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THE STRUCTURE OF A SILICON ANALOG OF THE PSYCHOTROPIC DRUG PERATHIEPIN: 5,5-DIMETHYL-10-(4-METHYLPIPERAZINYL)-10,11-DIHYDRO-5*H*-DIBENZO[*b*,*f*]SILEPIN HYDROFUMARATE

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Summary

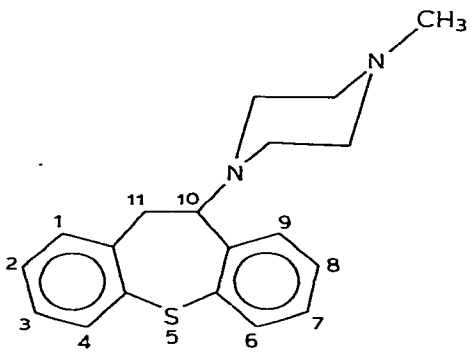
The solid state structure of the hydrofumarate salt of 5,5-dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin (II), a silicon analog of perathiepin (I) in which divalent sulfur is replaced by the $(CH_3)_2Si$ moiety, has been determined by X-ray diffraction methods. The compound, $C_{25}H_{32}N_2O_4Si$, crystallizes in the orthorhombic space group, $Pbc2_1$ with a 9.304(2), b 23.010(7), c 11.599(3) Å; the structure was refined by full-matrix least-squares techniques to a conventional R of 0.039 for 1858 counter reflections. The structure consists of a network of hydrogen-bonded hydrofumarate anions and the protonated heterocyclic unit. The tricyclic framework of the cation adopts a folded boat conformation with a dihedral angle between benzo group planes of 151.2°. In contrast to related systems, the piperazinyl substituent which has the expected chair conformation occupies a pseudoaxial site on the ethano bridge. Structural parameters of the tricyclic framework of the title compound and related compounds are compared.

Introduction

A number of widely administered psychotropic drugs have common molecular features: a dibenzo tricyclic framework with a central six- or seven-membered ring and a chain of three atoms separating a terminal amino function from the tricyclic moiety [1].

Tricyclic pharmaceuticals with a central seven-membered ring include the antidepressant carbocycle, amitriptyline [2]; imipramine hydrochloride, an antidepressant with nitrogen in the 5-position of the central ring [3], doxepin,

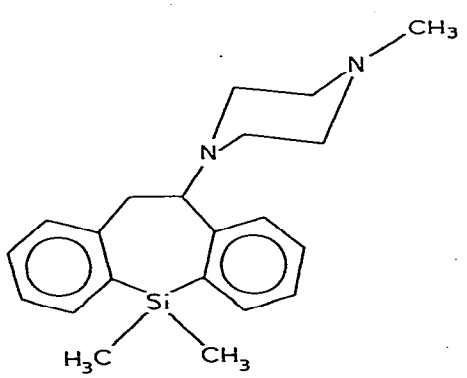
an antipuretic with oxygen in the 10-position of the central ring [2]; the neuroleptics loxapine with chlorine at the 2-position and nitrogen in the 5- and 10-positions, respectively [4,5], clozapine with chlorine at the 2-position and nitrogen atoms in the 5- and 11-positions [5] and perathiepin (I) with a sulfur heteroatom in the 5-position and the basic substituent at the 10-position [6].



(I)

It has been suggested that these tricyclic drugs act in the brain by inhibiting the process of the uptake of the biogenic amines, noradrenaline and 5-hydroxytryptamine, into the presynaptic nerve ending by simulating the conformation of a biologically important region of the biogenic amine and blocking the receptor site [7—9].

The pharmacological activity of tricyclic compounds with silicon in the central seven-membered ring has been documented. The neuroleptic activity of the dimaleate salt of 5,5-dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin (II) has been reported [6]. The activity of the silicon compound as a central nervous system depressant is weaker than that of perathiepin (I) by two orders of magnitude [6].



(II)

The pharmacological activity of silicon containing compounds is not limited to this silepin derivative. A related compound (3-dimethylaminopropyl)methyl-

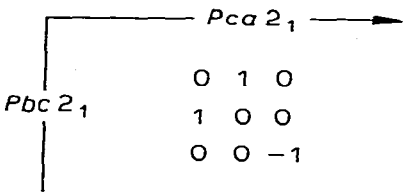
diphenylsilane hydrochloride exhibits tranquilizing activity [10]: Voronkov [11,12] has documented the biological activity of silicon containing compounds with a wide variety of effects.

As part of a synthetic [13,14] and structural [15] research program concerned with silicon analogs of tricyclic compounds, we wish to report the solid state structure of the hydrofumarate salt of 5,5-dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin hydrofumarate (II), a silicon analog of perathiepin in which divalent sulfur is replaced by the $(CH_3)_2Si$ moiety.

Experimental

Crystal data

Crystals of 5,5-dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin hydrofumarate, $C_{25}H_{32}N_2O_4Si$, are orthorhombic with *a* 9.304(2), *b* 23.010(7) and *c* 11.599(3) Å; cell parameters were determined by least-squares refinement of fifteen high angle reflections. A calculated density of 1.21 g cm^{-3} and an experimental density of 1.19(1) g cm^{-3} indicated four formula units per cell. Systematic absences of $0kl$ with k odd and $h0l$ with l odd are consistent with either space groups *Pbcm* or $Pbc2_1$; the latter is a nonstandard setting of $Pca2_1$ [16]. The presence of four formula weights per cell and the unlikelihood of crystallographically required symmetry favors the choice of $Pbc2_1$ as the space group. The transformation matrix to the standard setting is:



Data collection

A 0.7 × 0.4 × 0.3 mm crystal was attached to a glass fiber and placed on a Syntex $P2_1$ diffractometer. Intensity data were collected to $2\theta = 54°$ with Mo-K_α (λ 0.71069 Å) radiation (graphite monochromator) and the θ—2θ scan technique with a scan speed of 2.0° min^{-1}. Backgrounds were measured at each end of the scan (2θ scan range: 2θMo-$K_{\alpha 1}$—1.0° to 2θMo-$K_{\alpha 2}$ + 1.0°) for a total time equal to one-half the scan time. During data collection the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$. 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 counts, K = ratio of scan time to background time. No absorption corrections were made (μ 1.31 cm^{-1}). A total of 1858 intensities greater than $3\sigma(I)$ were obtained from 3031 reflections scanned.

TABLE 1

FINAL POSITIONAL ($\times 10^4$) AND ANISOTROPIC THERMAL ($\times 10^4$) PARAMETERS [a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	6068(5)	3707(2)	−642(4)	211(8)	21(1)	74(4)	12(2)	−26(5)	−3(2)
C(2)	4662(5)	3518(2)	−478(5)	155(8)	20(1)	99(4)	−9(2)	−52(5)	1(2)
C(3)	3864(5)	3744(2)	401(5)	133(7)	20(1)	108(5)	−10(2)	−20(5)	7(2)
C(4)	4447(5)	4166(2)	1098(4)	128(6)	18(1)	86(4)	3(2)	0(5)	3(2)
Si(5)	6354(1)	4983(1)	1960 [b]	106(1)	17.3(2)	57(1)	5.9(5)	1(1)	−5.5(4)
C(6)	8368(5)	5893(2)	2048(4)	177(7)	18(1)	93(4)	−1(2)	−12(6)	−3(2)
C(7)	9683(6)	6172(2)	1960(5)	200(8)	18(1)	113(5)	−18(2)	−55(7)	7(2)
C(8)	10883(6)	5886(2)	1510(5)	175(8)	22(1)	105(5)	−23(3)	−33(5)	16(2)
C(9)	10685(5)	5313(2)	1143(4)	122(6)	26(1)	92(4)	−9(2)	−9(5)	18(2)
C(10)	9289(4)	4399(2)	832(4)	87(5)	20(1)	62(3)	5(2)	9(3)	0(1)
C(11)	8225(5)	4313(2)	−176(4)	140(6)	21(1)	62(3)	9(2)	10(4)	0(1)
C(12)	6672(4)	4135(2)	78(3)	124(6)	16(1)	48(3)	2(2)	−18(4)	1(1)
C(13)	5851(4)	4376(2)	966(4)	102(5)	14(1)	59(3)	4(2)	−4(4)	4(1)
C(14)	8174(4)	5312(2)	1699(4)	129(6)	15(1)	67(4)	0(2)	−16(4)	3(1)
C(15)	9375(4)	5026(2)	1241(4)	104(5)	17(1)	64(3)	0(2)	−4(4)	8(1)
C(16)	6198(5)	4738(2)	3487(4)	162(7)	30(1)	67(4)	3(2)	15(5)	−4(2)
C(17)	4982(5)	5567(2)	1683(5)	173(7)	24(1)	121(4)	23(2)	−22(5)	−17(2)
N(18)	8996(3)	4014(1)	1834(3)	89(4)	15(1)	61(3)	3(1)	2(3)	−2(1)
C(19)	8926(4)	3398(2)	1477(4)	97(5)	17(1)	76(3)	7(2)	−7(3)	−7(1)
C(20)	8642(4)	3010(2)	2490(4)	94(5)	16(1)	94(4)	−1(2)	7(4)	−1(2)
N(21)	9839(3)	3066(1)	3331(3)	83(4)	19(1)	69(3)	7(1)	20(3)	4(1)
C(22)	9932(4)	3683(2)	3712(4)	120(6)	20(1)	64(3)	9(2)	−2(4)	−2(2)
C(23)	10141(4)	4076(2)	2684(4)	112(6)	16(1)	70(3)	0(2)	−12(4)	−1(1)
C(24)	9688(5)	2659(2)	4338(4)	158(7)	22(1)	88(4)	10(2)	42(5)	14(2)
O(25)	13259(3)	3011(1)	3488(3)	122(4)	32(1)	72(3)	12(2)	12(3)	−7(1)
O(26)	11959(3)	2626(1)	2101(3)	79(3)	31(1)	94(3)	14(1)	16(3)	−9(1)
C(27)	13134(4)	2726(2)	2575(4)	89(5)	21(1)	61(3)	8(2)	12(4)	7(2)
C(28)	14459(3)	2489(2)	2017(4)	77(4)	19(1)	74(4)	5(2)	12(4)	5(2)
C(29)	14451(4)	2205(2)	1051(4)	79(5)	19(1)	71(4)	5(2)	11(4)	5(2)
C(30)	15805(5)	1999(2)	506(4)	93(6)	15(1)	87(4)	6(2)	19(4)	5(2)
O(31)	16939(3)	1991(1)	1008(3)	82(4)	28(1)	120(3)	13(1)	8(3)	−3(1)
O(32)	15713(3)	1832(1)	−577(3)	111(4)	31(1)	88(3)	10(1)	27(3)	−5(1)

[a] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Fixed parameter.

TABLE 2

FINAL HYDROGEN ATOM POSITIONAL PARAMETERS (X 10^3) AND THERMAL PARAMETERS [a]

	x	y	z	B (Å^2)
H(C(1))	666	354	—128	5.4
H(C(2))	424	322	—100	5.0
H(C(3))	286	360	54	5.2
H(C(4))	384	433	173	4.7
H(C(6))	753	611	237	5.3
H(C(7))	979	658	223	5.5
H(C(8))	1179	609	144	5.4
H(C(9))	1153	511	80	5.0
H(C(10))	1026	429	54	3.8
H(C(11))′	864	401	—69	4.5
H(C(11))″	818	469	—60	4.5
H(C(16))′	686	440	362	5.5
H(C(16))″	518	462	365	5.5
H(C(16))‴	647	506	401	5.5
H(C(17))′	400	541	186	5.9
H(C(17))″	503	569	86	5.9
H(C(17))‴	518	591	219	5.9
H(C(19))′	986	329	112	3.9
H(C(19))″	813	335	90	3.9
H(C(20))′	857	260	222	4.2
H(C(20))″	772	313	287	4.2
H(N(21))	1075	297	292	3.7
H(C(22))′	1076	373	425	4.3
H(C(22))″	902	379	412	4.3
H(C(23))′	1016	449	296	4.0
H(C(23))″	1108	398	231	4.0
H(C(24))′	968	225	405	5.0
H(C(24))″	877	274	475	5.0
H(C(24))‴	1052	271	487	5.0
H(C(28))	1540	255	241	3.8
H(C(29))	1351	212	66	3.7
H(O(32))	1467	190	—97	5.2

[a] Isotropic thermal parameters have been assigned fixed values 10% greater than the equivalent B's of the atoms bonded to the hydrogen atoms.

Structure solution and refinement

The structure was solved with the program MULTAN *. A multisolution tangent refinement procedure using the Lessinger strategy [17] provided a solution with a combined figure of merit of 2.06 that led to a trial partial structure of thirteen atoms. The remaining nonhydrogen atoms were located in successive Fourier syntheses.

Least-squares refinement of the non-hydrogen atom positional parameters and isotropic thermal parameters gave an $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.097$. Refinement was continued with anisotropic thermal parameters for the nonhy-

* 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.

drogen atoms; the hydrogen atoms were included in the calculations at ideal locations with fixed distance of 1.0 Å from carbon and nitrogen and 1.08 Å from oxygen. The hydrogen atoms were assigned isotropic thermal parameters 10% larger than the equivalent B of the atom to which they are bonded. Scattering factors were taken from the International Tables for X-ray Crystallography; those for silicon were corrected for anomalous dispersion [18]. Tables 1 and 2 give the final positional and thermal parameters with associated estimated standard deviations. Final discrepancy values were $R_1 = 0.039$ and $R_2 = [\Sigma(w|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2} = 0.041$. The largest parameter shift in the final cycle of full matrix refinement was 7% of its standard deviation; the error of fit was 1.63. The highest residual electron density in the final difference map was 0.60 e Å^{-3}. A listing of structure factors is available *.

Discussion

The structure of 5,5-dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin hydrofumarate consists of a network of hydrogen-bonded acid-base pairs of hydrofumarate ions and protonated heterocyclic units. A stereoscopic view of one such acid-base pair is shown in Fig. 1. Fig. 1 also identifies the atom labels for the compound. Table 3 contains the values for the interatomic bond lengths and angles with estimated standard deviations.

Five parameters have been used [19,20] to describe the conformation of the tricyclic framework of 10,11-dihydro-dibenzo[*a*,*d*]cycloheptene and its analogs: (1) the dihedral angle between the benzo group planes; (2) the distance between the centers of the benzo groups; (3) the skew distance in the central ring as measured by the difference between nonbonded distances between the benzo carbon atoms at positions 12 and 15 and positions 13 and 14 (see Fig. 1); (4) the out of plane twist of the benzo rings, defined as the average value of the torsion angles about the vectors joining positions 12 and 15 and positions 13 and 14; and (5) the torsion angle about the bond between the atoms at the 10 and 11 positions in the ethano bridge. Values of these five parameters for the title compound are listed in Table 4 with corresponding values for the related thiepin compounds.

The structures of a number of psychoactive tricyclic compounds with central seven-membered rings and a piperazinyl substituent at the 10-position of the tricyclic framework have been determined [4,5,21,22]. In these compounds, the piperazinyl substituents have a chair conformation and the following three features in common: (1) the mean plane of the carbon atoms of the piperazinyl ring is roughly parallel to one of the benzo group planes, (2) the nitrogen atom (N(4) in Table 5) is at least 1.5 Å closer to the center of one of the benzo rings and (3) the same nitrogen atom is displaced from the plane of the closest benzo ring by less than 1 Å [22]. In contrast to these related systems which have the

* See NAPS document no. 03461 for 13 pages of supplementary material involving a listing of the observed and calculated structure factors, least squares planes and displacement of atoms from planes and nonhydrogen intermolecular contact distances. 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 $ 3.00 for microfiche or $ 5.00 for photocopies up to 30 pages, 15 c for each additional page. Make checks payable to Microfiche Publications. Outside the U.S.A. and Canada add postage of $ 3.00 for photocopy and $ 1.00 for microfiche.

TABLE 3

INTERATOMIC BOND LENGTHS AND ANGLES

Bond lengths (Å)

C(1)—C(2)	1.392(6)	C(11)—C(12)	1.530(6)
C(1)—C(12)	1.408(5)	C(12)—C(13)	1.398(5)
C(2)—C(3)	1.365(7)	C(14)—C(15)	1.401(5)
C(3)—C(4)	1.374(6)	N(18)—C(19)	1.477(5)
C(4)—C(13)	1.401(6)	N(18)—C(23)	1.459(5)
Si(5)—C(13)	1.870(4)	C(19)—C(20)	1.500(6)
Si(5)—C(14)	1.880(4)	C(20)—N(21)	1.486(5)
Si(5)—C(16)	1.865(5)	N(21)—C(22)	1.490(5)
Si(5)—C(17)	1.881(5)	N(21)—C(24)	1.504(5)
C(6)—C(7)	1.385(6)	C(22)—C(23)	1.509(6)
C(6)—C(14)	1.407(6)	O(25)—C(27)	1.251(5)
C(7)—C(8)	1.365(7)	O(26)—C(27)	1.245(5)
C(8)—C(9)	1.392(5)	C(27)—C(28)	1.496(5)
C(9)—C(15)	1.392(6)	C(28)—C(29)	1.297(6)
C(10)—C(11)	1.544(6)	C(29)—C(30)	1.487(5)
C(10)—C(15)	1.520(5)	C(30)—O(31)	1.205(5)
C(10)—N(18)	1.487(5)	C(30)—O(32)	1.317(5)

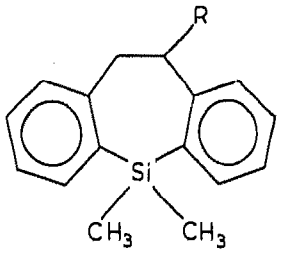
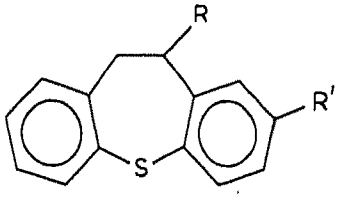
Bond angles (°)

C(2)—C(1)—C(12)	120.9(4)	Si(5)—C(14)—C(6)	116.9(3)
C(1)—C(2)—C(3)	119.6(4)	Si(5)—C(14)—C(15)	126.1(3)
C(2)—C(3)—C(4)	119.6(4)	C(6)—C(14)—C(15)	116.9(4)
C(3)—C(4)—C(13)	123.2(5)	C(9)—C(15)—C(10)	118.1(4)
C(13)—Si(5)—C(14)	115.3(2)	C(9)—C(15)—C(14)	120.4(4)
C(13)—Si(5)—C(16)	109.9(2)	C(10)—C(15)—C(14)	121.5(3)
C(13)—Si(5)—C(17)	104.9(2)	C(10)—N(18)—C(19)	111.2(3)
C(14)—Si(5)—C(16)	110.2(2)	C(10)—N(18)—C(23)	109.6(3)
C(14)—Si(5)—C(17)	107.2(2)	C(19)—N(18)—C(23)	108.4(3)
C(16)—Si(5)—C(17)	109.0(2)	N(18)—C(19)—C(20)	111.1(3)
C(7)—C(6)—C(14)	122.2(4)	C(19)—C(20)—N(21)	109.3(3)
C(6)—C(7)—C(8)	120.0(4)	C(20)—N(21)—C(22)	108.7(3)
C(7)—C(8)—C(9)	119.6(4)	C(20)—N(21)—C(24)	112.7(3)
C(8)—C(9)—C(15)	121.0(4)	C(22)—N(21)—C(24)	111.6(3)
C(11)—C(10)—C(15)	113.1(3)	N(21)—C(22)—C(23)	110.1(3)
C(11)—C(10)—N(18)	113.4(3)	N(18)—C(23)—C(22)	112.4(3)
C(15)—C(10)—N(18)	109.4(3)	O(25)—C(27)—O(26)	123.5(4)
C(10)—C(11)—C(12)	119.6(3)	O(25)—C(27)—C(28)	118.7(4)
C(1)—C912)—C(11)	116.8(4)	O(26)—C(27)—C(28)	117.7(4)
C(1)—C(12)—C913)	119.7(4)	C(27)—C(28)—C(29)	123.5(4)
C(11)—C(12)—C(13)	123.5(4)	C(28)—C(29)—C(30)	121.5(4)
C(4)—C(13)—Si(5)	115.1(3)	C(29)—C(30)—O(31)	122.8(4)
C(4)—C(13)—C(12)	116.9(4)	C(29)—C(30)—O(32)	116.3(4)
Si(5)—C(13)—C(12)	127.9(3)	O(31)—C(30)—O(32)	120.9(4)

piperazinyl substituent in a pseudoequatorial site, the piperazinyl substituent on the silepin compound occupies a pseudoaxial position on the ethano bridge. The mean plane of the carbon atoms of the piperazinyl ring is nearly perpendicular to the plane of one of the benzo rings; nitrogen atom, N(21), is equidistant from the centers of the benzo rings; and this nitrogen atom is displaced by more than 3.5 Å from the plane of the closest benzo ring. Table 5 summarizes the structural parameters that describe the orientation of the piperazinyl substituents.

TABLE 4

STRUCTURAL PARAMETERS DESCRIBING THE CONFORMATION OF THE TRICYCLIC FRAMEWORK OF 10,11-DIHYDRO-5H-DIBENZ[*a*, *d*]CYCLOHEPTENE DERIVATIVES AND RELATED COMPOUNDS [a]

	Dihedral angle (°)	Ring center distance (Å)	Skew (Å)	Twist (°)	10-11 Torsion angle (°)	Ref.
 —N⟨⟩NCH$_3$ · C$_4$H$_4$O$_4$	151.2	5.73	0.35	21.3	93.6	*b*
 —N⟨⟩N(CH$_2$)$_3$OH ; R′ = SCH$_3$	103.7	4.79	0.35	11.8	49.2	27
—N⟨⟩NCH$_3$; R′ = Cl	117.1	5.02	0.42	15.4	64.3	28 [c]
	120.4	5.07	0.40	16.2	68.3	

[a] Values calculated from published parameters. [b] This work. [c] First line of data refers to racemic octaclothepin, second line to dextrorotatory enantiomer.

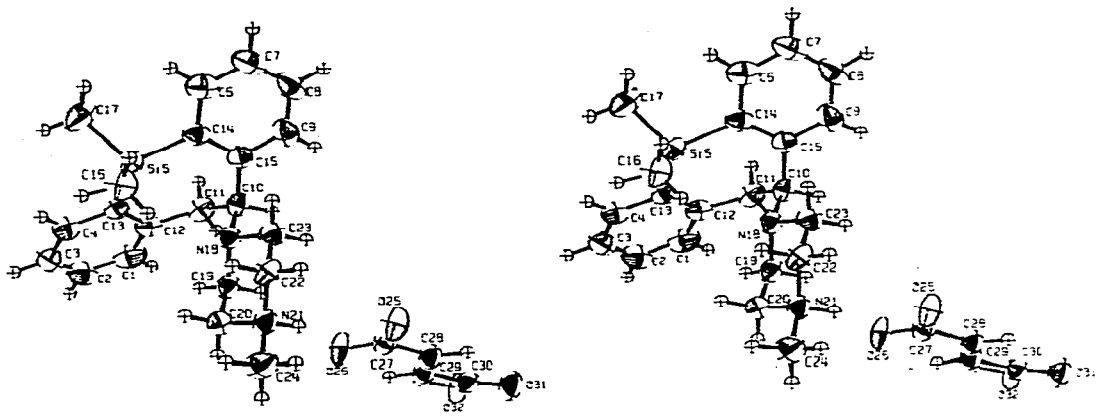


Fig. 1. A stereoscopic view of the unique portion of the structure of 5,5-Dimethyl-10-(4-methylpiperazinyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin hydrofumarate with atom labels.

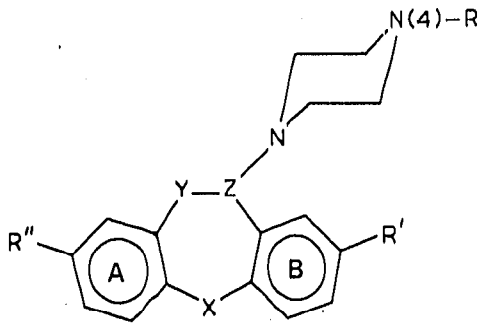
The orientation of the 10-substituent influences the magnitude of the dihedral angle between the benzo groups. The thiepin derivatives have pseudo-equatorial substituents at the 10-position; interactions between the substituent and the *peri* protons of the adjacent benzo ring can be relieved by increasing the fold of the tricyclic framework. This gives a ring system with a smaller dihedral angle and a shorter distance between ring centers (Table 4). As the separation of the benzo rings becomes smaller, the distance spanned by the ethano bridge decreases and the torsion about the 10,11 bond decreases. For the silepin with a substituent at the 10-position in the pseudoaxial orientation, an opposite effect takes place; the steric interaction between the piperazinyl group and the axial methyl group on silicon can be relieved by flattening the tricyclic framework. This gives rise to a larger dihedral angle, a greater ring separation, and a larger torsion angle. This difference in orientation of the piperazinyl substituent may account for the difference in psychotropic activity of the dimaleate salt of silepin derivative [6] as compared to the other compounds [23].

Silicon substitution in compounds with central seven-membered ring results in a tricyclic framework that is appreciably flatter than that observed for related thiepin derivatives. The orientation of the substituents on the ethano bridge also depends on the heteroatom; the silepin derivative has a pseudoaxial substituent that is nearly equidistant from the two benzo rings in the tricyclic framework, while thiepin derivatives have ethano bridge substituents in pseudo-equatorial orientations that are closer to one benzo ring than the other.

The hydrofumarate counter ion has a nonplanar conformation similar to that observed for other salts of fumaric acid [24]. The anion may be described as two planar C—CO_2 moieties twisted 15° with respect to each other. The carbon—carbon bond length in fumaric acid [25,26] and in hydrofumarate [24] and fumarate [27,28] salts are consistent with an isolated double bond that does not participate in π-bonding with the carbonyl or carboxylate groups. This allows rotation about the carbon—carbon single bonds to conform with packing requirements and the local balancing of charge [27]. These rotations, measured by the dihedral angle between the planes of the C—CO_2 moieties,

TABLE 5

STRUCTURAL PARAMETERS DESCRIBING THE ORIENTATION OF THE PIPERAZINYL SUBSTITUENT IN PSYCHOACTIVE TRICYCLIC COMPOUNDS [a]



–Y–Z–	>X	–R	–R'	–R''	Dihedral angle between piperazinyl group and benzo rings mean planes (°)		Distance between N(4) and benzo ring centroids (Å)		Perpendicular distance between N(4) and plane of benzo rings (Å)		Ref.
					A_{plane}	B_{plane}	A_{ring}	B_{ring}	A_{plane}	B_{plane}	
–N=C–	>O	–H	–Cl	–H	162.8	135.2	7.69	6.15	0.18	2.69	4
–N=C–	>O	$-CH_3$	–Cl	–H	157.9	134.6	7.74	6.20	0.09	2.31	4 [b]
–N=C–	>O	$-CH_3$	–Cl	–H	147.2	146.3	7.73	6.19	0.06	2.37	5 [c]
–N=C–	>NH	$-CH_3$	–H	–Cl	139.0	148.2	7.72	5.97	1.02	2.28	5
–N=C–	>NH	$-CH_3$	–Cl	–H	147.9	148.4	7.78	5.95	0.31	2.70	5
$-CH_2CH-$	>S	$-(CH_2)_3OH$	$-SCH_3$	–H	171.0	111.0	7.76	6.11	0.26	4.21	21
$-CH_2CH-$	>S	$-CH_3$	–Cl	–H	158.5	118.3	7.72	5.02	0.79	3.52	22 [d]
$-CH_2CH-$	>S	$-CH_3$	–Cl	–H	157.0	113.2	7.55	5.07	0.57	3.20	22 [e]
$-CH_2CH-$	$>Si(CH_3)_2$	$-CH_3$	–H	–H	100.9	120.2	6.17	6.10	3.76	5.07	– [f]

[a] Calculated from published atomic coordinates. [b] Monoclinic form. [c] Orthorhombic form. [d] Racemic mixture. [e] Dextrorotatory enantiomer. [f] This work.

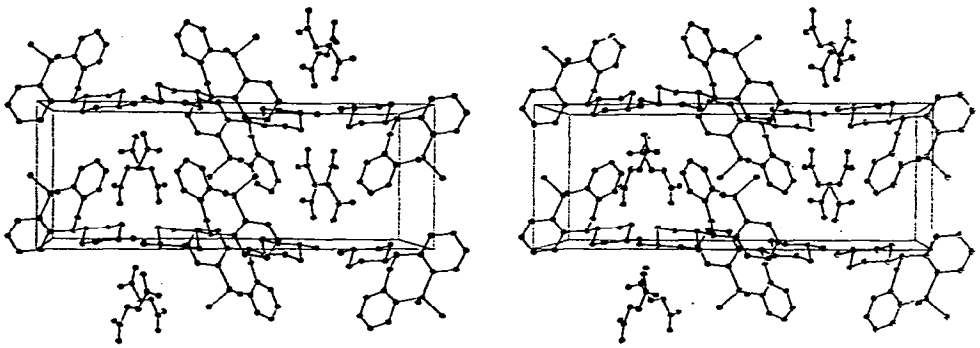


Fig. 2. A stereoscopic view of the unit cell contents.

range from 0° in fumaric acid [25,26] to 40° in sodium hydrofumarate [24].

The solid state structure of the title compound consists of chains of hydrofumarate ions held together by O···O hydrogen bonds 2.553(4) Å long. Slightly longer N···O bonds, 2.636(4) Å, bond the 10,11-dihydro-5*H*-dibenzo[*b*,*f*]-silepin moieties, through the protonated nitrogen atom in the piperazinyl substituent, to each unit of the hydrofumarate chain. A stereoscopic view of the contents of the unit cell is shown in Fig. 2. The only intermolecular approaches less than Van der Waals distances are the hydrogen bonds described above.

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