Conformational analysis and simulation of the structures of diisobutylsilanediol and dihydroxytetraalkyldisiloxanes and their analogs $[R_2(HO)Si]_2X$ ($X = CH_2$, S), precursors of liquid-crystalline phases

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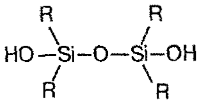
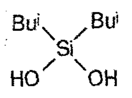
Molecular mechanics studies of structure formation in condensed phases of $[R_2(HO)Si]_2X$ ($X = CH_2$ (dihydroxydicarbosilanes) and X = S (dihydroxydisilthians)) compounds have been performed and the results have been compared with those obtained for previously known columnar mesophases of $[R_2(HO)Si]_2O$ (R = Et and Pr) (dihydroxydisiloxanes). Conformational analysis demonstrates the similarity in structure and cross-linking of dihydroxydisiloxanes and dihydroxydicarbosilanes and the difference between these compounds and dihydroxydisilthians. This allows the conclusion that for dihydroxydicarbosilanes the columnar mesophase formed by H-associates can occur. Simulation of dimeric and trimeric H-associates for $(Bu^i)_2Si(OH)_2$, which belong to the same class of mesophases, has been performed.

Key words: hydrogen bonds, liquid crystals, molecular simulation; silanediols, siloxanediols.

Presently, mesogenic compounds, the molecules of which cannot be anisometric, are known. Some representatives of the series of dihydroxydisiloxanes of the general formula $[R_2(HO)Si]_2O$ (R = Et and Pr)[1–3] as well as one silanediol $R_2Si(OH)_2$ ($R = Bu^i$), diisobutylsilanediol,[1,4–6] are among these compounds.



Dihydroxydisiloxanes (R = Alk)

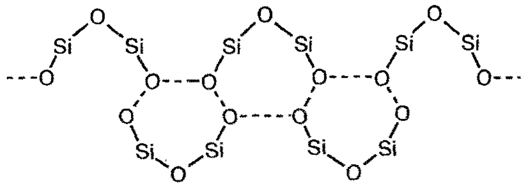


Diisobutylsilanediol

These compounds are assigned to a new class of liquid crystals,[1] phases with columnar H-bonded associates.

The crystal structures of mesogenic dihydroxydisiloxanes consist of infinite H-bonded ribbons (Scheme 1) that are nearly cylinder-shaped with a flexible alkyl exterior. According to the X-ray diffraction data,[1] mesophases of these compounds largely inherit their crystal structures.

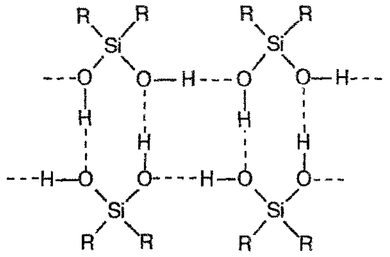
Scheme 1



Although forming the same system of cooperative hydrogen bonds, methyl- and phenyl-substituted dihydroxydisiloxanes exhibit no mesomorphism because of the absence of the flexible alkyl environment.[1,7,8]

Attempts to obtain single crystals of diisobutylsilanediol failed, and therefore, the structural studies of its homologs were performed.[9,10] The authors[9,10] believed that the structure of diisobutylsilanediol most closely resembles the structures of Pr^i- and Bu^t-substituted silanediols built of infinite H-bonded ribbons, which consist of dimers (Scheme 2).

Scheme 2



In this work based on the above-mentioned data on the relationship between the structure and the manifestation of mesomorphism, we performed a comparative computational analysis of the possibility of the occur-

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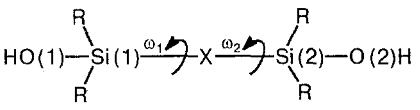
rence of the liquid-crystalline state for alkyl-substituted dihydroxydicarbosilanes and dihydroxydisilthians $[R_2(HO)Si]_2X$ (X = CH_2 and S; R = Alk) using molecular mechanics.

Computational analysis involved two stages. In the first stage, we compared the most important, in our opinion, intramolecular characteristics, which determine the structures of molecules of dihydroxydisiloxanes, dihydroxydicarbosilanes, and dihydroxydisilthians, namely, the torsion angles. The conformational energy maps were calculated for dihydroxydisiloxanes, dihydroxydicarbosilanes, and dihydroxydisilthians. In the second stage, dimeric and trimeric H-associates of molecules of these compounds were simulated and compared. In this stage, simulations of H-associates for diisobutylsilanediol and Pr^i-substituted silanediol were also performed for the purpose of revealing the energetically most favorable associates because the structures of diisobutylsilanediol in the crystal and in the mesophase were not established unambiguously.[4]

Isolated molecules. We used molecular mechanics[11] for solving the stated problems. Calculations were carried out using the MMX program (the version of the MM2 program[11] adapted to an IBM PC computer). A comparative analysis of isolated molecules of dihydroxydicarbosilanes and dihydroxydisilthians as well as the forms of dihydroxydisiloxanes previously studied was performed. The principal parameters determining the structures of these flexible molecules are the O(1)—Si(1)—X—Si(2) (ω_1) and O(2)—Si(2)—X—Si(1) (ω_2) torsion angles.



$$HO(1)-\underset{R}{\overset{R}{Si}}(1)\xrightarrow{\omega_1}X\xrightarrow{\omega_2}\underset{R}{\overset{R}{Si}}(2)-O(2)H$$

These angles were varied in the range 0—360° with a step of 20°. This allowed us to obtain a rather clear picture of the change in geometry and energy of the molecule and required little computer time. To save computer time, Me groups were chosen as alkyl substituents.

At each point (for each pair of torsion angles ω_1 and ω_2), energy minimization with respect to all parameters was achieved and two principal characteristics (the energy (E) and the O...O distance ($r_{O...O}$)) for three compounds, *i.e.*, six functions $f(\omega_1, \omega_2)$, were considered. These functions are symmetric with respect to the diagonals of the field of variables (ω_1 [0, 360] and ω_2 [0, 360]), which also decreased substantially the computer time. The functions $E(\omega_1, \omega_2)$ are represented graphically in Fig. 1. The $r_{O...O}(\omega_1, \omega_2)$/Å (see below) have minimum values when the torsion angles tend to zero and have maximum values when $\omega_1 = \omega_2 = 180°$:

ω_1/deg	ω_2/deg	X = O	X = CH_2	X = S
0	0	2.97	2.89	2.83
180	180	5.17	5.67	6.14

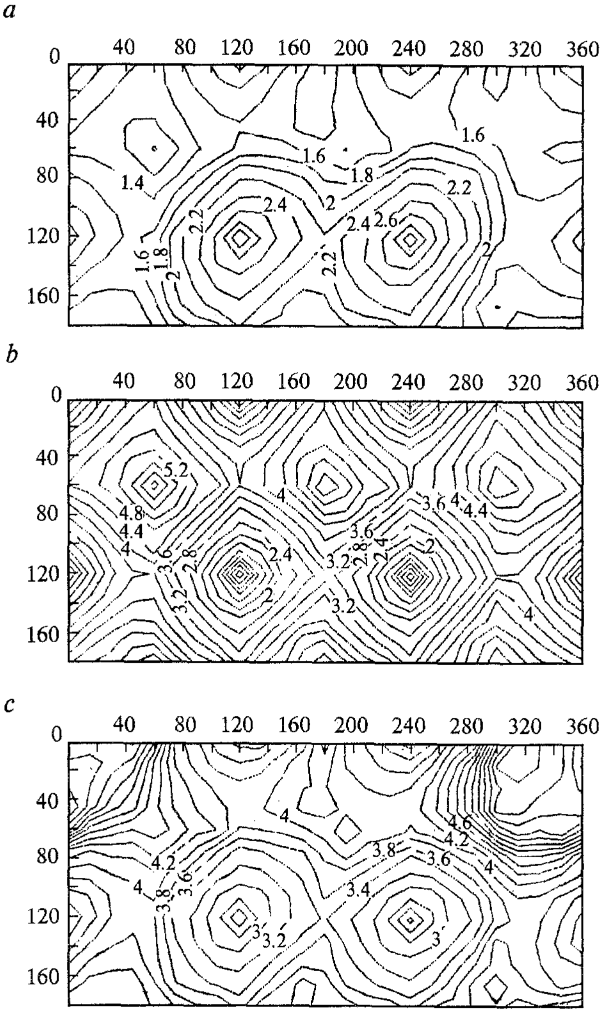


Fig. 1. Conformational energy maps for dihydroxydisiloxane (*a*), dihydroxydicarbosilane (*b*), and dihydroxydisilthian (*c*).

H-associates. Molecular mechanics calculations for H-associates were performed on an MicroVAX-3100 computer using the MM3 program.[11] The H-associates of compounds of the general formula $[Me_2(HO)Si]_2X$ (X = O, CH_2, and S) as well as diisobutylsilanediol and Pr^i-substituted silanediol were simulated.

We have restricted ourselves to consideration of dimeric and trimeric H-associates; of all the possible types, the most symmetrical ones were chosen. It was demonstrated with many phases formed by discotic molecules that these phases occur only when molecules have a rather high molecular symmetry.[12—14] Note that a total of approximately 20 theoretically possible types of dimeric and trimeric H-associates exist. The schemes of H-associates are represented as graphs in Fig. 2, in which the molecular skeleton is denoted by the arc $\overset{\frown}{HO\ OH}$.

We did not consider type *e* for $[Me_2(HO)Si]_2X$ compounds because, in our opinion, this trimer can be somewhat compact and flattened only for molecules

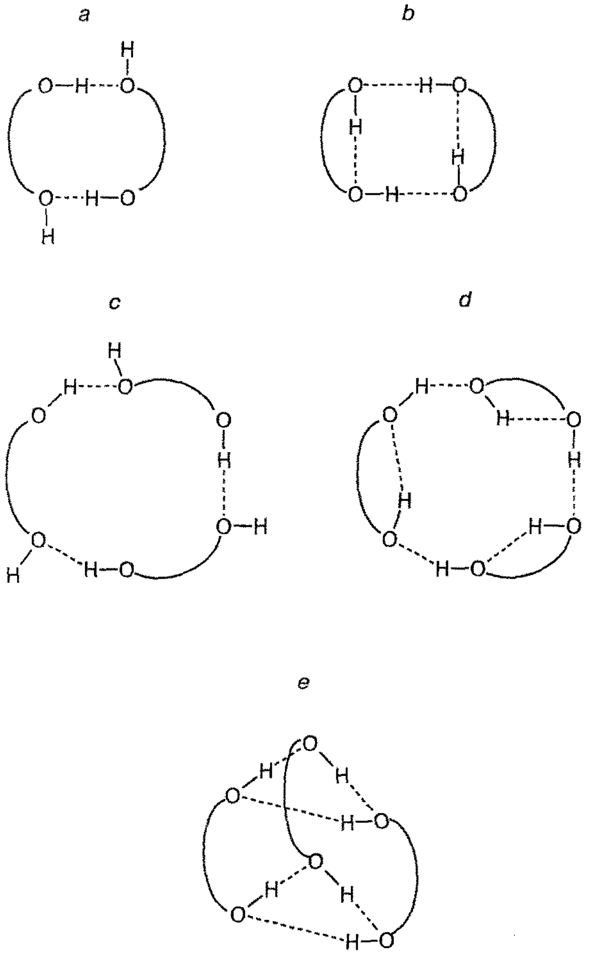


Fig. 2. Schemes of H-associates (see text for explanations).

with short arcs, for example, for silanediols. In silanediols in turn, intramolecular hydrogen bonds cannot be formed, and, therefore, H-associates of types *b* and *d*, which contain these bonds, were not taken into account for diisobutylsilanediol and Pr^i-substituted silanediol. Note that in H-associates of types *b*, *d*, and *e*, all possible hydrogen bonds occur, while in structures of types *a* and *c*, only half of the possible hydrogen bonds occur (see Fig. 2).

When dimer *a* for silanediols and dimer *b* for dihydroxydisiloxane, dihydroxydicarbosilane, and dihydroxydisilthian as well as trimers *d* and *e* were simulated no change in arrangement of hydrogen bonds occurred in the process of minimization, *i.e.*, neither cleavage nor formation of new hydrogen bonds was observed. Problems arose when trimeric H-associates of type *c* were calculated. In all compounds under study, new hydrogen bonds appear between the "free" H and O atoms, which results in associates with an unsymmetrical structure. In H-associates of diisobutylsilanediol and Pr^i-substituted silanediol, two molecules form dimer *a* and the third molecule is bonded to one or two centers capable of forming hydrogen bonds (two H atoms and two O atoms); in H-associates of $[Me_2(HO)Si]_2X$, intramolecular hydrogen bonds occur in one or two molecules.

Table 1. Optimized energies per molecule of H-associates of different types

Compound	E/kcal mol^{-1}				
	a	*b*	*c*	*d*	*e*
DSO	−19.13	−18.15	—	−19.17	—
DCS	−14.74	−14.67	—	−16.36	—
DST	—	−14.52	—	−16.59	—
DISD	−1.92	—	—	—	−3.75
DIPSD	−6.94	—	—	—	−9.16

Note: DSO is dihydroxydisiloxane; DCS is dihydroxydicarbosilane; DST is dihydroxydisilthian; DISD is diisobutylsilanediol; DIPSD is Pr^i-substituted silanediol.

Apparently, formation of additional (to those, which occur in associates shown in Fig. 2) hydrogen bonds is caused by the presence of empty space within the isolated trimer *c*, which is thus filled. Based on the results obtained, we believe that this trimer (*c*) should not exist, and therefore, this dimer is excluded from subsequent consideration.

The same problems arose when we searched for the optimum structure of dimer *a* for the compounds $[Me_2(HO)Si]_2X$. The reason is, apparently, identical to that mentioned above for trimer *c*. However, for dihydroxydisiloxane (X = O) and dihydroxydicarbosilane (X = CH_2), we succeeded in choosing such initial geometry that the optimized structure corresponds to structure *a*. For dihydroxydisilthian (X = S), when the energy of dimer *a* is minimized, either ordinary or bifurcated intramolecular hydrogen bonds are formed (Fig. 3).

The results of calculations are given in Table 1; the values of the energy per molecule for H-associates, in which not all O and H atoms are involved in hydrogen bonding, include an additional −2 kcal mol^{-1} per hydrogen bond, which does not actually occur but is potentially possible. This correction is caused by the assumption that in real structures, these associates are linked together through hydrogen bonds. This correction (−2 kcal mol^{-1}) is an average value of the calculated energies of hydrogen bonds, which are in the range from −2.1 to −1.9 kcal mol^{-1}.

Results and Discussion

When analyzing the conformational maps, we assumed that if these maps for different molecules are similar, the structures and conformational flexibility of these molecules are nearly identical, and, on the contrary, substantial differences in maps are indicative of the different structural behavior of the molecules. It follows from the comparison of the energy maps $E(\omega_1, \omega_2)$ shown in Fig. 1 that in the structure of dihydroxydisiloxane, the barriers to rotation about the X—Si(1, 2) bonds are substantially smaller than that of dihydroxydicarbosilane. For conformational rearrangements in these molecules, the following barriers were obtained (where $f(\omega_1, \omega_2)$ is the molecular conformation with the torsion angles ω_1 and ω_2):

Transition	E_{DSO} /kcal mol^{-1}	E_{DCS} /kcal mol^{-1}
$f(0, 60) \rightarrow f(0, 180)$	0.8	3.7
$f(60, 60) \rightarrow f(60, 180)$	0.7	3.0
$f(120, 60) \rightarrow f(120, 180)$	1.5	4.3

Positions of local maxima and minima on conformational maps of dihydroxydisiloxane and dihydroxydicarbosilane are similar and the periodicity of their alternation is ~60°. In particular, the points (60, 60), (60, 180), and (60, 300) correspond to minima, while the points (120, 120) and (120, 240) correspond to maxima. Therefore, in our opinion, differences in conformational maps of dihydroxydicarbosilane and dihydroxydisiloxane are insignificant and for dihydroxydicarbosilane, cross-linking of molecules (the presence of H-associates) and hence, occurrence of the mesomorphic state similar to that of dihydroxydisiloxane would be expected.

The conformational map of dihydroxydisilthian differs from those mentioned above. At the points (120, 120), (120, 240), and (60, 180), the situation is similar to that described above, whereas in the points (60, 60) and (60, 300), local minima are absent and these minima are observed for the conformations with the torsion angles of (0, 40) and (0, 320). Note also that the conformations $f(60, 60)$ for dihydroxydisiloxane and dihydroxydicarbosilane correspond to the global minima on the corresponding potential energy surfaces while in the case of dihydroxydisilthian, this minimum appears in the point (0, 40). This difference is caused by formation of an intramolecular hydrogen bond in the structures of dihydroxydisilthian when conformations occur, which favor short distances between oxygen atoms. When the O...O distances are large, the barriers to rotation about the X—Si(1, 2) bonds for this molecule approximate those determined for siloxanes. In particular, for dihydroxydisilthian, E is 1.4 kcal mol^{-1} and 3.4 kcal mol^{-1} for the transitions $f(120, 60) \rightarrow f(120, 180)$ and $f(0, 40) \rightarrow f(0, 180)$, respectively. This difference is caused by the decrease in potential energy when an intramolecular hydrogen bond is formed in the conformation with the torsion angles of (0, 40).

We believe that the differences in conformational maps of dihydroxydisilthian and dihydroxydisiloxane described above are significant. The tendency for the formation of an intramolecular hydrogen bond in dihydroxydisilthian can, apparently, affect the structure of an H-associate, and the hydrogen-bonding pattern is, apparently, different from the pattern that is actually observed in alkyl-substituted dihydroxydisiloxane and determines the occurrence of mesomorphism in these compounds.

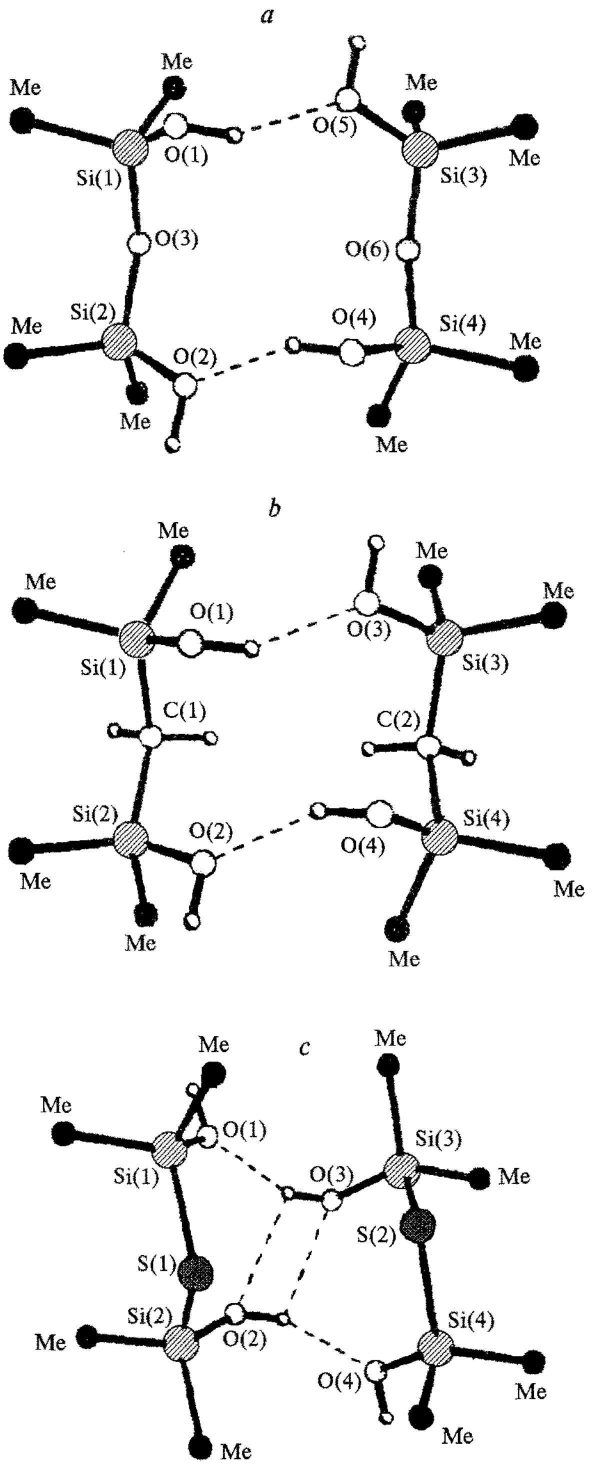


Fig. 3. Dimeric H-associates of dihydroxydisiloxane (*a*), dihydroxydicarbosilane (*b*), and dihydroxydisilthian (*c*).

The analysis of the results of simulation of H-associates for the compounds $[Me_2(HO)Si]_2X$ leads to analogous conclusions. A comparison of dimers of type *a* (see Fig. 3) demonstrates the similarity of dihydroxydisiloxane and dihydroxydicarbosilane and the difference between these compounds and dihydroxydisilthian, for which we failed to obtain this dimer (see above). Identical results of calculations for all three compounds in cases *b* and *d* (see Fig. 2, Table 1) are attributable to the fact that the energies of these H-associates correspond to minima but, probably, not to the global minima because the

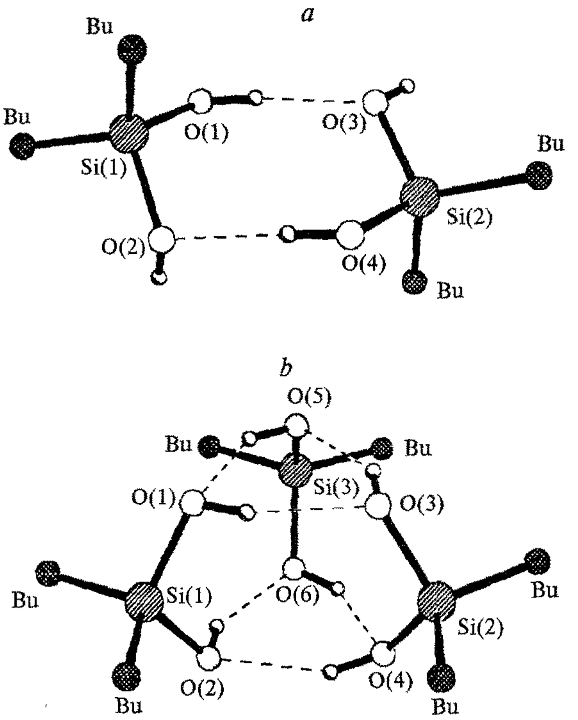


Fig. 4. H-associates of diisobutylsilanediol: *a*, dimers and *b*, trimers.

molecular environment was not taken into account. Only for specially chosen initial conditions, calculations give such minima.

As is evident from the data in Table 1, the energies of associates *a*, *b*, and *d* for dihydroxydicarbosilane and dihydroxydisiloxane are nearly identical, and comparative analysis provides no clear evidence that the formation of intramolecular hydrogen bonds is unfavorable. However, the obtained result correlates well with the results of X-ray structural analysis of dihydroxydisiloxanes,[1–3] which demonstrates that the network of hydrogen bonds observed in the crystal structure does not correspond to types *a*, *b*, and *d*. When performing calculations, we did not seek to obtain a picture of the crystal and liquid-crystal packing for the compounds under study. Our goal was to reveal the difference in structure formation with the participation of isolated molecules and H-associates (when these differences can manifest themselves); these differences were found when the energy of dimers *a* was minimized (see above).

The data obtained for diisobutylsilanediol (Fig. 4, see Table 1) indicate that the trimeric H-associate of type *e* is energetically more favorable. However, an analogous result was obtained also in the case of the Pr^i-substituted silanediol (see Table 1). For this compound, as is evident from the X-ray structural data,[10] dimer *a* occurs in the crystal structure. According to our calculations, this dimer is energetically less favorable. Based on these data, the following conclusions can be made. Because the molecules of diisobutylsilanediol and Pr^i-substituted silanediol differ only by alkyl substituents (Pr^i and Bu^i), this difference may be considered as insignificant for the formation of the framework of H-bonded associates. Then the analogy obtained in molecular mechanics calculations can be extended to the structure formation of these compounds in condensed phases as well. Therefore, the system of structure formation described previously[4] (H-bonded dimers, which form infinite ribbons) is acceptable for diisobutylsilanediol.

More recently,[15] a system of H-bonded trimers was proposed for diisobutylsilanediol. To our knowledge, this proposal was not confirmed experimentally as well; however, if this proposal is considered to be true, change from the Pr^i to the Bu^i substituent in the series of alkyl-substituted silanediols should substantially change the structure of the crystalline state. However, our calculations show that the stability of isolated H-associates is virtually unaffected by this change.

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References

1. A. P. Polishchuk, T. V. Timofeeva, M. Yu. Antipin, N. N. Makarova, N. A. Golovina, Yu. T. Struchkov, and O. D. Lavrentovich, *Metalloorg. Khim.*, 1991, **4**, 147 [*Organomet. Chem. USSR*, 1991, **4**, 77 (Engl. Transl.)].
2. A. P. Polishchuk, M. Yu. Antipin, T. V. Timofeeva, N. N. Makarova, N. A. Golovina, and Yu. T. Struchkov, *Kristallografiya*, 1991, **36**, 92 [*Sov. Phys. Crystallogr.*, 1991, **36** (Engl. Transl.)].
3. A. P. Polishchuk, N. N. Makarova, M. Yu. Antipin, T. V. Timofeeva, M. A. Kravers, and Yu. T. Struchkov, *Kristallografiya*, 1990, **35**, 446 [*Sov. Phys. Crystallogr.*, 1990, **35** (Engl. Transl.)].
4. J. D. Bunning, J. E. Lydon, C. Eaborn, P. H. Jackson, J. W. Goodby, and G. W. Gray, *J. Chem. Soc., Faraday Trans. 1*, 1982, 713.
5. C. Eaborn, *J. Chem. Soc.*, 1952, 149.
6. C. Eaborn and N. H. Hartshorne, *J. Chem. Soc.*, 1955, 549.
7. A. P. Polishchuk, T. V. Timofeeva, N. N. Makarova, M. Yu. Antipin, and Yu. T. Struchkov, *Liquid Cryst.*, 1991, **9**, 433.
8. V. E. Shklover, Yu. T. Struchkov, I. V. Karpova, V. A. Odinets, and A. A. Zhdanov, *Zh. Strukt. Khim.*, 1985, **26**, 125 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
9. N. H. Buttrus, C. Eaborn, P. B. Hitchcock, and A. K. Saxena, *J. Organomet. Chem.*, 1985, **248**, 291.
10. N. H. Buttrus, C. Eaborn, P. B. Hitchcock, and P. D. Lickis, *J. Organomet. Chem.*, 1986, **302**, 159.
11. U. Burkert and N. L. Allinger, *Molecular Mechanics*, ASC, Washington, DC, 1982.
12. T. V. Timofeeva, P. M. Zorkii, and A. P. Polishchuk, in *Problemy kristallokhimii* [*Problems of Crystal Chemistry*], Nauka, Moscow, 1990, 149 (in Russian).
13. A. M. Levelut, *J. Chem. Phys.*, 1983, **80**, 149.
14. O. B. Akopova, V. I. Bobrov, and Yu. G. Erykalov, *Zh. Fiz. Khim.*, 1990, **64**, 1460 [*Sov. J. Phys. Chem.*, 1990, **64** (Engl. Transl.)].
15. J. E. Lydon, 1990, Personal communication.

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