
**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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**To cite this Article** Darabi, Hossein Reza , Jadidi, Khosrow , Mohebbi, Ali Reza , Faraji, Laleh , Aghapoor, Kioumars , Shahbazian, Shant , Azimzadeh, Marjan and Nasseri, Sareh M.(2008) 'A Simple and Convenient Strategy for the Synthesis of Tolanophanes: Synthesis, Characterization and Conformational Analysis of a Novel Tolanophane', Supramolecular Chemistry, 20: 3, 327 — 333
**To link to this Article: DOI:** 10.1080/10610270701258642
**URL:** http://dx.doi.org/10.1080/10610270701258642

*Supramolecular Chemistry*, April–May 2008 Vol. 20 (3), pp. 327–333

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# A Simple and Convenient Strategy for the Synthesis of Tolanophanes: Synthesis, Characterization and Conformational Analysis of a Novel Tolanophane

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*(Received 23 December 2006; Accepted 3 February 2007)*



**The bromination/dehydrobromination of stilbenophanes as a practical, simple and efficient strategy is applied to the synthesis of tolanophanes 1a ($n = 2$) and 1b ($n = 4$). The method is significantly superior to the reported methods. A careful conformational study on a novel tolanophane 1b showed that the relative stability of its conformers is directly linked to both twist angle between the two arene rings and the orientation of the alkoxy groups. The strong interaction between 1b and $CDCl_3$ at −60°C is an unusual feature that is attributed to high restriction in its molecular motion.**

*Keywords*: Tolanophane; Stilbenophane; Bromination/dehydrobromination; Conformational restriction

## INTRODUCTION

Diphenylacetylenes (DPA) are fascinating building blocks for larger ethynylated aromatic systems. Many ethynylated aromatic systems, such as 1,4-bis(phenylethynyl) benzenes, display interesting structural, electronic, nonlinear optical, and luminescent properties [1,2]. The origin of many of these fascinating properties may be directly attributed to the relative orientation of the planar aromatic moieties [3–5]. Therefore, considering the low rotational barrier around the alkynyl-aryl single bond [6], the engineering control over the molecular conformation in DPAs is required. In this regard, the sterically constrained o,o′-alkoxy cyclic tolane, namely tolanophane **1**, is an excellent template to probe the relationship between the interannular angle of the phenyl rings and the spectroscopic properties [7,8].

The used methods for the synthesis of tolanophanes **1** are routes *a* and *b* as outlined in Scheme 1. Route *a* includes a Sonogashira coupling of terminal alkyne, followed by intramolecular Mitsunobu reaction [9]. Route *b* is a known ring-closing alkyne metathesis [8,10]. From the synthesis standpoint, the lack of general applicability, the use of harsh reaction conditions, time- and cost-consuming, tedious experimental procedures, and the disappointing or low yields of products are common drawbacks of both methods. Both methods have been widely employed in the synthesis of acyclic alkynes; however, examples are deficient in the synthesis of **1**.

Considering their interesting properties, together with their application in the construction of designed poly (phenyleneethynylenes) [11] and chemosensors [7], the development of an effective method for the synthesis of **1** [such as **1a** ($n = 2$) and **1b** ($n = 4$)] is still an important challenge. Moreover, to gain an understanding of the flexible nature of **1** ($n = 4$), and as well, to probe the influence of conformational restriction on its properties, the performance of an energy profile calculation with respect to the rotation around the CC triple bond is helpful.

## RESULTS AND DISCUSSION

### Synthesis and Properties

The synthetic strategy presented in this paper, as demonstrated in Scheme 1, is largely based on energetically difficult cyclization of the acyclic

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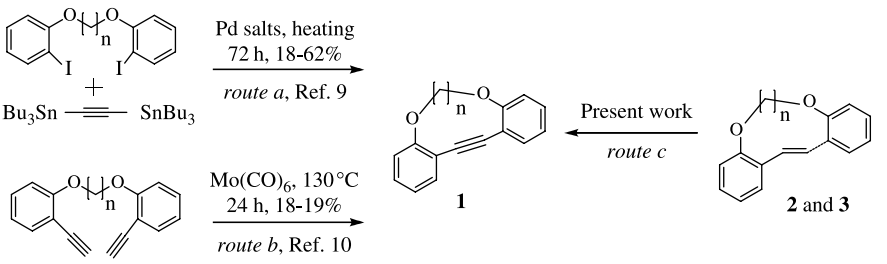
ISSN 1061-0278 print/ISSN 1029-0478 online © 2008 Taylor & Francis
DOI: 10.1080/10610270701258642




SCHEME 1 Synthetic routes for the preparation of **1**.

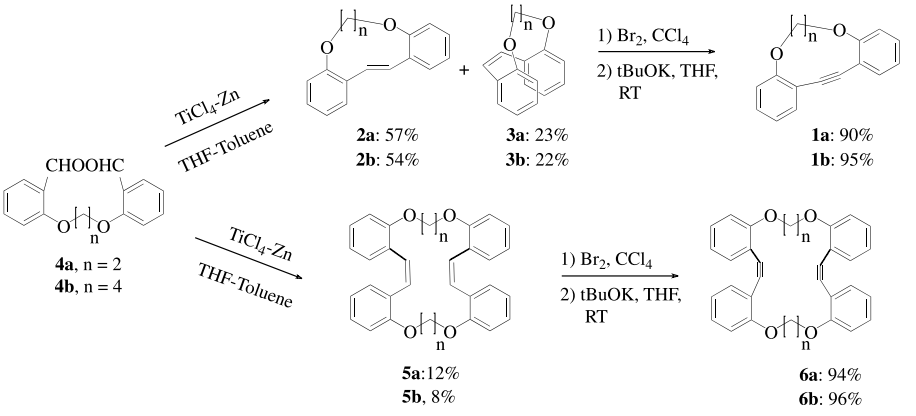
precursors in which the triple bond is introduced at the final reaction step. Perhaps the most obvious approach to the synthesis of cycloalkynes is the bromination/dehydrobromination of cycloalkenes which has been applied even to the synthesis of a variety of highly strained substrates such as nanorings [12–20]. In this context, we have taken the synthesis of the strained **1a** and less strained novel **1b** to show its superiority over the aforesaid methods. *Ab initio* calculations revealed these tolanophanes are stable enough to avoid undergoing ready addition of nucleophiles, thus allowing the application of the base promoted dehydrohalogenation method for constructing the triple bonds.

We achieved the synthesis of the (Z)- and (E)-stilbenophanes **2** and **3**, potential precursors to **1**, by a McMurry coupling reaction. A preliminary report from our laboratory has outlined a convenient high yielding synthetic method for the preparation of stilbenophanes [21–23]. Treatment of the corresponding dicarbaldehydes **4** with the low-valent titanium, prepared from $TiCl_4$ and Zn in THF, afforded geometric isomers of **2** and **3**, totally in 75–80% yields. As shown in Scheme 2, about 10% of isomeric mixture of **5a** and **5b** were also produced via a McMurry coupling of the two molecules of **4a** and **4b**, respectively.

The reaction of a crude mixture of **2** and **3** with bromine and subsequent treatment of the crude dibromide mixture with tBuOK furnished the tolanophanes **1a** and **1b** in quantitative yields. Similarly, tolanophanes **6a** and **6b** were prepared in quantitative yields from a mixture of isomers of **5a** and **5b**, respectively.

The structure of compound **2b** was confirmed by X-ray diffraction studies (Figs. 1 and 2). The crystal packing includes 16 molecules in which stilbene units overlap each other not only in a face-to-face interaction but in an edge-to-face interaction. Therefore, this crystal does not possess any open channels that result from the arrangement of the molecules. Like *E*-stilbenophanes **2** ($n = 3$) [22], an intramolecular weak C—H…O hydrogen bond (2.36 and 2.52 Å) in the structure of **2b** was observed, resulting from the possible pedal motion around aryl-alkene bond in molecule [24]. The angle between the planes formed by the two aromatic rings is 12.7°.

Cyclophanes **1**–**3** showed simple NMR spectra, confirming their symmetrical nature. The $^1$H NMR resonances for both aromatic and vinylic protons of *Z*-**3** appeared at higher field than those of *E*-**2**. A comparison of the carbon chemical shifts of tolanophane **1a** ($\delta = 95.4$ ppm) with **1b** ($\delta = 91.9$ ppm) shows a significant downfield shift of the sp carbons, suggesting the higher bending of triple bonds of **1a** due to its shorter alkyl moiety [25]. On the other hand, aromatic protons of **1a** appeared at $\delta = 7.09$–$7.39$ ($\Delta\delta = 0.30$ ppm), while for **1b** the




SCHEME 2 Synthesis of tolanophanes **1 and 6** via **4**.

| | |
|---|---|
| Empirical formula | $C_{18}H_{18}O_2$ |
| Formula weight | 266.32 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | a = 23.148(12) Å alpha = 90 deg. |
| | b = 7.173(4) Å beta = 98.89(5) deg. |
| | c = 35.41(2) Ågamma =90 deg. |
| Volume | 5809(5) $Å^3$ |
| Z, Calculated density | 16, 1.218 $Mg/m^3$ |
| Absorption coefficient | 0.078$mm^{-1}$ |
| F(000) | 2272 |
| Crystal size | 0.40 x 0.35 x 0.05mm |
| Theta range for data collection | 1.78 to 21.97 deg. |
| Limiting indices | $-24 \le h \le 24$, $-6 \le k \le 7$, $-36 \le l \le 25$ |
| Reflections collected / unique | 8108 / 3311 [R(int) = 0.0588] |
| Completeness to theta = | 21.97 93.1 % |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3311 / 0 / 361 |
| Goodness-of-fit on $F^2$ | 1.088 |
| Final R indices [I>2sigma(I)] | R1 = 0.0859, wR2 = 0.1913 |
| R indices (all data) | R1 = 0.1231, wR2 = 0.2125 |
| Largest diff. peak and hole | 0.428 and -0.302 e. $Å^{-3}$ |

FIGURE 1 Crystal data for colorless *E*-stilbenophane **2b**.

corresponding peaks expanded to $\delta = 6.93–7.43$ ($\Delta\delta = 0.50$ ppm), confirming the higher flexibility of **1b**.

While the NMR spectra of monomeric and dimeric tolanophanes (**1** and **6**) are very similar, the molecular ion peaks in the mass spectra ensure that the assignment was correct. Moreover, the carbon chemical shifts of tolanophanes **1a** and **1b** shows a significant downfield shift of the sp carbons compared to those of **6** [**6a:** $\delta = 90.1$ ($\Delta\delta = 5.3$ ppm), **6b:** $\delta = 89.8$ ($\Delta\delta = 2.1$ ppm)], respectively. It suggests the higher bending of triple bonds in **1a** and **1b** due to their smaller cavity than those of **6a** and **6b**, respectively.

## The Energy Profile Calculation on Molecular Conformations

Calculations have shown that twisting around the ethyne linkage from a planar to orthogonal geometry in the gas and solution phase requires 0.3 kcal/mol [6]. Therefore, the actual conformation is an equilibrium mixture of coplanar and orthogonal geometry which may be observed in crystal structure. To gain an understanding of the flexible nature of **1b**, we performed an energy profile calculation with respect to the rotation around the CC triple bond. In the attempt to grasp possible conformers **1b**, three local minima were located at both HF/3-21g(d) and B3LYP/6-31g(d) computational levels. Figure 3 offers the three optimum geometries at B3LYP/6-31g(d) level corresponding to the availability of three possible conformers in solution at room temperature which are labeled as "A", "B" and "C".

Table I contains their relative electronic as well as gas phase Gibbs free energies. Single point calculations at HF/6-311 + g(d)//HF/6-31g(d) and B3LYP/6-311 + g(d)//B3LYP/6-31g(d) levels did not change the main trends but sharpened the stability of "A".

To have a crude estimate on the role of intermolecular forces on stability trends the electric dipole moments of three conformers were also computed. Although there are almost large differences between electric dipole moments of the three conformers at HF/3-21g(d) level, these differences diminish by extending the basis set (HF/6-311 + g(d)) and taking into account the electron correlation effects (B3LYP/6-31g(d) and B3LYP 6-311 + g(d)).

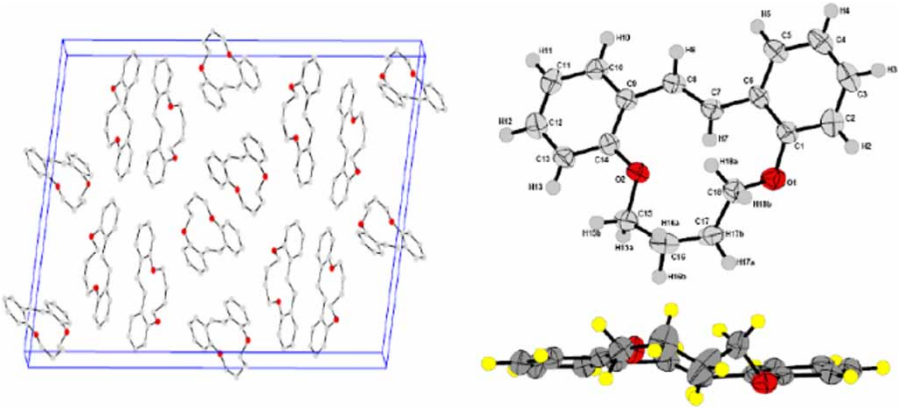


FIGURE 2 Ortep representation of the X-ray structure of compound **2b**. Left: Crystal packing; Right: plan view (top); side view (bottom).

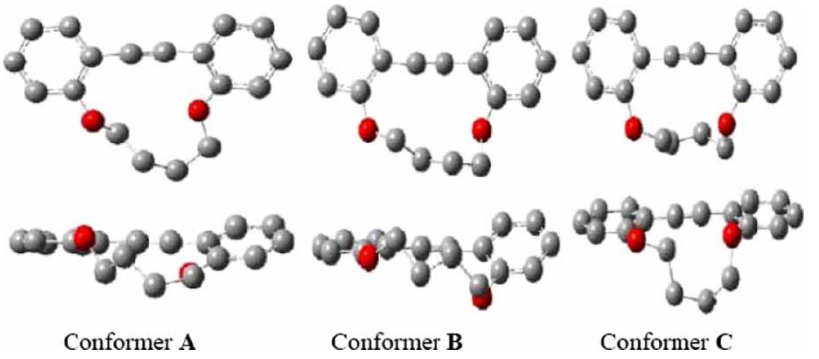



FIGURE 3 Two views of the optimized conformers of A, B and C related to tolanophane **1b**. The $\alpha$ values are 25°, 29° and 3°.



So, at our best computational level, B3LYP/6-311 + g(d), the difference does not exceed 0.2 Debye. This small difference may be interpreted as an evidence against the possibility of "qualitative" changes of stability trends due to intermolecular forces in dense phase (liquid form).

To check these results from another independent source and gain a deeper understanding of the structures of the cycle, theoretical NMR spectra were constructed employing GIAO methodology at HF/6-311 + g(d) level [26].

Although the experimental spectra has a simple structure consistent with an effective C2 symmetry, but the calculated theoretical spectra is more involved with several additional lines. This difference may be interpreted by assuming an internal dynamical process that makes the molecule to be an entity with $C_2$ symmetry. To confirm this assumption average $^1$H and $^{13}$C spectra were constructed.

Table II offers theoretical and the corresponding average as well as experimental $^1$H-NMR chemical shifts. In this average spectrum, the four ($CH_2$) groups of **1b** are classified into two sets, one contains the two central ($CH_2$) groups whereas the other one comprises the two ($CH_2$) groups attached to oxygen atoms (the TMS calculated hydrogen absolute chemical shift at HF/6-31g(d) computational level was employed as the reference in constructing the theoretical spectra).

In each set the "arithmetic mean" of chemical shifts has been compared with experimental values. As is evident from this table, without averaging the chemical shifts of $^1$H NMR spectra, there is large distribution of chemical shifts within each ($CH_2$) set irrelevant to simple structure of experimental spectra (with only two singlet lines), but the average chemical shifts within each set offers a striking similarity with experimental data.

As a result, the theoretical average $^1$H NMR chemical shifts of both conformers "A" and "B" are more in line with experimental chemical shifts. In this regard, the $^{13}$C NMR of sp carbons seems to be the best probe because its chemical shift reflects the related strain in the triple bonds due to bending, compared to its acyclic compound [25].

Table III offers theoretical $^{13}$C NMR chemical shifts and also the corresponding average chemical shift (arithmetic mean) of these carbons relative to same carbon atoms in acyclic 1,2-bis(2-methoxyphenyl)-ethyne **7**. Since theoretical chemical shifts of conformers of tolanophane **1b** and **7** were calculated at HF/6-311 + g(d) level, it is resonable to assume that error cancellation compensates for possible shortcomings of HF method.

As is clear from Table III, the agreement between experimental data and the theoretical average chemical shift of conformer "A" is striking. Since the average theoretical chemical shifts for other two conformers is considerably far from experimental value, so it seems that $^{13}$C NMR data confirms the dominance of conformer "A" in line with stability trend. On the other hand, since only the average

TABLE I Relative energies of the conformers of tolanophane **1b**[†]

| | Electronic energy | | | Gibbs free energy | | |
|---|---|---|---|---|---|---|
| Method/basis set | A | B | C | A | B | C |
| HF/6-31g(d) | 0 | 3.4 | 7.1 | 0 | 2.9 | 6.6 |
| B3LYP/6-31g(d) | 0 | 2.9 | 6.8 | 0 | 3.2 | 6.7 |
| HF/6-311 + g(d)[‡] | 0 | 4.3 | 9.6 | – | – | – |
| B3LYP/6-311 + g(d)[‡] | 0 | 3.6 | 7.5 | – | – | – |

[†] All energies are shown in Kcal.mol$^{-1}$. [‡]Single point calculations. The optimized geometries at B3LYP/6-31g(d) have been employed in these single point calculations. For basic statistical mechanics behind gas phase Gibbs free calculations see [27].

TABLE II Computed and experimental $^1$H-NMR chemical shifts (ppm) for ($CH_2$) groups of three conformers of **1b**

| | Chemical shifts (ppm) for ($CH_2$) groups[†] | | | | | |
|---|---|---|---|---|---|---|
| | Theoretical data | | Theoretical average | | Experimental | |
| Conformer | C | O | C | O | C | O |
| A | 1.66, 1.84<br>2.34, 2.37 | 3.70, 3.75<br>4.33, 5.47 | 2.05 | 4.31 | 2.09 | 4.26 |
| B | 1.26, 1.47<br>2.16, 3.38 | 3.88, 4.20<br>4.30, 4.38 | 2.07 | 4.19 | 2.09 | 4.26 |
| C | 1.21, 1.89<br>2.34, 2.48 | 3.83, 4.33<br>4.33, 4.35 | 1.98 | 4.21 | 2.09 | 4.26 |

[†] C is Central methylenes and O is O–attached carbons in **1b**.

TABLE III Computed and experimental $^{13}$C-NMR chemical shifts for bridge triple bonded carbon atoms of three conformers of **1b** (91.9 ppm) relative to **7** (89.7 ppm) [10]

| | Δδ between sp carbons of **1** and **7** (ppm) | | |
|---|---|---|---|
| Conformer | Calculated data | Calculated average | Experimental data |
| A | 2.68, 1.61 | 2.14 | 2.20 |
| B | 1.25, 0.18 | 0.71 | 2.20 |
| C | 1.61, 4.46 | 3.04 | 2.20 |

of computed chemical shifts for both $^{1}$H and $^{13}$C NMR conform with experimental NMR data, as have been discussed previously, some internal dynamical process must be present for conformer "A". In its simplest form, this internal motion possibly connects two local minima that correspond to left and right-handed form of conformer "A".

According to different levels of theory, it seems that the relative stability of these conformers is directly linked to both twist angle between the two arene rings and relative orientation of their alkoxy groups. The twisted forms of **1b** (conformers "A" and "B") compared to its planar form (conformer "C") are much more stable because they are considerably more distorted. On the other hand, the less stablility of "B" (about 3–4 kcal mol$^{-1}$) from "A" may be due to orientation of its alkoxy groups which are located at the same side of the molecule, where both alkoxy groups in "A" avoid each other. In this regard, the deformation of triple CC bond (the C(sp$^2$)—C(sp)—C(sp) bond angle) is increased from conformer "C" (~161°) to the conformer "B" (~168°) and then to the conformer "A" (~171°) and so, this regularity may also be invoked to justify the observed computational stability trend.

In terms of measurements of predominant conformation concerned with the molecular motion of **1b**, we also studied its NMR spectra at −60°C in $CDCl_3$. Tables IV and V list $^{1}$H and $^{13}$C NMR signals of **1b**. While the spectra pattern remained unchanged, a strong interaction between $CDCl_3$ and **1b** was observed.

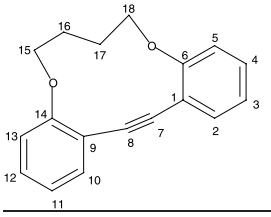
Most of the aromatic carbons of **1b** are in close contact with the $CDCl_3$. Signals of the aromatic carbons (Δδ), are shifted upfield at most in the magnitudes of 2.6 ppm. What is more interesting is the remarkably upfield shifts of carbon and hydrogen of $CDCl_3$ which is shifted upfield in the magnitudes of 23.5 ppm and 1.86 ppm, respectively. The phenomena can be ascribable to a strong intermolecular shielding effect in which the $CDCl_3$ axis is perpendicularly oriented to the plane of the benzene ring and pointed toward the center of the ring of benzene. Probably, the three chlore atoms are located over the $C_6$ axis and C-D bond points toward the benzene ring. So, it seems reasonable to assume that low temperatures cause a viscose medium, playing a significant role in hindering the torsional motion of the aryl groups.

In conclusion, we have demosnatrated a practical and efficient synthetic method which is significantly superior to the other reported methodologies. We also found that the relative stability of conformers **1b** is directly linked to not only twist angle between the two arene rings but the orientation of their alkoxy groups. Moreover, the NMR spectra of **1b** at −60°C showed an unusual feature that we attribute to high restriction in its molecular motion.

## EXPERIMENTAL SECTION

The experiments were conducted in flame-dried glassware under an inert atmosphere of argon unless otherwise noted. Melting points are determined on

TABLE IV $^{1}$H Chemical shift of **1b** at 25 and −60°C in $CDCl_3$




| | Chemical shifts (ppm) | | | | |
|---|---|---|---|---|---|
| | H1 | H2 | H3 | H4 | $CDCl_3$ |
| 25°C | 7.43 | 6.97 | 7.27 | 6.95 | 7.25 |
| −60°C | 7.42 | 7.01 | 7.38 | 6.97 | 5.39 |
| Δδ | 0.01 | 0.04 | 0.11 | 0.02 | 1.86 |

TABLE V $^{13}$C Chemical shift of **1b** at 25°C and −60°C in $CDCl_3$

| | Chemical shifts (ppm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 | $CDCl_3$ |
| 25°C | 161.1 | 115.1 | 131.2 | 121.4 | 129.6 | 114.9 | 91.9 | 70.6 | 26.6 | 77.0 |
| −60°C | 160.1 | 112.5 | 129.8 | 121.1 | 129.3 | 112.3 | 91.6 | 68.9 | 25.9 | 53.6 |
| Δδ | 1.0 | 2.6 | 1.4 | 1.4 | 0.3 | 2.6 | 0.3 | 1.7 | 0.7 | 23.4 |

Büchi 530 and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 300 and 500. All NMR samples were run in $CDCl_3$ and chemical shifts are expressed as ppm relative to internal $Me_4Si$. Infrared spectra (IR) were observed on FT-IR Mattson 1000 spectrometer. 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. The solvents and reagents used in each experiment were dried and purified according to accepted procedures. Salicylaldehyde, $TiCl_4$, HMPA, bromine, potassium tert-butoxide, 1,2-dibromoethane and 1,4-dibromobuthane all are commercially available and used without further purification.

### Synthesis of Stilbenophanes 2b, 3b and 5b by the McMurry Coupling of Dialdehyde 4b

To a stirred suspension of Zinc powder (502 mg, 8 mmol) in 25 ml dry THF, $TiCl_4$ (0.44 mL, 4 mmol) was injected slowly at 0°C. The mixture was gradually brought to room temperature and subsequently refluxed for 2 h. Then a solution of dialdehyde **4b** (298 mg, 1 mmol) in 10 ml of dry THF was added dropwise to the resulting dark brown solution at room temperature. The reaction mixture was stirred at reflux temperature. After disappearance of the substrate (TLC), the reaction mixture was treated with aq $K_2CO_3$ (10%) and stirred open to the atmosphere until oxidation of the titanium was completed (off-white suspension). The mixture was filtrated and the organic layer was separated. The aqueous suspension was extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and evaporated to afford the crude product. From the crude product, a mixture of trans/cis monomers **2b** and **3b** was separated from isomeric mixtures of dimer **5b** by flash chromatography on silica gel using a 1:9 mixture of ethyl acetate and hexane. In a further purification, the E isomer **2b** was separated by recrystallization from ethyl ether, while the Z isomer **3b** was purified by preparative thin-layer chromatography (PTLC) (silica gel; EtOAc-hexane, 1:9). The yield of each product is: E isomer **2b** (143 mg, 54%), Z isomer **3b** (58 mg, 22%) and dimer **5b** (45 mg, 8%).

Note that the above procedure is also applied for the synthesis of **2a** (136 mg, 57%), **3a** (55 mg, 23%) and **5a** (29 mg, 12%) via a McMurry coupling of the two molecules of **4a** [28].

It is noteworthy that the above crude products can be directly utilized for the preparation of the tolanophanes **1** and **6**, respectively, without the need for column chromatographic purification of any of the isomers.

Physical and spectral data for each compound follow:

#### *E-Stilbenophane 2b*

Colorless needles, mp: 135°C; $^1$H NMR (300 MHz, $CDCl_3$) δ 2.06 (m, 4H), 4.16 (m, 4H), 7.00 (d, 2H), 7.05 (t, 2H), 7.20 (t, 2H), 7.34 (s, 2H), 7.41 (d, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 26.02 (t), 71.82 (t), 118.19 (d), 122.75 (s), 128.06 (d), 128.20 (d), 128.22 (d), 129.91 (d), 157.60 (s); MS (EI), m/z (rel. Intensity %) 266 ($M^+$, 45), 181 (34), 165 (56), 55 (100).

#### *Z-Stilbenophane 3b*

Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$) δ 1.82 (s, 4H), 4.11 (s, 4H), 6.73 (s, 2H), 6.75–6.82 (m, 4 H), 6.99–7.12 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 25.0, 68.3, 113.5, 119.5, 126.6, 127.9, 128.3, 129.4, 154.4; MS (EI), m/z (rel. Intensity %) 266 (M + , 45).

### Synthesis of Tolanophane 1b

To a stirred mixture of **2b** and **3b** (133 mg, 0.50 mmol) in 15 ml of $CCl_4$ was added dropwise a solution of bromine in $CCl_4$. The red color of the solution fades gradually to a pale yellow during about 30 min. More bromine was added until a permanent red color indicates a slight excess of bromine in the flask. The reaction mixture was quenched by a dilute solution of sodium thiosulfate and then washed with water. The organic layer was dried over anhydrous sodium sulfate and evaporated to afford the dibromide quantitatively.

To a cooled mixture of crude dibromide (215 mg, 0.50 mmol) in THF (15 ml) was added, in portions, tBuOK (130 mg, 1.2 mmol). After being stirred for 90 min, the mixture was quenched with distilled water. The organic layer was separated, dried over anhydrous sodium sulfate and evaporated. A flash column chromatography on silica gel (ethyl acetate: hexane; 2:8) afforded pure product **1b** (125 mg, 95%).

Note that the above procedure was conducted on a mixture of **2a** and **3a** (119 mg, 0.50 mmol) and obtained **1a** (106 mg, 90%).

#### *Tolanophane 1a*

Colorless solid, $^1$H NMR (300 MHz, $CDCl_3$) δ 4.45 (s, 4H), 7.09 (d, 2H), 7.13 (t, 2H), 7.28 (t, 2H), 7.39 (dd, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 73.7 (t), 95.4 (s), 117.0 (d), 122.2 (s), 123.8 (d), 129.8 (d), 129.9 (d), 162.5 (s). MS (EI), m/z (rel. Intensity %) 236 ($M^+$, 80).

#### *Tolanophane 1b*

Colorless viscous oil, $^1$H NMR (300 MHz, $CDCl_3$) δ 2.09 (t, 4H), 4.26 (t, 4H), 6.93 (d, 2H), 6.97 (t, 2H), 7.27 (m, 2H), 7.43 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 26.59 (t), 70.64 (t), 91.89 (s), 114.85 (d), 115.11 (s), 121.44 (d), 129.58 (d), 131.17 (d), 161.10 (s). IR

(KBr, $cm^{-1}$) 3030, 2936, 2836, 1592, 1484, 1448, 1254, 1096, 1014, 751. MS (EI), m/z (rel. Intensity %) 264.2 ($M^+$, 100), 221 (45), 181 (36), 152 (24).

The same procedure was separately conducted on the isomeric mixture of **5a** (48 mg, 0.1 mmol) and **5b** (53 mg, 0.1 mmol) and gave **6a** (45 mg, 94%) and **6b** (51 mg, 96%), respectively.

### *Tolanophane 6a*

Colorless solid, $^1$H NMR (300 MHz, $CDCl_3$) δ 4.56 (s, 8H), 6.91 (d, 4H), 6.95 (d, 4H),7.24 (t, 4H), 7.46 (dd, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 68.7 (t), 90.1 (s), 114.2 (d), 114.9 (d), 121.6 (s), 129.5 (d), 133.5 (d), 159.4 (s). MS (EI), m/z (rel. Intensity %) 472 ($M^+$, 10).

### *Tolanophane 6b*

Colorless solid, $^1$H NMR (300 MHz, $CDCl_3$) δ 4.56 (s, 8H), 6.91 (d, 4H), 6.95 (d, 4H),7.24 (t, 4H), 7.46 (dd, 4H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 26.0 (t), 68.9 (t), 89.8 (s), 113.0 (d), 113.7 (d), 120.6 (s), 129.4 (d), 133.7 (d), 159.4 (s). MS (EI), m/z (rel. Intensity %) 528 ($M^+$, 10).

### *Supplementary Material*

X-ray data for compound **2b** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 608894. 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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