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Sandwich-type molecular recognition of acceptors by a bis-anthracene host

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A bis-anthracene host which has two anthryl groups side by side projecting in the same direction from an anthraquinone spacer has been synthesized. There is little interaction between the two anthracenes in 1 as judged by ^{1}H-NMR, UV-visible, and fluorescence spectra. The optimized geometry by molecular mechanics shows that the two anthracenes are arranged face to face. With the bis-anthracene effect, 1 forms charge-transfer 1:1 complexes with aromatic acceptors such as nitrofluorenones in chloroform. The complexation is enthalpically driven. In the complex of 1 and 2,4,7-trinitrofluorenone (TNF) in solution, TNF has been revealed to be sandwiched between the two anthracenes, based on the ^{1}H-NMR chemical shifts and the ring current calculation.

INTRODUCTION

Donor–acceptor (DA) complexes are of importance in view of their potential applicability to electronics.[1,2] Aromatic donors and aromatic acceptors form DA complexes as molecular crystals. To explore the use of DA complexes as photonic and electronic devices[3] in molecular systems,[4] it would be required for donors and acceptors to complex strongly at the supramolecular level. In general, however, the driving force for the stacking of a donor and an acceptor is too weak to form the DA complex as a supermolecule in solution.

Approaches from molecular recognition have been successful in this regard. Among many host compounds, molecular tweezers,[5] in which two aromatic chromophores connected by a single spacer, can have distinct advantages in terms of the size and topology of the guests that can be complexed.[6a] The non-macrocyclic receptors may sandwich planar compounds of infinite dimensions as well as intercalate into stacked systems. Thus far, only a few examples of molecular tweezers are known. Zimmerman[6] demonstrated that rigid molecular tweezers, in which a rigid spacer enforces a *syn* co-facial orientation of the two acridine donors, can complex with aromatic acceptors. Beer and Rothin[7] reported an allosteric bis-crown ether, which binds a diquat dication featured by the appearance of a charge-transfer absorption band.

Our interest in the supramolecular DA complexes prompted us to explore a new type of molecular tweezers which is as effective as those predecessors and can be synthesized with less difficulty. We report here on a new molecular tweezer, 1,8-bis[(9-anthryl)-methoxy]-9,10-anthraquinone (**1**), which can be synthesized in one step and effectively sandwiches aromatic acceptors.

RESULTS AND DISCUSSION

Synthesis

Several combinations of bases and solvents have been used to prepare ethers from alkyl halides and alcohols.[8] We attempted a few of them. Use of K_2CO_3 in dimethylformamide and K_2CO_3 and 18-crown-6 in acetone resulted in formation of a mass of insoluble products which could not be characterized. The present method, in which a phase-transfer catalyst, tetrabutylammonium chloride, was used, had an advantage in that almost pure product precipitated out of the solution. It was also the case for synthesis of the reference compound, anthrylmethoxyanthraquinone (**2**).

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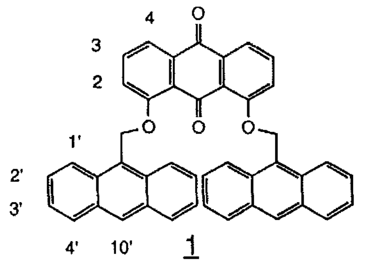

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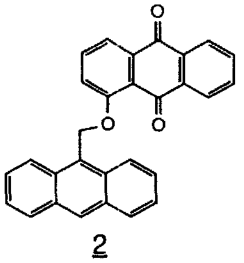

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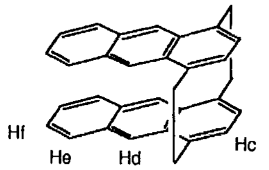

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Characterization of the free host in solution

Our primary concern is with the relative position and orientation of the two anthryl groups of **1**, since these are crucial factors which determine the dimensions of the cleft which accommodates guest molecules. The bis-anthracene has three rotatable bonds between the anthracene and the anthraquinone spacer, i.e. C(anthracene)–CH_2, CH_2–O, and O–C(anthraquinone). Therefore **1** is more flexible than Zimmerman's molecular tweezers.[6] Although this is an inferior point with respect to the preorganization the CPK model suggests that a conformation in which the two anthryl groups are arranged face to face appears to be the most suitable for avoiding steric hindrances. The interaction of the intramolecular anthracenes was examined by ^{1}H-NMR, electronic absorption, and fluorescence spectra. The most stable conformation was estimated from these experimental observations and molecular mechanics (MM) and molecular orbital (MO) calculations.

Because of large charges in chemical shifts owing to the anisotropic diamagnetic ring current in aromatic π-electron systems, ^{1}H-NMR is a powerful tool for revealing the time average solution conformation of systems involving aromatic moieties.[9,10] The resonances of anthracenes and methylenes of **1** shifted upfield by 0.10–0.22 ppm compared with those of the monoanthryl analogue **2**. The analysis is complicated by the presence of an anthraquinone unit, which affects the chemical shifts by its ring current, combined with the structural flexibility of **1** and **2**. Therefore, only rough estimation is possible in this case. Zimmerman *et al.*[6] analysed the conformation of the rigid molecular tweezers by comparing their chemical shifts with those of model compounds. The magnitude of the upfield shifts of **1** is about the same as those of their molecular tweezers (ca. 0.1–0.2 ppm), which have been concluded to have open clefts. Furthermore, the magnitude of these upfield shifts are much smaller than those seen in either *syn*[2.2](1,4)-anthracenophane (**3**) or [2.2](1,4)(9,10)-anthracenophane in which the inter-anthracene separations are 2.7–3.9 Å.[11a] These comparisons argue that **1** has an open cleft between the two anthracenes, which may be compared with that of the rigid molecular tweezers.[6]

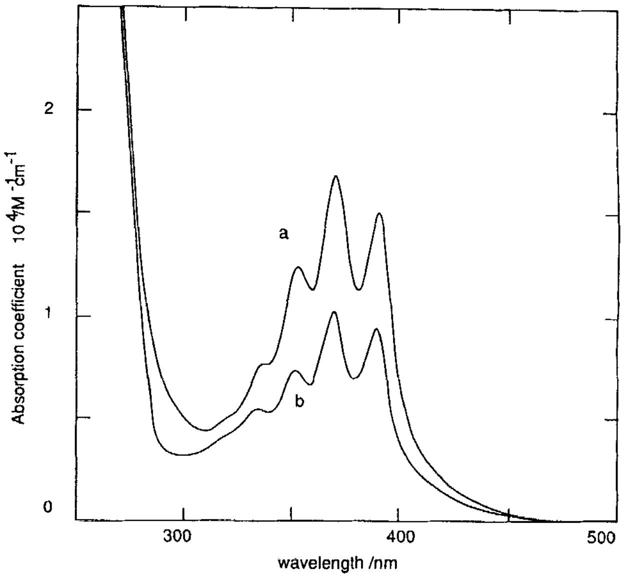


Figure 1 Electronic spectra of **1** (a) and **2** (b) in chloroform.

The ground state interaction of the intramolecular anthracenes was examined by electronic absorption spectra (Fig 1). The vibronic structure of the ^{1}La band characteristic of anthracene was clearly observed. The magnitude of hypochromism can be used to evaluate the intensity of the inter-anthracene interaction.[12] The absorption must be corrected for the contribution from the anthraquinone component. The molar absorption coefficient of 1-methoxy-2-methylanthraquinone at 370 nm is reported to be $3.2 \times 10^3 \, cm^{-1} M^{-1}$ in methanol.[13] Assuming that the absorption coefficients of the alkoxyanthraquinone moiety of **1** and **2** are equal to this value, those of the anthracene unit are calculated to be 6.8×10^3 and $6.9 \times 10^3 \, cm^3 cm^{-1} M^{-1}$ for **1** and **2**, respectively. Thus, there is no hypochromic effect observed. Neither broadening nor bathochromic shifts reported for the anthracenophanes[11a] are observed.

The bichromophore **1** exhibits no intramolecular excimer fluorescence which could be visualized by comparison with the fluorescence of the model compound **2**. The excimer emission is observed for bis-anthracenes linked with flexible polyoxyethylene chains[14] and for an anthraceno-crown ether[12e] when the intramolecular anthracenes are pulled into proximity. Therefore, the absence of the excimer fluorescence for **1** indicates that two anthracenes are isolated and have little probability of reaching close proximity within the excited monomer lifetime.[12e,15,16]

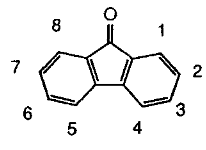
^{1}H-NMR gives information about the average position of protons relative to aromatic groups on an NMR time-scale (relatively long), absorption spectra gives information about the electronic interaction within the electronic transition timescale (very short), and the excimer gives information about the probability of reaching close proximity within the excited monomer lifetime (middle). All of these observations show that there is little interaction between the anthracene arms of the tweezers. Thus, we have concluded that the anthraquinone spacer of **1** effectively isolates the anthracenes regardless of the three rotatable bonds between the spacer and the anthracenes.

The geometry optimization was attempted by MM and MO calculations since the most stable conformation was yet to be determined. Energies were calculated by MM as a function of the distance (r) between H-10′ of one anthracene and H-10′ of the other, wherein the geometry was optimized at each r (Fig 2*a*). The minimum energy is found at $r = 3.0$ Å and the structure is shown in Fig 2(*b*). Two anthryl moieties point in the same direction from the anthraquinone spacer, lie face to face with each other, but are not parallel so as for the cleft to taper off. The optimized geometry obtained by the PM3 method[17] is similar but has a wider cleft ($r = 4.4$ Å).

A chair-shaped distortion of the central ring of the anthraquinone spacer is noted, which occurs in order to give sufficient distance between the ether oxygen atoms and the quinoid oxygen atom.* [18] It follows that the two ether oxygens approach each other, and consequently, so do the two anthracenes. This tendency is more apparent in the MM calculations than the MO. Thus the separation of anthracenes is sensitive to the degree of anthraquinone distortion.

Interaction with nitrofluorenones

Interaction of **1** and a series of nitrofluorenones was investigated by electronic absorption and ^{1}H-NMR spectroscopy. Investigated entries were fluorenone, 2-mono-, 2,7-di-, 2,4,7-tri-, and 2,4,5,7-tetra-nitrofluorenones.



fluorenone

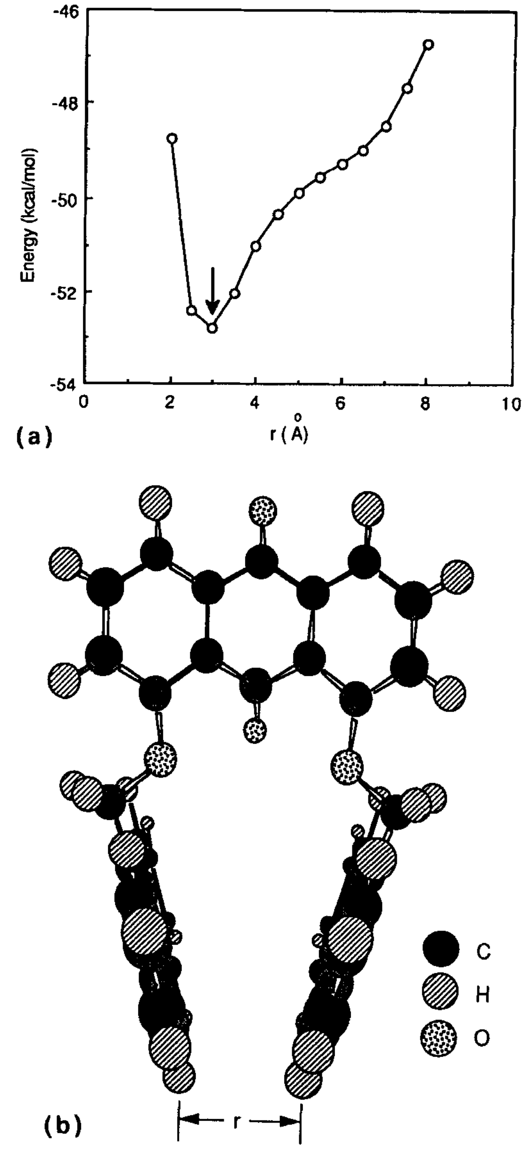


Figure 2 (a) Calculated energy by MM as a function of a fixed r, which is the distance between H-10′ of one anthracene and H-10′ of the other. The geometry is optimized at each r. (b) The minimum energy geometry ($r = 3.0$ Å).

Mixtures of **1** and fluorenones, which are substituted by at least one nitro group, exhibit a new absorption band, which is ascribed to charge transfer (CT) transitions (Fig 3). The maximum wavelengths are 454, 504, and 576 nm in the cases of di-, tri-, and tetra-nitrofluorenone, respectively. This result, i.e. increasing electron affinity, resulting in the absorption at longer wavelengths, is qualitatively in accordance with the CT theory[19] and argues that these absorptions are due to the CT transitions.

Complex formation (1:1) was confirmed by the Rose–Drago plots for trinitrofluorenone (TNF) and by both the Job (Fig 4) and the Rose-Drago plots for tetranitrofluorenone (TENF). Thermodynamic

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* Similar but smaller distortion was observed in the crystal structure of 1,5-dichloroanthraquinone (ref 18a). However, the anthraquinone ring of 1,8-dinitro-4,5-dihydroxyanthraquinone (ref 18b) and 1,5-dihydroxyanthraquinone (ref 18c) is almost planar.

Table 1 Charge transfer absorption and thermodynamic parameters for the complexation of **1**

Guest	λ_{CT} *(nm)*	ε_{CT} *$(M^{-1}cm^{-1})$*	K_{assoc} [a,b] *(M^{-1})*	ΔG° [a,b] *$(kJ\,mol^{-1})$*	ΔH° [a,c] *$(kJ\,mol^{-1})$*	ΔS° [a,c] *$(J\,K^{-1}mol^{-1})$*
DNF	454		< 10	> -5		
TNF	504	889	$(2.89 \pm 0.17) \times 10^2$	-14.0 ± 0.1	-41.0 ± 0.1	-90.6 ± 9.7
TENF[d]	576	830	$(2.17 \pm 0.02) \times 10^3$	-19.0 ± 0.0		

[a] 25°C.
[b] Indicated errors are the conditional standard deviations.[24]
[c] Indicated errors are the standard deviations.[26]
[d] Values for TENF are applied for samples within 1 h of preparation (see the text).
DNF = 2,7-dinitrofluorenone.

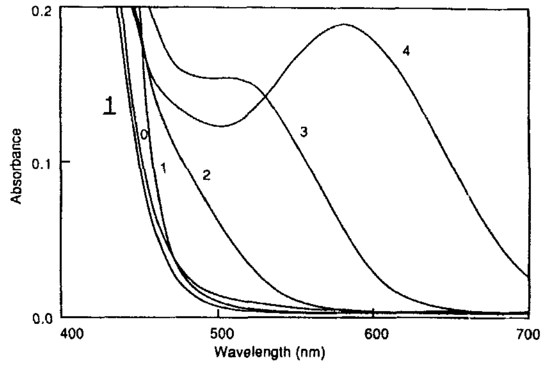

Figure 3 Charge transfer absorption bands of **1** and *n* (0–4, as indicated) nitro-substituted fluorenone in chloroform.

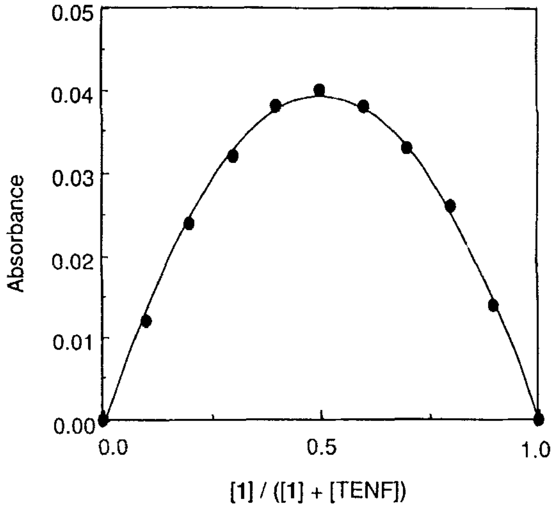

Figure 4 A Job's plot for the complex of **1** with TENF immediately after mixing (see text).

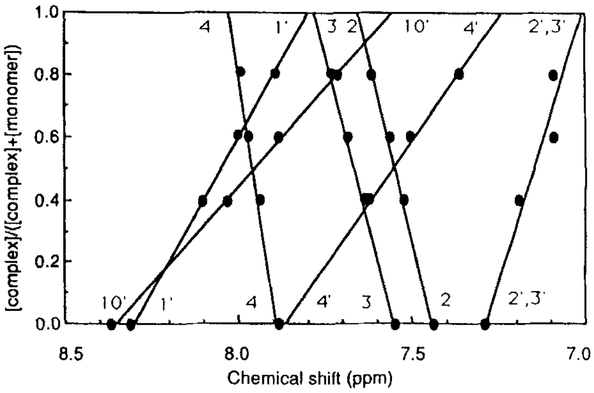

Figure 5 Complexation-induced upfield shifts (ppm) of **1**.

parameters were determined from the slope of van't Hoff plots and are summarized in Table 1. Although the entropy changes are negative, as expected from complex formation in organic solvents,[6b,20] the complexation is enthalpically driven. Increasing the number of nitro-substituents of the acceptor results in substantially stronger binding, which indicates that DA interaction* [21] is a major contributory force in stabilizing the complex.

A comment is needed for the case of TENF. Although the 1:1 complexation was clearly confirmed by the Job plot (Fig 4) for a while (ca. 1 h) after the sample preparation, a few hours later, precipitation was observed even though rather dilute (0.2 mM) solutions were used. Therefore, the thermodynamic parameters for TENF should be considered to apply to the initial complexation process only.†

The bis-system effect on binding efficiency is apparent from the comparison of **1** with **2**. An association increase by a factor of at least 29 is achieved; **2** and TNF associate too weakly ($K < 10\,M^{-1}$) to determine the association constant. Thus the co-operation of the two chromophores in the host is indispensable for recognizing these electron deficient compounds.

The ^{1}H-NMR revealed significant shifts for all signals of both **1** and TNF in the 1:1 complex. To be concise, protons of anthryl moieties and TNF shifted upfield and protons from the anthraquinone moiety shifted downfield. In Figure 5 are shown ^{1}H-NMR

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* DA interaction is composed of several interactions such as London dispersion, dipole–dipole and CT interaction (ref 21a–c).

† Characterization of the precipitate is now under way and will be reported later.

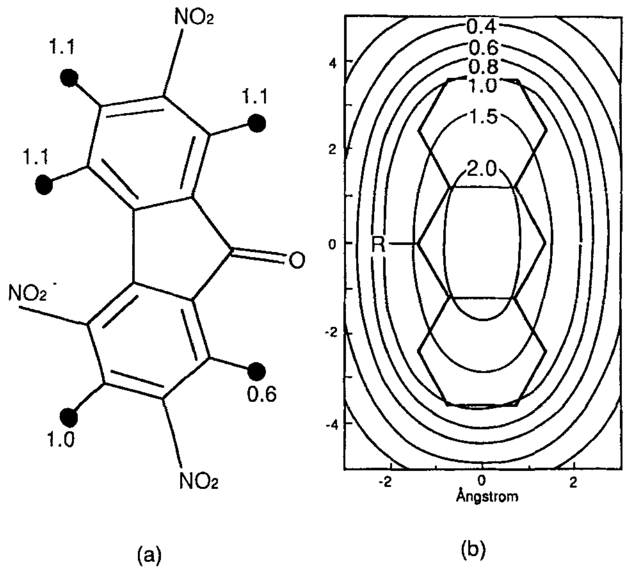
chemical shifts of **1** as a function of the ratio, [complex]/([complex] + [monomer]). The ratio was calculated from the association constant determined from the UV-visible titration (Table 1). The good linearity of all the shifts indicates that the chemical shift changes and the appearance of CT absorption are due to the exact same phenomenon, the complexation. The association constant of **1** and TNF derived from NMR is $3.00(\pm 0.06) \times 10^2\ M^{-1}$ and agrees with the value obtained from the UV-visible titration. It is clearly noted from the Figure that all the protons of the anthryl group shift upfield and the anthraquinone protons shift downfield. These changes indicate that anthracenes are above the plane of TNF and anthraquinone is at its side.

On the other hand, the calculated limiting chemical shifts of protons of TNF are 0.6–1.1 ppm (Fig 6*a*). The fact that most of TNF protons experience the upfield shift by 1.0–1.1 ppm, which are larger than those observed for **3** (0.5–0.7 ppm)[11a] indicates that TNF protons are influenced by the ring current of more than one anthracene as close as 3.4 Å, and hence it is located between the two anthryl groups of **1** as illustrated schematically in Figure 7.

To be more quantitative, chemical shifts induced by the ring current of methylanthracene, as a model of the anthryl group of **1**, were calculated using the quantum mechanical Haigh–Mallion equation (1)[22,23] (see Appendix):

$$\delta_R \times 10^{-6} = 4.06\,(H'/H'_{benzene}) \qquad (1)$$

Here, the ring current shift is expressed in ppm, and positive numbers indicate shifts to higher field. H′ is the secondary field induced by the ring current at the proton in question. A contour diagram of the induced upfield shift in the plane at 3.4 Å above the plane of methylanthracene is shown in Figure 6(*b*). The scale is the same as with Figure 6(*a*). It is obvious from the comparison of Figures 6(*a*) and 6(*b*) that one methylanthracene is not enough to explain the observed magnitude of these shifts, even by assuming maximum stacking. It follows that TNF must stack with more than one anthryl group simultaneously. Hence the observed shifts, together with the enhanced binding by the bis-system, makes good evidence for the sandwich-type structure of the complex in solution. The fact that the complexation shifts for H-1 and others differ by almost a factor of 2, suggests highly oriented complex. The determination of the specific orientation is, however, beyond the present data.



(a) (b)

Figure 6 (a) Structure of TNF and observed complexation-induced chemical shifts. (b) Contour diagram of the induced upfield shift in the plane at 3.4 Å above the plane of methylanthracene. Shifts are given in ppm. The scale of (a) and (b) is the same.

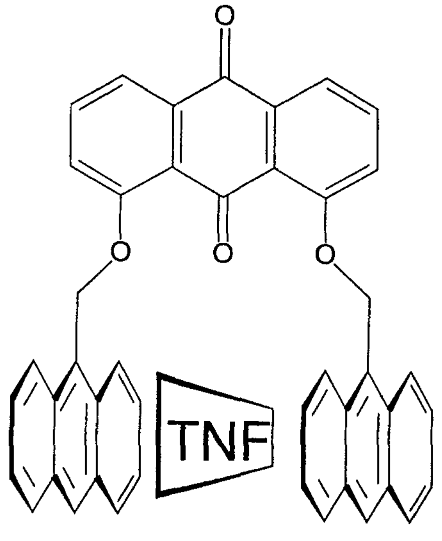


Figure 7 Sandwich structure of the complex of 1 with TNF.

In conclusion, TNF is sandwiched between the two anthryl groups of **1** as shown in figure 7 in solution, which is in consistent with the bis-effect and all of the ^1H-NMR results as discussed above. Thus, a new molecular tweezer, 1,8-bis[(9-anthryl)methoxy]-9,10-anthraquinone recognizes guest molecules and forms a DA complex as a supermolecule, of which functionality will be explored.

EXPERIMENTAL SECTION

Chloroform for spectroscopic measurements was distilled over P_2O_5, stored with molecular sieve 4A, and used within 1 week. Water was either doubly distilled or purified with a Millipore Milli-Q Labo system. Other chemicals were used directly as received. Proton magnetic resonance spectra were recorded on a JEOL GX-270 in $CDCl_3$. The chemical shifts are given in δ values from Me_4Si. Complicated peaks in the aromatic region were resolved and identified with two-dimensional COSY spectra and NOE techniques. UV-visible absorption spectra were recorded on a Photal MCPD-1000 or on an Hitachi 557 spectrophotometer. Fluorescence spectra were obtained on an Hitachi 650–40 spectrofluorimeter. The sample solutions were degassed by argon purging prior to the measurements. The IR spectrometer was a Perkin-Elmer 1600.

1,8-Bis[(9-anthryl)methoxy-9,10-anthraquinone (1)

A solution of 1,8-dihydroxyanthraquinone (0.24 g, 1 mmol) and 9-chloromethylanthracene (0.91 g, 4 mmol) in CH_2Cl_2 (30 ml) and a solution of tetrabutylammonium chloride (0.56 g, 2 mmol) and sodium hydroxide (0.12 g, 3 mmol) in water (25 ml) were placed in a two-necked flask equipped with a mechanical stirrer and a reflux condenser. The mixture was refluxed under vigorous stirring so as to mix the two phases well. After 38 h, a yellow precipitate was collected and washed with CH_2Cl_2 and water. The resulting precipitate was crystallized from chloroform/hexane to give crystals (0.21 g, 34%): m.p. 215–217°C (dec.); ^{1}H-NMR δ 8.37 [2H, s, anthryl (=a)H-10)], 8.32 (4H, d, aH-1), 7.89 [4H, d, aH-4; 2H, d, anthraquinone (=aq)H-4], 7.56 (2H, t, aqH-3), 7.45 (2H, d, aqH-2), 7.2–7.4 (8H, m, aH-2,3), 6.04 (4H, s, CH_2); IR (KBr pellets, cm^{-1}) 1670, 1584, 1456, 1311, 1261, 1236, 1014, 962, 887, 732; UV (chloroform, nm) 337 (log $\varepsilon/M^{-1}cm^{-1}$ 3.87), 352 (4.07), 368 (4.18), 388 (4.16); Anal. calcd. for $C_{44}H_{28}O_4$: C, 85.14; H, 4.55. Found: C, 84.87; H, 4.34.

1-(9-Anthryl)methoxy-9,10-anthraquinone (2)

A solution of 1-hydroxyanthraquinone (0.54 g, 2.4 mmol) and 9-chloromethylanthracene (1.1 g, 4.8 mmol) in CH_2Cl_2 (100 ml) and a solution of tetrabutylammonium chloride (0.67 g, 2.4 mmol) and sodium hydroxide (97 mg, 2.4 mmol) in water (50 ml) were used and the procedure was similar to the above. The precipitate was crystallized from chloroform, which gave pure **2** as a yellow solid (0.20 g, 20%): m.p. 219°C (dec.); ^{1}H-NMR δ 8.55 (1H, s, aH-10), 8.47 (2H, d, aH-1), 8.22 (2H, m, aqH-5,8), 8.06 (2H, d, aH-4), 8.00 (1H, m, aqH-4), 7.6–7.8 (2H, m, aqH-6,7), 7.4–7.6 (4H, m, aH-2,3), 6.26 (2H, s, CH_2); IR (KBr pellets, cm^{-1}) 1670, 1583, 1448, 1315, 1256, 1052, 961, 883, 732, 798; UV (chloroform nm) 332 (log $\varepsilon/M^{-1}cm^{-1}$ 3.78), 350 (3.94), 367 (4.11), 387 (4.07); MS *m/z* 404 (calcd. 404); Anal. calcd. for $C_{29}H_{18}O_3$: C, 84.03; H, 4.38. Found: C, 84.39; H, 4.07.

UV titration and analysis of the data

The changes in the absorbance due to the CT transition of the complex were followed for chloroform solutions including varying concentrations of nitrofluorenones and a fixed concentration (0.2 mM) of **1**. The data were analysed by using a non-linear least-squares curve-fitting procedure based on the treatment by Long and Drago.[24] However, their method implicitly assumes that the absorbance of the uncomplexed species is measured with no error, and uses it as a perfect reference point in determining ΔA values and hence complex parameters.[25] This point was modified to evaluate all the data equally weighted. Rose–Drago plots were also made to confirm the 1:1 complex formation. The thermodynamic parameters were determined by the least-square procedure[26] from the temperature dependence (25–43°C) of the association constant.

Computation methods

MS-BASIC programs were written on an Apple Macintosh computer to calculate the association constants, the simple Hückel molecular orbitals, and the ring-current chemical shifts. The MM and MO (PM3) calculations were conducted by Sony Tektronix CAChe (version 2.8) program on an Apple Computer Macintosh IIfx.

ACKNOWLEDGMENT

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APPENDIX

Ring current effects of the anthryl group

The ring current equation used in this study was the quantum-mechanical Haigh–Mallion equation[22,23] which has been successfully used to predict chemical shifts in many systems including e.g. hydrocarbons[23] and proteins.[9] The equation involves a constant of proportionality which should be determined empericallly. The factor 4.06 was found to be appropriate for protons outside the van der Waals dimension of the ring,[27] while the factor 1.56 was found to apply for protons attached to the ring in which the ring current is considered, as was first proposed by Haigh and Mallion.[23b]

Since the crystal structure of *syn*[2,2](1,4)-athracenophane **3** and its induced chemical shifts are known,[11] the cyclophane was used to test the validity of the proportionality constant. A plane 1,4-dimethylanthrace composed of the regular benzene hexagons was used as the current loop. The inductive model for the methyl group (the Coulomb integral for the methyl-substituted carbon, α-0.5β) was used in the simple Hückel molecular orbital calculation.[27]

Every given proton has four distinctive positions relative to the anthracene loop, since the anthracenophane has two types of crystal structure, each of which has two kinds of equivalent protons.[11b] The shifts were calculated for the four locations of each proton, followed by being averaged. The calculated and observed shifts are as follows (ppm): H_c, 0.48(obs), 0.39(cal); H_d, 0.71, 0.78; H_e, 0.63, 0.57; H_f, 0.52, 0.49. Thus the calculated results agree with experimental values within 20%. Now the applicability of the theory and the constant value, 4.06, are confirmed for the shielding region of the anthracene system.

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