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6,7-Dihydrodibenzo[e,*g*]azulen-8(5*H*)-one and 12,13-dihydrobenzo-[e]napth[2,1-*g*]azulen-14(11*H*)-one

A. Abdul Ajees,[a] M. N. Ponnuswamy,[a] S. Parthasarathy[a]* and C. A. M. A. Huq[b]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and [b]Department of Chemistry, The New College, Chennai 600 005, India
Correspondence e-mail: partha24@hotmail.com

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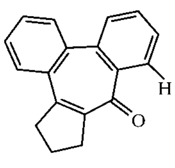
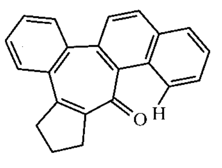
In the structures of the title compounds, 6,7-dihydrodibenzo-[*e*,*g*]azulen-8(5*H*)-one, $C_{18}H_{14}O$, (I), and 12,13-dihydrobenzo-[*e*]napth[2,1-*g*]azulen-14(11*H*)-one, $C_{22}H_{16}O$, (II), the azulene group is in a boat-envelope conformation. The structures are stabilized by weak C—H···O interactions.

Comment

Both the title compounds, (I) and (II), possess an azulene skeleton similar to that found in the natural products extracted from *Saussurea lappa*, a well known medicinal plant used in the indigenous system of medicine in India for the treatment of coughs, asthma, fever, dyspepsia and leprosy, and as a diuretic and anthelminthic. They are also extensively used in China, as powerful stimulants, carminatives and anti-spasmodics (Salooja *et al.*, 1950; Kalsi *et al.*, 1983).



(I)



(II)

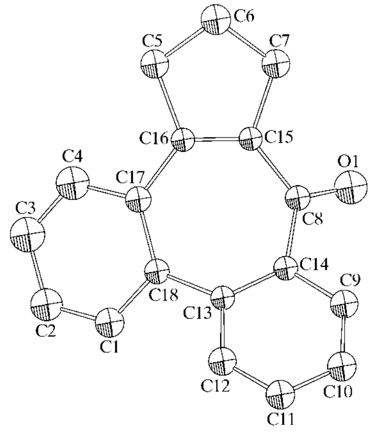


Figure 1
The molecular structure of (I) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

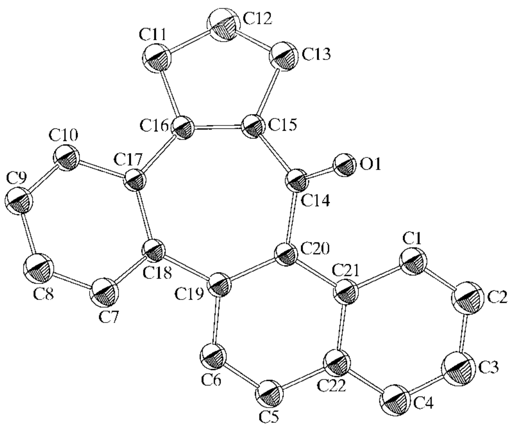


Figure 2
The molecular structure of (II) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

The structures of the two molecules are shown in Figs. 1 and 2, for (I) and (II), respectively. Selected bond lengths and angles are given in Tables 1 and 3, and the dimensions of possible hydrogen bonds are in Tables 2 and 4, for (I) and (II), respectively. In both molecules, the cycloheptane rings are in the boat conformation and the cyclopentane rings are in the envelope conformation. The puckering parameters evaluated using *PARST* (Nardelli, 1995) also confirm the above results. For the seven-membered rings in (I), q_2 = 0.527 (1), q_3 = 0.082 (2) and Q_T = 0.534 (1) Å, and φ_2 = 179.73 (15) and φ_3 = 148.7 (10)°, while in (II), q_2 = 0.652 (1), q_3 = 0.149 (1) and Q_T = 0.669 (1) Å, and φ_2 = 171.60 (12) and φ_3 = −166.7 (5)°. For the five-membered rings in (I), q_2 = 0.261 (2) Å and φ_2 = −142.3 (4)°, while in (II), q_2 = 0.280 (2) Å and φ_2 = 38.6 (3)°. The superposition of the non-H atoms in the common parts of the two molecules (Fig. 3) shows that they have practically the

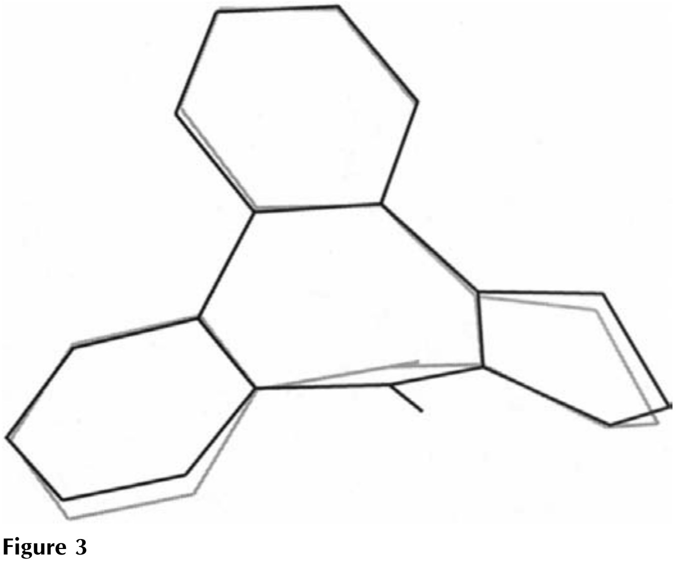


Figure 3
Superposition of the non-H atoms of the two molecules. The black line indicates compound (I), the grey line compound (II).

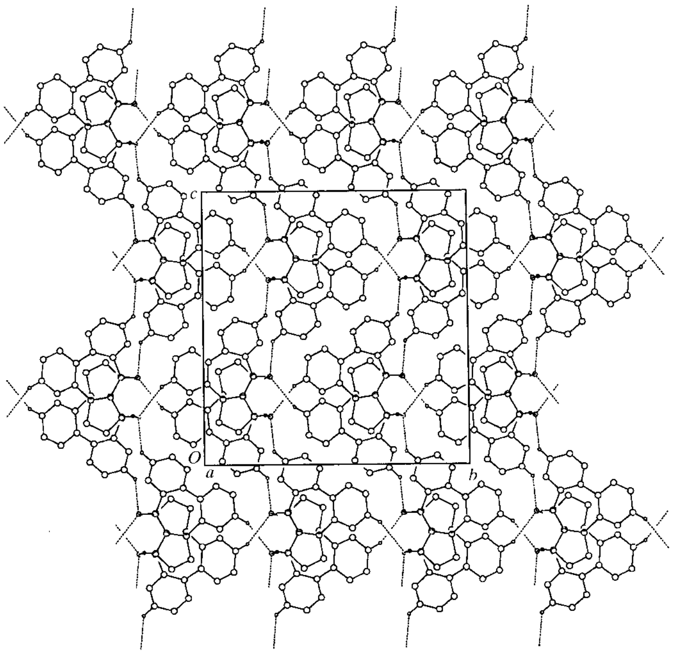


Figure 4
The packing diagram for (I) viewed along the *a* axis.

same geometry with an r.m.s. deviation of 0.19 Å (the r.m.s. deviation is 0.08 Å when the atoms in the azulene rings alone are superimposed).

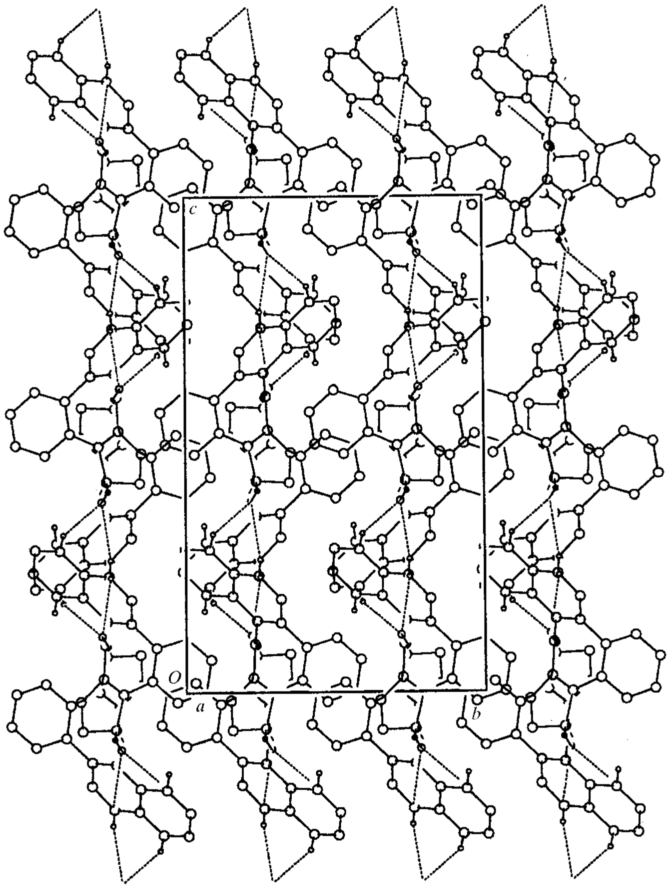


Figure 5
The packing diagram for (II) viewed along the *a* axis.

From the nature of the molecules in the two compounds it is clear that strong intermolecular hydrogen bonds are not possible, and in such cases C—H···O bonds play an important role in crystal packing (Desiraju, 1991, 1996). The significant shortening of some of the C—C bonds in the molecules [*e.g.* C9—C10 and C10—C11 in (I), and C3—C4 and C5—C6 in (II)] probably facilitates activation of the adjacent C*sp*^{2} atoms to act as donors. In both (I) and (II), the molecules are packed in columns parallel to the *c* axis. In (I) (Fig. 4), the adjacent columns are interlinked through C—H···O interactions. However, in (II) (Fig. 5), C—H···O interactions are confined to molecules within the columns and the columns are held together purely by van der Waals interactions.

Experimental

Compounds (I) and (II) were prepared by rearranging the vinyl carbinol with two equivalents of potassium hydride in refluxing tetrahydrofuran (Geetha *et al.*, 1982). Crystals suitable for X-ray diffraction studies were grown by slow evaporation from hexane solutions.

Compound (I)

Crystal data

$C_{18}H_{14}O$
$M_r = 246.29$
Orthorhombic, *Pbca*
$a = 8.0547\ (11)$ Å
$b = 17.378\ (2)$ Å
$c = 17.919\ (3)$ Å
$V = 2508.2\ (6)$ Å^3
$Z = 8$
$D_x = 1.304$ Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 14–25°$
$\mu = 0.616$ mm^{-1}
$T = 273\ (2)$ K
Rectangular prism, colourless
0.40 × 0.18 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2449 measured reflections
2449 independent reflections
1794 reflections with $I > 2\sigma(I)$
$\theta_{max} = 77.67°$

$h = 0 \rightarrow 9$
$k = 0 \rightarrow 22$
$l = -21 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C8	1.2011 (16)	C13—C14	1.3765 (18)
C5—C6	1.502 (2)	C13—C18	1.4681 (19)
C5—C16	1.555 (2)	C15—C16	1.3123 (18)
C6—C7	1.527 (2)	C16—C17	1.4596 (19)
C7—C15	1.530 (2)	C17—C18	1.459 (2)
C8—C14	1.5191 (19)		
C6—C5—C16	106.01 (12)	C16—C15—C8	127.43 (13)
C5—C6—C7	101.73 (13)	C16—C15—C7	109.86 (13)
C6—C7—C15	106.02 (12)	C15—C16—C17	126.62 (13)
O1—C8—C15	117.94 (13)	C15—C16—C5	109.43 (12)
O1—C8—C14	119.04 (13)	C18—C17—C16	126.94 (12)
C15—C8—C14	122.50 (12)	C17—C18—C13	126.32 (12)
C13—C14—C8	125.89 (12)		
C16—C5—C6—C7	24.55 (17)	C7—C15—C16—C5	−1.01 (17)
C5—C6—C7—C15	−25.26 (17)	C6—C5—C16—C15	−15.70 (18)
C18—C13—C14—C8	12.0 (2)	C15—C16—C17—C18	25.6 (2)
C15—C8—C14—C13	34.8 (2)	C16—C17—C18—C13	6.5 (2)
C14—C8—C15—C16	−38.7 (2)	C14—C13—C18—C17	−36.5 (2)
C8—C15—C16—C17	−3.8 (2)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.105$
$S = 1.033$
2449 reflections
229 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.2676P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0031 (3)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O1	0.949 (16)	2.438 (16)	2.799 (2)	102.3 (12)
C3—H3···O1^{i}	0.985 (19)	2.616 (19)	3.540 (2)	156.3 (15)
C7—H71···O1^{ii}	0.961 (19)	2.66 (2)	3.435 (2)	137.4 (14)
C10—H10···O1^{iii}	1.025 (19)	2.687 (19)	3.541 (2)	140.8 (14)

Symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

Compound (II)

Crystal data

$C_{22}H_{16}O$
$M_r = 296.35$
Orthorhombic, *Pbca*
$a = 11.8466$ (12) Å
$b = 12.4890$ (15) Å
$c = 20.703$ (2) Å
$V = 3063.0$ (6) Å^3
$Z = 8$
$D_x = 1.285$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14$–24°
$\mu = 0.599$ mm^{-1}
$T = 293$ (2) K
Rectangular prism, colourless
0.15 × 0.08 × 0.05 mm

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C14	1.2260 (16)	C14—C20	1.4904 (18)
C11—C16	1.5125 (19)	C15—C16	1.3453 (19)
C11—C12	1.527 (3)	C16—C17	1.4596 (19)
C12—C13	1.529 (2)	C17—C18	1.4175 (19)
C13—C15	1.5045 (19)	C18—C19	1.484 (2)
C14—C15	1.4575 (19)	C19—C20	1.3878 (19)
C16—C11—C12	103.50 (13)	C16—C15—C13	112.05 (12)
C11—C12—C13	104.58 (13)	C15—C16—C17	126.94 (13)
C15—C13—C12	102.23 (13)	C15—C16—C11	109.61 (13)
O1—C14—C15	121.13 (13)	C18—C17—C16	124.22 (12)
O1—C14—C20	121.47 (12)	C17—C18—C19	124.48 (12)
C15—C14—C20	117.08 (11)	C20—C19—C18	125.90 (12)
C16—C15—C14	125.97 (13)	C19—C20—C14	121.38 (12)
C16—C11—C12—C13	−26.59 (18)	C12—C11—C16—C15	15.95 (18)
C11—C12—C13—C15	27.14 (18)	C15—C16—C17—C18	−27.9 (2)
C20—C14—C15—C16	50.5 (2)	C16—C17—C18—C19	−11.7 (2)
C12—C13—C15—C16	−18.48 (18)	C17—C18—C19—C20	40.0 (2)
C14—C15—C16—C17	5.5 (2)	C18—C19—C20—C21	−178.10 (12)
C13—C15—C16—C11	1.68 (18)	C15—C14—C20—C19	−54.63 (18)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1	1.002 (17)	2.338 (17)	2.937 (2)	117.4 (12)
C5—H5···O1^{i}	0.972 (18)	2.617 (18)	3.4993 (19)	151.0 (14)
C4—H4···O1^{i}	0.973 (19)	2.714 (19)	3.604 (2)	152.3 (14)
C9—H9···O1^{ii}	0.972 (19)	2.768 (19)	3.653 (2)	151.7 (15)
C11—H111···O1^{iii}	1.038 (19)	2.652 (19)	3.658 (2)	163.3 (14)

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2949 measured reflections
2948 independent reflections
2160 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 70.85°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.110$
$S = 1.033$
2948 reflections
273 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 0.2784P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0028 (3)

For both compounds, all H atoms were located from the difference Fourier map and refined isotropically.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *SDP* (Frenz, 1978); data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1998); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1128). Services for accessing these data are described at the back of the journal.

References

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290.
Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1978). *The Enraf–Nonius CAD*-4 *SDP. Computing in Crystallography*, edited by H. Schenk, R. Olthof–Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
Geetha, P., Huq, C. A. M. A., Rajagopalan, K. & Swaminathan, S. (1982). *Tetrahedron Lett.* **23**, 569–560.
Johnson, C. K. & Burnett, M. N. (1998). *ORTEP*III. Version 1.0.2. University of Glasgow, Scotland.
Kalsi, P. S., Sharma, S. & Kaur, G. (1983). *Phytochemistry*, **22**, 1993–1995.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Salooja, K. C., Sharma, V. N. & Siddiqui, S. (1950). *J. Sci. Ind. Res. Sect. B*, **9**, 1–6.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. Both release 97–2. University of Göttingen, Germany.