Acta Cryst. (1987). C**43**, 1013–1014

Methyl 8-(4-Bromobenzoyloxy)-5,8a-dimethyl-1,4,4a,7,8,8a-hexahydro-7-oxo-(1β,4aβ,8α,8aβ)-naphthalene-1-acetate

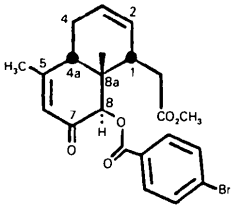
By Kenneth N. Trueblood* and You-Xi Liu†

J. D. McCullough Laboratory for X-ray Crystallography, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, *USA*

(*Received* 21 *October* 1986; *accepted* 23 *December* 1986)

Abstract. $C_{22}H_{23}BrO_5$, $M_r = 447{\cdot}3$, monoclinic, $P2_1/c$, $a = 13{\cdot}580\,(3)$, $b = 13{\cdot}137\,(4)$, $c = 12{\cdot}009\,(2)$ Å, $\beta = 96{\cdot}44\,(2)°$, $V = 2128{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}396$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 18{\cdot}9$ cm^{-1}, $F(000) = 920$, $T = 296$ K, $R = 0{\cdot}062$ for 1918 unique reflections with $I > 3\sigma(I)$. This bicyclic diester was prepared in the course of synthetic studies on quassinoids; its structure and conformation were essential in confirming the course of the synthesis. Although the molecule is chiral, the sample used was racemic. The geometry of the molecule and its packing in the crystal exhibit no unusual features.

Experimental. The title compound (Kloc, 1985) crystallized from ethyl acetate–hexane as clear colorless prisms. Dimensions of crystal used 0·22 × 0·18 × 0·51 mm, Syntex $P\bar{1}$ diffractometer, graphite monochromator; unit-cell parameters by least-squares refinement of 15 reflections ($23 \le 2\theta \le 30°$), θ–2θ scan, 4·0° min^{-1} from 1° below $K\alpha_1$ to 1° above $K\alpha_2$, $2\theta_{max} = 50°$ for the range $0 \le h \le 16$, $0 \le k \le 15$, $-14 \le l \le 14$, three reflections monitored every 97 reflections with maximum 3% intensity variation from average for two standards, but the third *increased* gradually by nearly 19%; since the focus of interest was the overall molecular structure and configuration, no effort was made to investigate or correct for this effect. In all, 4128 measured intensities (3778 unique data, 3181 with $I > 0$), 1918 with $I > 3\sigma(I)$ used in refinement, Lorentz and polarization but no absorption correction ($\mu = 18{\cdot}9$ cm^{-1}); structure solved by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), all atoms located on Fourier and difference Fourier maps except for four H atoms (on two different methyl groups). Aliphatic H atoms fixed in calculated positions based on those found, with C—H = 1·08 Å and tetrahedral angles, and not refined; the four aromatic and three ethylenic H atoms were fixed with C—H = 1·08 Å and 120° angles, and not refined. Anisotropic displacement parameters for all non-hydrogen atoms; refined by full-matrix least-squares procedure based on $|F|$, with 253 parameters, converged to $R = 0{\cdot}062$, $wR = 0{\cdot}107$ ($wR = 0{\cdot}087$ for all 3778 unique reflections, including 'unobserved', goodness of fit = 1·84), $w = 1/\sigma^2(F_o)$; ratio of maximum least-squares shift to e.s.d. for a position parameter in the final cycle of 0·22 and an average ratio of shift to e.s.d. of about 0·05, highest peak in final difference map 0·22 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations on a DEC VAX11/780 and VAX11/750, using a locally edited profile-analysis program, *MULTAN* (Main *et al.*, 1978), *SHELX*76 (Sheldrick, 1976), a local molecular geometry program, *MG*84, and a local molecular motion program (Trueblood, 1978). The illustrations were prepared with a locally edited version of *PLUTO* (Motherwell & Clegg, 1978). Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1‡ and selected bond lengths, and bond angles and torsion angles are given in Table 2. Librational corrections for rigid-body motion (Schomaker & Trueblood, 1968) and internal torsional motion (Trueblood, 1978) are smaller than the e.s.d.'s and have been neglected. The molecular conformation is illustrated in Fig. 1. The molecular geometry and packing are unexceptional.



* To whom correspondence should be addressed.

† Present address: Zhongshan University, Guangzhou, People's Republic of China.

‡ Lists of anisotropic displacement parameters, H-atom parameters and geometry, torsion angles and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43671 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/051013–02$01.50

© 1987 International Union of Crystallography

Related literature. Stevens & Vinogradoff (1985); Stevens, Angle, Kloc, Mak, Trueblood & Liu (1986); Kloc (1985).

Table 1. *Position and displacement parameters for* $C_{22}H_{23}BrO_5$

	x	y	z	$\langle u^2\rangle_{eq}$
C(1)	0·3596 (6)	0·4640 (5)	0·1556 (6)	0·047
C(2)	0·3377 (7)	0·3866 (6)	0·2387 (8)	0·059
C(3)	0·3999 (8)	0·3617 (6)	0·3275 (8)	0·066
C(4)	0·4977 (7)	0·4089 (6)	0·3530 (7)	0·057
C(4a)	0·5231 (6)	0·4929 (6)	0·2685 (7)	0·050
C(5)	0·5969 (7)	0·5638 (6)	0·3271 (7)	0·057
C(5*M*)	0·7028 (8)	0·5281 (8)	0·3448 (10)	0·088
C(6)	0·5681 (7)	0·6536 (7)	0·3682 (6)	0·058
C(7)	0·4657 (6)	0·6879 (6)	0·3494 (6)	0·047
O(7)	0·4410 (5)	0·7726 (4)	0·3727 (5)	0·064
C(8)	0·3903 (5)	0·6101 (5)	0·3008 (6)	0·040
C(8a)	0·4309 (6)	0·5468 (5)	0·2088 (6)	0·041
C(8a*M*)	0·4622 (6)	0·6181 (6)	0·1140 (6)	0·051
O(8)	0·3016 (4)	0·6650 (4)	0·2576 (4)	0·045
C(9)	0·2431 (6)	0·6947 (6)	0·3320 (6)	0·045
O(9)	0·2507 (4)	0·6657 (4)	0·4288 (4)	0·061
C(10)	0·1630 (5)	0·7620 (5)	0·2827 (6)	0·042
C(11)	0·1571 (6)	0·7943 (5)	0·1733 (6)	0·046
C(12)	0·0823 (6)	0·8585 (6)	0·1312 (6)	0·056
C(13)	0·0118 (7)	0·8899 (6)	0·1995 (7)	0·058
C(14)	0·0167 (8)	0·8576 (8)	0·3057 (8)	0·085
C(15)	0·0926 (7)	0·7964 (7)	0·3490 (7)	0·074
Br	−0·0930 (1)	0·9760 (1)	0·1390 (1)	0·091
C(16)	0·2671 (7)	0·5027 (6)	0·0869 (8)	0·062
C(17)	0·2211 (9)	0·4225 (9)	0·0061 (8)	0·079
O(17)	0·2657 (8)	0·3601 (9)	−0·0343 (10)	0·181
O(18)	0·1264 (6)	0·4396 (6)	−0·0216 (7)	0·100
C(18)	0·0759 (13)	0·3687 (12)	−0·1024 (12)	0·155

Displacement parameters are commonly called vibration parameters. Units of $\langle u^2\rangle$ are Å^2. Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter.

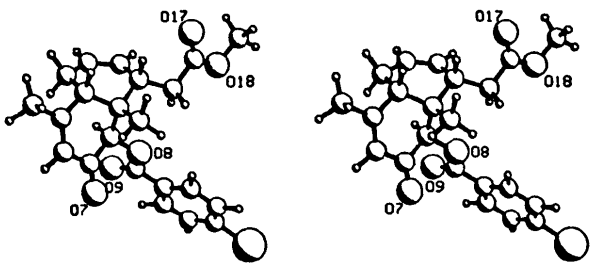


Fig. 1. A stereoview of the molecule.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for* $C_{22}H_{23}BrO_5$

C(1)–C(2)	1·478 (8)	O(8)–C(9)	1·320 (12)
C(2)–C(3)	1·326 (12)	C(10)–C(11)	1·375 (10)
C(4a)–C(5)	1·487 (12)	C(12)–C(13)	1·392 (11)
C(5)–C(6)	1·353 (12)	C(14)–C(15)	1·364 (13)
C(7)–C(8)	1·517 (9)	C(17)–O(18)	1·310 (15)
C(8a)–C(8a*M*)	1·569 (9)	C(1)–C(16)	1·512 (9)
C(9)–C(10)	1·473 (12)	C(4)–C(4a)	1·563 (10)
C(11)–C(12)	1·372 (11)	C(5)–C(5*M*)	1·505 (15)
C(13)–Br	1·897 (12)	C(7)–O(7)	1·204 (7)
C(17)–O(17)	1·158 (17)	C(8)–O(8)	1·449 (11)
C(1)–C(8a)	1·546 (8)	C(9)–O(9)	1·216 (15)
C(3)–C(4)	1·467 (11)	C(10)–C(15)	1·387 (13)
C(4a)–C(8a)	1·544 (11)	C(13)–C(14)	1·339 (12)
C(6)–C(7)	1·455 (10)	C(16)–C(17)	1·518 (14)
C(8)–C(8a)	1·534 (10)	O(18)–C(18)	1·46 (2)
C(2)–C(1)–C(8a)	111·7 (4)	C(2)–C(1)–C(16)	112·4 (5)
C(8a)–C(1)–C(16)	115·6 (4)	C(1)–C(2)–C(3)	123·7 (7)
C(2)–C(3)–C(4)	123·0 (7)	C(3)–C(4)–C(4a)	115·0 (6)
C(4)–C(4a)–C(5)	108·7 (6)	C(4)–C(4a)–C(8a)	113·5 (6)
C(5)–C(4a)–C(8a)	113·7 (6)	C(4a)–C(5)–C(5*M*)	117·1 (8)
C(4a)–C(5)–C(6)	120·7 (8)	C(5*M*)–C(5)–C(6)	122·1 (8)
C(5)–C(6)–C(7)	121·6 (7)	C(6)–C(7)–O(7)	122·5 (6)
C(6)–C(7)–C(8)	116·3 (5)	O(7)–C(7)–C(8)	121·2 (5)
C(7)–C(8)–C(8a)	111·2 (6)	C(7)–C(8)–O(8)	107·5 (6)
C(8a)–C(8)–O(8)	111·3 (6)	C(1)–C(8a)–C(4a)	107·8 (5)
C(1)–C(8a)–C(8)	114·9 (5)	C(1)–C(8a)–C(8a*M*)	109·2 (5)
C(4a)–C(8a)–C(8)	104·6 (6)	C(4a)–C(8a)–C(8a*M*)	109·8 (6)
C(8)–C(8a)–C(8a*M*)	110·4 (6)	C(8)–O(8)–C(9)	116·3 (8)
O(8)–C(9)–O(9)	124·2 (10)	O(8)–C(9)–C(10)	112·2 (8)
O(9)–C(9)–C(10)	123·5 (9)	C(9)–C(10)–C(11)	122·1 (7)
C(9)–C(10)–C(15)	119·4 (8)	C(11)–C(10)–C(15)	118·5 (7)
C(10)–C(11)–C(12)	120·2 (7)	C(11)–C(12)–C(13)	119·7 (7)
C(12)–C(13)–C(14)	120·2 (7)	C(12)–C(13)–Br	119·2 (6)
C(14)–C(13)–Br	120·6 (7)	C(13)–C(14)–C(15)	120·3 (8)
C(10)–C(15)–C(14)	120·9 (9)	C(1)–C(16)–C(17)	111·9 (7)
C(16)–C(17)–O(17)	124·2 (11)	C(16)–C(17)–O(18)	111·4 (9)
O(17)–C(17)–O(18)	124·0 (12)	C(17)–O(18)–C(18)	115·8 (10)

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KLOC, K. (1985). PhD Thesis. Univ. of California, Los Angeles.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78.* Program for drawing crystal and molecular structures. Univ. of Cambridge, England.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

STEVENS, R. V., ANGLE, S. R., KLOC, K., MAK, K. F., TRUEBLOOD, K. N. & LIU, Y.-X. (1986). *J. Org. Chem.* **51**, 4347–4353.

STEVENS, R. V. & VINOGRADOFF, A. P. (1985). *J. Org. Chem.* **50**, 4056–4062.

TRUEBLOOD, K. N. (1978). *Acta Cryst.* A**34**, 950–954.