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Structural Comparisons of a Perpendicular Diene with Known Derivatives

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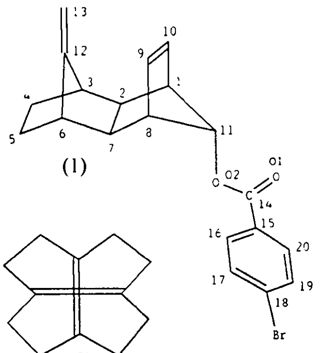
Abstract

The X-ray crystal structure determination of *endo,exo*-12-methylenetetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-9-en-*anti*-11-yl *p*-bromobenzoate, $C_{20}H_{19}BrO_2$ (1), is reported. The molecule consists of norbornene with an *anti-p*-bromobenzoate substituent at the methano bridge and an *exo*-methylenenorbornyl unit *endo*-fused to the ethano bridge. The ring C atom of the exocyclic double bond is pyramidalized significantly. Steric interactions are examined and some structural comparisons are made with other derivatives.

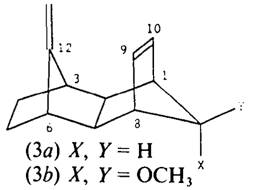
Comment

Parallel laticyclic π–π molecular orbital interactions (Goldstein & Hoffman, 1971) have been studied theoretically, spectroscopically (Elsässer, Hassenrück, Martin, Mayer, Lutz & Prinzbach, 1991; Martin & Mayer, 1983) and crystallographically (Ermer, Bödecker & Preut, 1984). Although a number of compounds exist which show perpendicular longicyclic π–π interactions (Paquette, Shen & Engel, 1989; Pinkerton, Schwarzenbach, Birbaum, Carrupt, Schwager & Vogel, 1984; Siemionko & Berson, 1980), an attempt to synthesize a perpendicular laticyclic diene (2) was unsuccessful (McMurry, 1989). However, the X-ray crystal structure of a perpendicular almost laticyclic benzo derivative has been reported (Butler, Gupta, Ng & Nyberg, 1980). The hydrocarbon (3*a*) is known (Lap & Paddon-Row, 1979), but it is a liquid at 268 K and polymerizes slowly at 298 K.

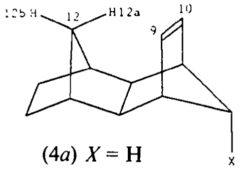


(1)

(2)



(3*a*) *X*, *Y* = H
(3*b*) *X*, *Y* = OCH$_3$
(3*c*) *X* = OH, *Y* = H



(4*a*) *X* = H
(4*b*) *X* = OPBB

The low-temperature X-ray crystal structure of the diene acetal (3*b*), whose π bonds are perpendicular and almost laticyclic, was reported recently (Lloyd, Arif & Allred, 1992). The dihedral angle between the least-squares plane of atoms C3, C6, C12 and that of atoms C1, C8, C9, C10 is 10.6 (5)° in (3*b*). The values of the intramolecular contacts C9···C12 [2.946 (2) Å] and C10···C12 [2.977 (2) Å] for (3*b*) are within the sum of the respective van der Waals radii (Bondi, 1964; Gordon & Ford, 1972). In addition, π splitting of 1.2 eV is observed in the He (I_α) photoelectron spectrum of (3*a*) (Gleiter, Jähne, Allred & Lloyd, 1993).

The two C—H σ bonds of the H12*b*—C12—H12*a* unit in the structure of (4) together have similar phase symmetry to that of an atomic 2*p* orbital (Jordan & Paddon-Row, 1992; Paddon-Row, Engle-

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† Deceased 8 July 1991.

hardt, Skelton, White, Jørgensen & Patney, 1987; Paddon-Row, 1985). Through-space σ–π orbital mixing lowers the first (π) ionization energy of (4*a*) relative to norbornene by 0.32 eV. This interaction is termed 'laticyclic hyperconjugation' in compounds containing the tetracyclic structural unit in (4). The low-temperature X-ray crystal structure of the *anti*-11-*p*-bromobenzoate (OPBB) derivative (4*b*) has been reported recently (Lloyd, Arif, Coots & Allred, 1994). Experimental structural comparisons between the topologically similar systems (1), (3) and (4) are the subject of this work.

The *p*-bromobenzoate ester (1) was prepared in connection with solvolysis studies of *anti*-norbornene derivatives and X-ray analysis proved possible (Lloyd, 1985).* The structure has since been redetermined with improved precision.

An *ORTEP* (Johnson, 1965) drawing of (1) is shown in Fig. 1. There are no non-hydrogen intermolecular contacts shorter than the sum of the respective van der Waals radii (Bondi, 1964; Gordon & Ford, 1972).

The tetracyclic hydrocarbon framework of (1) contains a non-crystallographic mirror plane defined by *M*(C2—C7), *M*(C4—C5), *M*(C9═C10), C(11) and C(12), where *M* is the midpoint of the respective bond. The bond C11—O2 is at an angle of 2.65° to the least-squares mirror plane, with O2 0.055 (3) Å out of the plane. The bond lengths C2—C3 and C6—C7 differ by 0.012 Å. Other differences between symmetry-related bonds are ≤0.005 Å. The bond angles C1—C11—O2 and C8—C11—O2 differ by 5.1°; the corresponding differences for (3*b*) and (4*b*) are 6.3 and 4.9°, respectively. All other differences between symmetry-related bond angles in (1) are ≤1.0°.

Differences between equivalent bond lengths in the tetracyclic entities are ≤0.016 Å for (1) *cf.* (3*b*) and (1) *cf.* (4*b*), with the exception that the C3—C12 and C6—C12 bonds are on average 0.033 Å shorter in (1) and (3*b*) than in (4*b*), as expected for allylic bonds. The C11—O2 bond is 0.021 Å longer in (1) than in (4*b*) and 0.047 Å longer than the *anti* C11—O2 bond in (3*b*). Differences between equivalent bond angles in the tetracyclic entity are ≤2.7° for (1) *cf.* (3*b*) and ≤3.2° for (1) *cf.* (4*b*). The e.s.d.'s are larger in (1) than in (3*b*) and (4*b*) by factors of *ca* 4 and 2, respectively.

Atom C13 of (1) is 0.188 (6) Å out of the C3, C6, C12 plane [plane 5 in the side-view *PLUTO* drawing (Motherwell & Clegg, 1978) shown in Fig. 2]. The angle between the C12—C13 bond and plane 5 is 8.07°. These values are similar to those of (3*b*) [0.194 (2) Å and 8.41°, respectively]. Apparently, neither the different crystal packing forces in (1) compared to those in (3*b*) nor the *syn* O1—CH_3 group of (3*b*) affect C12 pyramidalization significantly.

Some structural differences between (1), (3*b*) and (4*b*) are revealed by comparison of the angles between the least-squares planes (Fig. 2). Atoms C1, C10, C9, C8 (plane 2) are very nearly coplanar in (1). The atoms C1, C2, C7, C8 (plane 3), C2, C3, C6, C7 (plane 4) and C3, C4, C5, C6 (plane 6) deviate from coplanarity more than those of plane 2, but are coplanar to within 2σ. Puckering is largest for plane

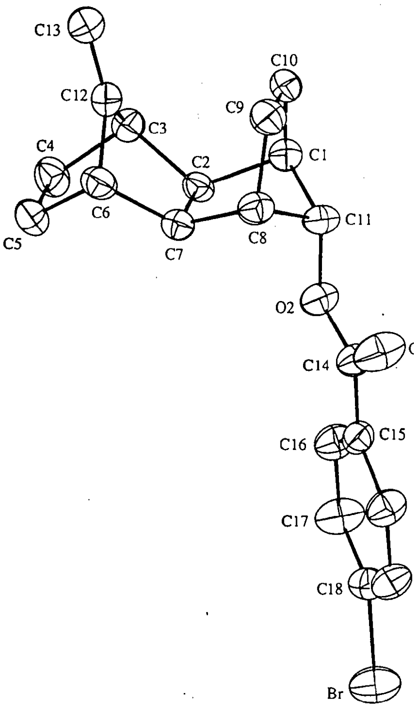

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1) with displacement ellipsoids at the 30% probability level.

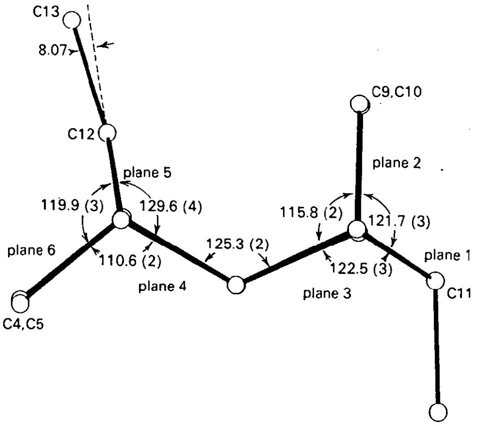

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) side view, looking down the C5—C4 and C9═C10 bonds, giving the interplanar angles (°) with e.s.d.'s.

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* Non-standard numbering of atoms was used in structure (1) in order to facilitate comparisons with other structures.

3 in structures (1) and (3*b*) and for planes 4 and 6 in (4*b*).

The interplanar angles $1\wedge2$ and $4\wedge5$ are nominally 4.0 and 0.8° smaller, respectively, in (1) than in (3*b*). Interplanar angles $1\wedge3$, $2\wedge3$, $3\wedge4$ and $4\wedge6$ are 3.2, 0.8, 0.1 and 0.8° larger, respectively, in (1) than in (3*b*), while the $5\wedge6$ angles are the same. Thus, the two structures are remarkably similar with the exception that the C11 bridge is bent upwards significantly (as drawn) in (1) compared to (3*b*). The C1—C11 and C8—C11 bonds are also shorter by an average of 0.013 Å in (1) *cf.* (3*b*). Although these effects are rather small, they undoubtedly reflect the different steric requirements of the dimethoxy ketal and *p*-bromobenzoate substituents. There may be some norbornenyl carbocation character in (1) similar to that suggested for (4*b*) (Lloyd, Arif, Coots & Allred, 1994). Repulsion between the *n* electrons of O1 and the C9=C10 π electrons in (3*b*) is an intriguing possibility that is consistent with the observed tilting of the C11 bridge in (3*b*) compared with (1). The non-bonding contacts O1···C9 and O1···C10 are 2.828 (2) and 2.768 (2) Å, respectively, in (3*b*).

The interplanar angles $1\wedge2$, $2\wedge3$, $3\wedge4$ and $5\wedge6$ are nominally 1.2, 0.9, 2.8 and 0.9° smaller, respectively, in (1) than in (4*b*). Interplanar angles $1\wedge3$, $4\wedge5$ and $4\wedge6$ are 2.1, 0.1 and 0.8° larger, respectively, in (1) than in (4*b*). Non-bonding C12···C9 and C12···C10 distances are 2.948 (8) and 2.983 (8) Å, respectively, for (1), compared with 3.087 (5) and 3.087 (5) Å, respectively, for (4*b*). These distances and the differences between the interplanar angles $1\wedge3$ and $3\wedge4$ are consistent with the somewhat smaller inter-bridge (C12···C9=C10) steric repulsion in (1) than in (4*b*). However, the similarities between structures of (1) and (4*b*) are more salient than the differences. Bridge tilting due to C12=C13···C9=C10 π–π and steric repulsions, appears to be nearly equivalent to that in (4*b*) arising from the C12—H12*a*···H9—C9=C10—H10 σ–π and steric repulsions.

Experimental

The synthesis of the alcohol (3*c*) has been described previously (Lloyd, Arif, Allred & Sharp, 1993). (3*c*) was esterified with *p*-bromobenzoyl chloride in pyridine/$CHCl_3$ (Lloyd, 1985). Since the diene is acid sensitive, ether extractions from 10% acetic acid/10% NaCl and washings with $NaHCO_3$ were performed at 277 K. The crude product was purified by column chromatography (Florisil), eluting with ether/pentane (1:9 *v*/*v*), and recrystallized from ether/pentane (1:2 *v*/*v*) to yield 80% of (1), m.p. 399.0-399.5 K; ^1H NMR (90 MHz, $CDCl_3$) δ 1.10-1.63 (*m*, 4H), 2.11-2.33 (*m*, 4H), 2.98 (*m*, 2H), 4.30 (*s*, 2H, $C=CH_2$), 4.38 (*m*, 1H), 5.72 (*t*, 2H, HC=CH), 7.57 (*d*, 2H), 7.87 (*d*, 2H). Dissolution of 71 mg of the ester (1) in 1.2 ml of ether and 2.0 ml of pentane, followed by the slow evaporation of the solvents at 253 K over one week gave prisms which were then filtered out. A crystal was selected from this sample for X-ray structure analysis.

Crystal data

$C_{20}H_{19}BrO_2$
M_r = 371.28
Triclinic
$P\overline{1}$
a = 6.837 (2) Å
b = 7.367 (2) Å
c = 17.699 (6) Å
α = 100.83 (2)°
β = 94.94 (3)°
γ = 107.49 (2)°
V = 825.35 Å^3
Z = 2

D_x = 1.494 Mg m^{-3}
D_m = 1.51 Mg m^{-3}
D_m by flotation in $ZnCl_2$
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 10-20°
μ = 2.4708 mm^{-1}
T = 296 K
Prism
0.30 × 0.21 × 0.15 mm
Colorless

Data collection

Syntex $P\overline{1}$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3176 measured reflections
2907 independent reflections
1682 observed reflections [$I \geq 3\sigma(I)$]
R_{int} = 0.011

θ_{max} = 25°
$h = 0 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -20 \rightarrow 20$
2 standard reflections monitored every 98 reflections
intensity variation: <3%

Refinement

Refinement on F
R = 0.0376
wR = 0.0409
S = 0.8990
1682 reflections
208 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.0003
$\Delta\rho_{max}$ = 0.301 e Å^{-3}
$\Delta\rho_{min}$ = −0.284 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Br	0.8859 (1)	0.5985 (1)	0.87957 (4)	5.85 (1)
O1	0.3270 (5)	0.9235 (6)	1.1465 (2)	5.4 (1)
O2	0.6467 (4)	1.0353 (5)	1.2154 (2)	3.60 (8)
C1	0.7291 (7)	1.1923 (7)	1.3547 (3)	3.4 (1)
C2	0.8724 (6)	1.3671 (6)	1.3276 (2)	2.9 (1)
C3	0.9960 (7)	1.5579 (7)	1.3884 (3)	3.6 (1)
C4	1.1396 (7)	1.6906 (8)	1.3437 (3)	4.2 (1)
C5	0.9871 (8)	1.7531 (7)	1.2913 (3)	4.4 (1)
C6	0.7732 (7)	1.6523 (7)	1.3136 (3)	3.8 (1)
C7	0.7173 (7)	1.4328 (6)	1.2772 (3)	3.1 (1)
C8	0.5028 (7)	1.2896 (7)	1.2836 (3)	3.6 (1)
C9	0.4650 (7)	1.3226 (7)	1.3676 (3)	4.0 (1)
C10	0.5958 (7)	1.2654 (7)	1.4091 (3)	3.8 (1)
C11	0.5575 (7)	1.1009 (7)	1.2831 (3)	3.4 (1)
C12	0.8423 (8)	1.6670 (7)	1.3985 (3)	3.8 (1)
C13	0.8052 (9)	1.7744 (8)	1.4623 (3)	5.1 (1)
C14	0.5058 (7)	0.9393 (7)	1.1506 (3)	3.6 (1)
C15	0.6061 (7)	0.8598 (6)	1.0863 (3)	3.1 (1)
C16	0.8112 (7)	0.8697 (7)	1.0961 (3)	3.9 (1)
C17	0.8941 (7)	0.7917 (8)	1.0344 (3)	4.7 (1)
C18	0.7692 (7)	0.7062 (7)	0.9637 (3)	3.9 (1)
C19	0.5666 (7)	0.6942 (7)	0.9518 (3)	4.1 (1)
C20	0.4831 (7)	0.7727 (7)	1.0138 (3)	4.1 (1)

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

Br—C18	1.904 (5)	C6—C12	1.508 (7)
O1—C14	1.187 (6)	C7—C8	1.555 (7)
O2—C11	1.458 (5)	C8—C9	1.520 (7)
O2—C14	1.356 (6)	C8—C11	1.543 (7)
C1—C2	1.550 (7)	C9—C10	1.321 (8)
C1—C10	1.516 (7)	C12—C13	1.342 (7)
C1—C11	1.544 (7)	C14—C15	1.495 (7)
C2—C3	1.552 (7)	C15—C16	1.376 (7)
C2—C7	1.569 (7)	C15—C20	1.395 (7)
C3—C4	1.547 (7)	C16—C17	1.382 (7)
C3—C12	1.506 (7)	C17—C18	1.373 (7)
C4—C5	1.562 (8)	C18—C19	1.356 (7)
C5—C6	1.550 (8)	C19—C20	1.390 (7)
C6—C7	1.540 (7)		
C11—O2—C14	114.4 (4)	C8—C9—C10	108.8 (5)
C2—C1—C10	109.1 (4)	C1—C10—C9	107.7 (4)
C2—C1—C11	100.9 (4)	O2—C11—C1	109.7 (4)
C10—C1—C11	96.4 (4)	O2—C11—C8	114.8 (4)
C1—C2—C3	119.7 (4)	C1—C11—C8	94.8 (4)
C1—C2—C7	103.6 (4)	C3—C12—C6	98.2 (4)
C3—C2—C7	103.0 (4)	C3—C12—C13	130.9 (6)
C2—C3—C4	106.2 (4)	C6—C12—C13	129.9 (6)
C2—C3—C12	103.6 (4)	O1—C14—O2	123.5 (5)
C4—C3—C12	97.8 (4)	O1—C14—C15	125.4 (5)
C3—C4—C5	103.8 (4)	O2—C14—C15	111.2 (5)
C4—C5—C6	102.9 (4)	C14—C15—C16	122.8 (5)
C5—C6—C7	106.4 (4)	C14—C15—C20	117.4 (5)
C5—C6—C12	98.6 (4)	C16—C15—C20	119.8 (5)
C7—C6—C12	103.3 (4)	C15—C16—C17	120.0 (5)
C2—C7—C6	103.5 (4)	C16—C17—C18	119.0 (5)
C2—C7—C8	102.6 (4)	Br—C18—C17	118.4 (4)
C6—C7—C8	119.8 (4)	Br—C18—C19	118.9 (4)
C7—C8—C9	109.6 (4)	C17—C18—C19	122.7 (5)
C7—C8—C11	100.7 (4)	C18—C19—C20	118.3 (5)
C9—C8—C11	95.9 (4)	C15—C20—C19	120.2 (5)

The structure was solved and refined using the direct-methods package *SDP* (Frenz, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, torsion angles and cell-packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71466 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1064]

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2-[1-Phenylsulfonyl-2-(3,4,5-trimethoxyphenyl)vinyl]-3-(phenylthio)indole

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Abstract

The title molecule, $C_{31}H_{27}NO_5S_2$, consists of an indole ring with phenylthio, phenylsulfonyl and 3,4,5-methoxyphenyl groups as exocyclic substituents. All the ring systems are planar. The indole ring is slightly folded along the C(8)—C(9) bond.

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