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Ethyl 1,3-dibromoazulene-6-carboxylate

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Key indicators

Single-crystal X-ray study
T = 95 K
Mean σ(C–C) = 0.007 Å
R factor = 0.042
wR factor = 0.092
Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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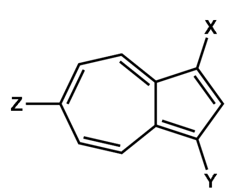
The title compound, $C_{13}H_{10}Br_2O_2$, was obtained during the synthesis of azulene derivatives. There are two independent molecules in the asymmetric unit. The azulene frameworks of the molecules are planar, with mean deviations of 0.01 and 0.02 Å from the ring planes.

Comment

A number of azulene derivatives are known with varying substitution patterns (Nefedov, 1973). We were more interested in synthesizing 2,6-disubstituted azulenes and perhydroazulenes, as the latter framework is a part of many natural products and is expected to be a potentially photochromic compound (Daub *et al.*, 1990). However, it is surprising that the crystal structures of only a few azulenes and their derivatives are known (Kaftory *et al.*, 1997). It is also worth noting that the substitution pattern of azulene and perhydroazulene derivatives plays an important role in determining the properties described above, and specific substitution at the 2- and 6-positions, which gives linear derivatives, was most important for our studies. We were able to obtain this pattern in many of our new derivatives with excellent overall yield. Compound (I) was formed as an unexpected product in 5–10% yield during the synthesis of 2,6-disubstituted perhydroazulene derivatives. Although (I) was obtained as a by-product in a very low yield, it was possible to increase the yield by prolonging the reaction time.



(I) X = Y = Br, Z = -COOEt

(II) X = Y = Br, Z = H

(III) X = Y = Cl, Z = H

(IV) X = Y = I, Z = ^{t}butyl

(V) X = Y = F, Z = isopropyl

(VI) X = Y = NO_2, Z = H

Comparison of (I) with known compounds such as (II)–(VI) reveals its importance for functional group interconversion at the 6-position, which is not easy in (IV) (Fabian *et al.*, 2000) and (V) (Tetreault *et al.*, 1999) and perhaps very difficult in (II) (Anderson *et al.*, 1957), (III) (Nefedov, 1973) and (VI) (Anderson *et al.*, 1964). Compound (I) can be used for a number of 2,6-disubstituted derivatives to study structure–property relationships.

There are two independent molecules (*A* and *B*) in the asymmetric unit. Fig. 1 shows molecule *A*. The azulene framework is planar, with a mean deviation of 0.01 and 0.02 Å for *A* and *B*, respectively, from the ring planes. The plane defined by all non-H atoms of the ethyl ester group is inclined from the ring plane of the azulene framework by 4.3 (4) and 3.3 (4)° in *A* and *B*. The bond lengths of the ten-membered ring systems, in the range 1.374 (8)–1.413 (7) Å (Table 1), do not show significant differences in molecules *A* and *B*. This is similar to what is observed in other substituted azulene derivatives (Kaftory *et al.*, 1997). Only the bonds between the bridgehead atoms of (I) are considerably longer [1.507 (6) Å and 1.495 (7) Å in molecules *A* and *B*, respectively].

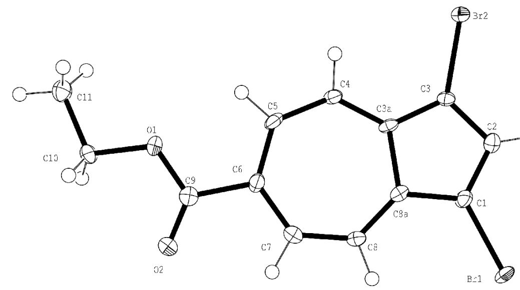


Figure 1
Structure of molecule *A* in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond distances (Å).

Br1—C1	1.881 (5)	Br1′—C1′	1.881 (5)
Br2—C3	1.882 (5)	Br2′—C3′	1.871 (5)
C1—C2	1.374 (8)	C1′—C8*A*′	1.386 (7)
C1—C8*A*	1.413 (7)	C1′—C2′	1.400 (8)
C2—C3	1.397 (7)	C2′—C3′	1.409 (7)
C3—C3*A*	1.398 (7)	C3′—C3*A*′	1.398 (8)
C3*A*—C4	1.376 (7)	C3*A*′—C4′	1.380 (7)
C3*A*—C8*A*	1.507 (6)	C3*A*′—C8*A*′	1.495 (7)
C4—C5	1.399 (8)	C4′—C5′	1.390 (8)
C5—C6	1.410 (8)	C5′—C6′	1.405 (8)
C6—C7	1.394 (7)	C6′—C7′	1.401 (7)
C6—C9	1.517 (8)	C6′—C9′	1.510 (7)
C7—C8	1.388 (8)	C7′—C8′	1.386 (8)
C8—C8*A*	1.377 (7)	C8′—C8*A*′	1.388 (8)

Experimental

2-(*tert*-Butyl-diphenylsilanyloxy)-4,4a,5,5a,6-pentahydrocyclopropa-[*f*]indan-5-carboxylic acid ethyl ester (6.0 g, 13.39 mmol) was dissolved in CCl_4 (300 ml) with stirring and cooled in an ice bath. Bromine (2.139 g, 13.39 mmol) dissolved in CCl_4 (20 ml) was added dropwise with stirring. When the addition was complete, triethylamine (6.62 g, 65.64 mmol) was added. Triethylamine hydrobromide began to form immediately. The mixture was refluxed for 18 h. The HBr salt was filtered off and the filtrate was evaporated. The resulting oil was washed with water, dried over $MgSO_4$ and filtered to yield the crude product. The mixture containing the 2,6-azulene derivative and (I) was purified through a column of silica gel using pentane as an eluant by increasing polarity with dichloromethane (1–10%). Compound (I), being less polar, eluted first (dark blue), followed by the 2,6-azulene derivative, and was recrystallized from dichloromethane and hexane to yield dark green needles.

Crystal data

$C_{13}H_{10}Br_2O_2$
$M_r = 358.03$
Orthorhombic, $Pca2_1$
$a = 17.032$ (2) Å
$b = 3.9694$ (5) Å
$c = 35.819$ (5) Å
$V = 2421.6$ (5) Å^3
$Z = 8$
$D_x = 1.964$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 806 reflections
$\theta = 2.5$–28.3°
$\mu = 6.68$ mm^{-1}
$T = 95$ (2) K
Needle, dark green
0.27 × 0.08 × 0.08 mm

Data collection

Bruker Smart APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: numerical (*SHELXTL*; Bruker, 2001)
$T_{min} = 0.266$, $T_{max} = 0.617$
15 805 measured reflections
5943 independent reflections
5714 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 28.3°$
$h = -22 \rightarrow 13$
$k = -5 \rightarrow 5$
$l = -47 \rightarrow 47$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.092$
$S = 1.11$
5943 reflections
310 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 8.7967P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -1.59$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 2880 Friedel pairs
Flack parameter: 0.141 (13)

H atoms were positioned geometrically and refined as riding, with C—H distances in the range 0.95–0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C_{methyl})$]. The highest peak is located 0.86 Å from atom C1 and the deepest hole 0.84 Å from atom Br1′.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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