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CRYSTAL AND MOLECULAR STRUCTURE OF 9-METHYL-9-PHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRONE

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Summary

The crystal and molecular structure of 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthrone has been determined from three-dimensional X-ray diffraction data. The title compound crystals are monoclinic, space group $P2_1/b$, $a = 12.818(2)$, $b = 16.508(2)$, $c = 7.694(1)$ Å, $\gamma = 105°, 34'(2)$, $Z = 4$ and $D_{cal} = 1.278$ g cm^{-3}. The structure was determined by direct methods and refined by full-matrix least-squares calculations in the block-diagonal anisotropic approximation for non-hydrogen atoms to $R = 0.043$ for 2190 independent reflections, registered at room temperature. This is the first crystal structure determination of a Si-dihydroanthracene derivative with two heterocycles and a planar carbon atom in the C10-position. The tricyclic fragment takes up a planar configuration, the silicon atom having a tetrahedral surrounding, with an endocyclic angle of 103.7(1)° and average bond length Si—C, 1.862(1) Å. The C—O, 1.220(2) Å, bond length in the carbonylic group exactly corresponds with the double bond length. Average distance N—C is 1.335(3) Å, angle C—N—C, 116.5(2)°.

Introduction

To date, the structure of the heterocyclic derivatives of 9,10-dihydroanthracenes with various numbers of different heteroatoms in the central ring has been investigated in detail [1—9]. A systematic study in the field of synthesis and properties of the nitrogen analogs of dihydrosilaanthracenes, dihydrosilaazaanthracenes, and their derivatives is being conducted in our departments

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[10,11]. These compounds may be of interest in the search for physiologically active compounds of this type [12—17]. The physiological activity of dihydrosilaanthracene was reported in ref. 18.

Study of the structure of the heterocyclic derivatives of 9,10-dihydroanthracenes made it possible to explain the effect of different factors on the conformation of the tricyclic ring fragment. Yet no information exists regarding the change in the molecular geometry induced by the replacement of the bridge tetrahedral carbon atom by a trigonal one. We suggest that such a substitution should lead to an effective planar state of the system and an increase of aromaticity. To enlighten this question we undertook the X-ray diffraction analysis of the title compound.

Experimental

The synthesis of the title compound was published earlier [19]. These colourless, transparent crystals belong to the monoclinic system. Crystal data: $C_{19}H_{15}NOSi$, M.W. = 301.42, $a = 12.818(2)$, $b = 16.508(2)$, $c = 7.694(1)$ Å, $\gamma = 105^\circ, 34'(2')$, $V = 1568.38$ Å, $Z = 4$, $D_{cal} = 1.278$ g cm^{-3}. Space group $P2_1/b$. Unit cell dimensions were refined on a DRON-1 diffractometer with a monocrystal auxiliary. The intensities of 2190 independent nonzero ($I > 2\sigma(I)$) reflections of the $hk0$—$hk7$ type were measured with a crystal of 0.2 × 0.3 × 0.4 mm on a diffractometer DAR-UM with a Cu-K_α-radiation (graphite monochromator) using a layer line registration method in a $3.5 \leqslant \theta^\circ \leqslant 67.5^\circ$ scan.

TABLE 1

COORDINATES AND ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si	0.1992(0)	0.3753(0)	0.1014(1)	0.0049	0.0028	0.0089	0.0023	0.0006	0.0
O	0.2212(2)	0.6481(1)	0.1747(2)	0.0139	0.0043	0.0291	0.0082	−0.0116	−0.0
N	0.0698(1)	0.5524(1)	−0.2679(2)	0.0088	0.0058	0.0157	0.0068	−0.0021	0.0
C(1)	0.2563(1)	0.4431(1)	0.2892(2)	0.0059	0.0044	0.0089	0.0038	0.0024	0.0
C(2)	0.3050(2)	0.4106(1)	0.4256(2)	0.0095	0.0056	0.0098	0.0053	0.0003	0.0
C(3)	0.3528(2)	0.4594(2)	0.5633(3)	0.0100	0.0078	0.0091	0.0046	−0.0015	0.0
C(4)	0.3507(2)	0.5425(2)	0.5718(3)	0.0103	0.0073	0.0106	0.0034	−0.0026	−0.0
C(5)	0.3024(2)	0.5762(1)	0.4415(3)	0.0083	0.0056	0.0135	0.0034	0.0002	−0.0
C(6)	0.2560(1)	0.5281(1)	0.2978(2)	0.0050	0.0043	0.0098	0.0030	0.0022	−0.0
C(7)	0.2116(1)	0.5729(1)	0.1595(2)	0.0058	0.0037	0.0147	0.0040	0.0022	−0.0
C(8)	0.1588(1)	0.5307(1)	−0.0026(2)	0.0045	0.0036	0.0111	0.0029	0.0020	0.0
C(9)	0.1175(1)	0.5798(1)	−0.1179(2)	0.0067	0.0042	0.0160	0.0049	0.0017	0.0
C(10)	0.0626(2)	0.4720(1)	−0.3094(3)	0.0079	0.0062	0.0123	0.0051	−0.0042	0.0
C(11)	0.1007(2)	0.4190(1)	−0.2047(2)	0.0068	0.0044	0.0121	0.0028	−0.0030	0.0
C(12)	0.1498(1)	0.4469(1)	−0.0462(2)	0.0045	0.0034	0.0108	0.0024	0.0014	0.0
C(13)	0.3089(1)	0.3407(1)	−0.0119(2)	0.0064	0.0033	0.0109	0.0041	0.0016	0.0
C(14)	0.4172(2)	0.3792(1)	0.0188(2)	0.0063	0.0056	0.0130	0.0040	0.0012	0.0
C(15)	0.4982(2)	0.3560(2)	−0.0720(3)	0.0072	0.0081	0.0208	0.0067	0.0055	0.0
C(16)	0.4718(2)	0.2947(2)	−0.1964(3)	0.0116	0.0064	0.0258	0.0100	0.0178	0.0
C(17)	0.3653(2)	0.2561(1)	−0.2307(3)	0.0144	0.0044	0.0259	0.0066	0.0137	−0.0
C(18)	0.2844(2)	0.2782(1)	−0.1393(3)	0.0092	0.0038	0.0208	0.0036	0.0026	−0.0
C(19)	0.0848(2)	0.2845(1)	0.1639(3)	0.0070	0.0041	0.0235	0.0022	0.0039	0.0

TABLE 2

COORDINATES AND ISOTROPIC THERMAL PARAMETERS OF HYDROGEN ATOMS. IN PARENTHESES ESTIMATED STANDARD DEVIATIONS ARE SHOWN. TEMPERATURE FACTOR $T = \exp[-B(\sin\theta/\lambda)^2]$

Atom	x	y	z	B (Å^2)
H(1)	0.308(2)	0.353(1)	0.419(3)	2.6
H(2)	0.389(2)	0.432(1)	0.655(3)	3.3
H(3)	0.378(2)	0.574(1)	0.665(4)	4.9
H(4)	0.297(2)	0.634(2)	0.450(3)	3.5
H(5)	0.118(2)	0.636(1)	−0.076(3)	2.6
H(6)	0.033(2)	0.451(1)	−0.429(3)	3.7
H(7)	0.093(2)	0.363(1)	−0.248(3)	2.6
H(8)	0.442(2)	0.424(1)	0.113(3)	3.6
H(9)	0.576(2)	0.390(1)	−0.038(3)	4.1
H(10)	0.527(2)	0.279(2)	−0.261(3)	4.6
H(11)	0.345(2)	0.215(2)	−0.315(4)	5.6
H(12)	0.207(2)	0.252(1)	−0.164(3)	4.5
H(13)	0.035(2)	0.302(1)	0.243(3)	4.2
H(14)	0.059(2)	0.248(1)	0.056(3)	4.5
H(15)	0.110(2)	0.248(1)	0.246(3)	3.6

The structure was obtained by the direct method using the RENTGEN-75 complex programme [20]. The sign determination was effected selecting 220 reflections with $|E(hkl)| \geqslant 1.51$. The location of non-hydrogen atoms was obtained by E-synthesis, and of the hydrogen atoms by R-synthesis. Structure refinement was conducted by the least-squares method in the block diagonal anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms, using the Cruikshank weight-scheme. Final value, R = 0.043. Absorption corrections were not taken into account ($\mu(\text{Cu-}K_\alpha)$ = 12.44 cm^{-1}).

Coordinates and thermal parameters of the atoms are listed in Table 1 and 2.

Results and discussion

A general view of the molecule with atom designations is shown in Fig. 1. Bond lengths and angles, with their standard derivations are given in Table 3.

The tricyclic fragment of the molecule, including the two heterocycles, is planar within the experimental error limit. The maximum deviation from the general plane passing through all the atoms of the tricyclic fragments is 0.04 Å (atoms C(1) and C(3)). The phenyl-substituent plane constitutes a dihedral angle of 70.7° with the main plane of the molecule, and 41.8° with the plane C(13)SiC(19). Hence the conformation of the title compound effectively differs from those of the non-planar molecules of phenotiazine [21], 9-siladihydroanthracene [9] and hydrochloride 9-methyl-9-(3-dimethyl aminopropyl)-9,10-dihydrosilaanthracene [16]. In the above compounds the molecular bending, defined by the dihedral angle between the planes of the two benzene rings equals 153.3°, 136° and 132.1°, respectively.

The silicon atom configuration is distorted tetrahedral. The C(1)-Si-C(12), 103.7(1)°, endocyclic angle has the maximum deviation from the ideal value of 109.5°. Bond lengths Si—C lie in the range 1.854(1)—1.869(1) Å. Preliminary

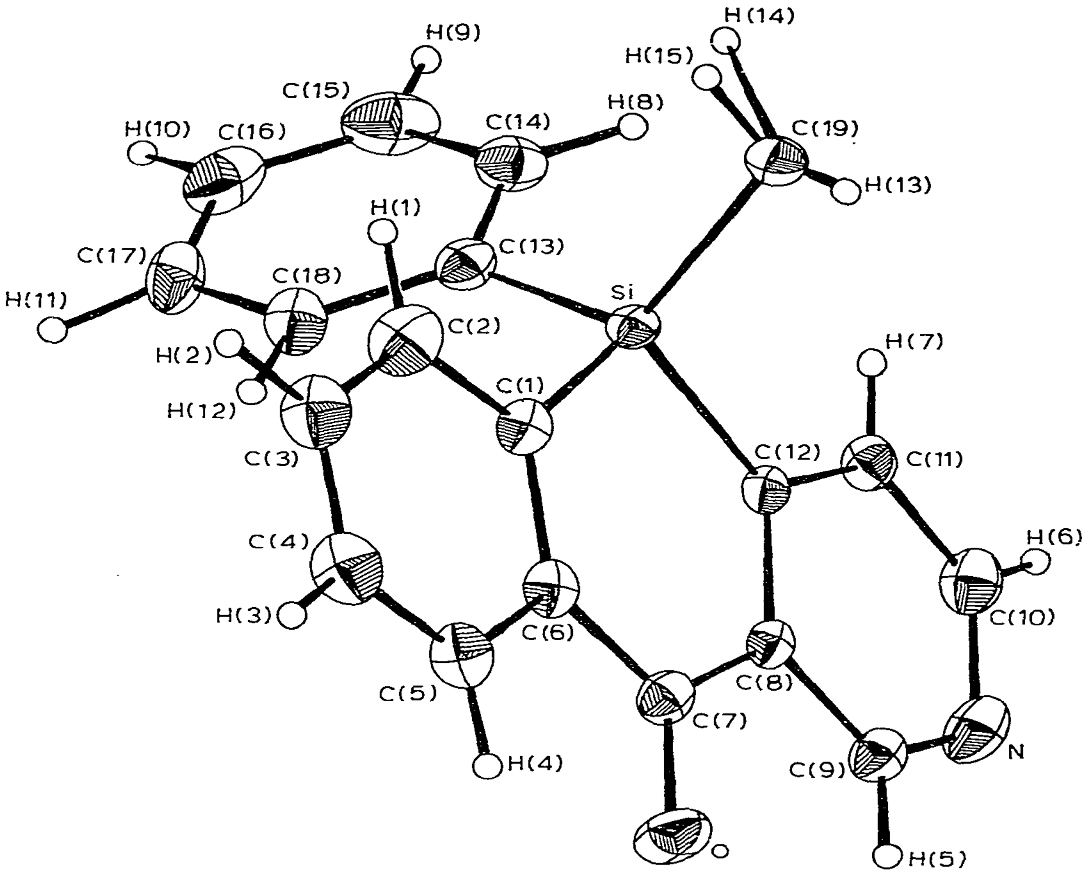

Fig. 1. An ELLIDS drawing of the molecule. The non-hydrogen atoms are represented by 30% probability thermal ellipsoids. The spheres shown for hydrogen atoms are arbitrary.

equalisation of the endocyclic bonds Si—C and the corresponding coordinate refinement of the atoms once again led to the values shown in Table 3. Probably this bond inequality is induced by the nitrogen atom in one of the cycles. The distribution of angles in this cycle corresponds with the results of microwave measurements [22]. An additional decrease of the C(8)—C(12)—C(11) angle to 116.6(2)°, as also for angles C(2)—C(1)—C(6), 117.9(2)°, and C(14)—C(13)—C(18), 117.3(2)°, is due to the electronic effect of the silicon atom [23,24].

The bond configuration of the carbonyl-carbon atom is almost planar. The C(7) atom is displaced from the plane of connected atoms O, C(6), C(8) by 0.02 Å. The bond length C(7)—O, 1.220(2) Å, exactly corresponds to that of a double bond. Fig. 2 shows the packing of the molecule in the crystals. Intermolecular distances less than the normal Van der Waals contacts were not observed.

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°) OF THE MOLECULE

Si—C(1)	1.854(1)	C(13)—C(18)	1.383(2)
Si—C(12)	1.869(1)	C(14)—C(15)	1.381(3)
Si—C(13)	1.869(1)	C(15)—C(16)	1.368(3)
Si—C(19)	1.857(1)	C(16)—C(17)	1.368(3)
O—C(7)	1.220(2)	C(17)—C(18)	1.388(3)
N—C(9)	1.327(2)	H(1)—C(2)	0.96(2)
N—C(10)	1.344(3)	H(2)—C(3)	1.02(3)
C(1)—C(2)	1.399(2)	H(3)—C(4)	0.91(3)
C(1)—C(6)	1.405(2)	H(4)—C(5)	0.98(3)
C(2)—C(3)	1.372(2)	H(5)—C(9)	0.98(2)
C(3)—C(4)	1.381(3)	H(6)—C(10)	1.02(2)
C(4)—C(5)	1.372(3)	H(7)—C(11)	0.96(2)
C(5)—C(6)	1.398(2)	H(8)—C(14)	0.99(2)
C(6)—C(7)	1.493(2)	H(9)—C(15)	0.92(3)
C(7)—C(8)	1.498(2)	H(10)—C(16)	0.95(3)
C(8)—C(9)	1.397(2)	H(11)—C(17)	1.03(2)
C(8)—C(12)	1.398(2)	H(12)—C(18)	1.02(2)
C(10)—C(11)	1.373(3)	H(13)—C(19)	0.99(3)
C(11)—C(12)	1.392(2)	H(14)—C(19)	1.03(3)
C(13)—C(14)	1.396(2)	H(15)—C(19)	0.98(3)
C(1)SiC(12)	103.7(1)	SiC(1)C(2)	119.8(1)
C(1)SiC(13)	109.9(1)	SiC(1)C(6)	122.2(1)
C(1)SiC(19)	112.5(1)	C(2)C(1)C(6)	117.9(2)
C(12)SiC(13)	108.7(1)	C(1)C(2)C(3)	121.9(2)
C(12)SiC(19)	109.8(1)	C(1)C(2)H(1)	119(1)
C(13)SiC(19)	111.7(1)	C(3)C(2)H(1)	119(1)
C(9)NC(10)	116.5(2)	C(2)C(3)C(4)	119.7(2)
C(2)C(3)H(2)	117(1)	SiC(12)C(8)	121.9(1)
C(4)C(3)H(2)	123(1)	SiC(12)C(11)	121.5(1)
C(3)C(4)C(5)	119.9(2)	C(8)C(12)C(11)	116.6(2)
C(3)C(4)H(3)	120(2)	SiC(13)C(14)	120.9(1)
C(5)C(4)H(3)	120(2)	SiC(13)C(18)	121.6(1)
C(4)C(5)C(6)	121.1(2)	C(14)C(13)C(18)	117.3(2)
C(4)C(5)H(4)	120(1)	C(13)C(14)C(15)	121.1(2)
C(6)C(5)H(4)	121(2)	C(13)C(14)H(8)	118(2)
C(1)C(6)C(5)	119.3(2)	C(15)C(14)H(8)	121(2)
C(5)C(6)C(7)	116.2(2)	C(14)C(15)C(16)	120.3(2)
C(1)C(6)C(7)	124.4(2)	C(14)C(15)H(9)	118(2)
C(6)C(7)C(8)	123.2(2)	C(16)C(15)H(9)	122(2)
OC(7)C(6)	119.2(2)	C(15)C(16)C(17)	119.8(2)
OC(7)C(8)	117.5(2)	C(15)C(16)H(10)	120(2)
C(7)C(8)C(9)	116.9(2)	C(17)C(16)H(10)	120(2)
C(7)C(8)C(12)	124.5(2)	C(16)C(17)C(18)	120.1(2)
C(9)C(8)C(12)	118.5(2)	C(16)C(17)H(11)	126(2)
NC(9)C(8)	124.5(2)	C(18)C(17)H(11)	114(2)
NC(9)H(5)	120(1)	C(13)C(18)C(17)	121.3(2)
C(8)C(9)H(5)	116(1)	C(13)C(18)H(12)	122(1)
NC(10)C(11)	123.2(2)	C(17)C(18)H(12)	117(1)
NC(10)H(6)	118(1)	SiC(19)H(13)	111(1)
C(11)C(10)H(6)	119(1)	SiC(19)H(14)	109(1)
C(10)C(11)C(12)	120.6(2)	SiC(19)H(15)	109(1)
C(10)C(11)H(7)	116(1)	H(13)C(19)H(14)	122(2)
C(12)C(11)H(7)	123(1)	H(13)C(19)H(15)	98(2)
		H(14)C(19)H(15)	106(2)

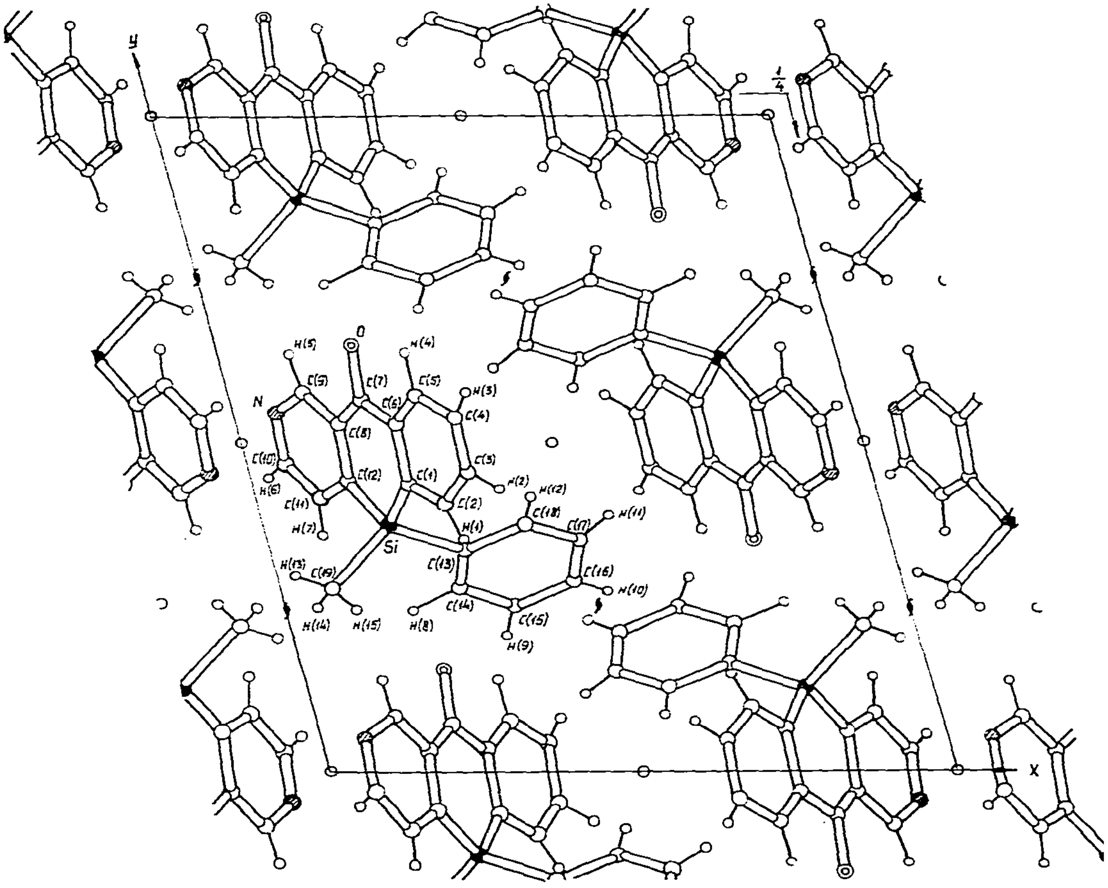

Fig. 2. Projection of the structure on the plane (001).

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References

1 O.A. D'yachenko, L.O. Atovmyan and S.V. Soboleva, Zh. Strukt. Khim., 17 (1976) 191.
2 O.A. D'yachenko, L.O. Atovmyan and S.V. Soboleva, Zh. Strukt. Khim., 16 (1975) 505.
3 O.A. D'yachenko, L.O. Atovmyan, T.Yu. Markova, N.G. Komalenkova, L.N. Shamshin and E.A. Che nyshev. Zh. Strukt. Khim., 15 (1974) 667.
4 S.V. Soboleva, O.A. D'yachenko and L.O. Atovmyan, Izvest. Akad. Nauk, SSSR, Ser. Khim., (1974) 1443.
5 O.A. D'yachenko, S.V. Soboleva and L.O. Atovmyan, Zh. Strukt. Khim., 17 (1976) 496.
6 A.B. Zolotoy, O.A. D'yachenko, L.O. Atovmyan, I.P. Yakovlev and V.O. Reikhcfel'd. Zh. Strukt. Khim., 21 (1980) 134.
7 A.B. Zolotoy, O.A. D'yachenko, L.O. Atovmyan, I.P. Yakovlev and V.O. Reikhcfel'd. J. Organomet Chem., 190 (1980) 267.

8 E.R. Corey, J.Y. Corey, W.F. Paton and M.D. Glick, Acta Cryst. B, 33 (1977) 1254.

9 A.I. Udelnov, V.E. Shklover, N.G. Bokii, E.A. Chernyshev, T.L. Krasnova, E.F. Shipanova and Yu.T. Struchkov; Zh. Strukt. Khim., 15 (1974) 83.

10 A.V. Varlamov, N.S. Prostakov, Navin Saxena and A.M. Klochkov; VIth Symposium on chemistry of heterocyclic compounds, Abstracts of papers, Brno. Czeckoslovakia, 1978, p. 80.

11 N.S. Prostakov, A.V. Varlamov and V.P. Zvolinski, Khim. Geterotsik. Soudinenii, (1972) 1579.

12 Ya.Ya. Baltkas, M.G. Voronkov and G.E. Zelgan, Izvest. Akad. Nauk. Latv. SSR, (1964) 102.

13 M.G. Voronkov, L.E. Alekseeva, B. Brizga, A. Zile, B.P. Kozakov, Ya. Kruzmetra, Ye. Lukevitz, E.E. Lyashenko, V.F. Mironov and V.F. Fedotov, Khim. Pharm. Zh., (1967) 26.

14 M. Frankel, M. Broze, D. Gertner, A. Rotman, Shenhar and A. Zilkha, J. Med. Chem., 11 (1968) 857.

15 M.G. Voronkov and E.Ya. Lukevits, Uspekhi Khimii, 38 (1969) 2173.

16 N.S. Prostakov and N.N. Mikheeva, Uspekhi Khimii, 31 (1962) 1191.

17 A.V. Varlamov, A.M. Klochkov, S.A. Vichkanova, S.B. Izosimova, V.V. Adchina, L.D. Shipulina and N.S. Prostakov, Khim. Pharm. Zh., 13 (1979) 39.

18 Y.Y. Corey, M.G. Dye, R.L. Farrell and M.V. Mitchell, J. Organometal. Chem., 153 (1978) 127.

19 A.V. Varlamov, A.M. Klochkov, N. Saxena and N.S. Prostakov, Ftoraya Moskovskaya Konferentsiya po Organicheskoi khimii i tekhnologii. Tezisi, Moscow, 1979, p. 38.

20 V.I. Andrianov, Z. Sh. Saffina and B.L. Tarnopolskii, RENTGEN-75, Chernogolovka, 1975.

21 J.D. Bell, J.F. Blount, O.V. Briscoe and H.C. Freeman, J. Chem. Soc., Chem. Commun., (1968) 1656.

22 G.O. Sørensen, L. Mahler and N. Rastrup-Andersen, J. Molec. Struct., 20 (1974) 119.

23 A. Domenicano, A. Vaciago and C.A. Coulson, Acta Cryst B, 31 (1975) 221, 1630.

24 Z.V. Zvonkova, Uspekhi Khimii, 46 (1977) 907.