Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1317). Services for accessing these data are described at the back of the journal.

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1-Cyano-2-*p*-bromophenylazulene and 2-Azulenylmethyl 2-Anthraquinoate†

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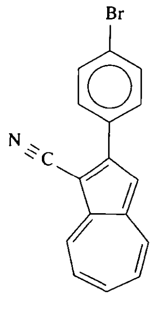
Abstract

The title azulene, $C_{17}H_{10}BrN$, (I), and ester, $C_{26}H_{16}O_4$, (II), are precursors for the preparation of the corresponding 1,8a-dihydroazulenes which are potentially photochromic compounds. In both compounds, the azulene moiety is found to be planar. All aromatic bonds in the azulenes lie in the range 1.369 (7)–1.416 (3) Å and the bridging bond between the seven- and five-membered rings is longer, 1.471 (3) and 1.478 (6) Å in (I) and (II), respectively.

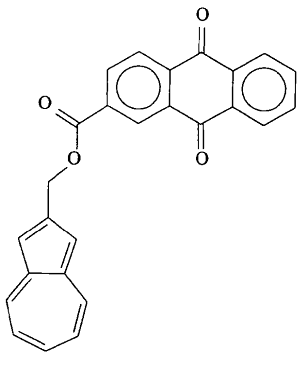
Comment

It is surprising that the crystal structures of only a few azulenes and their derivatives are known: azulene (Robertson, Shearer, Sim & Watson, 1962; Pawley, 1965), 2-aminoazulene (Takaki, Sasada & Nitta, 1959), azulene-*s*-trinitrobenzene complex (Hanson, 1965; Brown & Wallwork, 1965), azulene-1,3-dipropionic acid (Ammon & Sundaralingam, 1966), diazulenium azulene perchlorate (Sly, 1966), 1-(tricyanovinyl)azulene (Chetkina, Zavodnik & Bespalov, 1981), 1-benzoyl-4,6,8-trimethylazulene, 1-trifluoroacetyl-4,6,8-trimethylazulene (Tafeenko, Porshnev, Polyakov, Gerasimov, Cherkashin & Dyumaev, 1983) and bis(isothiocyanatotetrakis(4-methylpyridine)nickel(II) bis(azulene) clathrate (Lipkowski, Gluzinski, Suwinska & Andreetti, 1984).

Our interest in azulenes stems from the potential use of their 1,8a-dihydro derivatives as chemical and physical switches which can utilize a photochemically induced rearrangement (see, for example, Daub *et al.*, 1986, 1989; Daub, Gierisch & Salbeck, 1990; Daub, Fischer, Salbeck & Ulrich, 1990; Achatz, Fischer, Salbeck & Daub, 1991). Both compounds have been synthesized by a procedure outlined by Daub *et al.* (1986).



(I)



(II)

Crystals of (II) were poorly diffracting, leading to the small ratio of observed reflections to the number of refined parameters. An empirical absorption correction, based on azimuthal scans of several reflections, was applied for (I) (*TEXSAN*; Molecular Structure Corporation, 1992). The crystal structures of (I) and (II) (Figs. 1 and 2, respectively) show that the azulene moiety is planar (the out-of-plane displacements are less than 0.004 Å). A comparison of bond lengths and angles in the azulene moieties is given in Table 1. The

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† Alternative name: 2-azulenylmethyl 9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid.

bond lengths in the azulene groups lie in the range 1.369 (7)–1.416 (3) Å except for the C3a—C8a bond which is 1.471 (3) and 1.478 (6) Å in (I) and (II), respectively, and typical of an sp^2–sp^2 single bond. The range of bond angles within the five-membered ring is 105.8 (2)–109.7 (2)° and within the seven-membered ring is 126.5 (3)–130.1 (3)°.

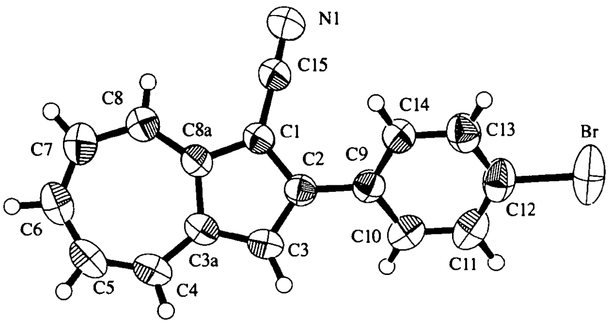

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

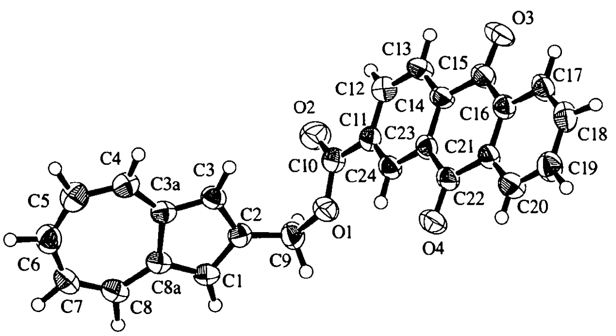

Fig. 2. The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Compounds (I) and (II) were prepared according to Daub *et al.* (1986).

Compound (I)

Crystal data

$C_{17}H_{10}BrN$
$M_r = 308.17$
Monoclinic
$P2_1/n$
$a = 8.910 (2)$ Å
$b = 3.973 (4)$ Å
$c = 37.261 (2)$ Å
$\beta = 92.900 (10)°$
$V = 1317.3 (14)$ Å^3
$Z = 4$
$D_x = 1.554$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 21 reflections
$\theta = 41.9$–$52.9°$
$\mu = 4.102$ mm^{-1}
$T = 293 (2)$ K
Needle
0.45 × 0.20 × 0.10 mm
Deep violet

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1992)
$T_{min} = 0.555$, $T_{max} = 0.664$
2718 measured reflections
2718 independent reflections

2058 reflections with $I > 2\sigma(I)$
$\theta_{max} = 77.60°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 4$
$l = -47 \rightarrow 46$
3 standard reflections every 200 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.122$
$S = 1.141$
2718 reflections
213 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.4972P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.012$
$\Delta\rho_{max} = 0.290$ e Å^{-3}
$\Delta\rho_{min} = -0.759$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0023 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{26}H_{16}O_4$
$M_r = 392.39$
Orthorhombic
$P2_12_12_1$
$a = 7.441 (6)$ Å
$b = 41.869 (6)$ Å
$c = 5.934 (7)$ Å
$V = 1848.7 (27)$ Å^3
$Z = 4$
$D_x = 1.410$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.5$–$14.0°$
$\mu = 0.095$ mm^{-1}
$T = 293 (2)$ K
Prism
0.40 × 0.30 × 0.20 mm
Deep violet

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1928 measured reflections
1928 independent reflections
1382 reflections with $I > 2\sigma(I)$

$\theta_{max} = 24.98°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 49$
$l = 0 \rightarrow 7$
3 standard reflections every 200 reflections intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.123$
$S = 1.255$
1928 reflections
336 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + 1.2666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.035$

$\Delta\rho_{max} = 0.244$ e Å^{-3}
$\Delta\rho_{min} = -0.229$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0040 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of selected geometric parameters (Å,°) for (I) and (II)*

	(I)	(II)
C1—C8a	1.413 (3)	1.403 (6)
C1—C15	1.414 (4)	–
C2—C9	1.464 (3)	1.485 (6)
C1—C2	1.416 (3)	1.402 (6)
C2—C3	1.396 (3)	1.403 (6)
C3—C3a	1.394 (4)	1.396 (6)
C4—C3a	1.392 (4)	1.383 (6)
C4—C5	1.381 (5)	1.401 (7)
C5—C6	1.377 (5)	1.382 (8)
C6—C7	1.376 (5)	1.392 (7)
C7—C8	1.394 (4)	1.369 (7)
C8—C8a	1.381 (4)	1.396 (6)
C8a—C3a	1.471 (3)	1.478 (6)
C2—C1—C8a	109.2 (2)	108.8 (4)
C1—C2—C3	107.8 (2)	108.9 (4)
C2—C3—C3a	109.7 (2)	108.9 (4)
C3—C3a—C8a	107.4 (2)	106.9 (4)
C4—C3a—C8a	126.5 (3)	127.3 (4)
C3a—C4—C5	129.4 (3)	128.7 (5)
C4—C5—C6	128.6 (3)	128.7 (5)
C5—C6—C7	130.1 (3)	129.8 (5)
C6—C7—C8	128.8 (3)	128.7 (5)
C7—C8—C8a	128.2 (3)	129.4 (5)
C8—C8a—C3a	128.3 (2)	127.3 (4)
C1—C8a—C3a	105.8 (2)	106.5 (4)

For both compounds, data collection: *MSC/AFC Data Reduction and Refinement Software* (Rigaku Corporation, 1988); cell refinement: *MSC/AFC Data Reduction and Refinement Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976) and *TEXSAN* (Molecular Structure Corporation, 1992); software used to prepare material for publication: *WORD*6.0.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1032). Services for accessing these data are described at the back of the journal.

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Tris(1-phenacyl-2-pyridone) Hydroxonium Tetrafluoroborate, a Hydrogen-Bonded Complex

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Abstract

The hydrolytic cleavage of 2-phenyloxazolo[3,2-*a*]pyridinium tetrafluoroborate results in the formation of the title tris(1-phenacyl-2-pyridone) hydroxonium tetrafluoroborate complex, $3C_{13}H_{11}NO_2.H_3O^+.BF_4^-$. The structure is built up from hydrogen-bonded cations and disordered BF_4^- anions. The strong hydrogen bonding causes considerable redistribution of electron density in the pyridone moiety.

Comment

Recently, it was found that mesoionic 2-oxo-3-benzoyloxazolo[3,2-*a*]pyridine can be transformed to oxazolo-[3,2-*a*]pyridinium tetrafluoroborate by the action of H_2SO_4 and HBF_4 (Babaev & Orlova, 1997). Having attempted to confirm the structure of this compound, we discovered that prolonged standing of the reaction mixture (one week at room temperature) resulted in the unexpected formation of *N*-phenacyl-2-pyridone, (I). Although the ring opening of the former compound is known to occur by the action of alkali (Pauls