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Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: PA1250). Les processus d'accès à ces archives est donné au dos de la couverture.

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2-*p*-Cyanophenyl-1,8a-dihydroazulene-1,1-dicarbonitrile and Methyl 1-Cyano-2-*p*-cyanophenyl-1,8a-dihydroazulene-1-carboxylate

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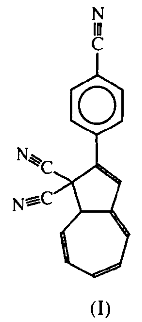
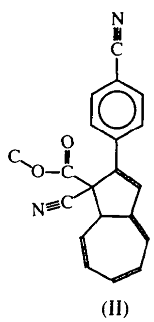
Abstract

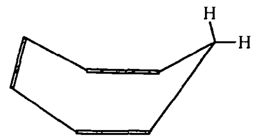
The title compounds, $C_{19}H_{11}N_3$ and $C_{20}H_{14}N_2O_2$, show solid-state photochromic properties. In both compounds, the dihydroazulene moiety was found to adopt the boat conformation.

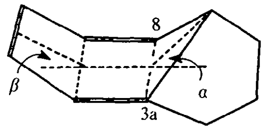
Comment

Our interest in 1,8a-dihydroazulenes stems from their use as chemical and physical switches caused by a photochemically induced rearrangement (see, for example, Daub *et al.*, 1989; Daub, Gierisch & Salbeck, 1990; Daub, Fischer, Salbeck & Ulrich, 1990; Achatz, Fischer, Salbeck & Daub, 1991). The crystal structures of few 1,8a-dihydroazulenes are known (see, for example, Brown, McPhail & Sim, 1966; Van de Grampel, Cuperus & Vos, 1971; Daub *et al.*, 1985, 1986).

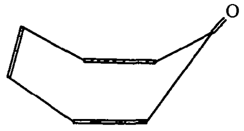

(I)


(II)


(III)



(IV)


(V)

Crystals of 2-*p*-cyanophenyl-1,8a-dihydroazulene-1,1-dicarbonitrile, (I), were poorly diffracting and there was a complete fall off of intensity above $\theta = 22.0°$. There is a clear distinction between C_{sp^2}—C_{sp^2} double and single bonds in the cycloheptatriene moiety. The formal double-bond lengths (Table 1) are in the range 1.338 (5)–1.345 (3) Å and the formal C_{sp^2}—C_{sp^2} single-bond lengths are in the range 1.434 (3)–1.441 (5) Å. The five-membered rings are almost planar [deviations from the mean planes are smaller than 0.077 (2) Å]. Irradiation of the photochromic compounds (I) and (II) (methyl 1-cyano-2-*p*-cyanophenyl-1,8a-dihydroazulene-1-carboxylate) results in an opening of the fused cyclopentene moiety. The expected consequence of the ring opening is the conformational change of the cycloheptatriene moiety. It is therefore interesting to note the expected differences of the conformation in both cases by comparing the conformation of cycloheptatriene in three systems: cycloheptatriene, (III), as the reference system, dihydroazulene, (IV), and heptafulvene, (V). The cycloheptatriene in all three systems adopts the boat conformation. A comparison of the three important parameters that describe the conformation is given in Table 2. The notation is shown in (IV) [definition of the α and β angles were taken from Daub *et al.*

(1985)]. There is a very small increase of the C3a···C8 distances in dihydroazulene attributed to the flattening of the cycloheptatriene moiety and expressed by the decrease of the β angle. Further flattening is observed in heptafulvene and it is shown by the decrease of both the α and β angles, followed by an increase of the C3a···C8 distances. The conclusion is that the cycloheptatriene in both photochromic compounds (I) and (II) is flattened during the irradiation.

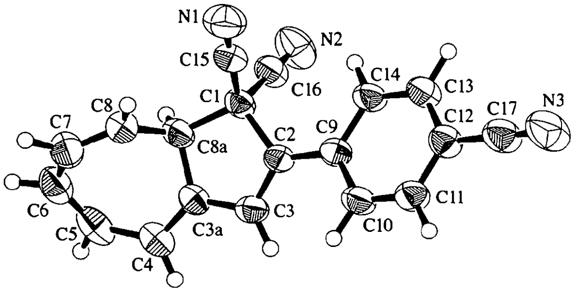


Fig. 1. The molecular structure of (I). The displacement ellipsoids are drawn at the 50% probability level.

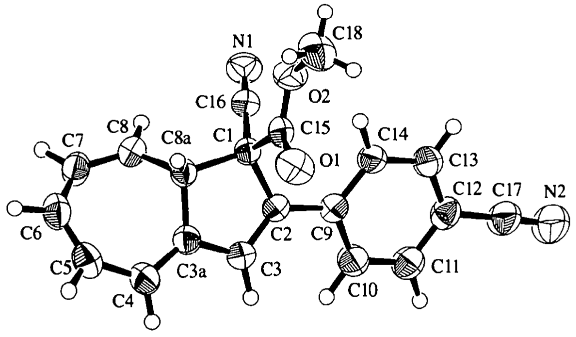


Fig. 2. The molecular structure of (II). The displacement ellipsoids are drawn at the 50% probability level.

Experimental

The procedure for the synthesis of similar compounds is given in Daub *et al.* (1986).

Compound (I)

Crystal data

$C_{19}H_{11}N_3$
$M_r = 281.31$
Triclinic
$P\bar{1}$
$a = 10.016\,(4)$ Å
$b = 9.185\,(4)$ Å
$c = 9.105\,(4)$ Å
$\alpha = 102.68\,(4)^\circ$
$\beta = 116.90\,(5)^\circ$
$\gamma = 84.62\,(3)^\circ$
$V = 728.8\,(5)$ Å^3
$Z = 2$
$D_x = 1.282$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3.1$–15.2°
$\mu = 0.078$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.30 \times 0.27 \times 0.15$ mm
Light yellow

Data collection

Phillips PW1100 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1788 measured reflections
1788 independent reflections
1308 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 22^\circ$
$h = -10 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.136$
$S = 1.085$
1788 reflections
244 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.0635P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$

$\Delta\rho_{\max} = 0.245$ e Å^{-3}
$\Delta\rho_{\min} = -0.139$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.013 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{20}H_{14}N_2O_2$
$M_r = 314.33$
Monoclinic
$C2/c$
$a = 17.965\,(2)$ Å
$b = 13.649\,(2)$ Å
$c = 16.987\,(2)$ Å
$\beta = 129.514\,(5)^\circ$
$V = 3213.4\,(7)$ Å^3
$Z = 8$
$D_x = 1.299$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 24 reflections
$\theta = 43.4$–44.9°
$\mu = 0.687$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.50 \times 0.20 \times 0.15$ mm
Light yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3212 measured reflections
3212 independent reflections
2448 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 77.60^\circ$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 17$
$l = -20 \rightarrow 16$
3 standard reflections
every 200 reflections
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.119$
$S = 1.099$
3212 reflections
274 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.9474P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.082$
$\Delta\rho_{\max} = 0.218$ e Å^{-3}
$\Delta\rho_{\min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.00148 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

	(I)	(II)
C1—C8a	1.571 (4)	1.587 (2)
C1—C15	1.477 (5)	1.538 (2)
C1—C16	1.482 (4)	1.474 (2)
C2—C9	1.458 (4)	1.467 (2)
C1—C2	1.545 (4)	1.540 (2)
C2—C3	1.349 (4)	1.340 (2)
C3—C3a	1.432 (4)	1.433 (2)
C4—C3a	1.344 (4)	1.345 (2)
C4—C5	1.439 (5)	1.438 (2)
C5—C6	1.338 (5)	1.345 (3)
C6—C7	1.441 (5)	1.434 (3)
C7—C8	1.338 (5)	1.342 (2)
C8—C8a	1.497 (4)	1.505 (2)
C8a—C3a	1.506 (4)	1.514 (2)
C2—C1—C8a	104.3 (2)	103.8 (1)
C1—C2—C3	108.5 (3)	109.7 (1)
C2—C3—C3a	113.4 (3)	113.3 (1)
C3—C3a—C8a	108.7 (2)	108.8 (1)
C4—C3a—C8a	122.1 (3)	123.8 (2)
C3a—C4—C5	124.4 (3)	124.9 (2)
C4—C5—C6	125.7 (4)	125.6 (2)
C5—C6—C7	125.9 (4)	125.9 (2)
C6—C7—C8	125.4 (4)	127.4 (2)
C7—C8—C8a	120.7 (3)	121.3 (2)
C8—C8a—C3a	107.9 (2)	107.8 (1)
C1—C8a—C3a	103.4 (2)	103.3 (1)

Table 2. *Comparison of cycloheptatriene conformation*

REFCODE†	α (°)‡	β (°)‡	C3a—C8a (Å)	Reference
System (III)				
DMDPCH	52.6	34.3	2.410 (7)	Stegemann & Lindner (1979)
HEHWIA	48.8	28.1	2.387 (4)	Burnett *et al.* (1994)
System (IV)				
(I)	53.5 (3)	27.3 (2)	2.428 (4)	Present work
(II)	50.9 (2)	25.16 (9)	2.439 (2)	Present work
CRCAAZ	50.4	6.6	2.39 (5)	
	58.5	9.5	2.39 (5)	Brown *et al.* (1966)
HPHAZO	47.2	24.5	2.453 (8)	Van de Grampel *et al.* (1971)
FAPMOY	53.1	26.4	2.417 (6)	Daub *et al.* (1986)
DELCUS	53.3	27.6	2.436 (4)	Daub *et al.* (1985)
System (V)				
BETBEH	8.2	0.9	2.499 (2)	Reichardt *et al.* (1985)
HEPFUL	24.7	15.7	2.492 (5)	Thomas & Coppens (1972)
MCHFUL	45.3	20.1	2.474 (7)	Shimanouchi *et al.* (1974)
TAFFAH	36.6	28.9	2.461 (4)	Badejo *et al.* (1990)

† The refcodes are those used by Cambridge Structural Database (Allen & Kennard, 1993). ‡ S.u. values for α and β angles are not given in the original articles.

Data collection: *PW*1100/20 *Software* (Phillips, 1973) for (I); *Rigaku MSC/AFC Software* (Rigaku Corporation, 1988) for (II). Cell refinement: *PW*1100/20 *Software* for (I); *Rigaku MSC/AFC Software* for (II). Data reduction: *PROCN* in *PW*1100/20 *Software* for (I); *Rigaku MSC/AFC Software* for (II). For both compounds, 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, 1993); software used to prepare material for publication: WORD6.0.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1031). Services for accessing these data are described at the back of the journal.

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N-3-Allylation of 2-(*N*,*N*-Dimethylaminomethyleneamino)-6-formylpteridin-4-one

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Abstract

The reaction of 2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one with allyl bromide in the presence of diazabicycloundecane as base leads

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