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6a,6b,12a,12b-Tetrahydrocycloocta[3,4]cyclobuta[1,2][8]annulene

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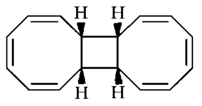
The *cis,syn,cis*-tricyclic [2+2]-dimer of cyclooctatetraene, $C_{16}H_{16}$, crystallizes in space group $Pca2_1$ with two molecules in the asymmetric unit. An extensive network of weak C—H···π(C═C) interactions between the two independent molecules, *A* and *B*, as well as *A*···*A* and *B*···*B* interactions, are observed in the supramolecular assembly. The C—H groups point more towards one C atom than to the centre of the C═C bond. Notable among the interactions are bifurcated (cyclobutane)C—H···C═C contacts that span transannularly the eight-membered ring.

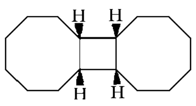
Comment

In recent years, the weak hydrogen bond-like interactions between C—H donor groups and π acceptors have been invoked with increasing frequency to explain diverse chemical and biological phenomena, such as biomolecular conformations, stereoselective reactions, chiral recognition and self-assembly processes, among others (Nishio *et al.*, 1998; Desiraju & Steiner, 1999). In addition, the role of C—H···π interactions in crystal packing has also been recognized through several examples wherein the solid-state architecture is determined by a network of weak hydrogen bonds involving alkene, alkyne and aromatic π-bonds as acceptors. However, most of the systems studied so far have been multifunctional, in which there could be some influence of other intermolecular forces, besides the C—H···π interactions, in determining the three-dimensional molecular packing (Steiner, 1995; Steiner *et al.*, 1995; Platts *et al.*, 1996; Batsanov *et al.*, 1996; Madhavi *et al.*, 1997; Lutz *et al.*, 1998; Harder, 1999; Takahashi *et al.*, 2001). Thus, the crystal structures of pure hydrocarbons can be more illuminating in delineating the interplay of weak C—H···π interactions in crystal packing.

While many examples of C—H···π interactions with alkyne and aromatic π-bonds are known (McMullan *et al.*, 1992), involvement of alkene π-bonds in such interactions has been rarely encountered. A recent report in this regard is the observation of C—H···π interactions in the low-temperature crystal structures of the simple hydrocarbons 1,7-octadiene and 1,9-decadiene (Bond, 2002). This finding prompts us to report on the crystal structure of the title compound, (I), which is an esoteric tricyclic hydrocarbon synthethized by Schröder & Martin (1966). There are two molecules in the asymmetric unit (denoted hereafter *A* and *B*; Fig. 1). The determination of the crystal structure in the related centrosymmetric space group, *Pbcm*, was not successful. Hence, the non-centrosymmetric space group was chosen. The two independent molecules are found to be related by a non-crystallographic center of symmetry. The distributions of the torsion angles within molecules *A* and *B* are essentially the same, the values about the corresponding bonds showing variations of not more than about 2.5° (Table 1). The r.m.s. fit of the atoms for the two molecules is 0.041 Å. The molecular symmetry of both molecules is close to twofold symmetry, deviating from the expected *mm*2 symmetry.



(I)



(II)

A careful study of the intermolecular distances and the relevant angles of approach revealed many C—H···π contacts of the types (cyclobutane)C—H···C═C and (cyclooctene)C═C—H···C═C between molecules *A* and *B*, as well as *A*···*A* and *B*···*B* interactions. The geometric parameters of the significant intermolecular C—H···π interactions that are within acceptable limits are given in Table 2. Significantly, the large number of C—H···C(π) interactions encountered in (I) exhibit favorable directional characteristics, although the C—H groups do not target the mid-point of the C═C double bond, but are displaced towards one of the C atoms of the C═C group (Desiraju & Steiner, 1999). It should be mentioned that there are four H···H short contacts

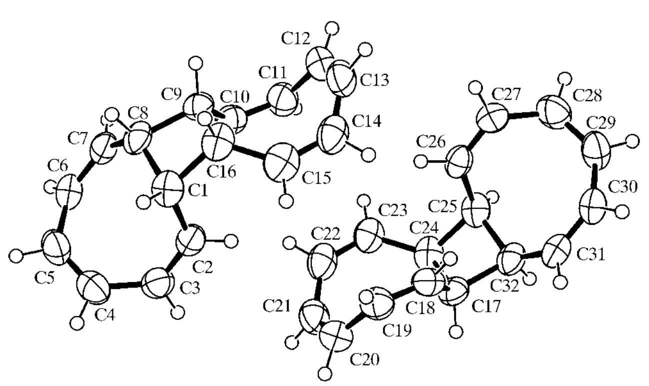


Figure 1
Views of molecule *A* (left) and molecule *B* (right) of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

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(H7$\cdots$H20, H9$\cdots$H22, H17$\cdots$H14 and H31$\cdots$H12), with distances in the range 2.34–2.56 Å, which are close to the sum of the H-atom van der Waals radii ($r_{\rm H}$ = 1.2 Å). Such a situation appears to be caused by the exigencies of packing considerations. Fig. 2(*a*) shows the infinite wave-like C—H$\cdots$C*sp*^{2} interactions between *A* molecules along the *b* axis. A similar pattern (Fig. 2*b*) is also observed between *B* molecules. In both cases, the less acidic cyclobutane ring H atoms participate in the interactions. To our knowledge, the participation of cyclobutane C—H groups in C—H$\cdots\pi$ interactions does not seem to have been observed. However, C—H$\cdots$O contacts involving a cyclobutane C—H group have been reported (Mehta *et al.*, 1999; Mehta & Vidya, 2000). A further novel aspect is that the cyclobutane H atoms in molecules *A* and *B* are involved in bifurcated C—H$\cdots\pi$ interactions, which span a 'transannular 1,6-hydrogen bridge' in one of the cyclooctatriene rings, and generate a structural motif reminiscent of anti-Bredt alkenes (Hopf, 2000). It is tempting to speculate that the formation of this novel hydrogen-bridged anti-Bredt motif may contribute towards the carbon-centred directional preference of the C—H$\cdots\pi$ contacts in molecules *A* and *B*.

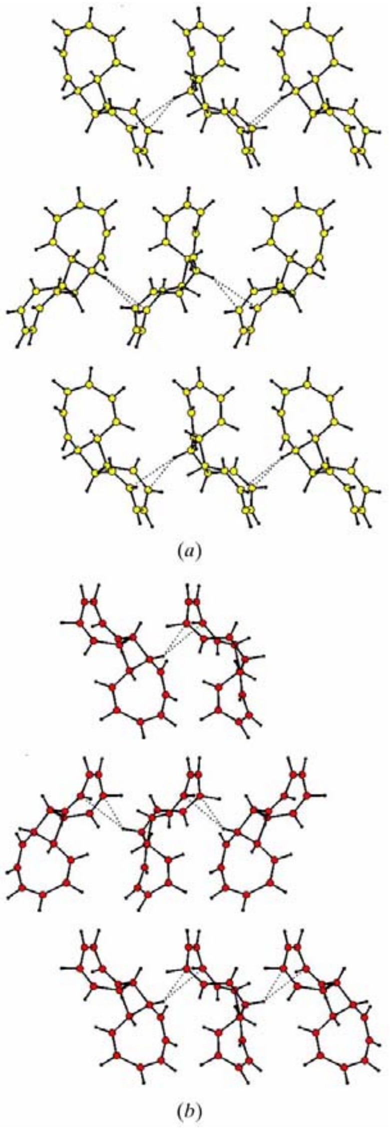

Figure 2
(*a*) C—H$\cdots\pi$ interactions between *A* molecules and (*b*) C—H$\cdots\pi$ interactions between *B* molecules.

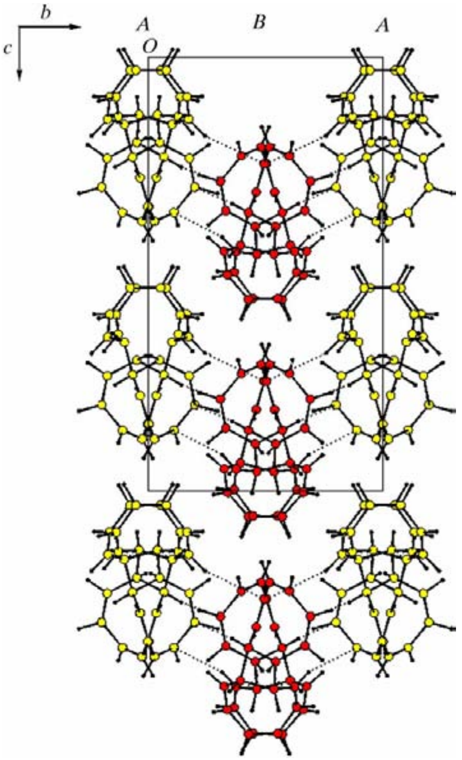

Figure 3
C—H$\cdots\pi$ interactions between *A* and *B* molecules, viewed along the *a* axis.

The overall pattern in the organization of the two crystallographically independent molecules in the crystal structure, viewed along the *a* axis [*a* = 12.016 (3) Å], is shown in Fig. 3. It is observed that rows of *A* and *B* molecules are arranged along the *c* axis of the unit cell, repeating in the sequence $\cdots A\cdots B\cdots A\cdots B\cdots$ along the *b* axis, with infinite strands of wave-like patterns along the *b* axis connecting molecules *A* and *B*. Molecules *A* and *B* along the *b* axis are connected through C—H$\cdots\pi$ interactions involving contacts of types (cyclobutane)C—H$\cdots$C═C and (cyclooctene)C═C—H$\cdots$C═C (Table 2).

It may be pertinent to raise the question of whether the molecular assembly observed in (I) could be attributed to the network of weak C—H$\cdots\pi$ interactions, particularly in view of the ongoing debate on their role. In this context, it is noteworthy that the intermolecular contact distances between C and H atoms are well above the sum of their van der Waals radii in the crystal structure of the perhydro derivative *cis,syn,cis*-tricyclo[8.6.0.0^{2,9}]hexadecane, (II) (Spek *et al.*, 1985). This lends support for the reality of C—H$\cdots\pi$ interactions in the unsaturated hexaene (I). Although some non-dispersive contributions from C—H$\cdots\pi$ interactions would be present, specific directional C—H···π forces appear to play a role in the observed pattern in the crystal structure of (I). It is reasonable to surmise that the unique tricyclic structure of hydrocarbon (I), with two conformationally flexible eight-membered rings, facilitates the generation of the extensive C—H···π network observed here.

In conclusion, we observe that in the crystalline state of (I), a pure hydrocarbon, an efficient network of C—H···π(sp^2) interactions operates in concert with non-directional van der Waals interactions to generate the observed supramolecular organization. The involvement of the less acidic cyclobutane H atoms in a bifurcated interaction, forming a transannular ‘hydrogen bridge’ in the eight-membered ring, is also a noteworthy feature in the compound.

Experimental

The synthesis of the *cis,syn,cis*-tricyclic [2+2]-dimer of cyclooctatetraene has been described by Schröder & Martin (1966). Suitable crystals were grown from a solution of (I) in dichloromethane and hexane by slow evaporation.

Crystal data

$C_{16}H_{16}$
$M_r = 208.29$
Orthorhombic, $Pca2_1$
$a = 12.016$ (3) Å
$b = 10.347$ (2) Å
$c = 19.233$ (4) Å
$V = 2391.1$ (9) Å^3
$Z = 8$
$D_x = 1.157$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1342 reflections
$\theta = 2.3$–23.4°
$\mu = 0.07$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.920$, $T_{\max} = 0.987$
16 681 measured reflections

2255 independent reflections
1899 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.3°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 23$

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.115$
$S = 1.05$
2255 reflections
289 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.3136P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected torsion angles (°).

C1—C2—C3—C4	5.5 (7)	C17—C18—C19—C20	−4.8 (6)
C2—C3—C4—C5	54.0 (7)	C18—C19—C20—C21	−56.3 (6)
C3—C4—C5—C6	4.2 (6)	C19—C20—C21—C22	−3.4 (8)
C4—C5—C6—C7	−52.9 (7)	C20—C21—C22—C23	55.2 (6)
C5—C6—C7—C8	−6.2 (7)	C21—C22—C23—C24	3.2 (6)
C9—C10—C11—C12	4.8 (6)	C25—C26—C27—C28	−4.9 (7)
C10—C11—C12—C13	56.7 (6)	C26—C27—C28—C29	−54.0 (7)
C11—C12—C13—C14	3.2 (8)	C27—C28—C29—C30	−4.3 (6)
C12—C13—C14—C15	−56.2 (6)	C28—C29—C30—C31	52.4 (7)
C13—C14—C15—C16	−3.3 (6)	C29—C30—C31—C32	5.7 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···C20$^{\rm i}$	0.93	3.05	3.834 (6)	143
C9—H9···C22$^{\rm ii}$	0.98	2.99	3.953 (4)	168
C16—H16···C6$^{\rm ii}$	0.98	2.94	3.584 (5)	124
C16—H16···C3$^{\rm ii}$	0.98	3.10	4.015 (5)	155
C17—H17···C14$^{\rm iii}$	0.98	2.94	3.895 (4)	166
C24—H24···C30$^{\rm iii}$	0.98	3.02	3.647 (6)	123
C24—H24···C27$^{\rm iii}$	0.98	3.04	3.965 (5)	157
C31—H31···C12$^{\rm iv}$	0.93	3.08	3.896 (6)	147

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

Due to the absence of any significant anomalous scatterers in (I), attempts to confirm the absolute structure by refinement of the Flack (1983) parameter in the presence of 2044 sets of Friedel equivalents led to an inconclusive value of −2 (10) (Flack & Bernardinelli, 2000). Therefore, the intensities of the Friedel pairs were merged before the final refinement and the absolute structure was assigned arbitrarily. The H atoms were placed in idealized positions (C—H = 0.93–0.98 Å) and were constrained to ride on their parent atoms, with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1180). Services for accessing these data are described at the back of the journal.

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