

**(RS)-6-Ethyl 2-carboxy-1,2,3,4-tetrahydroazulene-6-carboxylate**Zakir Hussain,<sup>a</sup> Thomas Oeser<sup>b\*</sup> and Henning Hopf<sup>a</sup><sup>a</sup>Institut für Organische Chemie, TU Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany, and <sup>b</sup>Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany  
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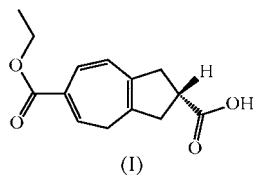
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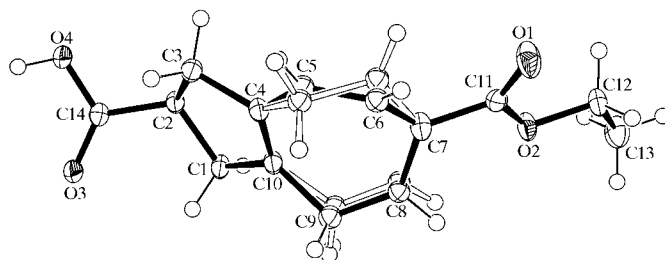
The title compound, C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>, was obtained during the synthesis of 2,6-disubstituted azulene derivatives. In the partially reduced azulene skeleton, the absence of a H atom at the ester substituent position of the seven-membered ring, as well as lengthened double bonds, indicate a conjugative stabilized system with two overlaid tautomers.

**Comment**

The synthesis of the azulene skeleton has received a good deal of attention over the past few decades (Nefedov, 1973*a,b*). Luhowy & Keehn (1977) synthesized azulenophane in order to study the charge-transfer interaction, and later Zindel *et al.* (1996) reported the synthesis of 2,6-substituted push-pull azulene. Recently, Mori *et al.* (2003) synthesized the 1,3-diazaazulene skeleton and described the mesomorphic properties of its various derivatives. We were interested in mesogenic materials based on the perhydroazulene skeleton. During our work on synthesizing the core skeleton, we employed various synthetic strategies to obtain 2,6-disubstituted perhydroazulene derivatives. We employed a slightly modified synthetic strategy as reported by Zindel *et al.* (1996) to obtain the title compound, (I), in order to investigate its structural and stereochemical features for input into further studies.



We prepared compound (I) by adding formic acid to the diester of (I) and stirring the mixture at room temperature for 15 h. Compound (I), obtained first as a light-coloured solid, was recrystallized from hexane as colourless irregular crystals. The structure analysis revealed an azulene frame-

**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. The open bonds indicate the minor sites of two overlaid tautomeric molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

work which was partially hydrogenated at the pentacyclic subunit. The geometric parameters of the seven-membered ring further revealed the presence of disorder between two tautomers. Their structures, shown as two overlaid molecules in Fig. 1, were refined with a disorder model involving atoms C5/C6/C8/C9 and C5A/C6A/C8A/C9A [with 53 (1):47 (1)% refined occupancy; the minor sites are shown with open bonds in Fig. 1].

We did not find a H atom at C7 in the difference Fourier map, but did observe two H atoms at each of C5A and C9, as well as only one H atom at C5 and at C9A. Due to the disorder of the seven-membered ring, these H atoms were included in the refinement in calculated positions which were re-idealized after every refinement run.

The disorder of the two tautomers is evident in an analysis of selected geometric parameters, listed in Table 1. The average value of the distances C5–C6, C5A–C6A, C8–C9 and C8A–C9A [1.392 (5) Å] is longer by about 0.07 Å than the average for chemically equivalent olefinic bonds (Allen *et al.*, 1995). For comparison, the C4=C10 double bond has a length of 1.337 (2) Å, which is in the expected range. Furthermore, the average value of 1.412 (4) Å for the bonds C6–C7, C6A–C7, C7–C8 and C7–C8A is about 0.05 Å shorter than comparable single-bond lengths tabulated by Allen *et al.* (1995). In addition, a very 'flat' conformation at the top atom, C7, was detected (selected torsion angles are given in Table 1), indicating conjugative interaction of the  $\pi$  system with the ester substituent.

In the extended structure of (I), stabilizing hydrogen bonds were found [O4–H4O $\cdots$ O3<sup>i</sup> = 1.74 (3) Å, O4 $\cdots$ O3<sup>i</sup> = 2.635 (3) Å and O4–H4O $\cdots$ O3<sup>i</sup> = 176.9 (2)°; symmetry code: (i)  $-x, -y + 1, -z - 1$ ], mediating aggregation of the azulene derivatives into dimeric pairs across a crystallographic centre of symmetry.

**Experimental**

A solution of the diester of (I) (1.0 mmol) in formic acid (50 ml) was stirred at room temperature for 15 h. The solvent was removed under reduced pressure and the crude product, originally obtained as a light-coloured solid, was recrystallized from hexane, giving a 95% yield of (I) as colourless irregular crystals.

## Crystal data

$C_{14}H_{16}O_4$   
 $M_r = 248.27$   
 Monoclinic,  $P2_1/c$   
 $a = 4.1002$  (4) Å  
 $b = 36.118$  (4) Å  
 $c = 8.3164$  (8) Å  
 $\beta = 103.157$  (2)°  
 $V = 1199.2$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.375$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4258 reflections  
 $\theta = 2.3$ – $28.3$ °  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Irregular, colourless  
 $0.18 \times 0.15 \times 0.14$  mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.982$ ,  $T_{\max} = 0.986$   
 11969 measured reflections

2953 independent reflections  
 2710 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 28.3$ °  
 $h = -5 \rightarrow 5$   
 $k = -48 \rightarrow 48$   
 $l = -11 \rightarrow 11$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.136$   
 $S = 1.17$   
 2953 reflections  
 165 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.8094P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.22$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

C4–C10	1.337 (2)	C7–C8	1.388 (4)
C4–C5	1.448 (4)	C7–C8A	1.435 (5)
C4–C5A	1.506 (5)	C8–C9	1.406 (5)
C5–C6	1.362 (5)	C9–C10	1.509 (4)
C6–C7	1.403 (4)	C8A–C9A	1.315 (6)
C5A–C6A	1.486 (7)	C9A–C10	1.440 (4)
C6A–C7	1.424 (4)		
C10–C4–C5–C6	22.9 (8)	C6A–C7–C8A–C9A	–5.6 (9)
C4–C5–C6–C7	11.2 (10)	C11–C7–C8A–C9A	–171.8 (4)
C10–C4–C5A–C6A	69.0 (6)	C7–C8A–C9A–C10	34.0 (8)
C4–C5A–C6A–C7	–60.6 (7)	C5A–C4–C10–C9A	–16.3 (5)
C5–C6–C7–C8	–58.1 (8)	C5–C4–C10–C9	12.7 (5)
C5–C6–C7–C11	145.1 (5)	C8A–C9A–C10–C4	–39.6 (6)
C5A–C6A–C7–C8A	19.8 (10)	C8–C9–C10–C4	–53.5 (5)
C5A–C6A–C7–C11	–173.5 (5)	C8–C7–C11–O1	–151.3 (3)
C6–C7–C8–C9	38.4 (7)	C6–C7–C11–O1	3.7 (4)
C11–C7–C8–C9	–165.5 (4)	C6A–C7–C11–O1	22.5 (4)
C7–C8–C9–C10	25.7 (6)	C8A–C7–C11–O1	–169.0 (3)

Each of atoms C5, C6, C8 and C9 was refined at two positions with 53 (1):47 (1)% refined occupancy. The displacement parameters of their disordered positions were only refined isotropically because some of the disorder sites were rather close together. Their positions were not initially located as separate sites in a difference map, but were rather generated by splitting the atomic positions with large anisotropic displacement parameters, as per a suggestion by *SHELXTL* (Bruker, 2001). The H atom of the carboxylic acid group was located in a difference Fourier map and refined isotropically. All other H atoms were found in a difference map but then placed in calculated positions and included in the refinement with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ , and their positions were re-idealized before each refinement cycle. The C–H bond distances of 0.95–0.99 Å were established according to criteria described in the *SHELXTL* manual (Bruker, 2001), with an increase of 0.01 or 0.02 Å for the low-temperature refinement.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1151). Services for accessing these data are described at the back of the journal.

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