stilbenophanes is of interest to provide molecular hosts in supramolecular chemistry [1–8]. Recently, we have reported the synthesis and selective complexation of isomers **1b** and **2b** with lithium ions. Moreover, we found that isomer *trans*-**1b** is the first example of a stilbenophane with a short intramolecular C–H \cdots O hydrogen bond in the solid state (crystal) [9]. We have also reported the synthesis, properties and structure of 2,2'-ortho(metaxylylene)stilbenophanes [10]. These interesting findings caused us to continue our study of this class of stilbenophanes.

Herein, we wish to focus on the synthesis and properties of **1a–3a**, the smallest members of this class of compounds known to date. The compounds are characterized by NMR, IR and mass spectroscopy.

Although all attempts to obtain a suitable crystal failed, *ab initio* calculations confirmed that calculated structures are in agreement with spectroscopic data. The calculations were performed at the Hartree-Fock (HF) level of theory using the STO-3G basis set for the fully optimized geometries.

Our approach strategy to the target molecules involves the intramolecular reductive coupling of dialdehydes **4**, using a two-step synthesis, from salicylaldehyde. In order to improve the yields of products, we investigated the McMurry reaction of dialdehydes **4** under several conditions. In general, the use of a mixed solvent of toluene–DME or toluene–THF, as shown in Table I, gives the best yield for products.



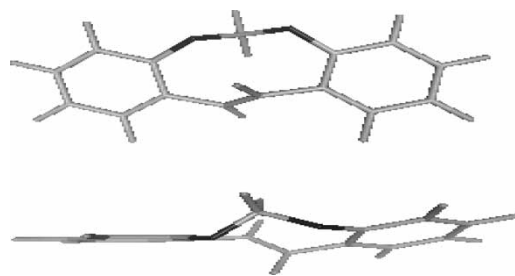
The results listed in Table I show that the stereochemical outcome of the intramolecular McMurry reaction is strongly influenced by the length of the alkyl bridge. Dialdehyde **4a**, unlike **4b**, obviously prefers an intermolecular coupling to intramolecular coupling and gave dimer **3a** as the major product. This means that the torsional angle between the two aldehyde groups in the molecule plays a basic role in the competition between inter- and intramolecular coupling, because this angle is directly dependent on the length of the alkyl bridge in **4**.

^1H and ^{13}C NMR spectra of **1a** and **2a** show different patterns in comparison with those of **1b** and **2b**, respectively. As shown in Fig. 1, in

*Corresponding author. E-mail: darabi@ccerci.ac.ir

TABLE I Synthesis of stilbenophanes 1–3 by McMurry coupling of dialdehydes 4

Dialdehyde	Solvent	1	2	3
4a	THF	1	2	15
4b	THF	13	7	–
4b	DME	10	8	–
4a	THF–toluene (2:1)	21	14	47
4a	DME–toluene (2:1)	15	25	48
4b	THF–toluene (2:1)	51	36	8

SCHEME 1 *ab initio* Calculated structure of **1a** by the STO-3G method. Top: plan view; bottom: side view.

trans-isomer **1a**, the vinylic protons (unlike in **1b** [9]) appear as two doublets. This shows that the vinylic protons are exposed to different chemical fields. As shown in Scheme 1, one proton of the vinylic group is nearer to the oxygens and is observed at lower field (5.42 ppm) than the other vinylic proton (5.11 ppm). The methylene protons are observed as a singlet at 5.45 ppm. The vinylic carbon signal was observed at 76.20 ppm, showing the existence of strain in the structure of **1a**. These data are in agreement with the *ab initio* structure calculated using the STO-3G method. The *cis*-isomer **2a** shows a different NMR pattern. While the vinylic protons appear as one sharp singlet at 6.90 ppm, the methylene protons are observed as a doublet at 5.02–5.05 ppm, which is in agreement with its calculated structure.

The energy minimization calculations were carried out by *ab initio* methods using STO-3G as the basis set [11]. Although the energy-minimized conformation/geometry depends very much on the local geometry from the starting model, we found that the energy-minimized structure in the case of **1b** is in good agreement with the X-ray structure in terms of

the conformation and the cavity dimensions of the stilbenophane.

On the basis of our calculations the *cis*-isomer **2a** cannot adopt a molecular geometry in which the ethylene and phenyl moieties are coplanar. The two phenyl units are facing each other in a virtually fixed arrangement perpendicular to the plane of the linking ethylene double bond.

However, the geometry of the *trans*-isomer **1a** is different. It has also non-coplanar structure. The molecule deviates from planarity by a twist of about 58° around the phenyl–ethylene single bonds in order to accommodate the hydrogens of the *trans*-ethylene moiety and oxygen at an intramolecular distance of about 2.56 and 3.89 Å, respectively (Table II).

The complexation ability of both isomers with alkali metal ions was studied by conductivity titration in acetonitrile. Both isomers **1a** and **2a** formed very weak complexes with lithium and other alkali ions ($pK < 1$). For the complex formation, we considered two possibilities: one is the case when the Li ion is in the center of the cavity and the other is the case where the Li ion is directed towards the outer

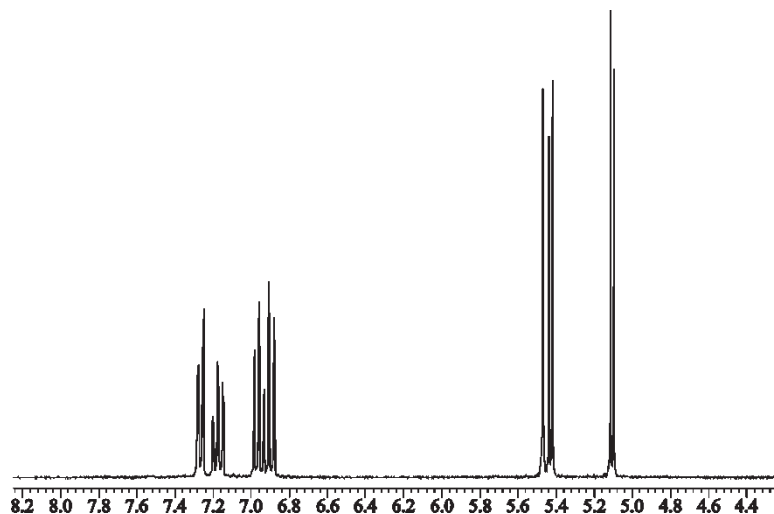
FIGURE 1 ^1H NMR spectra of (*E*)-stilbenophane **1a**.

TABLE II Selected data for the calculated structures of **1a,b** and **2a,b**

Entry	C=C*		Ar/Ar [†]		C1–C17=C16–C15		Ar/ethylene [‡]		CH...O	
	1	2	1	2	1	2	1	2	1	2
A	122	123.6	26.1	0.1	34	0.1	57.5	77.2	2.56	3.80
B	124.5	124	16.5	0.1	9.3	0.1	45.5	89.4	2.65	3.14

* Ethylene bond angle shown as C=C. [†] Angle between the planes formed by the two aromatic rings shown as Ar/Ar. [‡] Angle between the planes formed by the aromatic rings and ethylene bond shown as Ar/ethylene.

side of the phenyl rings. The theoretical calculations (STO-3G) confirmed the second possibility.

Further investigations on the synthesis and properties of analogous molecules are currently in progress.

EXPERIMENTAL

The experiments were conducted in flame-dried glassware under an inert atmosphere of argon unless otherwise noted. The solvents and reagents used in each experiment were dried and purified according to accepted procedures. Melting points were determined on Büchi 530 apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on Bruker-80 and 250 spectrometers. All NMR samples were run in CDCl₃ and chemical shifts are expressed in ppm relative to internal Me₄Si. Infrared spectra (IR) were observed on a FT-IR Mattson 1000 spectrometer. Mass spectra were obtained on a FTSONS instrument. Column chromatography was carried out with Merck Art.7734 kieselgel 60, 70-230 mesh ASTM. Tetrahydrofuran (THF) and dimethoxyethane (DME) were freshly distilled under a nitrogen atmosphere from sodium-benzophenone prior to use. Salicylaldehyde, HMPA, and dibromomethane all are commercially available and were used without further purification.

Synthesis of Bis(carbonyl) Ether **4a**

Compound **4a** was prepared according to the literature [12].

Bis(carbonyl) Ether **4a**: colorless crystals, mp 132°C; ¹H NMR (90 MHz, CDCl₃) δ 5.93 (s, 2H), 7.05–7.15 (m, 2H), 7.25–7.32 (m, 2H), 7.43–7.75 (dd, 2H), 10.34 (s, 2H); ¹³C NMR (22.5 MHz, CDCl₃) δ 188.43, 158.08, 135.80, 128.13, 124.95, 122.67, 114.19, 89.95; IR (KBr) [cm⁻¹] 2850, 1670, 1580, 740; *m/z* (rel. intensity, %) 256 (M⁺, 5), 135 (80), 121 (100), 77 (40).

Synthesis of Compounds **1a–3c**

Compounds **1a–3c** were prepared according to the literature [12] with the difference that both solvent

(THF-toluene, 2:1) and reflux time were changed. The reflux time was changed from 6–20 h to 4–6 h.

(Z)-Stilbenophane **1a**: colorless liquid, ¹H NMR (300 MHz, CDCl₃) δ 7.39 (d, *J* = 7.52 Hz), 7.16 (t, *J*₁ = 7.52 Hz, *J*₂ = 7.96 Hz), 6.96 (d, *J* = 0.89 Hz), 6.94 (d, *J* = 0.89 Hz), 6.93–6.89 (m), 6.90 (s), 5.02–5.05 (d); ¹³C NMR (75 MHz, CDCl₃) δ 153.96, 128.40, 125.14, 121.56, 121.27, 117.09, 90.30, 76.23; IR (KBr) [cm⁻¹] 3039, 2940, 1660, 1555, 1464, 1230, 1083, 1058, 968, 755; MS (EI), *m/z* (rel. intensity, %) 224 (20), 223 (90), 210 (80), 181 (60), 152 (50).

(E)-Stilbenophane **2a**: colorless needles; mp 140°C; ¹H NMR (300 MHz, CDCl₃) δ 7.25–7.27 (d, *J* = 7.70 Hz), 7.18 (t, *J* = 7.74, 7.96, 1.55 Hz), 6.97 (d, *J* = 7.52, 1.10 Hz), 6.91 (t, *J* = 7.30, 1.33, 1.10 Hz), 5.47 (s), 5.42 (d, *J* = 7.75 Hz), 5.11 (d, *J* = 7.75 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 145.91, 130.30, 127.17, 126.02, 124.48, 123.49, 123.46, 121.02, 120.79, 117.50, 117.44, 115.14, 111.03, 103.30, 73.98; IR (KBr) [cm⁻¹] 2995, 1619, 1460, 788; MS (EI) *m/z* (rel. intensity, %) 224 (10), 210 (90), 152 (5), 135 (15).

(E,Z)-Cyclic dimer **3a**: colorless needles; mp 149°C; ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, 2H), 7.18 (dd, 2H), 6.90–6.95 (m, 6H), 5.10 (d, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 153.34, 130.32, 127.47, 124.48, 123.46, 121.25, 120.59, 117.83, 116.02, 111.03, 103.28; MS (EI) *m/z* (rel. intensity, %) 448 (50).

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