| | | | |
|---|---|---|---|
| P(3)—N(2) | 1,71 (1) | P(9)—N(8) | 1,687 (9) |
| P(3)—N(4) | 1,653 (9) | P(9)—N(10) | 1,665 (9) |
| N(1)—N(2) | 1,39 (2) | N(7)—N(8) | 1,40 (1) |
| N(4)—N(5) | 1,42 (1) | N(10)—N(11) | 1,38 (1) |
| C(6)—O(6) | 1,22 (1) | C(12)—O(12) | 1,19 (1) |
| C(6)—N(5) | 1,37 (1) | C(12)—N(1) | 1,39 (2) |
| C(6)—N(7) | 1,37 (2) | C(12)—N(11) | 1,39 (1) |
| C—C (Phenyl) | 1,38 (2) (Mittelwert) | | |
| Bereich: | 1,34 (2)-1,41 (2) | | |
| C(Methyl)—N | 1,47 (3) (Mittelwert) | | |
| Bereich: | 1,43 (2)-1,50 (2) | | |
| S(1)—P(3)—O(1) | 117,3 (3) | S(2)—P(9)—O(2) | 117,9 (3) |
| O(1)—P(3)—N(2) | 96,4 (5) | O(2)—P(9)—N(8) | 96,4 (4) |
| O(1)—P(3)—N(4) | 106,9 (4) | O(2)—P(9)—N(10) | 107,2 (4) |
| N(2)—P(3)—N(4) | 105,0 (4) | N(8)—P(9)—N(10) | 103,8 (4) |

| | |
|---|---|
| C(1)—N(1)—N(2)—C(2) | −74 (1) |
| C(12)—N(1)—N(2)—P(3) | −89 (1) |
| C(1)—N(1)—N(2)—P(3) | 61 (1) |
| C(12)—N(1)—N(2)—C(2) | 136 (1) |
| C(4)—N(4)—N(5)—C(5) | −74 (1) |
| P(3)—N(4)—N(5)—C(6) | −106,8 (9) |
| C(4)—N(4)—N(5)—C(6) | 75 (1) |
| P(3)—N(4)—N(5)—C(5) | 104,2 (8) |
| C(7)—N(7)—N(8)—C(8) | −73 (1) |
| C(6)—N(7)—N(8)—P(9) | −84 (1) |
| C(7)—N(7)—N(8)—P(9) | 65 (1) |
| C(6)—N(7)—N(8)—C(8) | 138 (1) |
| C(10)—N(10)—N(11)—C(11) | −76 (1) |
| P(9)—N(10)—N(11)—C(12) | −100 (1) |
| C(10)—N(10)—N(11)—C(12) | 72 (1) |
| P(9)—N(10)—N(11)—C(11) | 112,9 (8) |
| C(1)—N(1)—C(12)—O(12) | −8 (1) |
| N(2)—N(1)—C(12)—O(12) | 142 (1) |
| C(1)—N(1)—C(12)—N(11) | 171,1 (9) |
| N(2)—N(1)—C(12)—N(11) | −38 (1) |
| C(11)—N(11)—C(12)—O(12) | 135 (1) |
| N(10)—N(11)—C(12)—O(12) | −10 (2) |
| C(11)—N(11)—C(12)—N(1) | −45 (1) |
| N(10)—N(11)—C(12)—N(1) | 171,2 (9) |
| C(7)—N(7)—C(6)—O(6) | −5 (2) |
| N(8)—N(7)—C(6)—O(6) | 144 (1) |
| C(7)—N(7)—C(6)—N(5) | 172 (1) |
| N(8)—N(7)—C(6)—N(5) | −39 (1) |
| C(5)—N(5)—C(6)—O(6) | 137 (1) |
| N(4)—N(5)—C(6)—O(6) | −9 (2) |
| C(5)—N(5)—C(6)—N(7) | −40 (1) |
| N(4)—N(5)—C(6)—N(7) | 174,1 (9) |
| N(1)—N(2)—P(3)—N(4) | 143,0 (8) |
| N(5)—N(4)—P(3)—N(2) | −45,9 (8) |
| N(7)—N(8)—P(9)—N(10) | 146,0 (7) |
| N(11)—N(10)—P(9)—N(8) | −51,8 (7) |

Die Struktur wurde mit direkten Methoden gelöst (*MULTAN*; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Eine sinnvolle Lösung der Struktur in der zentrosymmetrischen Raumgruppe Pnma konnte nicht erhalten werden. Diese Raumgruppe hätte bei $Z = 8$ und somit einem halben Molekül in der asymmetrischen Einheit eine Spiegelebene oder ein Symmetriezentrum im Molekül erfordert. Wie die gelöste Struktur zeigt, ist keine dieser Bedingungen auch nur annähernd erfüllt. Alle anderen Rechnungen wurden mit dem Programmsystem *Xtal*2.6 (Hall & Stewart, 1989) durchgeführt. Die gegen Ende der Verfeinerungen versuchte Verfeinerung der H-Atomlagen der Methylgruppen mit isotropen Temperaturfaktoren führte zwar zu einer Verbesserung der $R$-Werte, ergab aber keine sinnvollen Atomlagen. Diese H-Atome wurden deshalb unter Annahme einer jeweils gestaffelten Anordnung der Methylgruppen geometrisch gesetzt. Den betreffenden H-Atomen wurden die isotropen Temperaturfaktoren der an sie gebundenen C-Atome zugewiesen. Die Positionen der Phenyl-H-Atome wurden dagegen mit verfeinert mit festen isotropen Temperaturfaktoren. In der endgültig erhaltenen Struktur liegt die polare Achse in einer Richtung parallel zur gewellten 'Ringebene'. Eine Rechnung mit den Atomkoordinaten -$z$ ergab demzufolge kein abweichendes Ergebnis.

Wir danken Herrn Kollegen D. Lenz für die Hilfe bei den Messungen. Dem Fonds der Chemischen Industrie gilt unser Dank für finanzielle Unterstützung.

---

Die Liste der Strukturfaktoren, anisotropen Verschiebungsfaktoren, H-Atom Koordinaten und vollständigen geometrischen Daten sind bei dem British Library Document Supply Centre (Supplementary Publication No. SUP 71650: 21 pp.) hinterlegt. Kopien sind erhältich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF Aktenzeichen: SH1063]

---

## Literatur

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Bünger, T. (1983). Dissertation, Freie Universität Berlin, Deutschland.

Engehardt, U., Bünger, T. & Viertel, H. (1984). *J. Crystallogr. Spectrosc. Res.* **14**, 603–615.

Engelhardt, U. & Simon, A. (1992). *Acta Cryst.* **C48**, 492–495, 495–498.

Hall, S. R. & Stewart, J. M. (1989). Herausgeber. *Xtal*2.6 *Users Manual*. Univ. Western Australia, Australia, und Maryland, VStA.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. York, England, und Louvain, Belgien.

Simon, A. (1992). Dissertation, Freie Universität Berlin, Deutschland.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

---

*Acta Cryst.* (1994). **C50**, 777–781

# Structural Investigations of a Tetracyclic *endo*-Norborenyl Derivative

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*

(*Received* 29 *January* 1993; *accepted* 16 *November* 1993)

## Abstract

The X-ray crystal structure of *endo*,*exo*-tetracyclo[6.2.1.1$^{3,6}$.0$^{2,7}$]dodec-9-en-*anti*-11-yl *p*-bromobenzo-

---

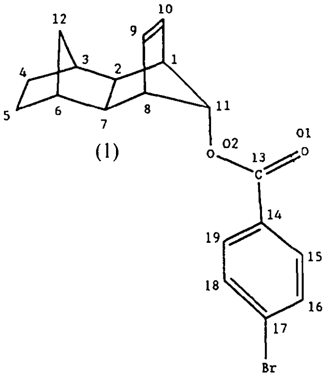
† Deceased 8 July 1991.

© 1994 International Union of Crystallography
Printed in Great Britain – all rights reserved

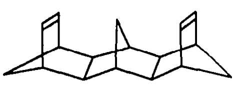
ate, $C_{19}H_{19}BrO_2$ (1), was determined at 148 K. The molecule consists of norbornene with an *anti-p*-bromobenzoate substituent at the methano bridge and an *exo*-norbornyl unit *endo*-fused to the ethano bridge. Structural comparisons are made with another derivative and steric interactions examined. The distance from the norbornyl methano bridge to the norbornene etheno bridge is consistent with laticyclic hyperconjugation in (1).

## Comment

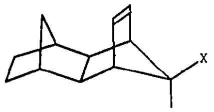
Recently, much theoretical and experimental work has gone into understanding the origins of long-range non-conjugated $\pi$-orbital interactions (Jordan & Paddon-Row, 1992; Elsässer, Hassenrück, Martin, Mayer, Lutz & Prinzbach, 1991). In this regard, laticyclic hyperconjugation contributes to substantial $\pi$ splitting (0.52 eV) in the hydrocarbon (2) and raises the $\pi$ energies in both (2) and (3*a*) relative to ethene (Paddon-Row, 1985).



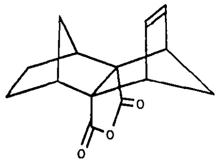
(1)



(2)



(3*a*) *X*, *Y* = H
(3*b*) *X*, *Y* = O
(3*c*) *X* = H, *Y* = OH



(4)

An abundance of theoretical and spectroscopic data exists for compounds containing the tetracyclic hydrocarbon framework (3). However, a search of the Cambridge Structural Database (1992) showed that X-ray structural data are limited to a few polychlorinated derivatives (Paddon-Row, Englehardt, Skelton, White, Jørgensen & Patney, 1987; Mackenzie, Miller, Muir & Manojlović-Muir, 1983) and an anhydride derivative (4) (Bartlett, Combs, Le, Watson, Galloy & Kimura, 1982).

Molecular orbital energies are often sensitive to small variations of structural parameters (Angermund, Claus, Goddard & Krüger, 1985; Ermer, Bell & Mason, 1989; Zahn & Ziegler, 1986). It would be desirable, therefore, to determine the structure of the tetracyclic entity (3) as unencumbered as possible by extraneous functional groups.

Single crystals of the hydrocarbon (2) could not be obtained for X-ray analysis (Paddon-Row, Englehardt, Skelton, White, Jørgensen & Patney, 1987). It has not yet been possible to obtain suitable crystals of norbornene (Ermer, Bell & Mason, 1989) or norbornane (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985). The hydrocarbon (3*a*) is an oil at 298 K (Stille & Witherell, 1964).

The structure of the *anti*-7-*p*-bromobenzoate derivative of norbornene has been reported (McDonald & Trotter, 1965) but the precision was low. More recently, the structure of the *anti*-7-*p*-nitrobenzoate derivate of norbornene was determined (Jones, Kirby & Parker, 1992).

The *p*-bromobenzoate ester (1) was prepared in connection with solvolysis studies of *anti*-norbornene derivatives (Lloyd, 1985) and X-ray analysis proved possible (Coots, 1983).* We have now redetermined the structure at a lower temperature. 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). There are three short intermolecular hydrogen contacts affecting the tetracyclic hydrocarbon entity [H1$^{i}$···H15$^{ii}$ 2.20 (6), H4$a^{i}$···H4$b^{iii}$ 2.44 (6) and H4$b^{i}$···H5$a^{iv}$ 2.44 (7) Å].

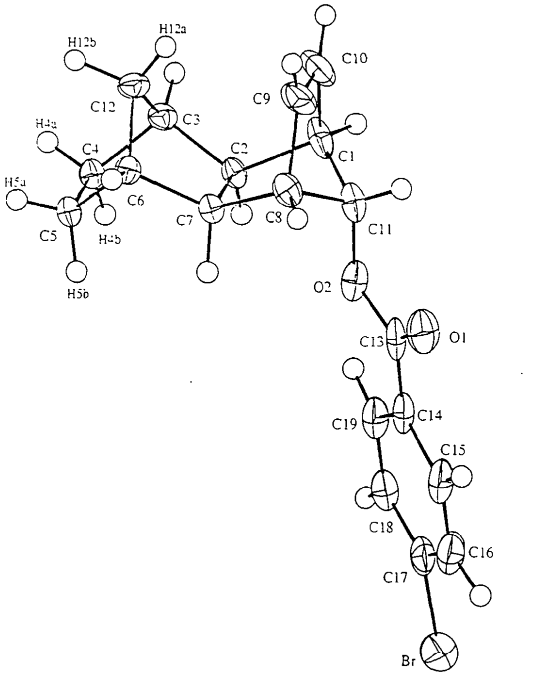


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the non-H atoms of one of the enantiomers of (1) with displacement ellipsoids shown at the 30% probability level.

---

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

The tetracyclic hydrocarbon framework 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 2.53° to the least-squares mirror plane, with O2 0.063 (3) Å out of the plane. The differences in length between the bonds C1—C11 and C8—C11 (0.014 Å) and the bonds C2—C3 and C6—C7 (0.011 Å) are near to the experimental uncertainty. Other differences between symmetry-related bonds are insignificant ($\leq$0.007 Å). The bond angles C1—C2—C3 and C6—C7—C8 differ by 1.4°, while C1—C11—O2 and C8—C11—O2 differ by 4.9°. All other differences between symmetry-related bond angles are $\leq$0.9°.

The differences between corresponding bond lengths in (1) and (4) are $\leq$0.023 Å, while differences between corresponding bond angles are $\leq$2.4°. The e.s.d.'s are smaller in (1) than in (4) by a factor of $\sim$2.

Some structural differences between (1) and (4) are revealed by a comparison of angles between least-squares planes [given for (1) in the side-view *PLUTO* (Motherwell & Clegg, 1978) drawing shown in Fig. 2]. Plane 1 is defined by atoms C1, C11 and C8. Atoms C1, C10, C9, C8 (plane 2) are very nearly coplanar, as are C1, C2, C7, C8 (plane 3). Although atoms C3, C2, C7, C6 (plane 4) and C3, C4, C5, C6 (plane 6) approach co-planarity to a lesser extent than the atoms in planes 2 and 3, they are coplanar to within $3\sigma$. The slight puckering may be the result of the intermolecular hydrogen contacts noted above.

The interplanar angles 1^2, 3^4 and 4^6 are nominally smaller by 3.4, 0.4 and 2.3°, respectively, in (1) than in (4). The interplanar angles 1^3, 2^3, 4^5 and 5^6 are larger in (1) than in (4) by 1.6, 1.8, 1.5 and 0.8°, respectively. The interplanar angle 4^6 is smaller in (1) than in (4), which is consistent with the greater steric size of the anhydride unit in (4) compared to that of H2 and H7 in (1). The C4—C5 bridge is tilted upwards in (4) compared to (1). This tilting is probably limited by H4*a*—C4—C5—H5*a*···H12*b*—C12 and C12—H12*a*···H9—C9=C10—H10 steric interactions on the opposing (top) face. The H12*a*···C9 and H12*a*···C10 non-bonding distances are 2.56 (5) and 2.57 (4) Å, respectively, in (1) and 2.48 Å in (4). Also, the C12···C9 and C12···C10 distances [both 3.087 (5) Å] are less than the sum of van der Waals radii in (1). These data are consistent with laticyclic hyperconjugation (Jordan & Paddon-Row, 1992) in this compound.

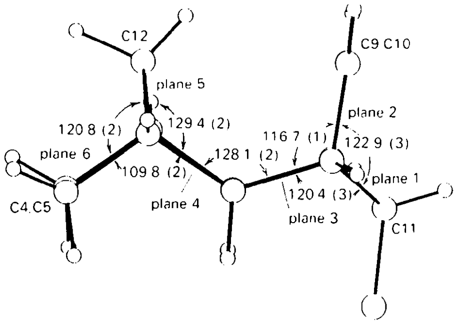


Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) side view, looking down the C5—C4 and C9=C10 bonds, giving the interplanar angles (°) with e.s.d.'s.

Interestingly, the interplanar angle 1^3 is larger and the angle 1^2 is compressed in (1) compared to (4). The non-bonding distances C2···O2, C7···O2, H2···O2 and H7···O2 are 2.752 (3), 2.792 (3), 2.53 (4) and 2.56 (4) Å, respectively. These contacts are consistent with a steric interaction that could widen angle 1^3 and compress angle 1^2 in (1) with respect to (4).

Although the compression of angle 1^2 in (1) relative to (4) is small, it is statistically significant and in the same direction as in a norbornenyl carbocation (Laube, 1989). The smaller 1^2 angle in (1) *cf.* (4) could be a manifestation of a C9=C10 $\pi$-bond interaction with the negative phase lobe of the C11 $sp^3$ orbital used in bonding to O2. This effect is apparently small, however, in the *anti*-7-norbornenyl system (Jones, Kirby & Parker, 1992). Furthermore, the C11—O2 bond in (1) is shorter than the analogous bond in the *anti*-7-norbornenyl 4-nitrobenzoate ester. The opposite would be expected if the above effect were important. Thus, steric factors seem to be responsible for the major differences between the structures of (1) and (4).

## Experimental

The ketone (3*b*) was synthesized using the procedure reported by McCulloch, Rye & Wege (1974). It was reduced to the *anti*-alcohol (3*c*) with $LiAlH_4$ in ether (Franzus & Snyder, 1965; Gassman & Pape, 1964). The overall yield of (3*c*) from norbornadiene was 26%. After purification by gas chromatography, (3*c*) was esterified with *p*-bromobenzoyl chloride in dry pyridine (Coots, 1983). The crude ester (1) was recrystallized from hexane in 72% yield, m.p. 357-358 K; $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 0.47-0.73 (1*H*, *m*), 1.01-1.80 (5*H*, *m*), 1.97-2.25 (4*H*, *m*), 2.90-3.06 (2*H*, *m*), 4.37 (1*H*, *t*), 5.97 (2*H*, *t*), 7.58 (2*H*, *d*), 7.86 (2*H*, *d*). Analysis: calculated for $C_{19}H_{19}BrO_2$ C 63.52, H 5.33%; found C 63.42, H 5.30%. Compound (1) was recrystallized twice more from hexane and then from ether/pentane (1:2 *v*/*v*). A small sample (32.2 mg) was placed in a 9 mm × 85 cm Pyrex tube. The ester was sublimed from 298 to 390 K (0.7 Pa) for 72 h using a 61 cm gradient tube heater (Scientific Instrument Accessories, Austin, TX, USA); a single crystal was obtained.

### *Crystal data*

| | |
|---|---|
| $C_{19}H_{19}BrO_2$ | Cu $K\alpha$ radiation |
| $M_r$ = 359.27 | $\lambda$ = 1.5418 Å |

Tetragonal
$I\bar{4}$
$a = 22.461\ (1)$ Å
$c = 6.191\ (1)$ Å
$V = 3123.23$ Å$^3$
$Z = 8$
$D_x = 1.528$ Mg m$^{-3}$

Cell parameters from 25 reflections
$\theta = 12$–$20°$
$\mu = 3.6314$ mm$^{-1}$
$T = 148$ K
Prism
0.25 × 0.22 × 0.16 mm
Colorless

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical, $\psi$ scan
$T_{\min} = 0.729$, $T_{\max} = 0.9833$
3094 measured reflections
3054 independent reflections

1514 observed reflections $[I \geq 3\sigma(I)]$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 7$
2 standard reflections
frequency: 60 min
intensity variation: <3%

*Refinement*

Refinement on $F$
$R = 0.0256$
$wR = 0.0262$
$S = 1.625$
1514 reflections
257 parameters
Only coordinates of H atoms refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.244$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.270$ e Å$^{-3}$
Extinction correction: $F_{\rm corr} = F_c/[1 + xF_c^2\sin^2(\theta)]^{1/4}$
Extinction coefficient: $x = 1.18\ (2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| Br | 0.03743 (2) | 0.42030 (2) | 0.01986 (9) | 3.858 (8) |
| O1 | 0.2050 (1) | 0.2351 (1) | −0.6196 (5) | 3.19 (6) |
| O2 | 0.1947 (1) | 0.1795 (1) | −0.3201 (4) | 2.54 (5) |
| C1 | 0.2540 (2) | 0.0916 (2) | −0.2288 (7) | 2.79 (8) |
| C2 | 0.1916 (1) | 0.0626 (1) | −0.1879 (6) | 1.74 (6) |
| C3 | 0.1855 (2) | −0.0024 (1) | −0.1133 (6) | 1.82 (6) |
| C4 | 0.1187 (1) | −0.0111 (1) | −0.0628 (5) | 1.67 (6) |
| C5 | 0.0891 (1) | −0.0100 (1) | −0.2901 (6) | 1.68 (6) |
| C6 | 0.1421 (1) | −0.0029 (1) | −0.4450 (6) | 1.70 (6) |
| C7 | 0.1631 (1) | 0.0624 (1) | −0.4187 (6) | 1.61 (6) |
| C8 | 0.2124 (2) | 0.0909 (1) | −0.5636 (6) | 2.24 (7) |
| C9 | 0.2674 (2) | 0.0511 (2) | −0.5692 (7) | 3.09 (8) |
| C10 | 0.2915 (2) | 0.0515 (2) | −0.3728 (8) | 3.33 (9) |
| C11 | 0.2372 (2) | 0.1373 (2) | −0.4023 (7) | 2.57 (7) |
| C12 | 0.1894 (1) | −0.0394 (2) | −0.3229 (6) | 1.99 (6) |
| C13 | 0.1855 (2) | 0.2284 (2) | −0.4388 (6) | 2.46 (7) |
| C14 | 0.1486 (2) | 0.2729 (2) | −0.3250 (6) | 2.31 (7) |
| C15 | 0.1325 (2) | 0.3250 (2) | −0.4350 (6) | 2.78 (7) |
| C16 | 0.0988 (2) | 0.3683 (2) | −0.3350 (7) | 3.10 (8) |
| C17 | 0.0813 (2) | 0.3596 (2) | −0.1237 (7) | 2.75 (7) |
| C18 | 0.0957 (1) | 0.3089 (2) | −0.0107 (8) | 2.70 (7) |
| C19 | 0.1298 (2) | 0.2652 (2) | −0.1120 (6) | 2.56 (7) |
| H4*a*† | 0.113 (2) | −0.049 (2) | 0.01 (1) | 4.0 |
| H4*b*† | 0.102 (2) | 0.019 (2) | 0.03 (1) | 4.0 |
| H9† | 0.283 (2) | 0.027 (2) | −0.68 (1) | 4.0 |
| H10† | 0.323 (2) | 0.030 (2) | −0.33 (1) | 4.0 |
| H12*a*† | 0.227 (2) | −0.043 (2) | −0.384 (9) | 4.0 |
| H12*b*† | 0.173 (2) | −0.083 (2) | −0.28 (1) | 4.0 |

† Located from the final Fourier synthesis and refined with a fixed isotropic displacement parameter.

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

| | | | |
|---|---|---|---|
| Br—C17 | 1.903 (3) | C6—C7 | 1.549 (4) |
| O1—C13 | 1.211 (4) | C6—C12 | 1.540 (4) |
| O2—C11 | 1.437 (3) | C7—C8 | 1.562 (4) |
| O2—C13 | 1.336 (4) | C8—C9 | 1.524 (5) |
| C1—C2 | 1.566 (5) | C8—C11 | 1.548 (5) |
| C1—C10 | 1.521 (5) | C9—C10 | 1.331 (6) |
| C1—C11 | 1.534 (4) | C13—C14 | 1.478 (5) |
| C2—C3 | 1.538 (4) | C14—C15 | 1.401 (5) |
| C2—C7 | 1.566 (4) | C14—C19 | 1.395 (5) |
| C3—C4 | 1.546 (4) | C15—C16 | 1.380 (5) |
| C3—C12 | 1.543 (4) | C16—C17 | 1.380 (5) |
| C4—C5 | 1.557 (4) | C17—C18 | 1.375 (5) |
| C5—C6 | 1.539 (4) | C18—C19 | 1.394 (5) |
| C11—O2—C13 | 116.7 (2) | C9—C8—C11 | 96.8 (2) |
| C2—C1—C10 | 110.2 (3) | C8—C9—C10 | 107.8 (3) |
| C2—C1—C11 | 99.8 (2) | C1—C10—C9 | 108.3 (3) |
| C10—C1—C11 | 97.0 (3) | O2—C11—C1 | 110.9 (3) |
| C1—C2—C3 | 121.5 (2) | O2—C11—C8 | 115.8 (2) |
| C1—C2—C7 | 102.7 (2) | C1—C11—C8 | 95.1 (2) |
| C3—C2—C7 | 103.6 (2) | C3—C12—C6 | 95.0 (2) |
| C2—C3—C4 | 105.4 (2) | O1—C13—O2 | 123.7 (3) |
| C2—C3—C12 | 104.7 (2) | O1—C13—C14 | 123.9 (3) |
| C4—C3—C12 | 99.0 (2) | O2—C13—C14 | 112.3 (3) |
| C3—C4—C5 | 103.3 (2) | C13—C14—C15 | 118.5 (3) |
| C4—C5—C6 | 103.5 (2) | C13—C14—C19 | 122.5 (3) |
| C5—C6—C7 | 105.6 (2) | C15—C14—C19 | 119.0 (3) |
| C5—C6—C12 | 99.9 (2) | C14—C15—C16 | 120.9 (3) |
| C7—C6—C12 | 104.1 (2) | C15—C16—C17 | 118.7 (3) |
| C2—C7—C6 | 102.9 (2) | Br—C17—C16 | 119.2 (3) |
| C2—C7—C8 | 103.5 (2) | Br—C17—C18 | 118.5 (3) |
| C6—C7—C8 | 122.9 (2) | C16—C17—C18 | 122.2 (4) |
| C7—C8—C9 | 110.4 (2) | C17—C18—C19 | 118.9 (4) |
| C7—C8—C11 | 99.2 (2) | C14—C19—C18 | 120.3 (3) |

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

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

---

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data, torsion angles and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71639 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1063]

---

## References

Angermund, K., Claus, K. H., Goddard, R. & Krüger, C. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 237–247.

Bartlett, P. D., Combs, G. L. Jr, Le, A.-X. T., Watson, W. H., Galloy, J. & Kimura, M. (1982). *J. Am. Chem. Soc.* **104**, 3131–3138.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Coots, R. J. (1983). PhD dissertation, Univ. of Utah, USA, p. 79.

Cambridge Structural Database (1992). Version 4.6. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

Doms, L., Van Hemelrijk, D., Van de Mieroop, W., Lenstra, A. T. H. & Geise, H. J. (1985). *Acta Cryst.* **B41**, 270–274.

Elsässer, D., Hassenrück, K., Martin, H.-D., Mayer, B., Lutz, G. & Prinzbach, H. (1991). *Chem. Ber.* **124**, 2863–2869.

Ermer, O., Bell, P. & Mason, S. A. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1239–1241.

Franzus, B. & Snyder, E. I. (1965). *J. Am. Chem. Soc.* **87**, 3423–3429.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Gassman, P. G. & Pape, P. G. (1964). *J. Org. Chem.* **29**, 160–163.
Gordon, A. J. & Ford, R. A. (1972). *The Chemist's Companion*, p. 109. New ork: John Wiley.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992). *Acta Cryst.* C**48**, 829–832.
Jordan, K. D. & Paddon-Row, M. N. (1992). *Chem. Rev.* **92**, 395–410.
Laube, T. (1989). *J. Am. Chem. Soc.* **111**, 9224–9232.
Lloyd, B. A. (1985). PhD dissertation, Univ. of Utah, USA.
Mackenzie, K., Miller, A. S., Muir, K. W. & Manojlović-Muir, Lj. (1983). *Tetrahedron Lett.* **24**, 4747–4750.
McCulloch, R. K., Rye, A. R. & Wege, D. (1974). *Aust. J. Chem.* **27**, 1929–1941.
McDonald, A. C. & Trotter, J. (1965). *Acta Cryst.* **19**, 456–463.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.
Paddon-Row, M. N. (1985). *J. Chem. Soc. Perkin Trans.* 2, pp. 257–263.
Paddon-Row, M. N., Englehardt, L. M., Skelton, B. W., White, A. H., Jørgensen, F. S. & Patney, H. K. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 1835–1850.
Stille, J. K. & Withcrell, D. R. (1964). *J. Am. Chem. Soc.* **86**, 2188–2192.
Zahn, T. & Ziegler, M. L. (1986). *Acta Cryst.* C**42**, 494–495.

---

*Acta Cryst.* (1994). C**50**, 781–784

# Structural Comparisons of a Perpendicular Diene with Known Derivatives

BARRY A. LLOYD*

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

ATTA M. ARIF AND EVAN L. ALLRED†

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

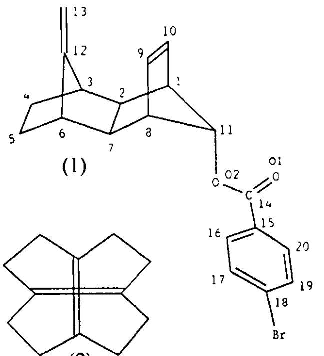
(*Received* 29 *January* 1993; *accepted* 5 *July* 1993)

## 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.

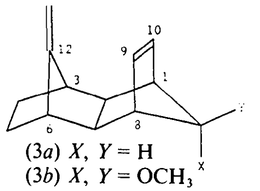
## Comment

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.

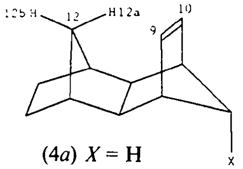


(1)

(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 ($I_\alpha$) 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-

---

† Deceased 8 July 1991.

©1994 International Union of Crystallography
Printed in Great Britain – all rights reserved