Journal of Organometallic Chemistry, 101 (1975) 177—186

THE STRUCTURE OF 5-*p*-*N*,*N*-DIMETHYLAMINOPHENYL-10,11-DIHYDRO-5H-DIBENZO[*b*,*f*]SILEPIN

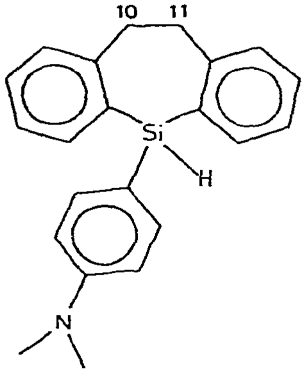
EUGENE R. COREY* and JOYCE Y. COREY
Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121 (U.S.A.)
and MILTON D. GLICK
Department of Chemistry, Wayne State University, Detroit, MI 48202 (U.S.A.)
(Received May 19th, 1975)

Summary

The structure of 5-*p*-*N*,*N*-dimethylaminophenyl-10,11-dihydro-5H-dibenzo[*b*,*f*]silepin has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.121(4)$, $b = 14.379(3)$, $c = 9.126(2)$ Å and $\beta = 99.57(2)°$. The observed and calculated densities ($Z = 4$) are 1.19 and 1.20 g cm^{-3}, respectively. Anisotropic refinement of nonhydrogen atoms with hydrogen atoms at fixed calculated positions gave a conventional *R*-factor of 4.6% for 2023 reflections with $F_0^2 > 3\sigma(F_0^2)$. The central seven-membered ring of the tricyclic system exhibits a folded boat conformation; the dihedral angle between the benzo groups is 137.2°. The benzo groups are twisted approximately 21° relative to one another and skewed such that the two carbons bonded to silicon are 0.33 Å closer to one another than the two benzo ring carbons one atom removed from the silicon. The nitrogen atom is displaced 0.04 Å from the plane of the adjacent carbon atoms.

Introduction

The pharmacological activity of tricyclic ring systems has been attributed in part to the conformation of the tricyclic moiety, but as yet there are insufficient structural data on tricyclic heterocycles to evaluate this effect. The solid state structure of 5-*p*-*N*,*N*-dimethylaminophenyl-10,11-dihydro-5H-dibenzo[*b*,*f*]-silepin (I) is reported in this paper. This is the first structural study of a silicon substituted aniline derivative. The structures of three dibenzo[*b*,*f*]heterocycles with sp^3-hybridized atoms in the 10 and 11 positions have been published:



(I)

4[2-(methylthio)dibenzo[*b,f*]thiepin-11-yl]-1-piperazinylpropanol hemihydrate [1], 5,5-diphenyl-10,11-dihydro-5H-dibenzo[*b,f*]germepin [2] and 5-(3-dimethylaminopropyl)-10,11-dihydro-5H-dibenzo[*b,f*]azepine hydrochloride [3]. No structural reports have been published for the related carbocycle with sp^3 hybridized carbon in the 5-position but two structures with sp^2 carbon in the 5 position have been published: 5-(bromomethylene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene [4] and 3-(10,11-dihydro-5H-dibenz[*a,d*]cycloheptene-5-ylidene)-1-ethyl-2-methylpyrrolidene hydrobromide [5]. (Structural formulas of the compounds are given in Table 3.)

Experimental

Crystals of the title compound were prepared by the method of Corey [6]. A summary of data collection and cell parameters is given in Table 1. The crystal was attached to a glass fiber and mounted on a Syntex $P2_1$ four-circle diffractometer. The space group was assigned on the basis of rotation and axial photographs and counter data. Fifteen reflections with 2θ between 15 and 27 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 MoKα 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 of thirty seconds were taken at each end of the scan.

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

---

* 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. Zalkin's hydrogen atom finding program.

TABLE 1

PHYSICAL CONSTANTS AND EXPERIMENTAL DATA: 5-*p*-*N*,*N*-DIMETHYLAMINOPHENYL-10,11-DIHYDRO-5H-DIBENZO[*b*,*f*]SILEPIN

Molecular formula	$C_{22}H_{23}NSi$
Number of molecules per cell	4
a	14.121(4) Å
b	14.379(3) Å
c	9.126(2) Å
β	99.57(2)°
density (calcd.), g cm^{-3}	1.20
density (found)	1.19
crystal size	0.38 × 0.39 × 0.48 mm
linear absorption coefficent	1.33 cm^{-1}
2θ scan range (deg)	2θ Mo-K_{α_1} — 1.0 to 2θ Mo-K_{α_2} + 1.0
number of independent data collected	3727
number of independent data for which $I > 3\sigma$ (I)	2023
2θ (max)	50° Mo-K_α

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.04 \times I)^2]^{1/2}$$

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 correction for absorption was made. Only those data for which $F^2 > 3\sigma(F^2)$ were used in the structure solution and refinement.

The structure was solved by an iterative application of the Sigma-2 relationship [7,8] using 208 normalized structure factors (E's) of magnitude 1.5 or greater. An E-map based on the set of phases for the solution with the largest consistency index (0.89) contained the positions of the 24 non-hydrogen atoms.

Least squares refinement of the positional and anisotropic thermal parameters of the 24 nonhydrogen atoms yielded $R_1 = 0.082$ and $R_2 = 0.127$. The hydrogen atoms were placed at ideal locations relative to the positional coordinates of all other atoms with C—H distances of 0.97 Å and an Si—H distance of 1.48 Å. Least squares refinement of positional and anisotropic thermal parameters of the nonhydrogen atoms with fixed positional and isotropic thermal parameters for hydrogen atoms set 1.0 $Å^2$ greater than the equivalent B for the atom to which they are bonded resulted in discrepancy values of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.046 \text{ and } R_2 = [\Sigma(w|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.056$$

The largest parameter shift in the final cycle of refinement was 8% of its standard deviation. The error of fit was 1.79. Scattering factors were taken from Vol. IV of the International Tables [9]. The highest residual electron density in the final difference map was 0.38 $eÅ^{-3}$. Table 2 lists the atomic coordinates and thermal parameters. A listing of structure factors is available[*].

---

[*] The Table of structure factors has been deposited as NAPS Document No. 02678 (10 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting \$ 5.00 for photocopies or \$ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside of the U.S.A. and Canada, postage is \$ 2.00 for a photocopy or \$ 1.00 for a fiche.

TABLE 2

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS FOR 5-*p*-*N*,*N*-DIMETHYLAMINOPHENYL-10,11-DIHYDRO-5H-DIBENZO-[*b*,*f*]SILEPIN [a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	0.25542(6)	0.44338(6)	−0.01896(9)	477(5)	514(5)	1203(12)	37(4)	36(6)	−14(6)
N	0.5381(2)	0.6484(2)	0.4456(3)	567(18)	871(22)	1763(47)	−98)16)	7(23)	−273(26)
C1	0.1449(2)	0.3980(2)	0.0463(3)	576(19)	407(11)	1156(43)	2(14)	51(22)	−41(21)
C2	0.0532(2)	0.3864(2)	−0.0391(3)	524(19)	335(16)	1329(44)	29(14)	116(23)	−119(21)
C3	−0.0210(2)	0.3517(2)	0.0294(4)	562(21)	464(20)	1857(57)	−11(16)	233(27)	−120(27)
C4	−0.0069(3)	0.3266(2)	0.1768(4)	783(25)	475(20)	1805(58)	−8(18)	440(32)	−45(27)
C5	0.0837(3)	0.3356(2)	0.2616(4)	960(29)	503(21)	1382(49)	−8(20)	351(31)	37(25)
C6	0.1570(2)	0.3713(2)	0.1970(3)	691(22)	530(20)	1296(48)	−7(17)	66(25)	10(24)
C7	0.0266(2)	0.4112(2)	−0.2011(3)	570(20)	515(10)	1308(45)	−92(15)	−46(23)	−80(23)
C8	0.1059(2)	0.4054(2)	−0.2992(3)	678(21)	513(20)	1200(44)	9(16)	47(24)	−156(23)
C9	0.2256(2)	0.5240(2)	−0.1808(3)	482(18)	498(18)	1186(43)	36(15)	179(22)	−31(22)
C10	0.1598(2)	0.4955(2)	−0.3053(3)	528(19)	544(20)	1125(43)	55(16)	161(22)	−36(23)
C11	0.1422(2)	0.5511(3)	−0.4308(3)	648(22)	692(23)	1300(47)	63(19)	171(24)	152(28)
C12	0.1871(3)	0.6354(3)	−0.4350(4)	668(24)	810(27)	1631(58)	146(21)	273(30)	268(32)
C13	0.2512(3)	0.6658(3)	−0.3138(5)	676(24)	612(23)	2271(67)	3(18)	461(33)	222(32)
C14	0.2705(2)	0.6102(2)	−0.1865(4)	556(20)	611(22)	1581(52)	−32(17)	214(25)	2(27)
C15	0.3384(2)	0.4999(2)	0.1342(3)	465(18)	564(20)	1264(44)	36(15)	16(21)	44(24)
C16	0.4377(2)	0.4843(3)	0.1507(3)	518(20)	738(23)	1437(50)	75(17)	108(25)	−123(28)
C17	0.5026(2)	0.5317(3)	0.2536(4)	421(18)	832(26)	1630(53)	62(17)	48(25)	−85(29)
C18	0.4735(2)	0.5982(2)	0.3468(3)	460(19)	654(21)	1301(45)	−24(16)	26(23)	30(26)
C19	0.3742(2)	0.6124(3)	0.3352(4)	525(21)	722(24)	1697(54)	−17(17)	161(27)	−271(28)
C20	0.3101(2)	0.5646(3)	0.2307(4)	442(18)	752(24)	1791(55)	34(17)	80(25)	−213(30)
C21	0.5066(3)	0.7099(3)	0.5525(5)	870(29)	982(32)	2208(80)	−256(24)	75(36)	−445(39)
C22	0.6403(3)	0.6348(3)	0.4530(4)	553(23)	1094(33)	2305(71)	−66(22)	−331(31)	−206(39)

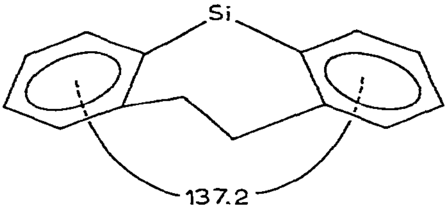
[a] Estimated standard deviation from the full variance-covariance matrix is given in parentheses for the least significant digit(s). The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$. The β's are multiplied by 10^5.

Discussion

The crystal structure of the title compound consists of discrete monomeric units. A stereoscopic molecular view excluding hydrogen atoms is given in Fig. 1 and a stereoscopic view of the unit cell contents including hydrogen atoms is given in Fig. 2*. All nonhydrogen atom intermolecular contacts are greater than 3.5 Å; the shortest intermolecular contact that involves a hydrogen atom is 2.8 Å between C(4) and a hydrogen atom bonded to C(9). Bond distances and angles are presented in Fig. 3.

The conformation of tricyclic ring systems has been described previously with four parameters [11]. The angles and distances used by Wilhelm and Kuhn were obtained from Dreiding models. The X-ray structural results are more conveniently described using the parameters given below.

The first is a bending angle defined as the dihedral angle between the planes of the benzo rings. This dihydrosilepin has a bending angle of 137.2° (II) between the experimentally planar rings.



(II)

The second and third parameters involve the twist (out of plane) and skew (in plane) of the two benzo rings relative to one another. The benzo rings are

(continued on p. 184)

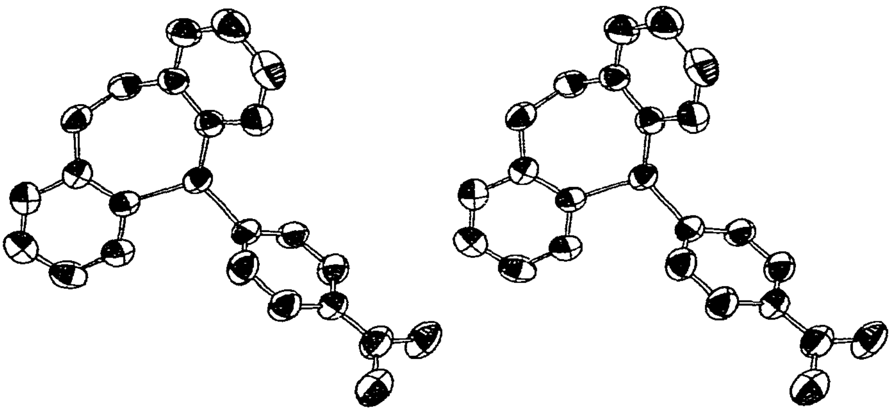


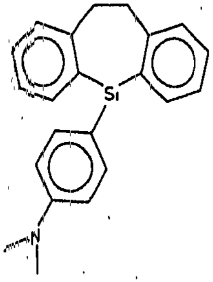
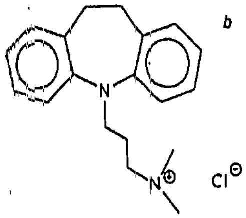
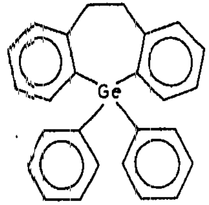
Fig. 1. A stereoscopic view of the 5-*p*-*N*,*N*-dimethylaminophenyl-10,11-dihydro-5H-dibenzo[*b*,*f*]silepin molecule. The atoms are represented by 50% probability thermal ellipsoids.

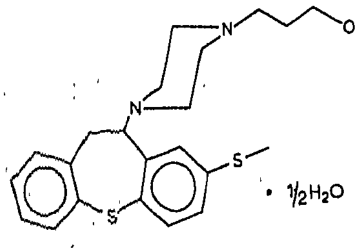
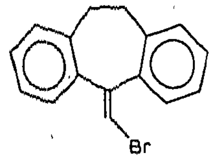
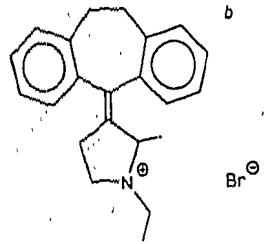
---

* This figure was prepared on and photographed from the plasma screen of a laboratory interactive computer system [10].

TABLE 3

COMPARISONS OF STRUCTURAL PARAMETERS OF RELATED TRYCYCLIC SYSTEMS

Compound	Dihedral angle (°) between benzo rings	Distance (Å) between centers of benzo rings	Distance (Å) between benzo carbons bonded to the heteroatom [a]	Distance (Å) between benzo carbon atoms one removed from the hetero-atom site[a]	Out of plane Twist of benzo rings (°)	Reference
	137.2	5.56	3.41	3.74	20.8	this work
 [b] Molecule A: Molecule B:	130.3 123.0	4.96 4.79	2.47 2.42	3.14 3.03	17.2 8.4	[3]
	156.4	5.74	3.28	3.47	1.0	[2]

		103.7	4.79	2.71	3.06	11.8	[1]
		119.9	4.91	2.60	3.14	13.4	[4]
 [b]	Molecule A: Molecule B:	114.4 116.8	4.78 4.87	2.48 2.54	3.09 3.15	12.5 15.0	[5]

---

[a] Carbon 5 in the carbocycles. [b] Two molecules per asymmetric unit.

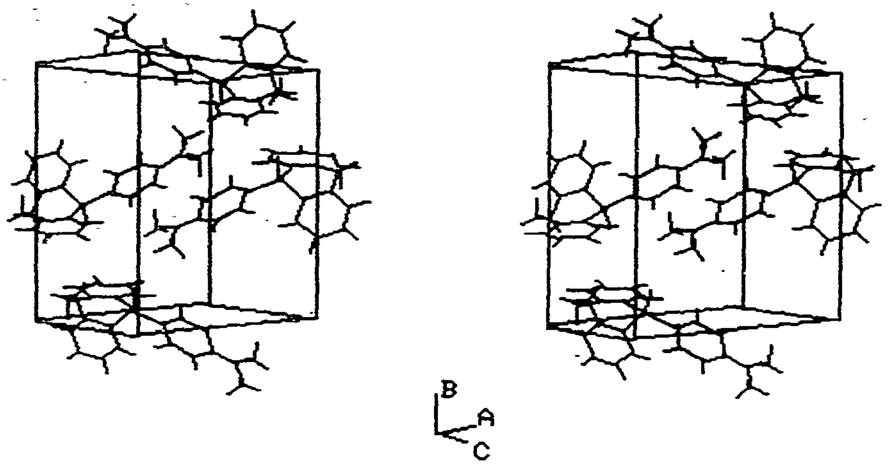
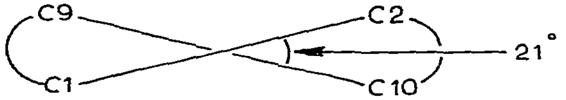


Fig. 2. A stereoscopic view of the unit cell contents including hydrogen atoms at calculated positions.

twisted in opposite directions by an angle of approximately 21° (III) and are skewed so that the carbon atoms bonded to the silicon (C(1)...C(9), 3.14 Å)



(III)

are closer than the carbon atoms one removed from the silicon (C(2)...C(10),

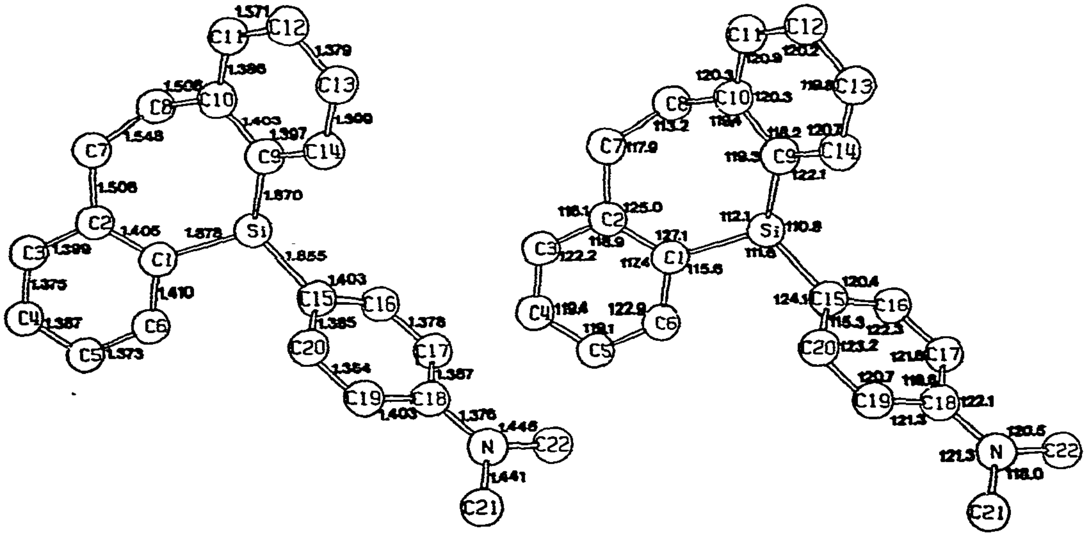


Fig. 3. Bond distances and angles. Estimated standard deviations for bond distances: Si—C, 0.003; N—C, 0.004 (except N—C(21), 0.005); C—C, 0.004 (except C(3)—C(4), C(4)—C(5), C(5)—C(6), C(11)—C(12), C(12)—C(13), and C(13)—C(14), 0.005). Estimated standard deviations for angles: C—Si—C, 0.1; Si—C—C, 0.2; C—N—C, N—C—C and C—C—C, 0.3 (except C(7)—C(8)—C(10), 0.2).

TABLE 4

TORSION ANGLES (°) IN THE SEVEN-MEMBERED RING

C(9)-Si-C(1)-C(2)	−27.3(3)
Si-C(1)-C(2)-C(7)	1.5(4)
C(1)-C(2)-C(7)-C(8)	−29.6(4)
C(2)-C(7)-C(8)-C(10)	90.7(3)
C(7)-C(8)-C(10)-C(9)	−73.1(3)
C(8)-C(10)-C(9)-Si	−7.1(4)
C(10)-C(9)-Si-C(1)	51.6(3)

3.74 Å). The average angles of 82.4 and 96.0° in the trapezoidal projection of the benzo carbons in the central ring provide a quantitative measure of the skewing in the system. A fourth parameter is the distance between the centers of the benzo rings which is 5.56 Å. These data are compared in Table 3 with similar information for other dibenzo tricyclic systems with central seven-membered rings. The table includes only compounds with sp^3 hybridized atoms at the 10,11-positions of the heterocycle and analogous carbocyclic systems. The twist

TABLE 5

DEVIATIONS (Å) OF ATOMS FROM SELECTED LEAST SQUARES PLANES[a]

Plane 1. $0.107X + 0.747Y - 0.657Z = 5.03$			
Si^b	−0.23	C(19)	−0.07
C(15)^b	−0.03	C(20)^b	−0.10
C(16)^b	0.09	C(21)	0.00
C(17)^b	0.10	C(22)	0.00
C(18)	0.00	N^b	−0.04
Plane 2. $0.497X - 0.832Y - 0.247Z = -4.01$			
Si^b	−0.56	C(8)^b	−0.80
C(1)	−0.13	C(9)	0.13
C(2)	0.12	C(10)	−0.12
C(3)^b	0.43	C(11)^b	0.30
C(6)^b	−0.09	C(14)^b	0.83
C(7)^b	0.12	C(15)^b	−0.01
Plane 3. $0.282X - 0.927Y - 0.248Z = -4.84$			
Si^b	0.00	C(6)	0.00
C(1)	0.01	C(7)^b	−0.01
C(2)	−0.01	C(8)^b	−0.66
C(3)	0.00	C(9)^b	0.76
C(4)	0.01	C(10)^b	0.31
C(5)	−0.01	C(15)^b	0.83
Plane 4. $0.818X - 0.445Y - 0.366Z = 0.068$			
Si^b	−0.13	C(10)	0.01
C(1)^b	1.15	C(11)	0.00
C(2)^b	1.75	C(12)	0.00
C(7)^b	1.48	C(13)	0.00
C(8)^b	0.08	C(14)	0.00
C(9)	−0.01	C(15)^b	0.03

[a] X, Y, Z, are orthogonal unit vectors defined by the equations: $X = a$, $Y = b$, $Z = a \times b$. The equation for the plane is $aX + bY + cZ = d$. [b] Atoms not included in the least squares plane.

angles are the averages of the torsion angles about the nonbonded vectors across the central ring that involve the benzo carbon atoms (e.g., C(2)-C(1)-C(9)-C(10) and C(1)-C(2)-C(10)-C(9). Torsion angles for the central ring are presented in Table 4 and indicate considerable ring strain.

The phenyl moiety of the dimethylaminophenyl substituent forms a dihedral angle of 110° with the best plane for the central ring benzo carbon atoms (C(1), C(2), C(9) and C(10); plane 2 in Table 5). The dimethylamino fragment is rotated 4.4° from the plane of the phenyl ring to which it is bonded with the nitrogen atom displaced 0.04 Å from the plane of the adjacent carbon atoms (C(18), C(21) and C(22); plane 1 in Table 5). The differences in C—N distances may be explained qualitatively by the sp^2 vs. sp^3 hybridization of the carbon atoms bonded to the nitrogen atom. The near planarity of the dimethylaminophenyl substituent may be a result of delocalization of electrons into silicon orbitals of π symmetry [12,13] and is supportive of the ground state bonding description of R_3Si substituted anilines [13]. The orientation of the dimethylaminophenyl substituent minimizes hydrogen—hydrogen interactions involving the hydrogens bonded to carbon atoms 6, 14, 16 and 20. The Si—C(15) bond distance of 1.855(3) Å is significantly shorter ($\sim 5\sigma$) than the Si—C(1) and Si—C(9) bond lengths of 1.878(3) and 1.870(3) Å, respectively. The latter two bond lengths are in agreement with Si—C bond distances compiled by Yokoi [14]. Table 5 also gives the displacement of selected atoms from the benzo ring least squares planes (planes 3 and 4 in Table 5).

Additional structural studies are in progress to determine the effect of heteroatom replacement of carbon and nitrogen on the bending and twist angles and the skewing of benzo groups in these tricyclic systems.

Acknowledgement

The authors thank the computer center at Wayne State University. J.Y.C. and E.R.C. acknowledge support by NIH research grant number R01NS10903 from National Institute of Neurological Diseases and Stroke, and wish to thank Hans Bock for helpful discussions.

References

1 M.H.J. Koch and G. Evrard, Acta Crystallogr., Sect. B, 30 (1974) 2925.
2 J.Y. Corey, E.R. Corey, M.D. Glick and J.S. Dueber, J. Heterocycl. Chem., 9 (1972) 1379.
3 M.L. Post, O. Kennard and A.S. Horn, Acta Crystallogr. Sect. B, 31 (1975) 1008.
4 K. Larsson, Acta Chem. Scand., 24 (1970) 1503.
5 Y. Tokuma, H. Nojima and Y. Morimoto, Bull. Chem. Soc. Jap., 44 (1968) 2665.
6 J.Y. Corey, J. Amer. Chem. Soc., 97 (1975) 3237.
7 R.E. Long, Ph.D. Thesis (Part III), University of California, Los Angeles, California (1965).
8 R. Sayre, Acta Crystallogr., 5 (1952) 60.
9 J.A. Ibers and W.C. Hamilton, Ed., "International Tables for X-ray Crystallography, "Vol. IV, The Kynoch Press, Birmingham, England (1974).
10 M.D. Glick and D.L. Fulton, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa, April 1975, COMP8.
11 M. Wilhelm and R. Kuhn, Pharmakopsychiat., 3 (1970) 317.
12 H. Alt and H. Bock, Tetrahedron, 27 (1971) 4965.
13 M.J. Drews, P.S. Wong and P.R. Jones, J. Amer. Chem. Soc., 94 (1972) 9122.
14 M. Yokoi, Bull. Chem. Soc. Japan, 30 (1957) 100, 106.