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CRYSTAL AND MOLECULAR STRUCTURE OF 2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE

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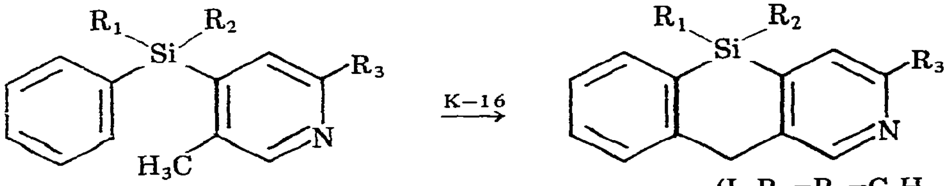
Summary

The crystal and molecular structure of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene has been determined by three-dimensional X-ray analysis. The crystal data are: space group $P\bar{1}$, a 11.339(2), b 11.151(2), c 19.808(4) Å, α 100.11(1), β 100.00(1), γ 121.20(2)°, $C_{25}H_{21}NSi$, $Z = 4$, $D_c = 1.20$ g cm^{-3}. The intensity data were measured on a 4-circle automatic diffractometer (Mo-K_α radiation). The structure was solved by direct methods using a multiple-solution procedure, and it was refined by large-blocks least-squares methods with anisotropic temperature factors for Si, N and C atoms and with isotropic temperature factors for the H atoms. The final R-factors are $R = 0.024$ and $R_w = 0.027$ for 2049 reflections with $I > 3\sigma(I)$. The investigated compound belongs to the family of quasi-heteromolecular crystals. Within the standard deviation limits the symmetrical non-bonded molecules A and A′ are characterised by equal bond lengths and slight differences of the valency angles in the central heterocycles, but differ in the conformation of the tricyclic fragments. The planes of the benzene and pyridine rings constitute a dihedral angle of 132.1° for A and 147.0° for A′, and the planes of the phenyl substituents 87.0° and 55.0°, respectively. The organosilicon heterocycles investigated have a boat conformation. Bond lengths Si—C lie in the range 1.853—1.871 Å, the average value of the endocyclic angle C—Si—C is 101.5(2)°. Average bond length N—C 1.339(7) Å and angle C—N—C 117.2(4)°.

Introduction

Condensed tricyclic compounds with a hydrogenated central cycle form an interesting class for the investigation of biological, especially psychotropic, activity among their derivatives [1—5]. A number of such compounds have already found application in pharmacology (derivative of phenothiazines and imipramine). Lately, the silicon analogs of phenothiazines [6,7] and imipramine [8] have been synthesized and their physiological activity investigated. For the first time we have been able to synthesize dihydrosilaazaanthracenes [9,10] which can be considered as analogs of phenothiazines, where the sulphur atom is replaced by a diorganosilyl group, and the nitrogen atom lies in the aromatic side ring. Dihydrosilaazaanthracenes I—III have been obtained by catalytic dehydrocyclisation of 5-methyltriorganosilylpyridines on K-16 catalyst at 530—560°C [10].



(I, R_1=R_2=C_6H_5, R_3=CH_3;
II, R_1=R_2=CH_3, R_3=H;
III, R_1=CH_3, R_2=C_6H_5, R_3=H)

The ready availability of these silylpyridines and the relatively simple method for their conversion into dihydrosilaazaanthracenes made it possible to start a systematic study of these structures, and the physiochemical properties and biological activity of these silicon- and nitrogen-containing tricyclic systems. Analytical and spectral characteristics of the title compound I have been published earlier [9]. Mass spectral study of 9,10-dihydro-9-sila-3-azaanthracenes and their derivatives [11] showed that the intensity of the molecular ion peak depends to a large extent on the nature of the substituents at the C(10) position. In this case the highest stability is shown by the molecular ions of ketones and oximes, having C=O and C=N groups at the C(10) position, whereas the dihydrosilaazaanthracene has the last stable molecular ion. The principal difference in the fragmentation paths of these compounds under electron impact has been studied. Thus the main fragmentation route of dihydrosilaazaanthracenes leads to the elimination of a benzene molecule with the formation of a rearranged $(M - C_6H_6)^{+\cdot}$ ion. The dissociative ionisation of dihydrosilaazaanthrones leads mainly to the loss of the $CH_3^\cdot$ and $C_6H_5^\cdot$ radicals situated at the silicon atom. This distinction in the mass spectral behaviour of silaazaanthracene and its ketone may be related with the difference in their structures. For a detailed study of this question the crystals of the title compound I and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthrone (IV) were investigated through X-ray analysis. The crystal and molecular structure of compound I is described in the present work. Similar results for compound IV were published earlier [12].

TABLE 1

2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE. COORDINATES OF Si (X10^{5}), N, C (X10^{4}), H (X10^{3}) AND ISOTROPIC THERMAL PARAMETERS OF THE ATOMS [a]

Atom	X	Y	Z	B (Å^{2})
Si	47953(10)	67811(10)	32577(5)	3.4
N	8181(3)	5597(4)	3686(2)	5.2
C(1)	5669(3)	8794(4)	3420(3)	4.2
C(2)	6351(5)	9501(5)	2972(2)	7.1
C(3)	7117(5)	11068(6)	3154(3)	8.9
C(4)	7180(5)	11864(4)	3773(3)	6.7
C(5)	6501(5)	11178(5)	4219(3)	7.0
C(6)	5749(4)	9656(4)	4041(2)	5.9
C(7)	3558(3)	6095(3)	3813(2)	3.7
C(8)	2205(4)	5888(4)	3619(2)	4.8
C(9)	1259(4)	5360(4)	4019(2)	5.4
C(10)	1647(4)	5027(4)	4615(2)	5.3
C(11)	2968(4)	5231(4)	4830(2)	5.2
C(12)	3901(4)	5755(4)	4422(2)	4.5
C(13)	3814(3)	5619(3)	2297(2)	3.6
C(14)	3279(3)	6017(3)	1754(2)	4.3
C(15)	2581(4)	5098(4)	1048(2)	5.0
C(16)	2392(4)	3740(3)	869(2)	5.0
C(17)	2929(3)	3330(3)	1393(2)	4.2
C(18)	3639(3)	4245(3)	2105(2)	3.6
C(19)	6195(3)	6377(3)	3481(2)	3.6
C(20)	5769(3)	4941(3)	3143(2)	3.7
C(21)	6801(4)	4630(4)	3259(2)	4.7
C(22)	8584(4)	6968(4)	4008(2)	4.9
C(23)	7622(4)	7388(3)	3910(2)	4.4
C(24)	4231(3)	3769(3)	2669(2)	4.4
C(25)	10121(4)	8016(4)	4511(3)	8.4
Si′	1906(10)	−18442(10)	17328(5)	3.5
N′	−2659(4)	−6811(3)	1605(2)	5.3
C(1)′	1578(4)	−1591(4)	1276(2)	3.9
C(2)′	1105(4)	−2605(4)	601(2)	5.1
C(3)′	2015(6)	−2491(6)	202(2)	7.0
C(4)′	3435(7)	−1341(7)	475(4)	8.1
C(5)′	3973(5)	−320(5)	1139(4)	7.8
C(6)′	3030(4)	−437(4)	1550(2)	5.9
C(7)′	1036(4)	−487(4)	2654(2)	4.6
C(8)′	2225(5)	−229(4)	3161(2)	6.4
C(9)′	2843(5)	816(5)	3837(2)	7.8
C(10)′	2295(6)	1614(5)	4022(2)	7.7
C(11)′	1148(5)	1405(5)	3539(3)	7.4
C(12)′	534(4)	369(4)	2864(2)	6.0
C(13)′	−1176(3)	−1670(3)	1180(2)	3.7
C(14)′	−798(3)	−620(4)	820(2)	4.5
C(15)′	−1803(5)	−495(4)	392(2)	5.3
C(16)′	−3247(5)	−1464(5)	310(2)	6.1
C(17)′	−3669(4)	−2516(5)	656(2)	6.0
C(18)′	−2661(4)	−2636(4)	1097(2)	4.7
C(19)′	−904(3)	−3808(3)	1723(2)	3.7
C(20)′	−2411(4)	−4532(4)	1573(2)	4.4
C(21)′	−3206(4)	−6015(4)	1515(2)	5.4
C(22)′	−1219(4)	−6115(4)	1758(2)	4.5
C(23)′	−341(3)	−4640(4)	1810(2)	4.1
C(24)′	−3160(4)	−3742(4)	1500(2)	6.2
C(25)′	−630(4)	−7022(4)	1844(2)	6.9
H(2)	639(3)	896(3)	253(2)	7.4(9)
H(3)	745(3)	1140(3)	280(2)	8.7(9)
H(4)	772(3)	1300(3)	391(2)	8.0(8)

TABLE 1 (continued)

Atom	X	Y	Z	B (Å^2)
H(5)	661(4)	1182(4)	471(2)	10.7(9)
H(6)	528(3)	915(3)	440(2)	7.8(8)
H(8)	196(3)	618(3)	320(1)	6.0(7)
H(9)	34(3)	525(3)	388(1)	6.3(8)
H(10)	100(3)	464(3)	491(1)	5.6(8)
H(11)	331(3)	500(3)	528(2)	7.9(7)
H(12)	485(3)	591(3)	461(1)	4.7(7)
H(14)	338(3)	697(3)	188(1)	4.6(7)
H(15)	218(3)	533(3)	65(1)	5.5(7)
H(16)	194(3)	313(3)	36(1)	4.9(7)
H(17)	285(3)	238(3)	125(1)	4.9(7)
H(21)	650(3)	354(3)	299(1)	6.7(7)
H(23)	796(3)	841(3)	416(1)	5.1(7)
H1(24)	416(3)	287(3)	240(1)	4.7(7)
H2(24)	360(3)	348(3)	298(1)	5.1(7)
H1(25)	1070(4)	781(4)	436(2)	11.3(1.0)
H2(25)	1018(5)	865(5)	492(2)	13.0(1.0)
H3(25)	1053(4)	894(5)	440(2)	11.4(1.0)
H(2)′	−1(3)	−344(5)	37(1)	6.9(7)
H(3)′	168(4)	−327(4)	−34(2)	10.9(9)
H(4)′	405(4)	−119(4)	19(2)	9.6(9)
H(5)′	481(3)	41(3)	133(2)	8.1(1.0)
H(6)′	349(3)	22(3)	206(2)	7.6(8)
H(8)′	265(3)	−78(3)	304(2)	8.0(8)
H(9)′	360(4)	90(4)	418(2)	10.1(9)
H(10)′	270(4)	226(4)	451(2)	11.2(9)
H(11)′	65(4)	190(4)	369(2)	10.4(9)
H(12)′	−25(3)	25(3)	253(2)	7.6(8)
H(14)′	18(3)	1(3)	86(1)	5.1(7)
H(15)′	−147(3)	26(3)	12(2)	8.0(7)
H(16)′	−396(3)	−140(3)	−2(2)	7.9(8)
H(17)′	−467(3)	−322(3)	59(1)	6.7(8)
H(21)′	−427(3)	−653(3)	136(1)	5.7(8)
H(23)′	74(3)	−414(3)	192(1)	5.4(7)
H1(24)′	−426(3)	−458(4)	122(2)	8.7(8)
H2(24)′	−307(4)	−324(4)	198(2)	9.9(8)
H1(25)′	−137(4)	−806(4)	165(2)	10.0(9)
H2(25)′	−38(4)	−699(4)	232(2)	9.8(9)
H3(25)′	33(4)	−662(4)	185(2)	9.6(9)

[a] The standard deviations are given in parentheses. For the anisotropic oscillating atoms the equivalent isotropic thermal parameters are given. The designations of the hydrogen atoms correspond to those of the carbon atoms to which they are connected.

Experimental

The compound crystallises in the triclinic system. Crystal data from single crystal diffractometry are: space group $P\bar{1}$, a 11.339(2), b 11.151(2), c 19.808(4) Å, α 100.11(1), $\beta = 100.00(1)$, $\gamma = 121.20(2)°$, $V = 2002$ Å^3; Mo-K_α, λ 0.71069 Å; $C_{25}H_{21}NSi$, $Z = 4$, $M = 363.54$, $D_c = 1.20$ g cm^{-3}, $F(000) = 768$, μ(Mo-K_α) = 1.26 cm^{-1}, m.p. 174°C.

Intensity data and cell dimensions were measured on a Syntex $P\bar{1}$ automatic diffractometer by the $\theta/2\theta$ scan technique with $4.2° \leqslant 2\theta \leqslant 41.6°$ using

TABLE 2

2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE. ANISOTROPIC THERMAL PARAMETERS OF Si ($\times 10^4$), N AND C ($\times 10^3$) WITH STANDARD DEVIATIONS IN PARENTHESES

Temperature factor $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si	420(6)	376(6)	501(6)	235(5)	135(5)	131(5)
N	64(2)	79(2)	73(2)	50(2)	22(2)	32(2)
C(1)	49(2)	49(2)	59(2)	29(2)	13(2)	16(2)
C(2)	114(3)	62(3)	96(3)	44(3)	57(3)	33(3)
C(3)	130(4)	71(4)	127(5)	38(3)	62(4)	57(3)
C(4)	77(3)	51(3)	105(4)	32(3)	5(3)	20(3)
C(5)	86(3)	53(3)	107(4)	34(3)	17(3)	10(3)
C(6)	74(3)	45(3)	88(3)	27(2)	23(2)	12(3)
C(7)	45(2)	37(2)	52(2)	24(2)	7(2)	6(2)
C(8)	58(3)	69(3)	67(3)	42(2)	19(2)	23(2)
C(9)	48(2)	76(3)	77(3)	35(2)	22(2)	12(2)
C(10)	72(3)	61(2)	72(3)	37(2)	38(2)	21(2)
C(11)	74(3)	71(3)	62(2)	45(2)	30(2)	22(2)
C(12)	52(2)	63(2)	56(2)	35(2)	14(2)	16(2)
C(13)	41(2)	44(2)	57(2)	26(2)	18(2)	20(2)
C(14)	47(2)	48(2)	67(3)	27(2)	17(2)	16(2)
C(15)	65(2)	69(3)	55(3)	40(2)	10(2)	20(2)
C(16)	57(2)	69(3)	50(2)	35(2)	5(2)	7(2)
C(17)	46(2)	47(2)	56(2)	25(2)	9(2)	6(2)
C(18)	40(2)	44(2)	54(2)	23(2)	17(2)	21(2)
C(19)	47(2)	41(2)	47(2)	24(2)	15(2)	15(2)
C(20)	47(2)	51(2)	49(2)	31(2)	13(2)	20(2)
C(21)	75(3)	64(2)	52(2)	48(2)	19(2)	21(2)
C(22)	47(2)	67(3)	73(3)	30(2)	20(2)	32(2)
C(23)	46(2)	46(2)	68(2)	24(2)	12(2)	15(2)
C(24)	64(2)	41(2)	58(2)	28(2)	13(2)	16(2)
C(25)	49(3)	80(3)	165(4)	29(2)	10(3)	31(3)
Si$'^{1}$	389(6)	410(6)	476(6)	200(5)	140(5)	117(5)
N'	60(2)	52(2)	74(2)	20(2)	31(2)	20(2)
C(1)'	47(3)	48(2)	62(3)	29(2)	19(2)	26(2)
C(2)'	67(3)	79(3)	64(3)	47(2)	30(2)	31(2)
C(3)'	123(4)	117(4)	95(3)	92(4)	71(4)	63(3)
C(4)'	126(5)	122(5)	155(5)	98(4)	102(5)	101(4)
C(5)'	58(3)	81(4)	181(6)	39(3)	56(4)	74(4)
C(6)'	50(3)	56(3)	115(3)	26(2)	29(3)	35(2)
C(7)'	56(2)	49(2)	69(3)	28(2)	22(2)	21(2)
C(8)'	84(3)	83(3)	72(3)	55(3)	3(3)	10(3)
C(9)'	105(4)	95(3)	62(3)	50(3)	—10(3)	4(3)
C(10)'	110(4)	78(3)	65(3)	41(3)	11(3)	—2(3)
C(11)'	104(4)	85(3)	73(3)	57(3)	10(3)	—7(3)
C(12)'	72(3)	75(3)	71(3)	45(2)	10(2)	5(2)
C(13)'	47(2)	45(2)	48(2)	24(2)	19(2)	14(2)
C(14)'	52(2)	54(2)	68(2)	33(2)	21(2)	17(2)
C(15)'	76(3)	73(3)	74(3)	52(3)	34(2)	31(2)
C(16)'	79(3)	95(3)	90(3)	65(3)	31(2)	45(3)
C(17)'	55(3)	93(3)	96(3)	48(2)	31(2)	39(3)
C(18)'	54(3)	68(3)	69(3)	38(2)	31(2)	30(2)
C(19)'	41(2)	49(2)	41(2)	20(2)	13(2)	14(2)
C(20)'	49(2)	57(3)	59(2)	24(2)	27(2)	25(2)
C(21)'	46(2)	64(3)	77(3)	20(2)	24(2)	24(2)
C(22)'	61(3)	45(2)	59(2)	23(2)	25(2)	20(2)
C(23)'	45(2)	46(2)	55(2)	21(2)	14(2)	14(2)
C(24)'	58(2)	91(3)	114(3)	48(2)	45(2)	57(3)
C(25)'	88(3)	60(3)	127(4)	45(2)	42(3)	41(3)

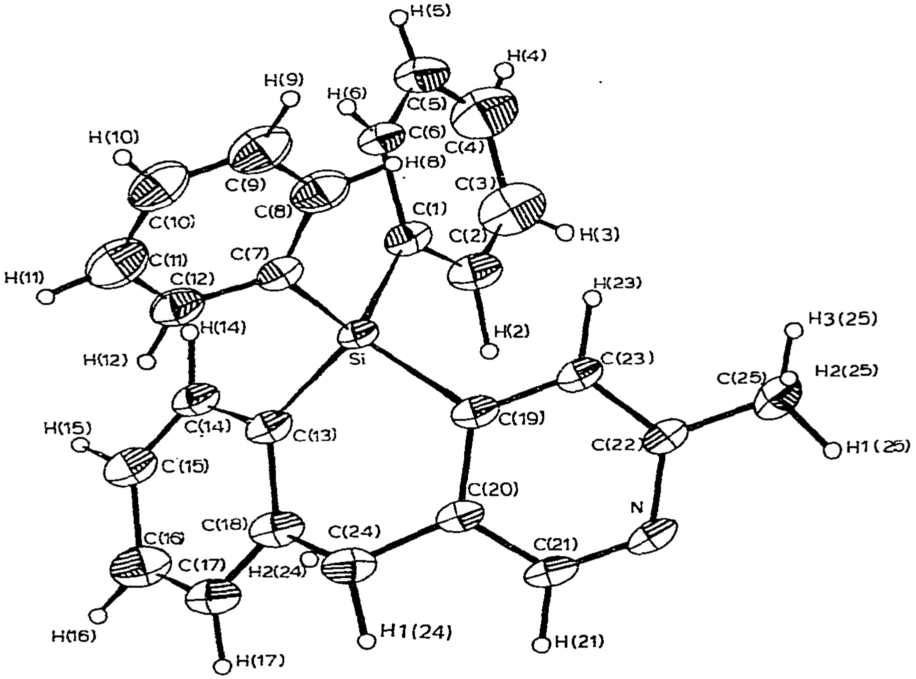


Fig. 1. The molecular structure of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene and the numbering scheme of the atoms. The thermal ellipsoids are at 30% probability.

graphite-monochromatized Mo-K_α radiation. Of the 4182 independent reflections, 2049 with $I > 3\sigma(I)$ were considered as observed and were used in all further calculations. Corrections were made for Lorentz and polarization effects in the structure factors $|F_0|$. Absorption and extinction effects were neglected.

Determination and refinement of the structure

It was found in the preliminary investigation that the strong reflections obeyed the approximate condition $h + k + l = 2n$, which corresponds to the non-standard pseudo-space group I$\bar{1}$. Thus in our structure 8 pseudo-centres of symmetry located at (1/4 1/4 1/4), (3/4 1/4 1/4), etc. are added to the 8 centres of symmetry in the space group $P\bar{1}$. It is obvious that two independent molecules in the asymmetric unit should be connected by the pseudo-centre of symmetry. The solution and initial refinement of the structure have some difficulties due to the above-mentioned pseudo-symmetry, but it does not affect the final results.

The structure was solved by direct methods using a multiple-solution procedure. The scale factor and the overall temperature factor were evaluated by Wilson's method. 540 reflections with $|E| > 1.60$ and 5820 Σ_2-relationships were used in direct methods. 512 different sets of signs were generated starting with 3 origin-defining and 9 sign-alternating reflections. An E-synthesis based on the set of signs with the third figure of merit (Σ_2-consistency) revealed that the structure strongly obeyed the pseudo-space group I$\bar{1}$. The structure was then developed in the space group $P\bar{1}$ by Fourier methods and initial least-squares refinements. In the final stage the structure was refined by large-blocks least-squares methods with anisotropic temperature factors for the Si, N, and C atoms and with isotropic temperature factors for the H atoms. All the H atoms were located in difference electron density syntheses. The full matrix was partitioned into 4 overlapping large-blocks along its diagonal. The function minimized in least-squares was $\Sigma w(|F_0| - |F_c|)^2$ with the weighting scheme: $\sqrt{w} = |F_0|/C_1$, if $|F_0| < C_1$; $\sqrt{w} = 1$, if $C_1 \leqslant |F_0| \leqslant C_2$ and $\sqrt{w} = C_1/|F_0|$, if $|F_0| > C_2$. The coefficients C_1 and C_2 were chosen such that the distribution of $\langle w(\Delta F)^2 \rangle$ was essentially independent of $|F_0|$ and $\sin\theta/\lambda$ ($C_1 = 36$ and $C_2 = 130$). In the final cycles of refinement all calculated shifts were less than one standard deviation for all parameters. A difference synthesis calculated at the end of refinement showed no peaks greater than 0.18 e Å^{-3}. The final R-factors are: $R = 0.024$ and $R_w = 0.027$ for 2049 observed reflections. Scattering factors for Si, N and C were taken from ref. 13 and for H from ref. 14. The final positional and thermal parameters are listed in Tables 1 and 2.

All calculations were carried out using a new system of crystallographic computer programs, LUCH-77, written by Dr. A.N. Chekhlov. Fig. 1 was drawn with the program ELLIDS also written by him. All computations were performed on a BESM-6 computer.

Results and discussion

Two independent crystallographic molecules of I, denoted as A and A′, lie in the asymmetric part of the cell. The general view of these molecules with atom designations for A is shown in Fig. 1. Bond lengths and angles are given in Table 3, whereas the geometrical data of separate fragments is shown in Table 4.

The tricyclic fragments of both molecules are non-planar with specific difference between their conformations. Thus the dihedral angle between the planes of the benzene and the pyridine rings in molecule A is 132.1°, and the planes of the phenyl substituents constitute an angle of 87.0° between themselves. The corresponding angles in molecule A′ are 147.0° and 55.0°. The silicon heterocycles in both molecules have a boat conformation. Deviations of the Si and C(24) atoms from the planes of the rest of the atoms in molecule A (0.620(1) and 0.530(3) Å, respectively) are slightly magnified relative to the same in molecule A′ (0.390(1) and 0.436(5) Å). Moreover in molecule A the silicon atom lies further from the central plane than the C(24) atom whereas in the molecule A′ it is just the opposite. Comparison of the structures of I and IV confirmed our assumption about the differences in their structures based on mass spectral data [11]. Here the planar conformation of the tricycle fragment corresponds to the more stable molecular ion of silaazaanthrone (IV).

It follows from Table 3, that the bond lengths and the valency angles between the chemically-equivalent atoms in A and A′ coincide within their standard deviations. This leads us to consider molecules A and A′ as crystal conformers, the existence of which is not due to intramolecular but intermolecular nonvalent interactions, which arise during the packing of the mole-

TABLE 3

2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE. BOND LENGTHS (Å) AND ANGLES (°)

	Molecule A	Molecule A′
Si—C(1)	1.859(4)	1.870(4)
Si—C(7)	1.867(4)	1.861(4)
Si—C(13)	1.854(4)	1.853(4)
Si—C(19)	1.867(4)	1.871(4)
N—C(21)	1.341(5)	1.339(7)
N—C(22)	1.336(7)	1.340(5)
C(1)—C(2)	1.364(6)	1.395(6)
C(1)—C(6)	1.380(6)	1.382(5)
C(2)—C(3)	1.427(9)	1.375(7)
C(2)—H(2)	0.99(4)	1.06(3)
C(3)—C(4)	1.349(9)	1.358(9)
C(3)—H(3)	0.89(4)	1.13(4)
C(4)—C(5)	1.350(8)	1.368(10)
C(4)—H(4)	1.04(4)	0.93(4)
C(5)—C(6)	1.385(8)	1.420(8)
C(5)—H(5)	1.05(4)	0.83(3)
C(6)—H(6)	1.03(3)	1.01(3)
C(7)—C(8)	1.397(5)	1.390(6)
C(7)—C(12)	1.379(6)	1.385(7)
C(8)—C(9)	1.389(6)	1.387(7)
C(8)—H(8)	0.98(3)	0.99(4)
C(9)—C(10)	1.366(7)	1.360(9)
C(9)—H(9)	0.96(3)	0.95(4)
C(10)—C(11)	1.367(6)	1.354(7)
C(10)—H(10)	0.99(3)	0.97(4)
C(11)—C(12)	1.390(5)	1.380(7)
C(11)—H(11)	1.05(4)	1.01(5)
C(12)—H(12)	0.99(3)	0.95(3)
C(13)—C(14)	1.394(6)	1.394(6)
C(13)—C(18)	1.410(6)	1.409(5)
C(14)—C(15)	1.381(6)	1.381(6)
C(14)—H(14)	1.00(3)	0.94(3)
C(15)—C(16)	1.383(7)	1.374(6)
C(15)—H(15)	0.98(3)	1.01(4)
C(16)—C(17)	1.375(6)	1.375(7)
C(16)—H(16)	0.96(3)	0.99(4)
C(17)—C(18)	1.389(5)	1.393(6)
C(17)—H(17)	1.00(3)	0.96(3)
C(18)—C(24)	1.516(5)	1.503(6)
C(19)—C(20)	1.399(6)	1.404(5)
C(19)—C(23)	1.381(5)	1.389(6)
C(20)—C(21)	1.378(6)	1.382(7)
C(20)—C(24)	1.506(5)	1.516(7)
C(21)—H(21)	1.07(4)	0.99(3)
C(22)—C(23)	1.391(6)	1.384(6)
C(22)—C(25)	1.508(5)	1.489(7)
C(23)—H(23)	1.00(3)	1.02(3)
C(24)—H1(24)	1.00(3)	1.06(3)
C(24)—H2(24)	0.99(3)	0.99(4)
C(25)—H1(25)	0.88(5)	0.96(5)
H(25)—H2(25)	0.96(5)	0.93(4)
C(25)—H3(25)	0.97(5)	0.94(4)
C(1)—Si—C(7)	110.8(2)	111.7(2)
C(1)—Si—C(13)	114.9(2)	110.0(2)
C(1)—Si—C(19)	110.6(2)	108.7(2)
C(7)—Si—C(13)	109.9(2)	109.9(2)
C(7)—Si—C(19)	109.2(2)	113.3(2)

TABLE 3

	Molecule A	Molecule A′
C(13)—Si—C(19)	101.0(2)	102.0(2)
C(21)—N—C(22)	117.3(4)	117.2(4)
Si—C(1)—C(2)	122.5(3)	117.7(3)
Si—C(1)—C(6)	120.2(3)	124.4(3)
C(2)—C(1)—C(6)	117.1(4)	117.8(4)
C(1)—C(2)—C(3)	120.3(5)	122.8(4)
C(1)—C(2)—H(2)	122(2)	118(2)
C(3)—C(2)—H(2)	118(2)	119(2)
C(2)—C(3)—C(4)	120.3(5)	118.6(6)
C(2)—C(3)—H(3)	113(3)	125(2)
C(4)—C(3)—H(3)	127(3)	116(2)
C(3)—C(4)—C(5)	120.1(5)	121.5(7)
C(3)—C(4)—H(4)	121(2)	120(3)
C(5)—C(4)—H(4)	119(2)	118(3)
C(4)—C(5)—C(6)	119.8(5)	119.8(6)
C(4)—C(5)—H(5)	119(2)	127(3)
C(6)—C(5)—H(5)	121(2)	113(3)
C(1)—C(6)—C(5)	122.4(4)	119.5(5)
C(1)—C(6)—H(6)	119(2)	123(2)
C(5)—C(6)—H(6)	119(2)	117(2)
Si—C(7)—C(8)	120.5(3)	123.0(3)
Si—C(7)—C(12)	123.1(1)	120.9(3)
C(8)—C(7)—C(12)	116.4(4)	116.0(4)
C(7)—C(8)—C(9)	121.4(4)	121.1(5)
C(7)—C(8)—H(8)	118(2)	121(2)
C(9)—C(8)—H(8)	120(2)	118(2)
C(8)—C(9)—C(10)	119.8(4)	120.6(5)
C(8)—C(9)—H(9)	121(2)	119(3)
C(10)—C(9)—H(9)	120(2)	120(3)
C(9)—C(10)—C(11)	120.8(4)	119.9(5)
C(9)—C(10)—H(10)	122(2)	117(3)
C(11)—C(10)—H(10)	117(2)	122(3)
C(10)—C(11)—C(12)	118.8(4)	119.7(5)
C(10)—C(11)—H(11)	123(2)	120(2)
C(12)—C(11)—H(11)	118(2)	120(2)
C(7)—C(12)—C(11)	122.8(4)	122.7(4)
C(7)—C(12)—H(12)	122(2)	119(2)
C(11)—C(12)—H(12)	116(2)	118(2)
Si—C(13)—C(14)	125.2(3)	122.3(3)
Si—C(13)—C(18)	116.8(3)	120.4(3)
C(14)—C(13)—C(18)	118.0(3)	117.5(4)
C(13)—C(14)—C(15)	121.7(4)	123.2(4)
C(13)—C(14)—H(14)	119(2)	118(2)
C(15)—C(14)—H(14)	120(2)	119(2)
C(14)—C(15)—C(16)	119.7(4)	118.5(4)
C(14)—C(15)—H(15)	124(2)	120(2)
C(16)—C(15)—H(15)	116(2)	121(2)
C(15)—C(16)—C(17)	119.8(4)	120.5(5)
C(15)—C(16)—H(16)	118(2)	118(2)
C(17)—C(16)—H(16)	122(2)	122(2)
C(16)—C(17)—C(18)	121.3(4)	121.6(4)
C(16)—C(17)—H(17)	119(2)	122(2)
C(18)—C(17)—H(17)	120(2)	116(2)
C(13)—C(18)—C(17)	119.6(3)	119.1(4)
C(13)—C(18)—C(24)	120.6(3)	121.0(4)
C(17)—C(18)—C(24)	120.0(3)	119.9(4)
Si—C(19)—C(20)	116.3(3)	118.5(3)
Si—C(19)—C(23)	125.8(3)	124.4(3)

TABLE 3 (cont.)

	Molecule A	Molecule A′
C(20)—C(19)—C(23)	117.8(3)	117.0(3)
C(19)—C(20)—C(21)	117.8(4)	117.2(4)
C(19)—C(20)—C(24)	121.2(3)	122.5(4)
C(21)—C(20)—C(24)	121.0(3)	120.2(4)
N—C(21)—C(20)	124.7(4)	125.7(4)
N—C(21)—H(21)	116(2)	117(2)
C(20)—C(21)—H(21)	119(2)	117(2)
N—C(22)—C(23)	121.9(4)	121.1(4)
N—C(22)—C(25)	116.3(4)	116.5(4)
C(23)—C(22)—C(25)	121.8(4)	122.3(4)
C(19)—C(23)—C(22)	120.5(4)	121.8(4)
C(19)—C(23)—H(23)	120(2)	119(2)
C(22)—C(23)—H(23)	120(2)	120(2)
C(18)—C(24)—C(20)	114.1(3)	117.7(4)
C(18)—C(24)—H1(24)	107(2)	108(2)
C(18)—C(24)—H2(24)	109(2)	109(3)
C(20)—C(24)—H1(24)	110(2)	105(2)
C(20)—C(24)—H2(24)	108(2)	108(2)
H1(24)—C(24)—H2(24)	108(3)	109(3)
C(22)—C(25)—H1(25)	111(3)	112(3)
C(22)—C(25)—H2(25)	112(3)	111(3)
C(22)—C(25)—H3(25)	108(3)	118(3)
H1(25)—C(25)—H2(25)	137(5)	96(4)
H1(25)—C(25)—H3(25)	95(5)	123(4)
H2(25)—C(25)—H3(25)	78(5)	90(4)

cules in the crystal lattice. The formation of the conformers A and A′ shows the existence of at least two potential energy minima for the molecule. Moreover, the conformer energy difference is probably commensurable with the energy of the crystal lattice. In both the symmetrically non-bonded molecules the configuration of the Si and Si′ atom bonds is tetrahedral with similar deviations. Hence in molecule A the Si—C bond lengths vary from 1.854(4) to 1.867(4) Å, and the angles C—Si—C from 101.0(2) to 114.9(2)°. In molecule A′ the values of similiar bond lengths and angles lie in the ranges 1.853(4) to 1.871(4) Å and 102.0(2) to 113.3(2)°. Here the maximum deviation from the tetrahedral values are observed for the endocyclic angles at the silicon atom 101.0(2)° for A and 102.0(2)° for A′. These values correspond to the lower limit of the range for endocyclic angles C—Si—C, 98.7(6)—111.0(4)°, calculated on the basis of the study of 16 compounds containing six-membered heterocycles.

The N atoms in the aromatic pyridine systems enforce a strong localisation effect which distorts the symmetry of the system. The average distance N—C is 1.339(7) Å, and angle C—N—C is 117.2(4)°. Probably the very slight increase in the endocyclic bonds between the Si atom with the pyridine cycle (1.867(4) and 1.871(4) Å) in comparison with the benzene cycle (1.853(4) and 1.854(4) Å) is due to the ability of the nitrogen atom to act as an electron acceptor. A similar tendency was observed by us in the study of the structure of IV. The substituents at the Si and Si′ as well as C(24), C(24)′ atoms are crystallographically non-equivalent. As is seen from Table 4 (planes I and X) cycles C(1)...C(6),

TABLE 4

2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE. EQUATIONS OF PLANES IN THE FORM $AX' + BY' + CZ' - D = 0$ [a] FOR SOME FRAGMENTS OF THE MOLECULES AND DEVIATIONS (Δ, Å) OF THE ATOMS FROM THEM

Plane	A	B	C	D	Δ (Å)					
I	−0.6112	0.0134	0.7914	0.0491	C(13) −0.009(3)	C(18) 0.010(3)	C(19) 0.009(3)	C(20) −0.010(3)	Si* 0.620(1)	C(24)* 0.530(3)
					C(1)* −0.043(4)	C(7)* 2.487(3)	H1(24)* 0.29(3)	H2(24)* 1.52(3)		
II	0.8321	−0.4529	0.3201	2.8489	C(1) 0.005(4)	C(2) −0.000(5)	C(3) −0.005(6)	C(4) 0.005(5)	C(5) −0.000(5)	C(6) −0.005(4)
III	0.4076	0.8571	0.3149	6.9303	C(7) −0.003(4)	C(8) 0.002(5)	C(9) 0.003(5)	C(10) −0.007(5)	C(11) 0.005(5)	C(12) −0.000(4)
IV	0.8735	−0.0825	−0.4797	1.4698	C(13) −0.007(3)	C(14) 0.001(3)	C(15) 0.006(4)	C(16) −0.009(3)	C(17) 0.003(3)	C(18) 0.005(3)
					Si* 0.017(1)	C(24)* 0.030(3)				
V	−0.2561	−0.1465	0.9555	2.3129	N 0.005(3)	C(19) 0.004(3)	C(20) 0.005(3)	C(21) −0.009(4)	C(22) 0.004(4)	C(23) −0.008(4)
					Si* −0.095(1)	C(24)* 0.026(4)	C(25)* 0.082(5)			
VI	0.2050	−0.8150	0.5420	3.9105	C(1)' −0.005(4)	C(2)' 0.003(5)	C(3)' 0.003(7)	C(4)' −0.007(9)	C(5)' 0.005(7)	C(6)' 0.001(5)
VII	−0.6216	−0.4198	0.6614	3.3059	C(7)' 0.007(4)	C(8)' −0.002(5)	C(9)' −0.004(5)	C(10)' 0.006(5)	C(11)' −0.001(5)	C(12)' −0.005(4)
VIII	0.0872	0.7185	0.6900	1.1249	C(13)' −0.005(4)	C(14)' −0.002(4)	C(15)' 0.006(5)	C(16)' −0.004(5)	C(17)' −0.003(5)	C(18)' 0.007(4)
					Si'* −0.059(1)	C(24)'* 0.090(5)				
IX	0.1168	0.2233	0.9677	3.2954	N' −0.001(3)	C(19)' −0.002(3)	C(20)' 0.009(4)	C(21)' −0.008(4)	C(22)' 0.008(4)	C(23)' −0.007(4)
					Si'* −0.119(1)	C(24)'* 0.081(4)				
X	0.1486	0.5003	0.8530	1.7668	C(13)' −0.003(4)	C(18)' 0.003(4)	C(19)' 0.003(4)	C(20)' −0.003(4)	Si'* 0.390(1)	C(24)'* 0.436(5)
					C(1)'* −0.766(4)	C(7)'* 2.173(4)	H1(24)'* 0.03(4)	H2(24)'* 1.42(4)		

[a] A, B, C are the direction cosines of normals to the plane in the orthogonal coordinate system X', Y', Z'; D = distance (Å) from the plane to the origin of the coordinates. Atoms not included in the plane calculation are indicated by asterisks.

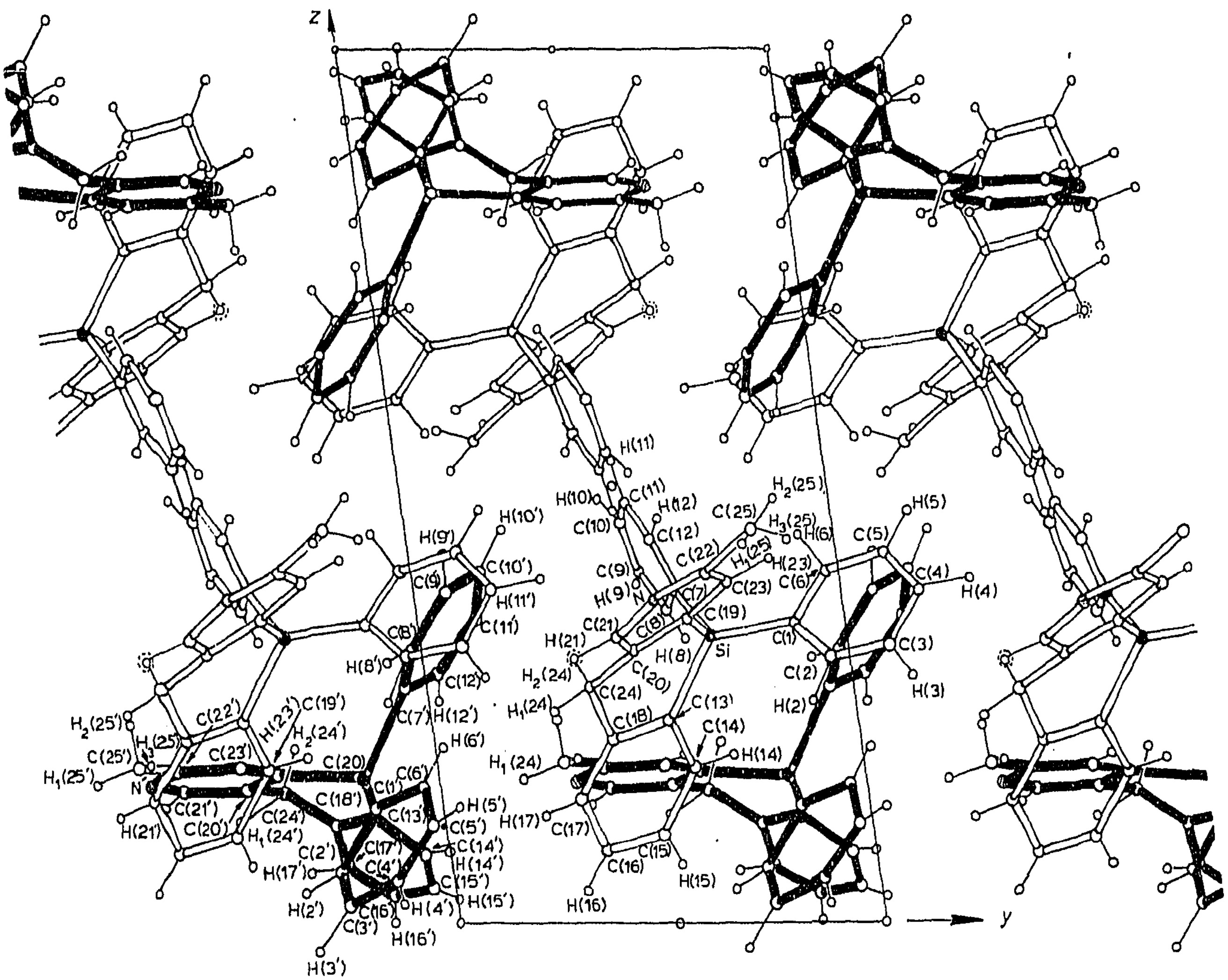


Fig. 2. Projection of the structure on the plane (100).

C(1)'...C(6)' and atoms H1(24), H1(24)', occupy equatorial positions, and cycles C(7)...C(12), C(7)'...C(12)' and atoms H2(24), H2(24)' axial positions. The average value of the bond lengths Si—$C_{(e)}$, 1.865(4) Å, and Si—$C_{(a)}$ 1.864(4) Å, are the same. Fig. 2 shows the packing of the molecules A and A' in the crystals. In agreement with the results of the present investigation and classification [15] I belongs to the quasi-heteromolecular crystal structure class $P\bar{1}$, $Z = 4$ (1,1).

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