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[2.2]Basketenoparacyclophane 18,20-dicarbonitrile

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Key indicators

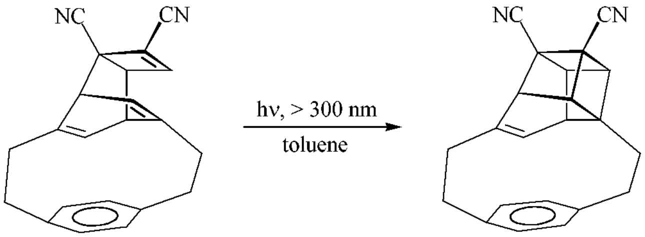
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.117
Data-to-parameter ratio = 12.7

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

The title compound, $C_{22}H_{18}N_2$, displays some release of the usual strain in [2.2]paracyclophanes (*e.g.* the bridge bonds are no longer lengthened), associated with the lengthening of the bridgehead contact C3···C14. However, the effect is not uniform; the basketene ring system introduces strain of its own (*e.g.* lengthened single bonds, wide angles at the corresponding bridge atoms).

Comment

When excess cyanoacetylene is heated in benzene solution at 433 K in a sealed ampoule, it [2+2]-cyclodimerizes to yield the highly reactive dicyanocyclobutadiene, which can be trapped by various diene systems, including those with aromatic character. Thus [2.2]paracyclophane and dicyanocyclobutadiene react to form four cycloadducts, which we have characterized (Witulski *et al.*, 1990). In these Diels–Alder adducts, two olefinic double bonds are oriented parallel to each other and in such close proximity that intramolecular photo-addition should be possible. This has now been confirmed for the dinitrile (1), which undergoes photo-addition to form compound (2) (see Scheme). The structure assignment of this novel birdcage hydrocarbon system is based on spectral data (Witulski, 1992) and the structure reported here (Fig. 1).



(1) (2)

The unreacted ring (C11–16) displays the usual paracyclophane distortion, in that the bridgehead atoms C11 and C14 lie 0.154 (3) and 0.142 (3) Å, respectively, out of the plane of the other four atoms (r.m.s. deviation 0.005 Å). There is elsewhere some release of the usual paracyclophane strain, because the bridgehead contact C3···C14 is lengthened to 3.023 (2) Å [*cf.* C6···C11 2.798 (2) Å]. Similarly, the bridge single bonds C1—C2 and C9—C10, usually lengthened to *ca* 1.58–1.59 Å in [2.2]parayclophanes (*e.g.* Jones *et al.*, 2002), revert to normal lengths. However, the angles in the bridges, usually widened to *ca* 112°, do not show a consistent narrowing to normal sp^3 values; the angle at C10 does narrow, that at C1 is essentially unaffected, and those at C9 and C2 widen much further (Table 1). The latter effect may reasonably be ascribed to strain from

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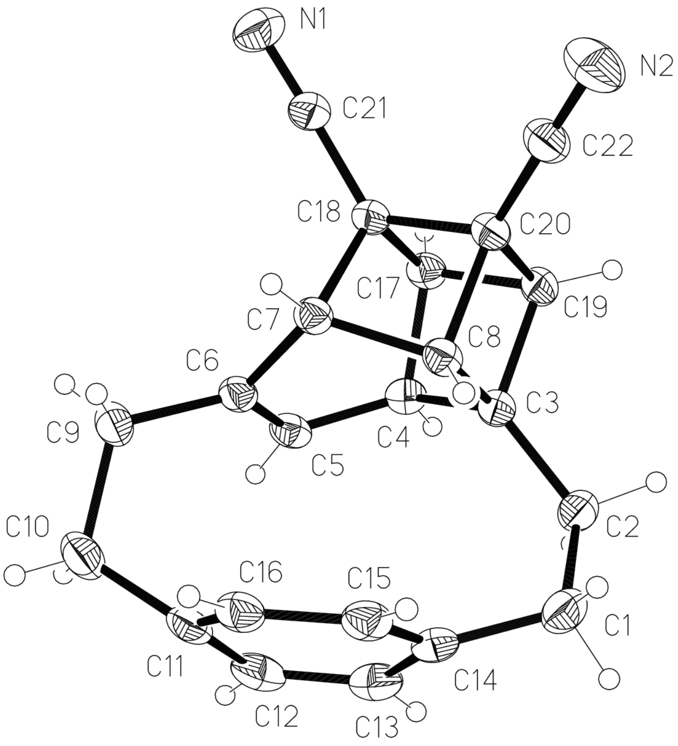

Figure 1
The molecule of the title compound (2) in the crystal. Ellipsoids represent 30% probability levels. H atom radii are arbitrary.

the basketene ring system, *cf*. the very narrow angle C5—C6—C7 112.85 (14)° at the sp^2 atom C6 [the localized double bond C5—C6 displays a normal length of 1.329 (2) Å]. Further evidence for this is provided by the lengthening of several basketene C—C single bonds to *ca* 1.57–1.58 Å, the longest being C3—C4 of 1.585 (2) Å (Table 1).

There are no noteworthy intermolecular contacts and, in particular, none of the type C—H$\cdots$*Cg*, where *Cg* represents the centroid of a cyclophane ring. We recently observed such contacts in cyclophane derivatives (Jones *et al.*, 2002), with H$\cdots$*Cg* *ca* 2.7 Å and acceptable linearity. Here, the only potential candidate would be H17$\cdots$*Cg*(C12,13,15,16), with H$\cdots$*Cg* 2.95 Å, but a narrow angle C—H$\cdots$*Cg* 124°.

Experimental

Irradiation of (1) in toluene with a 450 W mercury high pressure lamp for 5 h under nitrogen leads to (2) in 73% yield (after silica-gel chromatography and fractional crystallization from chloroform/pentane).

Crystal data

$C_{22}H_{18}N_2$
$M_r = 310.38$
Monoclinic, $P2_1/c$
$a = 6.6094$ (14) Å
$b = 17.251$ (3) Å
$c = 13.910$ (3) Å
$\beta = 97.272$ (16)°
$V = 1573.3$ (5) Å^3
$Z = 4$

$D_x = 1.310$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
$\theta = 10$–11.5°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.60 × 0.60 × 0.08 mm

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
5639 measured reflections
2760 independent reflections
2175 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

$\theta_{\rm max} = 25.0°$
$h = -7 \rightarrow 7$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 0$
3 standard reflections
every 147 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.117$
$S = 1.03$
2760 reflections
217 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 0.3931P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.539 (2)	C6—C9	1.521 (2)
C3—C8	1.562 (2)	C7—C8	1.560 (2)
C3—C19	1.577 (2)	C8—C20	1.576 (2)
C3—C4	1.585 (2)	C9—C10	1.554 (2)
C4—C5	1.485 (2)	C17—C19	1.548 (2)
C4—C17	1.551 (2)	C17—C18	1.562 (2)
C5—C6	1.329 (2)	C18—C20	1.578 (2)
C6—C7	1.499 (2)	C19—C20	1.552 (2)
C14—C1—C2	111.63 (14)	C12—C11—C16	117.37 (17)
C3—C2—C1	118.93 (14)	C15—C14—C13	117.46 (17)
C2—C3—C8	120.83 (13)	C19—C17—C4	90.84 (12)
C2—C3—C19	121.49 (13)	C19—C17—C18	90.82 (12)
C8—C3—C19	89.36 (11)	C4—C17—C18	108.58 (12)
C2—C3—C4	121.15 (14)	C21—C18—C17	118.16 (14)
C8—C3—C4	107.23 (12)	C21—C18—C7	118.29 (14)
C19—C3—C4	88.58 (11)	C17—C18—C7	109.73 (12)
C5—C4—C17	115.02 (13)	C21—C18—C20	125.62 (14)
C5—C4—C3	118.37 (13)	C17—C18—C20	88.79 (12)
C17—C4—C3	87.10 (11)	C7—C18—C20	90.18 (11)
C6—C5—C4	117.09 (14)	C17—C19—C20	90.25 (12)
C5—C6—C7	112.85 (14)	C17—C19—C3	87.50 (11)
C6—C7—C8	118.79 (13)	C20—C19—C3	90.59 (12)
C6—C7—C18	114.59 (13)	C22—C20—C19	128.15 (14)
C8—C7—C18	86.52 (11)	C22—C20—C8	125.85 (14)
C7—C8—C3	110.88 (12)	C19—C20—C8	89.76 (11)
C7—C8—C20	90.68 (11)	C22—C20—C18	124.57 (14)
C3—C8—C20	90.27 (11)	C19—C20—C18	90.13 (12)
C6—C9—C10	115.64 (15)	C8—C20—C18	85.81 (11)
C11—C10—C9	107.84 (14)		

H atoms were included at calculated positions, using a riding model. $U_{\rm iso}$(H) values were fixed at 1.2 times the $U_{\rm eq}$ of the parent atom.

Data collection: *P*3 (Nicolet, 1987); cell refinement: *P*3; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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