

A norbornenyl derivative with through-space ketone π -interaction

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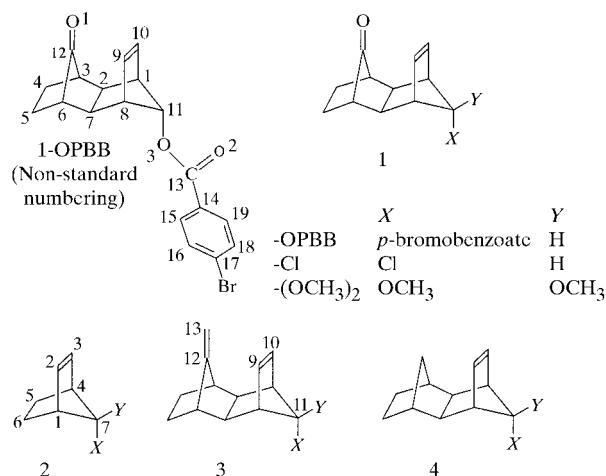
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The title compound, *endo,exo*-12-oxotetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dodeca-9-en-*anti*-11-yl *p*-bromobenzoate, C₁₉H₁₇BrO₃, consists of norbornene with an *anti-p*-bromobenzoate substituent at the methano bridge and an *exo*-fused norbornanone unit bonded to the ethano bridge. The spatially proximate ketone and alkene interact through space and the ketone C atom is substantially pyramidalized. Through-space ketone π -interaction is probably responsible for the low solvolysis rate of the *anti*-11-chloride derivative.

Comment

Our interest in the title structure, 1-OPBB, arises from our discovery that tetracyclic *anti*-norbornenyl derivative 1-Cl solvolyzes 2.4 times slower than the famous *anti*-7-norbornenyl chloride, 2-Cl (Kaselj *et al.*, 1999), 72 times slower than isoelectronic 3-Cl and 67 times slower than 4-Cl in 80%



dioxane-*d*₈/20% D₂O at 383 K (Lloyd *et al.*, 1995). Replacement of the exocyclic methylene group in 3-Cl with an O atom (O1) in 1-Cl thus results in a substantial solvolytic rate

† Deceased 8th July 1991.

difference although these atoms are five bonds removed from the solvolysis site (at C11).

Calculations show that solvolytic rate differences between 2, 3 and 4 are mostly determined by the respective transition-state energies rather than by the reactant energies (Chow, 1998), *i.e.* transition states are reached late on the respective reaction curves (Jones *et al.*, 1992). The X-ray crystal structure of *p*-bromobenzoate ester 1-OPBB was determined so that comparisons could be made with the previously published *endo,exo*-structures [3-OPBB (Lloyd, Arif & Allred, 1994) and 4-OPBB (Lloyd, Arif, Coots & Allred, 1994)] to see if the tetracyclic ring reactant structures are really similar, as predicted by the theory. A search of the Cambridge Structural Database in December 1999 yielded one other structure containing the tetracyclic enone unit (1), namely the C11 dimethoxyketal 1-(OCH₃)₂ (Lloyd, Ericson, Arif & Allred, 1993), but the C9=C10...C11 interaction, of interest in solvolysis, is complicated by the presence of the *syn* methoxy group (*Y*) in this structure.

An ORTEP-3 (Farrugia, 1997) drawing of the 1-OPBB structure is shown in Fig. 1. Non-standard atom numbering was used to facilitate comparisons with other compounds. The closest intermolecular non-hydrogen contacts are C5...O1ⁱ of 3.447 (3) Å and O2...C19ⁱⁱ of 3.307 (2) Å. The closest intermolecular hydrogen contacts are H5A...O1ⁱ of 2.52 (3) Å and O2...H19ⁱⁱ of 2.45 (2) Å [symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$; (ii) $1 - x, -y, 1 - z$]. Intermolecular contacts do not appear to be responsible for any major structural effects.

Reactivity has been related to the reactant C—X bond length (Kirby, 1994). The C11—O3 bond length is 0.010 (5) Å shorter in 1-OPBB than the corresponding bond in the 298 K (3-OPBB) structure; but the C11—O3 bond length is longer by 0.011 (4) Å in 1-OPBB than the corresponding bond in 4-OPBB. These small differences are near the precision limits,

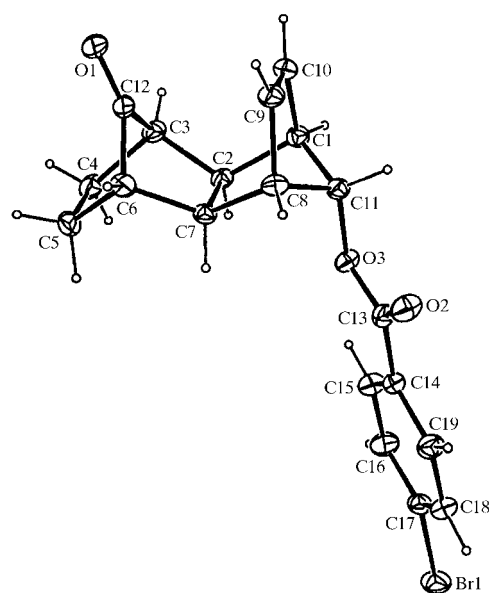


Figure 1
ORTEP-3 (Farrugia, 1998) drawing of 1-OPBB with displacement ellipsoids at the 30% probability level and spherical H atoms of arbitrary size.

and the C11—X bond lengths do not appear to correlate with the solvolytic reactivities of these compounds (Jones *et al.*, 1992).

Examination of the angles between least-squares planes reveals some significant structural differences [see the side view *PLUTO* (Motherwell & Clegg, 1978) drawing of 1-OPBB, Fig. 2]. Interplanar angles are given for compound 1-OPBB, and also for 3-OPBB, 4-OPBB, 1-(OCH₃)₂, and 3-(OCH₃)₂ (Lloyd *et al.*, 1992) in Table 2. The differences are well outside 3 σ . Interplanar angles may play a small role in solvolytic reactivity, although a simple structure/reactivity correlation is not obvious.

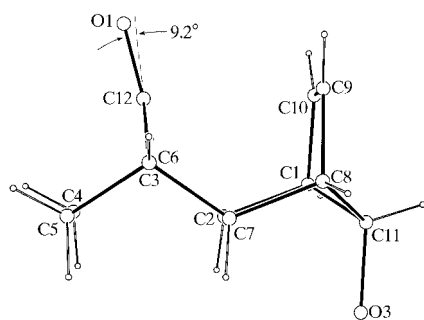


Figure 2
PLUTO (Motherwell & Clegg, 1978) side-view drawing of 1-OPBB with the C3 and C6 atoms eclipsed. See Table 2 for interplanar angles.

The O1 atom lies 0.194 (5) Å out of the C3—C12—C6 plane in 1-OPBB, making an angle of 9.2 (2)° with the plane. As in 1-(OCH₃)₂, pyramidalization is probably a consequence of ketone π -interaction through space (Robbins *et al.*, 1992). The pyramidalization at C12 observed in 1-(OCH₃)₂ is of a similar magnitude, and therefore must not be influenced very much by the *syn*-methoxy group (Y). The perpendicular distance of C12 from the C3—C6—O1 plane (Δ_c) is 0.088 (2) Å, which is large compared with that of other pyramidalized carbonyls (Kirby, 1994; Lloyd, Arif, Allred, Patton & Sharp, 1993). The H9—C9—C10—H10 plane is tilted 5 (2)°, with H9 and H10 towards the C12 side of the C8—C9—C10—C1 plane, which is similar to that observed in 3-OPBB and 4-OPBB. Some non-bonding distances are C9...C12 2.853 (3), C10...C12 2.883 (3), C9...C11 2.300 (3) and C10...C11 2.297 (2) Å, which are consistent with through-space laticyclic interaction in 1-OPBB (Chow, 1998).

The similarities between 1-OPBB and 3-OPBB are perhaps more noticeable than the differences. The low solvolytic reactivity of 1-Cl might be explained by electron withdrawal from C11 through space by the ketone group *via* the C9=C10 bridge, which would stabilize the reactant and destabilize the transition state. By contrast, the higher reactivity of 3-Cl is consistent with electron release towards C11 through space from the C12=C13 group *via* the C9=C10 bridge, which would destabilize the reactant and stabilize the transition state (Chow, 1998). There are likely to be differences in the π -electron clouds of each structure that are not observable at present.

Experimental

Compounds 1-OPBB and 1-Cl were synthesized from 1-(OCH₃)₂ (Lloyd, Ericson, Arif & Allred, 1993). The details of these syntheses and compound characterizations have been deposited. Crystals were prepared by dissolving a sample (350 mg) of pure ester 1-OPBB in CH₂Cl₂ (5.0 ml) and warming. This solution was placed on a cork ring inside a desiccator which was in a freezer (253 K). Also inside the desiccator was a sample (in a separate container) of 20 ml of ether (for vapor diffusion). After 24 h, prisms were filtered off. A crystal was selected, cleaved with a razor blade, and mounted.

Crystal data

C ₁₉ H ₁₇ BrO ₃	$D_x = 1.55 \text{ Mg m}^{-3}$
$M_r = 373.24$	Mo K α radiation
Monoclinic, $P2_1/a$	Cell parameters from 17290 reflections
$a = 11.3936 (3) \text{ \AA}$	$\theta = 4.39\text{--}32.59^\circ$
$b = 8.2659 (2) \text{ \AA}$	$\mu = 2.58 \text{ mm}^{-1}$
$c = 16.9840 (5) \text{ \AA}$	$T = 148.0 (1) \text{ K}$
$\beta = 90.6750 (17)^\circ$	Prism, colorless
$V = 1599.41 (7) \text{ \AA}^3$	$0.30 \times 0.23 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	4073 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan	$\theta_{\text{max}} = 32.59^\circ$
(<i>DENZO-SMN</i> ; Otwinowski & Minor, 1997)	$h = -16 \rightarrow 17$
$T_{\text{min}} = 0.51, T_{\text{max}} = 0.63$	$k = -10 \rightarrow 12$
8643 measured reflections	$l = -25 \rightarrow 25$
5678 independent reflections	Intensity decay <2.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 1.2341P]$
$R(F) = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.59 \text{ e \AA}^{-3}$
5678 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
276 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

O1—C12	1.210 (2)	C4—C5	1.561 (3)
O3—C11	1.448 (2)	C5—C6	1.548 (3)
C1—C10	1.512 (2)	C6—C12	1.526 (3)
C1—C11	1.534 (2)	C6—C7	1.532 (3)
C1—C2	1.557 (2)	C7—C8	1.556 (2)
C2—C3	1.538 (2)	C8—C9	1.516 (2)
C2—C7	1.577 (2)	C8—C11	1.537 (3)
C3—C12	1.525 (3)	C9—C10	1.328 (3)
C3—C4	1.545 (3)		
C10—C1—C11	97.88 (14)	C6—C7—C8	117.96 (14)
C10—C1—C2	107.69 (14)	C6—C7—C12	103.82 (15)
C11—C1—C2	100.82 (14)	C8—C7—C2	102.70 (13)
C3—C2—C1	117.55 (14)	C9—C8—C11	97.73 (14)
C3—C2—C7	103.82 (14)	C9—C8—C7	108.66 (14)
C1—C2—C7	102.75 (13)	C11—C8—C7	100.16 (13)
C12—C3—C2	103.59 (14)	C10—C9—C8	107.93 (16)
C12—C3—C4	96.62 (15)	C9—C10—C1	107.99 (15)
C2—C3—C4	106.21 (15)	O3—C11—C1	109.80 (13)
C3—C4—C5	103.82 (16)	O3—C11—C8	115.40 (14)
C6—C5—C4	104.24 (16)	C1—C11—C8	94.89 (14)
C12—C6—C7	103.11 (15)	O1—C12—C3	130.44 (19)
C12—C6—C5	96.41 (17)	O1—C12—C6	129.82 (19)
C7—C6—C5	107.16 (15)	C3—C12—C6	98.47 (14)

Table 2

Comparison of the angles ($^{\circ}$) between least-squares planes in 1-OPBB and related compounds.

Planes 1–6 are defined by atoms C1–C11–C8, C8–C9–C10–C1, C1–C2–C7–C8, C2–C3–C6–C7, C3–C12–C6, and C3–C4–C5–C6, respectively (see Fig. 2).

	1-OPBB	3-OPBB	4-OPBB	1-(OCH ₃) ₂	3-(OCH ₃) ₂
Plane 1–Plane 2	124.4 (1)	121.7 (3)	122.9 (3)	126.9 (2)	125.7 (1)
Plane 1–Plane 3	121.5 (1)	122.5 (3)	120.4 (3)	119.6 (1)	119.3 (1)
Plane 2–Plane 3	114.2 (1)	115.8 (2)	116.7 (1)	113.5 (1)	115.1 (1)
Plane 3–Plane 4	123.2 (1)	125.3 (2)	128.1 (2)	122.9 (1)	125.2 (1)
Plane 4–Plane 5	130.6 (1)	129.6 (4)	129.4 (2)	130.8 (2)	130.3 (2)
Plane 4–Plane 6	111.5 (1)	110.6 (2)	109.8 (2)	111.6 (1)	109.8 (1)
Plane 5–Plane 6	118.0 (1)	119.9 (3)	120.8 (2)	117.6 (1)	119.9 (2)

C–H bond distances for 1-OPBB range from 0.90 (3) Å for C18–H18 to 0.99 (2) Å for C1–H1, and the s.u.'s range from 0.02 to 0.03. The H-atom U_{eq} values range from 0.021 (5) Å² for H7 to 0.055 (7) Å² for H5A and H18.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1998) and *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1550). A crystal packing diagram has also been deposited. Services for accessing these data are described at the back of the journal.

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