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The conformational analysis of organoelemental and organometallic molecules

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ABSTRACT. The results obtained using the mechanical model of a molecule to calculate the conformation and conformational transformations of the molecules of organoelemental and organometallic compounds have been reviewed. The conformational characteristics of the molecules of hydrocarbons and their organoelemental analogues have been compared. The present state and future prospects of the use of the mechanical model in calculations for the molecules of π-complexes and metal clusters have been described.

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I. Introduction

Conformational analysis in the wider sense involves the study of the relative arrangement of the parts of a molecule and the possibility of a change in this arrangement, taking place without the rupture of chemical bonds, and also the search for the relationship between the reactivity of molecules and their conformation. This analysis includes an examination of both the geometric (bond lengths, valence and torsional angles, non-valence contacts) and the energetic (the relative energies of the conformers and isomers, the barriers to internal rotation, etc.) characteristics of the molecules. The conformers are studied by experimental methods and calculations, and the accessibility of the latter has increased considerably with the significant development of computer technology.

The principal experimental methods for studying the conformation of molecules at present are X-ray diffraction (XRD), neutron diffraction (for molecules in the crystalline state), NMR (for molecules in the liquid state), gas-phase electron diffraction (GED), and spectral methods (for molecules in the gaseous state). All these methods have their advantages and limitations, the most significant limitation being that the results of a study of the structure of molecules in one phase state (particularly for the conformation of non-rigid molecules) cannot be transferred to another phase state without additional analysis (most frequently by calculation).

The calculation methods for studying the conformation of molecules now include semi-empirical and non-empirical quantum-chemical methods, and also empirical methods which use the mechanical model of a molecule (MMM)†, based on the atom–atom approximation.

The possibility of examining a wide range of materials and the considerable saving of machine time (compared with quantum-chemical methods) has now enabled the MMM to occupy an important place among methods used to study molecular conformations. The MMM began to be used for simple organic molecules about 40 years ago,[1,2] and is now used extremely widely in organic and bio-organic chemistry.[3–6] The MMM has also been used for a fairly long time in coordination chemistry.[7,8] In these fields, the method, which has passed through a period of methodological construction and development, is used to solve specific chemical problems. The present paper reviews for the first time the available data on new fields of application of the MMM in the study of the conformational characteristics of organoelemental and organometallic molecules (in particular π-complexes), which have developed significantly only in recent years.

II. The mechanical model of a molecule

The mechanical model of a molecule is an empirical approximation based on the Born–Oppenheimer principle, which makes it possible to examine the motion of nuclei and electrons separately. In this model, the molecule is regarded as a system of interacting atoms, and the intramolecular and non-valence interactions are central in character. For each type of atom there are "ideal" values of the valence angles and bond lengths, deviations from which require the expenditure of energy. To reproduce the experimental values of the dihedral angles and the barriers to rotation about the bonds in the molecules, the model is usually supplemented by a so-called torsional component characterising the expenditure of energy due to the deviation from the optimum relative orientation of the fragments of the molecules joined by chemical bonds. Where necessary, the model also takes account of the energy of electrostatic interactions, hydrogen bonds, etc.

Thus the conformational energy of a molecule (representing the fraction of its total energy which depends on the conformation) can be written as

$$U_{conf} = U_{non\text{-}v} + U_{bd} + U_{ang} + U_{tors} + U_{el} + \ldots$$

† A number of equivalent names are used in the Soviet and other literature for calculations of this type, for example "molecular mechanics", "force-field calculations", etc.

Here, the energy of the non-valence interaction ($U_{non\text{-}v}$) is the sum of the paired interactions of all the atoms (atom–atom approximation), and is most frequently described by the Lennard–Jones ("6–12") or Buckingham ("6-exp") potentials:

$$U_{non\text{-}v} = -Cr^{-6} + Ar^{-12},$$
$$U_{non\text{-}v} = -Cr^{-6} + A\exp(-Br),$$

where r represents the interatomic distances, and A, B, and C are empirical constants, obtained, for example, from the virial coefficients and the equilibrium interatomic distances for the inert gases.

The terms U_{bd} and U_{ang} are the energies required to deform all the bonds and valence angles in the molecule from the ideal values (l_0 and θ_0), for which the mean-statistical values are often taken‡, to the actual values (l and θ). For the small deformations usually observed with change in the conformation, Hooke's law (the harmonic approximation) is applicable:

$$U_{bd} = 0.5K_l(l-l_0)^2,$$
$$U_{ang} = 0.5K_\theta(\theta-\theta_0)^2,$$

where K_l and K_θ are the force constants of the bonds and angles, obtained from the vibrational spectra of the simple molecules. The torsional energy (U_{tors}) is written as

$$U_{tors} = 0.5U_0(1+\cos n\varphi),$$

where U_0 is the torsional constant (inherent barrier), selected from experimental or quantum-chemical data on the barriers to internal rotation, φ the dihedral (torsional) angle for the kth bond, and n the multiplicity of the barrier to rotation.

The energy of the electrostatic interactions (U_{el}) is taken into account fairly infrequently, sometimes in the dipole–dipole or, more often, in the monopole approximation:

$$U_{el} = q_i q_j/\varepsilon r_{ij},$$

where q_i and q_j are the charges on the ith and jth atoms (obtained from a quantum-chemical calculation) situated at a distance r_{ij} from one another, and ε the dielectric constant (usually, $\varepsilon = 1$).

The geometry of an isolated (free) molecule corresponds to a conformational energy minimum. Thus the determination of the optimum molecular conformation involves the search for a minimum value of U_{conf}.

Depending on the form of representation of the coordinates of the atoms in the molecule (Cartesian or coordinates expressed in terms of the bond lengths and valence and torsional angles—the so-called "tree system"), different methods of minimising U_{conf} are used, and these have been described in detail.[3,4] In the general case, the problem of determining the optimum geometry of a molecule reduces to the search for a minimum of a function of $(3N-6)$ variables, where N is the number of atoms in the molecule. Fairly frequently, however, most of the geometric parameters of the molecule can be fixed, so that the problem is simplified, and reduces to scanning the values of U_{conf} over several variables (constructing the corresponding graphs and conformational maps). The search for the minimum of U_{conf} over all variables is naturally possible only for molecules in which the number of atoms is not too large, up to ~100, whereas when the number of parameters is restricted, it is possible to examine the conformation of very large molecules, for example proteins. The molecule is usually described in the Cartesian system of coordinates in the first case, and using the "tree system" in the second. Both of these methods of specifying the geometry and the corresponding methods for finding the minimum of U_{conf} have been used in a large number of computer programs. The first of these methods is employed, for example, in the widely used programs MM2 and MMP2 of Allinger and co-workers[4] and in Boyd's program MOLBD3,[9] and the second is used in the program ECEPP of Scheraga and co-workers[10] for calculating peptide structures.

The choice of parameters for conformational calculations will not be dealt with in detail. The most widely encountered method of finding the parameters—the constants in the expressions for the components of U_{conf}—is by variation for a series of simple compounds of the same type to achieve the best agreement between the calculated and experimental data (the geometric parameters of the molecules, the barriers to internal rotation, etc.) or corresponding data obtained in a non-empirical quantum-chemical calculation. Data on the specific sets of parameters proposed by different authors for groups of compounds of the same type will be given in the appropriate sections.

III. Conformational calculations for organoelemental molecules

The similarity in the structures of hydrocarbons and organoelemental compounds in which one or several C atoms have been replaced by the atoms of an element X = Si, Ge, Sn, Pb is fairly obvious (the tetrahedral coordination of the atoms C and X, the formation of ordinary σ-bonds, the absence of lone pairs of electrons). Conformationally, however, the molecules of hydrocarbons and their organoelemental analogues (linear and cyclic) may differ considerably. This led to the idea of using the MMM to calculate the conformations of these molecules to investigate the reasons for their similarities and differences.[11–13] Two large groups of compound forming acyclic and cyclic molecules will be considered as an example of how this problem was solved.

1. Acyclic organoelemental molecules

Parameters of the potentials have been proposed[11–13] for the calculations for organoelemental molecules (X = Si, Ge, Sn), and a number of calculations have been carried out for fairly simple molecules, to verify the suitability of the proposed parameters. Most of the calculations have been carried out for organosilicon molecules,[11,12] since they have been more fully characterised by physicochemical methods. The good agreement between the calculated and experimental data made it possible to use the proposed parameters with confidence for carrying out specific calculations.

The relative energetic advantage of the conformers and the barriers to conformational transformations have been examined[13] for various simple hydrocarbons and their organoelemental analogues in which one of the C atoms has been replaced by an X atom. In the compounds $MeHX_3$, Me_2XH_2, and Me_3XH, on going from X = Si to X = Ge and Sn, the barrier to rotation about the C–X bond decreases considerably, the values being 1.6 (X = Si), 1.2 (X = Ge), and 0.65 (X = Sn) kcal mol^{-1} respectively. This is attributed to the decrease in the contribution of the non-valence interactions to the magnitude of the barrier, as a result of the increase in the length

‡The mean-statistical values of the geometric parameters are calculated for the isolated molecules in the gas phase from GED data or for the molecules in the crystal from XRD data, collected in the Cambridge Structural Data Bank.

of the C–X bond, and to the simultaneous decrease in the torsional constant for this bond, which has the values 0.5, 0.38, and 0.22 kcal mol^{-1} for X = Si, Ge, and Sn respectively.

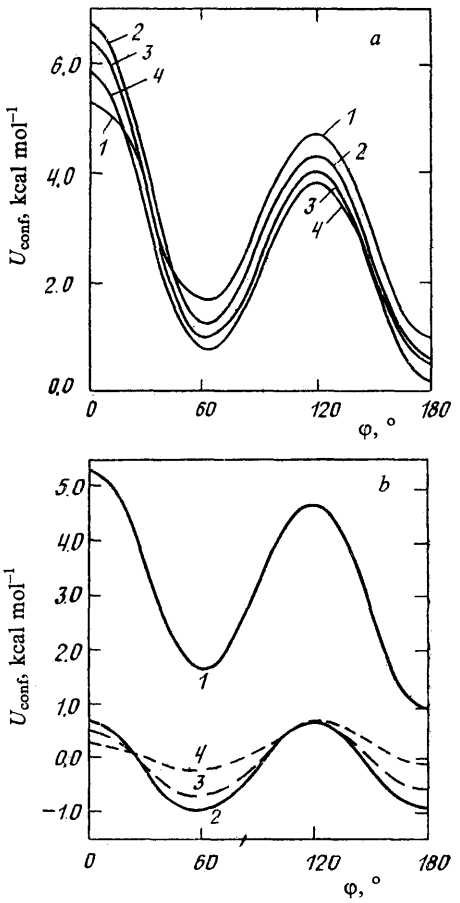


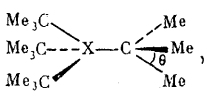
Figure 1. Dependence of U_{conf} on the angle of rotation about the central bond in the molecules $CH_3CH_2CH_2XH_3$ (*a*) and $CH_3CH_2XH_2CH_3$ (*b*), where X = C (*1*), Si (*2*), Ge (*3*), and Sn (*4*).[10]

The introduction of an organoelemental substituent on one of the C atoms has little influence on the magnitude of the barrier to rotation about the C–C bond. Thus for the molecules $CH_3CH_2XH_3$, these barriers have the values 3.78, 3.87, and 3.98 kcal mol^{-1} for X = Si, Ge, and Sn respectively.

A calculation made it possible to estimate[10] the ratio of the relative energies of the *gauche* (or crossed, φ = 60°) and *anti* (or *trans*, φ = 180°) conformations (rotation about the central bonds) for the molecules $MeCH_2CH_2XH_3$ and $MeCH_2XH_2Me$. In the first case (Fig. 1*a*), the introduction of the atom X into the terminal group does not change the conformation of the molecule relative to n-butane, and only leads to a slightly greater difference in the energies of the eclipsed and staggered conformations. This is understandable, since in this case the central bond does not change, and the terminal groups are "repelled" more strongly in the eclipsed conformation, since they are brought closer together by the increase in the length of the C–X and X–H bonds. In the second case, the *trans*- and *gauche*-conformers of $MeCH_2XH_2Me$ (unlike the corresponding conformers of n-butane) have similar energies (Fig. 1*b*). The explanation is that the increase in the length of the central bond in the molecule is associated with an increase in the contribution made to U_{conf} by the energy of attraction between the H atoms of the terminal methyl groups, favouring the approach of these groups, that is the energy of the *gauche*-conformation approaches that of the *trans*-conformation.

Mislow and co-workers[14–19] examined not only the relative advantage of the conformers and the values of the barriers to rotation but also the mechanism of internal rotation in molecules, in particular the mechanism of the rotation of several bulky substituents situated on one C or X central atom. Thus the rotation of the t-butyl groups in the $HSi(Bu\text{-}t)_3$ molecule was analysed.[19] Here, two mechanisms of internal rotation of the alkyl substituents are possible: independent and coupled, that is involving the simultaneous rotation of at least one other substituent. In the case being considered, only coupled rotation takes place. The rotation of the t-butyl groups can take place in two ways: all three t-butyl groups may be present simultaneously in the staggered (*S*) orientation (*SSS*, barrier to rotation 5.1 kcal mol^{-1}), or one of the groups may be present in the eclipsed (*E*) orientation, and the other two in the staggered orientation (*ESS*, barrier 6.8 kcal mol^{-1}). The fact that the magnitude of the second barrier is close to the experimental value obtained from NMR data, $\Delta G^{\neq}$ = 6.1 ± 0.3 kcal mol^{-1}, was taken as evidence that the actual mechanism of internal rotation is of the *ESS* type.

For two series of sterically crowded molecules $X[CMe_3]_4$ and $X[SiMe_3]_4$, where X = C, Si, Ge, Sn, and Pb, calculations have been carried out[18] to determine the geometric parameters of the molecules (there are no published experimental data for molecules of the first type) and to compare the energies of their conformers with *T* and S_4 symmetry. The results of the calculation for the molecules



where X = C, Si, Ge, Sn, Pb, are summarised in Fig. 2. Fig. 2 shows that the difference in the values of U_{conf} for the energetically more favourable (*T*) and less favourable (S_4) conformers (ΔU_{conf}) decreases with increase in the atomic number of the central atom. At the same time, the angle θ increases, and its value approaches the usual tetrahedral value. For the first member of the series (X = C), for which the steric crowding is greatest, the decrease in this angle is fairly large. The same trend in the change in the geometric and energetic parameters was detected in the series of molecules $X[SiMe_3]_4$.

A search for the most favourable conformations and an analysis of the routes of conformational rearrangements has also been carried out for aryl-substituted§ derivatives of methane and silane.[15,16] The most favourable conformations were found to be that with D_{2d} symmetry for the CPh_4 molecule, and that with S_4 symmetry for the $SiPh_4$ molecule.[15] It was pointed out[15] that this result was not obtained for these compounds in earlier calculations,[20] since the authors of these calculations did not vary all the geometric parameters, but only the values of the torsional angles round the C–Ph or Si–Ph bonds. For the molecules CR_4 and SiR_4, where R = *o*-tolyl or 2,6-xylyl, the S_4 conformers were found to be most

§The parameters of the potentials for conformational calculations for molecules containing an Si–Ar bond have been published.[15]

favourable.[15] A calculation to analyse the mechanism of internal rotation in molecules of this type showed[15] that the rotation of the substituents in this case, as in the case of the t-butyl derivative of silane, is not independent, and the route of the conformational transformation can be represented by the sequence of conformers shown in Fig. 3. Although the molecules with the *o*-tolyl substituents are less symmetrical, and a large number of conformational transformation routes are possible for these molecules, the most favourable mechanism of rotation for these molecules was found to be similar to that found for the Ph-derivatives. The calculated values of the barriers to the internal rotation of the substituents for the molecules of $SiPh_4$ and $Si(o\text{-}CH_3C_6H_4)_4$, 14.9 kcal mol^{-1} and 19.6 kcal mol^{-1} respectively, lie in the range of values of the activation energy of the topo-isomerisation process obtained experimentally from NMR data.

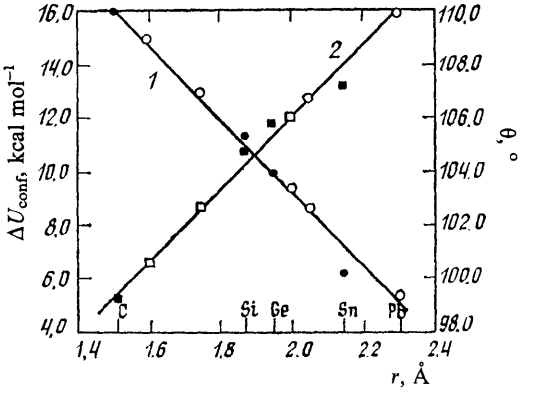


Figure 2. Dependences of the difference in the energies ΔU_{conf} (*1*) between the *T*- and S_4-conformers and of the angle θ (*2*) on the C–X bond length in $X(CMe_3)_4$ molecules, where X = C, Si, Ge, Sn, Pb;[18] the black points correspond to the actual structures, and the white points to model structures with intermediate values of the C–X bond lengths.

Stereo-isomerisation has been examined[14] for a large number of triaryl-substituted molecules. The authors cited used a simplified approach, in which the same parameters [as for the $HC(Mes)_3$ molecule] were used for the molecules $Z(Mes)_3$, where Z = B, CH, SiH, GeH, N, P, and As, and Mes = mesityl, and only the length of the Z–Mes bond was changed. The calculation of the routes for the simultaneous internal rotation of one, two, and three substituents (Fig. 4) showed that the simultaneous rotation of two aryl fragments is most favourable in this case. The calculated and experimental values of the barriers to rotation in these molecules are compared in Fig. 5. The calculation provides a qualitatively correct description of the change in the magnitude of the barrier with change in the Z–Mes bond length, but it does not reproduce the experimental values quantitatively. This last feature (the high values of the barriers) was attributed to the use of a simplified model, in which the lengths of the bonds formed by the central atom Z in the molecule were not varied.

Halogen-substituted alkylsilanes of the type $Si(CH_2Hal)_4$, $H_2Si(CHal_3)_2$, and $Hal_2Si(CHal_3)_2$, where Hal = F, Cl, Br, have been studied.[21,22] For the tetra-substituted molecules,[21] for all Hal, the conformation with D_{2d} symmetry is most favourable. The order of the relative advantage of the conformers is different for different halogens, however: $D_{2d} > C_s > C_2 > C_1 > S_4$ for F, $D_{2d} > C_4 > C_1$ for Cl, and $D_{2d} > S_4$ for Br. The conformation with C_2 symmetry is most favourable for the dialkyl-substituted molecules $H_2Si(CHal_3)_2$, and that with C_{2v} symmetry is most favourable for $Hal_2Si(CHal_3)_2$. The calculated barriers to the internal rotation of the substituents are 5.7, 14.5, and 14.8 kcal mol^{-1} for F, Cl, and Br respectively in the molecules $H_2Si(CHal_3)_2$, and 2.2, 8.2, and 8.5 kcal mol^{-1} respectively for $Hal_2Si(CHal_3)_2$.

Parameters making it possible to use the mechanical model of a molecule to carry out calculations for allylsilanes have been proposed.[23] The parameters were selected by fitting the results of calculations using the MMM to the results of non-empirical quantum-chemical calculations using different basis sets. The torsional potential of the rotation about the central bond in the fragment C=C–C–Si was found to be close to the usual value for rotation about a $C(sp^2)$–$C(sp^3)$ bond. The minimum energy

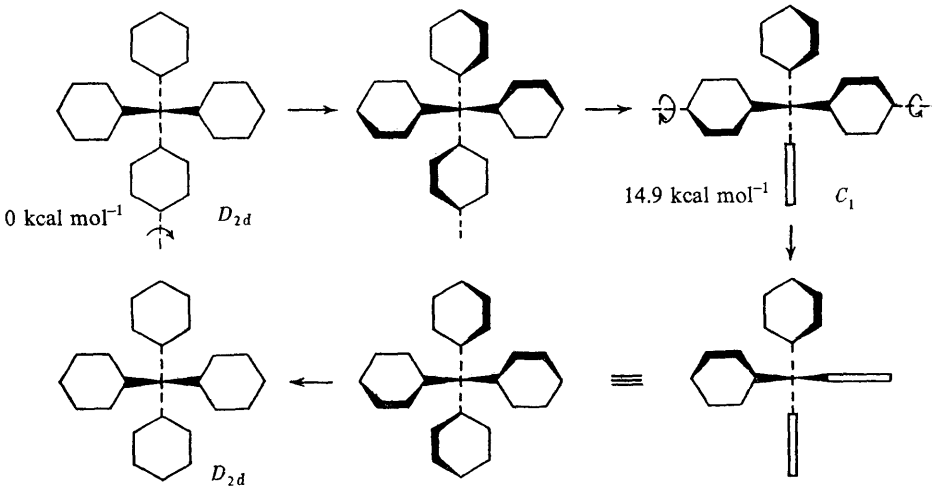


Figure 3. Internal rotation pathway in tetraphenylmethane.[15]

corresponds to the conformation of allylsilane with a torsional angle of rotation round the central bond equal to ~100°; the values of the *cis*- and *trans*-barriers differ slightly, and according to the data obtained using the MMM (in agreement with quantum-chemical calculations) are equal to 2.09 kcal mol^{-1} and 2.75 kcal mol^{-1} respectively.

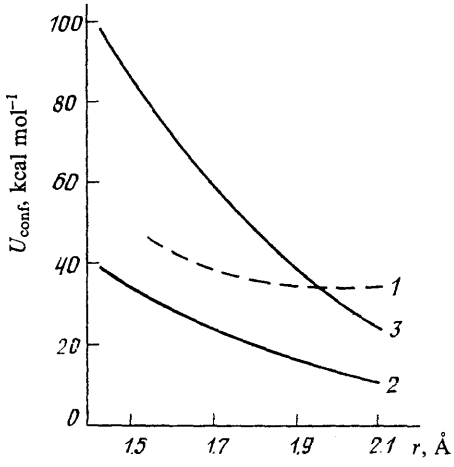


Figure 4. Calculated energies of the transition state for different mechanisms of the stereo-isomerisation of $Z(Mes)_3$ molecules: *1*, rotation of one mesityl substituent; *2*, two substituents; and *3*, three substituents (r is the $Z-C_{Mes}$ bond length).[14]

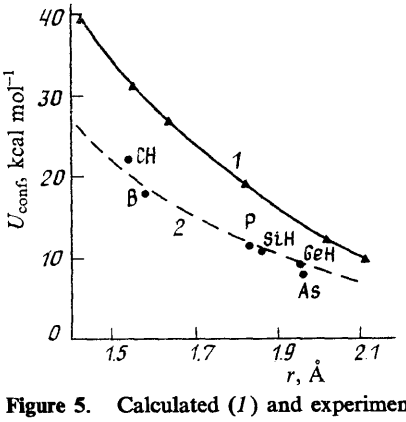
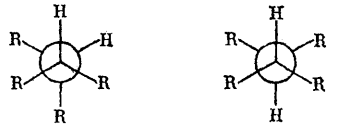


Figure 5. Calculated (*1*) and experimental (*2*) values of the energy of stereo-isomerisation for $Z(Mes)_3$ molecules (r is the length of the $Z-C_{Mes}$ bond).[14]

A parametrisation which makes it possible to carry out conformational calculations for molecules containing chains of several Si atoms was described by Mislow and co-workers[24] and developed in later studies.[25] The simplest representatives of this series are the alkyl-substituted disilanes $(R_2HSi)_2$, where R = Me, t-Bu, and Cy (cyclohexyl).[26] For the compound with R = Me, the energies of the *gauche*- and *anti*-conformations



according to the calculations, differ by 0.2 kcal mol^{-1}, but the barriers to the transformations $G \rightleftarrows G^-$ and $G \rightleftarrows A$ are fairly small: 0.97 kcal mol^{-1} and 1.34 kcal mol^{-1} respectively. The dependence of U_{conf} on the angle of rotation about the Si–Si bond in the $[(t\text{-Bu})_2HSi]_2$ molecule is shown in Fig. 6. In this case the barriers to the corresponding conformational transformations are significantly larger: 24.9 kcal mol^{-1} for $G \rightleftarrows G^-$ and 15.1 kcal mol^{-1} for $G \rightleftarrows A \rightleftarrows A^- \rightleftarrows G^-$; the last value is close to the experimental value obtained by NMR ($\Delta G^{\neq}$ = 13.8 ± 0.3 kcal mol^{-1}). For $(Cy_2HSi)_2$, for which the number of possible conformers is appreciably greater than in the previous cases (45 *gauche*- and 27 *anti*-forms), the most favourable conformer was again found to be one of the *gauche*-conformers, whose structure shows good agreement with that found in the crystal by XRD.

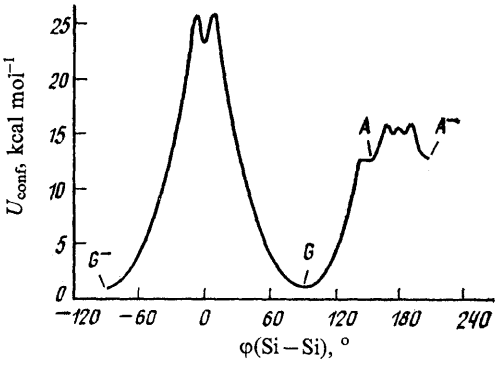


Figure 6. Dependence of U_{conf} on the angle of rotation about the Si–Si bond in the $[(t\text{-Bu})_2HSi]_2$ molecule.[26]

The stereochemistry of similar tetra-aryl-substituted disilanes has been studied[27] using the MMM, XRD, and NMR. For the $(Ph_2HSi)_2$ molecule, the energies of five *G*- and *A*-conformers are similar (the energies of the most favourable C_2– and C_i-conformers are –7.12 kcal mol^{-1} and –6.68 kcal mol^{-1} respectively). For the $(Mes_2HSi)_2$ molecules (in contrast to the alkyl derivatives described above), the *anti*-conformation becomes much more favourable [$U_{conf}(A)$ = 10.55 kcal mol^{-1}, $U_{conf}(G)$ = 13.08 kcal mol^{-1}]. The results of the calculation for the two molecules show good agreement with NMR data (in solution, the Ph-derivative exists as a mixture of conformers, whereas for the Mes-derivative the *anti*-form with C_2 symmetry predominates) and with XRD data for these compounds, according to which both derivatives are present in the crystals as the *anti*-conformers.

Molecules containing chains of several Si atoms have been examined.[24,25] The study of these molecules is a necessary stage in the determination of the structure of polymeric silane molecules. The parametrisation used in the works cited, and hence the results of the calculations, differ slightly. Table 1 compares the results of the calculations with the available experimental data for the molecules studied. The results obtained with the parametrisation proposed by Hönig and Hassler[25] show better agreement with the experimental data (Table 1). This last feature apparently explains why this version of the parameters was used to calculate the conformation of the polymer chains of polysilane $H(H_2Si)_nH$ and polydimethylsilane $Me(Me_2Si)_nMe$.[29] In the work cited, a calculation of the conformations of polysilane molecules containing n = 30, 10, and 5 units was used to analyse the dependence of the qualitative results obtained on the length of the chain being studied. The minimum chain length making it possible to model all its possible conformations was found to be that with n = 5. The data obtained for the chain with n = 5 can be used to obtain a sufficiently full description of the conformtion of longer chains. This made it possible, in the study of the conformation of polydimethylsilane, to consider only a fragment of the chain with n = 5. These calculations were repeated by Welsh and co-workers[30] with slight restrictions, in that account was taken of only the non-valence and torsional components of the energy, and also by Tashiro and co-workers,[31] where the parametrisation for the silanes (for the program MM2) was calibrated from the results of quantum-chemical calculations for model molecules.

Table 1. Comparison of the results of conformational calculations and experimental data for silane molecules.

Molecule	Confirmation	U^{rel}_{conf}, kcal mol^{-1}		ΔU, kcal mol^{-1} (method)
		Hummel et al. (Ref.24)	Hönig and Hassler (Ref.25)	
Disilane**	*S*	0.0	0.0	1.22 (IR)
	E	1.20	1.20	
Hexamethyldisilane	*S*	0.0	0.0	—
	E	1.05	1.20	
Tetrasilane	*A*	0.10	0.31	0.0 (ESCA)
	G	0.0	0.0	
Decamethyltetrasilane	*A*	0.0	0.0	0.55 (NMR, IR)
	G	0.12	0.55	

*See the paper by Hönig and Hassler[25] for references to experimental work.

**According to a non-empirical quantum-chemical calculation,[28] the relative energies of the *S*- and *E*-conformers are 0.0 and 3.8 kcal mol^{-1} respectively.

The results of the calculations for a chain with n = 5, carried out by Damewood and West[29] and Welsh and co-workers[30] (Table 2), and also by Tashiro and co-workers,[31] agree well with one another, and indicate that the *GG*-conformer is the most favourable. The differences, given below, in the conformational energies of the *anti*- (planar zigzag) and *gauche*- (spiral) conformers for alkane and silane chains[31] indicate an increase in the energetic advantage of the *gauche*-conformer for the silane and of the anti-conformer for the alkane with increase in the chain length:

n	4	5	7	13	17	21	30
ΔU (C_nH_{2n+2}), kcal mol^{-1}	0.86	1.62	2.99	7.09	10.01	12.88	19.05
ΔU (Si_nH_{2n+2}), kcal mol^{-1}	0.07	0.02	−0.16	−0.53	−0.83	−1.12	−1.82

Table 2. Relative energies of different conformers of polysilane and polydimethylsilane, kcal mol^{-1}.

Conformer	Polysilane		Polydimethylsilane	
	Profeta et al. (Ref.23)	Stolevik and Bakken (Ref.22)	Profeta et al. (Ref.23)	Stolevik and Bakken (Ref.22)
AA	0.51	0.7	0.42	0.9
AG	0.21	0.4	0.00	0.8
GG	0.00	0.0	0.08	0.0
G^+G^-	0.41	0.4	—*	38.4

*Large quantity, not calculated.

A statistical analysis of the conformational stability of polysilane chains has been carried out.[30] The calculation showed that the characteristic ratio

$$C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0/nL^2,$$

where $<r^2>_0$ is the mean-square distance between the ends of the chain, n the number of units, and L the length of the unit in the chain, is 4.02 for polysilane, and 12.2−15.0 for polydimethylsilane (depending on the method used to calculate the conformational energy). Comparison of these values with the values of C_∞ for polyethylene (6.7) and polydimethylsiloxane (6.4) indicates that the polydimethylsilane molecule is less flexible than these polymers.

The influence of lateral substituents on the conformation of a polysilane chain has not been studied by calculation, but it can be followed from experimental studies of the structure of polymers of the type $R-(SiR_2)_n-R$. The polymer with R = n-pentyl has a spiral chain conformation (7/3 spiral), and that with R = n-hexyl has a planar zigzag conformation, which is apparently stabilised by the regular packing of the lateral substituents.[32,33] In the opinion of the authors cited,[32] the existence of extended chain fragments with the *trans*-conformation is responsible for the unusual spectral properties of the hexyl-derivative (the displacement of the absorption band to the low-wavenumber range 370−380 nm), not observed for its homologues with n < 6.

The fluorescence of the n-hexyl-derivative in the near ultraviolet range (λ_{max} = 300−400 nm) has also been attributed to the presence of planar *trans*-fragments.[34] Experimental data and quantum-chemical calculations indicate that the chain in this macromolecule effectively breaks down into a number of planar chromophores separated by sections with the *gauche*-conformation, between which rapid exchange of energy takes place.[34]

No experimental data have yet been published on the stucture of diphenyl-substituted polysilanes $R-(SiPh_2)_n-R$, but their conformation can be characterised from XRD data for the oligomers with

chain length $n = 4-7$.[35,36] The conformation of the phenyl-substituted polysilanes changes from planar to spiral with increase in the length of the oligomer chain. This last feature (and the fact that, as shown above, the chain with $n = 5$ repeats the conformation of the corresponding polymer) indicates that the corresponding polymers also contain chain fragments with the spiral conformation.

2. Organoelemental molecules containing cyclic fragments

A number of authors[12,37-41] have examined the influence of organoelemental substituents on the conformation of saturated cyclic hydrocarbons, and also the relative advantage of different arrangements of the substituents in them, in particular the equatorial (*e*) and axial (*a*) arrangements. Calculation has shown[12] that in mono-substituted cyclohexanes containing organoelemental substituents, as in those containing organic substituents, the equatorial arrangement is most favourable; its energetic preference compared with the axial arrangement (ΔE) for different substituents is given below:

R	Me	SiH_3	Me_2CH	Me_2SiH	Me_3C	Me_3Si
ΔE, kcal mol^{-1}	1.77	1.26	2.05	1.94	5.41	3.41

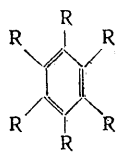
In this case, equatorial substituents have practically no influence on the conformation of the ring, whereas axial substituents lead to slight flattening.

In 1,2-disubstituted cyclohexanes[37] with comparatively small substituents (Me, SiH_3), the di-equatorial *trans*-arrangement is most favourable, as indicated both by calculations using the MMM and by non-empirical quantum-chemical (QC) calculations[37] (Table 3). For bulky substituents, the di-axial conformation is more favourable (Table 3). For $SiMe_3$ this is the only favourable conformation, but for CMe_3 the twist conformation has a similar energy. The results of the calculation show good agreement with NMR data,[36] which show that the solution of the first compound contains one conformer, whereas the solution of the second contains a mixture of two conformers.

Table 3. Relative energies of 1,2-disubstituted cyclohexanes (kcal mol^{-1}) from MMM data and QC calculation.

Conformation	Me		SiH_3		CMe_3	$SiMe_3$
	MMM	QC	MMM	QC	MMM	MMM
e,a-cis	1.62	1.96	0.78	1.16	5.29	1.80
a,a-trans	2.44	2.76	0.70	1.69	0.0	0.0
e,e-trans	0.0	0.0	0 0	0.0	6.73	1.70
twist-trans	5.40	8.15	5.80	6.50	0.41	2.34

The influence of bulky substituents, including group IV elements, on the conformation of the aromatic ring in hexa-substituted benzenes, and also the possibility and the mechanism of the internal rotation of these substituents, have been studied by Mislow and co-workers.[38-41] The problem was solved by a combination of experimental methods (NMR, XRD) and calculations. The following series of compounds was studied:



(I)—(VI)

(I): R = CH_2Me (Ref.38),
(II): R = $CHMe_2$ (Ref.39),
(III): R = $SiHMe_2$ (Ref.40),
(IV): R = CMe_3 (Ref.41),
(V): R = $SiMe_3$ (Ref.41),
(VI): R = $GeMe_3$ (Ref.41).

According to the calculations, which show good qualitative agreement with XRD data, the ethyl, isopropyl, and dimethylsilyl substituents do not distort the planar structure of the aromatic ring. These distortions are detected, however, when the bulkier trimethylgermyl substituent is introduced. The C—C bond length in the benzene ring is increased considerably (to 1.418 Å) relative to the value 1.384 Å in non-substituted benzene, the ring acquires a flattened chair conformation, and the arrangement of the $GeMe_3$ substituents, which are displaced considerably from the average plane of the central ring, is described as a "superchair" conformation. The average value of the torsional angles Ge—C—C—Ge is 57.1° (XRD), in good agreement with the results of the calculation. The same trend in the distortion of the benzene ring was found from the results of the calculation for molecules (IV) and (V).

The conformation corresponding to the energy minimum for all three molecules with substituents XMe_3 [(IV)—(VI)] has D_3 symmetry. A second possible conformation for these molecules, with S_6 symmetry, is much less favourable (by 16—18 kcal mol^{-1}).

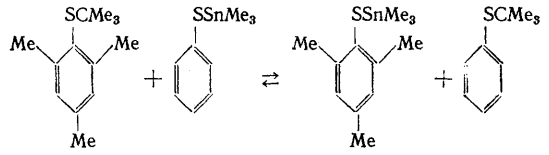
Molecules (I)—(III) have a large number of conformers [8 for (I) and 9 for (II) and (III)]. Calculation of their relative energies showed that for molecule (I), the most favourable conformation is that with D_{3d} symmetry (Me groups arranged alternately above and below the plane of the benzene ring), and for molecules (II) and (III) the C_{6h} conformation is most favourable (the H atoms of the substituent lie in the plane of the ring and occupy the space between the groups of neighbouring substituents). The calculation also made it possible to reach conclusions about the mechanism of internal rotation of the substituents in molecules (I)—(III). Two possibilities were examined—coupled (correlated) and "stepwise" (non-correlated) rotation of the ethyl, isopropyl, and dimethylsilyl groups. The second version of the rotation makes it possible to select the conformational transformation route with the lowest barrier. For example, for molecule (III), according to the calculations, the coupled rotation of the substituents can take place with an energy barrier of ~90 kcal mol^{-1}, whereas for stepwise rotation the barrier is ~35 kcal mol^{-1}. NMR data¶ for this compound give for the barrier the value $\Delta G \geqslant 22$ kcal mol^{-1}. Much better agreement is observed for the barriers to rotation of the substituents in molecules (I) and (II): 11.8 and 15.7 (calculation) and 11.5 and 14.2 (experiment) kcal mol^{-1} respectively. This proves the stepwise mechanism of internal rotation in molecules (I)—(III).

The optimum orientations and the barriers to internal rotation of the substituent R in molecules ArSR (R = CH_3, CMe_3, $SnMe_3$ and $SnPh_3$) have been compared.[42] The calculations showed that the substituent R usually does not lie in the plane of the aromatic

¶ The energy of the internal rotation was measured by a dynamic NMR method for π-complexes of compounds (I)—(III) with $Cr(CO)_3$.[41] The authors cited[41] consider that the steric influence of tricarbonylchromium is slight, and that the conclusions about the mechanism of rotation in the isolated molecules C_6R_6 are unaffected.

fragment (the dihedral angle C–C–S–R is 80–90°). For Ar = Ph, internal rotation is possible for all the substituents except CMe_3. For Ar = Mes, this rotation is unlikely for all types of substituent.

The conformational energies of the starting materials and reaction products have also been calculated[42] for the exchange reaction:



The replacement of the t-butyl group, which experiences greater steric hindrance, by the trimethylstannyl group is accompanied by a decrease in the sum of U_{conf} for the reaction products compared with the sum for the starting materials by ~8 kcal mol^{-1}, that is the equilibrium should be displaced to the right.

The conformational characteristics of saturated molecules with one or several X atoms in the ring have been studied.[11,12,43,44] It is fairly obvious that these molecules should differ from the corresponding cycloalkanes, primarily because of the non-equivalence of the bond lengths in the ring. For silacyclopentane, the relative advantage of the conformers decreases in the order:[44]

half-chair (C_2) 8.42 kcal mol^{-1} → envelope (C_s) 11.77 kcal mol^{-1} →
→ planar conformation (C_{2v}) 14.23 kcal mol^{-1}

and the calculated values of the geometric parameters of the most stable conformer (C_2) agree with experimental data on its structure in the gas phase.[45] The introduction of methyl substituents into different positions in silacyclopentane (1-; 1,2-*cis*-; 1,2-*trans*-) does not lead to a significant change in its conformation.[44] When the ring does not contain a heteroatom (cyclopentane), the conformations C_2 and C_s are energetically equivalent.

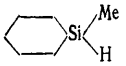
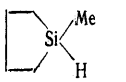
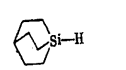
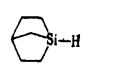
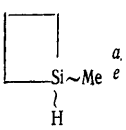
For silacyclohexane, the energy difference between the most favourable chair conformation and the next most favourable twist conformation (according to different data) is 3–4 kcal mol^{-1}.[11,43] For silacyclohexane, in contrast to cyclohexane, the ring is flattened slightly in the region of the Si atom and "wrinkled" in the region of the C atom lying opposite (according to calculation,[44] the endocyclic angles at these atoms are 104.2° and 113.5° respectively).

Comparison of the energies of mono-substituted silacyclohexanes[44] showed that for the 2-, 3-, and 4-methyl-derivatives, the equatorial isomers are more favourable (their energies are lower than those of the axial isomers by 1.87, 1.66, and 1.27 kcal mol^{-1} respectively). For 1-methylsilacyclohexane, the data on the relative advantage of the isomers differ slightly; Cartledge[44] considers the axial isomer to be more favourable, whereas Ouelette and co-workers[12] consider the equatorial isomer to be more favourable (difference in the energies 0.2 kcal mol^{-1} and 0.3 kcal mol^{-1} respectively). Both results indicate, however, that these isomers have similar energies.

For cyclic compounds of the type being considered, the calculations effectively reproduce the barriers to inversion of the ring. Thus for 1,1-dimethylsilacyclohexane, calculation gives the value 5.46 kcal mol^{-1}, and experiment gives the value 5.5 kcal mol^{-1} (in the analogous hydrocarbon, the corresponding values are slightly higher, 8.99 kcal mol^{-1} and 10–11 kcal mol^{-1}).

It has been shown[44] that the MMM can be used to establish the relationship between the structure and reactivity of compounds. The calculations were carried out for a series of cyclic and polycyclic molecules with one Si atom in the ring. It was previously assumed that in these compounds, the hydrolysis of the Si–H bond under basic catalysis conditions depends on the degree of strain of the coordination site including the Si atom, that is, in the language of molecular mechanics, on the contribution of U_{ang}(Si) to the total conformational energy. To verify this suggestion, the correlation between U_{ang}(Si) for several molecules and the hydrolysis rate constant was analysed (the corresponding data are given in Table 4 and Fig. 7). The graph in Fig. 7 shows that the strain in the angle at the Si atom is linearly dependent on lg k_{rel}, and the correlation coefficient (0.991) indicates that this relationship is not accidental.

Table 4. Strain in the angles at the Si atom and reactivity of a series of silanes in hydrolysis.[44]

Molecule, conformation	Endocyclic angles C–Si–C, °	U_{ang}(Si), kcal mol^{-1}	lg k_{rel}
 *a* *e*	104.6 104.9	0.4 0.4	0
	91.7	1.9	2
	102.2 102.2 102.2	2.1	2
	94.3 94.3 102.2	6.2	4
 *a* *e*	75.0 75.7	10.3 9.9	5.5

The study by experimental methods and calculations of the structure of cyclic and more particularly macrocyclic polysilanes is to a large extent determined by their unusual properties: the formation of charge-transfer complexes, radical-anions and radical-cations, and absorption in the ultraviolet range.[46]

A series of conformational calculations has been carried out[25,47] for cyclic silanes $(SiR_2)_n$ with small rings (n = 4–6) and different substituents, in particular with R = H, Me, Cl, Br, I. The authors cited compared the results of the calculations with earlier results obtained by calculations and experimental studies. The data obtained[25,47] are summarised in Table 5. Table 5 shows that for four-membered silane rings (as for cyclobutane), the folded conformation is more favourable. A similar result for $(SiH_2)_4$ was obtained by a non-empirical quantum-chemical calculation,[48] according to which the relative advantage of the D_{2d} conformation

Table 5. Relative conformational energy of cyclic silanes $(SiR_2)_n$, $n = 4-6$ (kcal mol^{-1}).

Molecule	Conformation (symmetry)	Substituents							
		H (Ref.24)	H (Ref.25)	Me (Ref.24)	Me (Ref.25)	Ph (Ref.47)	Cl (Ref.25)*	Br (Ref.25)*	I (Ref.25)*
$(SiR_2)_4$	folded (D_{2h})	—	0.0	—	—	—	0.0	0.0	0.0
	planar (D_{4h})	—	0.26	—	—	—	1.17	0.55	1.10
$(SiR_2)_5$	envelope (C_s)	0.01	—	0.0	—	—	0.0	0.02	0.0
	twisted (C_2)	0.0	—	0.0	—	—	0.0	0.0	0.05
	planar (D_{5h})	0.44	—	0.44	—	—	2.08	3.54	4.90
$(SiR_2)_6$	chair (D_{3d})	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	twisted boat (D_2)	1.96	2.22	2.34	2.89	18.90	1.58	2.10	2.65
	boat (C_{2v})	2.32	2.49	3.83	4.14	—	2.34	3.47	4.88
	twisted (C_2)	4.14	3.49	4.11	4.23	—	3.44	2.34	5.07
	envelope (C_s)	—	3.80	—	4.52	—	3.71	5.65	5.62

*Calculation carried out with allowance for the electrostatic component.

compared with the D_{4h} conformation is 0.54–0.74 kcal mol^{-1} (calculations in different basis sets). This difference in energy indicates conformational non-rigidity of the four-membered silane rings. The conformational non-rigidity of four-membered silane rings is also indicated by experimental data. Thus according to XRD data, the molecules of $(SiMe_2)_4$ [49] and $[Si(SiMe_3)_2]_4$ [50] are planar, and the molecules of $[Si(i\text{-}Pr)_2]_4$,[51] $[SiMe(Bu\text{-}t)]_4$,[52] and $(SiPh_2)_4$ [53] are folded; the angles of bending in the last three molecules are 37.1, 37.0, and 12.8° respectively. For the last two molecules, calculation using the MMM [47] led to good agreement between the experimental and calculated geometric parameters.

For cyclopentasilanes with different substituents, as for cyclopentane, the two conformers C_s and C_2 have similar energies. For the Ph-derivative, whose structure was studied in the crystal, an intermediate conformation was found.[54]

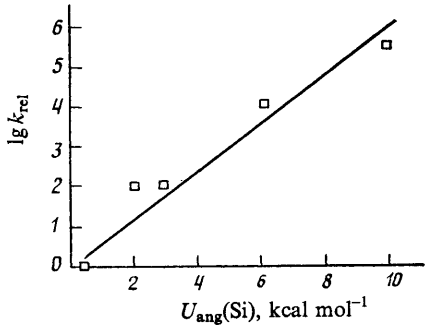


Figure 7. Dependence of lg k_{rel} for the hydrolysis of the SiH group on the strain in the valence angles at the Si atom.[44]

The optimum conformation of cyclohexasilane and its derivatives is the chair conformation, in agreement with experimental data for $(SiH_2)_6$ (GED),[55] $(SiMe_2)_6$ (XRD),[56] and $(SiMePh)_6$ (XRD).[57] According to calculations[24,58,59] and GED data,[55] the cyclohexasilane molecule is less flattened than the cyclohexane molecule [the valence angles in the $(SiH_2)_6$ and $(CH_2)_6$ rings are 111.4° and 110.3° respectively, and the torsional angles are 54.9° and 57.9°]. This is understandable, since the bonds in the ring in the $(SiH_2)_6$ molecule are appreciably longer than those in the $(CH_2)_6$ molecule, so that the repulsion of the groups occupying the *gauche*-positions will be smaller in $(SiH_2)_6$ than in $(CH_2)_6$ (by analogy with the non-cyclic tetrasilane).

For the seven-membered cyclosilane $(SiMe_2)_7$, according to XRD data and calculation,[60] the characteristic conformation is the twisted chair (*TC*) conformation. The same conformation is also the most favourable for cycloheptane. The calculation showed, however, that the relative advantage of other conformers† (Table 6), and also the conformational transformation routes, are different for $(SiMe_2)_7$ and its hydrocarbon analogue.

Even greater structural and energetic differences compared with the hydrocarbon analogues were observed[61] for the $(SiMe_2)_8$ molecule. This is obvious from a comparison of the conformational energies (kcal mol^{-1}) of a number of conformers:

	TCC	*CC*	*CR*	*TBC*	*BC*	*TB*	*TC*	*C*	*BB*	*B*
$(SiMe_2)_8$ (Ref.61)	0.0	0.4	0.9	2.3	2.6	3.7	4.3	6.3	9.2	10.7
$(CMe_2)_8$ (Ref.62)	—	—	1.22	2.37	0.0	—	9.96	9.51	1.67	12.13

†The torsional angles and the generally accepted notation for the conformers of cyclic molecules (*C* = chair, *B* = boat, *TC* = twisted chair, *TB* = twisted boat, *CR* = crown, *BB* = boat–boat, *CC* = chair–chair, *TCC* = twisted chair–chair, *TBB* = twisted boat–boat, etc.) have been described in detail.[63]

The authors cited[61] also noted a significant increase in the valence angles in the ring at the Si atoms (118–123°), which exceed the equilibrium value (111.7°); the same was previously observed for $(SiMe_2)_7$.[60] Thus with increase in the size of the ring, the differences in the structures and conformational behaviour of the molecules of cyclic silanes and the corresponding hydrocarbons increase.

Table 6. Relative energy (kcal mol^{-1}) of the conformers of $(SiMe_2)_7$ and $(CH_2)_7$.[60]

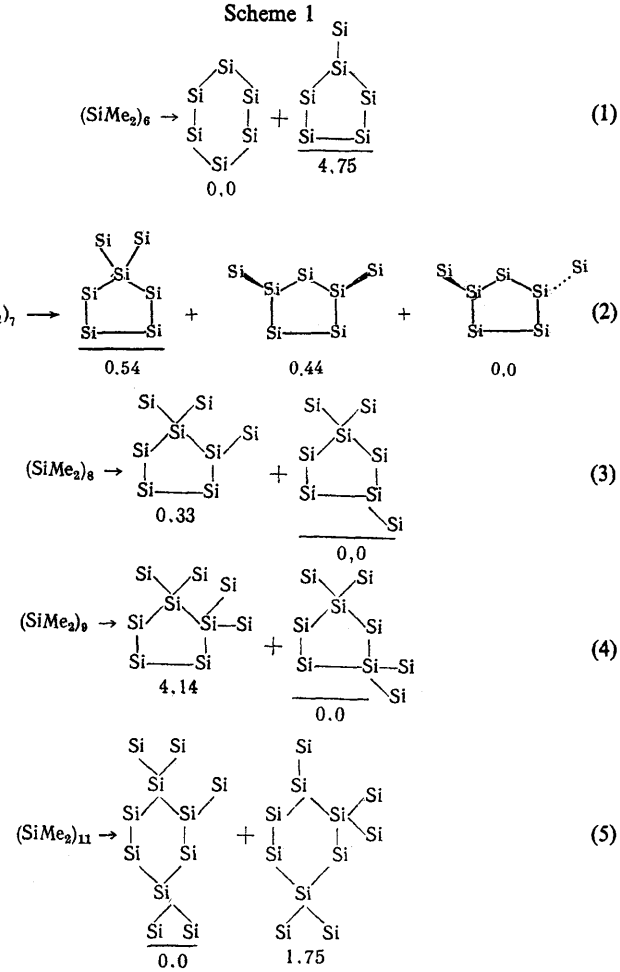
Conformer	$(SiMe_2)_7$	$(CH_2)_7$ *
TC	0.0	0.0
C	0.9	0.63–1.58
TB	2.6	2.40–5.64
B	4.2	2.60–5.66
TT	2.9	8.1–9.6

*The scatter in the data of different authors cited by Shafiee[60] are given.

Molecules with larger ring dimensions have been less extensively studied. Data have been published[64] on the structures of the molecules $(SiMe_2)_{13}$ and $(SiMe_2)_{16}$ in the crystals. Comparison of their conformations with those of their hydrocarbon analogues, in which the ring most frequently can be "placed" in the diamond lattice, shows appeciable differences in both cases. A calculation of the geometric characteristics of hypothetical conformers of the $(SiMe_2)_{13}$ molecule with the "pentagonal" or "trigonal" conformations (the conformer consists of five or three approximately planar fragments), observed for the hydrocarbons $(CR_2)_{13}$, showed that these conformations cannot be produced in the case of the cyclosilane, since they lead to shortened contacts between the methyl groups. The values of the torsional angles in the $(SiMe_2)_{13}$ and $(SiMe_2)_{16}$ rings differ considerably from the values corresponding to the *trans-* and *gauche*-arrangements of the units, indicating again that the silanes have a greater conformational flexibility than the hydrocarbons.

In the standard version of the MMM, electronic effects (for example conjugation) are not taken into account in explicit form. This makes it possible to use the mechanical model to detect those cases where the part played by electronic effects (irrespective of their nature) is considerable. An example of this use of the MMM is provided by studies[58,59] of a large group of alkyl-substituted penta- and hexasilanes. These compounds are products of the isomerisation of permethylated cyclic silanes $(SiMe_2)_n$ with $n = 5-11$, and a characteristic feature of the reaction, which takes place in the presence of the catalyst $AlFeCl_6$, is that the isomerisation of each of the rings usually gives a product consisting of a single isomer (Scheme 1). Scheme 1 shows only the energetically most favourable isomers (the Me groups are not shown). The values of ΔU_{ster} (kcal mol^{-1}) are given. The isomers whose yields are 95% are underlined.

Scheme 1



It is suggested that in these reactions, decrease in the ring size leads to a gain in the so-called σ-conjugation energy‡. The σ-conjugation energy for the molecules being considered can be estimated as follows. The gain in free energy for the isomer formed is written as the sum

$$\Delta H = \Delta H_{ster} + \Delta H_{bd} + \Delta H_{\sigma}.$$

Data on the ratio of the isomers (reaction products) make it possible to estimate ΔH, the MMM can be used to calculate ΔH_{ster}, and the value of ΔH_{bd} (a characteristic of the bonds in the molecules) is assumed[58,59] to be the same for all the isomers. These quantities can then be used to calculate ΔH_{σ}.

For $(SiMe_2)_6$ (Scheme 1), the ratio of the initial and final isomers is 99:1, which gives for ΔH the value 2.7 kcal mol^{-1}. With allowance for the difference ΔH_{ster} indicated in the Scheme, ΔH_{σ} for this pair of isomers is 7.4 kcal mol^{-1}, that is in this case the formation of the product with the five-membered ring is determined by not steric but electronic factors. The same is characteristic of the isomers obtained from $(SiMe_2)_7$; in this case, ΔH_{σ} is 3.2 kcal mol^{-1}.

For the products of the isomerisation of 8-, 9-, and 11-membered cyclosilanes, the preference for the formation of a given isomer is determined by steric factors. Summarising the results of calculations

‡The concept of σ-conjugation has been discussed in detail.[65]

and the experimental study of the ratio of the quantities of isomers obtained, the authors cited[58,59] point out that in the formation of cyclic isomers with the same number of silicon atoms in the ring and different arrangements of the $SiMe_3$ substituents, a decisive role in the "choice" of product is played by steric factors [see reactions (3)–(5) in Scheme 1]. When the numbers of silicon atoms in the ring or the positions of the substituents are different [reactions (1) and (2)], the electronic σ-conjugation effect predominates.

In the opinion of the present authors, however, no absolute significance should be given to the separation of the contributions into steric and electronic (this is indicated by a detailed quantum-chemical analysis of these contributions in four- and five-membered cyclosilanes[48]). These conformational calculations also lead to the conclusion that the force field suitable for the description of cyclosilanes with $n \geqslant 6$ should not be extended automatically to the description of smaller rings.

The range of substances which have now been examined using the MMM includes compounds containing the bonds X–O, X–N, X–S, etc., such as organoelemental peroxides, siloxanes, and silazanes.

Siloxanes. The MMM has been applied to the organosiloxanes,[66,67] an extensive class of compound with wide practical applications in polymer chemistry.[68] The selection of the required parameters of the potentials describing the siloxane bond has been carried out for various simple linear and cyclic siloxanes: $(H_3Si)_2O$, $(Me_3Si)_2O$, $(Me_2SiO)_3$, $(H_2SiO)_4$, and $(Me_2SiO)_4$.[66] These parameters supplement the set of parameters proposed by Allinger and Tribble[11] for the description of the molecules of silanes and carbosilanes.

A detailed analysis of the conformational possibilities of the tetrasiloxane ring, which is the basic structural fragment of a number of polymers, has been carried out.[67,69] An eight-membered ring with fixed bond lengths and valence angles has two degrees of freedom,[70,71] namely two torsional angles, and the values of the remaining six torsional angles are determined by the ring closure conditions.[72] A calculation for non-substituted cyclotetrasiloxane[69] showed that in the space of the two independent torsional angles (φ_1 and φ_2), the extensive range shown in Fig. 8 is allowed (within the isoenergetic line 10 kcal mol^{-1}). The values of the remaining torsional angles also lie in this range.

The tetrasiloxane ring is much more flexible than the cyclo-octane ring;[69] a typical value of the difference between the energies of the symmetrical conformers§ is 0.1–0.2 kcal mol^{-1}, and the least favourable planar conformer differs from the most favourable conformer by only 3.4 kcal mol^{-1}. It was also shown that for a given conformation, a smooth change in the torsional angles without an appreciable change in energy is possible. The small difference in the conformational energies is associated with a large variety of unsymmetrical structures of the tetrasiloxane ring observed in the crystals;[74] these structures can be represented approximately as the superposition of the symmetrical canonical forms of the eight-membered ring. The conformational non-rigidity of the siloxane molecules is apparently one of the reasons for the greater "friability" of siloxane crystals compared with organic molecular crystals.[75]

A smaller siloxane ring (cyclotrisiloxane) compared with the tetrasiloxane ring is characterised by the single energetically most favourable planar conformation.[66]

§The canonical symmetrical forms of the eight-membered rings according to Hendrickson[63,73] were examined.

According to XRD data[76] and calculation,[76] in the carboxysiloxane six-membered ring of the $CH_2CH(COOH)CH_2SiMe_2OSiMe_2$ molecule the siloxane fragment CSiOSiC also remains planar, whereas the CCC angle deviates from this plane by 57°, that is the ring as a whole has the "sofa" conformation.

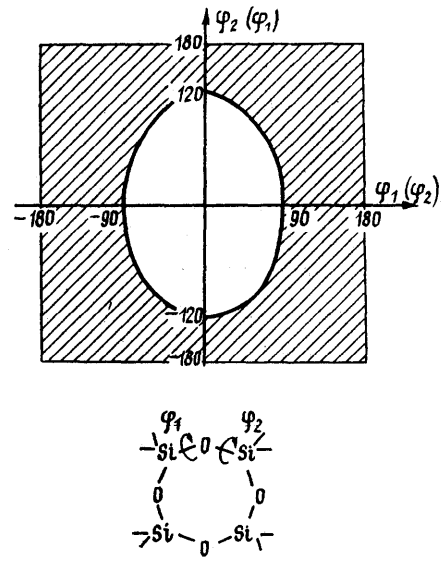
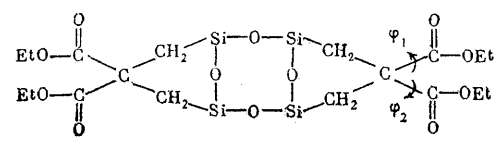


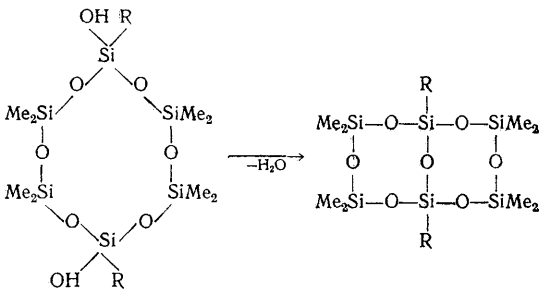
Figure 8. Range of existence of cyclotetrasiloxane in the space of the torsional angles φ_1 and φ_2 (the forbidden region is hatched).[69]

For various organosiloxanes, calculations have established the relationship between the conformational characteristics of the molecules and their chemical behaviour. Thus in the tricyclic molecule



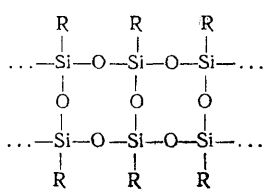
the pseudo-equatorial ester group can undergo practically free rotation (angle φ_1), whereas for the pseudo-axial group there are two ranges of allowed values of φ_2 close to ~60° and ~240°, separated by a high barrier.[77] The orientation of the pseudo-axial group in the crystal (φ_2 = 60°[77]) lies in one of the allowed ranges, and should not change on transfer to solution. This ester group occupies a shielding position relative to the carboxysiloxane group and, partly, the siloxane ring, and this (together with the redistribution of charges on the atoms of the ring, taking place under the influence of the ester substituent) probably explains the lowered reactivity of this compound in ionic splitting reactions.

The possibilities of change in the conformation of a twelve-membered siloxane ring on dehydration, taking place with the formation of a bicyclic product, have been examined.[78,79]



According to the calculation, in the ring with the *cis*-arrangement of the OH groups the approach of these groups is possible without a significant change in U_{conf} for the molecule to a distance corresponding to the formation of an H-bond between them (O...O ~ 2.94 Å). Dehydration at this bond apparently gives the bicyclic product. For the *trans*-isomer, this approach is impossible, and the formation of a cyclic product can take place only with rupture of the bonds in the ring at intermediate stages of the reaction. The conformation of the molecule of the *cis*-isomer predicted in the work cited[78] showed good agreement with that subsequently found in the crystal,[80] where the ring again has the boat form, and the OH groups are joined by an intramolecular H-bond (O...O 2.71 Å).

The bicyclic product obtained in the reaction is the simplest fragment of the cyclic–linear ladder polymer



A calculation[67] carried out for the bicyclic molecule showed that for it, at least two conformations with similar energies are possible (in the first, the molecule has C_2 symmetry, and both rings have the *BB* conformation, and in the second, one ring has the *CB* conformation, and the other the *LC* conformation), differing from the conformation found in the crystal.[81]

For the molecules of oligomers containing three cyclic fragments, where the side rings are joined in *cis*- and *trans*-fashion to the central ring, the calculated geometric parameters (particularly for the central ring) show fairly good agreement with those obtained by XRD.[74,82] These results indicate that introduction into the bicyclic molecule does not restrict the mobility of the eight-membered siloxane rings, whereas tricyclic (and hence polycyclic) connection makes this ring fairly rigid.

The calculation also showed slight energetic preference for *trans*-connection for the tricyclic molecule, compared with *cis*-connection (8.17 kcal mol^{-1} and 7.55 kcal mol^{-1} respectively). This indicates that for the ladder polymer, the *trans*-connection of the rings (Fig. 9*a*) is more favourable than alternate *trans*- and *cis*-connection (Fig. 9*b*).

In the above studies, the structure of the polymer chain was estimated from the results of calculations for its fragments represented by oligomer molecules. Other authors[83–85] examined the structure of infinite linear siloxane chains $(R_2SiO)_n$ in the isolated state and in the crystalline regions of the polymer. The calculation for the isolated chains $(R_2SiO)_n$, where R = Me, Et, Pr,[83] and Ph [85] showed that the spiral conformation is energetically most favourable. For polydimethylsiloxane, several possible conformations were examined, corresponding to the planar zigzag and the spirals 4_1 and 6_1 (with four and six units in each period). The spiral 4_1 version was found to be energetically most favourable, but the difference between its energy and that of the next most favourable version 6_1 is small (energy difference ~0.1 kcal mol^{-1}), while the production of the planar zigzag conformation is unlikely. For the molecules of polydiethyl- and polydipropylsiloxanes, several conformations of similar energy were detected, having approximately the same spiral step (~2.35 Å) but differing in the orientation of the substituents and the angle of rotation about the virtual bond O...O characterising the connection of the chain units. The final selection of the most favourable conformation in these cases made it possible to carry out a search for the optimum packing of the molecules in the crystal, corresponding to a minimum value of $U_{conf} + U_{interm}$, where the last term characterises the intermolecular non-valence interactions.[84] The search for this packing was carried out using the space groups and unit cell parameters obtained in an X-ray diffraction study of the crystalline polymers. For the tetragonal polydipropylsiloxane and the monoclinic polydiethylsiloxane, the most favourable conformation in the crystal is the spiral with 4_1 symmetry.

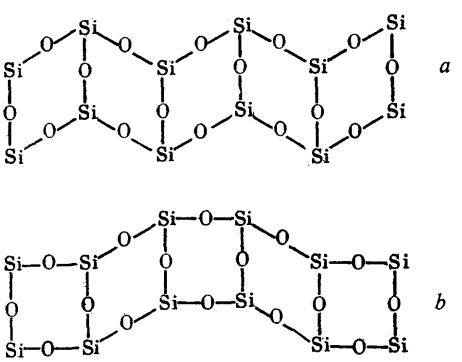


Figure 9. Cyclic–linear polyorganosiloxanes with *trans*- (*a*) and *cis*–*trans*- (*b*) connection of the rings.

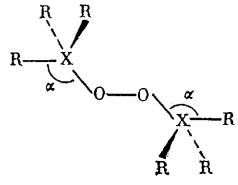
The same conformation is characteristic of polydiphenylsiloxane in the free state and in the crystal.[85] In the last case the authors cited note that the conformation is the same in the two states mentioned. Thus for all the polyorganosiloxanes examined (at least in the crystalline state), the most favourable conformation is the spiral 4_1, with slight differences which are due to the increase in the volume of the substituents and which correspond to an increase in the spiral step and in the valence angles at the O atoms.

Peroxides. The conformational characteristics of organosilicon and organic peroxides with similar structures have been examined.[86–89] A common feature of the molecules of simple peroxides is the "half-opened book" conformation with torsional angle ω about the O–O bond equal to 90–150°. For molecules

with bulky organoelemental and organic substituents, this angle may reach 180°, that is the molecule as a whole has the *trans*-conformation.

The conformations of a series of peroxides $Me_2RSiOOSiRMe_2$, where R = Me, CH_2Ph, and *p*-C_6H_4Cl, have been calculated.[86] The values of the angle ω in these compounds are 143.5° (GED),[90] 180°, and 180° (XRD)[88] respectively. The aim of the calculation was to determine whether the *trans*-conformation in the last two compounds is due to the effect of the crystalline environment, or whether it is characteristic of these molecules in the free state. It was found that for the molecule with R = Me, the optimum angle is ω = 140°; for the molecule with the slightly larger substituent R = CH_2Ph, two ranges of favourable conformations corresponding to angles ω = 140° and 180° were detected, the energy of the first being lower by 0.7 kcal mol^{-1}; and, finally, for the molecule with R = *p*-C_6H_4Cl the only favourable conformation is the *trans*-conformation (ω = 180°). Thus the molecule of the peroxide with R = CH_2Ph apparently adopts the *trans*-conformation under the influence of the crystal field. With more bulky substituents, this conformation is also characteristic of the isolated molecule. The same regularities were found in calculations for the molecules of organic peroxides R_3COOCR_3.[87,89]

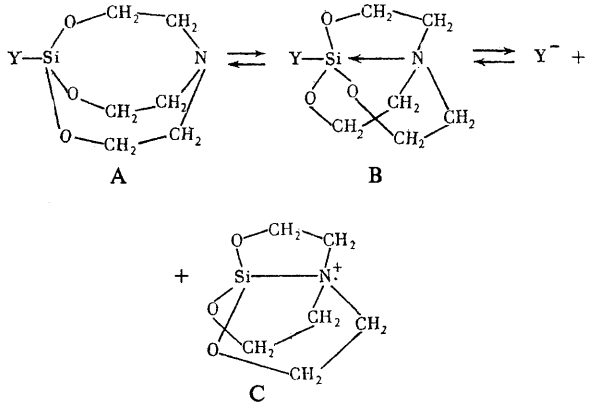
The MMM does not reproduce all the characteristics of the structure of peroxide molecules. X-Ray diffraction[87–89] has shown that in organic and organoelemental peroxides



the value of the valence angle O–X–R (α), including the X–R bond in the *trans*-orientation to the O–O bond, is always smaller than the tetrahedral value, and equal to ~100°. It has been shown[89] that the tendency for this angle to decrease is not reproduced satisfactorily in calculations using the MMM, but is effectively described by the semi-empirical CNDO/2 quantum-chemical method, indicating that this effect is predominantly electronic.

In the molecules of $Me_3COOCMe_3$ and $Me_3SiOOSiMe_3$, GED [90] did not detect a decrease in the angle α, whereas X-ray gave for the first molecule a value of α equal to 100.7°.[89] This difference is due to the fact that the GED refinement was carried out using a model with fixed symmetry of the Me_3X groups (C_{3v}),[90] which could not have led to a decreased value of one of the valence angles.

Silatranes. As noted in the Introduction, the range of applicability of the MMM is usually restricted to those cases of change in the structure of molecules where there is no rupture or formation of chemical bonds. Earlier, however, attempts had already been made to modify the mechanical model in order to examine processes of molecular rearrangement accompanied by a change in the coordination of various atoms, that is essentially not conformational but chemical transformations. An example from organoelemental compounds is provided by studies[91–94] in which a method for carrying out these calculations was developed for the case of the 1-methylsilatrane molecule. The last of the works cited,[94] in which the most fully developed calculation procedure was used, can be considered in more detail. The authors cited examined the hypothetical conversion of the energetically unfavourable *exo*-form of the silatrane A into the ionic product C, which is also unfavourable, via the *endo*-form B, which is the only one to actually exist:



The authors cited[94] regard this process as a model substitution reaction of the S_N2 type. To take account of the change in the coordination number of the silicon atom, the dependence of the equilibrium values and force constants of the valence angles on the bond orders (*P*) at the Si atom was introduced into the model. The nature of the change in the bond orders in this reaction was the subject of a special study;[95] in particular, in the *exo*-form $P_{Si-N} = 0$, and in the *endo*-form $P_{Si-N} = P_{Si-Y}$.

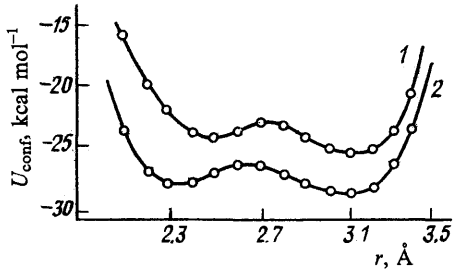


Figure 10. Dependence of the conformational energy on the distance Si...N for the molecules of 1-methylsilatrane (*1*) and 1-chlorosilatrane (*2*).

The calculated dependence of the energy (U_{conf}) on the distance Si–N (reaction coordinate) for the molecules with Y = Me and Cl is shown in Fig. 10. Curves *1* and *2* have minima corresponding to the *endo*-form which actually exists, and to the *exo*-form which has not been detected; the geometric parameters of the first show good agreement with those found for molecules of this kind by GED and XRD. The calculation showed that with the usual parametrisation (tetrahedral coordination of the silicon atom), these curves will have only one minimum, corresponding to the *exo*-form.

The authors cited[95] point out that the differences in the energies of the forms and the barriers to the transformation calculated for both molecules do not explain the fact that the silatrane molecules

exist only in the *endo*-form and the fact that quantitative agreement between calculation and experiment can be achieved only by taking account of the energy of the hypervalent bonding Y—Si ← N. In spite of these shortcomings, the results obtained are fairly encouraging, since they make it possible to obtain geometric parameters of the molecules which are close to the actual values, at the point corresponding to the minimum on the reaction coordinate.

IV. Conformational calculations for organometallic molecules

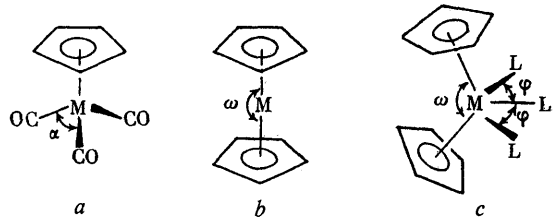
The previous section examined molecules in which the atom X has a definite (most frequently four-fold) coordination, analogous to the coordination of the C atom (sp^3) in organic molecules; this made possible an exhaustive description of its immediate environment using the X—R bond lengths and valence angles. The examination of structural data on the nature of the ligand environment of a metal atom (M) in organometallic complexes (mononuclear and polynuclear π-complexes and metal clusters) shows that in these compounds there is no rigidly fixed coordination of the M atom,[96,97] so that it cannot be described in terms of ideal values of the valence angles at the M atom. This feature, and also the widely encountered view that the structure of these molecules is determined chiefly by electronic factors, apparently explain why, until recently, there has been practically no application of the mechanical model to the examination of organometallic molecules¶.

1. Mononuclear metal complexes

Until recently, the only example of the application of the MMM to π-complexes was that described by Dashevskii and co-workers.[98] For molecules of the type $(C_5H_5)_2M$, the authors cited calculated the dependence of the energy of the non-valence inter-ligand interaction on the angle of relative rotation of the parallel cyclopentadienyl (Cp) rings. In agreement with the experimental data, it was shown that the barrier to this rotation is low, and that, depending on the M—C(Cp) distance, the molecule may have the staggered ($\varphi = 36°$, $d \lesssim 2.05$ Å) or eclipsed ($\varphi = 0°$, $d > 2.05$ Å) conformation of the ligands. A calculation has also been carried out for the $(C_5H_5)_2TiCl_2$ molecule, assuming ideal tetrahedral coordination of the Ti atom.[98] The minimisation of U_{conf} gave a ligand arrangement agreeing with that obtained by electron diffraction (the angle Cl—Ti—Cl is 105° or 102°, and the dihedral angle between the Cp ligands 125° or 121°, according to calculation and GED respectively).

Later, a simplified version of the MMM was proposed,[100–102] which makes it possible to predict fairly reliably the geometric characteristics of π-complexes. This model of a mononuclear π-complex ("hinge" model) is based on the view that the coordination sphere of the metal is uniformly occupied by the ligands,[99,103] and the criterion of uniform filling is the attainment of a minimum energy of the non-valence inter-ligand interaction. In this case the geometric characteristics of each of the organic ligands are calculated using the usual MMM scheme; the constants characterising the rigidity of the valence angles at the metal atom are taken as zero, and the metal—ligand distances are fixed by specifying high values of the deformation constants of the bond lengths M—L.

For a comprehensive verification of the proposed model, π-complexes of three main types were examined:[101,102,104] a, the half-sandwich compounds $CpM(CO)_3$ (Fig. 11*a*); b, the sandwich compounds $(C_5R_5)_2M$ with R = H or Me (Fig. 11*b*); and c, wedge-sandwich compounds with additional ligands $(C_5R_5)_2ML_n$, where L = H, Cl, CO (Fig. 11*c*). For the half-sandwich molecules, the calculation was carried out for values of the bond lengths M—Cp (centre of gravity of the Cp ligands) equal to 1.730 Å and 1.957 Å, and values of the M—CO bond lengths equal to 1.826 Å and 1.894 Å, characteristic of metals of the first and second transition series. The calculated values of the inter-ligand angles α (Fig. 11*a*), equal to 95.2—96.4° for the first set of distances and 98.7—99.7° for the second, show good agreement with XRD data for $CpMn(CO)_3$ [105] (M—Cp 1.79 Å, M—CO 1.79 Å, α = 91—94°), $[CpFe(CO)_3]^+PF_6^-$ (M—Cp 1.68 Å, M—CO 1.82 Å, α = 92—95.6°), and $CpRe(CO)_3$ (M—Cp 1.96 Å, M—CO 1.90 Å, α = 89.9—90.5°). Increase in the covalent radius of the atom M leads to a decrease in the steric strain in the coordination sphere and to slightly less satisfactory quantitative agreement between the calculated and experimental values of the angles α, although qualitatively the geometry of the "piano stool" is reproduced correctly.



a *b* *c*

Figure 11. Types of π-complex studied:[101,102] *a*, half-sandwich $CpM(CO)_3$; *b*, sandwich $(C_5R_5)_2M$; and *c*, wedge-sandwich with additional ligands $(C_5R_5)_2ML_n$.

A calculation[102] carried out for the half-sandwich complex $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ (Fig. 12) effectively reproduced all the experimentally observed structural characteristics.

In sandwich molecules with the parallel arrangement of the CP ligands, the inter-ligand contacts C...C are usually close to the normal van der Waals distances, so that regular filling of the coordination sphere of the metal atom is observed. At the same time, the structures of a number of bis-cyclopentadienyl derivatives Cp_2M, where M = Si, Ge, Sn, Pb, As,[106–109] have molecules with a wedge-sandwich configuration. According to quantum-chemical calculations, this arrangement of the Cp rings is due to the presence of a localised lone pair of electrons of the atom M in the equatorial plane of the wedge-sandwich.[106] An alternative explanation of the

¶The MMM is applied fairly extensively[7] to the molecules of coordination compounds in which the values of the valence angles at the M atoms are fixed. At the same time, in coordination chemistry, use is also made of models in which the most favourable arrangement of the ligands is determined by the minimum of the energy of interaction of points arranged on a sphere and approximating the ligands.[99]

wedge-shaped arrangement of the rings[101,102] takes account of only the non-valence inter-ligand interaction, and corresponds to the mutual attraction of the Cp ligands, where the non-valence contacts between the ligands when M has a large radius correspond to an attractive van der Waals interaction.

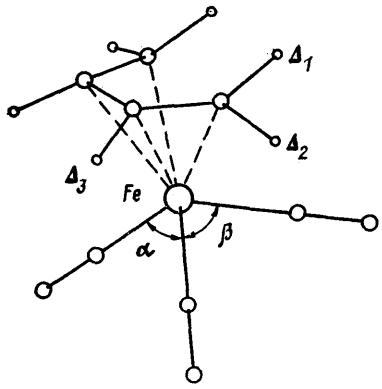


Figure 12. Structure of the $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ molecule; the geometric parameters have the following values: α = 93.7° and 92.0°, β = 98.3° and 100.0°; Δ_1 = 0.65 Å and 0.50–0.65 Å, Δ_2 = −0.14 Å and from −0.15 Å to −0.20 Å, Δ_3 = −0.48 Å and from −0.05 Å to −0.15 Å from calculation and experiment respectively (Δ is the deviation of the hydrogen atom from the average plane of the ligand).[102]

A calculation[101] of the optimum configuration of metallocenes, characterised by the angle ω (see Fig. 11*b*), in the range of distances M–Cp from 1.6 Å to 2.5 Å at intervals of 0.05 Å showed preference for the wedge-sandwich configuration for the molecules Cp_2M and $(C_5Me_5)_2M$ for distances M–Cp greater than 1.80 Å and 2.05 Å respectively. Qualitative agreement was observed between the calculated and experimental values of the geometric parameters in these molecules (Fig. 13). The slight quantitative differences[101,102] are attributed to the appreciable conformational flexibility of the wedge-shaped sandwich, and hence to the influence of the crystal field on its geometry, found by XRD. This effect is illustrated, for example, by the difference in the angles ω in the Cp_2Sn molecule in the gas phase (GED) and in the crystal (XRD) and by the coexistence in the $(C_5Me_5)_2Si$ crystal[109] of two symmetrically independent molecules with markedly different angles ω, equal to 180° and 154.7°. The model used also effectively explains the increase in the angle ω when bulky substituents are introduced; the experimental values of this angle in Cp_2Sn[106] (GED), $(C_5Me_5)_2Sn$,[105] and $(C_5Ph_5)_2Sn$[110] are 125, 144, and 180°; and in Cp_2Ge[108] and $[C_5H_2(SiH_3)_3]_2Ge$[111] 129.6° and 171° respectively. Thus in the approximation used (and in agreement with experiment) it has been shown that with increase in the radius of the atom M, the structure of the metallocene molecule changes from parallel to wedge-sandwich under the influence of van der Waals forces.

For wedge-sandwich metallocene derivatives with additional ligands, where there is more "compact" filling of the coordination sphere of the metal by the ligands, better agreement between the calculated and experimental values of the angles at the central atom M should be expected. This is confirmed by the data in Table 7, where the calculated and experimental values of the angles ω and φ are compared (see Fig. 11*c*). The experimentally observed decrease in the angle φ on going from the complexes with the d^0 electron configuration of the atom M to the d^1 and d^2 complexes is satisfactorily explained in the MMM by steric factors, although usually this change in the geometry is interpreted on the basis of the molecular-orbital model as the result of the electrostatic repulsion of the ligands in the bisector plane and the electrons localised in the "rear" orbitals of the metal atom.[112] Here, the difference between the calculated and experimental values of the angles is small for φ, and slightly greater for ω. This result shows that calculations using the MMM can be used to reproduce qualitatively fairly fine structural effects previously attributed to electronic factors.

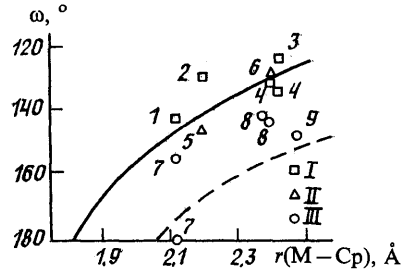


Figure 13. Calculated dependence of the angle ω on the distance M–Cp in Cp_2M (continuous line) and $(C_5Me_5)_2M$ (broken line); I, experimental values for Cp_2M molecules; II, the same for $(C_5H_4Me)_2M$; III, the same for $(C_5Me_5)_2M$; *1*, Cp_2As (XRD);[107] *2*, Cp_2Ge (XRD);[108] *3*, Cp_2Sn (GED);[106] *4*, Cp_2Sn (XRD, two independent molecules);[106] *5*, $(C_5H_4Me)_2Ge$ (GED);[106] *6*, $(C_5H_4Me)_2Sn$ (GED);[106] *7*, $(C_5Me_5)_2Si$ (XRD, two independent molecules);[109] *8*, $(C_5Me_5)_2Sn$ (XRD, two independent molecules);[106] *9*, $(C_5Me_5)_2Pb$ (XRD).[106]

These results[101,102,104] show the possibilities provided by the study of organometallic π-complexes by the MMM method, whose development should apparently take the direction of a search for an improved parametrisation.

Here, mention may be made of another purely geometric model, whose conceptual basis is similar to that of the method examined above, and which also makes it possible to obtain the characteristics of the coordination environment of the metal atom in the molecules of π-complexes. This model is based on Tolman's approach,[113] which makes it possible to describe the filling of the coordination sphere of the metal atom using the body (conical) angles characterising the projection of the ligand on to the coordination sphere of the metal. An analysis[114] of a large number of examples, including lanthanide π-complexes, was used to formulate the "packing centre" rule, according to which the sum of the products of the fraction of the body angle corresponding to the ligand and the length of the vector characterising the relative position of the ligand is close to zero. This rule makes possible an *a priori* quantitative description of the relative arrangement of the ligands in mono- and

dinuclear complexes with a sufficiently high accuracy. The authors cited point out that this rule is analogous to the requirement of a minimum energy for the non-valence interaction of the ligands in their optimum arrangement.

Table 7. Calculated[101] and experimental[105] values of the geometric parameters of molecules of the type $(C_5R_5)_2ML_n$.

Compound	M–Cp, Å	M–L, Å	φ, °		ω, °	
			calc.	exper.	calc.	exper.
Cp_2NbH_3	2.06	1.70	73.7	63	138.5	141.5
Cp_2TaH_3	2.07	1.77	71.8	62.9	139.1	139.9
Cp_2ZrCl_2	2.20	2.44	94.7	97.2	134.0	127.0
Cp_2TiCl_2	2.12	2.36	90.4	95.2	135.3	129.1
Cp_2NbCl_2	2.09	2.47	86.9	85.6	138.3	130.5
$[Cp_2MoCl_2]^+$	1.99	2.39	83.1	87.9	140.0	131.5
Cp_2MoCl_2	1.98	2.47	81.9	82.0	141.4	130.5
Cp_2MoH_2	1.94	1.69	81.0	75.5	139.3	145.8
$Cp_2Ti(CO)_2$	2.03	2.03	86.9	87.9	133.4	138.6
$Cp_2Zr(CO)_2$	2.18	2.19	82.5	89.2	132.9	143.4
$[Cp_2V(CO)_2]^+$	1.92	1.96	88.6	92	131.1	137.9
$(C_5Me_5)_2Ti(CO)_2$	2.07	2.01	82.2	83.3	146.1	147.9
$(C_5Me_5)_2Zr(CO)_2$	2.20	2.15	80.3	86.3	147.4	147.4
$(C_5Me_5)_2Hf(CO)_2$	2.17	2.14	81.6	87	146.1	148.2

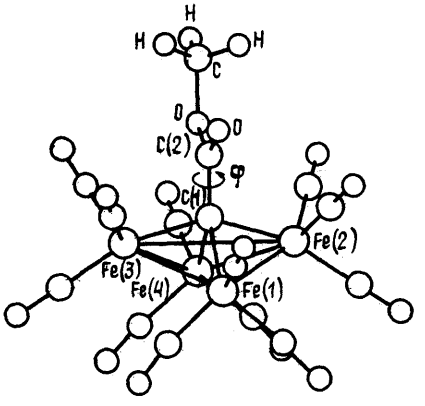


Figure 14. Structure of the $Fe_4(CO)_{12}CC(O)OCH_3$ molecule.[115]

In the opinion of the present authors, this rule should be fulfilled effectively only for sufficiently "compact" filling of the coordination sphere by ligands (for example, for the molecules MCp_3, where M represents a lanthanide, examined in the work cited[114]). It is fairly obvious that in the wedge-shaped sandwich molecules of the same lanthanides (for example for the wedge-sandwich $SmCp_2$ and $EuCp_2$) this rule is not fulfilled, but the conformation of these molecules is effectively described using the hinge model mentioned above.

In a number of cases, in the examination of the conformation of the molecules of mononuclear and polynuclear π-complexes, the feature of particular interest is not the arrangement of the ligands in the immediate environment of the metal atom but the relative arrangement of the parts of the complex or the orientation of the substituents in the ligands. In these cases, when carrying out a conformational analysis, the coordination environment is most frequently fixed, and only a limited number of the parameters being considered are varied. Examples of such calculations, which were begun only recently, have been published.[115,116]

In the first of the works cited, U_{conf} was calculated to establish the relationship between the nature of the substituent R = COOMe, CH_2, and Me and the reactivity of the iron cluster $Fe_4(CO)_{12}CR$, which has the "butterfly" shape (Fig. 14). For R = COOMe (the structure of this cluster has been established experimentally by XRD[115]), the calculated orientation of the substituent showed good agreement with experiment. A similar position of the substituent was found in the model molecule with R = CH_2. For the cluster with R = Me, the total conformational energy is many times greater than that for R = CH_2, because of the short contacts between the hydrogen atoms of the CH_3 group and the carbonyl ligands. This

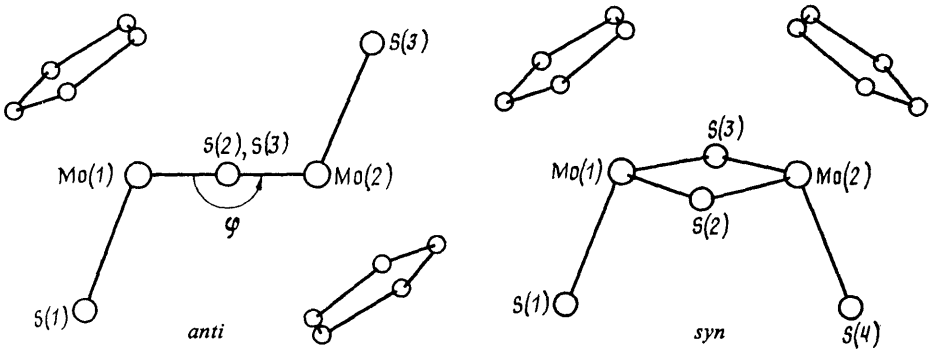


Figure 15. *syn*- and *anti*-forms of the molecules $[(C_5R_5)MoS(\mu\text{-}S)]_2$, where R = H, Me.[116]

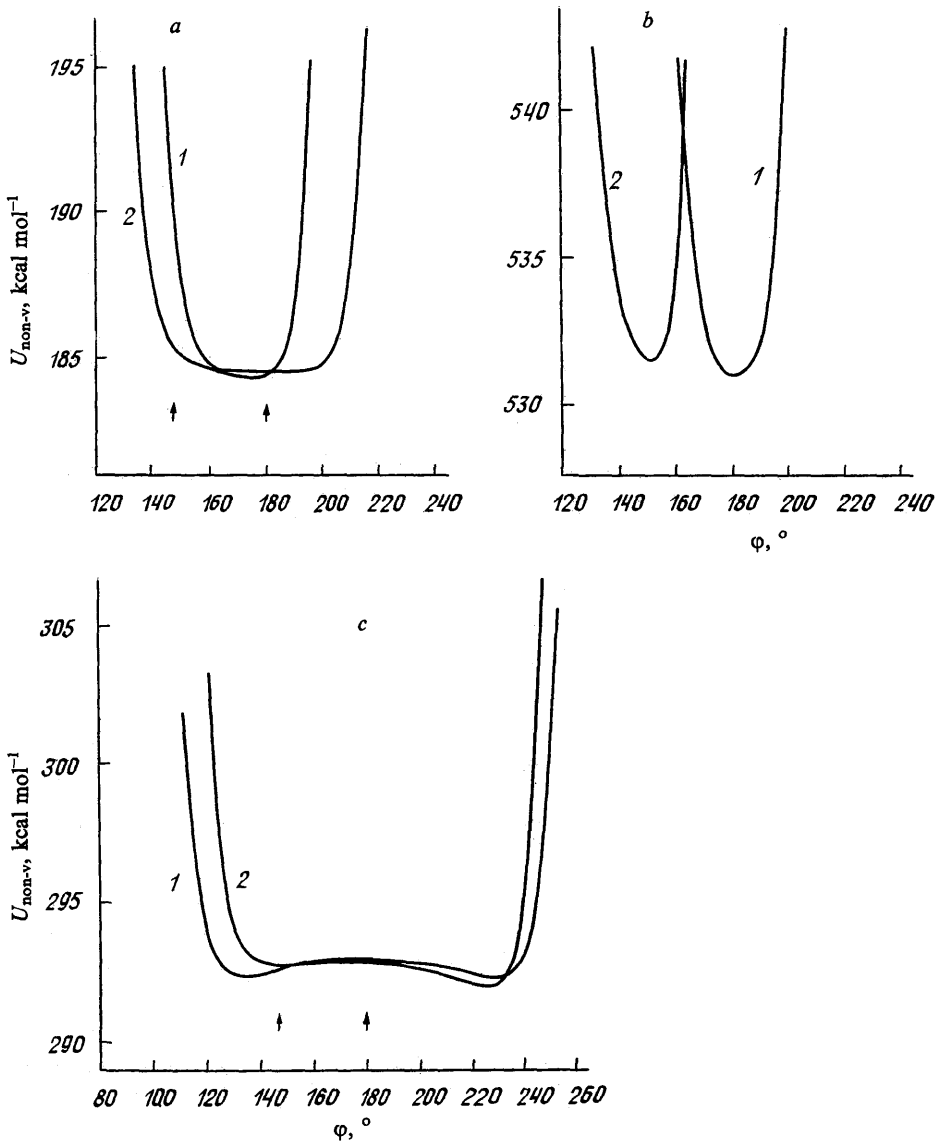


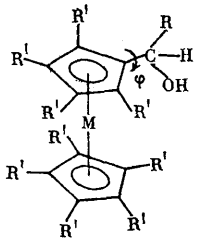
Figure 16. Dependence of the energy of the van der Waals interaction on the pseudo-torsional angle (Mo—S...S—Mo) in the molecules $[C_5R_5Mo(\mu\text{-}S)]_2$ with R = H (*a*) and Me (*b*) and in the molecule $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2$ (*c*); the arrows indicate the values of φ found experimentally in the crystal; *1*, *anti*-isomer; *2*, *syn*-isomer.[116]

last feature led the authors cited to the conclusion that the addition of any group to this cluster through the sp^3 hybridised C atom cannot take place without a change in the structure of the cluster itself.

The same approach was used to study the possibility of variation in the relative arrangement of the parts of the molecules in the dinuclear complexes $[LMoS(\mu\text{-}S)]_2$, where L = $C_2H_4S_2$, C_5H_5, and C_5Me_5.[116] The *syn*- and *anti*-isomers, in which, for a fixed ligand environment of each of the metal atoms, the relative arrangement of these atoms was varied by changing the pseudo-torsional angle Mo—S...S—Mo (φ) (Fig. 15), were examined. The graphs giving the dependence of U_{conf} on φ (Figs. 16*a*—16*c*), including only the non-valence component, show that in the non-crowded molecules with L = $C_2H_4S_2$ and C_5H_5 the angle φ changes over a fairly wide range, which also includes the values of these angles for the corresponding isomers in the crystal. For both of these molecules, the *syn*- and *anti*-isomers have similar energies. The energy difference between these isomers is appreciable only for the complex with the bulkier ligand C_5Me_5. This complex is characterised by narrow ranges of allowed values of the angle φ. At present, only the energetically most favourable *anti*-isomer of this complex has been detected.[116] The slight difference in the energies of the *syn*- and *anti*-isomers (0.59 kcal mol^{-1}), however, does not exclude the existence of the second isomer.

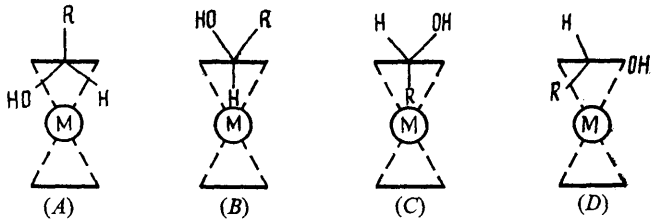
To investigate unusual intramolecular hydrogen bonds, Shubina and co-workers[117–119] undertook a combined spectral, X-ray

diffraction, and calculation study of various carbinol derivatives of metallocenes



U

where M = Fe, Ru; R = H, Me, Ph, Mes, etc.; and R' = H, Me. The conformational calculation in this case should have revealed the steric predisposition of these molecules to the formation of H-bonds of different types: OH...M (involving the metal atom) or OH...π (involving the π-electron system of the cyclopentadienyl ligand). Fig. 17 shows several possible orientations of the carbinol group relative to the metallocene ring. From geometric criteria, an O–H...M bond can be formed in case (*A*), an O–H...π bond can be formed in cases (*B*) and (*C*), neither of these bonds is formed in case (*D*).



(*A*) (*B*) (*C*) (*D*)

Figure 17. Schematic representation of possible orientations of the carbinol group in metallocenes.

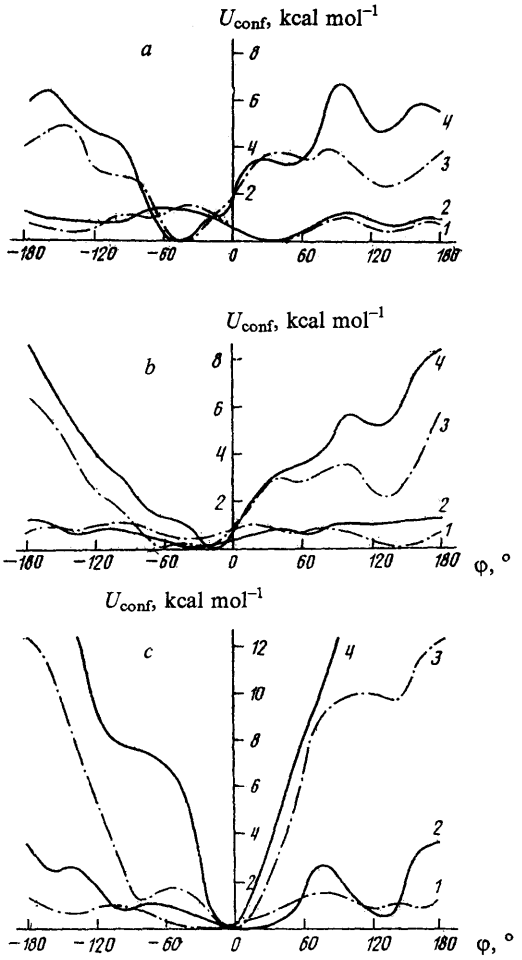
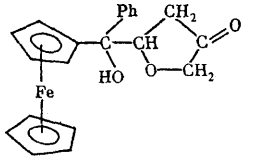


Figure 18. Dependence of the conformational energy of carbinol derivatives of metallocenes on the angle of rotation φ of the carbinol group (M = Fe—continuous line, M = Ru—dot–dash line): *a*, R = Me; *b*, R = Ph; *c*, R = Mes; curves *1* and *2* characterise the molecules with R = H, and curves *3* and *4* the molecules with R = Me.

The dependence of U_{conf} on the angle of rotation φ (C–C–C–O) of the carbinol group has been calculated. The angle φ has negative values for orientation of the OH group towards the metal, and positive values for the arrangement of the OH group above the Cp ring. The calculation showed that for carbinol-substituted metallocenes and nonamethylmetallocenes (M = Fe, Ru) with R = H, there are no ranges of preferential orientation of the OH group. For R = Me, Ph, and Mes (Figs. 18*a*–18*c*), these ranges are distinguished sufficiently clearly only for the nonamethylmetallocene derivatives. For R = Me, the OH group is orientated towards M when M = Fe, and has two orientations when M = Ru; when R = Ph, the OH group is oriented towards the M atom for both metals, but the probability of approach of the OH group to the metal is greater for M = Ru; when R = Mes, the OH group may be turned towards the metal (M = Ru) or may lie in the plane of the Cp ligand (M = Fe), which does not favour the formation of intramolecular H-bonds. In the last case, the calculation shows good agreement with XRD data,[117] according to which the torsional angle φ is 7°.

For the molecule $(C_5Me_5)Fe(C_5Me_4CH(OH)Bu\text{-}t)$ with one bulky substituent on the carbinol group and the molecule



V

with two bulky substituents on the carbinol group, the calculation[118] (Fig. 19) indicates that the OH group is oriented towards the metal (negative range of values of the angles φ); this orientation is fairly "rigid" for the first molecule, and less "rigid" for the second. This is in good agreement with the results of a study of the second complex in the crystal[120] (φ = −50.5° from the calculation, and φ = −42.9° from the experiment). The arrangement of the OH group in these molecules makes probable only the formation of the O–H...M bond.

The results of all the calculations are consistent with the infrared spectra of the complexes, which show that they contain O–H...M bonds in those cases where, from steric considerations, only the orientation of the OH group towards the metal is possible, and that two types of bond, O–H...M and O–H...π, are present when there is no steric hindrance.

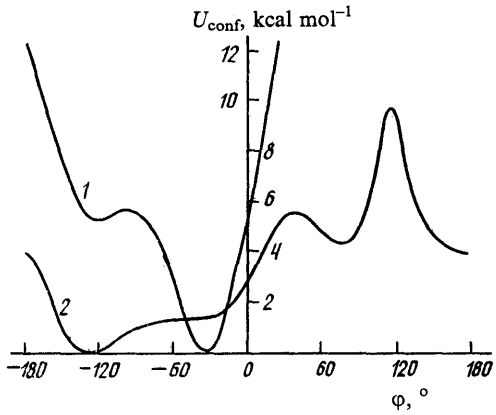


Figure 19. Dependence of the conformational energy on the angle of rotation of the carbinol group φ in the molecules of $(C_5Me_5)Fe[C_5Me_4CH(OH)(Bu\text{-}t)]$ (*1*) and $(C_5H_5)Fe[C_5H_4CPh(OH).(C_4H_5O_2)]$ (*2*).

The orientation of substituents on an asymmetric atom plays an important role in stereoselective reactions. Conformational calculations revealing the role of this factor for organic molecules have been described in detail.[4] Similar calculations were recently carried out[121] for a large number of organometallic complexes containing carbonyl, cyclopentadienyl, phosphine, and acyl ligands on an asymmetric metal atom. The aim of these calculations was to establish the relative orientation of the acyl ligands assuming rigidly fixed coordination (square planar, octahedral, etc.) of the metal atom and a fixed arrangement of the other ligands. The calculations were carried out with allowance for only the energy of the non-valence interaction in the model molecules, which contained the phosphine groups PH_2Ph, and the acyl groups C(O)Me. Fig. 20 shows the Newman projections of complexes of different types, in which the position of the C(O)Me group corresponds to the energy minimum. Complexes ML_4 with square planar, tetrahedral, and pseudo-octahedral (for complexes with Cp ligands) coordination, complexes ML_5 with square-pyramidal and trigonal-bipyramidal coordination, and complexes ML_6 with octahedral coordination were examined.

For all these complexes, the dependence of U_{conf} on the angle of rotation of the C(O)Me group for different filling of the coordination sphere by bulky (PPh_3, Cp) and less bulky (CO) ligands was analysed.[121] The introduction of bulky ligands in most cases does not change the optimum arrangement of the substituents, but it makes the range of allowed orientations narrower, and in some cases decreases the number of such ranges.

The calculation showed a similarity in the orientations of the acyl group in the octahedral and pseudo-octahedral complexes, where one of the faces of the coordination polyhedron is occupied by a Cp ligand replacing three CO groups. The authors cited[121] consider that this similarity [for example in the complexes (4) and (11), and (5) and (12), in Fig. 20] illustrates the so-called isolobal analogy between octahedral and pseudo-octahedral complexes.

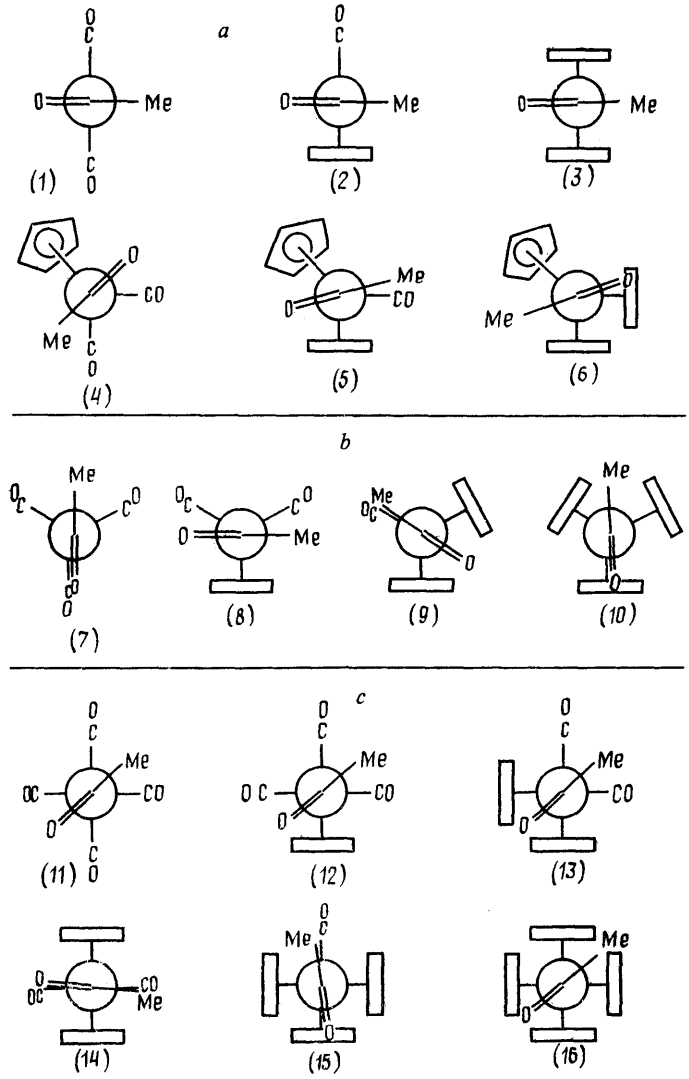


Figure 20. Newman projections of acyl complexes of metals along the line [Me(O)]C–M–CO, corresponding to the minimum energy in complexes ML_4 (*a*), ML_5 (*b*), and ML_6 (*c*); *1–3*, square planar; *4–6*, pseudo-octahedral (tetrahedral); *7–10*, trigonal-bipyramidal; *11–16*, octahedral; the rectangle denotes the ligand PPh_3; in complexes *1–3* and *7–16* the CO group under the plane of the diagram is not shown.

The most interesting and complex conformational calculations for organometallic molecules known at present are the calculations for the molecular complexes of cyclodextrins with ferrocenylacrylic esters

with the 1 : 1 composition, carried out simultaneously by two groups of authors.[122,123] The aim of these calculations was to find the conformation of the clathrate and to establish the mechanism and conformation of the product of the acylation of β-cyclodextrin by ferrocene derivatives (Fig. 21).

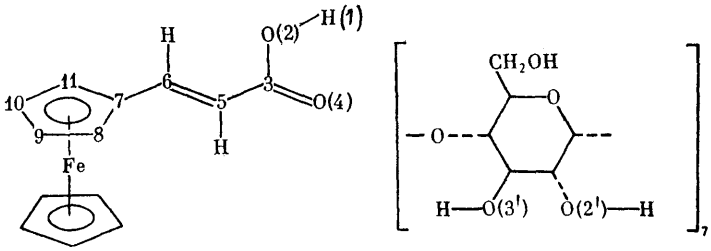


Figure 21. Structure of the molecule of the ferrocenylacrylic ester and the elementary unit of the β-cyclodextrin molecule.

In the first stage of the calculation, the conformations of the isolated molecules forming the complex were determined. It was found, in particular, that the substituent in the ferrocene derivative† has an almost planar structure, and that the *cis*- and *trans*-conformers with respect to the C(3)–C(5) bond have similar energies (with slight preference for the latter). The second stage of the calculation involved the search for the optimum arrangement of the molecule of the ferrocenylacrylic ester in the cavity of the β-cyclodextrin molecule. In this search, in each of the molecules, account was taken of all the components of the conformational energy and the non-valence and electrostatic components of the intermolecular interaction.

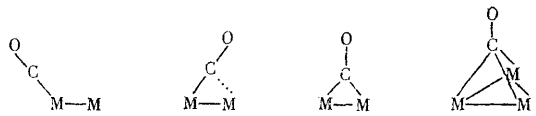
The calculation showed the existence of the three most favourable orientations of the molecule of the ferrocenylacrylic ester in the β-cyclodextrin cavity.[122] In the first of the orientations, the C(3) atom of the ferrocenylacrylic ester approaches the O(2′) atom of β-cyclodextrin, and in the second and third orientations it approaches the O(3′) atom (see Fig. 21). Their relative advantage has the values 0.0, 3.0, and 5.0 kcal mol^{-1} respectively. Calculation of the conformational energy of the acylation products (with allowance for the different arrangements of the parts in the unreacted complex) revealed a slight preference for the product corresponding to the first of these orientations. Evidence in support of the first product is also provided by the fact that the conformation of the acylating agent in this case [acylation at the O(2′) atom] undergoes the smallest change. These conclusions were confirmed by an independent calculation.[123]

2. Metal clusters

The most complex organometallic materials for which the MMM is used at present are cluster molecules. The arrangement of the ligands on the surface of metal clusters, like that round a single M atom, is not rigidly fixed, and may change when the molecule is transferred from the crystal to solution, and in solution the ligands can migrate over the surface of the cluster, that is many clusters are stereochemically non-rigid.[124,125] These features obviously make it difficult to use the ordinary version of the MMM in calculations of the ligand environment of clusters. Earlier, however, it was suggested that the nature of the ligand environment of the metallic nucleus of a cluster is determined by the closest packing of the ligands on its surface.[126] The development of this suggestion has led in recent years to modified versions of the MMM which make it possible to calculate the geometric characteristics of the ligand environment of clusters, using (as in the case of mononuclear complexes) the criterion of the minimum energy of the inter-ligand van der Waals interaction.[127,128]

Thus the authors cited[127,128] developed a model in which the ligands were regarded as points on a sphere approximating the surface of the cluster, between which only the repulsion interaction was specified. The proposed model provides a qualitatively correct description of clusters with CO ligands, but does not reproduce all the details of their structure. It is understandable that the carbonyl ligand can be approximated satisfactorily by a point on a sphere, but this can hardly apply to larger π-bonded hydrocarbon or phosphine ligands, so that the application of this model is restricted considerably.

A more complex version of the MMM, free from the above limitations, has also been developed[125] for carbonyl clusters. The main complication in the description of the ligand environment of the molecules of metal clusters lies in the fact that for the M–L bonds it is difficult to specify the ideal values of the bond lengths and their force constants, since the actual concept of a bond in these molecules is somewhat indefinite. For example, the CO ligand may be terminal, half-bridging, or bridging between two or three metal atoms:



It is considered[125] that in cluster molecules of this type the ligands are joined not to one or several M atoms but to the entire metallic nucleus of the cluster. It is clear that the angle characteristics are also indefinite in this case. Here, therefore, as in mononuclear metal complexes, the non-valence inter-ligand interactions predominate.

The following model has been proposed[123] to take account of these difficulties. All the metal atoms are regarded as spheres with a radius r_m equal to half the length of the M–M bond (usually, in clusters, $r_m \simeq 2.6/2 = 1.3$ Å). Around the centres of the metal atoms, spheres are described with radius r_t equal to the "ideal" (corresponding to the energy minimum) length of the M–C bond with a terminal CO group (1.75 Å). Assuming a definite length r_b for the "ideal" bond M–C with a bridging CO group (in the present case 2.0 Å), the radius of the so-called "trial" sphere r_p (the significance of the notation is clear from Fig. 22) is calculated. As the trial sphere is moved over the surface of the metal core of the cluster, an equipotential surface is constructed from the points of contact; all the points of the surface correspond to a minimum energy of the metal–carbonyl interaction. Examples of these equipotential surfaces for di- and trinuclear clusters are shown in Fig. 23. A similar representation of the surface was adopted for protein molecules[129] in an examination of their solvate layer, from

† The parameters of the potentials for ferrocene derivatives, which make it possible to use the program MM2 for their calculation, have been published.[122,123]

which a mathematical description of this surface was obtained. The movement of a carbonyl ligand arranged at right angles to the equipotential surface is regarded as equally energetically favourable in all directions over the metal cluster.

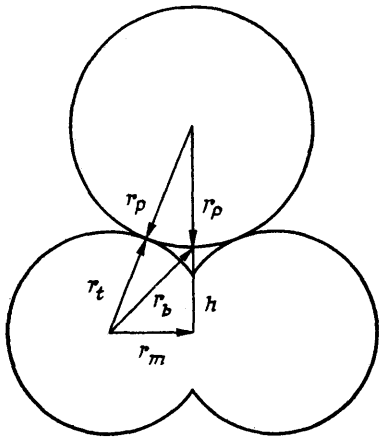


Figure 22. Diagram (section) of the relative arrangement of the metal atoms and the "trial" sphere in a dinuclear cluster.[123]

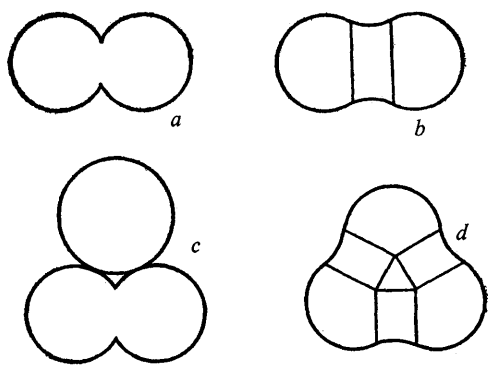


Figure 23. Construction of the equipotential surface of clusters: *a*, metal cores M_2 with intersecting (at a distance r_m) spheres of radius r_t; *b*, the same with a trial sphere of radius r_p touching the fragment M_2; *c*, the equipotential surface of a dinuclear cluster; *d*, the equipotential surface of a trinuclear cluster.[123]

The energies of bond stretching and valence angle deformation are written with allowance for the position of the carbonyl group.

For a terminal CO group, the bond stretching energy is given by

$$E_s = 71.94\, K_s (r - r_t)^2 [1 - 2.0 (r - r_t)],$$

where r is the M–C distance, and K_s the force constant of the bond.

For bridging bonds

$$E_s = 71.94\, K_s (r' - r_p)^2 [1 + 2.0 (r' - r_p)],$$

where r' is the distance from the C atom to the centre of the trial sphere.

The dependence of the energy on the angle of slope of the ligand is given by the expression:

$$E_\theta = 0.021941\, K_\theta (\theta - \theta_0)^2 [1 + 7.0 \cdot 10^{-8} (\theta - \theta_0)^4],$$

where θ is the angle between the C–O bond and the normal to the surface of the cluster, and θ_0 is the ideal value, equal to 0. The angle constant K_θ is small, and the values of the C–M–C angles are determined almost entirely by van der Waals interactions. The geometry of the metal core is not varied in the calculation.

The proposed model[125] was used to carry out calculations for a large number of carbonyl clusters containing from one to four metal atoms. Good agreement between the calculated and experimentally determined coordination was observed for the mononuclear complexes $M(CO)_n$ (n = 4–7). For n = 7, the isomers with coordination of different types (singly-capped octahedron, singly-capped trigonal pyramid, pentagonal bipyramid) have similar energies. In the dinuclear molecules $M_2(CO)_n$ (n = 8, 9), a large number of isomers is detected for the complexes with the less extensively filled coordination layer (n = 8), in agreement with the experimental data. The trinuclear clusters $M_3(CO)_{12}$ are characterised by the existence of three most favourable types of ligand coordination with overall symmetry of the molecules D_{3h}, D_3 (all CO groups terminal), and C_{2v} (two CO groups bridging). For tetranuclear clusters $M_4(CO)_n$ (n = 12–14, 16) with a small number of ligands in the coordination sphere, several versions of the environment corresponding to an energy minimum are possible, whereas increase in the number of ligands usually gives one most favourable type of ligand environment.

The author cited[125] considers that a promising development of the model which he proposed involves the inclusion in it of ligands of different types; this requires the selection of new metal cluster–ligand interaction parameters. The parameters describing the geometry of the organic ligands themselves can be taken, for example, from papers by Allinger and co-workers.[4] The calculation of the ligand environment using this model requires special fairly complex programs.

Mention may be made of another recently published calculation[130] of the geometric characteristics of the molecule of a tetrahedral cluster $M_4(CO)_{14}$ by the usual version of the MMM method with parameters proposed by the authors cited for the interactions including the metal atoms. The calculation was carried out to investigate the influence of steric crowding on the increase in the lengths of the M–M bonds relative to the same bond lengths in the non-crowded molecules. The calculation showed that a definite contribution to the additional elongation of the M–M bonds is made by the C...C non-valence interactions of adjacent CO ligands, but it was not possible to reproduce the values of the M–M bonds characteristic of the cluster $[Fe_3Cr(CO)_{14}][(PPh_3)_2N]_2$, studied by XRD by the same authors.[130]

Brief mention may be made of the possibilities provided by calculations of the conformations of isolated clusters without a ligand environment, which have been described in sufficient detail.[131,132] The atom–atom approximation has for long been used successfully for their description. The calculation of the optimum configuration of clusters of any size, consisting of inert gas atoms, was carried out by minimising the energy of the system using the hard-spheres potential, the Lennard–Jones potential, the Morse potential, etc.[131] The use of long-range potentials gives a significantly smaller number of possible isomers. For small clusters, the number

of isomers with similar energies is fairly large, and decreases with increase in the number of atoms in the aggregate. The same conclusions also apply to metal clusters for which calculations have recently been carried out using special potentials.[133]

The above data, together with the extensive experimental material on the structure of the molecules of metal clusters characterised by different types of arrangement of the metal atoms,[124,134] indicate that the ligand environment may have a significant influence on the metallic core of the cluster. For a complete description of the structure of cluster molecules, it is apparently necessary to develop a model involving the combined calculation of the optimum configuration of the metallic core and the ligand environment with allowance for their constant mutual influence. At the present level of computer technology, this model should be developed in the near future.

V. Summary

The material presented leads to various conclusions about the present possibilities provided by conformation analysis by calculation in the study of organoelemental and organometallic molecules.

It is fairly obvious that for organoelemental molecules in which the coordination of the atom of the element is analogous to that of the carbon atom, the working instrument of conformational analysis by calculation, namely the mechanical model of the molecule, has a sufficiently well developed methodological base (parametrisation and programs). This makes it possible to analyse the conformations of a large number of acyclic, cyclic, and polycyclic organoelemental molecules (mainly organosilicon molecules), and to compare their conformations with those of the corresponding hydrocarbons. It has been found that in spite of the similarity in the coordination of the atoms of carbon and the element, quantitative differences between organic and organoelemental molecules are observed in the values of the barriers to internal rotation and in the ratio of the energies of the conformers, together with qualitative differences in the optimum conformations corresponding to the energy minimum.

The existing level of development of calculation methods for molecules of this class makes it possible to solve for these molecules not only stereochemical problems (the search for the most favourable conformers and the optimum stereo-isomerisation paths) but also the problems of establishing the relative reactivity of molecules and distinguishing the dominant factors (steric or electronic) in chemical transformations. In the near future, the fields of application of the MMM for organoelemental molecules should be as varied as that for organic compounds.

For organometallic molecules and metal clusters, for which conformational calculations have been actively carried out only in the last few years, the situation is different. It has now been shown possible to apply the MMM to molecules of this type, but the parametrisation for mononuclear complexes has not yet been sufficiently developed, and apparently requires improvement. The same applies to the molecules of metal clusters, where in addition to improvement of the parametrisation it is also necessary to continue the search for models making possible the simultaneous description of the arrangement of the atoms in the metallic core and in the ligand environment.

The above results of calculations for organometallic molecules and their comparison with the results of experimental studies for molecules of this type indicate unambiguously the complete qualitative agreement between the results and indicate that the use of the MMM in the stereochemistry of organometallic compounds is promising.

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