

### Experimental Section

**General Procedures.** Mass spectra were obtained using a Finnigan TSQ-45 triple quadrupole mass spectrometer under the following conditions: source temperature, 120 °C; ammonia gas pressure, 0.35 Torr; electron energy, 70 eV; electron multiplier 1300-1500 V. The collision cell pressure was 1.3 mTorr, and the collision energy was 30 eV.  $^{13}\text{C}$  NMR spectra were obtained at 75 MHz in  $\text{CDCl}_3$  with TMS as an internal standard.

**Compounds 1-5.** Compounds 1 and 2 were purchased from the Aldrich Chemical Co. Compounds 4 and 5 were prepared by hydrogen-deuterium exchange according to the method of Epp, Boyd, and Berchtold,<sup>22</sup> using phenols 2 and 1, respectively, as the starting materials. The fully proton decoupled  $^{13}\text{C}$  NMR spectrum of compound 4 contained singlet resonances at 155.40 (ipso carbon atom), 120.55 (para carbon atom), and 115.26 (ortho carbon atoms)

ppm and a low-intensity triplet (meta carbon atoms) at 129.41 ppm. The fully proton-decoupled  $^{13}\text{C}$  NMR spectrum for compound 5 contained singlet resonances at 155.25 (ipso carbon atom) and 129.52 (meta carbon atoms) ppm and low-intensity triplet resonances at 120.59 (para carbon atom) and 115.17 (ortho carbon atoms) ppm. Compound 3 was prepared by irradiation of *p*-chlorophenol in  $\text{CD}_3\text{OD}$  as described by Muller, Parlar, and Korte.<sup>23</sup> The fully proton-decoupled  $^{13}\text{C}$  NMR spectrum of compound 3 had singlet resonances at 155.59 (ipso carbon atom), 129.50 (meta carbon atoms), and 115.28 (ortho carbon atoms) ppm and a low-intensity triplet (para carbon atom) at 120.59 ppm.

**Acknowledgment.** The authors thank the Lewis Research Center (NASA) for donation of the mass spectrometer used in this work and the Standard Oil Company for partial financial support.

(22) Van Epp, J. E., Jr.; Boyd, D. R.; Berchtold, G. A. *J. Org. Chem.* 1981, 46, 1817.

(23) Muller, J. P. H.; Parlar, H.; Korte, F. *Synthesis* 1976, 524.

## From *p*-Dimethoxybenzene toward Crown Benzenophanes: 1,3,10,14-Tetraoxa[3.5]paracyclophane

Henning Hopf\* and Ralf Utermöhlen

*Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30,  
D-3300 Braunschweig, Germany*

Peter G. Jones

*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30,  
D-3300 Braunschweig, Germany*

Jean-Pierre Desvergne and Henri Bouas-Laurent\*

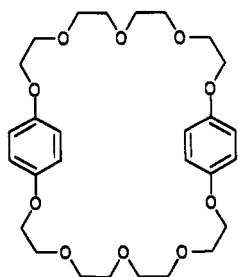
*Laboratoire de Photochimie Organique, URA 348, F-33405 Talence Cedex, France*

Received February 21, 1992

The title compound tetraoxa[3.5]paracyclophane (6) has been prepared and studied in order to investigate the evolution of spectroscopic properties in going from the monomer unit *p*-dimethoxybenzene (9) via the noncyclic bichromophoric reference compound 3b to 6. The X-ray structural analysis of 6 shows that the distance between the two aromatic carbon atoms linked to the smaller bridge is shorter than the van der Waals distance. The resulting electronic interaction is reflected by the perturbation of the UV spectrum of 6 (in particular by a distinct hypochromic effect) and in its charge-transfer complexes with TCNE and TCNQ, as compared to 9 and 3b. The fluorescence quantum yields show significant quenching as compared to 9. This process is related to the formation of a new, structureless red-shifted band with a maximum at  $26\,670\text{ cm}^{-1}$ , comparable to that of the excimer of 9. From a Stern-Volmer plot the self-quenching rate constant of the latter,  $k_q \approx 1.2 \times 10^9\text{ mol}^{-1}\text{ s}^{-1}$  is derived.

### Introduction

Crown ethers continue to attract interest as synthetic organic host molecules. Among a plethora of recent examples, the dibenzocrown ether  $\text{BBO}_5\text{O}_5$  (B = benzene),

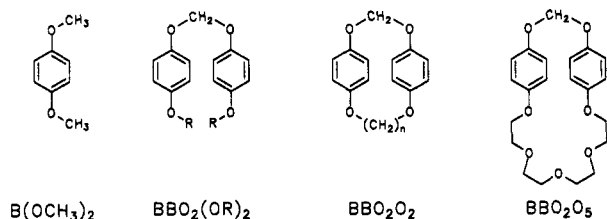


$\text{BBO}_5\text{O}_5$

studied by Stoddard and co-workers, encapsulates a molecule of paraquat. This was the prototype for preparing new catenanes and rotaxanes with great potential for various applications in molecular electronics.<sup>1</sup> Formally, this compound may also be regarded as belonging to the paracyclophane family, whose first members show special spectroscopic and chemical properties because of the close proximity of their aromatic subunits.<sup>2</sup> However, the free ligand  $\text{BBO}_5\text{O}_5$  can undergo considerable con-

(1) (a) Stoddard, J. F. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H. J., Dürr, H., Eds.; VCH Verlagsgesellschaft: Weinheim, 1990; pp 251-263. (b) Stoddard, J. F. *Chem. Br.* 1991, 27, 714-718.

(2) (a) Keehn, P. M., Rosenfeld, S. M. Eds. *The Cyclophanes*, Vol. I and II; Academic Press: New York, 1983. (b) Vögtle, F. *Cyclophan-Chemie*; Teubner Studienbücher: Stuttgart, 1990. (c) Vögtle, F., Ed. *Cyclophanes*, *Top. Curr. Chem.* 1983, 113, 1; 1983, 115, 2. (d) Diederich, F. *Cyclophanes*; The Royal Society of Chemistry: London, 1991.



**Figure 1.** Telescopic molecules: from *p*-dimethoxybenzene ( $B(OCH_3)_2$ ) to a crown benzenophane; an array of molecules to assess the evolution of physical and chemical properties.

formational changes, and there is virtually no significant intramolecular interaction between the two benzene rings. In other words, the molecule appears to resemble the crown ethers (complexing function) more than the small rigid cyclophanes (strong intramolecular interaction between the rings).

Addressing the question of the balance between these two functions, i.e., flexibility vs rigidity, one notes that  $BBO_5O_5$  incorporates two *p*-dimethoxybenzene ( $B(OC_6H_3)_2$ ) units, which could be assembled in molecules of progressive complexity on the way to  $BBO_5O_5$  as shown in Figure 1. This arrangement of "telescopic" molecules is expected to trace the evolution from a simple para-disubstituted benzene derivative to an elaborate crown ether via the biochromophore<sup>3</sup>  $BBO_2(OR)_2$  and the tetraoxaphane  $BBO_2O_2$ .

Our study of this building process is divided into two parts. The present article refers to the first members of this series up to a tetraoxaphane ( $BBO_2O_2$ ,  $n = 3$ ). A second paper will then be devoted to the crown ether.

In the first part of this paper the synthesis of the new compounds and the required intermediates is described. The second part deals with the crystal structure of the title compound 6. Finally, the results of the electronic absorption and fluorescence emission are reported and discussed.

**Synthesis. Preparation of 1,3,10,14-Tetraoxa[3.5]-paracyclophane (6).** The main targets were the small, strained tetraoxaphanes  $BBO_2O_2$ . Our attempts to isolate the first members of the series with  $n = 1$  and 2 have met with failure so far. However, the derivative with  $n = 3$ , the title compound 6, could be prepared as described below. An extension to systematically prepare the subsequent members of the series ( $n \geq 4$ ) has not yet begun.

The synthesis of 6 started with the commercially available mono benzyl ether of hydroquinone (1); this was first "dimerized" to the acetal 2—following a procedure by Dehmlow<sup>4</sup>—by treating it with solid potassium hydroxide in dichloromethane employing tetrabutylammonium hydrogen sulfate (TBAB) as phase-transfer catalyst, the yield being almost quantitative (95%).

Removal of the benzyl protective groups by catalytic hydrogenation with a 10% palladium-on-charcoal catalyst subsequently provided the crucial intermediate 3a, again in practically quantitative yield (95%). For comparison (vide infra) the dimethoxy derivative 3b was prepared in 95% yield by subjecting *p*-methoxyphenol (4) to the same Dehmlow procedure<sup>4</sup> with dichloromethane in the presence of solid potassium hydroxide and TBAB. Derivative 3b has been prepared previously from phenol;<sup>5</sup> however, this

reported route requires more steps, noncommercially available starting materials, and proceeds in lower overall yields.

The construction of the second bridge to obtain 6 was accomplished in two stages<sup>6</sup>: 3a was treated with 1 equiv of potassium hydroxide in methanol/TBAB and the resulting phenolate was then quenched by addition of 1.5 equiv of 1,3-dibromopropane. The desired intermediate ether 5 could be isolated in 38% yield from the reaction mixture by column chromatography; it was accompanied by traces of the corresponding dibromide (= bis ether), indicating that 3a had been converted into the bis phenolate to a very limited extent. For the cyclization to the title compound 6, high-dilution (hd) conditions were used: employing a motor-driven syringe, a solution of 5 in 2-butanol was added over 45 h to a suspension of potassium carbonate and sodium iodide in a large volume of 2-butanol. After a lengthy workup (see Experimental Section) the [3.5]phane 6 was isolated in 39% yield.

The spectroscopic data are as expected for an [*m.n*]-paracyclophane<sup>7</sup> and are hence only summarized in the Experimental Section. The final structural proof for 6 was obtained by the X-ray structural investigation discussed below.

Bis phenol 3a is an attractive precursor for the preparation of other oxaphanes and/or their open-chain analogs. When 3a was reacted with either dibromomethane or bromochloromethane in ethanol in the presence of potassium hydroxide, it dimerized again, providing the open-chain "hydroquinone-tetramer" 7 in excellent yield (90%). In contrast, the cyclic products 8 were obtained when 3a was treated with dichloromethane as the bridging reagent in the presence of base/TBAB under high-dilution conditions. Although the raw yield of this transformation appeared acceptable (ca. 20%), the product, finally obtained in small amounts (<5%), was shown by mass spectrometry and NMR spectroscopy to consist of a mixture of the cyclic compounds 8 with  $n = 3, 5$ , and 7. Interestingly, the tetraoxaphane 8,  $n = 1$ , which we also required for our investigations, was missing from the product mixture, its formation probably being prevented by the buildup of too much strain during the ring-forming process ( $S_N2$  reaction). No attempt has yet been made to separate the oligomers 8 although these oxaphanes probably also possess interesting structural and spectroscopic properties. In an exploratory experiment, it was shown that their synthesis can be drastically simplified by reacting hydroquinone with dichloromethane in the presence of base (potassium hydroxide) and a phase-transfer catalyst (TBAB). Besides the oxaphanes 8 obtained via 3a, in this latter case, however, the oligomers with  $n = 2, 4$ , and 6 were also formed, as shown by NMR and mass spectrometry of the purified product mixture. Again, no 8,  $n = 1$ , was produced.<sup>8</sup>

### X-ray Structural Analysis of 6

A crystal suitable for an X-ray structural investigation was obtained by recrystallizing 6 from chloroform/hexane. The molecule of 6 is shown in Figure 3.

The ring planes in cyclophane systems are usually calculated excluding the bridgehead atoms, since these are displaced toward the center of the molecule. In the current

(3) For the relevance of the term biochromophore which denotes two nonconjugated chromophores, see: Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* 1980, 52, 2633 and references cited therein.

(4) Dehmlow, E. V.; Schmidt, J. *Tetrahedron Lett.* 1976, 95. Cf. E. V.; Dehmlow, E. S. Dehmlow, *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1983; p 104.

(5) Baker, W. *J. Chem. Soc.* 1931, 1765.

(6) Although a one-pot reaction appears a priori more attractive, the two-stage procedure gave better results, which is understandable especially in the case of heterogeneous media.

(7) (a) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* 1969, 91, 3534. (b) See ref 2b.

(8) Utermöhlen, R.; Bouas-Laurent, H.; Hopf, H. Unpublished work.

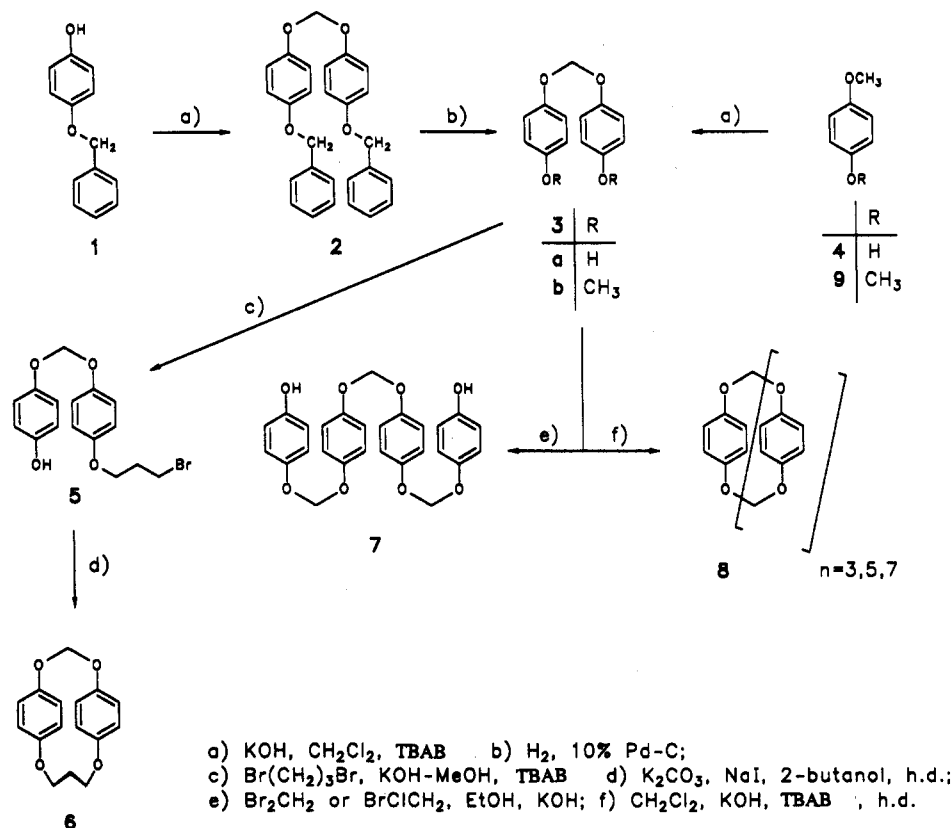


Figure 2. Synthesis of 1,3,10,14-tetraoxa[3.5]paracyclophane (6).

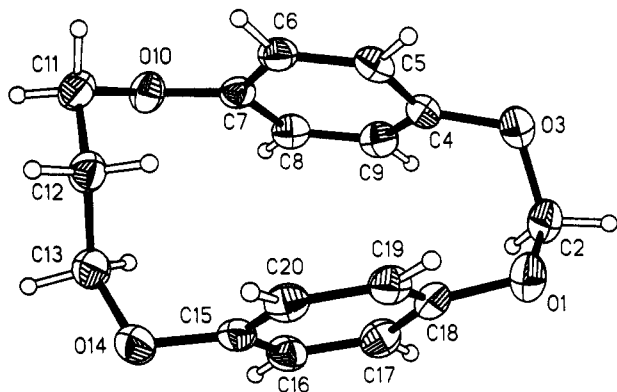


Figure 3. Molecule of compound 6 in the crystal. Thermal ellipsoids are drawn at the 50% level; H atom radii are arbitrary.

structure, the relatively long bridges are associated with small displacements (0.04–0.06 Å), amplified slightly for the oxygen atoms (0.15, 0.18, 0.13, 0.14 Å for O1, 3, 10, 14, respectively). The bridgehead separations are C4...C18 3.01, C7...C15 3.93 Å. The conformation of the longer bridge is described by the torsion angles  $-55$ ,  $-55$ ,  $161$ , and  $-75^\circ$  about the bonds starting from C10–C11. As in the longer bridge of [2.4]paracyclophane, the central C–C bonds are slightly short (1.519 Å).<sup>9</sup>

#### Spectroscopic Properties

(1) **Ultraviolet Absorption Spectroscopy.** (a) **Spectroscopic Properties of Compounds 6, 3b, and 9.** The spectra of the tetraoxaphane 6 and the reference compounds 3b and *p*-dimethoxybenzene (9) were recorded in methylcyclohexane (MCH) and methanol as representatives of nonpolar, aprotic and polar, protic solvents,

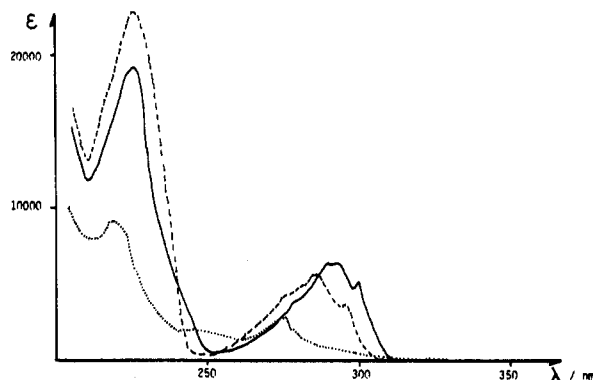


Figure 4. Electronic absorption spectra of 6 (···), 3b (---), and 9 (—) in methylcyclohexane at room temperature; concn.  $4 \times 10^{-6}$  to  $4 \times 10^{-4}$  M. For comparison, the intensity of the monochromophoric compound 9 was doubled ( $\epsilon \times 2$ ).

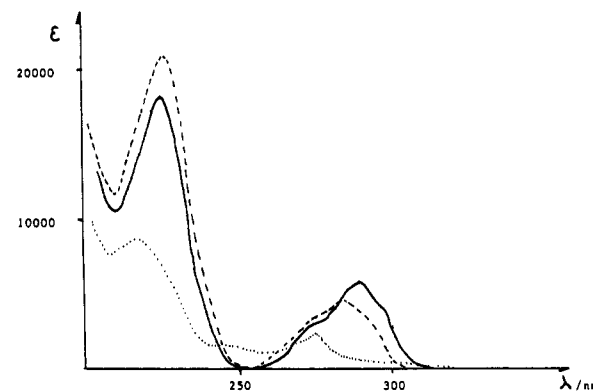


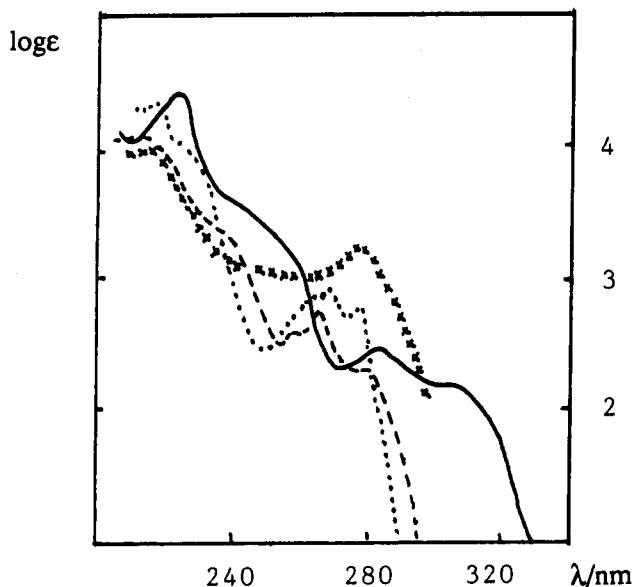
Figure 5. Electronic absorption spectra of 6 (···), 3b (---), and 9 (—) in methanol at room temperature; concn.  $1.5 \times 10^{-4}$  to  $2.5 \times 10^{-4}$  M. For comparison, the intensity of the monochromophoric compound 9 was doubled ( $\epsilon \times 2$ ).

(9) Jones, P. G.; Pechlivanidis, Z.; Hopf, H. *Z. Naturforsch.* 1989, 44b, 860.

**Table I. Charge-Transfer Complexes of Various Cyclophanes and Model Aromatic Compounds with TCNE and TCNQ (Absorption Maxima and Stability Constants As Determined from Scatchard Plots (cf. Figures 8 and 9, Respectively))**

compound	solvent	$\bar{\nu}_1$ max (cm <sup>-1</sup> ) ( $\lambda_1$ max, nm)	$\bar{\nu}_2$ max (cm <sup>-1</sup> ) ( $\lambda_2$ max, nm)	$\Delta\bar{\nu}$ (cm <sup>-1</sup> )	<i>K</i>	acceptor	ref
benzene	<i>a</i>		25 800 (387.5)			TCNE	
<i>p</i> -xylene <sup>c</sup>	<i>a</i>	21 740 (460)	23 810 (420)	2070	7.5 (0.6)	TCNE	23 (24)
anisole	<i>a</i>	19 600 (510)	25 800 (387.5)	6200		TCNE	16
9	<i>a</i>	15 820 (632)	26 315 (380)	10 500	1.3	TCNE	16, this work
3b	<i>a</i>	17 240 (580)	27 025 (370)	9785	0.75	TNCE	this work
6	<i>a</i>	17 240 (580)	27 780 (360)	10 200		TCNE	this work
[2.2]paracyclophane	<i>a</i>	19 230 (520)				TCNE	14
[3.4]paracyclophane	<i>a</i>	18 585 (538)	21 505 (465)	2920		TCNE	14
Q[2.2] <sup>d</sup>	<i>a</i>	13 515 (740)	18 520 (540)	5005		TCNE	18
9	<i>b</i>	16 950 (590)			2.1	TCNQ	this work
3b	<i>b</i>	19 230 (520)				TCNQ	this work
6	<i>b</i>	18 180 (550)				TCNQ	this work
12	<i>a</i>	13 890 (720)				TCNQ	22

<sup>a</sup>In dichloromethane. <sup>b</sup>In acetonitrile. <sup>c</sup>Note the significant discrepancy between the *K* values obtained by the authors. Kochi's results<sup>24</sup> are closer to the ones reported here. <sup>d</sup>Quintuple layered [2.2]paracyclophane.<sup>18</sup>

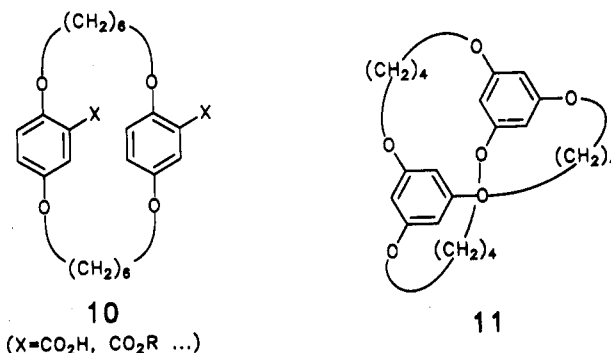


**Figure 6.** Electronic absorption spectra of [2.2]- (—), [3.4]- (---), and [3.6]paracyclophane (···) in ethanol<sup>11</sup> and of 6 (xxx) in methanol.

respectively. They are recorded in Figures 4 and 5. No significant solvent effects are discernible, which indicates that the electronic transitions do not have any important polar character and that hydrogen bonding effects are negligible. The long wavelength band of the bichromophore spectrum undergoes a hypsochromic shift as compared to that of 9. The striking feature is a strong *hypochromic* effect for the whole spectrum of 6 with the exception of the 240–260-nm region. This effect, generally observed in rigid systems, demonstrates a high degree of parallelism between the transition moments<sup>10</sup> of superimposed chromophores. In addition, the maxima seem to be shifted to the blue but one observes an absorption around 250 nm and a long tail all the way down to 350 nm. This apparent splitting has been observed by Cram and co-workers for a series of strained paracyclophanes.<sup>11</sup> Although the influence of the two strongly donating OR substituents on the electronic absorptions is more important than that of two alkyl groups, it seems instructive to draw the spectrum of 6 in methanol to the same scale ( $\log \epsilon$ ) as some selected paracyclophane spectra reported by Cram. As can be seen in Figure 6, the spectrum of

tetraoxaphane 6, a [3.5]paracyclophane, resembles that of the strained [2.2]- and [3.4]paracyclophanes, respectively, rather than that of the less strained dissymmetrical [3.6]paracyclophane. It would be appropriate to compare the spectra of 6 with those of [3.5]paracyclophane but the latter apparently has not been recorded or published. That the UV spectrum of 6 is similar to the spectra of strained [*m.n*]paracyclophanes may be related to the geometry of the molecule established by X-ray structural analysis (cf. Figure 3). The short three-membered bridge forces the two aromatic carbon atoms C<sub>4</sub> and C<sub>13</sub> to a much closer distance (3.01 Å) than expected from the sum of the van der Waals "half thickness" of the two benzene rings.

Other polyoxaphanes such as the [8.8]tetraoxaphane 10<sup>12</sup> or hexaoxaphanes such as 11<sup>13</sup> have been prepared but they do not show any significant strain; their electronic spectra have not been investigated.



**(b) Charge-Transfer Spectra.** One of the remarkable characteristics of cyclophanes, especially the [2<sub>*n*</sub>]- and the [*m.n*]cyclophanes, is the cooperative effect between the aromatic rings. The title compound 6, the bichromophore 3b, and *p*-dimethoxybenzene (9, PDMB) from CT complexes with both TCNE and tetracyanoquinodimethane (TCNQ). The different spectra were recorded in dichloromethane and acetonitrile; the major data are collected in Table I, and the spectra (in dichloromethane) are represented in Figure 7. For comparison some characteristic data and/or spectra of related molecules are inserted. The presence of two CT bands for benzene derivatives has long been known and interpreted theoretically.<sup>15,16</sup> The same phenomenon has been noted recently

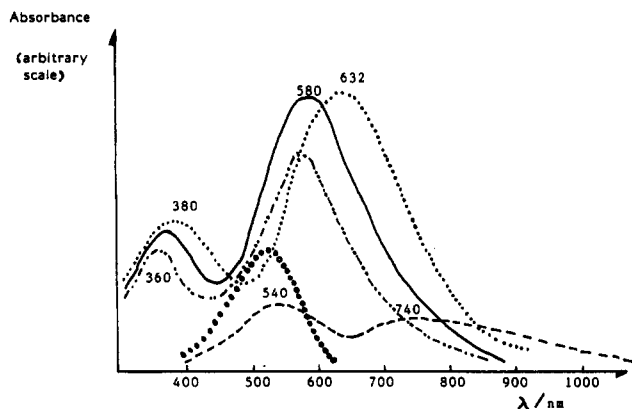
(12) Adams, S. P.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* 1982, 104, 1602.

(13) Curtiss, W. D.; Stoddart, J. F.; Jones, G. H. *J. Chem. Soc., Perkin Trans. I* 1977, 785.

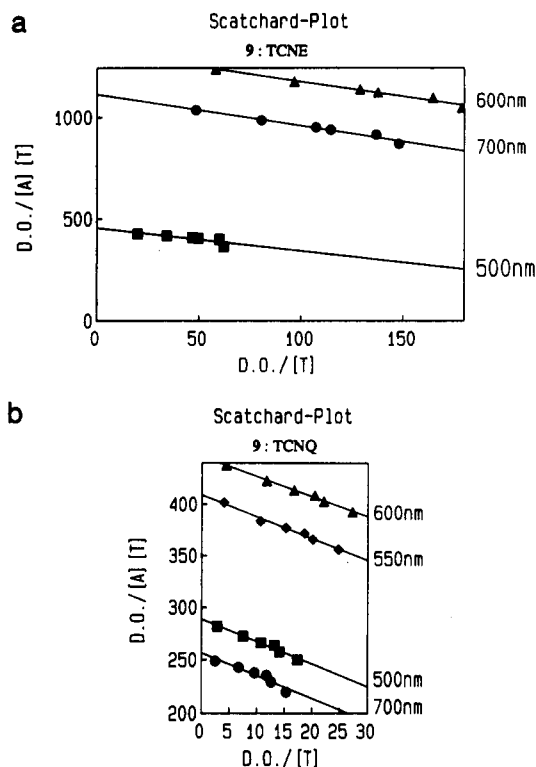
(14) Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* 1959, 81, 5971.

(10) Tinoco, I., Jr. *J. Am. Chem. Soc.* 1960, 82, 4785; 1969, 83, 5047.

(11) Cram, D. J.; Allinger, N. L.; Steinberg, H. *J. Am. Chem. Soc.* 1954, 76, 6132.

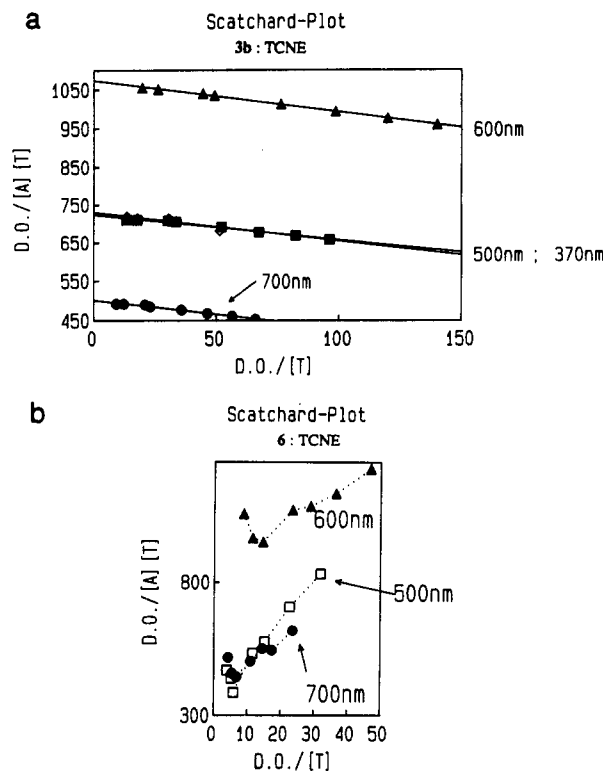


**Figure 7.** Charge-transfer (CT) complex spectra of some cyclophanes and their reference molecules with tetracyanoethylene (TCNE) in dichloromethane: **9** (···), **3b** (—), **6** (---), [2.2]paracyclophane (○), quintuple layered para-cyclophane<sup>18</sup> (---).



**Figure 8.** Scatchard plots for the determination of the association constant ( $K$ ) of *p*-dimethoxybenzene (**9**): (a) with TCNE in dichloromethane at 500, 600, and 700 nm,  $K = 1.3$ ; (b) with TCNQ in acetonitrile at 500, 600, and 700 nm,  $K = 2.1$ .  $[A]$  = concn. of **9**;  $[T]$  = concn of TCNE or TCNQ; D.O. = absorbance of the medium at a given wavelength (see Experimental Section).

for a number of naphthalene derivatives.<sup>17</sup> The present data for **9** are in full agreement with those of Voigt.<sup>16</sup> In agreement with theory, the large bathochromic effect observed for the first band ( $\nu_1 = 15\,820\text{ cm}^{-1}$ ) denotes the strong conjugative effect of the two *p*-methoxy groups with the benzene ring (cf.  $\nu_1 = 19\,600\text{ cm}^{-1}$  for anisole and  $21\,740\text{ cm}^{-1}$  for *p*-xylene<sup>16,23</sup>). Examining the emergence of this band in the paracyclophane series, Cram noted a systematic bathochromic shift<sup>14</sup> as compared to *p*-xylene. In-



**Figure 9.** Scatchard plots for the determination of the association constant ( $K$ ) of (a) bichromophore **3b** with TCNE in dichloromethane ( $[A]$  = concn. of **3b**,  $[T]$  = concn of TCNE,  $K = 0.75$ ) and (b) cyclophane **6** with TCNE in dichloromethane ( $[A]$  = concn of **6**,  $[T]$  = concn of TCNE). Here the Scatchard equation does not apply. D.O. = absorbance of the medium at a given wavelength.

cluded in this study was [3.4]paracyclophane, which is of special interest for the present investigation. In the multilayered phane series studied systematically by Misumi and co-workers<sup>18</sup> this effect apparently culminates in the quintuple-layered cyclophane (see Figure 7). The behavior of compounds **3b** and **6**, on the other hand, contrasts with that of the paracyclophanes as the former derivatives show a significant hypsochromic shift ( $\approx 1400\text{ cm}^{-1}$ ) as compared to the reference monochromophoric molecule **9**. It therefore appears that the second ring not only does not show a cooperative effect but—probably for steric reasons—rather induces some hindrance to conjugation. If the two alkoxy groups were not in conjugation with the ring, the spectra would look like that of anisole whose first band is shifted by  $3780\text{ cm}^{-1}$  with respect to **9**.

The association constants were determined using the Scatchard equation<sup>19,20</sup> (see Figures 8 and 9, respectively) and are reported in Table I. Good correlation was found for **9** and **3b** with TCNE in dichloromethane and **9** with TCNQ in acetonitrile, but not for the tetraoxaphane **6** which does not seem to undergo a simple 1:1 association with the acceptor molecules. The association constants are low but they are the result of a combination of several parameters, and for the time being they should be taken as experimental facts until a complete thermodynamic study has been performed.

Similar trends are observed for the CT complexes of **9**, **3b**, and **6** with TCNQ (see Table III). The data measured

(15) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969; pp 67–73 and pp 288–293.

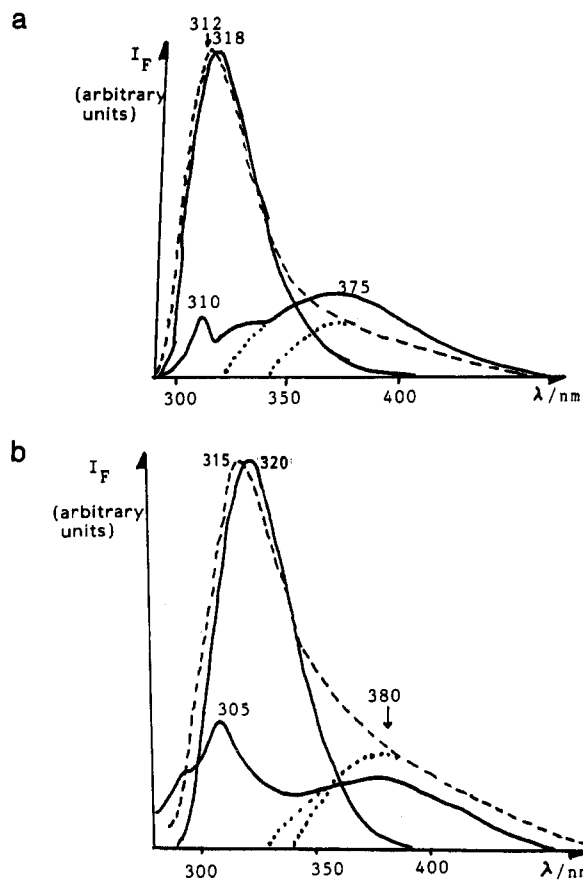
(16) (a) Voigt, E. M. *J. Am. Chem. Soc.* 1964, 86, 3611. (b) Mobley, M. J.; Rieckhoff, K. E.; Voigt, E. M. *J. Phys. Chem.* 1978, 82, 2005.

(17) Oevering, H.; Paddon-Row, N. N.; Heppener, M.; Oliver, A. M.; Cotaris, E.; Verhoeven, J. W.; Husch, N. S. *J. Am. Chem. Soc.* 1987, 109, 3258.

(18) Misumi, S. In *Cyclophanes*, Vol. II; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Chapter 10, pp 573–628.

(19) Foster, R. *Molecular Complexes*, Vol. II; Crane, Russak and Co.: New York, 1974; Chapter 3, pp 107–172.

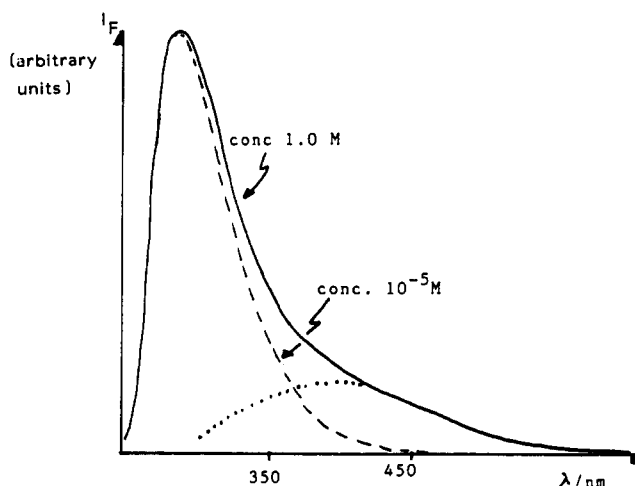
(20) Deranleau, D. A. *J. Am. Chem. Soc.* 1969, 91, 4050.



**Figure 10.** Fluorescence spectra, corrected for absorption and emission of **9** (—), **3b** (---), and **6** (—, lower curve); degassed solutions; concn.  $10^{-5}$  M in methylcyclohexane (a) and methanol (b) at 25 °C. Spectra of **9** and **3b** were normalized at the first vibronic band. Excimer spectra (···) are obtained by subtraction.

for **9** are at variance with those of Pierre et al.<sup>21</sup> Of special relevance is the CT band at  $\nu_{\max}$  13 890  $\text{cm}^{-1}$  (720 nm) for compound **12**,<sup>22</sup> which seem to suggest that the mutual orientation and distance between TCNQ and **6** (or **9**) are not ideal for optimal association.

(2) **Fluorescence.** Fluorescence emission is one of the most interesting properties of aromatic hydrocarbons<sup>25</sup>; at low concentration ( $10^{-6}$  to  $10^{-4}$  M) one observes emission by monomolecular species, but as concentration increases a new, red-shifted, structureless band can appear, caused by the formation of a bimolecular species, the *excimer*.<sup>26,27</sup> The term denotes an excited dimeric species which is stable only in the excimer state, i.e., the ground state, for this particular geometry, is dissociative. During the 1960s, experiments and theoretical investigations<sup>28–30</sup> were performed to characterize the spectroscopic states involved in the transitions, the stabilization energy, and the geom-



**Figure 11.** Fluorescence spectra corrected for absorption and emission of *p*-dimethoxybenzene (**9**) at 25 °C; degassed methanol solutions, concn.  $10^{-5}$  M (---, right angle), 1.0 M (—, front face). The excimer spectrum (···) is obtained as the difference between the high concentration and the low concentration (monomer) spectra which were both normalized at their maximum intensities.

etry of aromatic excimers, in particular for benzene and its alkyl derivatives. Although benzene itself forms a fluorescent excimer in the liquid state ( $\lambda_{\max} = 320$  nm),<sup>25,31</sup> it was convenient to examine the *intramolecular excimers* formed in bichromophores. In contrast to the [4.4]paracyclophane, in which the benzene rings are independent of each other in the ground state, the structureless fluorescence spectrum of [2.2]paracyclophane is that of an *excited dimer* rather than an excimer since the absorption spectrum shows a ground-state dimer interaction. Significantly, [6.6]paracyclophane shows a normal monomolecular fluorescence spectrum.<sup>33</sup>

Thus, the fluorescence emission is a very sensitive method to assess the mutual interaction of the aromatic rings in a cyclophane or—in general—a bichromophore, and it applies well to compounds **6** and **3b**, as described here. The spectra, recorded in *dilute* methylcyclohexane (MCH) and methanol solutions are reproduced in Figures 10a,b. Both display a structureless emission, red-shifted with respect to the monomer model compound **9**; within experimental error, this band reaches its maximum for both the cyclophane and the bichromophore at 375 nm in MCH and at 380 nm in methanol; the difference in position is probably not significant. The spectra of **6** and **3b** apparently arise from a “monomer” (290–330 nm) and an “excimer” (330–450 nm) contribution. However, the absorption spectra reveal mutual interactions between the two aromatic rings, which are also reflected in the fluorescence spectra where small but definitive shifts are observed between the maximum wavelength of the model molecule **9** and those of **6** and **3b** (for instance in MCH  $\lambda_{\max}(\mathbf{9}) = 318$  nm ( $31\,445$   $\text{cm}^{-1}$ ) for (**6**)  $\Delta\nu \approx 800$   $\text{cm}^{-1}$  and for (**3b**)  $\Delta\nu \approx 600$   $\text{cm}^{-1}$ ). A preliminary study of the fluorescence decay by the single photon counting technique indicates single ( $\tau_F = 2.5$  ns), double, and possibly triple exponential decay for **9**, **3b**, and **6**, respectively—a clear indication of the complexity of these systems. A more precise description of the different components of the

(21) Gagnaire, G.; Gellon, G.; Pierre, J. L. *Tetrahedron Lett.* 1988, 29, 933.

(22) (a) Tatemitsu, H.; Natsume, B.; Yoshida, M.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* 1978, 3459. (b) H. A.; Staab, H. E. Henke, *Tetrahedron Lett.* 1978, 1955.

(23) Merrifield, R. E.; Phillips, W. D. *J. Am. Chem. Soc.* 1958, 80, 2778.

(24) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* 1981, 46, 4116.

(25) Birks, J. *Photophysics of Aromatic Molecules*; J. Wiley: London, 1970; (a) pp 330–350, (b) p 130.

(26) Stevens, B. *Nature* 1961, 192, 725.

(27) Braslawsky, S. E.; Houk, K. N. Glossary of terms used in photochemistry, *Pure Appl. Chem.* 1988, 60, 1055.

(28) Murrell, J. N.; Tanaka, J. *Mol. Phys.* 1964, 7, 363.

(29) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* 1963, 39, 1186.

(30) Vala, M. T., Jr.; Hillier, I. H.; Rice, S. A.; Jortner, J. *J. Chem. Phys.* 1966, 44, 23.

(31) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

(32) Hirayama, F. *J. Chem. Phys.* 1965, 42, 3163.

(33) Vala, M. T., Jr.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* 1966, 43, 23.

(34) Desvergne, J. P.; Bitit, N.; Castellan, A.; Bouas-Laurent, H.; Soullignac, J. C. *J. Luminescence* 1987, 37, 175.

**Table II. Fluorescence Quantum Yield of 6, 3b, and 9 in Dilute Degassed Solution at 25 °C. For Comparison, Data for *p*-Xylene and Two Anthracene Derivatives<sup>24</sup> Are Included.**

solvent	compound					
	6	3b	9	<i>p</i> -xylene	9,10-dimethoxy-anthracene	9,10-didimethyl-anthracene
MCH <sup>a</sup>	0.03	0.09	0.26	0.40 <sup>b</sup>	0.41 <sup>b</sup>	0.63 <sup>b</sup>
MeOH	0.02	0.08	0.20			

<sup>a</sup>MCH = methylcyclohexane. <sup>b</sup>In cyclohexane.

spectra must await the results of a thermodynamic study. Apparently the excimer of 9 has not been described. The fluorescence self-quenching in methanol was followed by the front face technique up to a concentration of 1.0 M. The resulting spectra, reproduced in Figure 11, enable the characterization of the excimer with a maximum wavelength of 375 nm (26666 cm<sup>-1</sup>). This transition energy cannot be analyzed in a simple way,<sup>25</sup> but, since it is the same for the three compounds, it is reasonable to assume that the geometry of the excimer is similar. The Stern-Volmer plot (Figure 12b) gives  $K_{SV} \approx 3 \text{ M}^{-1}$  (see Experimental Section). Taking  $\tau_F = 2.5 \text{ ns}$  for 9 in methanol (2.7 ns in ethanol<sup>31</sup>) one finds for the bimolecular rate of quenching

$$k_q = K_{SV}/\tau_F = 1.2 \times 10^9 \text{ M}^{-1}/\text{s}^{-1}$$

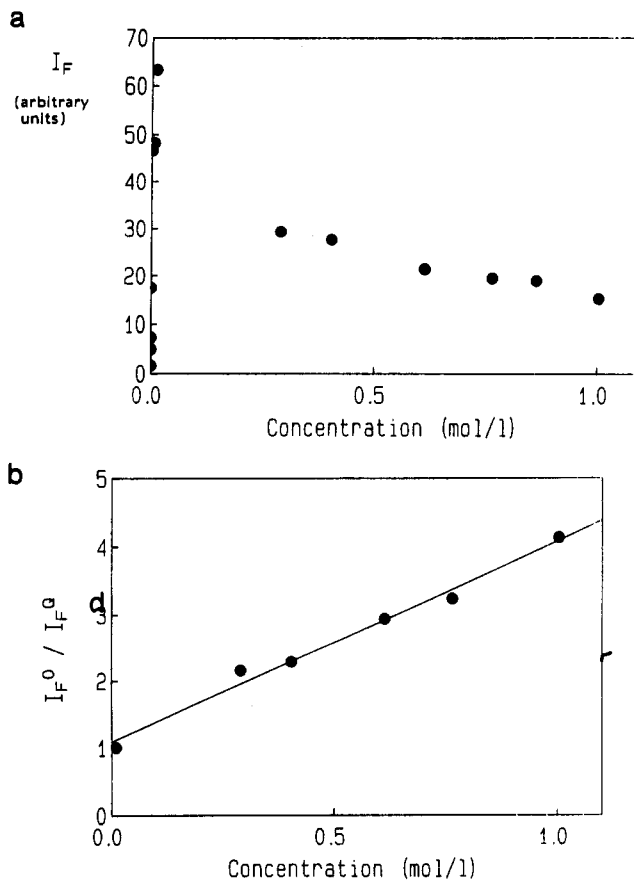
The fluorescence quantum yields of degassed solutions (MCH and methanol) are collected in Table II. Compared with alkyl substituents, the methoxy groups are more conducive to radiationless deactivation pathways, as can be seen in the benzene and anthracene series. The most important quenching process is intramolecular; it is, as expected, more pronounced for the cyclophane than for the biochromophore.

### Conclusion

The objective of this work was to examine the evolution of the physical and chemical properties of a set of molecules formally constructed from of the same basic unit, namely, *p*-dimethoxybenzene (9). The successful synthesis of the new tetraoxaphane 6 in four steps (overall yield 10%) and of the noncyclic bichromophoric compound 3b made it possible to achieve the first step of this project: a comparative study of the spectroscopic properties of 9, 3b, and 6. The UV absorption spectra, including those of the charge-transfer complexes with TCNE and TCNQ, and the fluorescence spectra clearly reflect the interaction between the two rings of the tetraoxaphane and the pronounced influence of the four phenolic oxygen atoms as compared with the [*m,n*]paracyclophanes. Moreover, the mass spectrum of 6 (see Experimental Section) suggests that its radical cation should be particularly stable. Finally, preliminary experiments indicate that 6 and 3b are photosensitive. Further spectroscopic and photochemical studies on the above and related compounds are in progress.

### Experimental Section

**General.** IR spectra were recorded on a Perkin-Elmer Model 1420 spectrometer and UV spectra on a Beckman UV 5230 instrument. For routine NMR spectra, a Varian EM-360 was employed; for more detailed work a Bruker AM 400 was available (CDCl<sub>3</sub> as solvent; internal TMS as standard for the <sup>1</sup>H NMR spectra ( $\delta = 0$ ) and CDCl<sub>3</sub> ( $\delta = 77.05$ ) for the <sup>13</sup>C NMR spectra, respectively). The degree of substitution of the C atoms was determined by the DEPT-135 method. Mass spectra were run on a Finnigan 8430 instrument at 70 eV. Melting points were taken on a Kofler hot-stage apparatus and are uncorrected. Electronic absorption spectra were run on Varian 219 and



**Figure 12.** (a) Fluorescence intensity ( $I_F$ ) in arbitrary units as a function of concentration of *p*-dimethoxybenzene (9);  $\lambda_{exc} = 30 \text{ nm}$  in methanol. The intensity is measured at right angles at low concentration ( $10^{-5}$  to  $10^{-2} \text{ M}$ ) and by the front face technique at high concentration.

Beckman UV 5230 spectrometers. Fluorescence spectra, corrected for absorption and emission, were recorded on a Hitachi Perkin-Elmer MPF 44 or a SPEX spectrofluorimeter. Fluorescence quantum yields were measured using fluorene as external reference ( $\phi_F = 0.54$  in ethanol<sup>25</sup> and 0.80 in cyclohexane<sup>31</sup>). Singlet lifetimes were determined by the time-correlated single photon timing technique, using the Applied Photophysics Systems as described in ref 34. All fluorescence measurements were performed on samples carefully purified by HPLC (Milton-Roy HPLC-system, dichloromethane-heptane, 1:1 (v/v), 25-cm aminosilane column). The various samples were degassed by the freeze-and-thaw technique until the vacuum ( $10^{-5} \text{ Torr}$ ) remained constant. The self-quenching of *p*-dimethoxybenzene (9) was studied in aerated solutions. In the concentration range ( $3.5 \times 10^{-5}$ )–( $1.04 \times 10^{-2}$ ) M, the intensity of reflected light increased continuously and then dropped as the concentration was increased up to 1.0 M. The values of the reflected light intensity ( $I_F$ ) vs the concentration of 9 were used to plot the Stern-Volmer curve according to the relation  $I_F^0/I_F = 1 + K_{SV}[Q]$ , where  $[Q]$  refers to the quencher concentration;  $I_F^0$  was determined for  $[Q] = [9] = 1.04 \times 10^{-2} \text{ M}$ .

**Solvents.** Dichloromethane, methylcyclohexane, and acetonitrile were commercial high-purity solvents (Spectrosol quality); methanol was carefully distilled on a 1-m fractionating column before use. Methylcyclohexane was selected as solvent since it is liquid down to  $-126.5 \text{ °C}$ , enabling a further study of fluid solutions at low temperatures.

**Syntheses.** **Bis(4-(benzyloxy)phenoxy)methane (2).** A solution of 20 g (0.1 mol) of *p*-(benzyloxy)phenol (Aldrich) in 150 mL of dichloromethane was stirred in a 500-mL flask over 16.2 g (ca. 0.3 mol) of solid potassium hydroxide in the presence of 3.39 g (0.01 mol) of TBAB as phase-transfer catalyst. After 40 h at room temperature the reaction mixture was filtered through a short column of silica and the resulting clear filtrate concentrated in the rotary evaporator. On cooling, 20.2 g (95%) of 2 precipitated rapidly. For analytical purposes a sample was recrystallized from



ether/hexane, mp 209 °C: IR (KBr)  $\nu$  = 2900 (s), 2880 (s), 1590 (w), 1510 (vs), 1470 (s), 1452 (s), 1412 (m), 1380 (s), 1280 (m), 1220 (vs, br), 1141 (m), 1100 (s), 1020 (vs, br), 915 (s), 818 (vs), 760 (s), 731 (vs), 700  $\text{cm}^{-1}$  (vs); UV (cyclohexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 206 (4.547), 228 (4.458), 282 (3.690, sh), 286 (3.721), 294 nm (3.541, sh);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.35 (m, 10 H, Ar-H), 7.02 and 6.89 (AA'BB'-m, 8 H, Ar-H), 5.56 (s, 2 H,  $\text{OCH}_2\text{O}$ ), 4.99 (s, 4 H,  $\text{OCH}_2\text{Ar}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 154.26 (s), 151.25 (s), 137.13 (s), 128.54 (d), 127.90 (d), 127.44 (d), 117.88 (d), 115.75 (d), 92.87 (t), 70.53 (t); MS  $m/z$  (vol intensity) = 412 ( $\text{M}^+$ , 20), 290 (3), 213 (10), 105 (6), 91 (100). Anal. Calcd for  $\text{C}_{27}\text{H}_{24}\text{O}_4$  (412.48): C, 78.55; H, 5.82. Found: C, 78.57; H, 5.77.

**Bis(4-hydroxyphenoxy)methane (3a).** 2 (8.25 g, 0.02 mol) was dissolved in 275 mL of ethyl acetate and hydrogenated at normal pressure and room temperature over 0.4 g of palladium-on-charcoal (10% Pd). After the uptake of 900 mL of hydrogen (calcd amount 896 mL) the catalyst was removed by filtration and the solvent evaporated in vacuo. The remaining oil slowly crystallized on standing in the refrigerator; yield 4.45 g (96%). For determination of the spectral data a sample was recrystallized from ether/pentane (1:1, v/v), mp 221 °C: IR (KBr)  $\nu$  = 3400 (s, br), 1520 (s), 1510 (vs), 1450 (m), 1365 (m), 1240 (s), 1218 (s), 1200 (vs), 1040 (m), 1012 (vs), 827 (s), 810 (m), 727  $\text{cm}^{-1}$  (m); UV (*n*-hexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 212 (4.038), 226 (4.268), 283 nm (3.753);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 9.08 (s, 2 H, OH), 6.88 (AA'BB' half spectrum, 4 H, Ar-H), 6.69 (AA'BB' half spectrum, 4 H, Ar-H), 5.56 (s, 2 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 152.41 (s), 149.15 (s), 117.60 (d), 115.65 (d), 92.13 (t); MS  $m/z$  (vol intensity) = 232 (44,  $\text{M}^+$ ), 123 (100), 95 (48), 93 (50), 81 (24), 65 (59), 43 (75). Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_4$  (232.23): C, 67.24; H, 5.17. Found: C, 67.12; H, 5.22.

**Bis(4-methoxyphenoxy)methane (3b).** A solution of 10.8 g (0.1 mol) of commercial (Aldrich) *p*-methoxyphenol (4) in 150 mL of dichloromethane was stirred over 16.2 g of solid potassium hydroxide in the presence of 3.39 g (0.01 mol) of TBAB at room temperature for 40 h. The solution was then filtered through a short (15 cm) silica gel column, and the resulting clear filtrate was concentrated on a rotary evaporator. On cooling 3b (11.5 g, 95%) crystallized. Although the ether has been described in the literature,<sup>5</sup> the determination of its spectral data using modern equipment seemed desirable: IR (KBr)  $\nu$  = 1508 (vs), 1290 (m), 1225 (vs), 1200 (vs), 1182 (s), 1150 (m), 1030 (vs, br), 1010 (vs, br), 825 (vs), 710  $\text{cm}^{-1}$  (m); UV (*n*-hexane)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 201 (4.246), 226 (4.330), 281 (3.664, sh), 285 (3.714), 289 (3.670, sh), 295 nm (3.516, sh);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.03 (AA'BB' half spectrum, 4 H, Ar-H), 6.83 (AA'BB' half spectrum, 4 H, Ar-H), 5.58 (s, 2 H,  $-\text{CH}_2-$ ), 3.77 (s, 6 H,  $\text{CH}_3\text{O}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 155.10 (s), 151.08 (s), 117.95 (d), 114.64 (d), 93.03 (t), 55.66 (q); MS  $m/z$  (rel intensity) = (45,  $\text{M}^+$ ), 137 (100), 123 (6), 109 (22), 107 (25), 77 (23). Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_4$  (260.29): C, 69.23; H, 6.15. Found: C, 69.19; H, 6.04.

**(4-Hydroxyphenoxy)(4-((3-bromopropyl)oxy)phenoxy)methane (5).** A mixture of 7.5 g (32 mmol) of 3a, 10 g (49 mmol) of 1,3-dibromopropane, 2 g (6 mmol) of TBAB, and 1.82 g (32 mmol) of potassium hydroxide in 70 mL of methanol was stirred for 65 h under nitrogen at room temperature. The solvent and excess dibromoalkane were removed in vacuo, and to the remaining solid residue 200 mL of water and 100 mL of chloroform were added. The two phases were separated, and the aqueous layer was washed three times with 50-mL portions of chloroform. After drying the combined organic extracts with sodium sulfate, the solvent was removed by rotary evaporation. The remaining oil slowly solidified in the refrigerator, and finally 4.1 g (37.5%) of 5 was isolated as colorless needles. The material was used without further purification in subsequent transformations; for analytical purposes a sample was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:1, v/v): IR (KBr)  $\nu$  = 3480 (s), 3370 (s), 1510 (vs), 1465 (m), 1435 (m), 1385 (m), 1291 (m), 1210 (vs, br), 1178 (s), 1110 (m), 1042 (vs, br), 822 (s), 730  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.03 (AA'BB' half spectrum, 2 H, Ar-H), 6.96 (AA'BB' half spectrum, 2 H, Ar-H), 6.83 (AA'BB' half spectrum, 2 H, Ar-H), 6.74 (AA'BB' half spectrum, 2 H, Ar-H), 5.57 (s, 2 H,  $-\text{OCH}_2\text{O}$ ), 4.05 (t,  $J$  = 5.84 Hz, 2 H,  $-\text{CH}_2\text{O}$ ), 3.59 (t,  $J$  = 6.44 Hz, 2 H,  $\text{CH}_2\text{Br}$ ), 2.28 (m, 2 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 154.13, 151.20, 151.02, 150.92 (all s), 118.17, 117.94, 116.05, 115.47 (all d), 92.98, 65.88,

32.37, 30.09 (all t); UV (methanol)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 207 (4.08), 227 (4.31), 286 nm (3.69); MS  $m/z$  (rel intensity) = 354/352 (18,  $\text{M}^+$ ), 245/243 (38), 232 (6), 215 (4), 163 (36), 123 (100), 110 (12), 95 (40), 93 (29). Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_4\text{Br}$  (353.21): C, 54.39; H, 4.82; Br, 22.63. Found: C, 54.40; H, 4.90; Br, 22.13.

**1,3,10,14-Tetraoxa[3.5]paracyclophane (6).** A solution of 1 g (2.8 mmol) of 5 in 50 mL of 2-butanol was added by means of a motor-driven syringe within 24 h to a refluxing solution of 2 g (14 mmol) of potassium carbonate and 0.2 (1.3 mmol) of sodium iodide in 1.5 L of 2-butanol. After completion of the addition the still warm solvent was removed with a rotary evaporator, and the remaining solid residue was dried for several hours in a desiccator. The reaction product was subsequently refluxed in 200 mL of chloroform for 10 min, the insoluble material was removed by filtration, and the solvent of the clear filtrate was evaporated. The raw product crystallized, and from it 0.28 g (39%) of 6 was isolated by thick layer chromatography (silica gel, chloroform), colorless needles, mp 158 °C: IR (KBr)  $\nu$  = 1500 (vs), 1210 (vs), 1100 (m), 1090 (m), 970 (s), 932 (w), 925 (w), 845  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.73 (AA'BB' half spectrum, 4 H, Ar-H), 6.53 (AA'BB' half spectrum, 4 H, Ar-H), 5.73 (s, 2 H,  $-\text{OCH}_2\text{O}$ ), 4.08 (t,  $J$  = 6.41 Hz, 4 H,  $-\text{OH}_2\text{CH}_2-$ ), 1.99 (m, 2 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 153.77 (s), 152.52 (s), 121.42 (d), 119.89 (d), 96.25 (t), 67.17 (t), 25.71 (t); UV (methanol)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 209 (3.82 sh), 219 (3.88), 247 (3.21, sh), 272 (3.26, sh), 276 (3.34), 287 nm (2.86); MS  $m/z$  (rel intensity) = 272 (100,  $\text{M}^+$ ), 163 (23), 123 (14), 109 (9). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4$  (272.30): C, 70.58; H, 5.88. Found: C, 54.02; H, 4.36.

**Preparation of the "Tetrameric" Hydroquinone 7.** To a boiling solution of 4.64 g (0.02 mol) of the bisphenyl 3a in 7 mL of ethanol and 6.95 g (0.04 mol) of dibromomethane was added a solution of 0.37 g (0.006 mol) of potassium hydroxide in 7 mL of ethanol within 1 h. After refluxing for additional 45 min, the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The raw product was dissolved in ethyl acetate and the insoluble potassium bromide washed out with water. The organic phase was dried with sodium sulfate, and, after solvent removal, tetramer 7 (1.22 g, 90%) was isolated by column chromatography on silica gel using ethyl acetate/hexane = 1:2 (v/v) as the eluent: IR (KBr)  $\nu$  = 3303 (s, br), 1507 (vs), 1455 (m), 1412 (m), 1198 (vs), 1145 (m), 1038 (s), 1014 (vs), 834  $\text{cm}^{-1}$  (s);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 9.09 (s, 2 H, OH), 7.03 (s, 8 H, "inner" aromatic rings), 6.88 (AA'BB' half spectrum, 4 H, "outer" aromatic rings), 6.68 (AA'BB' half spectrum, 4 H, "outer" aromatic rings), 5.71 (s, 2 H, "inner"  $-\text{OCH}_2\text{O}$ ), 5.63 (s, 4 H, "outer"  $-\text{OCH}_2\text{O}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 153.42, 152.45, 152.23, 149.91 (all s), 118.56, 118.28, 118.23, 116.57 (all d), 92.57 (t), 92.25 (t); MS  $m/z$  (rel intensity) = 476 (1.4,  $\text{M}^+$ ), 366 (5.8), 245 (9), 232 (10), 123 (40), 95 (100). Anal. Calcd for  $\text{C}_{27}\text{H}_{24}\text{O}_8$  (476.48): C, 68.07; H, 5.04. Found: C, 68.08; H, 5.09.

**Preparation of Crown Ethers 8 ( $n = 3$  to 7).** A solution of 3 g (0.013 mol) of 3a in 15 mL of ethyl acetate and 250 mL of dichloromethane was added with a motor-driven syringe within 48 h to a boiling and vigorously stirred solution of 15 g (0.29 mol) of potassium hydroxide and 3.3 g (0.01 mol) of TBAB in 1 L of dichloromethane. The reaction mixture was filtered, the remaining solid was dissolved in water (with 1.4 g of insoluble polymeric material remaining), the aqueous phase was washed thoroughly with dichloromethane, and the organic phases were united. After drying with sodium sulfate the solvent was removed by rotary evaporation. The raw-product mixture obtained (240 mg) was further purified by column chromatography on silica gel with dichloromethane/hexane = 12/1 (v/v), finally providing 130 mg of a mixture of the crown ethers 8. Although these compounds were not obtained in analytically pure form, it could be shown by NMR spectroscopy and mass spectrometry that the homologs with  $n = 3, 5$ , and 7 were present. 8 ( $n = 3$ ):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.78 (s, 16 H, Ar-H), 5.59 (s, 8 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 152.10 (s, Ar-C), 118.7 (d, Ar-C), 93.22 (t,  $-\text{CH}_2-$ ); MS:  $m/z$  (rel intensity) = 488 (100,  $\text{M}^+$ ), 366 (16), 245 (18), 135 (38), 123 (23). 8 ( $n = 5$ ):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.96 (s, 24 H, Ar-H), 5.61 (s, 12 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 151.84 (s, Ar-C), 117.52 (d, Ar-C), 91.47 (t,  $-\text{CH}_2-$ ); MS  $m/z$  (rel intensity) = 732 (100,  $\text{M}^+$ ), 610 (10), 488 (30), 366 (34), 245 (24), 135 (54), 123 (100). 8 ( $n = 7$ ):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.99 (s, 32 H, Ar-H), 5.60 (s, 16 H,  $-\text{CH}_2-$ );  $^{13}\text{C}$  NMR



(100 MHz, CDCl<sub>3</sub>)  $\delta$  = 152.17 (s, Ar-C).

**Stoichiometry of CT Complexes and Determinations of Association Constants *K*.** The stoichiometry of the CT complexes of 9, 3b, and 6 with TCNE in dichloromethane was found to be 1:1, employing the usual Job method.<sup>19</sup>

For the present situation (1:1 complexes, activity coefficients equal to unity) the association constant may be expressed in the following way on the molar scale (the index<sub>0</sub> represents initial concentration, A = acceptor, D = donor):

$$K = [\text{AD}]/([\text{A}]_0 - [\text{AD}]) - ([\text{D}]_0 - [\text{AD}])$$

When  $[\text{A}]_0 \ll [\text{D}]_0$  this equation may be rewritten according to the classical expressions of Benesi-Hildebrand, Scott, or Scatchard. Foster points out<sup>19</sup> (after Deranleu<sup>20</sup>) that "if a termolecular complex is present, the effect on the curvature of the various plots is most marked in the case of the Scatchard plot". This is the reason why the "Scatchard" equation was employed in the present study:  $A/[D]_0[A]_0 = (-K(\epsilon))/[A]_0 + K\epsilon$ , where *A* is the absorbance of the complex at a given wavelength and for a given concentration for the acceptor A.

**X-ray Crystal Structure Determination of Compound 6.** The compound crystallizes in the noncentrosymmetric space group *Pc* with cell dimensions *a* = 8.381 (3), *b* = 10.288 (3), and *c* = 8.368 (2) Å,  $\beta$  = 116.38 (2)°, *V* = 646.4 Å<sup>3</sup> (at -95 °C), *Z* = 2. The near equality of the *a* and *c* axes allows the construction of a metrically orthorhombic cell, but the true symmetry is no higher than

monoclinic (*R*<sub>int</sub> 0.27 for orthorhombically merged "equivalents"). Data were collected on a Siemens four-circle diffractometer using Mo K $\alpha$  radiation ( $2\theta_{\text{max}}$  55°, 1435 unique observed reflections). The structure was solved by direct methods and refined to *R* 0.032, *R*<sub>w</sub> 0.037. H atoms were included using a riding model. Full details of the structure determination are available as supplementary material.

**Acknowledgment.** We are indebted to the DAAD (Germany) and the ANRT (France) for a PROCOPE grant. H.R.L. is grateful to the Alexander von Humboldt Foundation for financial support. We furthermore thank Dr. F. Fages for discussions and Ms Christina Antonius for assistance.

**Registry No.** 1, 103-16-2; 2, 142746-15-4; 3a, 86072-79-9; 3b, 56207-34-2; 3b-TCNE, 142746-22-3; 3b-TCNQ, 142746-25-6; 4, 150-76-5; 5, 142746-16-5; 6, 142746-17-6; 6-TCNE, 142746-23-4; 6-TCNQ, 142746-26-7; 7, 142746-18-7; 8 (*n* = 3), 142746-19-8; 8 (*n* = 5), 142746-20-1; 8 (*n* = 7), 142746-21-2; 9-TCNE, 19199-93-0; 9-TCNQ, 142746-24-5; Br(CH<sub>2</sub>)<sub>3</sub>Br, 109-64-8.

**Supplementary Material Available:** Complete crystallographic details (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## Preparation and Properties of Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) and Its Derivatives. Novel Organic Semiconductors

Yoshiro Yamashita,\* Shoji Tanaka, Kenichi Imaeda, Hiroo Inokuchi, and Mizuka Sano†

*Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and Division of Natural Sciences, International Christian University, Mitaka, Tokyo 181, Japan*

Received May 18, 1992

Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) (3a) and its derivatives 3b-f were prepared by using a Wittig-Horner reaction. The conductivity of BTQBT was good as a single component. The X-ray structural analysis reveals that the planar molecule forms a sheetlike network by short S---S contacts. The conductivities of the derivatives 3b-f were poorer than that of BTQBT, indicating that the unique crystal structure of BTQBT is needed for the good conductivity. The selenadiazolo analogues 9a,b were also prepared. The conductivities were a little higher than that of BTQBT due to the stronger intermolecular interactions caused by the selenium atom.

Recently, much attention has been focused on organic conductors, and a large number of organic metals have been reported.<sup>1</sup> Organic superconductors have also been prepared.<sup>2</sup> Those organic conductors are comprised of more than two components. However, multicomponent systems have disadvantages such as instability to air, solvent, or heat treatment. Therefore, it is important to develop single-component organic conductors from viewpoints of fundamental research as well as applied science.<sup>3</sup> It is also a challenging theme to prepare such molecules since usual organic compounds are good insulators as single components.

Some compounds have been designed to exhibit electrical conductivities as single components. For example, tetrathiafulvalene (TTF) derivatives 1a,b containing long alkyl chains or methyltelluro substituents show conductivities of 10<sup>-5</sup> S cm<sup>-1</sup>, which are attributed to strong intermolecular interactions between adjacent molecules.<sup>4,5</sup>

In the former case, the van der Waals attractive force among alkyl chains results in strong intermolecular interactions (fastener effect).<sup>4</sup> In the latter case, tellurium atom contacts provide a transport of electrons in the crystal.<sup>5</sup> Stable heterocyclic biradicals 2a were recently found to show good conductivities. In this case the importance of intermolecular interactions based on selenium-selenium contacts for the good conductivities is pointed out since the corresponding sulfur analogues 2b

(1) Bechgaard, K. In *Structure and Properties of Molecular Crystals*; Pierrot, M., Ed.; Elsevier: Amsterdam, 1990; pp 235-295.

(2) Inokuchi, H. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1747; *The Physics and Chemistry of Organic Superconductors*; Saito, G., Kagoshima, K., Eds.; Springer-Verlag: Berlin, Heidelberg, 1990.

(3) Metzger, R. M.; Panetta, C. A. *New J. Chem.* 1991, 15, 209.

(4) Inokuchi, H.; Saito, G.; Wu, P.; Seki, K.; Tang, T. B.; Mori, T.; Imaeda, K.; Enoki, T.; Higuchi, Y.; Inaka, K.; Yasuoka, N. *Chem. Lett.* 1986, 1263. Imaeda, K.; Enoki, T.; Shi, Z.; Wu, P.; Okada, N.; Yamochi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* 1987, 60, 3163.

(5) Inokuchi, H.; Imaeda, K.; Enoki, T.; Mori, T.; Maruyama, Y.; Saito, G.; Okada, N.; Yamochi, H.; Higuchi, Y.; Yasuoka, N. *Nature* 1987, 329, 39.

† International Christian University.