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A dimer of 7-cyanodibenzobarrelene

Peter G. Jones,[a]* Peter Bubenitschek,[b] Henning Hopf[b] and Bernhard Witulski[b]

[a]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and [b]Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

Key indicators

Single-crystal X-ray study
T = 178 K
Mean σ(C–C) = 0.009 Å
R factor = 0.073
wR factor = 0.222
Data-to-parameter ratio = 10.0

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

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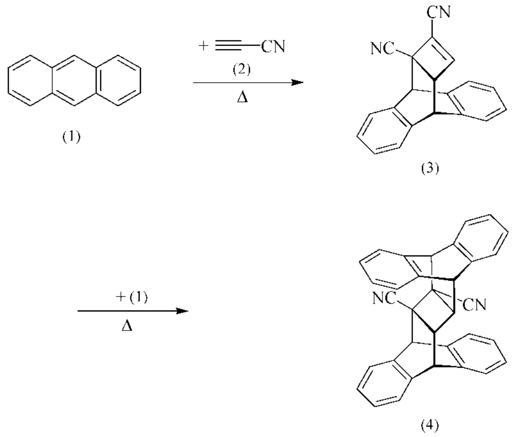
The molecule of the title compound, 2,3-dicyanotetrabenzopentacyclo[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-5,11,13,15-tetraene chloroform monosolvate, $C_{34}H_{22}N_2\cdot CHCl_3$, displays approximate twofold symmetry. The four-membered ring has slightly lengthened C—C bonds and a ring pucker of 11.9 (7)°. The solvent molecule is involved in a C—H···π contact.

Comment

Heating a solution of anthracene, (1), and cyanoacetylene, (2), in a 1:4 molar ratio in benzene at 433 K results in the formation of a complex mixture of cycloadducts (Hopf & Witulski, 1995), among them the 1:2 adduct, (3), and a 2:2 adduct, (4), isolated in 4% yield, the structure of which we were unable to derive from spectroscopic data alone. The compound was therefore subjected to X-ray structure determination, the results of which are presented here, confirming structure (4).



Although several mechanisms can be proposed to account for the formation of the triply layered product, (4), the one involving the addition of excess (1) to the intermediate (3) is particularly attractive. Indeed, when (3) and (1) are heated in toluene at 433 K (ratio 1:2), compound (4), which is formally a head-to-tail dimer of 7-cyanodibenzobarrelene, was produced in 18% yield.

Compound (4) (Fig. 1) displays no imposed symmetry, but has approximate twofold symmetry. It crystallizes with one molecule of chloroform. Molecular dimensions may be regarded as normal, *e.g.* the four-membered ring displays slightly lengthened C—C bonds and a ring pucker of 11.9 (7)° (Allen, 1984). The exocyclic bonds C9—C11 and C9′—C11′ are also significantly lengthened (Table 1).

The crystal packing involves three contacts that might be classified as C—H···*X* hydrogen bonds (*X* = N or Cl; Table 2). A more significant interaction, however, is between the chloroform H atom and the centroid (*Cent*) of ring C1*A*′–C4*A*′, with an H···*Cent* distance of 2.65 Å (non-normalized) and a C—H···*Cent* angle of 160°.

Experimental

The compound was prepared according to Witulski (1992) and recrystallized from chloroform/pentane.

Crystal data

$C_{34}H_{22}N_2 \cdot CHCl_3$
$M_r = 577.90$
Orthorhombic, $P2_12_12_1$
$a = 10.626$ (4) Å
$b = 16.048$ (5) Å
$c = 16.580$ (7) Å
$V = 2827.3$ (18) Å^3
$Z = 4$
$D_x = 1.358$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 50 reflections
$\theta = 10$–11°
$\mu = 0.35$ mm^{-1}
$T = 178$ (2) K
Prism, colourless
0.7 × 0.4 × 0.2 mm

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
3618 measured reflections
3618 independent reflections
2199 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.5°$

$h = -13 \rightarrow 0$
$k = -20 \rightarrow 0$
$l = -21 \rightarrow 0$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.222$
$S = 1.03$
3618 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.087P)^2 + 5.5143P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -0.97$ e Å^{-3}
Absolute structure: Flack (1983), no Friedel pairs
Flack parameter = 0.4 (2)

Table 1
Selected geometric parameters (Å, °).

C9—C11	1.602 (9)	C12—C12′	1.560 (8)
C11—C12	1.563 (8)	C9′—C11′	1.589 (9)
C11—C11′	1.571 (9)	C11′—C12′	1.578 (8)
C12—C11—C11′	89.4 (4)	C11—C11′—C12′	89.5 (4)
C12′—C12—C11	90.5 (4)	C12—C12′—C11′	89.3 (4)
C11′—C11—C12—C12′	8.5 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N′^{i}	0.95	2.70	3.641 (9)	172
C6′—H6′···N′^{ii}	0.95	2.59	3.455 (9)	152
C9—H9···Cl1^{iii}	1.00	2.82	3.776 (7)	161

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$.

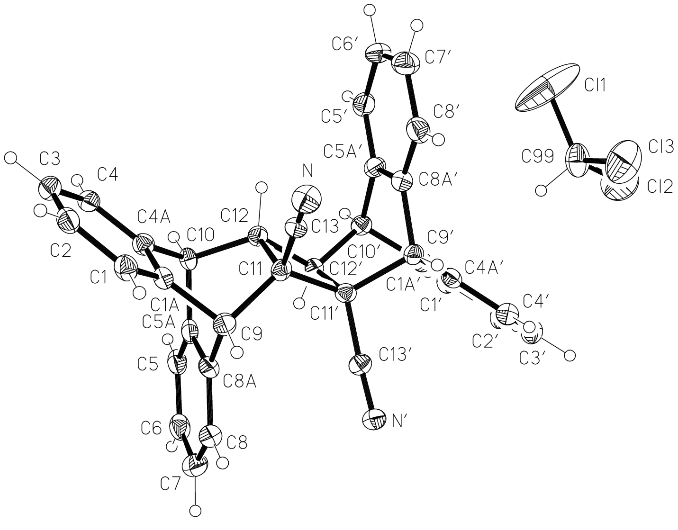


Figure 1
The structure of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H-atom radii are arbitrary.

H atoms were included using a riding model with fixed C—H bond lengths (aromatic = 0.95 Å and methine = 1.00 Å); $U_{\rm iso}$(H) values were fixed at 1.2$U_{\rm eq}$ of the parent atom. The Flack (1983) parameter was indeterminate. The only major features of residual electron density are found in the solvent region.

Data collection: *P*3 (Nicolet, 1987); cell refinement: *P*3; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); 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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