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## Structures of Two Trichromophoric Anthraceno Cryptands

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**Abstract.** 6,9,17,20-Tetraoxa-3,12-diaza[14.8<sup>3,12</sup>](9,10)-anthracenophane (*A*<sub>22</sub>), C<sub>30</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>, and 7,10,19,-

22-tetraoxa-4,13-diaza[16.8<sup>4,13</sup>](9,10)anthracenophane (*A*<sub>33</sub>), C<sub>32</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>. *A*<sub>22</sub> compound: *M*<sub>r</sub> = 492, monoclinic, *Pc*, *a* = 9.816 (4), *b* = 14.493 (4), *c* = 10.523 (5) Å, β = 118.26 (3)°, *V* = 1318.6 Å<sup>3</sup>, *Z* = 2,

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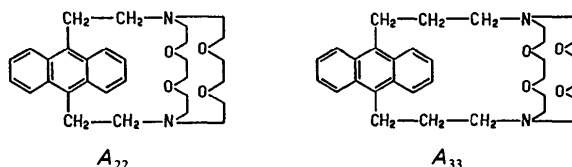
$D_x = 1.244 \text{ g cm}^{-3}$ , Cu  $K\alpha$ ,  $\lambda = 1.5405 \text{ \AA}$ ,  $\mu = 6.60 \text{ cm}^{-1}$ ,  $F(000) = 532$ ,  $T = 298 \text{ K}$ , final  $R = 0.043$ ,  $wR = 0.050$  for 1864 observed reflexions with  $I > 3\sigma(I)$ . As expected the nitrogen lone pairs point towards the aromatic nucleus.  $A_{33}$  compound:  $M_r = 520$ , triclinic,  $P\bar{1}$ ,  $a = 10.399(2)$ ,  $b = 10.577(3)$ ,  $c = 15.244(2) \text{ \AA}$ ,  $\alpha = 77.98(3)$ ,  $\beta = 109.61(2)$ ,  $\gamma = 117.23(2)^\circ$ ,  $V = 1401.4 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.233 \text{ g cm}^{-3}$ , Cu  $K\alpha$ ,  $\lambda = 1.5405 \text{ \AA}$ ,  $\mu = 6.47 \text{ cm}^{-1}$ ,  $F(000) = 564$ ,  $T = 298 \text{ K}$ , final  $R = 0.026$ ,  $wR = 0.030$  for 1582 observed reflexions with  $I > 3\sigma(I)$ . The nitrogen lone pairs are on the outside of the molecule, remote from the aromatic nucleus. Free space inside the molecules (both  $A_{22}$  and  $A_{33}$ ) appears to be too small to accept ions such as  $\text{Na}^+$  or  $\text{K}^+$ . Crystalline conformations are not consistent with the photophysical behaviour of the compounds in methanol and acetonitrile.

**Introduction.** The fluorescence spectra of aromatic compounds can be modified in the presence of salts. It is generally reported that addition of cations (McCullough & Yeroushalmi, 1983; Kitamura, Imabayashi & Tazuke, 1983) or anions (Watkins, 1974) produces fluorescence quenching. These effects can be magnified or changed by linking cation-complexing ligands (such as coronands) with the chromophores (Löhr & Vögtle, 1985; Takagi & Ueno, 1984). For instance, Sousa & Larson (1977) observed variations of luminescence quantum yields of several naphtho-*x*-crown-6 ethers in the presence of alkali-metal cations. Shizuka, Takada & Morita (1980) and Wolfbeis & Offenbacher (1984) reported an increase in fluorescence intensity of dibenzo-18-crown-6 ether by addition of alkali-metal cations. With tetrapyrro crown ethers, Tundo & Fendler (1980) noticed an alteration of monomer/excimer fluorescence ratio *versus*  $\text{K}^+$ , providing evidence of conformational changes of host upon complexation of the guest. Cation-modulated fluorescence was applied by Nishida, Katayama, Katsudi, Nakamura, Takagi & Ueno (1982) to the estimation of  $\text{Ca}^{2+}$ .

A more pronounced photophysical response to the presence of a cation was expected from a system that had a powerful fluorophore bound to a stronger ligand than a crown ether. As fluorophore, the anthracene ring was selected for its remarkable photophysical (high fluorescence yield) and photochemical properties as well as its synthetic flexibility (Bouas-Laurent, Castellan & Desvergne, 1980).

A preliminary account of the preparation and luminescence studies of the new cryptands  $A_{22}$  and  $A_{33}$  was reported recently (Konopelski, Kotzyba-Hibert, Lehn, Desvergne, Fagès, Castellan & Bouas-Laurent, 1985). These trichromophoric complexing systems were found to be very sensitive to the solvent polarity and the presence of protons or metal cations.

We were intrigued, in particular, by the striking difference between the fluorescence spectra of the two free ligands in methanol: whereas  $A_{22}$  exhibits a fairly high fluorescence yield ( $\Phi_F = 0.68$ ) but no detectable exciplex emission (Fig. 1a),  $A_{33}$  shows a low quantum yield ( $\Phi_F = 0.04$ ) with a characteristic intramolecular exciplex fluorescence (Fig. 1b).



An exciplex fluorescence is expected for systems in which tertiary amines are held in close proximity to an aromatic acceptor (Davidson & Whelan, 1983; Davidson, 1983). This was indeed observed for both  $A_{22}$  and  $A_{33}$  in acetonitrile where the fine structure has almost completely disappeared (Fig. 2).

A plausible explanation rests in the possibility of solvation of the two nitrogen atom lone pairs by methanol in  $A_{22}$  but not in  $A_{33}$ . Thus, in protonic solvents, the conformation of the nitrogen lone pairs

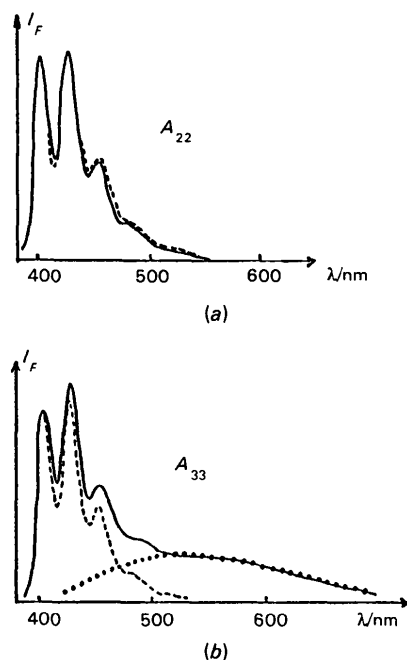


Fig. 1. Corrected fluorescence emission spectra. Intensities ( $I_f$ ) are in arbitrary units. (a)  $A_{22}$  (—) and the reference compound (9,10-di-*n*-propylanthracene) (-----) in  $\text{CH}_3\text{OH}$ ; concentration  $\approx 10^{-5} \text{ M}$ ; room temperature. (b)  $A_{33}$  in  $\text{CH}_3\text{OH}$ : free ligand (—); and in the presence of an excess of  $\text{H}^+$  (-----); exciplex (.....); concentration  $\approx 10^{-5} \text{ M}$ ; room temperature. Intensities ( $I_f$ ) are in arbitrary units.

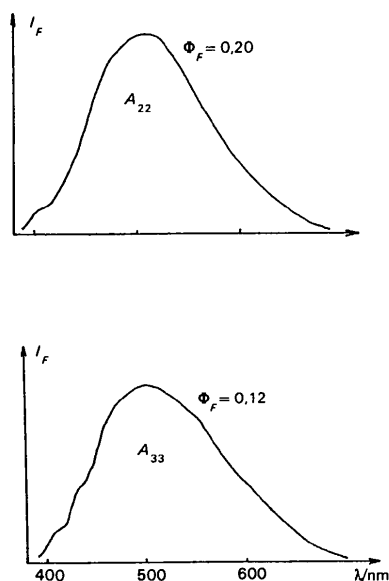


Fig. 2. Corrected fluorescence emission spectra of  $A_{22}$  and  $A_{33}$  in  $\text{CH}_3\text{CN}$  at room temperature; concentration  $\approx 10^{-5}M$ . Intensities ( $I_F$ ) are in arbitrary units.

Table 1 (cont.)

	x	y	z	$B_{eq}$
$A_{33}$				
C(14)	0.6299 (4)	0.4618 (4)	0.6254 (2)	3.0 (1)
C(2)	0.4375 (4)	0.2194 (3)	0.6235 (2)	2.9 (1)
C(7)	0.4326 (4)	0.2290 (3)	0.7146 (2)	2.9 (1)
C(1)	0.5407 (4)	0.3328 (4)	0.5806 (2)	2.9 (1)
C(9)	0.6187 (4)	0.4735 (3)	0.7148 (2)	3.0 (1)
C(3)	0.3352 (4)	0.0893 (4)	0.5773 (2)	3.5 (1)
C(13)	0.7338 (4)	0.5834 (4)	0.5848 (2)	3.6 (2)
O(33)	1.0965 (3)	0.4483 (3)	0.8339 (2)	4.5 (1)
C(10)	0.7091 (4)	0.6092 (4)	0.7552 (2)	3.8 (2)
C(5)	0.2350 (4)	-0.0138 (4)	0.7089 (3)	4.2 (2)
C(8)	0.5259 (4)	0.3555 (3)	0.7610 (2)	3.0 (1)
C(6)	0.3299 (4)	0.1066 (4)	0.7553 (2)	3.8 (2)
C(11)	0.8025 (4)	0.7214 (4)	0.7124 (3)	4.2 (2)
O(23)	0.7463 (3)	-0.0334 (3)	0.8003 (2)	4.1 (1)
C(12)	0.8166 (4)	0.7084 (4)	0.6262 (3)	4.1 (2)
C(15)	0.5316 (4)	0.3653 (4)	0.8600 (2)	3.7 (2)
C(21)	0.8837 (4)	0.1275 (4)	0.6971 (2)	3.8 (2)
C(4)	0.2372 (4)	-0.0214 (4)	0.6183 (3)	4.0 (2)
C(32)	0.9848 (4)	0.4252 (4)	0.8768 (3)	4.3 (2)
C(25)	0.6236 (5)	-0.1828 (4)	0.9162 (3)	5.1 (2)
N(20)	0.8831 (3)	0.1915 (3)	0.6024 (2)	3.2 (1)
C(31)	0.9572 (4)	0.2857 (4)	0.9341 (3)	4.5 (2)
O(26)	0.6635 (3)	-0.0768 (3)	0.9771 (2)	4.8 (1)
C(35)	1.2224 (4)	0.5834 (4)	0.7183 (3)	4.9 (2)
C(17)	0.5606 (4)	0.3103 (4)	0.4924 (2)	3.1 (1)
N(30)	0.8516 (3)	0.2490 (3)	0.9886 (2)	4.0 (1)
C(38)	1.0343 (4)	0.2568 (4)	0.5891 (3)	3.9 (2)
O(36)	1.1317 (3)	0.4875 (3)	0.6458 (2)	4.5 (1)
C(34)	1.1322 (4)	0.5786 (4)	0.7784 (3)	4.8 (2)
C(22)	0.7284 (4)	0.0289 (4)	0.7068 (3)	4.0 (2)
C(18)	0.6482 (4)	0.2188 (4)	0.5107 (2)	3.3 (1)
C(37)	1.1584 (4)	0.3639 (4)	0.6578 (3)	4.2 (2)
C(24)	0.6041 (4)	-0.1261 (4)	0.8163 (3)	4.7 (2)
C(16)	0.6786 (4)	0.3677 (4)	0.9309 (2)	3.8 (2)
C(27)	0.8203 (5)	-0.0083 (4)	1.0216 (3)	4.8 (2)
C(28)	0.8550 (4)	0.1307 (4)	1.0575 (3)	4.8 (2)
C(19)	0.8081 (4)	0.2891 (4)	0.5733 (2)	3.5 (1)
C(29)	0.6995 (4)	0.2325 (4)	0.9332 (2)	4.1 (2)

Table 1. Atomic positional parameters and  $B_{eq}$  for  $A_{22}$  and  $A_{33}$

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}$
$A_{22}$				
C(8)	0.0332 (4)	0.1832 (3)	0.3379 (4)	3.8 (1)
C(2)	0.2793 (4)	0.1214 (2)	0.3649 (4)	3.3 (1)
C(14)	0.0418 (4)	0.0798 (3)	0.1539 (4)	3.6 (1)
C(1)	0.2040 (4)	0.0790 (2)	0.2274 (4)	3.4 (1)
C(10)	-0.2094 (4)	0.1328 (3)	0.1275 (4)	4.8 (2)
C(3)	0.4438 (4)	0.1122 (3)	0.4543 (4)	4.1 (2)
C(6)	0.2808 (5)	0.2157 (3)	0.5592 (4)	4.4 (2)
C(7)	0.1957 (4)	0.1733 (3)	0.4188 (4)	3.6 (1)
C(4)	0.5179 (5)	0.1512 (3)	0.5880 (4)	4.7 (2)
O(23)	0.4906 (3)	0.3928 (2)	0.1930 (3)	4.8 (1)
C(9)	-0.0426 (4)	0.1321 (3)	0.2087 (4)	3.6 (1)
O(36)	0.0332 (3)	0.2804 (2)	-0.2331 (3)	4.7 (1)
C(13)	-0.0451 (5)	0.0309 (3)	0.0202 (4)	4.5 (2)
C(31)	-0.0395 (5)	0.4224 (3)	0.1254 (4)	4.5 (2)
O(33)	-0.1504 (3)	0.3952 (2)	-0.1256 (3)	4.8 (1)
C(11)	-0.2847 (5)	0.0857 (3)	0.0008 (5)	5.3 (2)
N(30)	0.0214 (4)	0.3767 (2)	0.2670 (3)	3.9 (1)
N(20)	0.2788 (4)	0.1818 (2)	0.0258 (3)	3.4 (1)
C(24)	0.5457 (5)	0.4390 (3)	0.3285 (5)	5.1 (2)
C(5)	0.4357 (4)	0.2035 (3)	0.6394 (4)	4.7 (2)
C(17)	0.2976 (5)	0.0372 (2)	0.1639 (4)	3.9 (1)
C(27)	0.2887 (5)	0.4444 (3)	0.4052 (5)	5.7 (2)
C(28)	0.1209 (5)	0.4400 (3)	0.3852 (4)	5.1 (2)
C(32)	-0.0685 (5)	0.3502 (3)	0.0112 (4)	4.6 (2)
O(26)	0.2956 (4)	0.4933 (2)	0.2965 (3)	6.0 (1)
C(34)	-0.2121 (5)	0.3319 (3)	-0.2422 (4)	5.1 (2)
C(12)	-0.2031 (5)	0.0342 (3)	-0.0525 (5)	5.4 (2)
C(18)	0.3808 (5)	0.1097 (3)	0.1212 (4)	3.9 (2)
C(22)	0.3904 (5)	0.3187 (3)	0.1748 (5)	4.8 (2)
C(38)	0.1930 (5)	0.1488 (3)	-0.1253 (4)	4.6 (2)
C(21)	0.3614 (5)	0.2674 (3)	0.0389 (4)	4.0 (2)
C(15)	-0.0553 (5)	0.2496 (3)	0.3801 (4)	4.8 (2)
C(25)	0.4464 (5)	0.5154 (3)	0.3274 (5)	6.2 (2)
C(35)	-0.1169 (5)	0.3196 (3)	-0.3172 (4)	4.9 (2)
C(16)	-0.1030 (5)	0.3374 (3)	0.2880 (5)	5.0 (2)
C(37)	0.0311 (6)	0.1878 (3)	-0.2063 (5)	5.4 (2)

could be 'out-out' in the former and 'in-in' or 'in-out' for the latter (Simmons & Park, 1968). In aprotic solvents, conformations could be 'in-in' for both compounds. It seemed thus appropriate to examine the structures of  $A_{22}$  and  $A_{33}$  by X-ray analysis.

**Experimental.** Nonius CAD-4 diffractometer. Variable scan rate ( $\theta, \omega$ ). Monochromated (graphite)  $\text{Cu } K\alpha$  radiation. No significant change in intensity observed by monitoring three independent reflexions. No absorption correction. All heavy atoms located by direct methods (Main *et al.*, 1980). H-atom positions calculated before isotropic refinement. C, O and N atoms refined anisotropically by block-diagonal least-squares refinements.  $\sum w(|F_o| - |F_c|)^2$  minimized with empirical  $w$  and finally with absolute weights. Local programs *CRISAFFI* and *CRISUTIL* (Marsau, 1972) for refinements and computation. Atom scattering factors for hydrogen from Stewart, Davidson & Simpson (1965).  $f$  curves from *International Tables for X-ray Crystallography* (1974) with analytical approximation.

(a)  $A_{22}$ : crystal of  $A_{22}$  ( $0.8 \times 0.5 \times 0.5$  mm) from toluene solution. Lattice parameters calculated by least squares of 21 independent reflexions. 1957 unique reflexions observed with  $I > 3\sigma(I)$ .  $\theta_{\max} = 60^\circ$ . Final  $R = 0.043$ ,  $wR = 0.050$ ,  $S = 2.6$ ,  $(\Delta/\sigma)_{av} = 0.1$ ,  $\Delta\rho = 0.28 \text{ e } \text{\AA}^{-3}$ . Absolute  $w = 1/\sigma^2(F_o)$ .

(b)  $A_{33}$ : crystal of  $A_{33}$  (0.5 × 0.1 × 0.2 mm) from toluene solution. Lattice parameters calculated by least squares of 20 reflexions. 4147 unique reflexions. Range of  $h, k, l$ : -11-11, -11-11, 0-17. 1582 reflexions observed with  $I > 3\sigma(I)$ .  $\theta_{\max} = 60^\circ$ . Final  $R = 0.026$ ,  $wR = 0.030$ ,  $S = 0.41$ ,  $(\Delta/\sigma)_{\text{av}} = 0.08$ ,  $\Delta\rho = 0.2 \text{ e \AA}^{-3}$ . Absolute  $w = 1/\sigma^2(F_o)$ .\*

**Discussion.** Atomic parameters are given in Table 1 and bond lengths in Table 2.

$A_{22}$ : Orthogonal projections of  $A_{22}$  obtained by the program *SNOOPI* (Davies, 1983) are shown in Fig. 3. The molecule is a cage where the oxygen atoms point outwards. With the hydrogen atoms H(121), H(131), H(125) and H(135), the oxygens sketch a cradle as previously depicted in 18-crown-6 macrocyclic polyethers (Truter, 1976) or diazopolyoxamacrorings (Moras, 1971). The oxygen atoms delineate a nearly planar quadrilateral, the centre being at 2.8 Å from each vertex. The free space inside the molecule appears to be too small for accepting ions such as Na<sup>+</sup> ( $R = 0.97 \text{ \AA}$ ) or K<sup>+</sup> ( $R = 1.33 \text{ \AA}$ ). A strong interaction between the nitrogen lone pairs and the aromatic ring is implied by this conformation.

$A_{33}$ : The molecule displays a different conformation to  $A_{22}$ . Two oxygens are located outside (26 and 36) and the two others (23 and 33) inside the crown framework. The nitrogen lone pairs are outside the cavity (Fig. 4). The nitrogen atoms (20 and 30) appear to be too remote from the aromatic ring to be involved in significant interaction (Fig. 4). Cations such as Na<sup>+</sup> and K<sup>+</sup> are too bulky to fit into the cavity because of the presence of the hydrogen atoms H(219), H(229), H(122), H(132), H(134) and H(124). The interatomic distances between these hydrogens and the aromatic ring atoms are given in Fig. 4. The figures in parentheses denote distances from the mean plane of the anthracene nucleus. The introduction of a medium-size cation into the cavity could occur only with major conformational change of the macrocyclic skeleton. Studies of cation complexes are required to resolve the matter. Torsional angles for compounds  $A_{22}$  and  $A_{33}$  are listed in Table 3.

In the crystalline state, the nitrogen lone pairs of  $A_{22}$  are oriented, inside the complexing cavity, towards the aromatic ring whereas they point outside for  $A_{33}$ . These molecular conformations revealed in the crystal (grown from toluene solutions) are not consistent with the photophysical behaviour of the compounds in methanol and acetonitrile.

A rapid interconversion 'in-out' of the nitrogen lone pairs might explain their fluorescence in fluid solution.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42688 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) for  $A_{22}$  and  $A_{33}$

	$A_{22}$	$A_{33}$		$A_{22}$	$A_{33}$
C(1)-C(2)	1.415 (4)	1.408 (4)	C(17)-C(18)	1.523 (4)	1.538 (4)
C(1)-C(14)	1.403 (4)	1.412 (4)	C(18)-N(20)	1.466 (4)	-
C(1)-C(17)	1.497 (4)	1.508 (4)	C(18)-C(19)	-	1.525 (4)
C(2)-C(3)	1.439 (5)	1.443 (4)	C(19)-N(20)	-	1.478 (3)
C(2)-C(7)	1.416 (4)	1.434 (4)	N(20)-C(21)	1.453 (5)	1.460 (3)
C(3)-C(4)	1.363 (5)	1.353 (4)	C(21)-C(22)	1.513 (4)	1.508 (4)
C(4)-C(5)	1.389 (5)	1.408 (4)	C(22)-O(23)	1.407 (4)	1.429 (3)
C(5)-C(6)	1.357 (5)	1.361 (4)	O(23)-C(24)	1.430 (4)	1.423 (4)
C(6)-C(7)	1.446 (5)	1.430 (4)	C(24)-C(25)	1.472 (6)	1.498 (4)
C(7)-C(8)	1.415 (4)	1.406 (4)	C(25)-O(26)	1.393 (5)	1.427 (4)
C(8)-C(9)	1.411 (5)	1.404 (4)	O(26)-C(27)	1.374 (5)	1.423 (4)
C(8)-C(15)	1.498 (5)	1.514 (4)	C(27)-C(28)	1.560 (5)	1.519 (4)
C(9)-C(10)	1.444 (5)	1.438 (4)	C(28)-N(30)	1.480 (5)	1.462 (4)
C(9)-C(14)	1.431 (5)	1.440 (4)	N(30)-C(31)	1.474 (4)	1.462 (4)
C(10)-C(11)	1.362 (5)	1.352 (4)	C(31)-C(32)	1.516 (5)	1.505 (4)
C(11)-C(12)	1.392 (5)	1.409 (4)	C(32)-O(33)	1.431 (4)	1.421 (4)
C(12)-C(13)	1.367 (5)	1.353 (4)	O(33)-C(34)	1.417 (4)	1.418 (4)
C(13)-C(14)	1.439 (5)	1.432 (4)	C(34)-C(35)	1.492 (5)	1.494 (4)
C(15)-C(16)	1.532 (5)	1.540 (4)	C(35)-O(36)	1.429 (4)	1.425 (4)
C(16)-N(30)	1.455 (5)	-	O(36)-C(37)	1.375 (5)	1.420 (3)
C(16)-C(29)	-	1.533 (4)	C(37)-C(38)	1.513 (5)	1.515 (4)
C(29)-N(30)	-	1.469 (4)	C(38)-N(20)	1.483 (4)	1.468 (3)



Fig. 3.  $A_{22}$ : projection on the mean anthracene plane and the free space inside the molecule of  $A_{22}$ .

