4-Aminopyridinium 2-(anthracen-9-yl)-3-oxo-3H-inden-1-olate monohydrate

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The title compound, $2C_5H_7N_2^+ \cdot 2C_{23}H_{13}O_2^- \cdot H_2O$, formed as a by-product in the attempted synthesis of a nonlinear optical candidate molecule, contains two independent 4-aminopyridinium cations and 2-(anthracen-9-yl)-3-oxo-3H-inden-1-olate anions with one solvent water molecule. This is the first reported structure containing these anions. The two anions are not planar, having different interplanar angles between the anthracenyl and inden-1-olate moieties of 59.07 (5) and 83.92 (5)°. The crystal packing, which involves strong classical hydrogen bonds and one C—H···π interaction, appears to account for both the nonplanarity and this difference.

Comment

Organic ionic salts have long been considered as promising materials for use in nonlinear optics (NLO) (Marder *et al.*, 1994). This is because such compounds can exhibit large first-order hyperpolarizabilities (β), can be easily tuned (for example, by changing the counter-ion), and have high melting points and crystal hardnesses (Yang *et al.*, 2007). By way of example, the crystalline organic salt 4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) is a very promising NLO material and has been shown to have a very large NLO susceptibility, with r_{11} values of 53 pm V^{-1} at 1310 nm and 92 pm V^{-1} at 720 nm (Pan *et al.*, 1996). In our previous work, we have successfully synthesized a series of ionic chromophores in order to observe the impact on the second-order NLO response of changing the donor group, the polarity of the solvent or the counter-ion (*i.e.* tosylate, naphthalene-2-sulfonate and iodide) (Teshome *et al.*, 2010). As part of our ongoing work to develop novel NLO materials, we were interested in preparing a compound containing an electron-rich indanedione acceptor, a dihydroanthracene–azo interconnection and a 1,4-dihydropyridin-4-ylidene donor unit [*viz.* compound (3) in the reaction scheme].

Our initial attempt to prepare this target molecule by adding 2-(anthracen-9-yl)indane-1,3-dione to the diazonium

salt of 4-aminopyridine (reaction scheme) was unsuccessful, as we only recovered the original diketone unchanged. One possible reason for this is the lack of stability of the diazonium
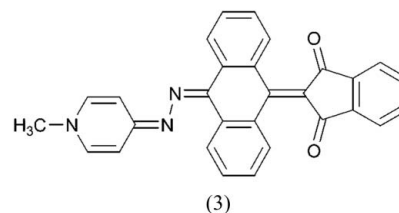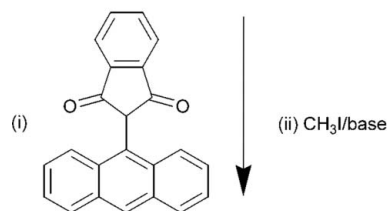
salt of 4-aminopyridine, (2), which has been reported to be very unstable (Bunsel & Keum, 1983), so it may have decomposed before reacting with the anthracenyl component. Consequently, we decided to prepare the diazonium salt *in situ* by dissolving the amine and diketone together at 273–278 K and adding sodium nitrite and hydrochloric acid. This resulted in the rapid appearance of an orange precipitate which, following isolation and characterization, was found to be the title compound, (I), and not the desired diazo intermediate. As a matter of procedure, we then resynthesized (I) using the method described in the *Experimental* section, which involves coupling the sodium salt of 2-(anthracen-9-yl)indane-1,3-dione with 4-aminopyridinium chloride.
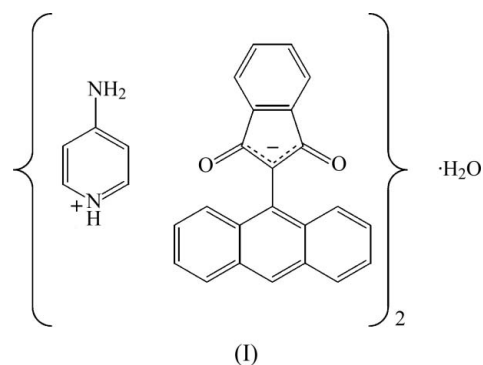
Only one structure, 1-n-butyl-3-(1,3-dioxoindan-2-yl)pyridinium [Cambridge Structural Database (CSD, Version 5.32 with November 2010 updates; Allen, 2002) refcode DUCWUT (Magomedova & Bel'skii, 1986)], has been reported in which deprotonation of the indane-1,3-dione ring has occurred, but
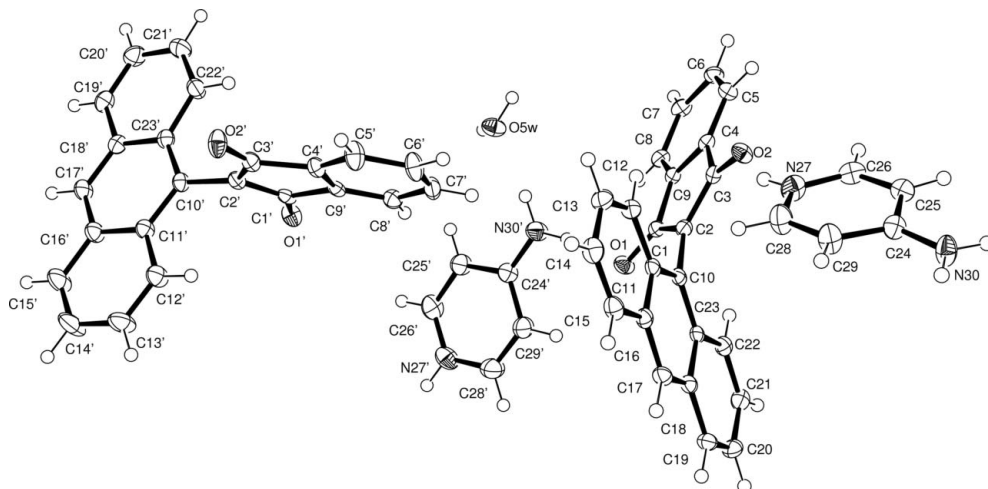
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Figure 1
The molecular structure and atom-numbering scheme for the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

in that case the coordinated pyridinium ring is formally charged, giving overall molecular neutrality. There are 25 structures in the CSD containing the neutral 1*H*-indene-1,3(2*H*)-dione entity, for example, JOTGII (Kolev *et al.*, 1992), but (I) represents the first report of a unique 3-oxo-3*H*-inden-1-olate anion coupled with the (more commonly observed) 4-aminopyridinium cation.

A view of the asymmetric unit contents and atom-labelling scheme of (I) is shown in Fig. 1. Along with a single water molecule, there are two independent cations and anions, with the labels of the second matching the first with an appended prime (*e.g.* C2 and C2′). There are minor differences in bond lengths and angles between the two anions, with examples given in Table 1. The nonhydrogen bond lengths have an r.m.s. fit of 0.0055 Å for the two anions, compared with an r.m.s. fit of 0.0044 Å for the two cations (*PLATON*; Spek, 2003). As shown in Table 1, the anions have quite different geometries from a typical 1*H*-indene-1,3(2*H*)-dione molecule (JOTGII), particularly with respect to the bond lengths of the five-membered ring, but they are somewhat similar to those found in the two independent molecules in the DUCWUT structure. Specifically, the C1—C2 and C2—C3 distances average to shorter distances of 1.420 (14) Å in (I) and 1.429 (5) Å in DUCWUT, compared with 1.526 (4) Å in JOTGII [an average of 1.538 (11) Å was found for these bonds in four similar molecules: SEZKAK (Kumar *et al.*, 2007), CEZCAM (Das *et al.*, 2007) and HOHWIK (Siaka *et al.*, 1998; two symmetry-independent molecules)]. Likewise, the C3—C4 and C1—C9 bonds average to longer values of 1.507 (7) Å in (I) and 1.504 (8) Å in DUCWUT, compared with 1.479 (1) Å for JOTGII. Of all the remaining bond lengths in the anions, including the six-membered ring, only two are significantly different: the average of the C5—C6 and C7–C8 bonds in (I), at 1.404 (3) Å, is slightly longer than its counterparts of 1.391 (13) Å in DUCWUT and 1.377 (6) Å in JOTGII [an average value of 1.375 (8) Å was found in the set of similar structures noted above]. The C6—C7 distances are shorter, at 1.379 (2) and 1.363 (11) Å in (I) and DUCWUT, respectively,

compared with 1.395 (4) Å in JOTGII. The geometry of the anthracenyl part of the anion is identical to that reported for 3-(9-anthryl)-1-methoxy–2,3-dihydro-1*H*-benz[*de*]anthracene (PAMRIE; Langer & Becker, 1992) and 2-(9-anthryl)-2-propanol (VAFNEV01; Langer & Becker, 1993), except for the connection link (C2—C10) bonds which have single-bond lengths in these compounds. The likely source of these variations in geometry is discussed below.

The individual five- and six-membered rings vary from being statistically planar [*e.g.* atoms C11–C16, mean out-of-plane distance of the constituent atoms = 0.003 (2) Å; atoms C4′–C9′, mean out-of-plane distance = 0.001 (2) Å] to approximately planar [*e.g.* atoms C1–C4/C9 = 0.026 (2) Å]. Both the 3-oxo-3*H*-inden-1-olate and anthracenyl rings are essentially planar, with average mean out-of-plane distances for the two independent anions of 0.013 (2) and 0.038 (2) Å, respectively. The most significant difference between the two anions involves the relative orientations of these anthracenyl and indane-1,3-dione rings: the interplanar angles are 59.07 (5) and 83.92 (5)° for the anions containing atoms O1 and O1′, respectively. Even more significant is the fact that, in the only really comparable structure (DUWCUT), the interplanar angles are much closer to, but not exactly, zero, at 6.1 (2) and 10.4 (2)° for the two independent molecules. Examination of the intermolecular packing (Fig. 2) confirms that these ring orientations allow close hydrogen-bonding contacts between anion and cation acceptors and donors, and a C—H⋯π interaction. It seems likely that the anion charge here is localized on the 3-oxo-3*H*-inden-1-olate rings, rather than partially delocalized through both rings as seen in DUCWUT; indeed, this would enhance the acceptor status of the O atoms. This is consistent with the fact that the link bond C2—C10 is significantly shorter in DUCWUT by 0.048 (7) Å, and also with the bond-length differences noted above with shorter average C1—C2 and C2—C3 distances.

Over 88 compounds containing the 4-aminopyridinium cation are found in the CSD and those reported here show identical dimensions. For example, the average C24—
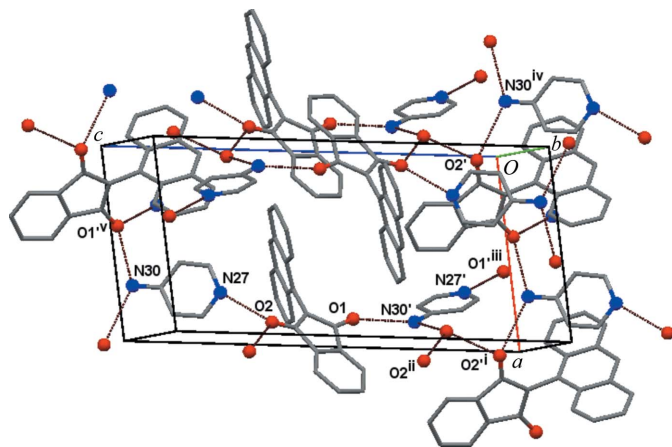
Figure 2
A partial packing diagram (*Mercury*; Macrae *et al.*, 2008) of the unit-cell contents of (I), showing key interactions. Contact atoms are shown as balls; see Table 2. H atoms have been omitted for clarity. [Symmetry codes: (i) $x + 1$, y, z; (ii) $-x + 2$, $-y + 1$, $-z + 1$; (iii) $-x + 1$, $-y$, $-z$; (iv) $x - 1$, y, $z - 1$; (v) x, y, $z + 1$.]

N30(amino) distance here is 1.332 (2) Å, compared with 1.328 (2) Å in 4-aminopyridinium picrate (KUVLAP; Ramesh *et al.*, 2010).

Overall, the crystal packing of (I) is dominated by strong (classical) hydrogen bonds (Table 2 and Fig. 2), building a three-dimensional matrix based on $D(2)$ primary graph-set motifs (Bernstein *et al.*, 1995) using all amine and water H atoms. These motifs combine to generate three discrete $D_2^1(3)$ secondary motifs which involve bifurcated interactions at the acceptor atoms (*e.g.* O2′, entries 1 and 5 in Table 2) and sets of $D_2^2(n)$ motifs, where n = 4, 5, 7, 8 or 9. Thus, the ketone O atoms act as acceptors for both amine and pyridinium donors of the 4-aminopyridinium cation. The single water molecule acts as a hydrogen-bond donor to the two independent anions, and as an acceptor to the amino H atom of one 4-amino-pyridinium cation. The alignment of the anthracenyl groups permits a significant C—H···π interaction (last entry in Table 2) between two symmetry-independent anions. There are also very weak C—H···O interactions with water atom O5W, which are included in Table 2 for completeness, and other fortuitous weak C—H···π interactions, but no significant π–π interactions.

This packing is in striking contrast with that of the related compound DUCWUT, where lattice binding is provided by C—H···O interactions only, with no C—H···π-type or other interactions involving the pyridinium ring atoms. It is noteworthy that, although the $D(2)$ motif interactions are observed in DUCWUT, there are also several intramolecular C—H···O interactions displaying the $S(6)$ motif that are only possible because of the near coplanarity of the adjacent indane-1,3-dione and pyridinium rings (dihedral angle ∼ 0°; Table 1, last entry).

The formation of this unexpected product, (I), is considered to be due to the negative charge on the 2-(anthracen-9-yl)-3-oxo-3*H*-inden-1-olate anion residing predominantly across the 1–3 diketone system. Therefore, it is not able to impart the requisite negative charge onto the anthracene unit to make it

sufficiently reactive toward the diazonium salt derived from 4-aminopyridine. Consequently, formation of the title salt occurs in preference and the equilibrium of the reaction is presumably driven by precipitation. Alternative synthetic routes are under investigation.

Experimental

To a cooled solution of 2-(anthracen-9-yl)indane-1,3-dione (1.6 g) in distilled water (40 ml) was added KOH (1 g), and the mixture was stirred for 30 min. A solution of 4-aminopyridinium chloride (0.7 g) in distilled water (10 ml) was then added dropwise, whereupon a red solid formed almost immediately. After 10 min, the solid product was collected by filtration, washed with several small portions of distilled water and air-dried to give a red powder. The crude product was purified by recrystallization from ethanol. Crystals of (I) were obtained by dissolving the compound in chloroform–acetone–toluene (4:5:1 *v*/*v*/*v*) and allowing the solution to evaporate slowly, whereupon dark-red crystals formed [m.p. 491–493 K (decomposition)]. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.33 (*s*, 1H), 8.02–7.95 (*m*, 3H), 7.88 (*d*, *J* = 5.0 Hz, 2H), 7.50 (*s*, 2H), 7.40 (*t*, 2H), 7.30 (*m*, 3H), 7.22 (*s*, 2H), 6.60 (*d*, *J* = 5.0 Hz, 2H), 2.04 (*s*, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 188.4, 182.5, 158.4, 141.4, 140.8, 134.6, 133.8, 133.1, 131.4, 130.8, 129.3, 128.9, 127.9, 126.8, 124.7, 123.6, 123.5, 117.1, 108.5, 103.7. MS, negative mode: found *m*/*z* 321.0915; $C_{23}H_{13}O_2$ requires *m*/*z* 321.0916, Δ = 0.3 p.p.m. Positive mode, found *m*/*z* 95.0618; $C_5H_7N_2$ requires *m*/*z* 95.0609, Δ = 9.5 p.p.m.

Crystal data

$2C_5H_7N_2{}^+\cdot2C_{23}H_{13}O_2{}^-\cdot H_2O$	$\gamma = 105.265\,(2)°$
$M_r = 850.94$	$V = 2143.78\,(14)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.1990\,(3)$ Å	Mo $K\alpha$ radiation
$b = 13.9977\,(6)$ Å	$\mu = 0.09$ mm^{-1}
$c = 17.9153\,(7)$ Å	$T = 116$ K
$\alpha = 100.962\,(2)°$	$0.70 \times 0.31 \times 0.18$ mm
$\beta = 97.628\,(2)°$	

Data collection

Bruker APEXII CCD diffractometer	41534 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	7568 independent reflections
$T_{min} = 0.637$, $T_{max} = 0.746$	6771 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.097$	
$S = 1.12$	
7568 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
610 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Ten reflections affected by the beam stop were omitted from the final refinement. Aromatic ring H atoms were constrained to an ideal geometry, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. All N-bound H atoms were placed in positions determined from a difference Fourier map and refined freely, with $U_{iso}(H) = 1.2U_{eq}(N)$. Water H atoms were located in a difference Fourier map and then refined freely, with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SADABS* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008);

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Table 1
Key structural parameters (Å, °) for (I) and related compounds (see Fig. 1 and *Comment*).

Atom labels used are those for anion 1 of (I).

Parameter	(I), anion 1	(I), anion 2	DUCWUT, molecule 1	DUCWUT, molecule 2	JOTGII
O1—C1	1.2494 (19)	1.2691 (19)	1.238 (5)	1.229 (5)	1.220 (3)
O2—C3	1.2610 (19)	1.252 (2)	1.242 (5)	1.246 (6)	1.212 (4)
C1—C2	1.437 (2)	1.401 (2)	1.429 (7)	1.437 (6)	1.523 (4)
C2—C3	1.414 (2)	1.427 (2)	1.426 (6)	1.425 (6)	1.530 (3)
C3—C4	1.510 (2)	1.515 (2)	1.493 (7)	1.504 (6)	1.479 (4)
C4—C9	1.391 (2)	1.391 (2)	1.380 (7)	1.378 (6)	1.389 (4)
C1—C9	1.502 (2)	1.499 (2)	1.507 (6)	1.513 (6)	1.480 (3)
C4—C5	1.376 (2)	1.378 (2)	1.383 (7)	1.380 (6)	1.396 (3)
C2—C10	1.485 (2)	1.488 (2)	1.438 (6)	1.438 (6)	1.514 (3)
C10—C11	1.417 (2)	1.408 (2)	1.410 (6)	1.406 (6)	1.383 (3)
C10—C23	1.417 (2)	1.414 (2)	1.391 (5)	1.388 (6)	1.382 (4)
C1—C2—C10	123.66 (14)	122.07 (14)	125.7 (4)	125.4 (4)	117.8 (2)
C3—C2—C10	128.04 (14)	129.16 (14)	125.8 (4)	125.4 (4)	113.3 (2)
C1—C2—C10—C11	−118.71 (17)	95.13 (19)	3.0 (7)	−6.9 (7)	−140.5 (2)

molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C18–C23 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O5W—H5W1···O2[i]	0.90 (2)	1.91 (2)	2.8064 (19)	169 (2)
O5W—H5W2···O2[ii]	0.86 (2)	1.94 (2)	2.8043 (18)	177 (2)
N27—H27···O2	0.90 (2)	1.89 (2)	2.705 (2)	150.4 (18)
N27′—H27′···O1′[iii]	0.92 (2)	1.79 (2)	2.695 (2)	169 (2)
N30—H30A···O2′[iv]	0.91 (2)	2.08 (2)	2.975 (2)	167.5 (19)
N30—H30B···O1′[v]	0.91 (2)	1.97 (2)	2.863 (2)	164.3 (19)
N30′—H31′···O5W	0.92 (2)	1.92 (2)	2.842 (2)	173 (2)
N30′—H32′···O1	0.92 (2)	1.92 (2)	2.8364 (19)	171 (2)
C5—H5···O5W[ii]	0.95	2.59	3.451 (2)	151
C5′—H5′···O5W[vi]	0.95	2.59	3.435 (2)	148
C15′—H15′···Cg1[vii]	0.95	2.51	3.452 (2)	170

Symmetry codes: (i) $x + 1, y, z$; (ii) $−x + 2, −y + 1, −z + 1$; (iii) $−x + 1, −y, −z$; (iv) $x + 1, y, z + 1$; (v) $x, y, z + 1$; (vi) $x − 1, y, z$; (vii) $x − 1, y, z − 1$.

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