Synthesis and Optoelectrochemical Properties of Stilbenophanes Having Carbazole Moieties

Perumal Rajakumar,*a Karuppannan Sekar,^b Nagarathinam Venkatesan^a

^a Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India Fax +91(44)22352492; E-mail: perumalrajakumar@gmail.com

^b Department of Chemistry, Anna University Constituent College Dindigul, Dindigul 624 622, India

Received: 20.07.2012; Accepted after revision: 06.09.2012

Abstract: A series of stilbenophanes having N-arylated carbazole moieties possessing small and large cavities have been synthesized via McMurry coupling of the corresponding dialdehyde derived from N-arylation of carbazole with various dibromide followed by formylation. The electrochemical, photophysical, and complexation properties of all the stilbenophanes with electron-deficient guest molecules like TCNQ, TCNE, and PQT were also carried out at different concentrations.

Key words: carbazole, stilbenophanes, fluorescence, redox potential

In cyclophanes,¹ the π -electron-rich subsystems when placed in the close proximity in parallel arrangement can form intense intramolecular electronic interactions,² both through bonds as well as through space. Carbazole is a well-known π -electron-rich chromophore which can act as a good photoconducting material due to the strong electron-donating ability of the nitrogen atom. Carbazolebased supramolecule systems are finding growing applications in the field of electronics and optoelectronics^{3,4} including organic light-emitting diodes (OLED)^{5,6} and solar cells.7 Though various carbazole-based oligomers and polymers are reported in the literature, very few examples are known of carbazole-based cyclophanes, including diethynylcarbazole macrocycles with solar-cell properties,⁸ fluorescent nanofibril film,9 carbazole-linked fullerene (C_{60}) ¹⁰ carbazolopyridinophane,¹¹ macromolecules^{12–15} containing carbazole and its derivatives, have attracted considerable interest on account of their unique electrooptical properties, which make such molecules potential candidates for diverse applications in photoluminescence and chemoluminescence. Recently, Chen et al.¹⁶ reported stilbene-like carbazole dimer-based electroluminescent materials for OLEDs. The McMurry reaction is an effective way to form a C=C bond under moderate conditions and has been employed to form conjugated cyclophanes in few cases.^{17,18} Though the intermolecular¹⁹ and intramolecular²⁰ McMurray coupling reaction in cyclophane chemistry is well documented, to the best of our knowledge, no carbazole-based conjugated stilbenophanes with large cavities have been reported so far. We report herein the design, synthesis, and characterization of

SYNLETT 2012, 23, 2504–2510 Advanced online publication: 28.09.2012

DOI: 10.1055/s-0032-1317324; Art ID: ST-2012-B0610-L

© Georg Thieme Verlag Stuttgart · New York

a new type of conjugated shape-persistent stilbenophane derivatives 1-5 (Figure 1) using various aromatic spacer units through McMurry olefination reaction. The electrochemical and photophysical properties of the all the stilbenophanes were also carried out.

The synthetic pathway leading to stilbenophanes 1-5 having N-arylated carbazole moieties is outlined in Scheme 1. The McMurry reaction, in these cases, led to the reductive coupling of two carbonyl groups to form intermolecular dimerization products. The N-arylation of dibromides **6**– **10** with 2.2 equivalents of carbazole in the presence of CuI, 1,10-phenanthroline, and K₂CO₃ in *p*-xylene afford-



Scheme 1 Reagents and conditions: i) carbazole (2.2 equiv), CuI, K_2CO_3 , 1,10-phenanthroline, *p*-xylene, 180 °C, 48 h, 11a (82%), 11b (73%), 12 (85%), 13 (60%), 14 (53%), 15 (72%); ii) POCl₃, DMF, DCE, reflux, 12 h, 16a (72%), 16b (67%), 17 (44%), 18 (48%), 19 (56%), 20 (51%); iii) TiCl₄ (20 equiv), Zn (40 equiv), pyridine (2 drops), THF, reflux, 12 h, 1a (18%), 1b (15%), 2 (17%), 3 (15%), 4 (12%), 5 (15%).



Figure 1 Structures of the shape-persistent stilbenophanes 1-5

ed biscarbazole compounds **11–15** in 82%, 73%, 85%, 60%, 53%, and 72% yields, respectively.

The ¹H NMR spectrum of the biscarbazole $11a^{21}$ showed a three-proton singlet at $\delta = 1.63$ ppm for the methyl protons, and two sets of three-proton triplet at $\delta = 7.30$ ppm (J = 7.5 Hz) and $\delta = 7.44$ ppm (J = 7.8 Hz) for the protons at 2-, 3- and 6-, 7-position of the carbazole unit, a singlet at $\delta = 7.62$ ppm for inner proton of the *m*-xylyl unit in addition to the other carbazole protons. In the ¹³C NMR spectrum, biscarbazole compound **11a** showed methyl carbon at $\delta = 21.6$ ppm, in addition to ten peaks in the aromatic region. Further, the structure of the biscarbazole compound **11a** was confirmed by the appearance of the molecular ion peak at m/z = 422 in the mass spectrum (EI) and from elemental analysis. Similarly, the structure of the biscarbazole compound **11b–15** was also confirmed from spectroscopic and elemental analysis. Formylation of biscarbazole **11–15** using POCl₃–DMF in DCE under refluxing conditions gave dialdehyde **16–20** in 72%, 67%, 44%, 48%, 56%, and 51% yields, respectively.

The ¹H NMR spectrum of the dialdehyde **16a**²² showed a singlet at $\delta = 1.65$ ppm for the methyl protons, and a oneproton singlet at $\delta = 7.26$ ppm for the inner proton of the *m*-xylyl unit, a singlet at $\delta = 10.13$ ppm for aldehyde protons in addition to the aromatic protons. In the ¹³C NMR spectrum, dialdehyde **16a** showed a methyl carbon at $\delta =$ 21.6 ppm, an aldehydic carbon at $\delta = 191.6$ ppm in addition to 15 signals in the aromatic region. The mass spectrum (EI) of the dialdehyde **16a** showed a peak at *m*/*z* = 478 corresponding to the molecular ion. Further, the structures of the dialdehydes **16b–20** were confirmed by spectroscopic and elemental analysis.

Addition of the dialdehyde 16-20 to a solution of 20 equivalents of TiCl₄ and 40 equivalents of Zn in THF followed by refluxing for 12 hours resulted in the formation of aromatic stilbenophanes 1-5 in 18%, 15%, 17%, 15%, 12%, and 15% yields, respectively. The ¹H NMR spectrum of the stilbenophane $1a^{23}$ (Figure 2) showed a sixproton singlet at $\delta = 2.48$ ppm for the methyl protons, a four-proton singlet at $\delta = 6.83$ ppm for olefinic protons, and a two-proton singlet at $\delta = 7.57$ ppm for the inner proton of the *m*-xylyl unit in addition to the other aromatic protons. In the ¹³C NMR spectrum, stilbenophane 1a showed a methyl carbon at $\delta = 21.5$ ppm, in addition to 17 peaks in the aromatic region. Further, the structure of the carbazolostilbenophane 1a was confirmed from the appearance of the molecular ion peak at m/z = 894 in the FAB mass spectrum. Similarly, the structure of the stilbenophane 1b-5 is also confirmed from spectral and analytical data.²⁴⁻²⁸ The ¹H NMR spectrum of the stilbenophanes 1–5 shows a single peak at $\delta = 6.81-6.87$ ppm, which shows that all the stilbenophanes exist as the *cis*-isomers in CDCl₃ solution.

The initial geometries of *cis* and *trans* isomers of **1a** were built using GaussView.²⁹ These geometries (*cis* and *trans*) were optimized using density functional theory³⁰ (DFT)based Becke's three-parameter hybrid exchange and Lee– Yang–Parr correlation^{31,32} (B3LYP) functional employing 6-31G* basis set. The geometry optimizations were carried out without any geometrical constrains. To ensure the optimized geometries correspond to true minima in potential energy surface, vibrational frequencies were computed using DFT (B3LYP/6-31G*) level for both the isomers. All these calculation were carried out using Gaussian 09 package.³³

The optimized structures and their corresponding energy values of *cis* and *trans* isomers of **1a** are shown in Figure



Figure 2 ¹H NMR spectrum (CDCl₃, 300 MHz) of stilbenophanes 1a

3. The calculated minimized energy difference between *cis* and *trans* isomer is 4.99 kcal/mol. Further the calculated HOMO–LUMO energy difference for the *cis* and *trans* isomers are 4.00 and 3.71 eV, respectively. The results obtained from the molecular orbital calculations further reinforce that the *cis* isomer is more stable than the *trans* isomer, which is in good agreement with the experimental findings.

The photophysical properties of the stilbenophane derivatives 1-5 were examined by UV-vis and fluorescence spectroscopic techniques in CH₂Cl₂. The absorption and emission spectra of the compounds in CH₂Cl₂ are shown in Figure 4 and Figure 5. In general, absorption spectra of all the stilbenophanes exhibited two absorption bands, a strong absorption band ranged at $\lambda = 294-348$ nm being assigned to the π - π * local electron transition of the carbazole and aromatic spacer unit and a less intense absorption band at longer wavelength ranged at $\lambda = 338-378$ nm, which was assigned to $\pi - \pi^*$ transition of the carbazole-dimer core of the stilbenophane.¹⁶ Stilbenophanes 1a, 1b, 2, and 4 with spacer units such as benzene, anisole, pyridine, and carbazole have no significant shift in the absorption band. However, due to the presence of thiophene and fluorene spacer units in stilbenophane 3 and 5 a red-shift was observed along with their increasing intensity which is due to high electron-donating ability and the extent of π -conjugation length in the cyclophanes.³⁴

Photoluminescence (PL) spectra of all the stilbenophanes 1–5 were recorded, and a strong absorption was observed at $\lambda = 294-348$ nm with a broad band located in the region at $\lambda = 391-589$ nm (blue to greenish region), and their emission maxima were significantly red-shifted with altering the spacer units such as carbazole, thiophene, and

fluorene. This is may be an effective π -conjugation in the cyclophanes (Table 1). The broad absorption and emission spectra show no vibrational bands in the absorption spectra of the cyclophanes and less shift value of nearly



Figure 3 The optimized geometries and energy values of *cis* and *trans* isomer (hydrogen atoms are omitted for clarity; gray color for carbon and blue color for nitrogen). a) Relative energy (*cis* isomer) = 0.00 kcal/mol, HOMO–LUMO gap = 4.00 eV. b) Relative energy (*trans* isomer) = 4.99 kcal/mol, HOMO–LUMO gap = 3.71 eV

100 nm between the absorption and emission wavelength maxima, which shows that the stilbenophanes have high rigidity and planarity.³⁵

Table 1 Optical Properties of	of Stilbenophanes 1–5
-------------------------------	-----------------------

Stilbenophane	$\lambda_{max} (nm)^a$ Absorption (nm)	Emission (nm)
1a	298, 340	425 ^b
1b	299, 338	427 ^b
2	294, 338	391 ^b
3	328, 359	526 ^c
4	305, 342	467 ^d
5	348, 378	589 ^e

^a All the spectra were recorded at 1×10^{-5} M in CH₂Cl₂.

^b Excited at $\lambda = 294$ nm.

^c Excited at $\lambda = 330$ nm.

^d Excited at $\lambda = 305$ nm.

^e Excited at $\lambda = 348$ nm.



Figure 4 UV-vis absorption of stilbenophanes 1–5 in CH_2Cl_2 (1×10⁻⁵ M solution)



Figure 5 Photoluminescence spectra of stilbenophanes 1–5 in CH_2Cl_2 (1×10⁻⁵ M solution) excited in the range of $\lambda = 294-348$ nm

Half-wave redox potentials vs. Ag/AgCl of the stilbenophanes 1–5 were obtained by cyclic voltammetry in CH_2Cl_2 at room temperature (scan rate: 100 mV/s, supporting electrolyte: *n*-Bu₄NPF₆, Pt as a working and a counter electrode). All the carbazolophanes exhibited one set of redox waves corresponding to the carbazole moiety attached to the aromatic spacer units (Figure 6). Usually stilbene-like carbazole dimer exhibits¹⁶ two reversible one-electron redox waves which show some electronic communication between two carbazole moieties and cause them to oxidize separately. However, stilbenophanes 1–5 exhibit only one set of redox quasi-reversible waves, which shows each carbazole unit is electronically isolated from the other carbazole molecules.

Compared with ferrocence (for which we found the difference between the anodic and cathodic peaks, $\Delta E_p = 74 \text{ mv}$ vs. Ag/AgCl in CH₂Cl₂ at room temperature), all the redox processes of the stilbenophanes **1–5** are quasi-reversible. The redox potentials are found to be different ranging between 580–690 mV (Table 2) due to various spacer units present in the molecules. In the presence of heterocyclic spacer units like pyridine, carbazole, and thiophene the redox potential decreases when compared to the benzene spacer units. Such low redox-potential behavior may be useful for electrochemical sensor studies of various electron-deficient guest molecules.

Table 2 Electrochemical Parameters Obtained for the Cyclophanes in $\rm CH_2Cl_2$ at 25 $^{\circ}\rm C$

Carbazolophane	$E^{1}_{1/2} (mV)^{a}$	$\Delta E_{p}^{-1} (mV)$	
1a	640	240	
1b	630	210	
2	580	200	
3	600	160	
4	590	190	
5	690	200	

^a $E^{1}_{1/2}$ is the average of the cathodic and anodic peak potential of the redox process. ΔE^{1}_{p} is the difference between the cathodic and anodic peak potential of the redox process.

Table 3 Complexation of TCNQ with Stilbenophanes 1-5

Carbazolophane	$K_{\rm a} ({\rm mol^{-1}}{\rm dm^3})$	$\epsilon (M^{1} \text{cm}^{1})$
1a	2.00×10 ⁴	2.50×10 ⁵
1b	3.37×10 ⁴	3.33×10 ⁵
2	5.00×10 ⁴	2.00×10 ⁵
3	4.00×10^{4}	2.50×10 ⁵
4	5.00×10 ³	2.00×10^{6}
5	4.00×10 ³	2.50×10^{6}



Figure 6 Cyclic voltammograms of stilbenophanes 1a (a) and 3 (b) in CH₂Cl₂ (1×10⁻⁵ M solution)

The charge-transfer complexation behavior of the carbazolostilbenophanes 1-5 guest molecules like TCNQ, TCNE, and PQT was then investigated.³⁶ The stilbenophanes having carbazole moiety showed UV-vis absorption maxima in the range of $\lambda = 338-378$ nm in MeCN-CH₂Cl₂ medium, respectively. However, the acceptors TCNQ, TCNE, and PQT showed absorption maxima at λ = 286.8, 274.0, and 263.0 nm, respectively, in the same solvent medium. Stilbenophanes 1a,b, 2-5 form chargetransfer complexes with TCNQ as evidenced by the appearance of absorption maxima at $\lambda = 410, 425, 412, 428$, 434, and 512 nm, respectively. The equilibrium constant for the charge-transfer complex was determined by the Benesi-Hildebrand equation.³⁷ From the stability constant, it is clear that 2 and 3 complexes more strongly with TCNQ than the stilbenophanes 1a, 1b, 4, and 5 (Table 3).

Among the stilbenophanes 1–5, small cavity cyclophanes 1–3 form charge-transfer complexes with TCNE as evi-

denced by the absorption maxima at $\lambda = 417$, 426, 428, and 431 nm, respectively. The stability constant for the formation of the charge-transfer complex of **1–3** with TCNE is 4.28×10^3 , 2.60×10^4 , 1.2×10^4 , and 3.22×10^4 mol⁻¹ dm³. When such experiments were carried out with PQT, charge-transfer complexation did not occur.

Table 4 Benesi–Hildebrand Treatment Data of the CT ComplexFormed between the Stilbenophane 2 and TCNQ $(\lambda_{max} = 412 \text{ nm})^{a,b}$

Concentration of the guest [A] (M)	Absorbance [A ₀]	[D]/A ₀ M	1/[A] (M)
0.0000049	0.306	3.267×10 ⁻⁵	204081
0.0000098	0.454	2.188×10 ⁻⁵	102040
0.0000147	0.695	1.439×10 ⁻⁵	68027
0.0000196	0.922	1.084×10 ⁻⁵	51020
0.0000245	0.954	1.048×10 ⁻⁵	40816

^a Concentration of cyclophane [D] $\mathbf{2} = 10^{-5}$ M

^b $K_{\rm a} = 5.00 \times 10^4 \text{ M}^{-1}$, $\varepsilon = 2.00 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, SD = 97.35%.



Figure 7 Plot between 1/[A] and $[D]/[A_0]$ for stilbenophane 2

In conclusion, conjugated stilbenophanes 1–5 are readily synthesized in a single step via tandem intermolecular McMurry coupling reaction with alternating cavity size. Preliminary electrochemical, photophysical, and complexation studies shows this type of aromatic stilbenophanes are useful candidates for further development of organic light emitting diodes (OLED) and organic solar cells (OSC). Further synthesis of similar stilbenophanes and detailed investigations of the complexation behavior with electron-deficient guest molecules are in progress.

Acknowledgment

K.S. thanks CSIR-New Delhi for providing SRF. The authors thank V. Rajapandian and Dr. V. Subramanian, Chemical Laboratory, CSIR-CLRI, Adyar, Chennai-20 for molecular orbital calculations. The authors thank CSIR-New Delhi, for financial assistance, DST-FIST for providing NMR facility to the department and SAIF-CDRI Lucknow for providing mass spectral data.

References and Notes

- For an excellent recent monograph, see: *Modern Cyclophane Chemistry*; Gleiter, R.; Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004.
- (2) For a recent review, see: Tusji, T. In Modern Cyclophane Chemistry; Gleiter, R.; Hopf, H., Eds.; Wiley-VCH: Weinheim, 2004, 81–104.
- (3) Morin, J.-F.; Leclere, M.; Adés, D.; Siove, A. *Macromol. Rapid Commun.* **2005**, *26*, 761.
- (4) Wong, K.-T.; Hung, T.-H.; Chao, T.-C.; Ho, T.-I. *Tetrahedron Lett.* 2005, 46, 855.
- (5) Adhikari, R. M.; Mondal, R.; Shah, B. K.; Neckers, D. C. J. Org. Chem. 2007, 72, 4727.
- (6) Promarak, V.; Ichikawa, M.; Meunmart, D.; Sudyoadsuk, T.; Saengsuwana, S.; Keawin, T. *Tetrahedron Lett.* 2006, 47, 8949.
- (7) Ning, Z.; Zhang, O.; Wu, W.; Pei, H.; Liu, B.; Tian, H. J. Org. Chem. 2008, 73, 3791.
- (8) Zhao, T.; Liu, Z.; Song, Y.; Xu, W.; Zhang, D.; Zhu, D. J. Org. Chem. 2006, 71, 7422.
- (9) Naddo, T.; Che, Y.; Zhang, W.; Balakrishnan, K.; Yang, X.; Yen, M.; Zhao, J.; Moore, J. S.; Zang, L. J. Am. Chem. Soc. 2007, 129, 6978.
- (10) Nakamura, Y.; Suzuki, M.; Imai, Y.; Nishimura, J. Org. Lett. 2004, 6, 2797.
- (11) Brown, A. B.; Gibson, T. L.; Clayton Baum, J.; Ren, T.; Smith, T. M. Sens. Actuators, B 2005, 110, 8.
- (12) Sanda, F.; Nakai, T.; Kobayashi, N.; Masuda, K. Macromolecules 2004, 37, 2703.
- (13) Morin, J. F.; Leclerc, M.; Ades, D.; Siove, A. Macromol. Rapid Commun. 2005, 26, 761.
- Brunner, K.; Dijken, A. V.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. J. Am. Chem. Soc. 2004, 126, 6035.
- (15) Cabaj, J.; Idzik, K.; Soloducho, J.; Chyla, A. *Tetrahedron* 2006, 62, 758.
- (16) Chen, C.-H.; Lin, J. T.; Yeh, M.-C. P. *Tetrahedron* **2006**, *62*, 8564.
- (17) Chung, M.-K.; Qi, G.; Stryker, J. M. Org. Lett. 2006, 8, 1491.
- (18) Chen, H.-B.; Yin, J.; Wang, Y.; Pei, J. Org. Lett. **2008**, 10, 3113.
- (19) Hopf, H.; Mlynek, C. J. Org. Chem. 1990, 55, 1361.
- (20) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P. *Tetrahedron Lett.* 1995, *36*, 1239.
- (21) Compound 11a
 - White solid; yield 82%; mp 110–112 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.63$ (s, 3 H), 7.30 (t, 4 H, J = 7.5 Hz), 7.44 (t, 4 H, J = 7.8 Hz), 7.51–7.56 (m, 6 H), 7.62 (s, 1 H), 8.15 (d, 4 H, J = 7.8 Hz). ¹³C NMR (75 MHz, CDCl₃): $\delta = 21.6$, 109.8, 120.2, 120.5, 122.5, 123.6, 126.1, 126.6, 139.2, 140.7, 141.7. MS (EI): m/z = 422 [M⁺]. Anal. Calcd (%) for C₃₁H₂₂N₂: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.24; H, 5.34; N, 6.78.

(22) Dialdehyde 16a

- White solid; yield 72%; mp 102–104 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.65$ (s, 3 H), 7.26 (s, 1 H), 7.38–7.43 (m, 2 H), 7.52–7.59 (m, 8 H), 7.99 (dd, 2 H, J = 8.6, 1.2 Hz), 8.22 (d, 2 H, J = 7.5 Hz), 8.68 (s, 2 H), 10.13 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 21.6, 110.0, 110.3, 120.9, 121.6, 122.7, 123.4, 123.9, 127.3, 127.5, 127.7, 129.8, 138.4, 141.6, 142.6, 144.2, 191.6. MS (EI): <math>m/z = 478$ [M⁺]. Anal. Calcd (%) for C₃₃H₂₂N₂O₂: C, 82.83; H, 4.63; N, 5.85. Found: C, 82.96; H, 4.72; N, 5.94.
- (23) Stilbenophane 1a White solid; yield 18%; mp 172–173 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.48 (s, 6 H), 6.83 (s, 4 H), 7.18 (d, 4 H,

© Georg Thieme Verlag Stuttgart · New York

 $J = 8.4 \text{ Hz}, 7.27-7.43 \text{ (m, 16 H)}, 7.49 \text{ (d, 4 H, } J = 8.1 \text{ Hz}), 7.57 \text{ (s, 2 H)}, 8.01 \text{ (s, 4 H)}, 8.08 \text{ (d, 4 H, } J = 7.5 \text{ Hz}). ^{13}\text{C}$ NMR (75 MHz, CDCl₃): $\delta = 21.5$, 109.4, 109.8, 120.2, 120.4, 121.4, 122.1, 123.4, 123.6, 126.0, 126.3, 126.7, 129.4, 130.0, 138.8, 139.5, 140.5, 141.6. MS–FAB: $m/z = 894 \text{ [M^+]}$. Anal. Calcd (%) for C₆₆H₄₄N₄: C, 88.76; H, 4.97; N, 6.27. Found: 88.92; H, 4.82; N, 6.42.

(24) Stilbenophane 1b

White solid; yield 15%; mp 164–166 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.43 (s, 6 H), 3.63 (s, 6 H), 6.84 (s, 4 H), 7.14 (d, 4 H, *J* = 8.3 Hz), 7.22–7.39 (m, 16 H), 7.47 (d, 4 H, *J* = 8.1 Hz), 8.02 (s, 4 H), 8.06 (d, 4 H, *J* = 7.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ = 21.2, 52.8, 109.6, 109.9, 120.1, 120.6, 121.7, 122.4, 123.7, 123.9, 126.0, 126.4, 126.9, 129.7, 130.3, 138.7, 139.4, 140.5, 151.2. MS–FAB: *m/z* = 954 [M⁺]. Anal. Calcd (%) for C₆₈H₄₈N₄O₂: C, 85.69; H, 5.08; N, 5.88. Found: C, 85.82; H, 5.22; N, 5.98.

(25) Stilbenophane 2

White solid; yield 17%; mp 186–187 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.81$ (s, 4 H), 7.18 (d, 4 H, J = 8.3 Hz), 7.24–7.40 (m, 12 H), 7.47 (d, 4 H, J = 8.1 Hz), 7.63 (d, 4 H, J = 6.7 Hz), 7.87 (t, 2 H, J = 6.8 Hz), 8.04 (s, 4 H), 8.10 (d, 4 H, J = 7.6 Hz). ¹³C NMR (75 MHz, CDCl₃): $\delta = 109.8$, 110.4, 116.7, 120.2, 120.5, 121.6, 122.2, 123.6, 126.2, 126.6, 129.8, 130.4, 138.8, 139.6, 140.6, 151.6 MS–FAB: m/z = 868 [M⁺]. Anal. Calcd (%) for C₆₂H₃₈N₆: C, 85.89; H, 4.42; N, 9.69. Found: C, 85.72; H, 4.30; N, 9.60.

(26) Stilbenophane 3

White solid; yield 15%; mp 191–193 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.85$ (s, 4 H), 7.23–7.47 (m, 20 H), 7.64 (d, 4 H, J = 6.9 Hz), 7.99 (s, 4 H), 8.08 (d, 4 H, J = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃): $\delta = 109.8$, 110.4, 120.3, 121.1, 121.4, 122.6, 123.8, 123.8, 126.4, 126.8, 129.5, 130.7, 136.0, 140.6, 141.7. MS–FAB: m/z = 878 [M⁺]. Anal. Calcd (%) for C₆₀H₃₆N₄S₂: C, 82.16; H, 4.14; N, 6.39. Found: C, 82.27; H, 4.31; N, 6.52.

(27) Stilbenophane 4

White solid; yield 12%; mp 191–193 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.45 (t, 6 H, *J* = 7.1 Hz), 4.40 (q, 4 H, *J* = 7.1 Hz), 6.87 (s, 4 H), 7.08 (s, 4 H), 7.12–7.27 (m, 8 H), 7.31–7.52 (m, 12 H), 7.61 (d, 4 H, *J* = 6.9 Hz), 7.72 (s, 4 H), 7.93 (d, 4 H, *J* = 8.1 Hz), 8.08 (d, 4 H, *J* = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ = 13.7, 38.1, 109.1, 110.2, 111.2, 120.1, 121.2, 121.4, 122.3, 122.6, 123.4, 123.7, 126.4, 124.6, 126.7, 126.9, 129.4, 130.6, 136.2, 140.4, 141.8. MS–FAB: *m/z* = 1100 [M⁺]. Anal. Calcd (%) for C₈₀H₅₄N₆: C, 87.40; H, 4.95; N, 7.64. Found: C, 87.54; H, 4.82; N, 7.51.

(28) Stilbenophane 5

White solid; yield 15%; mp 202–204 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.39$ (t, 12 H, J = 7.2 Hz), 2.00 (q, 8 H, J = 7.2 Hz), 6.84 (s, 4 H), 7.26–7.35 (m, 8 H), 7.46 (t, 4 H, J = 6.9 Hz), 7.56 (s, 4 H), 7.60–7.68 (m, 12 H), 7.93 (d, 4 H, J = 8.1 Hz), 8.11 (s, 4 H), 8.18 (d, 4 H, J = 7.8 Hz). ¹³C NMR (75 MHz, CDCl₃): $\delta = 8.6$, 30.9, 56.5, 109.1, 110.2, 120.3, 121.8, 122.9, 125.2, 126.1, 129.8, 130.4, 133.8, 136.8, 138.2, 139.7, 140.8, 142.6, 146.5, 148.8, 151.7, 153.5. MS–FAB: 1154 [M⁺]. Anal. Calcd (%) for C₈₆H₆₄N₄: C, 89.55; H, 5.59; N, 4.86. Found: C, 89.72; H, 5.74; N, 4.96.

- (29) Frisch, A.; Dennington, R. D. II.; Keith, T. A. *GaussView version 3.0*; Gaussian Inc: Pittsburgh (PA, USA), 2003.
- (30) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, **1986**.
- (31) Becke, A. D. Phys. Rev. A: At., Mol., Opt. Phys. 1988, 38, 3098.
- (32) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B: Condens. Matter 1988, 37, 785.

- (33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision A.02; Gaussian Inc: Wallingford (CT, USA), 2009.
- (34) Promarak, V.; Ruchirawat, S. Tetrahedron 2007, 63, 1602.
- (35) Lai, R. Y.; Kong, X.; Jenekhe, S. A.; Bard, A. J. J. Am. Chem. Soc. 2003, 125, 12631.
- (36) Determination of the Association Constant by UV-Vis Spectroscopy (Benesi–Hildebrand Method) In a typical experiment, 3 mL of a standard stock solution of the cyclophane in MeCN–CH₂Cl₂ was placed in a quartz cuvette. A known amount of the electron-deficient guest molecule was added in incremental amounts and the changes in absorbance of the CT bands were recorded. Table 4 shows the charge-transfer complexation studies of stilbenophanes **2** with various concentrations of TCNQ. Plots of [concn of cyclophane]/absorbance vs. **1**/concentration of guest were linear (Figure 7). From the slope and the intercept values K_a (K_a = intercept × slope⁻¹) and ε (ε = intercept⁻¹) were evaluated (Table 4). The plots were linear, suggesting that the predominant species in solution was a 1:1 complex..
- (37) Benesi, H. A.; Hildebrand, J. H. J. Am. Chem. Soc. 1949, 71, 2703.

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.