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The Water Inclusion Complex of a Fluorescent Diprotonated Anthracenocryptand

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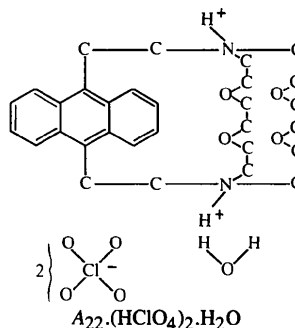
Abstract

6,9,17,20-Tetraoxa-3,12-diaza[14.8^{3,12}](9,10)anthracenophane perchlorate monohydrate, A₂₂·(HClO₄)₂·H₂O (C₃₀H₄₂N₂O₄²⁺·2ClO₄⁻·H₂O), is a diprotonated form of a molecular receptor described previously. The N⁺—H bonds are oriented inside the cavity which encapsulates one molecule of water. The single-crystal fluorescence spectra of the free base (A₂₂) and of the title compound are reported.

Comment

The crystal structure and the fluorescence emission spectra of the free ligand A₂₂ have already been reported (Guinand *et al.*, 1986). In non-protic solvents (such as toluene, acetonitrile or THF) a typical exciplex fluorescence (broad red-shifted band) is recorded, whereas in protic solvents (methanol) or in acidic media the spectra display a structured pattern, typical of an anthracene derivative in a very dilute solution. Indeed, an exciplex emission is known to occur between the nitrogen lone pairs and aromatic ring if the conformation is favourable (Davidson, 1983; Fages, Desvergne & Bouas-Laurent, 1989), *i.e.* in the case of A₂₂, when the lone pairs are oriented inside the cavity pointing toward the π cloud ('in-in' conformation). This is the conformation observed in crystalline A₂₂. From these data and the above observations, it was concluded that in protic media the conformation of the nitrogen lone pairs

could be essentially 'out-out'. In order to confirm the role played by protonation on the conformation of the N atoms, a single-crystal analysis of A₂₂·(HClO₄)₂ was performed.



Surprisingly, from the first steps of the structure resolution, the N atoms appeared to be in the 'in-in' conformation and the ClO₄⁻ anions held aloof from the protons. Difference Fourier map analyses revealed the presence of one molecule of water encaged inside the molecular cavity, principally coordinated with two O atoms (O23 and O36). The H atoms of this water molecule have been determined using a difference Fourier map after the last refinement cycle. Other H atoms were calculated after isotropic refinement of the 'heavy' atoms and refined isotropically. An attempt to determine the positions of the H atoms fixed on the N atoms (H120, H130) on the difference Fourier map failed, probably because the unique electron is not localized on H. If we assume the proton fixed on the N atoms with a distance of 1 Å between the centre of the protons and the corresponding N atom, the geometry of the inclusion complex can be characterized by the following bond distances and angles (see Fig. 2): H160···O36 = 1.7 (1) (H of the water molecule), H260···O23 = 2.2 (1) (H of the water molecule), H⁺120···O60 = 1.9 (1) (H fixed on N20), H⁺130···O60 = 2.0 (1) Å (H fixed on N30), O36···H160—O60 = 149 (8), O23···H260—O60 = 140 (7), H⁺120···O60···H⁺130 = 161 (7)°. The distances between protons and the anthracenic mean plane *P* are H⁺120—*P* = 2.65 (9), H⁺130—*P* = 2.63 (9) Å.

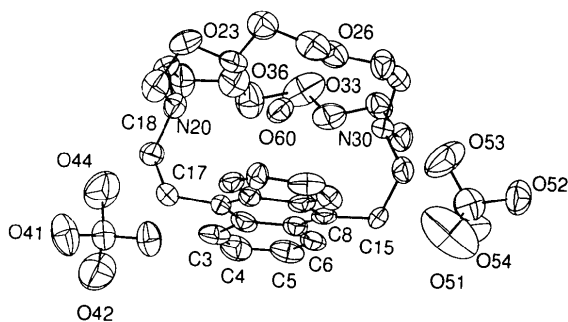


Fig. 1. View of the title compound showing the partial labelling of the non-H atoms (ellipsoids at 50% probability).

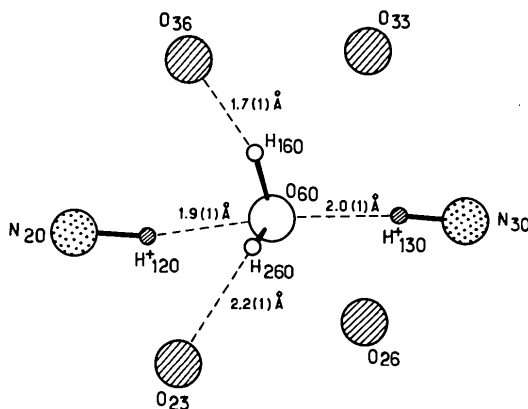


Fig. 2. Environment of the water molecule inside the cavity.

Compared with the structure of the free ligand A_{22} and the complex A_{22}/Ag^+ (Andrianatoandro *et al.*, 1995), the cavity of the protonated compound is flattened (Fig. 3) as observed in the complex A_{22}/Tl^+ (Fages, Desvergne & Bouas-Laurent, 1989). The N...N distance is 5.84(1) Å (5.18 and 5.09 Å in the free ligand and the Ag^+ complex, respectively). The distance between the encaged water molecule and the mean plane of the anthracenic ring is $d = 2.96(1)$ Å (3.09 and 3.20 Å in the Ag^+ and Tl^+ complexes, respectively).

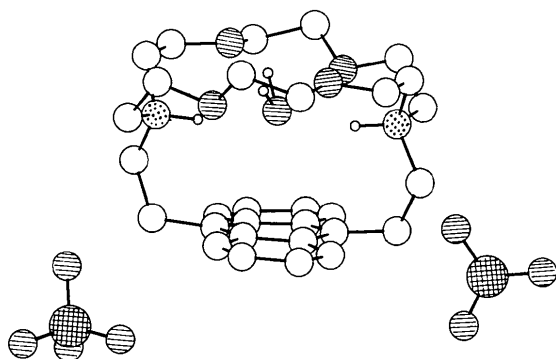


Fig. 3. Molecular conformation of $A_{22} \cdot (HClO_4)_2 \cdot H_2O$ (viewed along a direction near the great axis of the anthracene).

Other examples concerning inclusion of water or CH_3OH in protonated aza-crown ethers (Lehn & Vierling, 1980; Gokel & Garcia, 1977; Méndez, Singleton, Slawin, Stoddart & Williams, 1992; Gokel, 1991) or cryptands (Lehn, 1978*a,b*) have been described.

In the crystalline state, $A_{22} \cdot 2H^+$ containing a molecule of water exhibits a structured fluorescence emission spectrum which corresponds to a non-perturbed *meso*-disubstituted anthracene, whereas pure A_{22} exhibits a red-shifted structureless band due to an intramolecular exciplex involving the nitrogen lone pairs and the aromatic ring (Konopelski *et al.*, 1985; Fages *et al.*, 1989) (Fig. 4). The protonation of the nitrogen lone

pairs prevents such an interaction with the π cloud of the anthracene, and the fluorescence decay was found to be exponential (7.5 ns) as expected, supporting the occurrence of only one fluorescent excited species.

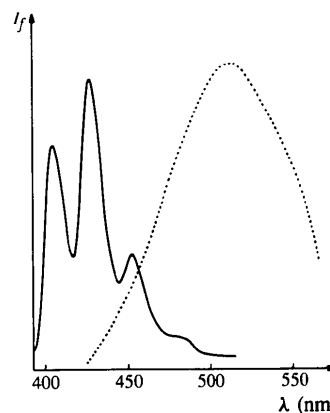


Fig. 4. Single-crystal corrected fluorescence spectra of the free ligand A_{22} (dotted line) and of $A_{22} \cdot (HClO_4)_2 \cdot H_2O$ (full line) at room temperature.

Taking into consideration the conformations of the two N atoms, the structure shows that the two protons are 'in-in' in contrast with previous hypothesis, because the 'in-in' structure is stabilized by the water inclusion. This interesting system deserves further investigation.

Experimental

Crystal data

$C_{30}H_{42}N_2O_4^{2+} \cdot 2ClO_4^- \cdot H_2O$
 $M_r = 711.6$
 Monoclinic
Cc
 $a = 12.258(7)$ Å
 $b = 22.289(4)$ Å
 $c = 13.297(6)$ Å
 $\beta = 104.64(4)^\circ$
 $V = 3515.2$ Å³
 $Z = 4$
 $D_x = 1.344$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 21 reflections
 $\theta = 7-13^\circ$
 $\mu = 0.255$ mm⁻¹
 $T = 293$ K
 Plate
 $0.6 \times 0.2 \times 0.03$ mm
 Colourless
 Crystal source: methanolic solution of A_{22} and perchloric acid

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (North, Phillips & Matthews, 1968)
 $T_{min} = 0.935$, $T_{max} = 1.000$
 3033 measured reflections
 2971 independent reflections
 2009 observed reflections
 $|I| > 3\sigma(I)$

$R_{int} = 0.0106$
 $\theta_{max} = 23^\circ$
 $h = -13 \rightarrow 13$
 $k = 0 \rightarrow 24$
 $l = 0 \rightarrow 14$
 3 standard reflections monitored every 200 reflections
 intensity decay: none

Refinement

Refinement on *F**R* = 0.061*wR* = 0.056*S* = 1.47

2009 reflections

572 parameters

H atoms refined isotropically

w = 1/[$\sigma^2(F) + 0.0004F^2$](Δ/σ)_{max} = 0.086

$$\Delta\rho_{\max} = 0.3 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.3 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV, Table

2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
C1	0.3541 (11)	0.1630 (5)	-0.0470 (11)	3.4 (7)
C2	0.2579 (12)	0.1657 (6)	-0.0005 (10)	3.8 (8)
C3	0.2022 (10)	0.1111 (6)	0.0186 (11)	4.5 (9)
C4	0.1188 (11)	0.1146 (6)	0.0651 (11)	4.9 (9)
C5	0.0785 (11)	0.1696 (6)	0.0944 (12)	4.7 (8)
C6	0.1262 (10)	0.2184 (6)	0.0751 (10)	3.8 (8)
C7	0.2169 (10)	0.2219 (6)	0.0260 (11)	3.5 (7)
C8	0.2659 (10)	0.2757 (6)	0.0028 (10)	3.4 (8)
C9	0.3552 (11)	0.2734 (6)	-0.0515 (11)	3.7 (7)
C10	0.3992 (11)	0.3268 (6)	-0.0853 (10)	3.8 (8)
C11	0.4846 (11)	0.3222 (7)	-0.1344 (11)	4.9 (9)
C12	0.5309 (11)	0.2684 (6)	-0.1531 (10)	3.5 (8)
C13	0.4900 (10)	0.2203 (6)	-0.1258 (11)	3.7 (8)
C14	0.3995 (10)	0.2159 (6)	-0.0722 (10)	3.1 (7)
C15	0.2278 (11)	0.3361 (6)	0.0360 (11)	3.4 (7)
C16	0.3189 (11)	0.3695 (6)	0.1148 (11)	4.4 (8)
C17	0.4035 (11)	0.1012 (6)	-0.0613 (11)	4.2 (8)
C18	0.4562 (11)	0.0684 (6)	0.0377 (11)	4.4 (8)
N20	0.5498 (8)	0.1020 (4)	0.1100 (8)	3.8 (7)
C21	0.6508 (12)	0.1041 (6)	0.0659 (11)	4.9 (9)
C22	0.7416 (11)	0.1505 (6)	0.1207 (12)	5.3 (9)
O23	0.6883 (7)	0.2092 (4)	0.1052 (8)	4.7 (5)
C24	0.7631 (11)	0.2528 (6)	0.1533 (12)	5.2 (10)
C25	0.6999 (11)	0.3116 (7)	0.1434 (12)	5.6 (10)
O26	0.6221 (7)	0.3113 (4)	0.2046 (7)	4.7 (5)
C27	0.5750 (11)	0.3683 (6)	0.2160 (12)	4.8 (9)
C28	0.4831 (11)	0.3598 (6)	0.2739 (12)	5.1 (9)
N30	0.3764 (8)	0.3315 (5)	0.2123 (8)	3.4 (6)
C31	0.2932 (11)	0.3264 (6)	0.2784 (11)	4.2 (8)
C32	0.3267 (11)	0.2848 (6)	0.3629 (11)	4.5 (8)
O33	0.3315 (7)	0.2257 (4)	0.3216 (7)	5.3 (6)
C34	0.3562 (12)	0.1788 (8)	0.3977 (11)	7.4 (11)
C35	0.3693 (13)	0.1190 (7)	0.3466 (13)	6.3 (10)
O36	0.4651 (8)	0.1250 (4)	0.3043 (8)	5.4 (6)
C37	0.4961 (12)	0.0667 (6)	0.2750 (11)	5.1 (9)
C38	0.5864 (11)	0.0737 (7)	0.2173 (12)	4.8 (8)
Cl40	0.4990 (3)	0.0929 (1)	-0.3399 (3)	4.4 (2)
O41	0.5599 (8)	0.0670 (4)	-0.4080 (9)	7.7 (7)
O42	0.3920 (8)	0.0666 (5)	-0.3516 (10)	9.3 (8)
O43	0.4918 (8)	0.1554 (4)	-0.3500 (8)	5.8 (6)
O44	0.5631 (10)	0.0796 (5)	-0.2340 (9)	9.1 (7)
Cl50	0.3506 (4)	0.5055 (2)	-0.0691 (4)	5.9 (2)
O51	0.3467 (13)	0.5017 (7)	-0.1774 (10)	14.8 (11)
O52	0.3481 (8)	0.5669 (4)	-0.0435 (9)	6.4 (6)
O53	0.4498 (9)	0.4776 (5)	-0.0084 (12)	11.1 (9)
O54	0.2546 (9)	0.4761 (6)	-0.0522 (10)	10.4 (8)
O60	0.4728 (7)	0.2166 (4)	0.1763 (7)	4.3 (5)
H120	0.5165 (8)	0.1469 (4)	0.1221 (8)	5.3 (8)*
H130	0.3877 (8)	0.2892 (4)	0.1921 (8)	5.0 (8)*

* *B*_{iso}.Table 2. Selected geometric parameters (\AA , °)

C1—C2	1.46 (2)	C21—C22	1.56 (2)
C1—C14	1.38 (2)	C22—O23	1.46 (2)
C1—C17	1.54 (2)	O23—C24	1.38 (2)

C2—C3	1.45 (2)	C24—C25	1.51 (2)
C2—C7	1.43 (2)	C25—O26	1.41 (2)
C3—C4	1.32 (2)	O26—C27	1.42 (2)
C4—C5	1.41 (2)	C27—C28	1.53 (2)
C5—C6	1.29 (2)	C28—N30	1.49 (2)
C6—C7	1.43 (2)	N30—C31	1.51 (2)
C7—C8	1.41 (2)	C31—C32	1.44 (2)
C8—C9	1.46 (2)	C32—O33	1.43 (2)
C8—C15	1.53 (2)	O33—C34	1.43 (2)
C9—C10	1.42 (2)	C34—C35	1.52 (2)
C9—C14	1.44 (2)	C35—O36	1.44 (2)
C10—C11	1.37 (2)	O36—C37	1.43 (2)
C11—C12	1.38 (2)	C37—C38	1.51 (2)
C12—C13	1.27 (2)	Cl40—O41	1.43 (1)
C13—C14	1.47 (2)	Cl40—O42	1.41 (1)
C15—C16	1.52 (2)	Cl40—O43	1.40 (1)
C16—N30	1.55 (2)	Cl40—O44	1.46 (1)
C17—C18	1.50 (2)	Cl50—O51	1.43 (2)
C18—N20	1.50 (2)	Cl50—O52	1.41 (1)
N20—C21	1.50 (2)	Cl50—O53	1.42 (1)
N20—C38	1.52 (2)	Cl50—O54	1.41 (1)

C2—C1—C14	119 (1)	C21—N20—C38	108 (1)
C2—C1—C17	118 (1)	N20—C21—C22	114 (1)
C14—C1—C17	123 (1)	C21—C22—O23	107 (1)
C1—C2—C3	121 (1)	C22—O23—C24	110 (1)
C1—C2—C7	121 (1)	O23—C24—C25	108 (1)
C3—C2—C7	119 (1)	C24—C25—O26	111 (1)
C2—C3—C4	119 (1)	C25—O26—C27	114 (1)
C3—C4—C5	123 (1)	O26—C27—C28	108 (1)
C4—C5—C6	118 (1)	C27—C28—N30	115 (1)
C5—C6—C7	126 (1)	C16—N30—C28	112 (1)
C2—C7—C6	115 (1)	C16—N30—C31	107.2 (9)
C2—C7—C8	120 (1)	C28—N30—C31	110 (1)
C6—C7—C8	125 (1)	N30—C31—C32	114 (1)
C7—C8—C9	120 (1)	C31—C32—O33	109 (1)
C7—C8—C15	121 (1)	C32—O33—C34	115 (1)
C9—C8—C15	120 (1)	O33—C34—C35	110 (1)
C8—C9—C10	121 (1)	C34—C35—O36	106 (1)
C8—C9—C14	119 (1)	C35—O36—C37	109 (1)
C10—C9—C14	120 (1)	O36—C37—C38	109 (1)
C9—C10—C11	119 (1)	N20—C38—C37	116 (1)
C10—C11—C12	124 (1)	O41—Cl40—O42	112.4 (7)
C11—C12—C13	118 (1)	O41—Cl40—O43	111.7 (6)
C12—C13—C14	126 (1)	O41—Cl40—O44	106.8 (7)
C1—C14—C9	121 (1)	O42—Cl40—O43	111.7 (6)
C1—C14—C13	125 (1)	O42—Cl40—O44	106.5 (7)
C9—C14—C13	114 (1)	O43—Cl40—O44	107.4 (6)
C8—C15—C16	114 (1)	O51—Cl50—O52	107.5 (8)
C15—C16—N30	114 (1)	O51—Cl50—O53	110.7 (8)
C1—C17—C18	115 (1)	O51—Cl50—O54	108.5 (8)
C17—C18—N20	114 (1)	O52—Cl50—O53	110.6 (7)
C18—N20—C21	110 (1)	O52—Cl50—O54	109.9 (7)
C18—N20—C38	113 (1)	O53—Cl50—O54	109.5 (7)

Data collection: *Structure Determination Package* (Enraf-Nonius, 1985). Cell refinement: *Structure Determination Package*. Data reduction: local programs. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: local programs. Molecular graphics: local program. Software used to prepare material for publication: local program.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Z)-5-(2-Thienylmethylene)-2,4-imidazolidinedione

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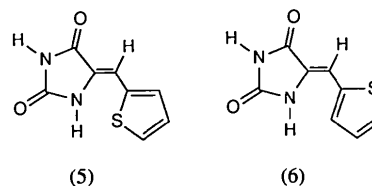
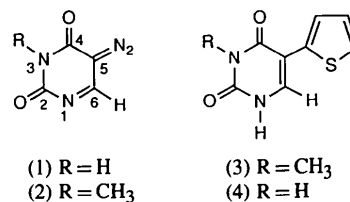
(Received 15 March 1994; accepted 5 December 1994)

Abstract

The major product formed in the thermolysis of 5-diazouracil in thiophene at 423–433 K has been identified as the unexpected compound (Z)-5-(2-thienylmethylene)-2,4-imidazolidinedione, C₈H₆N₂O₂S, by X-ray analysis. The molecule is a hydantoin derivative with a thienylmethylene group substituted at the 5-position. The structure is disordered in that the thiophene ring exists in two orientations which are related by an approximate 180° rotation about the C(6)—C(7) bond. All of the N and O atoms are involved in an intermolecular hydrogen-bonding network *via* N—H...O interactions. This network consists of an infinite chain along the *a*-axis direction and a cyclic trimer arrangement which branches from this chain. The molecules are arranged in the unit cell in pleated sheets which are approximately perpendicular to the *c* axis.

Comment

Recently, Mathur & Shechter (1990) reported some spectacular differences in the thermal behaviour of 5-diazouracil, (1), and 5-diazo-3-methyluracil, (2). Thermolysis of (2) in thiophene at 423–433 K yields 3-methyl-5-(2-thienyl)uracil, (3). Thermolysis of (1) under the same conditions, however, has now been found to give (Z)-5-(2-thienylmethylene)-2,4-imidazolidinedione, (5), as the major product and 5-(2-thienyl)uracil, (4), as the minor product. Details of the X-ray analysis of (5) are now reported.



The title molecule consists of a 2,4-imidazolidinedione ring (also known as hydantoin) with a thienylmethylene group substituted at the 5-position. The structure is disordered with respect to rotation of the thiophene group by approximately 180° about the C(6)—C(7) bond. The orientation shown in structure (5) is adopted by 80% of the molecules and the orientation seen in structure (6) is adopted by 20%. While introduction of a disorder model improved this structure considerably, the bond lengths within the thiophene ring remain unsatisfactory. The C(7)—C(8) bond length is slightly too long for a double bond and the C(8)—C(9) bond length is too short for a single bond. The metric parameters for the hydantoin ring agree well with those reported for (*E*)-5-(methoxymethylene)-2,4-imidazolidinedione (Gallucci, Mathur & Shechter, 1992); the largest discrepancy is in the N(1)—C(2) bond length which is 1.362 (3) Å for (5) and 1.346 (2) Å for the methoxymethylene derivative. The two external angles at C(5) are significantly different from one another; N(1)—C(5)—C(6) is 131.1 (2)° and C(4)—C(5)—C(6) is 123.3 (2)°. This distortion is in the direction expected for a Z isomer. The molecule is not planar and the dihedral angle between the least-squares plane through atoms S, C(7), C(8), C(9) and C(10) and the least-squares plane through atoms C(5), N(1), C(2), N(3), C(4), O(2) and O(4) is 171°.

A displacement ellipsoid diagram of (5) is shown in Fig. 1. The packing diagram (Fig. 2) shows that