Lid-type Inclusion of Pyrene-1,3,6,8-tetrasulphonate Anion by β-Cyclodextrin

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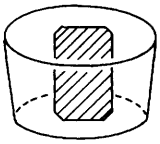
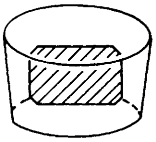
U.v. absorption and induced circular dichroism studies have indicated a new type of inclusion behaviour ('lid-type') in cyclodextrin–arene 1 : 1 host–guest complexes exemplified by the pyrene-1,3,6,8-tetrasulphonate–β-cyclodextrin complex.

Cyclodextrins (CDXs) and arenes often form inclusion complexes with 1:1 stoicheiometry. The most well known type is axial inclusion, in which the long axis of the arene is parallel to the CDX axis. Several *p*-disubstituted benzenes,[1] naphthalenes,[2] anthracenes,[3] tetracenes,[3a] and pyrenes[4] are accommodated by β-CDX in this manner [see (**1**)]. In a second type the short axis of the arene is parallel to the CDX axis [see (**2**)], as in the inclusion of 1,8-diaminonaphthalene by β-CDX.[2] Many unsymmetrically substituted arenes, heterocyclic arenes,[5] and dyes[6] from β-CDX complexes of intermediate type. In all these cases, however, the plane of the arene is believed to be almost parallel to the CDX axis. In the lid-type inclusion reported here, both short and long axes of the arene are nearly normal to the CDX axis [see (**3**)].

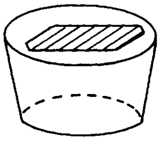
Unsubstituted pyrene is one of the best sized molecules for axial inclusion by β-CDX.[4] For the present study tetrasodium pyrene-1,3,6,8-tetrasulphonate (PYTS; Kodak) was used, for the following reasons. (i) Four sulphonate groups would sterically prevent axial inclusion. (ii) Since the inside of the CDX cavity is hydrophobic,[7] the more hydrophobic pyrene skeleton rather than a sulphonate moiety, would be included first. In addition, symmetrically attached polar sulphonate groups might assist an ideal lid-type inclusion. (iii) The polarization direction of the absorption bands of pyrene derivatives is known.[8] Accordingly, it is possible to deduce the



(**1**)



(**2**)



(**3**)

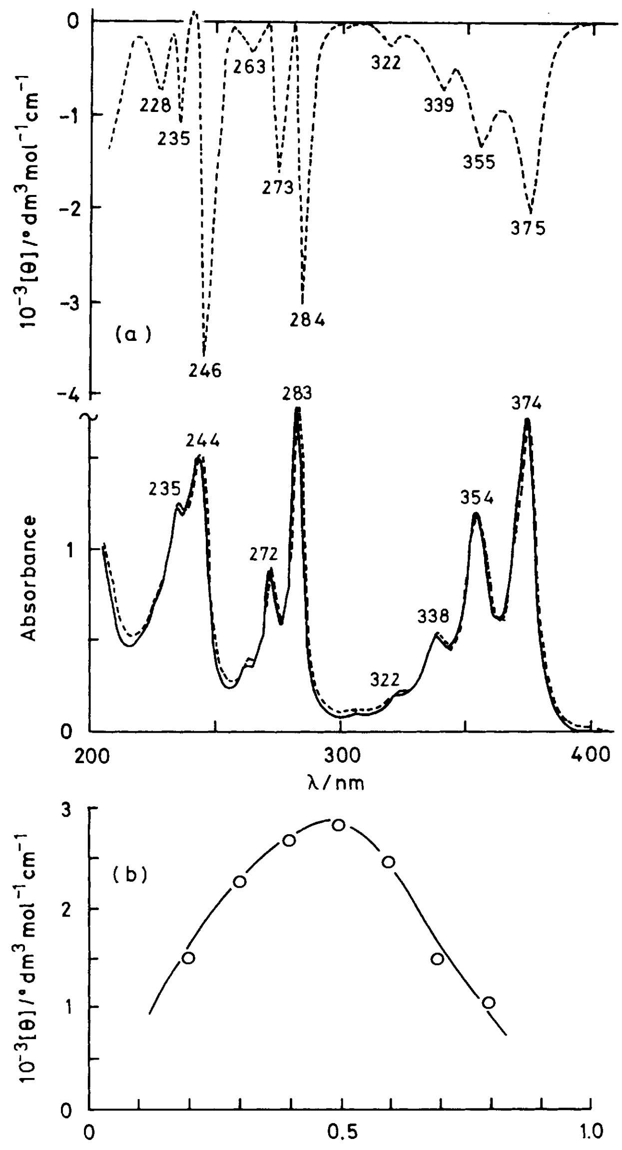


Figure 1. (a) C.d. and absorption spectra of 4.446×10^{-5} M-PYTS in the presence (dotted line) and absence (solid line) of 10^{-2} M-β-CDX (pH 9.0); path length 10 mm. Numbers indicate the positions of absorption peaks or of i.c.d. negative peaks in the presence of β-CDX. (b) Job's continuous variation plots for the determination of the complex stoicheiometry; [PYTS] + [β-CDX] = 4×10^{-3} M (constant); monitored at 322 nm using 1 mm path cell. A data processor was used for i.c.d. data collection.

inclusion type from the sign of induced circular dichroism (i.c.d.) spectra, on the basis of the assumption that transitions polarized parallel to the CDX axis produce a positive i.c.d., whereas those with perpendicular polarization produce a negative i.c.d.[1—5]

Figure 1(a) shows u.v. absorption and i.c.d. spectra of PYTS in the absence and presence of β-CDX. The change in absorption spectrum on addition of β-CDX (red shift of 2—3 nm) is not large in comparison with that for normal arene–CDX inclusion, in which the arene penetrates deeply into the cavity.[1—6] However, this is indeed the result of 1 : 1 complexation, as evidenced by continuous variation plots [Figure 1(b)].

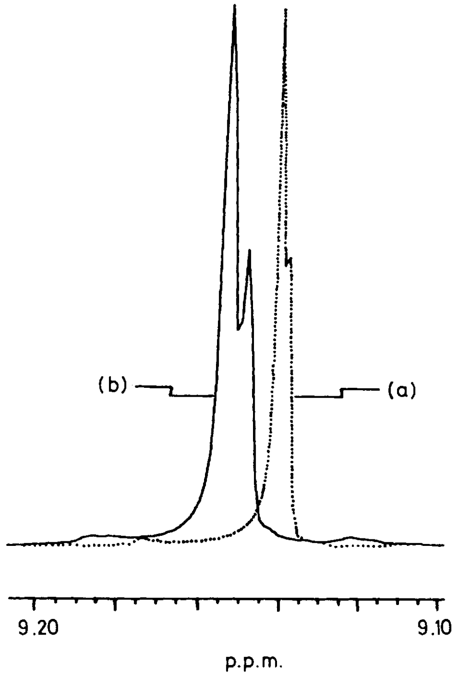


Figure 2. 500 MHz ^{1}H N.m.r. spectra of 10^{-3} M-PYTS in 99.85% D_2O in the absence (a) and presence (b) of 2×10^{-2} M-β-CDX (standard H_2O in D_2O, 4.670 p.p.m.).

Although several peaks are seen in the absorption spectra, only the peak around 275—290 nm is known to be polarized along the short axis; all others are polarized along the long axis.[4,8] The i.c.d. spectrum showed negative peaks corresponding almost exactly to all absorption peaks. If we interpret this phenomenon on the basis of the foregoing argument (iii), the inclusion appears to be approximately lid-type; the i.c.d. showed negative peaks for both long- and short-axis-polarized absorption bands. A Corey–Pauling–Koltun molecular model supports this type of inclusion.

^{1}H N.m.r. studies confirmed the association of PYTS with β-CDX (Figure 2). Two PYTS singlets at 9.138 (2H) and 9.140 p.p.m. (4H) were shifted to 9.149 and 9.154 p.p.m., respectively, on addition of β-CDX, indicating some interaction. However, it was not clear whether the lid-type inclusion was occurring at the 'primary' or the 'secondary' face of β-CDX.

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