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Synthesis, crystal structure and silver complexation of a novel saddle-shaped stilbenophane: NMR and theoretical study on the complex

Hossein Reza Darabi[a]*, Marjan Azimzadeh Arani[a], Abbas Motamedi[a], Rohoullah Firouzi[a], Rainer Herges[b], Ali Reza Mohebbi[b], Sarah M. Nasseri[b] and Christian Näther[c]

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A new *Z*,*Z*-stilbenophane was synthesised and characterised. According to an X-ray structure analysis, the structure has a saddle shape, with the π-electrons of the double bonds and the oxygen atoms pointing towards the centre of a cavity. The ligand forms a 1:1 complex with Ag^+. Both NMR spectra and theoretical analysis (Gauge-independent atomic orbitals (GIAO) and Quantum theory of atoms in molecules (QTAIM)) suggest that the silver cation is bound within the molecular cavity. The metal is coordinated by the two olefinic double bonds and the four oxygen atoms in an approximately octahedral environment. The coordination motif is unusual because the soft silver cation prefers the interaction with the four hard oxygen atoms over the bonding to the arene units, which is frequently observed in Ag^+ arene complexes.

Keywords: stilbenophane; saddle shape; host–guest systems; silver; theoretical study

1. Introduction

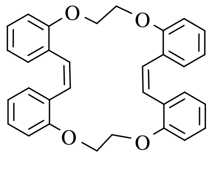
It is known that the binding power of a host is governed by the size, shape, rigidity and non-covalent interactions of the cavity. Particularly important is the fact that highly flexible hosts often make binding entropically unfavourable. To tune the binding ability of a host, a careful design of the host with an appropriate rigidity is necessary (*1*). Cyclophanes and crownophanes are interesting classes of macrocyclic hosts, which can be used as platforms for the design of supramolecular systems (*2*). The unique chemical and physical properties of the host–guest structures are the key to the future development of nanomolecular devices, chemosensors, etc. (*3*).

The ability of Ag^+ to complex with crown ethers (*4*), as well as π-electron systems (*5*), is well known. Its kinetically stable complexes as reagents in the radiation therapy of cancer (*6*) are generally obtained with cyclophanes (*7*).

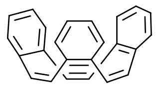
Stilbenophanes, cyclophanes containing stilbene moieties, show different behaviours in coordination with Ag^+. A detailed survey shows that the coordination of Ag^+ with cofacial *Z*-stilbenes preferably occurs through the arene unit (*8–10*). By contrast, the olefinic cavity of bowl-shaped all-*Z*-[*n*]benzo[4*n*]annulenes, such as **2**, incorporates Ag^+ to show the efficiency of cavity shapes in the complexation (*11*). In the *Z*-stilbene crown ether **3** containing multiple binding sites, the 'soft' π-electrons of the double bonds and 'hard' oxygen atoms make a well-defined cavity for complexation with Ag^+, without any participation of the arene units (*12*). On the other hand, the π-electron-rich cleft of phenyl rings of the sterically congested stilbene crown ether **4** offers a suitable site for complexation (*13*).

Since the *Z*-stilbene crown ethers **3** and **4** are proven to be suitable ligands but with a different coordination site for Ag^+, we became interested in the behaviour of *Z*,*Z*-**1** with Ag^+. Although the saddle-shaped stilbenophane *Z*,*Z*-**1** contains multiple binding sites in a suitable geometry, the π-electrons of the double bonds and the oxygen atoms are pointing towards the centre of a cavity to make a favourable binding site.

In continuation of our investigation on stilbenophanes (*14*), herein, we report the synthesis and structure of *Z*,*Z*-**1** and its complexation with Ag^+ to study its properties as a host compound by both NMR spectra and theoretical analysis.



Z,*Z*-**1**



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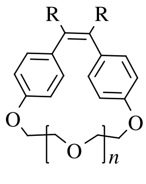

3 (*n* = 3); R = H
4 (*n* = 4); R = Ph

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2. Results and discussion

2.1 Synthesis and structure of stilbenophane **Z**,**Z-1**

A recent report from our laboratory outlined a convenient high-yielding synthetic method for the preparation of stilbenophanes (*14a*). The starting material for the McMurry reactions, the bis(carbaldehyde) **6**, was obtained from 2-hydroxybenzaldehyde by reaction with the 1,2-dibromoethane under reflux conditions (*15*).

As shown in Scheme 1, treatment of **6** with the low-valent titanium, prepared from $TiCl_4$ and Zn in tetrahydrofuran (THF), afforded bridged stilbenes **1** (20%) and **5** (45%), with a combined yield of 65%. Note that there is a competition between the intermolecular and intramolecular McMurry coupling of the dialdehyde **6**, which produced dimers **1** and monomers **5**, respectively. To increase the intermolecular coupling of the dialdehyde **6** and to maximise the formation of **1**, the reaction was performed under more concentrated conditions in THF.

It was gratifying to note that dimers **1** and monomers **5** are easily separable by column chromatography. However, the separation of three isomers containing *cis–cis* (*Z*,*Z*-**1**), *trans–trans* (*E*,*E*-**1**) and *cis–trans* stilbene moieties (*Z*,*E*-**1**) is more difficult. Nevertheless, the desired isomer *Z*,*Z*-**1** was separated from the mixture by a careful column chromatography followed by crystallisation (7%). On the other hand, the attempts towards complete purification of two other isomers *E*,*E*-**1** and *Z*,*E*-**1** were not successful. On the basis of ^1H NMR, the molar ratio of isomers *Z*,*E*-**1** and *E*,*E*-**1** was 1.5:1, respectively (13%).

The assignment of *cis*- and *trans*-geometries was based on ^1H NMR. The *cis*-geometry was assigned to the isomer with lower chemical shift values for the vinylic protons.

Stilbenophane *Z*,*Z*-**1** showed simple NMR spectra, confirming its symmetrical structure. In the ^1H NMR chemical shift region of aromatic hydrogens (δ 6.7–7.2 ppm), the expected four signals are observed: two doublets (H-3 and H-6) and two triplets (H-4 and H-5). Moreover, the expected singlets of alkenes and aliphatic protons were observed at δ 6.6 and 3.7 ppm, respectively. In the ^{13}C NMR spectrum, eight signals were observed, which is in agreement with a time-averaged C_{2v} symmetry in solution.

The ^1H NMR of a mixture of *E*,*E*-**1** and *E*,*Z*-**1** shows that the methylene protons of *E*,*E*-**1** resonance at 4.43 as singlet, while for *E*,*Z*-**1** at 4.16 and 4.24 as two triplets. On the other hand, the alkene hydrogens of *E*,*E*-**1** appeared as singlet at 7.47, and for *E*,*Z*-**1** as two singlets at 6.61 and 6.87 ppm.

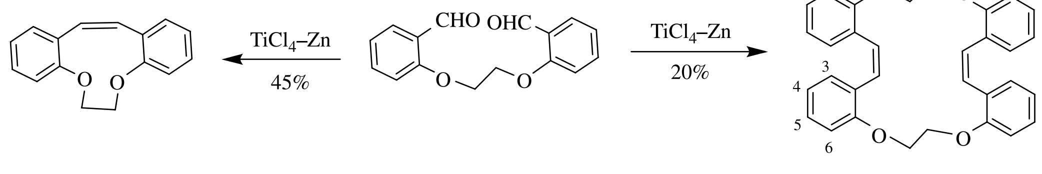
A single crystal of *Z*,*Z*-**1** suitable for the X-ray analysis was obtained from an acetonitrile solution. The ORTEP drawing is shown in Figure 1 (*16*). The structure crystallises in a ‘chiral’ space group ($P4_32_12$). Because no strong anomalous scattering atoms are present, the absolute structure cannot be determined. Therefore, the Friedel opposite was merged in the refinement and the absolute structure was assigned based on the known absolute structure of the starting material.

The X-ray results reveal several structural features of *Z*,*Z*-**1**. The molecule has a saddle-shaped structure with a two-fold axis (C_2). It contains a rectangular cavity with dimensions that are defined by the distance between the centre of the two non-facing phenyl ring (8.0 Å) and the facing oxygen atoms (4.0 Å). The ethene bridges exhibit a *cis* configuration, in agreement with the ^1H NMR spectrum, with considerably widened bond angles (av. 131.0°). The olefinic bridges are almost perpendicular with respect to each other with a torsional angle of about 88°. The phenylene rings of each stilbene moiety are rotated by about 66° out of plane with respect to the double bond. As a consequence, the π-electrons of both the double bonds and the oxygen atoms point into the cavity to accommodate the guest.

In the crystal structure, the molecules are densely packed and are stacked into the direction of the crystallographic *c*-axis in order that the π–π interactions between the phenyl rings are maximised (Figure 2). From this arrangement, very small channels are formed in the direction of the *c*-axis, in which the H atoms of the ethene bridges are directed.

2.2 Complexation of **Z**,**Z-1** with silver

A stoichiometric solution of *Z*,*Z*-**1** and $AgClO_4$ was prepared in dry THF. Evaporation of the solvent produced



E-**5** (25%)
Z-**5** (20%)

6

Z,*Z*-**1** (7%)
E,*Z*-**1** and *E*,*E*-**1** (13%)

Scheme 1. Intermolecular and intramolecular McMurry coupling of the dialdehyde **6** for the formation of products **1** and **5**, respectively.

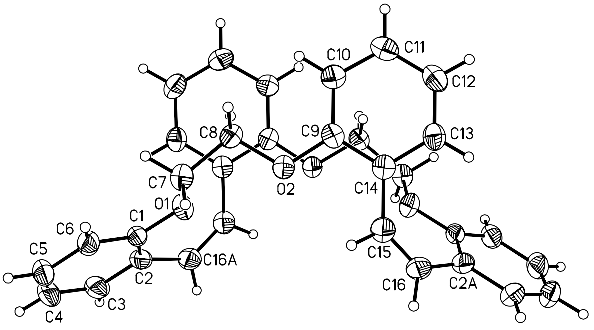


Figure 1. ORTEP drawing of *Z*,*Z*-**1** at 220 K (50% probability): C15–C16, 1.33 Å; C16···C16A, 6.49 Å; O2···O2A, 4 Å; O1···O1A, 6.5 Å; C11···C11A, 5.2 Å; C14–C15–C16, 131.1 Å.

brown crystals of a new material, *Z*,*Z*-**1**@Ag^+, which readily dissolved in chloroform, in contrast to $AgClO_4$. The ^1H NMR spectral patterns of *Z*,*Z*-**1** and *Z*,*Z*-**1**@Ag^+ are clearly different (see the ^1H NMR spectra in the Supporting Information). A remarkable downfield shift of alkene groups by $\Delta\delta = 0.48$ hints at a strong interaction between Ag^+ and the alkene groups. In the aromatic region, only minor changes of the signals were observed. Only the triplet peaks of H-4 and H-5 shifted downfield by $\Delta\delta = 0.15$ with respect to *Z*,*Z*-**1**. The absence of any change in the ^1H NMR spectrum of *Z*,*Z*-**1**@Ag^+ upon addition of excess silver salt indicates the 1:1 stoichiometry of the complex. In the ^{13}C NMR, and the INEPT spectra of *Z*,*Z*-**1** and *Z*,*Z*-**1**@Ag^+, downfield shifts of the ipso-carbons ($\Delta\delta = 1.4$–3.3 ppm) as well as the sp^3 carbons ($\Delta\delta = 1.3$ ppm) are observed.

Unfortunately, attempts to obtain suitable single crystals of *Z*,*Z*-**1**@Ag^+ for X-ray studies failed. Therefore, detailed theoretical calculations at the B3LYP/DGDZVP level of theory were performed to obtain more information of the complex structure. Our calculations for the structure of the free ligand *Z*,*Z*-**1** are in very good agreement with the X-ray structure. The calculated (B3LYP/DGDZVP Gauge-independent atomic orbitals (GIAO)) ^1H NMR shifts are also consistent with the observed signals, if a fast conformational equilibrium of the C_2-symmetric structure is assumed (Figure 3).

Upon complexation with Ag^+, all ^1H NMR signals shift downfield. Most affected are the protons *para* to the double bonds, which in the free ligand appear at higher field and in the complex at lower field as the corresponding *ortho* protons. All trends predicted by the theoretical calculations are in excellent agreement with the experiment. The coalescence of the $-O-CH_2-CH_2-O-$ protons is due to the restricted conformation (racemisation) of the C_2 structure of the complex.

As shown in Figure 4, the Ag^+ occupies a position at the centre of the cavity of the molecule binding to both the oxygen atoms and alkene groups of the host. The distance between the silver ion and oxygen atoms (O_3 and $O_4 = 2.74$ Å; O_1 and $O_2 = 2.89$ Å) and olefinic carbon atoms (C_7 and $C_8 = 2.75$ Å; C_5 and $C_6 = 2.57$ Å) is shorter than that between the closest carbon atom of the phenyl rings (3.24 Å).

2.2.1 *Topological analysis of the charge density*

The topological analysis of the charge density distribution developed within the framework of Quantum theory of atoms in molecules (QTAIM) (*17*) is used as a useful and powerful tool for evaluating the bonding interaction in organometallic compounds (*18*). The computational details and terminology associated with QTAIM have been inserted in the Supporting Information (S1).

Figure 4 presents a part of the molecular graph of *Z*,*Z*-**1**@Ag^+ (calculated at the B3LYP/3-21G(d) level) in which the Ag^+ is penetrated into the *Z*,*Z*-**1** cavity. Accordingly, six bond critical points (BCPs) in the molecular graph are found between the silver ion and all

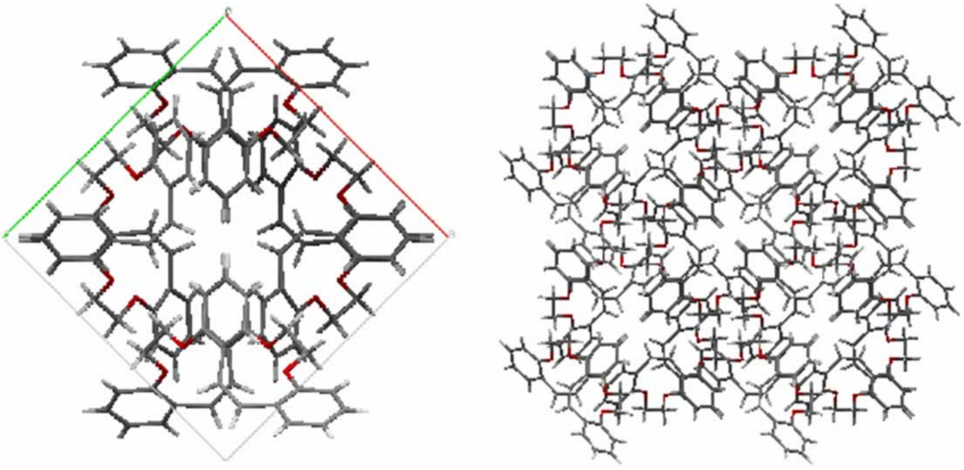


Figure 2. Crystal structure of *Z*,*Z*-**1** in the direction of the crystallographic along the *c*-axis.

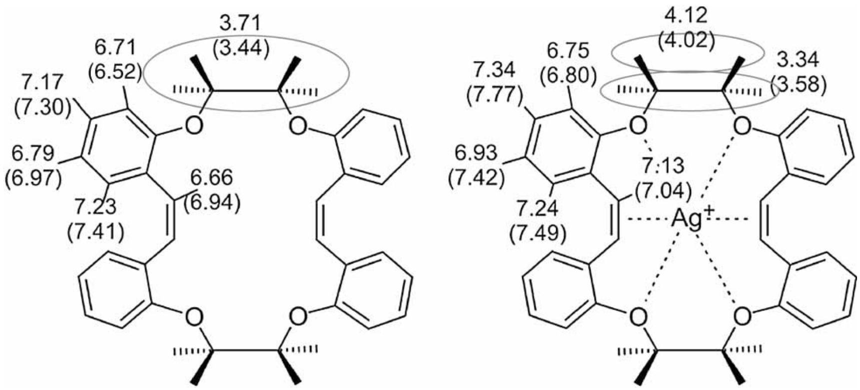


Figure 3. Observed and calculated (B3LYP/DGDZVP GIAO in parentheses) ^{1}H NMR shifts of stilbenophane *Z*,*Z*-**1** (left) and its silver complex *Z*,*Z*-**1**@Ag$^+$ (right).

four oxygen atoms and two ethylene groups in *Z*,*Z*-**1**. Then, silver ion in *Z*,*Z*-**1**@Ag$^+$ is a six-coordinate according to the number of BCPs (*18a*, *19*).

Several useful indicators, such as ρ_{BCP} (the electron density at the BCP) (*17*), $\nabla^2\rho_{\mathrm{BCP}}$ (the Laplacian of the electron density) (*20*) and local energy density at the BCP ($H_{\mathrm{BCP}} = G_{\mathrm{BCP}} + V_{\mathrm{BCP}}$) (*21*, *22*), have been employed to differentiate and classify the binding sites of the ligand with silver. The details and ranges with respect to each indicator have been comprehensively incorporated in the Supporting Information (S2).

Table 1 summarises the topological results for the Ag—C (alkene) and Ag—O interactions from a QTAIM analysis of the resultant wave functions (see also the Supporting Information, S3). The topological properties at the BCPs for the Ag—C and Ag—O interactions show relatively small values for ρ_{BCP} ($0.01 < \rho_{\mathrm{BCP}} < 0.04$), i.e. of the order of 10^{-2} au (*19b*) and positive values for the $\nabla^2\rho_{\mathrm{BCP}}$ ($0.07 < \nabla^2\rho_{\mathrm{BCP}} < 0.10$). Since the greater the ρ_{BCP}, the stronger the interaction, Ag—C$_5$ and Ag—C$_6$ are the strongest bonding interactions and Ag—O$_1$ and Ag—O$_2$ are the weakest bonding interactions. On the other hand, $|V_{\mathrm{BCP}}|$ and G_{BCP} values are small ($0.018 < |V_{\mathrm{BCP}}| < 0.034$ and $0.018 < G_{\mathrm{BCP}} < 0.029$) and $|V_{\mathrm{BCP}}|$ is very slightly greater than G_{BCP}. Likewise, the negative total energy density is very close to zero ($-0.0053 < H_{\mathrm{BCP}} < -0.0006$) and $|V_{\mathrm{BCP}}|/G_{\mathrm{BCP}}$ is near to 1 ($1.04 < |V_{\mathrm{BCP}}|/G_{\mathrm{BCP}} < 1.13$). Theoretical values of $\nabla^2\rho_{\mathrm{BCP}}$, ρ_{BCP},

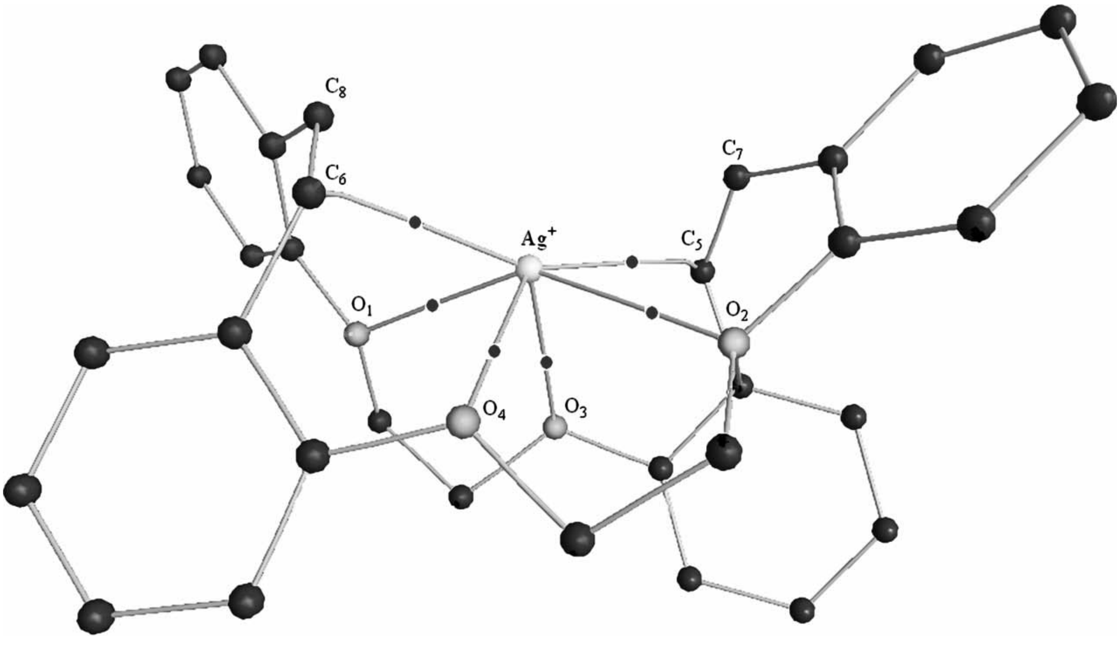


Figure 4. Projection of a part of the molecular graph of *Z*, *Z*-**1**@Ag$^+$ determined by the topology of the B3LYP electron density. The atoms are identified as follows: black, carbons; grey, oxygens. The lines and small points are bond paths and BCPs, respectively. Hydrogen atoms and the other bond paths and BCPs are omitted for clarity (see the whole molecular graph in the Supporting Information; Figure 3).

Table 1. Topological and energetic properties calculated at the BCPs of the binding sites of ligand with silver.[a]

Bond	Bond length	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	V_{BCP}	G_{BCP}	$\lvert V_{BCP}\rvert/G_{BCP}$
Ag—O_1	2.89	0.0168	0.0688	−0.0006	−0.0184	0.0178	1.0339
Ag—O_2	2.89	0.0168	0.0688	−0.0006	−0.0184	0.0178	1.0338
Ag—O_3	2.74	0.0262	0.1003	−0.0039	−0.0328	0.0289	1.1334
Ag—O_4	2.74	0.0262	0.1003	−0.0039	−0.0328	0.0289	1.1333
Ag—C_5	2.57	0.0359	0.0944	−0.0053	−0.0341	0.0289	1.1825
Ag—C_6	2.57	0.0359	0.0944	−0.0053	−0.0341	0.0289	1.1825

[a] Units of distance, the electron density, Laplacian of the electron density and local energetic properties (G_{BCP}, V_{BCP} and H_{BCP}) are in Å, e Å^{-3}, e Å^{-5} and kJ/mol per atomic unit volume, respectively.

G_{BCP}, $|V_{BCP}|$, H_{BCP} and $|V_{BCP}|/G_{BCP}$ indicate 'closed-shell' interactions for six independent BCPs between the Ag^+ and *Z*,*Z*-**1**, which should be classified into 'donor–acceptor' bonds (*20*, *23*).

3. Conclusion

The synthesis and characterisation of stilbenophane *Z*,*Z*-**1**, which can be viewed as a combined crown ether and π-ligand, and its silver complex *Z*,*Z*-**1**@Ag^+ are reported. Stilbenophane *Z*,*Z*-**1** has a saddle shape with a suitable cavity for cation binding. In the free ligand *Z*,*Z*-**1**, both the double bonds and the four oxygen atoms point towards the centre of the cavity. Consequently, based on the NMR spectra and a theoretical analysis in the silver complex, *Z*,*Z*-**1**@Ag^+, the Ag^+ prefers to occupy a position at the centre of the cavity binding to the oxygen atoms (Ag—O: 2.74, 2.89 Å) and alkene groups (Ag—C: 2.75, 2.57 Å). Topological charge density analysis developed within QTAIM suggests that the silver cation is bound within the molecular cavity. On the basis of the values obtained for the topological parameters, relatively low ρ_{BCP}, G_{BCP} and $|V_{BCP}|$ values (of the order of 10^{-2} au) and a positive $\nabla^2\rho_{BCP}$ value and negative H_{BCP} (but very near to zero) are obtained; Ag—O and Ag—C closed-shell interactions fall into 'donor–acceptor' bonds.

This is a rare example with an interaction of 'soft' silver and 'hard' oxygen atoms combined with a π-coordination to olefinic units and without any bonding to arenes.

4. Experimental section

The experiments were conducted in flame-dried glassware under an inert atmosphere of argon unless otherwise stated. The solvents and reagents used in each experiment were dried and purified according to standard procedures. Melting points are determined on a Büchi 530 instrument and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 and 500 MHz spectrometer. All NMR samples were run in $CDCl_3$ and chemical shifts are expressed as parts per million relative to internal Me_4Si. Mass spectra were obtained on a Fisons instrument. Column chromatography was carried out with the use of Merck Art. 7734 Kieselgel 60, 70–230 mesh ASTM. THF was freshly distilled under a nitrogen atmosphere from sodium–benzophenone prior to use. Salicylaldehyde, HMPA and 1,2-dibromoethane are all commercially available and used without further purification.

4.1 *Preparation of stilbenophane* Z,Z-1

Anhydrous THF (100 ml) was added to Zn dust (2.2 g, 34 mmol) under an argon atmosphere. $TiCl_4$ (3 ml, 27 mmol) was added to the mixture at 0°C and the black suspension thus obtained was warmed to room temperature, and then refluxed for 2 h. A solution of dialdehyde **6** (2.4 g, 8 mmol) in THF (50 ml) was added dropwise to the above black reaction mixture at room temperature, and the resulting mixture was refluxed for an additional 12 h. The reaction mixture was cooled to room temperature and quenched with 10% aqueous K_2CO_3 (30 ml). The organic layer was separated and the aqueous suspension was extracted with diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, evaporated and chromatographed on silica gel using a 1:9 mixture of ethyl acetate and hexane to afford *Z*-**5** (20%), *E*-**5** (25%), *Z*,*Z*-**1** (7%) and a mixture of *E*,*Z*-**1** and *E*,*E*-**1** (13%), respectively.

4.2 *Selected spectroscopic data*

NMR: at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$.

4.2.1 *Stilbenophane* E-**5**

Colourless solid, ^1H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 4.16$ (s, 4H), 7.05 (d, 2H), 7.12 (t, 2H), 7.14 (s, 2H), 7.20 (t, 2H), 7.33 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 73.2$, 122.6, 124.5, 127.6, 128.4, 132.2, 133.5, 158.1; MS (EI), *m/z* (relative intensity %) 238.1 (M^+, 100).

4.2.2 *Stilbenophane* Z-**5**

Colourless solid, ^1H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 4.20$ (s, 4H), 6.78 (s, 2H), 6.91 (m, 4H), 6.99 (d, 2H), 7.11 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 71.8$, 120.3, 123.2, 128.3, 130.1, 130.2, 131.5, 156.2; MS (EI), *m/z* (relative intensity %) 238.1 (M^+, 100).

4.2.3 *Stilbenophane* Z,Z-**1**

Colourless needles, ^1H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 3.71$ (s, 8H), 6.66 (s, 4H), 6.71 (d, 4H), 6.79 (t, 4H), 7.17 (t, 4H), 7.23 (d, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 65.9$, 111.30, 120.03, 125.27, 127.84, 127.86, 129.76, 155.43; MS (EI), *m/z* (relative intensity %) 476.2 (M^+, 100).

4.2.4 *Complex* Z,Z-**1**@*Ag*$^+$

Compound Z,Z-**1** (100 mg, 0.2 mmol) and 14.2 mg $AgClO_4$ were dissolved in 10 ml THF and the solution was stirred at room temperature for 60 min. It was filtered and the solvent was evaporated to give a brown powder. ^1H NMR (300 MHz, $CDCl_3$, 25°C): $\delta = 3.34$ (br, 4H), 4.12 (br, 4H), 6.75 (d, 4H), 6.93 (t, 4H), 7.13 (s, 4H), 7.24 (d, 4H), 7.34 (t, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 64.6$, 110.0, 120.7, 122.3, 124.6, 129.9, 130.2, 154.0. Anal. calcd for $C_{32}H_{28}AgClO_8$: C, 56.30; H, 4.14. Found: C, 56.62; H, 4.58%.

Supporting information available

NMR spectra and theoretical calculations of *Z,Z*-**1** and *Z,Z*-**1**@Ag^+.

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(16) *Crystal structure analysis Z,Z*-**1**. Empirical formula $C_{32}H_{28}O_4$, MW = 476.54, $a = 12.7958(6)$, $c = 15.0174(8)$ Å, $V = 2458.8(2)$ Å^3, $T = 220(2)$ K, $\rho_{\mathrm{calcd}} = 1.287\ \mathrm{g\,cm^{-3}}$, $\mu = 0.088\ \mathrm{mm^{-1}}$, tetragonal, space group $P4_32_12$, $Z = 4$, STOE Imaging Plate Diffraction System (IPDS-1), Mo-K_α ($\lambda = 0.71073$ Å), 23,895 measured reflections in the range of $5° \leq 2\theta \leq 56°$, 1745 independent reflections used for refinement. $R_{\mathrm{int}} = 0.0685$. Structure solution was done with SHELXS-97. Structure refinement was performed against F^2 using SHELXL-97; 164 parameters, R_1 for 1581 reflections with $F_0 > 4\sigma(F_0) = 0.0333$, wR_2 for all reflections = 0.0866, GoF = 1.046, residual electron density 0.151/−0.162 e/Å^3. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealised geometry and refined isotropic using a riding model. The absolute structure cannot be determined. Therefore, Friedel opposites were merged in the refinement. X-ray data for compound Z,Z-**1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 680701. 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).

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