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THE STRUCTURES OF 5-METHYL-5-PHENYL-5*H*-DIBENZO[*b,f*] SILEPIN AND ITS SATURATED ANALOG

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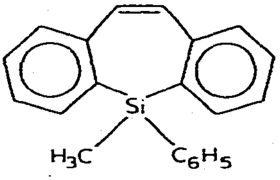
Summary

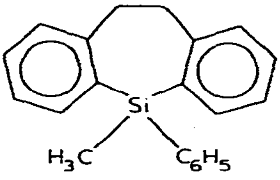
The structures of 5-methyl-5-phenyl-5*H*-dibenzo[*b,f*] silepin (I) and 5-methyl-5-phenyl-10,11-dihydro-5*H*-dibenzo[*b,f*] silepin (II) have been determined from three-dimensional X-ray data collected by counter methods. I crystallizes in the orthorhombic space group *Pnam* with *a* 7.596(3), *b* 18.102(5) and *c* 12.190(2) Å; observed and calculated densities ($Z = 4$) are 1.17 and 1.18 g cm^{-3}, respectively. II crystallizes in the monoclinic space group $P2_1/c$ with *a* 11.115(3), *b* 7.920(3), *c* 20.765(5) Å and β 111.71(2)°; observed and calculated densities ($Z = 4$) are 1.17 g cm^{-3}. Anisotropic refinement of nonhydrogen atoms, with hydrogen atoms included at fixed ideal locations, gave conventional *R*-factors of 4.5% (I) and 5.0% (II). Compound I exhibits the boat conformation for the tricyclic framework and is located on a crystallographically required mirror plane. Compound II has the expected folded boat conformation. The torsion angle about the 10,11-bond is 0.0° for I, a crystallographic symmetry requirement, and 89.9° for II. Mean Si—C bond distances are 1.863 Å(I) and 1.875 Å(II). The dihedral angles between the planar benzo groups are 129.7°(I) and 137.2°(II); introduction of unsaturation at the 10,11-position decreases the dihedral angle in the tricyclic system, i.e., the tricyclic system is more bent.

Introduction

In our continuing investigation into the effects of Group IV heteroatom replacement on the structural features of tricyclic ring systems, we have determined the solid state structures of the two compounds, 5-methyl-5-phenyl-5*H*-dibenzo-[*b,f*] silepin (I) and 5-methyl-5-phenyl-10,11-dihydro-5*H*-dibenzo[*b,f*] silepin (II).



(I)



(II)

The tricyclic framework in these heterocycles is related to those found in a number of pharmacologically active compounds which display central nervous system activity. A set of parameters has been developed to describe the structural features of dibenzo-tricyclic systems; these parameters include the dihedral angle between benzo planes, distance between benzo ring centers and the twist (out of plane) and skew (inplane) of the two benzo rings relative to one another [1]. We now report the effect on these parameters when a multiple bond is introduced into the central ring of the tricyclic compound.

Experimental

Crystals of the title compounds were prepared by J. Corey. Cell parameters and some data collection information are given in Table 1. Crystals of both compounds were attached to glass fibers and mounted on a Syntex $P2_1$ four-circle diffractometer. Space groups were assigned on the basis of rotation and axial photographs and counter data. Fifteen reflections with 2θ greater than 15 degrees were centered using a programmed centering routine. Cell constants and errors were obtained by least squares refinement of these angles. Intensity data were collected with monochromatic Mo-K_α radiation which had been diffracted by a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the crystal.

TABLE 1

CRYSTAL DATA FOR 5-METHYL-5-PHENYL-5*H*-DIBENZO[*b,f*]SILEPIN (I) AND 5-METHYL-5-PHENYL-10,11-DIHYDRO-5*H*-DIBENZO[*b,f*]SILEPIN (II)

	I	II
Molecular formula	$C_{21}H_{18}Si$	$C_{21}H_{20}Si$
Molecular weight	298.46	300.48
Crystal system	orthorhombic	monoclinic
Space group	*Pnam*	$P2_1/c$
a	7.596(3)	11.115(3)
b	18.102(5)	7.920(3)
c	12.190(2)	20.765(5)
β	—	111.71(2)
Number of molecules per cell	4	4
Density, found (calcd.) (g cm^{-3})	1.17 (1.18)	1.17 (1.17)
Volume (Å^3)	1676.2(9)	1698.4(9)
Linear absorption coefficient (cm^{-1})	1.37	1.35
Crystal dimensions (mm)	0.11 X 0.16 X 0.20	0.13 X 0.14 X 0.33
Number of independent data collected	1799	2658
Number of independent data for which $I > 3\sigma(I)$	568	1171

During data collection, the intensities of three standard reflections were measured every 47 reflections for I and every 97 reflections for II with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those described previously [*]. Standard deviations were assigned as follows:

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.03 \times I)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counting time, and K is the ratio of scan time to background time. No corrections were made for absorption, anomalous dispersion or extinction. Scattering factors were taken from Vol. IV of the International Tables [2].

Intensity data for I were collected with the $\theta - 2\theta$ scan technique. All reflections with $2\theta \leqslant 50^\circ$ were measured with a scan speed of 2.0 deg min^{-1}. Backgrounds were measured at each end of the scan (2θ scan range: $2\theta\text{Mo-}K_{\alpha 1} - 1.0$ to $2\theta\text{Mo-}K_{\alpha 2} + 1.0^\circ$) for a total time equal to one-half the scan time.

Intensity data for II were collected by the ω-scan technique. This quick data set was obtained by sampling the tops of all peaks with $2\theta \leqslant 45^\circ$. The normal number of steps collected was 13 with 11 steps used in the intensity calculations. A maximum of 3 additional steps were taken if the maximum intensity step was too close to either end of the normal scan range; additional steps were necessary for less than 1% of the reflections scanned. The normal total scan range was 1.0° in ω with a scan speed of 2.0 deg min^{-1}. Backgrounds were measured at either side of the peak with a 1.0 deg displacement from the $K_{\alpha 1,2}$ peak position for a total time equal to one-half the scan time.

The structure of I was solved with program MULTAN. The locations of 11 of the 13 nonhydrogen atoms in the asymmetric unit were obtained from the initial E-map. The positions of the remaining two atoms were found in a Fourier synthesis using phases calculated with the partial structure. Full matrix isotropic least squares refinement resulted in discrepancy values of:

$$R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.103 \text{ and } R_2 = [\Sigma(w|F_o| - |F_c|)^2 / \Sigma w F_o{}^2]^{1/2} = 0.110$$

Least squares refinement was completed with anisotropic thermal parameters for nonhydrogen atoms and inclusion of hydrogen atoms at fixed positions with isotropic thermal parameters 10% greater than the equivalent B for the atom to which they are bonded. The hydrogen atoms were placed at ideal calculated locations with C—H distances of 1.0 Å after each least squares cycle. Final discrepancy indices were $R_1 = 0.045$ and $R_2 = 0.041$. The largest parameter shift in the final cycle of refinement was less than 10% of its standard deviation. The error of fit was 1.45 and the highest residual electron density in the final difference map was 0.19 eÅ^{-3}. Table 2 lists the atomic coordinates and thermal parameters; the fixed isotropic B values for the hydrogen atoms ranged from 6.6 to

(continued on p. 23)

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[*] 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) MULTAN, Germain, Main and Woolfson's program for structure solutions; (6) FINDHATOM, T.J. Anderson's modification of A. Zalkin's hydrogen atom finding program.

TABLE 2

ATOMIC COORDINATES (X10^4) AND ANISOTROPIC THERMAL PARAMETERS[a] (X10^4) FOR 5-METHYL-5-PHENYL-5*H*-DIBENZO[*b*,*f*] SILEPIN

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−790(9)	3984(4)	161(7)	395(19)	65(3)	167(8)	−51(7)	−10(13)	37(4)
C(2)	−285(14)	3499(5)	−642(7)	628(32)	95(5)	113(8)	−119(11)	−90(16)	23(5)
C(3)	1162(12)	3064(4)	−502(6)	594(29)	72(3)	92(7)	−104(8)	26(12)	−9(4)
C(4)	2156(8)	3129(3)	451(5)	390(17)	50(2)	90(5)	−44(5)	32(9)	−10(3)
Si(5)	3106(3)	3763(1)	2500 *[b]	241(5)	27(1)	86(2)	7(2)	0 *	0 *
C(6)	−529(7)	4571(3)	1952(5)	252(12)	40(2)	198(9)	0(4)	−40(1)	11(3)
C(7)	158(8)	4050(3)	1140(5)	287(15)	39(2)	118(6)	−30(5)	42(9)	18(3)
C(8)	1703(7)	3623(2)	1279(4)	255(12)	31(2)	88(5)	−21(4)	−5(8)	5(3)
C(9)	5029(10)	3132(3)	2500 *	376(23)	43(3)	153(8)	37(7)	0 *	0 *
C(10)	3973(8)	4739(3)	2500 *	156(14)	29(2)	80(6)	−1(5)	0 *	0 *
C(11)	5400(10)	6154(4)	2500 *	316(20)	38(3)	140(8)	−34(7)	0 *	0 *
C(12)	4344(7)	5099(3)	1539(4)	337(14)	43(2)	90(5)	−32(5)	4(7)	1(3)
C(13)	5062(8)	5805(3)	1528(4)	425(17)	49(2)	106(5)	−57(5)	−3(9)	7(3)

[a] Estimated standard deviation from the full variance-covariance matrix is given in parentheses for the least significant digit(s). The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] * indicates parameters fixed by symmetry.

TABLE 3

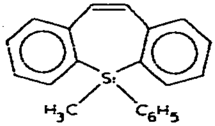
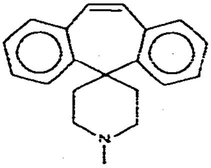
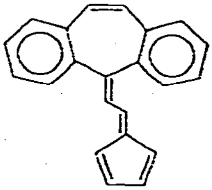
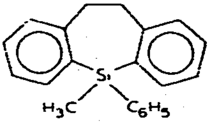
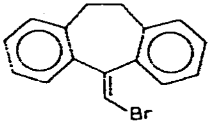
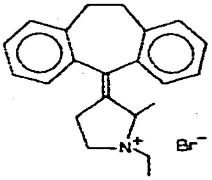
ATOMIC COORDINATES (X10^4) AND ANISOTROPIC THERMAL PARAMETERS [a] (X10^4) FOR 5-METHYL-5-PHENYL-10,11-DIHYDRO-5*H*-DIBENZO[*b,f*]-SILEPIN

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	5839(7)	2060(9)	1687(3)	139(9)	385(19)	31(2)	−54(11)	23(4)	−8(6)
C(2)	4990(6)	3339(13)	1397(4)	118(9)	524(27)	38(3)	−11(14)	24(4)	47(7)
C(3)	5075(6)	4835(11)	1748(4)	117(9)	423(21)	47(3)	64(12)	38(5)	59(7)
C(4)	6062(6)	5060(8)	2394(3)	117(7)	302(15)	37(2)	27(10)	34(4)	25(5)
Si(5)	8279(1)	4065(2)	3569(1)	117(2)	158(3)	32(1)	20(2)	33(1)	3(1)
C(6)	10974(6)	3978(7)	4074(3)	133(7)	215(13)	36(2)	8(9)	31(3)	−4(4)
C(7)	12221(5)	3556(8)	4137(3)	117(8)	262(16)	48(2)	−8(8)	27(3)	−10(5)
C(8)	12397(5)	2351(8)	3706(3)	101(7)	274(16)	47(3)	22(9)	33(4)	19(5)
C(9)	11350(6)	1565(7)	3228(3)	129(8)	199(13)	38(2)	31(8)	41(3)	11(4)
C(10)	9017(6)	996(8)	2589(3)	144(8)	305(15)	52(2)	11(10)	34(4)	−38(5)
C(11)	7720(5)	790(7)	2672(3)	152(8)	215(14)	47(2)	−20(9)	36(4)	−14(5)
C(12)	9863(5)	3213(6)	3582(3)	109(7)	158(11)	26(2)	6(7)	27(3)	3(4)
C(13)	10077(5)	1967(6)	3158(3)	131(4)	158(12)	33(2)	11(8)	34(3)	3(4)
C(14)	6814(5)	2221(8)	2342(3)	106(7)	239(15)	34(2)	−15(9)	29(4)	−2(5)
C(15)	6950(4)	3752(8)	2699(2)	100(7)	207(13)	31(2)	25(8)	30(3)	22(5)
C(16)	8463(5)	6360(6)	3779(3)	183(9)	154(12)	56(2)	24(8)	48(4)	−5(4)
C(17)	7803(5)	2976(6)	4245(2)	101(6)	185(12)	26(2)	17(7)	23(3)	−3(4)
C(18)	6674(5)	3460(6)	4339(3)	127(7)	224(13)	35(2)	36(7)	35(3)	9(4)
C(19)	6285(5)	2683(8)	4831(3)	121(7)	297(16)	40(2)	23(9)	46(3)	2(5)
C(20)	7009(6)	1420(8)	5235(3)	165(9)	309(17)	41(2)	43(10)	48(4)	24(5)
C(21)	8104(6)	891(8)	5147(3)	179(9)	321(16)	50(2)	94(10)	59(4)	56(5)
C(22)	8498(5)	1658(8)	4652(3)	125(7)	277(15)	42(2)	62(8)	40(3)	28(5)

[a] See footnote in Table 2.

TABLE 4

COMPARISON OF STRUCTURAL PARAMETERS FOR I AND II AND RELATED CARBOCYCLES

Compound	Dihedral angle (°)	Distance (Å) between centers of benzo rings	Skew (Å) [a]	Twist (°)	Ref.
	129.7	5.33	0.33	00.0	This work
	121	4.87	0.63	2.7	6
	134.1	4.99	0.55	4.2	7
	137.2	5.53	0.28	17.4	This work
	119.9	4.91	0.54	13.4	8
 [b]	114.4 116.8	4.78 4.87	0.61 0.61	12.5 15.0	9

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[a] Difference in distances of carbon atoms related across the central ring. [b] Two molecules per asymmetric unit.

10.3 Å^2. A listing of structure factors is available *.

Compound II is isostructural with 5-methoxy-5-phenyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin [3]. The final coordinates for the 15 atoms in the tricyclic framework of the latter compound were used to calculate phases for a Fourier map of II. The positions of all nonhydrogen atoms were taken from the resultant electron density map. Full matrix least squares refinement with anisotropic thermal parameters for C and Si and inclusion of hydrogen atoms in the same manner as described for I gave final discrepancy values $R_1 = 0.050$ and $R_2 = 0.048$. The largest parameter shift in the final refinement cycle was less than 10% of its standard deviation; the error of fit was 1.68. The highest residual peak in the final electron density map was 0.21 eÅ^{-3}. Table 3 gives the final atomic coordinates and thermal parameters; the fixed isotropic B values for the hydrogen atoms ranged from 5.5 to 7.6 Å^2. A listing of structure factors is available *.

Discussion

The crystal structures of the title compounds consist of discrete monomeric units. No unusual packing distances are present; the shortest intermolecular distances involving nonhydrogen atoms are 3.73 Å in I and 3.62 Å in II. Stereoscopic drawings of each molecule excluding hydrogen atoms are given in Fig. 1 and 2. Appropriate bond distances and angles are recorded for I in Fig. 3; bond distances and angles for II are in Fig. 4. Values of the angles and distances in the rings follow the trends associated with second row element substituents on benzene rings [4].

Compound I contains a crystallographically required mirror plane of symmetry and exhibits the boat conformation for the tricyclic system. Compound II has the expected folded boat conformation [1,3,5].

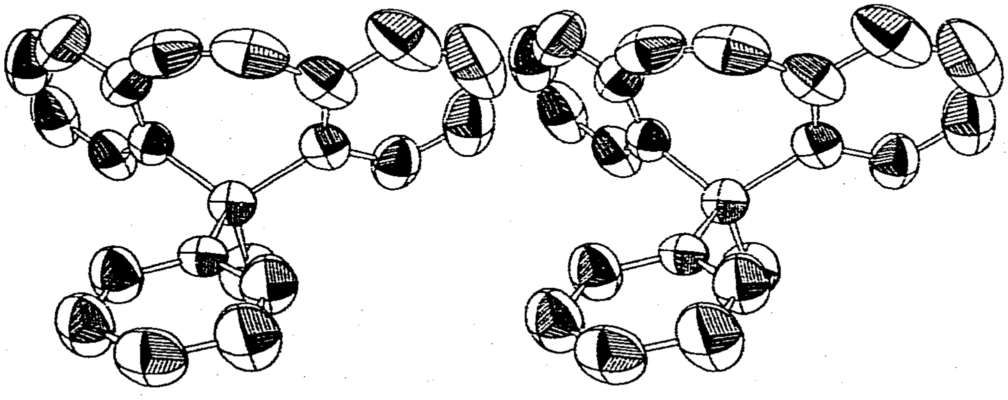

Fig. 1. A stereoscopic drawing of 5-methyl-5-phenyl-5*H*-dibenzo[*b*,*f*] silepin (I) with atoms represented by 50% probability ellipsoids.

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* See NAPS document no. 02914 for 9 pages of supplementary material involving a listing of the observed and calculated structure factors for $C_{21}H_{18}Si$ I and $C_{21}H_{20}Si$ II. 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 checks payable to Microfiche Publications.

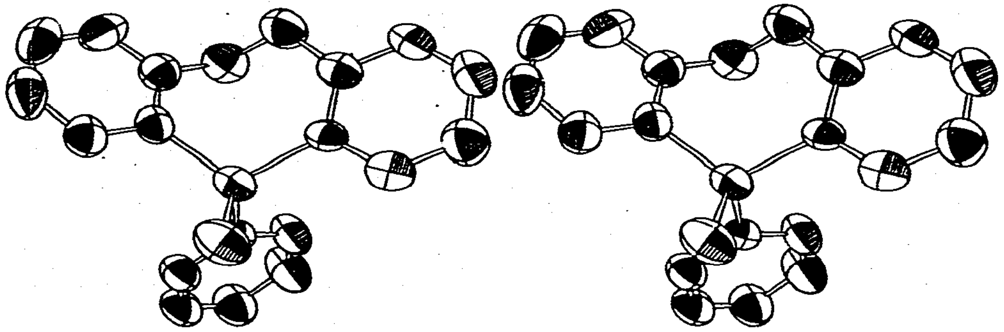

Fig. 2. A stereoscopic drawing of 5-methyl-5-phenyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin, (II), with atoms represented by 50% probability ellipsoids.

A comparison of the structural parameters that have been developed to describe tricyclic systems is presented in Table 4 for the silicon derivatives, I and II, as well as related carbocycles. The dihedral angle between benzo planes for I is smaller than that for II, i.e. the tricyclic framework of I is more bent. The range of dihedral angles observed in 10,11-dihydrodibenzo[*b*,*f*]silepin struc-

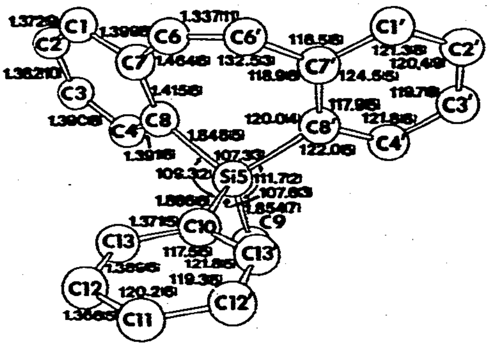

Fig. 3. Bond distances (Å) and angles (°) for I. The crystallographic mirror plane bisects the C(6)—C(6′) bond and contains Si(5), C(9), C(10) and C(11).

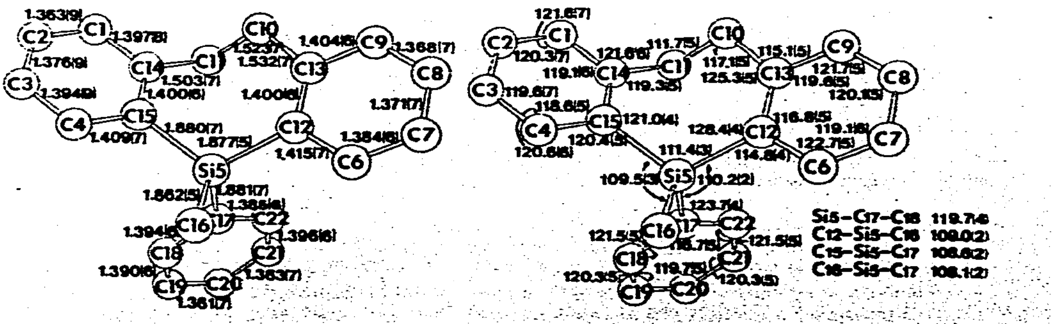

Fig. 4. Bond distances (Å) and angles (°) for II.

tures is 137.2 to 141.8° [1,3,5]. Data for comparison of this parameter in carbocyclic systems with sp^3 carbon at the 5-position are not available at this time. An sp^2 carbon atom at the 5-position results in an increase of the dihedral angle upon introduction of unsaturation in the 10,11-position. The degree of twist in the tricyclic framework decreases with introduction of unsaturation. The twist angle is related to the torsion angle about the 10,11 bond. In I the torsion angle is 0.0° as required by the mirror plane; in II this angle is 89.9° (the range of this torsion angle for 10,11-dihydrodibenzo[*b,f*]silepins is 88.3—92.4° [1,3,5]).

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