

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Structure with Through-Space Cyclopropyl π -Interaction

BARRY A. LLOYD*

Department of Chemistry, Weber State University, Ogden, Utah 84408, USA

ATTA M. ARIF, ROBERT J. COOTS AND EVAN L. ALLRED†

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

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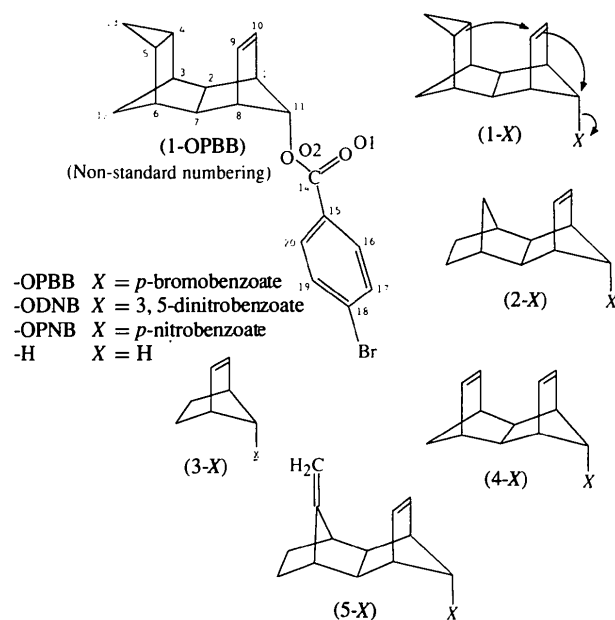
Abstract

The crystal structure determination of *endo,endo*-pentacyclo[7.2.1.1^{3,7}.0^{2,8}.0^{4,6}]tridec-10-en-*anti*-12-yl *p*-bromobenzoate, C₂₀H₁₉BrO₂ (1-OPBB), is reported. The molecule consists of norbornene with an *anti-p*-bromobenzoate substituent at the methano bridge, and with an *endo*-norbornyl unit *endo*-fused to the ethano bridge. The norbornyl unit also has an *exo*-cyclopropyl ring on the two-C-atom bridge opposite the ring

fusion. Interbridge steric interactions are discussed, and some comparisons are made with other norbornenyl derivatives.

Comment

A variety of compounds having cyclopropyl π -orbital interactions have been studied theoretically and spectroscopically (Hoffmann, Huel & Landmann, 1983; Martin & Mayer, 1983; Elsässer, Hassenrück, Martin, Mayer, Lutz & Prinzbach, 1991). The cyclopropyl π -interaction in hydrocarbon (1-H) is substantial (Prinzbach, Sedelmeier & Martin, 1977). The magnitude of the interaction is very dependent on the orbital geometries and is linked to reactivity in anchimerically assisted solvolysis reactions (March, 1992).



Solvolysis reactions have been followed *via* ¹H NMR spectroscopy for a few norbornenyl 3,5-dinitrobenzoate structures at 383 K in 80% dioxane-D₈/20% D₂O (v/v) (Lloyd, 1985). Under these conditions, esters (1-ODNB), (2-ODNB), (4-ODNB) and (5-ODNB) undergo solvolysis reactions 480, 28, 160 and 30 times faster, respectively, than the already enormously reactive *anti*-7-norbornenyl ester (3-ODNB). The rate enhancement of (1-ODNB) over (3-ODNB) is likely due (at least in part) to 'π'-electron donation from a cyclopropyl Walsh HOMO [see electron arrows for (1-ODNB) above] to the reaction center (C11 LUMO) *via* relay through the C₉=C₁₀ π bond (HOMO). The ribbon topologies require that the through-space interactions should destabilize the reactant and stabilize the transition state leading to the carbocation intermediate for (1-ODNB) relative to (3-ODNB) (Inagaki, Fujimoto

† Deceased, 8th July 1991.

& Fukui, 1976). This idea is similar to that proposed previously for the analogous diene (4-ODNB) (Allred, Lyon & Stroebel, 1979, and references therein).

In addition to long range through-space π -electron donation, interbridge steric and/or hyperconjugation effects are involved in solvolyses of these and other similar compounds. For example, the rate enhancement of (2-ODNB) over (3-ODNB) must be exclusively a steric/hyperconjugation effect, since remote π -electron donation is impossible. In an effort to confirm the existence of the remote π -electronic effect in (4-ODNB), deuterium-isotope studies were reported for some solvolyses (Allred, Lyon & Stroebel, 1979). These conductimetric kinetic data were later recalculated using four different approaches (linear least squares, multiple linear regression, Guggenheim method and nonlinear least squares), which showed that the original data were not precise enough to demonstrate the existence of such small isotope effects (Lloyd, 1985). This study must be viewed as inconclusive.

More recently, an attempt has been made to correlate the C10—C1—C11 and C9—C8—C11 angles (from the X-ray crystal structures of some norbornenyl *p*-bromobenzoates) with their respective solvolytic reactivities (Lloyd, 1985; Coots, 1983). In structures (1-OPBB), (2-OPBB), (4-OPBB) and (5-OPBB) where these angles are smaller than in (3-OPNB) or (3-OPBB), reactivity is higher. However, the largest observed difference in these bond angles [(1-OPBB) *versus* an analogous angle in (3-OPBB)] is only 4.1°, which while significant, is not far from the precision limits. It is nevertheless believed that small changes in structure can dramatically affect reaction rates (Menger, 1987). Our values for angles C10—C1—C11 and C9—C8—C11 in (4-OPBB) are 95.6(4) and 97.5(5)°, respectively; the analogous angles (C2—C1—C7 and C3—C4—C7) in (3-OPBB) are both 98.4(3)° (Coots, 1983), which agrees well with the values for (3-OPNB) of 98.3(2) and 98.1(2)° (Jones, Kirby & Percy, 1992). With one exception, C10—C1—C11 and C9—C8—C11 are nominally smaller in (1-OPBB) than in (2-OPBB), (3-OPNB), (3-OPBB), (4-OPBB) and (5-OPBB), by 1.1 and 2.5, 2.4 and 3.8, 2.5 and 4.1, 0.3 (larger) and 3.2, and 0.5 and 1.6°, respectively.

The crystal structure of the *p*-bromobenzoate ester (1-OPBB) is reported below.* An ORTEPII (Johnson, 1976) drawing of (1-OPBB) is shown in Fig. 1.

A search of the Cambridge Crystallographic Database in October 1993 yielded only one other structure similar to (1-OPBB), but it has an *endo,exo*-fusion at C2 and C7 such that through-space cyclopropyl π -interaction would be small (Caughlan, Smith, Jennings & Voeks, 1976). A *syn*-derivative of structure (4) is also known (Ermer, Bödecker & Preut, 1984).

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

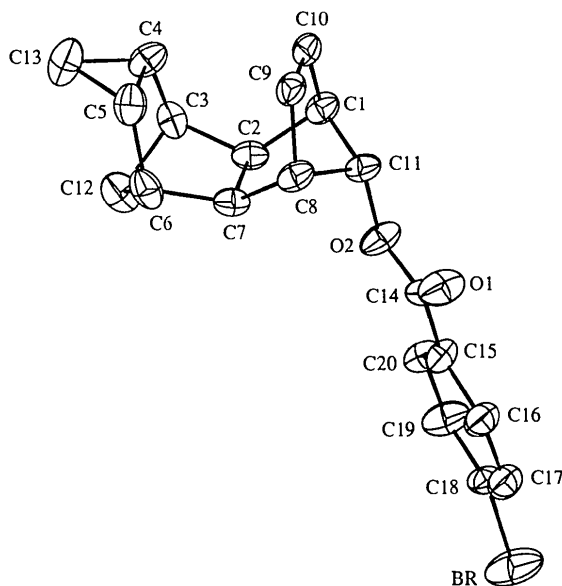


Fig. 1. ORTEPII (Johnson, 1976) drawing of non-H atoms of (1-OPBB) with displacement ellipsoids at the 30% probability level.

The pentacyclic hydrocarbon unit of (1-OPBB) is approximately bisected by a mirror plane through M (C2—C7), M (C4—C5), M (C9—C10), C11, C12 and C13, where M is the midpoint of the respective bond. The largest difference in symmetry-related bond lengths is 0.029 Å (C2—C3 *versus* C6—C7), which is near 3σ of a given bond length. The largest significant difference of symmetry-related bond angles in the pentacyclic unit is 1.9°, for C3—C2—C7 *versus* C2—C7—C6. The difference between bond angles C8—C11—O2 and C1—C11—O2 is 4.5°. A similar inequality was observed in the structure of (2-OPBB) (Lloyd, Arif, Coots & Allred, 1994) and that of (5-OPBB) (Lloyd, Arif, & Allred, 1994). There are no non-hydrogen-bond intermolecular contacts ≤ 3.43 Å.

Other planes can be defined as C1, C8, C11 (plane 1), C1, C10, C9, C8 (plane 2), C1, C2, C7, C8 (plane 3), C3, C2, C7, C6 (plane 4), C3, C4, C5, C6 (plane 5), C3, C6, C12 (plane 6) and C4, C5, C13 (plane 7), shown in a PLUTO (Motherwell & Clegg, 1978) side-view drawing (Fig. 2). The respective atoms of planes 2–5 are no more than 1σ out of the corresponding least-squares plane. Torsion angles for the atoms of planes 2–5 are 0°, to within 1σ , which is consistent with minimal twisting of the hydrocarbon framework.

Some significant angle differences are apparent on comparison of interplanar angles of structure (1-OPBB) *versus* those of the other structures. The $1^{\wedge}2$ interplanar angle is smaller in (1-OPBB) by 3.1, 4.6, 3.1 and 1.9° *versus* (2-OPBB), (3-OPBB), (4-OPBB) and (5-OPBB), respectively. With two exceptions, the $1^{\wedge}3$ angle is larger in (1-OPBB) by 1.3, 1.1 (smaller), 3.0 and 0.8° (smaller) *versus* (2-OPBB), (3-OPBB), (4-OPBB) and (5-OPBB),

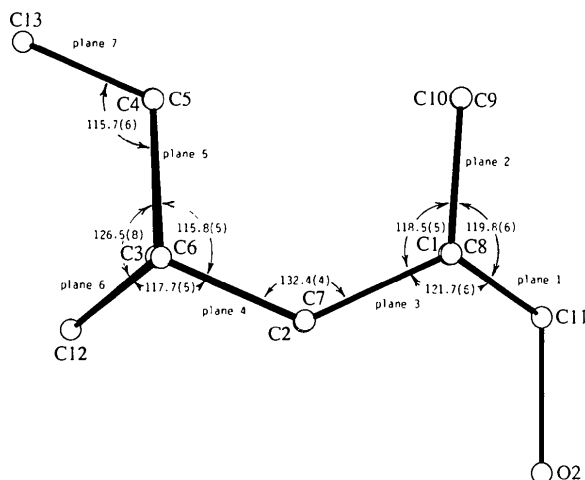


Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) side view looking down the C2—C7 bond showing interplanar angles ($^{\circ}$).

respectively. With one exception, the $2^{\wedge}3$ angles are larger in (1-OPBB) by 1.8, 5.7 (smaller), 0.2 and 2.7° versus (2-OPBB), (3-OPBB), (4-OPBB) and (5-OPBB), respectively. The $3^{\wedge}4$ angle in (1-OPBB) is larger by 4.3, 4.4 and 7.1° versus (2-OPBB), (4-OPBB) and (5-OPBB), respectively. The compressed $1^{\wedge}2$ and widened $1^{\wedge}3$, $2^{\wedge}3$ and $3^{\wedge}4$ angles of (1-OPBB) are consistent with increased interbridge H5—C5—C4—H4...H9—C9=C10—H10 steric and electronic repulsions versus the analogous interactions in the other structures.

The intramolecular contacts in (1-OPBB) C5...C9 2.921 (10) and C4...C10 2.917 (9) Å are within the sum of the respective van der Waals radii (Bondi, 1964; Gordon & Ford, 1972), and are consistent with the observed through-space cyclopropyl π -interaction of (1-H). The C12...C13 contact of 2.697 (11) Å is also consistent with interbridge steric repulsion.

The C11—O2 bond length is 0.23, 0.16 and 0.24 Å longer in (1-OPBB) than in (2-OPBB), (3-OPBB) and (4-OPBB), respectively, which is consistent with the higher reactivity of (1-ODNB). However, the (1-OPBB) C11—O2 bond is only 0.02 Å longer than the analogous bonds in (3-OPNB) and (5-OPBB). The latter results are consistent with the late transition-state idea (Jones, Kirby & Percy, 1992).

We believed initially that structures with significant π - π through-space interaction [e.g. (1-X), (4-X) and (5-X)] would have a different C10—C1—C11 and C9—C8—C11 angle—reactivity dependence than those with only steric π interactions [e.g. (2-X) and (3-X)]. While the data for (4-X) (Coots, 1983) are consistent with this idea, those of (1-X) and (5-X) are not. For (5-OPBB), it appears that the π - π repulsion may be of similar magnitude to the steric π interaction of (2-OPBB) (Lloyd, Arif & Allred, 1994). Direct experimental evidence for remote π -electron donation by relay during solvolysis, therefore, remains equivocal.

Although the effects are small, some trends seem to be emerging from these structural data. The C11—O2 bond lengths and/or angles (such as $1^{\wedge}2$, $1^{\wedge}3$, $2^{\wedge}3$ and/or $3^{\wedge}4$) do correlate roughly with reactivity. Greater precision of the atomic positions and/or electron-density deformation data may be needed to elucidate the possible relationships.

Experimental

Crystals of the title compound were obtained by recrystallization from ether/petroleum ether at 253 K (full details of the preparation have been deposited).

Crystal data

C₂₀H₁₉BrO₂
M_r = 371.28
 Monoclinic
*P*2₁/*c*
a = 11.350 (3) Å
b = 13.838 (3) Å
c = 10.509 (3) Å
 β = 100.15 (2) $^{\circ}$
V = 1624.72 Å³
Z = 4
D_x = 1.518 Mg m⁻³

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 10–20 $^{\circ}$
 μ = 2.5103 mm⁻¹
T = 296 K
 Prism
 0.28 × 0.25 × 0.20 mm
 Colorless

Data collection

Syntex *P* $\bar{1}$ diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scan
 T_{\min} = 0.72, T_{\max} = 1.00
 3914 measured reflections
 3732 independent reflections
 1376 observed reflections
 $[I > 2\sigma(I)]$

R_{int} = 0.0401
 θ_{max} = 23 $^{\circ}$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 16$
 $l = -12 \rightarrow 12$
 2 standard reflections monitored every 98 reflections
 intensity decay: < 3%

Refinement

Refinement on *F*
R = 0.0622
 wR = 0.0625
S = 2.382
 1376 reflections
 208 parameters
 H-atom positions calculated but not refined
 Unit weights applied

$(\Delta/\sigma)_{\text{max}}$ = 0.0001
 $\Delta\rho_{\text{max}}$ = 0.449 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.337 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Br	0.2106 (2)	0.04135 (7)	0.08421 (1)	6.90 (3)
O1	0.0494 (6)	-0.4184 (4)	0.2212 (7)	5.0 (2)
O2	0.1770 (5)	-0.4475 (4)	0.0848 (6)	4.2 (1)
C1	0.2152 (8)	-0.6049 (6)	-0.0079 (8)	3.3 (2)
C2	0.3471 (8)	-0.5816 (6)	0.0534 (8)	3.2 (2)
C3	0.4581 (8)	-0.6451 (7)	0.0441 (9)	3.6 (2)
C4	0.4336 (9)	-0.7492 (7)	0.0760 (8)	3.9 (2)
C5	0.4329 (9)	-0.7487 (7)	0.2197 (9)	4.0 (2)

C6	0.4539 (8)	-0.6439 (7)	0.2602 (8)	3.9 (2)
C7	0.3458 (8)	-0.5824 (6)	0.2040 (8)	3.2 (2)
C8	0.2134 (8)	-0.6048 (6)	0.2097 (8)	3.4 (2)
C9	0.1774 (8)	-0.7057 (6)	0.1551 (9)	3.2 (2)
C10	0.1782 (8)	-0.7053 (6)	0.0275 (9)	3.6 (2)
C11	0.1496 (8)	-0.5505 (6)	0.0867 (8)	3.4 (2)
C12	0.5412 (9)	-0.6100 (8)	0.1687 (8)	4.4 (2)
C13	0.5308 (1)	-0.8047 (8)	0.170 (1)	5.3 (3)
C14	0.1157 (8)	-0.3897 (6)	0.1561 (9)	3.6 (2)
C15	0.1438 (8)	-0.2866 (6)	0.1355 (9)	3.3 (2)
C16	0.0926 (8)	-0.2183 (6)	0.2081 (9)	4.0 (2)
C17	0.1097 (8)	-0.1205 (7)	0.1918 (9)	4.0 (2)
C18	0.1809 (9)	-0.0923 (6)	0.1048 (9)	4.1 (2)
C19	0.235 (1)	-0.1568 (7)	0.0310 (9)	4.8 (3)
C20	0.2153 (9)	-0.2553 (6)	0.0486 (8)	4.0 (2)

Table 2. Selected geometric parameters (Å, °)

Br—C18	1.899 (6)	C5—C6	1.518 (9)
O1—C14	1.172 (8)	C6—C7	1.524 (9)
O2—C11	1.460 (7)	C6—C12	1.569 (9)
O2—C14	1.367 (8)	C7—C8	1.546 (9)
C1—C2	1.556 (9)	C8—C9	1.537 (8)
C1—C10	1.517 (8)	C8—C11	1.559 (8)
C1—C11	1.540 (8)	C9—C10	1.343 (9)
C2—C3	1.553 (8)	C14—C15	1.486 (8)
C2—C7	1.585 (8)	C15—C16	1.403 (8)
C3—C4	1.516 (9)	C15—C20	1.393 (9)
C3—C12	1.551 (9)	C16—C17	1.382 (9)
C4—C5	1.512 (9)	C17—C18	1.379 (9)
C4—C13	1.549 (9)	C18—C19	1.394 (9)
C5—C13	1.521 (9)	C19—C20	1.399 (9)
C11—O2—C14	115.7 (5)	C7—C8—C11	100.6 (5)
C2—C1—C10	112.1 (5)	C9—C8—C11	94.3 (5)
C2—C1—C11	99.8 (5)	C8—C9—C10	108.7 (5)
C10—C1—C11	95.9 (5)	C1—C10—C9	107.4 (6)
C1—C2—C3	126.1 (5)	O2—C11—C1	109.9 (5)
C1—C2—C7	103.6 (5)	O2—C11—C8	114.4 (5)
C3—C2—C7	102.1 (5)	C1—C11—C8	95.3 (4)
C2—C3—C4	110.0 (5)	C3—C12—C6	93.9 (5)
C2—C3—C12	98.6 (5)	C4—C13—C5	59.0 (4)
C4—C3—C12	102.6 (5)	O1—C14—O2	124.3 (6)
C3—C4—C5	104.5 (5)	O1—C14—C15	125.9 (6)
C3—C4—C13	118.3 (6)	O2—C14—C15	109.8 (6)
C5—C4—C13	59.6 (4)	C14—C15—C16	116.6 (6)
C4—C5—C6	104.8 (5)	C14—C15—C20	124.0 (6)
C4—C5—C13	61.4 (4)	C16—C15—C20	119.5 (5)
C6—C5—C13	119.7 (6)	C15—C16—C17	120.8 (6)
C5—C6—C7	110.4 (5)	C16—C17—C18	118.1 (6)
C5—C6—C12	101.5 (5)	Br—C18—C17	119.2 (5)
C7—C6—C12	98.5 (5)	Br—C18—C19	117.1 (5)
C2—C7—C6	104.0 (5)	C17—C18—C19	123.7 (6)
C2—C7—C8	102.7 (5)	C18—C19—C20	117.0 (6)
C6—C7—C8	126.5 (5)	C15—C20—C19	121.0 (6)
C7—C8—C9	111.3 (5)		

Lorentz and polarization corrections were applied. The structure was solved by direct methods. Non-H atoms were refined anisotropically. Programs used were from the *Enraf-Nonius CAD-4 SDP* package (Frenz, 1978).

We thank the University of Utah University Research Committee for supporting this work.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates, and complete synthesis of (1-OPBB) have been deposited with the IUCr (Reference: SZ1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Iodo-2-*p*-tolyl-1-tellura-2-azaindene

THOMAS A. HAMOR, ANATOLY G. MASLAKOV AND WILLIAM R. McWHINNIE

Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET, England

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Abstract

The structure of C₁₄H₁₂INTe consists of discrete molecules in which the Te atom is three-coordinate with Te—C and Te—I distances of 2.102 (5) and 2.936 (1) Å, respectively, and a Te···N interaction of 2.230 (4) Å. The I atom is *trans* to the N atom [I—Te···N 170.3 (1)°].