C13	0.1678 (1)	0.2003 (5)	0.4856 (11)	7.84
C14	0.1954 (2)	0.1066 (6)	0.4682 (13)	10.87
C15	0.2297 (2)	0.1368 (7)	0.4230 (14)	12.04
C16	0.2383 (2)	0.2614 (7)	0.3945 (15)	12.85
C17	0.2117 (1)	0.3588 (5)	0.4121 (11)	8.67
C2	0.1072 (1)	0.4666 (4)	0.2274 (7)	3.52
C21	0.0833 (1)	0.3446 (4)	0.2279 (8)	4.22
C22	0.0939 (1)	0.2490 (4)	0.0981 (8)	4.26
C23	0.1290 (1)	0.2403 (5)	0.0333 (9)	6.07
C24	0.1369 (2)	0.1525 (5)	−0.0888 (10)	8.14
C25	0.1103 (2)	0.0703 (5)	−0.1473 (9)	7.33
C26	0.0754 (2)	0.0765 (5)	−0.0819 (10)	6.93
C27	0.0667 (1)	0.1655 (5)	0.0371 (9)	5.42
C3	0.1050 (1)	0.5602 (4)	0.0934 (8)	3.94
C31	0.0758 (1)	0.5554 (4)	−0.0360 (8)	4.73
C32	0.0370 (1)	0.6005 (4)	0.0220 (8)	3.99
C33	0.0337 (1)	0.7153 (4)	0.1059 (9)	5.06
C34	−0.0014 (1)	0.7573 (5)	0.1567 (9)	5.95
C35	−0.0327 (1)	0.6840 (5)	0.1272 (8)	5.48
C36	−0.0295 (1)	0.5688 (5)	0.0484 (8)	5.56
C37	0.0053 (1)	0.5257 (5)	−0.0076 (8)	4.97
C4	0.1321 (1)	0.6500 (4)	0.1148 (8)	3.92
C41	0.1423 (1)	0.7595 (4)	0.0034 (8)	4.90
C42	0.1773 (1)	0.7335 (4)	−0.0993 (8)	4.17
C43	0.1873 (1)	0.6093 (5)	−0.1442 (8)	4.79
C44	0.2180 (1)	0.5879 (6)	−0.2454 (8)	6.05
C45	0.2379 (1)	0.6914 (7)	−0.3019 (9)	6.50
C46	0.2286 (1)	0.8135 (6)	−0.2594 (10)	6.99
C47	0.1982 (1)	0.8365 (5)	−0.1570 (9)	5.82
C5	0.1530 (1)	0.6233 (4)	0.2690 (7)	4.16
C51	0.1550 (1)	0.7387 (4)	0.3871 (9)	4.95
C52	0.1174 (1)	0.7976 (4)	0.4334 (8)	4.29
C53	0.0943 (1)	0.7350 (4)	0.5433 (8)	4.94
C54	0.0598 (1)	0.7875 (5)	0.5880 (9)	5.80
C55	0.0483 (1)	0.9034 (5)	0.5239 (9)	5.49
C56	0.0709 (2)	0.9658 (4)	0.4155 (9)	5.90
C57	0.1051 (1)	0.9146 (4)	0.3701 (8)	5.28

Table 2. *Bond lengths* (Å) *and angles* (°)

C1—C2	1.328 (5)	C2—C21	1.515 (5)
C1—C5	1.507 (6)	C3—C31	1.490 (6)
C2—C3	1.470 (6)	C4—C41	150.0 (6)
C3—C4	1.346 (5)	C5—C51	1.539 (6)
C4—C5	1.502 (6)		
C1—C11	1.515 (6)		
$C(CH_2)$—C(Ph)	1.505 (6)–1.532 (5)	C(Ph)—C(Ph)*	1.3504 (7)–1.393 (7)
C2—C1—C5	109.5 (4)	C4—C3—C31	127.8 (4)
C1—C2—C3	109.9 (3)	C3—C31—C32	113.0 (4)
C2—C3—C4	108.3 (4)	C31—C32—C33	119.8 (4)
C3—C4—C5	109.8 (4)	C31—C32—C37	120.5 (4)
C4—C5—C1	102.5 (3)	C3—C4—C41	127.4 (4)
C2—C1—C11	127.3 (4)	C5—C4—C41	122.7 (4)
C11—C1—C5	123.2 (4)	C4—C41—C42	114.0 (3)
C1—C11—C12	114.7 (4)	C41—C42—C43	121.4 (4)
C11—C12—C13	120.3 (5)	C41—C42—C47	119.7 (4)
C11—C12—C17	121.0 (4)	C1—C5—C51	116.6 (4)
C1—C2—C21	128.8 (4)	C4—C5—C51	114.9 (4)
C3—C2—C21	121.0 (4)	C5—C1—C11	123.2 (4)
C2—C21—C22	113.5 (4)	C5—C51—C52	115.4 (4)
C21—C22—C23	123.7 (4)	C51—C52—C53	120.2 (4)
C21—C22—C27	119.2 (4)	C51—C52—C57	122.1 (4)
C2—C3—C31	123.8 (4)		
C(Ph)—C(Ph)—C(Ph)	117.0 (5)–121.3 (5)		

*Inaccurate bond lengths concerning the atoms C14, C15 and C16 are not considered.

Data reduction: *SDP* (Frenz, 1988). Program used to solve structure: *SHELXS86* (Sheldrick, 1986). Program used to refine structure: *SHELX76*.

The ω-scan width was $(0.80+0.35\tan\theta)°$ and the maximum scan time 60 s. Refinement was by full-matrix least-squares methods. H-atom positions were calculated [d(C—H) = 0.95 Å] with a fixed U_{iso} of 0.06 (—CH_2—) or 0.08 Å^2 (C_6H_5—).

0108-2701/93/030600-03$06.00

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55672 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1006]

References

Evrard, G., Piret, P., Germain, G. & Van Meerssche, M. (1971). *Acta Cryst.* B**27**, 661–666.

Frenz, B. A. (1988). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Hirsch, S. S. & Bailey, W. J. (1978). *J. Org. Chem.* **43**, 4090–4093.

Janiak, C. & Schumann, H. (1991). *Adv. Organomet. Chem.* **33**, 291–393.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Liebling, G. & Marsh, R. E. (1965). *Acta Cryst.* **19**, 202–205.

Schumann, H., Görlitz, F. H. & Schäfers, M. (1993). *Acta Cryst.* C**49**. In the press.

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

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ of Göttingen, Germany.

Acta Cryst. (1993). C**49**, 600–602

(+)-2,2′-(1,1′-Binaphthyl)phosphate Salt of Methyl (11*R*)-11-{[2-(4-Benzylpiperidino)-ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]oxepin-2-carboxylate

NORIAKI HIRAYAMA*

Department of Biological Science and Technology, Tokai University, 317 *Nishino, Numazu, Shizuoka* 410-03, *Japan*

TORU SUGAYA AND SHINJI TOMIOKA

Sakai Research Laboratories, Kyowa Hakko Kogyo Co. Ltd, 1-1-53 *Takasu-cho, Sakai, Osaka* 590, *Japan*

ETSUO OHSHIMA AND HIROYUKI OBASE

Pharmaceutical Research Laboratories, Kyowa Hakko Kogyo Co. Ltd, Nagaizumi, Shizuoka 411, *Japan*

(*Received* 7 *May* 1992; *accepted* 24 *August* 1992)

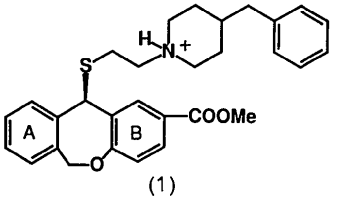
Abstract

The absolute configuration of methyl 11-{[2-(4-benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]-

oxepin-2-carboxylate was determined unequivocally based on the known absolute configuration of (+)-2,2′-(1,1′-binaphthyl)phosphoric acid [(+)-BNPPA]. The dihedral angle between the two phenyl rings is 43.3°.

Comment

Sodium 11-{[2-(4-benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]oxepin-2-carboxylate is a novel anti-allergic agent and also possesses thromboxane A_2 antagonist activity (Ohshima *et al.*, 1989). Although its racemic compound shows antagonistic activity against thromboxane A_2, optical resolution has been successfully accomplished using (+)- or (−)-BNPPA as a resolving agent (Sugaya, Kuge, Tomioka & Tamaki, 1992). In order to determine the absolute configuration of methyl 11-{[2-(4-benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]oxepin-2-carboxylate [(+) form], we have undertaken the X-ray analysis of its (+)-BNPPA salt (1).



(1)

The absolute configuration of the C11 atom was determined to be *R* based on the known chirality of (+)-BNPPA. The molecular structure of methyl (11*R*)-11-{[2-(4-benzylpiperidino)ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]oxepin-2-carboxylate is shown in Fig. 1. The 6,11-dihydrodibenz[*b*,*e*]oxepin skeleton adopts a folded conformation. The dihedral angle between the two phenyl rings [43.3 (2)°] is much larger than in isoxepac (31.5°) and its methyl ester (34.2°), but smaller than in isoxepac ethyl ester (49.0°; Matsuzawa, Hirayama, Ohshima & Obase, 1992). The planarity of ring *A* ($\chi^2 = 13.0$) is significantly higher than that of ring *B* ($\chi^2 = 66.4$). The two S—C bonds are remarkably asymmetrical. The piperidine ring adopts a chair conformation. The torsion angles C1a—C11—S—C14, C10a—C11—S—C14 and C11—S—C14—C15 are 155.8 (3), −74.2 (3) and −76.6 (4)°, respectively. One methanol molecule is contained in an asymmetric unit.

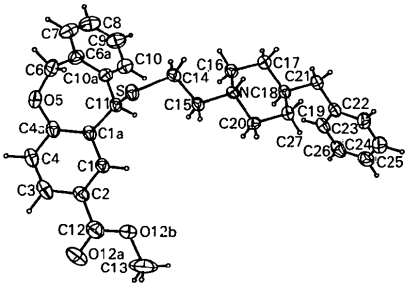


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of methyl (11*R*)-11-{[2-(4-benzylpiperidinyl)ethyl]thio}-6,11-dihydrodibenz[*b*,*e*]oxepin-2-carboxylate. Heavy atoms are shown with 30% probability ellipsoids and H atoms as spheres of arbitrary radius.

Experimental

Crystal data

$C_{30}H_{34}NO_3S.C_{20}H_{10}O_4P.CH_4O$
$M_r = 866.0$
Orthorhombic
$P2_12_12_1$
$a = 16.465$ (2) Å
$b = 30.163$ (3) Å
$c = 9.061$ (1) Å
$V = 4500$ (1) Å^3
$Z = 4$
$D_x = 1.28$ Mg m^{-3}
$D_m = 1.29$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 31$–$43°$
$\mu = 1.49$ mm^{-1}
$T = 293$ K
Prism
0.3 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4750 measured reflections
4656 independent reflections
4121 observed reflections [$|F_o| > 3.0\sigma(|F_o|)$]
$R_{int} = 0.035$
$\theta_{max} = 70°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 36$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 83.33 min
intensity variation: 0.007%

Refinement

Refinement on *F*
Final $R = 0.060$
$wR = 0.085$
$S = 2.40$
4121 reflections
550 parameters
H-atom parameters not refined
$w = 4F_o^2/[(I_o)^2 + (0.04I_o)^2]^{1/2}/\mathrm{Lp}$
$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.52$ (6) e Å^{-3}
$\Delta\rho_{min} = -0.11$ (6) e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 3.0×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
S	1.01206 (7)	0.61795 (4)	−0.5656 (2)	4.01 (2)
O5	0.8657 (3)	0.5234 (1)	−0.4109 (5)	6.02 (9)
O12a	0.6783 (4)	0.5913 (2)	−0.9741 (7)	11.7 (2)
O12b	0.7404 (3)	0.6529 (1)	−0.9124 (5)	6.7 (1)
N	1.0624 (2)	0.7514 (1)	−0.5670 (4)	3.24 (7)
C1	0.8166 (3)	0.6131 (2)	−0.6712 (6)	3.93 (9)
C1a	0.8536 (3)	0.5930 (1)	−0.5519 (6)	3.77 (9)
C2	0.7615 (3)	0.5905 (2)	−0.7587 (6)	4.6 (1)
C3	0.7411 (3)	0.5469 (2)	−0.7209 (7)	5.4 (1)
C4	0.7762 (3)	0.5271 (2)	−0.6032 (7)	5.2 (1)
C4a	0.8344 (3)	0.5488 (2)	−0.5213 (6)	4.6 (1)

C6	0.9434 (4)	0.5335 (2)	−0.3515 (8)	5.5 (1)
C6a	0.9386 (3)	0.5724 (2)	−0.2461 (6)	4.7 (1)
C7	0.9489 (4)	0.5668 (2)	−0.0939 (7)	6.3 (1)
C8	0.9445 (4)	0.6017 (3)	−0.0027 (7)	7.0 (2)
C9	0.9282 (4)	0.6430 (2)	−0.0557 (7)	6.7 (2)
C10	0.9171 (4)	0.6499 (2)	−0.2066 (6)	5.0 (1)
C10a	0.9236 (3)	0.6143 (2)	−0.3036 (5)	3.97 (9)
C11	0.9132 (3)	0.6223 (1)	−0.4663 (5)	3.39 (8)
C12	0.7244 (4)	0.6106 (2)	−0.8920 (8)	6.2 (1)
C13	0.7091 (6)	0.6739 (5)	−1.048 (1)	13.8 (3)
C14	1.0599 (3)	0.6693 (2)	−0.5107 (6)	4.1 (1)
C15	1.0232 (3)	0.7071 (1)	−0.5969 (6)	3.77 (9)
C16	1.0551 (3)	0.7656 (2)	−0.4077 (5)	3.78 (9)
C17	1.0908 (3)	0.8111 (2)	−0.3841 (6)	4.2 (1)
C18	1.0516 (3)	0.8457 (1)	−0.4824 (5)	3.67 (9)
C19	1.0618 (3)	0.8308 (2)	−0.6420 (6)	4.04 (9)
C20	1.0252 (3)	0.7855 (1)	−0.6687 (5)	3.77 (9)
C21	1.0881 (3)	0.8926 (2)	−0.4534 (6)	4.7 (1)
C22	1.0432 (3)	0.9292 (1)	−0.5335 (6)	4.2 (1)
C23	1.0797 (4)	0.9530 (2)	−0.6496 (8)	6.1 (1)
C24	1.0388 (4)	0.9866 (2)	−0.7199 (8)	7.2 (2)
C25	0.9620 (4)	0.9968 (2)	−0.6834 (8)	6.7 (2)
C26	0.9235 (4)	0.9737 (2)	−0.5729 (9)	6.3 (1)
C27	0.9644 (3)	0.9403 (2)	−0.4980 (6)	4.8 (1)
P(*B*)	0.78687 (6)	0.76373 (4)	0.5695 (2)	3.77 (2)
O1(*B*)	0.8498 (2)	0.7291 (1)	0.5650 (5)	5.31 (8)
O2(*B*)	0.7173 (2)	0.7613 (1)	0.6739 (4)	4.58 (7)
O3(*B*)	0.7423 (2)	0.7708 (1)	0.4121 (4)	3.93 (6)
O4(*B*)	0.8358 (2)	0.8101 (1)	0.5856 (4)	3.97 (6)
C1(*B*)	0.7892 (3)	0.7862 (1)	0.2945 (6)	3.72 (9)
C2(*B*)	0.8105 (3)	0.7555 (2)	0.1848 (7)	5.0 (1)
C3(*B*)	0.8545 (4)	0.7693 (2)	0.0650 (7)	5.1 (1)
C4(*B*)	0.8800 (3)	0.8130 (2)	0.0550 (6)	4.6 (1)
C(5*B*)	0.8594 (3)	0.8448 (2)	0.1657 (5)	3.66 (9)
C6(*B*)	0.8088 (3)	0.8302 (1)	0.2871 (5)	3.51 (8)
C7(*B*)	0.9296 (4)	0.8274 (2)	−0.0654 (6)	5.7 (1)
C8(*B*)	0.9588 (4)	0.8699 (2)	−0.0707 (7)	6.4 (1)
C9(*B*)	0.9394 (4)	0.9003 (2)	0.0391 (6)	5.3 (1)
C10(*B*)	0.8906 (3)	0.8885 (2)	0.1553 (6)	4.2 (1)
C11(*B*)	0.7816 (2)	0.8607 (1)	0.4072 (5)	3.51 (8)
C12(*B*)	0.7386 (3)	0.9010 (2)	0.3794 (6)	4.3 (1)
C13(*B*)	0.7198 (3)	0.9302 (2)	0.4988 (7)	5.3 (1)
C14(*B*)	0.7395 (3)	0.9179 (2)	0.6430 (8)	5.8 (1)
C15(*B*)	0.7757 (3)	0.8779 (2)	0.6722 (6)	4.9 (1)
C16(*B*)	0.7959 (3)	0.8495 (1)	0.5509 (5)	3.57 (8)
C17(*B*)	0.7120 (3)	0.9123 (2)	0.2333 (7)	5.6 (1)
C18(*B*)	0.6711 (4)	0.9521 (2)	0.2134 (9)	8.1 (2)
C19(*B*)	0.6584 (4)	0.9813 (2)	0.331 (1)	8.6 (2)
C20(*B*)	0.6807 (4)	0.9703 (2)	0.4688 (9)	6.7 (2)
O(SOL)*	0.6256 (6)	0.7810 (3)	0.926 (1)	15.3 (2)
C(SOL)*	0.6355 (8)	0.8215 (4)	0.989 (1)	13.8 (8)

*Refined isotropically. *B* and SOL denote (+)-BNPPA and the solvent molecules, respectively.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

S—C11	1.865 (4)	C4—C4a	1.378 (8)
O5—C6	1.420 (7)	C6a—C10a	1.387 (7)
N—C20	1.510 (6)	C14—C15	1.508 (6)
C1a—C11	1.531 (6)	O5—C4a	1.363 (7)
C6a—C7	1.400 (8)	N—C16	1.510 (6)
C10a—C11	1.504 (7)	C1a—C4a	1.398 (6)
S—C14	1.808 (5)	C6—C6a	1.516 (8)
N—C15	1.508 (5)	C10—C10a	1.392 (7)
C1—C1a	1.381 (7)		
C11—S—C14	100.8 (2)	C4a—O5—C6	119.9 (4)
C15—N—C16	112.8 (3)	C15—N—C20	108.6 (3)
C16—N—C20	111.0 (3)	C4a—C1a—C1	118.2 (4)
C4a—C1a—C11	126.5 (4)	C1—C1a—C11	115.3 (4)
C1a—C4a—C4	120.3 (5)	C1a—C4a—O5	126.7 (5)
C4—C4a—O5	113.0 (4)	C6a—C6—O5	111.0 (4)
C10a—C6a—C7	120.1 (5)	C10a—C6a—C6	118.6 (5)
C7—C6a—C6	121.3 (5)	C11—C10a—C10	119.1 (4)
C11—C10a—C6a	122.3 (4)	C10—C10a—C6a	118.6 (5)
S—C11—C1a	105.9 (3)	S—C11—C10a	111.2 (3)
C1a—C11—C10a	118.5 (4)	S—C14—C15	109.3 (3)
C14—C15—N	113.9 (4)		

Program used throughout the analysis: CAD-4 *SDP-Plus* (Frenz, 1983). Program used to solve structure: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Program used to draw the picture: *ORTEP*II (Johnson,1976). Refinement was by full-matrix least-squares methods.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55535 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1015]

References

Frenz, B. A. (1983). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Matsuzawa, E. S., Hirayama, N., Ohshima, E. & Obase, H. (1992). *Acta Cryst.* C**48**, 2016–2019.

Ohshima, E., Takami, H., Sato, H., Obase, H., Sasaki, Y., Ohmori, K., Miki, I., Karasawa, K. & Kubo, K. (1989). 10th Symp. Med. Chem. Abstracts, p. 101.

Sugaya, T., Kuge, Y., Tomioka, S. & Tamaki, K. (1992). *Bull. Pharm. Soc.* **40**, 238–239.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1993). C**49**, 602–604

Tetramethyl *tert*-Butylcalix[4]arene Tetraketone

GEORGE FERGUSON AND JOHN F. GALLAGHER

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

M. ANTHONY MCKERVEY

Department of Chemistry, Queens University, Belfast BT9 5AG, Northern Ireland

(*Received* 27 *May* 1992; *accepted* 6 *October* 1992)

Abstract

The title molecule, 25,26,27,28-tetraacetonyloxy-5,11,17,23-tetra-*tert*-butylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19,21,23-dodecaene, has twofold crystallographic symmetry and adopts a distorted cone conformation in the solid state.

0108-2701/93/030602-03$06.00