to prepare material for publication: *SHELXL93*. Geometric calculations: *PARST* (Nardelli, 1983*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual *trans*-Fused Cyclopentane Ring System at 158 K

MARK LAUTENS, ALAN J. LOUGH AND WILLIAM TAM

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

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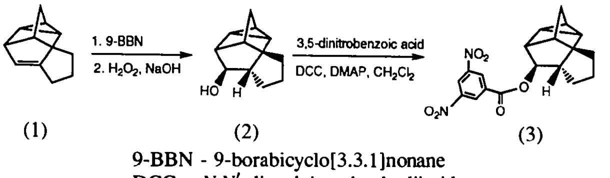
Abstract

The crystal structure of the title compound, pentacyclo[$6.4.0^{1,5}.0^{1,8}.0^{7,11}.0^{10,12}$]dodecan-6-yl 3,5-dinitrobenzoate, $C_{19}H_{18}N_2O_6$, establishes the cyclopentane ring junctions in the molecule to be *trans* fused. The C_{sp^3}—C_{sp^3} bond lengths range from 1.505 (4) to 1.568 (4) Å.

Comment

Recently, we reported the first examples of a transition metal-catalyzed intramolecular homo-Diels–Alder reaction (Lautens, Tam & Edwards, 1992; Lautens, Lautens & Smith, 1990). Pentacyclene, (1), was synthesized *via* this method. Hydroboration of pentacyclene, (1), with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by oxidative work-up, afforded alcohol (2) as a single regio- and stereoisomer with unusual *trans*-fused cyclopentane rings (Motherwell & Shipman, 1990). In order to confirm that the cyclopentane ring junctions are *trans* fused, alcohol (2) was converted into ester (3) and the structure determined by X-ray diffraction analysis.



9-BBN - 9-borabicyclo[3.3.1]nonane
DCC = *N,N'*-dicyclohexylcarbodiimide
DMAP = 4-(dimethylamino)pyridine

The effects of strain are reflected in the the bond lengths and angles of the molecule. This can be observed for the C_{sp^3} atoms. The bond length C9—C10 is 1.505 (4) Å, while C7—C8 is significantly longer at 1.568 (4) Å. The smallest angle is 59.2 (2)° for C10—C12—C11, while the largest is 128.4 (2)° for C8—C1—C2. The structure of one other molecule containing a *trans*-fused system of rings has been reported (Van Hijfte, Little, Peterson & Moeller, 1987).

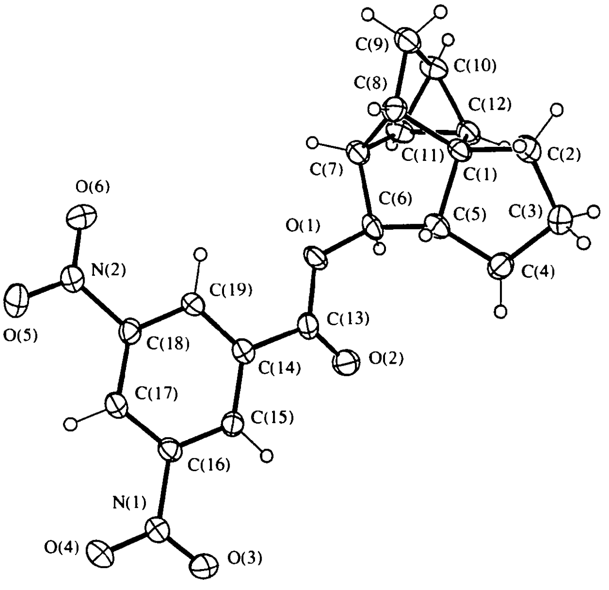


Fig. 1. View of compound (3) with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres. The junction of the *trans*-fused cyclopentane rings is the C1—C5 bond.

Experimental

Hydroboration–oxidation of pentacyclene, (1), followed by esterification of the alcohol (2) with 3,5-dinitrobenzoic acid, *N*,*N*′-dicyclohexylcarbodiimide and 4-(dimethylamino)-pyridine afforded the title compound, (3) (see scheme above). Suitable crystals were grown from a methanol/pentane/diethyl ether (1:1:1) solution.

Crystal data

$C_{19}H_{18}N_2O_6$
$M_r = 370.35$
Monoclinic
$P2_1/c$
$a = 13.199\ (3)$ Å
$b = 6.108\ (1)$ Å
$c = 20.971\ (4)$ Å
$\beta = 92.53\ (2)°$
$V = 1689.0\ (7)$ Å^3
$Z = 4$
$D_x = 1.456$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 5.06–11.00°$
$\mu = 0.110$ mm^{-1}
$T = 158$ K
Needle
0.25 × 0.15 × 0.10 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3112 measured reflections
2974 independent reflections
2067 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0230$

$\theta_{\max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 7$
$l = -24 \rightarrow 24$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R(F) = 0.0503$
$wR(F^2) = 0.1391$
$S = 1.043$
2974 reflections
245 parameters
H atoms riding (C—H = 0.96 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.479$ e Å^{-3}
$\Delta\rho_{\min} = -0.277$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.89719 (12)	0.3638 (3)	0.85435 (8)	0.0255 (4)
O2	0.87327 (13)	0.0189 (3)	0.89053 (9)	0.0361 (5)
O3	0.51989 (14)	−0.1604 (3)	0.94447 (9)	0.0326 (5)
O4	0.39604 (13)	0.0607 (4)	0.91826 (9)	0.0375 (5)
O5	0.46807 (13)	0.7364 (3)	0.80379 (9)	0.0340 (5)
O6	0.6166 (2)	0.7715 (4)	0.76583 (11)	0.0481 (6)
N1	0.48577 (15)	0.0096 (4)	0.92056 (10)	0.0260 (5)
N2	0.5564 (2)	0.6771 (4)	0.79883 (10)	0.0276 (5)
C1	1.1458 (2)	0.5392 (4)	0.89910 (12)	0.0230 (6)
C2	1.1961 (2)	0.5882 (5)	0.96548 (13)	0.0307 (6)
C3	1.1970 (2)	0.3590 (5)	0.99787 (13)	0.0313 (7)
C4	1.1162 (2)	0.2144 (5)	0.96123 (13)	0.0300 (6)
C5	1.0612 (2)	0.3776 (4)	0.91745 (12)	0.0231 (6)
C6	1.0074 (2)	0.3293 (4)	0.85259 (12)	0.0235 (6)
C7	1.0505 (2)	0.5060 (4)	0.80900 (12)	0.0249 (6)
C8	1.0912 (2)	0.6973 (4)	0.85295 (12)	0.0251 (6)
C9	1.1745 (2)	0.8072 (5)	0.81667 (13)	0.0287 (6)
C10	1.2300 (2)	0.6028 (4)	0.79851 (13)	0.0280 (6)
C11	1.1523 (2)	0.4235 (4)	0.78910 (12)	0.0265 (6)
C12	1.2162 (2)	0.4372 (4)	0.85167 (12)	0.0256 (6)
C13	0.8409 (2)	0.1947 (4)	0.87279 (12)	0.0242 (6)
C14	0.7299 (2)	0.2519 (4)	0.86896 (11)	0.0217 (6)
C15	0.6613 (2)	0.1099 (4)	0.89646 (11)	0.0222 (6)
C16	0.5589 (2)	0.1621 (4)	0.89228 (11)	0.0215 (6)
C17	0.5214 (2)	0.3475 (4)	0.86195 (11)	0.0209 (6)
C18	0.5919 (2)	0.4811 (4)	0.83437 (11)	0.0220 (6)
C19	0.6951 (2)	0.4399 (4)	0.83761 (11)	0.0221 (6)

Table 2. *Selected geometric parameters* (Å, °)

O1—C13	1.339 (3)	C5—C6	1.535 (3)
O1—C6	1.472 (3)	C6—C7	1.539 (4)
O2—C13	1.209 (3)	C7—C11	1.511 (3)
O3—N1	1.230 (3)	C7—C8	1.568 (4)
O4—N1	1.224 (3)	C8—C9	1.521 (4)
O5—N2	1.230 (3)	C9—C10	1.505 (4)
O6—N2	1.221 (3)	C10—C11	1.507 (4)
N1—C16	1.484 (3)	C10—C12	1.522 (4)
N2—C18	1.475 (3)	C11—C12	1.530 (3)
C1—C12	1.524 (3)	C13—C14	1.505 (3)
C1—C8	1.525 (3)	C14—C19	1.391 (4)
C1—C2	1.545 (3)	C14—C15	1.397 (4)
C1—C5	1.552 (3)	C15—C16	1.388 (3)
C2—C3	1.556 (4)	C16—C17	1.380 (4)
C3—C4	1.560 (4)	C17—C18	1.384 (3)
C4—C5	1.518 (4)	C18—C19	1.384 (3)
C13—O1—C6	117.3 (2)	C1—C8—C7	92.4 (2)
O4—N1—O3	124.6 (2)	C10—C9—C8	97.5 (2)
O4—N1—C16	118.0 (2)	C9—C10—C11	107.4 (2)
O3—N1—C16	117.4 (2)	C9—C10—C12	106.9 (2)
O6—N2—O5	123.5 (2)	C11—C10—C12	60.7 (2)
O6—N2—C18	118.0 (2)	C10—C11—C7	109.3 (2)
O5—N2—C18	118.5 (2)	C10—C11—C12	60.1 (2)
C12—C1—C8	97.4 (2)	C7—C11—C12	102.0 (2)
C12—C1—C2	114.6 (2)	C10—C12—C1	107.6 (2)
C8—C1—C2	128.4 (2)	C10—C12—C11	59.2 (2)
C12—C1—C5	111.6 (2)	C1—C12—C11	104.7 (2)
C8—C1—C5	103.6 (2)	O2—C13—O1	125.5 (2)
C2—C1—C5	100.7 (2)	O2—C13—C14	123.6 (2)
C1—C2—C3	102.3 (2)	O1—C13—C14	110.9 (2)
C2—C3—C4	107.6 (2)	C19—C14—C15	120.1 (2)
C5—C4—C3	103.0 (2)	C19—C14—C13	121.2 (2)
C4—C5—C6	126.9 (2)	C15—C14—C13	118.7 (2)
C4—C5—C1	103.7 (2)	C16—C15—C14	118.6 (2)
C6—C5—C1	102.3 (2)	C17—C16—C15	123.1 (2)
O1—C6—C5	111.7 (2)	C17—C16—N1	118.2 (2)
O1—C6—C7	107.8 (2)	C15—C16—N1	118.6 (2)
C5—C6—C7	102.9 (2)	C16—C17—C18	116.3 (2)
C11—C7—C6	106.7 (2)	C17—C18—C19	123.4 (2)
C11—C7—C8	97.2 (2)	C17—C18—N2	119.0 (2)
C6—C7—C8	107.4 (2)	C19—C18—N2	117.5 (2)
C9—C8—C1	105.4 (2)	C18—C19—C14	118.5 (2)
C9—C8—C7	105.7 (2)		

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclohepta-3,5-dien-1-yl 3,5-Dinitrobenzoate

FRANK H. ALLEN

Cambridge Crystallographic Data Centre,
12 Union Road, Cambridge CB2 1EZ, England

JUDITH A. K. HOWARD, NIGEL A. PITCHFORD AND PATRICK G. STEEL

Chemistry Department, University of Durham,
South Road, Durham DH1 3LE, England

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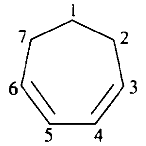
Abstract

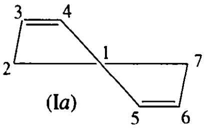
The cyclohepta-3,5-diene ring in the title compound, $C_{14}H_{12}N_2O_6$, is the first example of a 'free' ring to be characterized by crystal structure analysis. All previous examples are either bridged, fused to other rings or have exocyclic conjugative substituents attached to the ring sp^2-C atoms. All but one of these examples adopts the C_2-symmetric (twist) conformation, despite the fact that experimental gas-phase and computational results show a C_s-symmetric (envelope) conformation for the free ring. The 'free' cyclohepta-3,5-diene in the title compound clearly adopts a C_s-symmetric conformation with C1 displaced from the plane of the other six ring atoms. The ring is forced to adopt the C_2-symmetric conformation in more complex systems so as to minimize unfavourable intramolecular non-bonded repulsions.

Comment

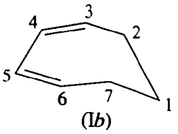
Cyclohepta-3,5-diene, (I), has been studied by a variety of experimental and computational techniques. Crews (1971) interpreted NMR data in terms of a distorted twist conformation (I*a*) of C_2 symmetry. However, electron diffraction (Chiang & Bauer, 1966; Hagen & Traetteberg, 1972) and microwave data (Avirah, Molloy & Cook, 1979) were interpreted unequivocally in terms of a C_s-symmetric conformation (I*b*), having all atoms except C1 coplanar. Molecular-mechanics calculations by Burkert & Allinger (1982) and by Favini, Maggi & Todeschini (1983) indicated that the experimentally observed C_s form (I*b*) was energetically preferred by 7–8 kJ mol^{-1} over the C_2 form (I*a*). This result was almost exactly reproduced by Saebo & Boggs (1982) using *ab initio* methods.



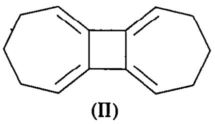
(I)

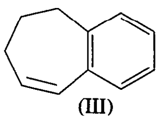


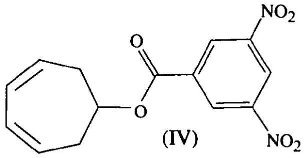
(I*a*)



(I*b*)


(II)


(III)



(IV)

Recently (Allen, Garner, Howard & Pitchford, 1994), we performed a conformational analysis of non-bridged examples of (I) using available crystallographic results from the Cambridge Structural Database (Allen *et al.*, 1991, hereinafter CSD). To our initial surprise we found that 13 of the 20 crystallographic observations of (I) adopted the C_2-symmetric conformation (I*a*). A further six examples were distorted by small-ring fusion at the 1–2 bond and exhibited a conformation that is typical of cyclohepta-1,3,5-trienes. Only one example, the symmetrically related ring in (II), adopted the energetically preferred C_s conformation (I*b*). Closer examination of the 13 C_2 conformers showed that in ten cases either one (seven examples) or both (three examples) of the 'double' bonds in (I) arose from benzo-fusion