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Synthesis, Characterization and Properties of Two Novel *E*- and *Z*-Stilbenophanes: Their Lithium-selective Complexation and C–H···O Short Hydrogen Bonds in the X-ray Structure of the *E*-Isomer

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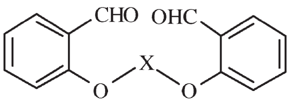
Dedicated to Professor Masaji Oda on the Occasion of his 60th Birthday.

Stilbenophanes 1c and 2c were synthesized in good yields. Among alkali ions, both isomers only formed 1:1 complexes with lithium selectively. An X-ray structure of 1c shows a statistical disorder which leads to two refined positions for the ethylene moiety. The existence of a weak intramolecular C–H···O hydrogen bond in its structure was confirmed by both X-ray analysis and theoretical calculation.

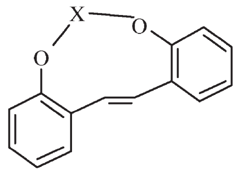
Keywords: Stilbenophanes; Intramolecular hydrogen bonds; Complexation; Lithium selectivity; X-ray structure

The design and synthesis of stilbenophanes as molecular hosts is an area of interest in supramolecular chemistry [1–7]. Recent investigations have shown that the binding power of a host is governed by the size, shape, rigidity, and the non-covalent interactions of the cavity. Particularly important is the fact that highly flexible hosts often make binding entropically unfavorable. To tune the binding ability of a host, one should carefully design the host with appropriate rigidity [8]. In the course of our study, we have considered a series of stilbenophanes **1** and **2**, the cyclic compounds of which are composed from both aromatic moieties and a flexible etheric chain.

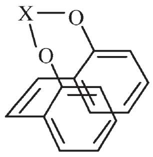


3a-e

a, X = CH_2
b, X = $(CH_2)_2$
c, X = $(CH_2)_3$
d, X = $(CH_2)_4$
e, X = $(CH_2)_5$



1a-e



2a-e

Our interest in this area is to study the structure, conformation and cavity dimensions of these cyclophanes for their use as hosts to form complexes with guests of suitable dimensions. The dimensions of the cavity depend on the spacer group and its connectivity to the arene units. To the best of our knowledge, however, 2,2′-*ortho*-bridged-stilbenophanes **1e** and **2e** have only been reported [9].

In this paper, we wish to report the synthesis and interesting properties of **1c** as the first example of a stilbenophane with an intramolecular C–H···O

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hydrogen bond together with its *cis* isomer **2c**. They can be prepared from the dialdehyde **3c** using the low-valent titanium species obtained from $TiCl_4$ and zinc [10–12]. The crude products were purified on silica gel eluted with hexane and then hexane–ethyl acetate (7:3) to afford, in order of elution, stilbenophanes **1c** and **2c** in 51 and 36% yield, respectively, together with cyclic dimer (8%). ^{1}H NMR and GC-Mass of the cyclic dimer show that it is a mixture of stereoisomers which are hardly separable by column chromatography.

A significant difference in the total yields of **1c** and **2c** was found when reaction solvent was changed from THF (20%) or DME (18%) to THF : toluene (2:1) (87%).

^{1}H and ^{13}C NMR spectra of **1c** and **2c** are in agreement with the C_2 and C_s symmetry of the molecules, respectively. In both isomers, the vinylic protons appear as one sharp singlet. The number of observed signals agrees with the expected number of carbons in both isomers. The methylene groups are shielded with respect to their positions in the open-chain compound **3**. When **1c** was compared with **1e**, it was found that the vinylic protons in the former are at higher fields (δ 6.88) than those of **1e** (δ 7.69) [9]. This may be explained by the higher rigidity of **1c** due to its shorter alkyl moiety. The ^{1}H NMR spectra of **1c** did not show any significant change with varying temperature from 30 to -90°C. Hence, it can be concluded that the rotation of single bonds between benzene rings and the *trans* double bond are fast even at -90°C.

X-RAY STRUCTURE†

The molecular structure of **1c** was established by X-ray crystallographic analysis at 193 K (Fig. 1).‡ X-ray data does not show any symmetrical sub-units to give C_1 symmetry for its structure. The observed statistical disorder leads to two refined positions for the HC═CH group (C161–C171 and C162–C172). Therefore, the C═C bond lengths are not very accurate, compared to the C═C distances between non-disordered carbon atoms. Concerning the standard deviations, the bond lengths C161–C171 and C162–C172 may be described as normal C–C double bonds.

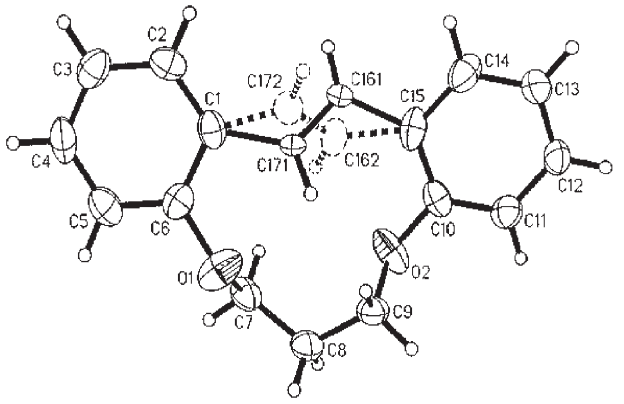

FIGURE 1 Molecular structure of **1c** with disorder behaviour (thermal ellipsoids are given with 40% probability). Selected bond lengths [Å], angles [°], and torsion angles [°]: C(162)–C(172) 1.28 (9), C(161)–C(171) 1.36 (1), C(15)–C(162) 1.508 (7), C(15)–C(161) 1.510 (5), C(15)–C(162)–C(172) 129.4 (4), C(15)–C(161)–C(171) 111.8 (5), O(2)–C(10)–C(15) 119.2 (2), C(15)–C(161)–C(171)–C1 8.9 (4), C(15)–C(162)–C(172)–C14.4 (5).

The split positions are not fixed in solution because of the single set of NMR signals for the HC═CH group. The two positions in the solid state are probably existing due to the weak C–H···O hydrogen bonds C171–H171···O1 (C171···O1 = 253.6(6) pm) and C162–H162···O2 (C162···O2 = 250.2(6) pm). In the other words, the existence of the two fixed split positions in the solid state must originate from the torsion rotation around the C–Ph bonds in solution, which cannot be detected by VT NMR measurements even at -90°C. This indicates that the rotation barrier around C–Ph bonds is too low. The similar unusual behavior has also been reported and discussed for *E*-stilbenes [13].

The deformation of the benzene rings from a regular hexagon rings is 6.5° and the angle between the planes formed by the two aromatic rings is 14°. The two phenyl moieties may be aligned parallel as the molecule deviates from planarity by a twist of about 41° around the phenyl–ethylene single bonds. The average C–C distance in the aromatic rings is equal to 1.38 Å. The energy-minimized structure based on semiempirical AM1 calculation is in good agreement with the X-ray structure (Table I).¶

The complexation ability of both isomers with alkali metal ions was studied by conductivity titration in acetonitrile. Amongst the alkali metal

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[†] X-ray data for compound **1c** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 180825. Copies of the data may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033. e-mail: deposit@ccdc.cam.ac.uk).

[‡] Crystallographic data were collected on a IPDS (Stoe) diffractometer with graphite-monochromated Mo Kα ($\lambda = 71.073$ pm) at 193 K. The structure was solved using direct methods with SHELXS-97. *Crystal data* for colourless **1c**: $C_{17}H_{16}O_2$, $M = 152.31$, orthorhombic, space group $Pca2_1$, $a = 1734.5(1)$, $b = 1096.0(1)$, $c = 697.1(1)$ pm, $V = 1325.2(2) \times 10^6$ pm^3, $Z = 4$, $d_{\text{calcd}} = 1.265$ g/cm^3, 2428 independent reflections were used in the refinement. Refinement of 192 parameters gave $wR2 = 0.0898$ and $R1 = 0.0365$ for 1855 data with $F_O > 4\sigma(F_O)$.

[¶] Theoretical calculation was performed with the Gaussian 98 program system with gradient geometry optimization.

[§] Both isomers formed very weak complexes with other alkali ions (p$K < 1$).

TABLE I The selected data of X-ray and AM1 structure of **1c**

Method	Ar/Ar	Ar/ethylene	CH···O	C15–C16 = C17–C1
X-ray	14	41	2.53	6.65
AM1	12.94	34.9	2.61	4.86

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.

cations, both isomers formed exclusively 1:1 complexes with lithium selectively. It is worthy to note that the complexation of $LiClO_4$ is more efficient with **1c** than with **2c** ($pK_{\mathbf{1c}} = 4.147$, $pK_{\mathbf{2c}} = 2.272$, $pK_{\mathbf{1c}}/pK_{\mathbf{2c}} = 1.825$).[§] Crystals of the lithium complex suitable for X-ray crystallographic characterization have yet to be obtained. For the complex formation, we considered two possibilities; one is the case when Li ion is in the centre of cavity and the other is the case when Li ion is directed toward the outer side of phenyl rings. AM1 calculation confirmed the second possibility.

Ultraviolet irradiation (high mercury pressure lamp) of the deoxygenated solutions of **1c** and **2c** in benzene for 1 h promoted the photoisomerization of the olefinic moiety. The GC analysis of an irradiated solution of *cis* isomer **2c** showed the development of a new peak assignable to **1c** with 90% conversion, while irradiation of **1c** only gave 33% of **2c**. This fact indicates that the strain in the framework of **2c** should promote the isomerization towards **1c**.

Under polarography conditions, isomer **2c** (−1.81 V) is more easily reduced than **1c** (−2.13 V). None of these isomers show any reversible oxidation wave, indicating that the cationic species of these molecules are highly reactive under the measurement conditions. Of course, the strain energy of **2c** is not so high to convert into **1c** under electronic conditions during the repeated scan. Both stilbenophanes are reduced at considerably more negative potentials than *trans* and *cis*-stilbenes. It may be due to the electron-donating properties of the oxygen atoms and the more structured skeleton of the stilbenophanes.

Further investigations on the synthesis of analog molecules are currently in progress.[‖] Their chemistry, electronic properties and their complexes are under investigation.

EXPERIMENTAL SECTION

All 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 are determined on Büchi 530 and are not corrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker-80. Mass spectra were obtained on a FTSONS instrument. The cyclic voltammetry system is a Metrohm 746 UA trace analyzer. The auxiliary electrode is a Pt wire. The reference electrode is Ag/AgCl. The measurements were performed in DMF containing 0.1 M tetrabutylammonium bromide under nitrogen atmosphere. The conductometer is a Philips PW 9526 digital conductivity meter.

Synthesis of bis(carbonyl) ether **3** was conducted according to the literature [9].

Bis(carbonyl) ether **3**: Colorless crystals, mp: 94–96°C; ^1H NMR (90 MHz, $CDCl_3$) δ 2.30 (m, 2H), 4.22 (t, 4H), 6.85–7.05 (m, 4H), 7.35–7.57 (m, 2H), 7.75–7.84 (dd, 2H), 10.35 (s, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 28.79, 64.41, 112.19, 120.67, 124.45, 128.33, 135.80, 160.38, 189.13; IR (KBr) [cm^{-1}] 3040, 2920, 1720, 1580, 1410, 1240, 1083, 1150, 820, 740; UV/Vis ($CHCl_3$): λ_{max} [nm] (ε) 253.7 (47300); MS (EI), m/z (rel. intensity %) 284 (M^+, 10), 162 (15), 135 (50), 121 (100), 77 (80).

Synthesis of products **1c**–**2c** is according to the literature [9], with these differences that both solvent (THF/toluene: 2/1) and reflux time were changed. The reflux time was changed from 6–20 to 4–6 h.

E-Stilbenophane **1c**: Colorless needles, mp: 92–94°C; ^1H NMR (90 MHz, $CDCl_3$) δ 2.07 (m, 2H), 4.12 (t, 4H), 6.88 (s, 2H), 7.12–7.40 (m, 8H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 30.68, 70.59, 113.10, 122.30, 124.15, 128.37, 129.20, 132.92, 157.72; IR (KBr)[cm^{-1}] 3042, 2942, 1664, 1558, 1464, 1231, 1083, 1052, 963, 750; UV/Vis (hexane): λ_{max} [nm] (ε) 282.80 (10625); MS (EI), m/z (rel. intensity %) 252 (M^+, 100), 223 (20), 209 (20), 195 (10), 181 (45), 165 (50), 145 (75), 133 (90), 119 (70), 91 (20).

Z-Stilbenophane **2c**: Colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.98 (m, 2H), 4.08 (t, 4H), 6.68 (s, 2H), 6.62–7.06 (m, 8H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 27.28, 68.69, 111.39, 120.70, 124.15, 128.24, 128.48, 132.10, 156.90; IR (KBr) [cm^{-1}] 2992, 1614, 1453, 783; UV/Vis (hexane): λ_{max} [nm] (ε) 289.1 (12500); MS (EI), m/z (rel. intensity %) 252 (M^+, 90).

Cyclic dimer: Colorless solid, ^1H NMR (90 MHz, $CDCl_3$) δ 2.1–2.5 (m, 4H), 4.10–4.40 (m, 8H), 6.65 (d, 2H), 6.87 (d, 2H), 6.64–7.42 (m, 16H); MS (EI), m/z (rel. intensity %) 504 (M^+, 43), 133 (69), 91 (58).

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