Journal of Organometallic Chemistry, 146 (1978) 95—101

THE STRUCTURE OF 5,5-DIMETHYL-5,6,11,12-TETRAHYDRO-5H-DIBENZO[b,f]SILOCIN

EUGENE R. COREY* and JOYCE Y. COREY

Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121 (U.S.A.)

and MILTON D. GLICK

Department of Chemistry, Wayne State University, Detroit, MI 48202 (U.S.A.)

(Received August 18th, 1977)

Summary

The structure of 5,5-dimethyl-5,6,11,12-tetrahydro-5H-dibenzo[b,f]silocin (I) has been determined from X-ray data collected by counter methods. I crystallizes in the orthorhombic space group Pbca with a = 15.577(4), b = 22.368(5) and c = 8.640(2) Å; observed and calculated densities (Z = 8) are 1.11 g cm^{-3}. Anisotropic full-matrix least squares refinement of nonhydrogen atoms, with hydrogen atoms included at fixed ideal locations gave a conventional R-factor of 5.0%. This is the first crystal structure of the dibenzo[b,f]metallocin framework with a single heteroatom in the central ring. The tricyclic framework adopts a distorted boat conformation in the solid state in contrast to dibenzcyclooctadiene. The dihedral angle between the planes of the two halves of the tricyclic framework (the benzo groups with the two central ring atoms bonded to them) is 111.4°.

Introduction

The conformation of tricyclic systems with medium-sized central rings has been of considerable interest [1-4]. We have been studying solid state conformations of 6:6:6 and 6:7:6 tricyclic heterocycles [5,6] which have central ring sizes that allow only boat-like conformations. The 6:8:6 system, dibenz[a,e]cyclooctadiene and heterocyclic analogs may adopt three distinct possible conformations: chair, boat and twist-boat [3]. This paper reports the first crystal structure of this 6:8:6 system with a single heteroatom in the central ring. The title compound, 5,5-dimethyl-5,6,11,12-tetrahydro-5H-dibenzo[b,f]silocin, adopts a distorted boat conformation. Preliminary crystallographic data show that the carbocycle, dibenz[a,e]cyclooctene, has the chair conformation in the solid state [1]. A pulsed nuclear

magnetic resonance study of the title compound has assigned one of three motions to methyl reorientation and the remaining two motions are unassigned but may be associated with flexing of the central ring [7]. The structure of a diheteroatom compound with the same framework, 2-chloro-6,11-dihydro-6H-dibenzo[b,f][1,4]thiazocine-12-carboxamide, has been reported and a boat-like conformer similar to that of the silocin is observed [8].

Experimental

Crystals of the title compound were synthesized from 5-chloromethyl-5-methyl-10,11-dihydro-5H-dibenzo[b,f]silepin by a ring expansion reaction [9] followed by reaction with methyllithium. A summary of crystal and experimental data for the silocin is given in Table 1. A crystal was attached to a glass fiber and mounted on a Syntex $P2_1$ diffractometer. The space group was assigned on the basis of rotation and axial photographs and counter data. Cell constants and errors were obtained by least squares refinement of angles for fifteen reflections centered with a programmed centering routine. Intensity data were collected with monochromatic MoK_α radiation which had been diffracted by a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the crystal. The θ-2θ scan technique was used with a 2.0 degree per minute scan speed. Background counts were taken at each end of the scan for a time equal to one-half the scan time.

During data collection, the intensities of three standard reflections were measured every 97 reflections; the intensities of the standard reflections decreased gradually to approximately 79% of the original values. De-

TABLE 1

PHYSICAL CONSTANTS AND EXPERIMENTAL DATA: 5,5-DIMETHYL-5,6,11,12-TETRAHYDRO-5H-DIBENZO[b,f]SILOCIN

Molecular formula	$C_{17}H_{20}Si$
Molecular weight	252.43
Crystal system	orthorhombic
Space group	Pbca
a	15.577(4) Å
b	22.368(5)
c	8.640(2)
Number of molecules per unit cell	8
Volume ($Å^3$)	3010(1)
Density (calcd.), g cm^{-3}	1.11
Density (found)	1.11
Linear absorption coefficient, MoK_α (cm^{-1})	1.46
Crystal dimensions (mm)	0.24 x 0.26 x 0.30
Number of independent data collected	3408
Number of independent data for which $I > 2.5\sigma(I)$	1245

cay factors were used to compensate for decreased intensity and the data were reduced to F^2 and $\sigma(F^2)$*. Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{counter}(I)^2 + (0.03 \times I)^2]^{1/2}$ where $\sigma_{counter} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counting time, and K is the ratio of scan time to background time. No absorption correction was made; data for which $F^2 > 2.5\sigma(F^2)$ were used in the structure solution and refinement.

The structure was solved by iterative application of the Sigma-2 relationship using 201 normalized structure factors (E's) of magnitude 1.3 or greater. An E-map based on the set of phases with the largest consistency index (0.86) revealed the positions of the nonhydrogen atoms.

Least squares refinement of the positional and anisotropic thermal parameters of the 18 nonhydrogen atoms with the hydrogen atoms at ideal locations with C-H distances of 1.0 Å resulted in discrepancy values of $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.050$ and $R_2 = [\Sigma(w|F_o|-|F_c|)^2/ wF_o^2]^{1/2} = 0.049$. Isotropic thermal parameters for the hydrogen atoms were fixed at values 10% greater than the equivalent B for the atom to which they are bonded. The largest parameter shift in the final cycle of refinement was 11% of its standard deviation. The error of fit was 1.71. Scattering factors for the atoms were taken from Vol. IV of the International Tables [10]. The highest resi-

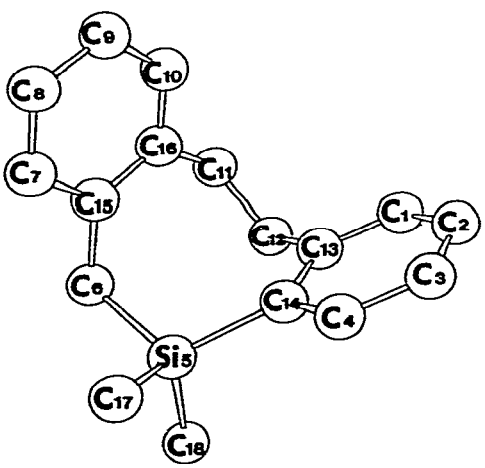

Fig. 1. Atom labeling for 5,5-dimethyl-5,6,11,12-tetrahydro-5H-dibenzo[b,f]-silocin.

*Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin and H. Levy's full-matrix least squares program and function and error program; (4) ORTEP, C.K. Johnson's program for drawing crystal models; (5) FASTES, E.R. Corey's normalization program; (6) REL, R.E. Long's program for iterative application of the Sigma-2 relationship; (7) FINDHATOM, T.J. Anderson's modification of A. Zallin's hydrogen atom finding program.

TABLE 2

FINAL POSITIONAL ($x10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($x10^4$) FOR 5,5-DIMETHYL-5,6,11,12-TETRAHYDRO-5H-DIBENZO[b,f]SILOCIN[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	313(3)	3761(2)	5251(6)	49(3)	39(2)	163(9)	8(2)	-4(4)	-3(3)
C2	25(4)	3186(4)	5319(7)	52(3)	50(2)	305(13)	-13(2)	4(5)	11(5)
C3	559(4)	2727(2)	5016(8)	67(4)	30(2)	378(14)	-19(2)	8(6)	16(4)
C4	1406(3)	2844(2)	4600(6)	61(3)	21(1)	247(10)	-3(2)	-1(5)	4(3)
Si5	2880(1)	3546(1)	3983(1)	38(1)	24(1)	143(2)	-1(1)	-8(1)	6(1)
C6	2995(3)	4206(2)	2625(5)	50(3)	33(1)	158(7)	-9(2)	-12(4)	18(3)
C7	2392(3)	3913(2)	66(5)	57(3)	32(1)	137(7)	-1(2)	21(4)	17(3)
C8	1733(4)	3875(2)	-1012(5)	71(3)	32(1)	123(7)	-4(2)	0(5)	6(3)
C9	960(3)	4140(2)	-701(6)	63(3)	38(2)	150(9)	-4(2)	-23(4)	16(3)
C10	842(3)	4433(2)	690(6)	57(3)	32(1)	154(8)	9(2)	-9(4)	22(3)
C11	1317(3)	4841(2)	3238(6)	94(4)	22(1)	191(9)	9(2)	-11(5)	2(3)
C12	1469(3)	4533(2)	4809(5)	84(3)	22(1)	144(8)	6(2)	-8(4)	-15(3)
C13	1153(3)	3892(2)	4856(4)	48(2)	23(1)	95(6)	1(1)	-6(4)	-7(2)
C14	1730(3)	3425(2)	4508(4)	43(2)	17(1)	123(7)	-3(1)	-8(3)	3(2)
C15	2276(3)	4216(2)	1469(5)	53(3)	20(1)	144(8)	-9(1)	-4(4)	18(2)
C16	1489(3)	4481(2)	1780(5)	60(3)	17(1)	141(8)	2(1)	-9(4)	9(3)
C17	3565(3)	3670(2)	5713(5)	49(2)	43(2)	196(9)	-9(2)	-31(4)	16(3)
C18	3265(3)	2872(2)	2940(6)	66(3)	37(1)	228(10)	14(2)	15(5)	-4(3)

[a] Estimated standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s). The form of the anisotropic thermal parameter is $\exp-[h^2\beta_{11}+k^2\beta_{22}+\ell^2\beta_{33}+2hk\beta_{12}+2h\ell\beta_{13}+2k\ell\beta_{23}]$.

TABLE 3

HYDROGEN ATOM FIXED POSITIONAL ($x10^3$) AND THERMAL PARAMETERS FOR 5,5-DIMETHYL-5,6,11,12-TETRAHYDRO-5H-DIBENZO[b,f]SILOCIN

	x	y	z	B(Å^2)		x	y	z	B(Å^2)
C1H	-9	410	549	6.1	C11H	167	521	307	6.6
C2H	-59	310	560	8.2	C11H'	70	494	307	6.6
C3H	35	231	509	7.8	C12H	96	470	537	5.7
C4H	180	250	436	6.3	C12H'	199	456	549	5.7
C6H	359	415	222	5.6	C17H	329	398	639	6.5
C6H	299	455	337	5.6	C17H'	420	373	568	6.5
C7H	296	372	-16	5.5	C17H"	351	332	643	6.5
C8H	182	366	-201	6.0	C18H	385	289	245	7.3
C9H	48	412	-147	6.3	C18H'	283	277	213	7.3
C10H	27	462	92	5.7	C18H"	321	251	363	7.3

dual electron density in the final difference map was 0.21 eÅ^{-3}. Tables 2 and 3 list the atomic coordinates and thermal parameters; Figure 1 indicates the numbering scheme. A listing of structure factors is available*.

* see NAPS document no. 03187 for 7 pages of supplementary material involving a listing of observed and calculated structure factors for $C_{17}H_{20}Si$. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y., 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make check payable to Microfiche Publications.

Discussion

The tricyclic framework of 5H-dibenzo[b,f]silocin adopts a distorted boat conformation in the solid state. A stereoscopic view of the conformation is shown in Figure 2. Bond distances and angles are presented in Table 4. Mean distances for the different bond types are C_{benzo}-C_{benzo}, 1.384 (range: 1.347-1.411); C_{benzo}-$C_{methylene}$, 1.512 (range: 1.502-1.519); Si-C, 1.869 (range: 1.856-1.894Å). Figure 3 is a stereoscopic drawing of the contents of the unit cell including hydrogen atoms.

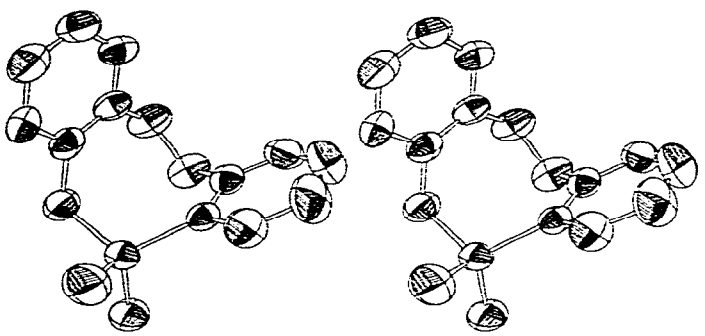

Fig. 2. A stereoscopic drawing of 5,5-dimethyl-5,6,11,12-tetrahydro-5H-dibenzo[b,f]silocin with atoms represented by 50% probability ellipsoids.

TABLE 4
BOND DISTANCES (Å) AND BOND ANGLES (°)

C1-C2	1.363(7)	C7-C8	1.388(6)
C1-C13	1.384(6)	C7-C15	1.401(6)
C2-C3	1.347(7)	C8-C9	1.369(6)
C3-C4	1.392(7)	C9-C10	1.381(6)
C4-C14	1.395(5)	C10-C16	1.383(6)
Si5-C6	1.894(4)	C11-C12	1.541(6)
Si5-C14	1.868(4)	C11-C16	1.519(6)
Si5-C17	1.857(4)	C12-C13	1.516(6)
Si5-C18	1.856(5)	C13-C14	1.411(5)
C6-C15	1.502(6)	C15-C16	1.389(6)
C2-C1 -C13	121.5(5)	C9-C10-C16	122.2(4)
C1-C2 -C3	120.5(5)	C12-C11-C16	117.8(3)
C2-C3 -C4	119.5(5)	C11-C12-C13	113.3(4)
C3-C4 -C14	122.1(4)	C1-C13-C12	121.0(4)
C6-Si5-C14	110.7(2)	C1-C13-C14	119.8(4)
C6-Si5-C17	109.1(2)	C12-C13-C14	119.2(4)
C6-Si5-C18	107.5(2)	C4-C14-Si5	119.7(3)
C14-Si5-C17	112.2(2)	C4-C14-C13	116.6(4)
C14-Si5-C18	108.1(2)	Si5-C14-C13	123.7(3)
C17-Si5-C18	109.1(2)	C6-C15-C7	118.2(4)
Si5-C6 -C15	110.7(3)	C6-C15-C16	122.5(4)
C8-C7 -C15	121.0(4)	C7-C15-C16	119.2(4)
C7-C8 -C9	119.5(5)	C10-C16-C11	118.5(5)
C8-C9 -C10	119.5(5)	C10-C16-C15	118.6(4)
		C11-C16-C15	122.8(4)

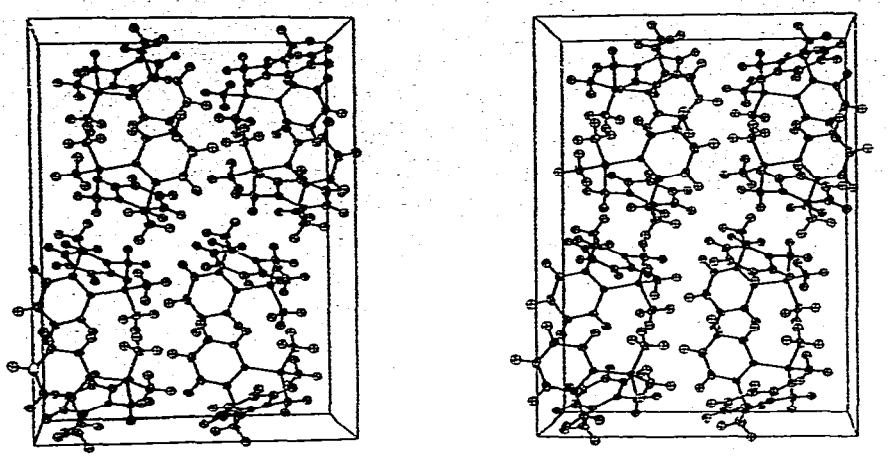

Fig. 3. A stereoscopic view of the contents of the unit cell viewed down the c-axis.

The undistorted boat conformation has been described as the intersection of three planes [3]; two of the planes consist of the nonhydrogen atoms of the o-phenylene moieties and the third plane contains the four nonbenzenoid atoms of the central ring. Table 5 gives the displacements of atoms from the three planes whose intersections describe the near boat conformation of I. Planes 1 and 2, the benzo atoms and the two central ring atoms bonded to them, have only small displacements of atoms from the best planes

TABLE 5

EQUATION OF BEST PLANES AND DISPLACEMENTS (Å) OF ATOMS FROM THE PLANES[a]

Plane 1.	-0.259X + 0.050Y - 0.965Z = -4.085		
C1	0.00	C11[b]	1.40
C2	0.00	C12	-0.01
C3	-0.02	C13	0.01
C4	0.00	C14	0.01
Si5	0.00	C15[b]	2.41
C6[b]	1.16	C16[b]	2.50
Plane 2.	0.337X + 0.839Y - 0.426Z = 8.549		
Si5[b]	-1.84	C11	0.04
C6	-0.04	C12[b]	-1.04
C7	0.03	C13[b]	-2.42
C8	0.01	C14[b]	-2.87
C9	-0.01	C15	0.02
C10	-0.04	C16	-0.01
Plane 3.	-0.607X - 0.542Y - 0.581Z = -9.045		
Si5	0.02	C13[b]	0.79
C6	-0.21	C14[b]	0.99
C11	0.30	C15[b]	1.04
C12	-0.26	C16[b]	1.31

[a]X,Y,Z are orthogonal unit vectors defined by the equations: X = a, Y = b, Z = a x b. [b] atoms not included in the least squares plane.

(0.04Å at most). The four nonbenzo atoms in the ring (plane 3) do not constitute a planar set and account for the distortion from the idealized boat conformation. This distortion may be described as a twisting of the benzo rings relative to one another (i.e., a slightly folded boat). The degree of twist can be measured by the mean value of 20° for the torsion angles about the nonbonded vectors C13···C16 and C14···C15 (individual values: 21.1 and 19.4°, respectively). The dihedral angle between planes 1 and 2 is 111.4°.

Torsion angles about the bonds of the eight-membered ring are in Table 6. The torsion angles about the Si5-C6 and C11-C12 bonds must be 0° for the idealized boat conformer [3]. Torsion angles in the eight-membered ring of 2-chloro-6,11-dihydro-6H-dibenzo[b,f][1,4]thiazocine-12-carboxamide, a di-heteroatom compound with the same boat-like framework as the silocin, show a similar range of values [8].

TABLE 6

TORSION ANGLES (°) IN THE EIGHT-MEMBERED RING

C14-Si5- C6-C15	-39
Si5- C6-C15-C16	86
C6-C15-C16-C11	8
C15-C16-C11-C12	-64
C16-C11-C12-C13	-32
C11-C12-C13-C14	88
C12-C13-C14-Si5	1
C13-C14-Si5-C6	-42

Acknowledgement

J.Y.C. and E.R.C. acknowledge support from NIH research grant RO1NS10903 from National Institute of Neurological Diseases and Stroke.

References

1 W. Baker, R. Banks, D.R. Lyon and F.G. Mann, J. Chem. Soc., (1945) 27.
2 W.D. Ollis, J.F. Stoddart and I.O. Sutherland, Tetrahedron, 30 (1974) 1903.
3 R. Crossley, A.P. Downing, M. Nógrádi, A. Braga de Oliveira, W.D. Ollis and I.O. Sutherland, J.C.S. Perkin I, (1973) 205.
4 R.P. Gellatly, W.D. Ollis and I.O. Sutherland, J.C.S. Perkin I, (1976) 913.
5 E.R. Corey, J.Y. Corey, W.F. Paton and M.D. Glick, Acta Crystallogr. Sect. B, 33 (1977) 1254.
6 E.R. Corey, J.Y. Corey and M.D. Glick, J. Organometal Chem., 129 (1977) 17.
7 D.W. Larsen, J.Y. Corey, T.A. Smentkowski and F.E. Stary, J. Organometal. Chem., 135 (1977) 161.
8 H.L. Yale, F. Sowinski and E.R. Spitzmiller, J. Heterocycl. Chem., 9 (1972) 899.
9 E.A. Francis and J.Y. Corey, J. Organometal. Chem., 61 (1973) C20.
10 J.A. Ibers and W.C. Hamilton, Ed., "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press, Birmingham, England (1974).