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CONFORMATIONAL ANALYSIS OF OVERCROWDED AROMATIC MOLECULES

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Abstract A method for calculating the conformation of overcrowded aromatic molecules with any out-of-plane distortions has been elaborated. Conformations of 1,4,5,8-tetrachloronaphthalene, a number of polycyclic condensed hydrocarbons, and 5,6-dichloro-11,12-diphenylnaphthacene have been calculated. As the results agree with the experimental data for the investigated structures, it has been concluded that the conformations of overcrowded aromatic compounds can be calculated *a priori* by the method proposed.

INTRODUCTION

THE fundamental aim of conformational analysis is to calculate theoretically the molecular structure, i.e. to predict the geometry of a molecule and in some cases the chemical and thermochemical properties.

A mechanical model[1, 2] of a molecule is often used successfully in conformational calculations, and according to this model the most favourable configuration is obtained as a result of compromise between the tendency of bond angles to maintain ideal values and non-bonded atoms to move apart to some equilibrium distance. Each bond angle is supposed to be elastic and interaction of non-bonded atoms can be described by the potentials depending upon only interatomic distances.

Calculation of conformation is based on determination of minimum of the strain energy defined later. It is important to stress that in our model valence bonds are supposed to be absolutely rigid according to experiments performed with the accuracy of 0·01 Å.

In overcrowded molecules, steric hindrance (interaction of nonbonded atoms) leads to serious distortion when compared with ideal models and in aromatic systems in addition to distortion in bond angles, atoms departing from the plane of symmetry of a molecule or from planes of some of its parts, and rotation of some groups (nitro- and carboxy-group or phenyl ring) around formal single bonds, which to some degree are conjugative, may increase this degree of distortion. Therefore, when conformation of overcrowded aromatic systems is considered, strain energy should include the energies of non-planar distortions and rotation around the bonds.

The method of calculating the conformation of aromatic systems, proposed in this paper appears to be more realistic than the earlier suggestions put forward by Westheimer[3] and Coulson and Haigh.[4]

Conformation calculation for aromatic systems

We consider that the potential function of deformation of any aromatic molecule should consist, in general, of the following four components:

(1) *Energy of interaction between non-bonded atoms* U_1, i.e. the sum of energies of interaction between all non-bonded atomic pairs,

$$U_1 = \sum_{k>s} f_m(r_{ks}) \tag{1}$$

where f_m are interaction potentials of non-bonded atoms k and s, r_{ks} is their distance (m indicates a type of potential, for example C...C, C...H, etc.).

We shall make use of 6-exp potentials to describe non-valent interactions

$$f(r) = -Mr^{-6} + N\exp(-qr) \tag{2}$$

where r -distance between atoms M, N and q are the constants depending upon only the atoms themselves.

(2) *Elasticity energy of bond angles* U_2. Deviations in valence angles against ideal values (120°) are supposed to obey Hook's law

$$U_2 = \tfrac{1}{2}\sum_i C_i(\Delta\alpha_i)^2 \tag{3}$$

where $\Delta\alpha_i$—the deviations of bond angles from ideal values, C_i—elastic constants, accepted to be the same for angles carrying a definite central atom in vertex and reflecting a definite hybridization state.

(3) *Energy of non-planar distortions* U_3. As aromatic molecules tend to keep the plane arrangement of atoms, a comparison of the experimental data with the calculated conformation gives an appropriate model describing the strain of out-of-plane distortions.

We introduced angles β_j to determine the local distortions but not the deviations from the mean plane as was done by Coulson and Haigh.[4]

Our parameters β_j for side-chain atoms or for "key" atoms of polyatomic substituents (N atom of a NO_2 group, etc.) are defined as the angles formed by the exocyclic bonds of a carbon substituent with the plane of two adjacent bonds of the benzene ring (in case of naphthalene or polycyclic aromatic systems, each benzene ring is considered to be a side-chain with respect to adjacent rings). In the deformation of benzene rings, β_j are the angles between the planes passing through the adjacent pair of bonds, for example, angles between the planes $C_1C_2C_3$ and $C_2C_3C_4$.

The formula

$$U_3 = \tfrac{1}{2}\sum_j C_j^* \sin^2\beta_j \tag{4}$$

where C_j^*—corresponding elastic constants, was accepted for the strain energy dependence.

As in general, the bond angles depend on the out-of-plane parameters (e.g. $\angle C_2C_1Cl = \alpha^* = 120° - \varepsilon_1 + \varepsilon_2$ in tetrachloronaphthalene, see Fig. 2), the true value α of a corresponding bond angle may be produced from the equation:

$$\cos\alpha = \cos\alpha^* \cos\beta$$

where β is a dihedral angle between corresponding bond and plane (C–$ClC_9C_1C_2$ in our example). When out-of-plane deformations are small one may neglect this dependence and consider that the bond-angles in vertex add up to 2π.

(4) *Rotation energy around the bond* U_4. The energy dependence of the angle between the plane of a polyatomic group and the plane of the benzene ring to which the first is attached by means of a single bond has been given in the form:

$$U_4 = \frac{U_0}{2}(1 - \cos 2\varphi) \tag{5}$$

because in two plane systems, the period is equal to π. Although the validity of this formula for small angles is trivial, in general the dependence U_4 on φ may be more complex, and this expression must be regarded as the first term of Fourie series.

The total strain energy is the sum of the above four components. In order to solve conformational problems, the energy must be expressed in terms of independent geometric parameters of the molecule, and paper[2b] gives methods of introducing such parameters for planar deformations in aromatic systems.

The energy minimum is found by special computer programmes described in the Appendix. These programmes, intended for numerical computation on ECM M-20 or BESM-3M, give the *exact* position of the local minimum and the corresponding energy value. If a potential surface has a few minima, their positions can be found by means of an appropriate technique. In this paper we consider only the cases which are characterized by a single deep minimum (neglecting rotamer problem). The calculation of a number of minima is of great importance, e.g. in the examination of polypeptide conformations (G. M. Lipkind, V. G. Dashevsky and E. M. Popov, to be published).

Parameters of conformation calculations

The mechanical model may be based on Born Ophenheimer approximation, resulting from the Schröedinger equation. According to this approximation, the electron energy of a molecule is determined with great accuracy by mutual positions of nuclei. Consequently, any molecule can be considered as a system of interacting atoms. However, in such an approach, the parameters have to be determined empirically (the same situation arises in theory of vibration spectra of molecules).

Interaction potentials of non-bonded atoms are usually determined from kinetics, absorption, heat of sublimation and other experimental data. The potential values thus obtained describe the interaction of atoms at distances close to the equilibrium, but if these results are extrapolated to such small distances as those between atoms inside the molecule, the error is so great that such potentials are not suited for conformational calculations. Regarding the elastic constants, one may say that use of spectroscopic deformation constants in conformational analysis is inexpedient because they implicitly involve the non-valent interactions and consequently cannot be stable invariants. Therefore there is some sense in determining the potential curves and elastic constants independently from experimental data based on geometry of overcrowded molecules.

Methods to determine and confirm the parameters in conformational analysis are similar to the trial and error method of X-ray structural analysis. The deviation coefficient for aliphatic planar conjugated and planar aromatic systems is defined as

$$R = \sum_i \frac{|\Delta\alpha_{i,\text{theor}} - \Delta\alpha_{i,\text{exp}}|}{|\Delta\alpha_{i,\text{exp}}|} \tag{6}$$

where $\Delta\alpha_i$ is the deviation in valence angles against the ideal.

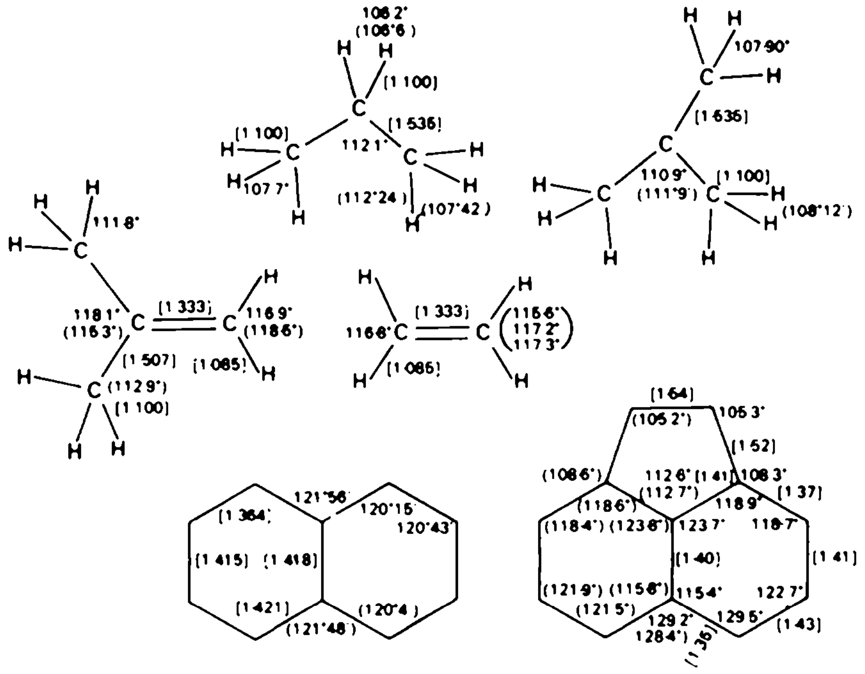


Fig. 1 Equilibrium configurations of some hydrocarbon molecules which are calculated with the use of potentials and elastic constants given in text. In parentheses are the experimental data. In square brackets are assumed values of bond lengths.

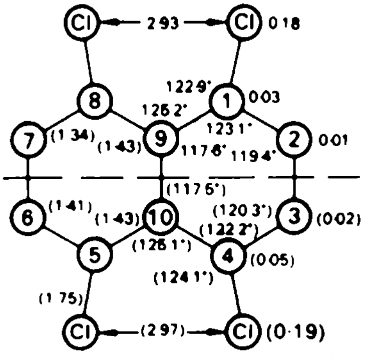
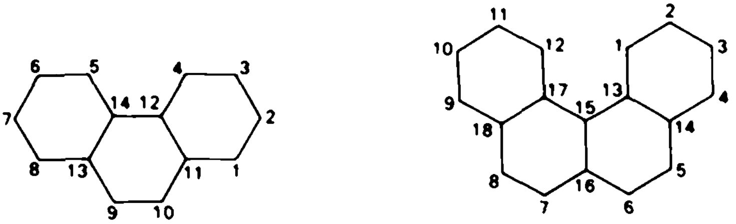


Fig. 2 Calculated and experimental (in parentheses) geometry of 1,4,5,8-tetrachloronaphthalene molecule. Deviations of atoms from the mean plane are given in Å.

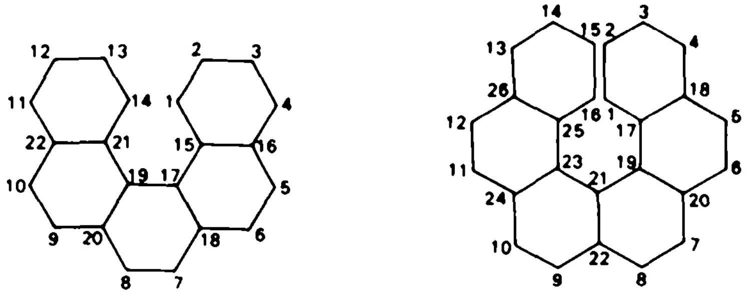
experiment can be expressed by these parameters. It is convenient to introduce a coordinate system as shown in Fig. 2 to express the distances between non-bonded atoms and dihedral angles of the ring 1-9-10-4, 10-9-1-2, 9-1-2-3, and 1-2-3-4. The calculated distances have been substituted into potential functions and summed up over all non-valent interactions. Calculation of the out-of-plane distortion energy is not difficult if we keep in mind the relative weights of mentioned dihedral terms—2:4:4:2. Thus the minimum energy was found using only 7 independent parameters which required 7 8 min to solve by a computer.

In the conformational calculation of tetrachloronaphthalene all nonbonded interactions were taken into consideration because of convenience of programming when operating with coordinates of atoms. The other programme written made use of only the nearest neighbours' interactions and also the interactions $C_1 \cdots C_4$, $C_9 \cdots C_2$, $Cl_1 \cdots Cl_8$, $Cl_1 \cdots H_2$ etc. The results in equilibrium geometry were the same within limits of 0·1° for ε_i and β_j. Therefore in the following examples the nearest neighbours and several important interactions which may change the geometry of a molecule were considered. The calculation of *all* interactions, including attraction of atoms, is valuable for the precise estimation of heats of formation.

2. *Polycyclic condensed systems.* A study of the conformation (Fig. 3) of phenanthrene, 3,4-benzophenanthrene, 3:4, 5:6-dibenzophenanthrene, and phenanthro-[3.4-c]phenanthrene (hexahelicene) makes possible to predict by analogy the structure of a large number of polycyclic aromatic systems not yet investigated.



Phenanthrene Benzophenanthrene



Dibenzophenanthrene Hexahelicene

FIG. 3 Numeration of the atoms in several condensed aromatic molecules.

We did not make use of either the traditional Hückel methods to calculate the bond orders or the experimental bond lengths (except phenanthrene molecule), but all the C—C bonds in the aromatic rings were accepted as being equal to 1·40 Å. Since we are interested chiefly in non-planar deformations, the differences in bond lengths were ignored, but it should be remembered that bond angles can not be calculated with accuracy.

There is no need to search the potential minima over all degrees of freedom since this takes too much time for a computer, and because there are independent parameters which do not considerably affect the final geometry of a molecule. Two out-of-plane parameters for each benzene ring, due to symmetry conditions, were sufficient for a complete determination of carbon skeleton. The C–H bonds were accepted to lie in the planes of the corresponding C atoms in all cases except two for which one out-of-plane parameter was used (C_4–H and C_5–H in phenanthrene, C_1–H and C_{12}—H in benzophenanthrene etc). A similar statement applies to C–CH$_3$ and C–Cl bonds in dimethyl and chloro derivatives. Two ε-parameters have been used only for phenanthrene: one for the angle $C_4C_{12}C_{14}$ and the other for HC_4C_{12}. The potential function of phenanthrene was minimized to 9 parameters, benzophenanthrene to 9, dibenzophenanthrene to 11, and hexahelicene to 13.

The calculations indicate that the phenanthrene molecule is planar, and the $H_4 \cdots H_5$ distance should be increased to 1·86 Å contrary to 1·72 Å in the ideal model, due to an increase in the $C_4C_{12}C_{14}$ angle to 123·1° (Experimental value is 123·0°[20]). In other molecules non-planar deformations are considerable, though deviations of valence angles from 120° also take place.

The calculated conformations of benzophenanthrene and dibenzophenanthrene agree with the experimental[21–23] and calculated data[24, 25] obtained by the method of Coulson and Senent. The structure of the hexahelicene molecule has not been investigated but the nature of its conformation is *a priori* clear and is reflected in its name. Let us give the calculated atomic deviations from the mean plane for hexahelicene molecule: C_1 1·47; C_2 1·94; C_3 2·09; C_4 1·85; C_5 1·20; C_6 0·87; C_7 0·35; C_8 0·20; C_{17} 0·70; C_{18} 1·13; C_{19} 0·24; and C_{20} 0·40 Å (the bond C_{21}—C_{22} is in middle plane).

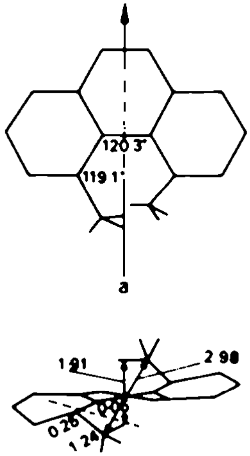


Fig. 4 Conformation of 4,5-dimethylphenanthrene molecule. The deviations of some atoms from the mean plane, interatomic distances (in Å), and valence angles are shown. Down is the view along an axe a.

The interaction of C and H atoms were considered separately in calculation of configuration for methyl substituted polycyclic condensed systems (usually the group Me is considered as a whole); and special geometric parameters were introduced for rotation of the Me "umbrella". This enabled us not only to determine the geometry with good accuracy, but also to find strain energies in equilibrium configuration, essential for thermochemical estimations.

Figure 4 gives the calculated geometric structure of 4,5-dimethylphenanthrene (bond lengths of phenanthrene[20] were used) as no X-ray data are available. The deformation in this case is very great, especially when compared with phenanthrene; moreover there is a loss in coplanarity of the phenanthrene ring together with departure of the Me group from the middle plane.

The above example is suitable to demonstrate how the equilibrium position of Me groups is found. The geometric parameter φ for rotation of the Me group, counting from the ideal conformation when one of the C—H bonds is in the plane of the molecule, has been introduced; and two Me groups have been considered to be "antisymmetric", i.e. only one parameter φ has been needed. In this molecule and in the examples below, the equilibrium φ corresponds to a maximum moving off from the nearest H atoms belonging to two different Me groups. The minimization of the potential functions with a number of fixed φ, which is of interest for the investigation of the hindrance to rotation and calculation of the barriers, has not been undertaken.

The calculated geometry of 1,12-dimethylbenzophenanthrene agrees well with the experimental.[21] As regards 1,14-dimethyldibenzophenanthrene, the deviations of C_{15} and C_1 atoms from the middle plane equal 0·46 and 1·32 Å; while (according to our calculations) for dibenzophenanthrene they are 0·45 and 1·30 Å; i.e. the difference is not as great for phenanthrene or benzophenanthrene[21] compared with the corresponding Me substitutes. Further, the calculations show that deformations in 1,16-dimethylhexahelicene are almost the same as in hexahelicene. The deformations of dibenzophenanthrene and hexahelicene are so great, that when new substituents enter no considerable strain is contributed. It is also of interest to note that in the above Me substituted dibenzophenanthrene and hexahelicene unlike the corresponding substituted phenanthrene and benzophenanthrene, mutual interaction of Me groups is not so essential as repulsion of C and H atoms in the Me group from the atoms of "opposite" benzene rings (for example, in hexahelicene mutual repulsion C_{17} and C_{25} atoms).

The differences in strain energies of equilibrium configurations of some methyl substituted compounds agree well with measured differences of combustion heats. Thus, the heat of isomerization for 4,5-dimethylphenanthrene into the 2,7-isomer according to calculation equals 14·2 kcal/mole, and for 1,12-dimethylbenzophenanthrene to the 1·5-isomer it is 11·5 kcal/mole; and corresponding experimental values[26] are 12·6 and 11·0 kcal/mole. It is curious that according to calculation (no experimental data found) the maximum heat of isomerization for dimethyldibenzophenanthrene is only 4·3 kcal/mole and for dimethylhexahelicene about 2 kcal/mole. Specific structure account for these low values of isomerization heat; in fact, as we have pointed out, new substitutions are not associated with high losses in deformation energy.

According to calculations the distance between "pressed" C atoms in polycyclic condensed systems is nearly 3·0 Å. This value was often shown in structural studies and was used in calculations by a rigid sphere method. Our calculations also have shown that the "pressed" distance is of this magnitude. The distances of this type obtained theoretically are 2·99 Å for 4,5-dimethylphenanthrene, 2·94 Å for benzophenanthrene, 2·98 Å for dibenzophenanthrene and 3·01 Å for hexahelicene.

3. *Dichlorodiphenylnaphthacene*. In the 5,6-dichloro-11,12-diphenylnaphthacene molecule, steric hindrance is due to the close disposition of phenyl rings and chlorine atoms in the ideal model. Here, the C atoms of the phenyl rings are placed one above the other. Although, the rotation of a phenyl ring around the C–C phenylnaphthacene bond, sharply decreases the strain energy it is clear that one type of deformation seems to be obviously inadequate. Even if phenyl rings rotate through 90°, nonvalence distances between C atoms in two phenyl rings remain inadmissibly small—2·42 Å.

Conformation problems for dichlorodiphenylnaphthacene involve the search of a minimum for functions with 10 variables. In general, a complete determination of geometry requires a large number of variables; however, when the number of variables increases, the time required to search the minimum by a computer increases rapidly. Ten independent geometric parameters are quite sufficient to reveal the basic geometric characteristics of the dichlorodiphenylnaphthacene molecule.

The geometric parameters were introduced in the following manner: four parameters for distortions in valence angles, corresponding to $C_2C_1C_2$, C_1C_2Cl, $C_9C_{10}C_9$, and $C_{10}C_9C_{11}$ (numeration is according to the "structure" in[27]), five parameters for non-planar deformations—deviations of bonds C_1–C_2, C—Cl, C_{10}–C_9, C_9–C_{11} and C_8–C_7, from corresponding planes; rotation angle of phenyl ring with respect to middle plane of benzene ring, with which it is connected. Some other data were assumed; for example the C_7—H bond was supposed to lie in the plane of the terminal benzene ring, which is planar by itself, etc. The bond lengths used were recorded.[27]

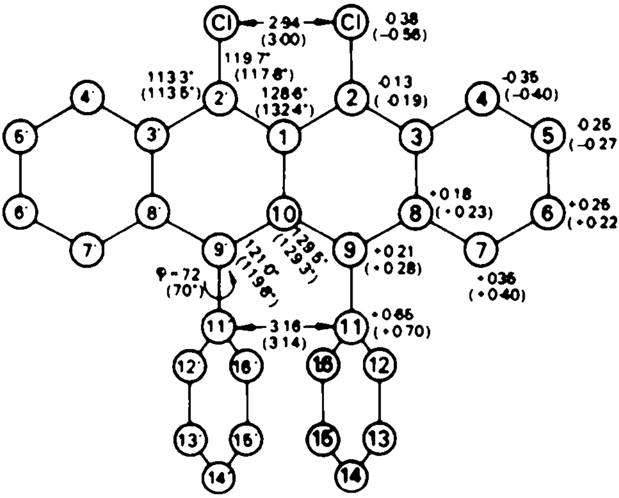


FIG. 5 Conformation of 5,6-dichloro-11,12-diphenylnaphthacene molecule. Experimental data are in parentheses

Figure 5 gives both calculated and experimental data. Although in some cases the difference between calculated and experimental values exceeds the experimental error (*viz.* valence angles $C_2C_1C_2$ and ClC_2C_1), the calculated results may be considered as satisfactory. It is natural, that if the potential surface is complicated the conformational calculation is less accurate. The errors of this calculation are to a great degree dependent on the limitations imposed on the number of variables and the assumptions made.

Not only the main features, but also some fine details of molecular configuration may be obtained by calculation: the inner benzene rings in the naphthacene nucleus are almost planar (planarity of benzene rings is characteristic of polynuclear condensed systems considered above), phenyl rings are rotated and, the angle of rotation almost equals the experimental one, and C_9—C_{11} bond departs out of plane of adjacent benzene ring, etc. It is interesting to note, that the angles ClC_2C_1 and $C_{10}C_9C_{11}$ are ca. 120°, i.e. they do not increase from the ideal, contrary to expectation. This is, obviously, due to the deformation of the angles ClC_2C_3 and $C_8C_9C_{11}$ which, in turn, result from the deformation of the angles $C_2C_1C_2$, and $C_9C_{10}C_9$. This demonstrates that it is not easy to see in advance even the character of deformation and the machine calculations are of great importance.

The above examples show that a mechanical model enables one to interpret and predict, *a priori*, the conformations of overcrowded aromatic systems having any type of deformation. We did not consider cases of possible formation of hydrogen bonds, the influence of intermolecular action on optimal conformation, etc. When necessary, new terms, taking into account these effects, can be added to the potential function; however the above method should give useful information on a large number of molecular structures which are of interest for crystallographers and theoretical chemists without any further additional assumptions.

APPENDIX

The potential functions of conformation problems usually contain variables of a rather different character, some influence the function substantially and in others this is not the case (e.g. parameters ε_i, β_r and φ in dichlorodiphenylnaphthacene). In these, the so-called "ravine" situation[28] often rises and the Steepest Descend method fails. It appears that the choice of direction with the use of second derivatives is more effective. Therefore we applied the method elaborated by Prof. A. Ja. Povzner and Dr. V. S. Posviansky at the Institute of the Chemical Physics, Academy of Sciences, USSR.

Let us expand our potential function $U(x)$ into a power series at the point x_0

$$U(x) = U(x_0) + \sum_i a_i \Delta x_i + \tfrac{1}{2}\sum_{i,j} b_{ij} \Delta x_i \Delta x_j + \ldots$$

where

$$a_i = \left(\frac{\partial U}{\partial x_i}\right)_{x=x_0}, \qquad b_{ij} = \left(\frac{\partial^2 U}{\partial x_i \partial x_j}\right)_{x=x_0}$$

If we neglect the higher terms, then the minimum of the function $U^{(2)}_{(x)}$ (index 2 means that we take in consideration only second derivatives) is found resolving a system of linear equations

$$b_{ij} \Delta x_i = a_i \qquad i = 1, 2, 3, \ldots n$$

The point x_1 which is solution of this system, is to be jointed to x_0 and vector $x_1 - x_0$ defines the direction of descend. When local minimum in this direction will be found, its position must be assumed as a new x_0, and a process of defining a new direction is repeated. The iteration procedure goes on until the variations of independent geometric parameters would be in the limits of 0.01.

The main difficulty of this method is calculation of the second derivatives. In principle, these derivatives of our functions can be found analytically, but because of tedious work on coding, we restricted the calculations to the simple cases, e.g. ethylene. In other cases we have calculated, instead of the derivatives, the corresponding differences. The

$$a_i = \frac{U(x_i + h) - U(x_i - h)}{2h},$$

$$b_{ij} = \frac{U(x_i + h; x_j + h) - U(x_i + h; x_j - h) - U(x_i - h; x_j + h) + U(x_i - h; x_j - h)}{4h^2},$$

where h is small change in argument.

Thus, for the determination of the matrices $|a_i|$ and $|b_{ij}|$ the potential function must be calculated $2m(m + 1) + 2m = 2m(m + 2) = 2[(m + 1)^2 - 1]$ times. The search of a minimum in the direction does not take much time and, consequently, computer time increases roughly as the squares of natural numbers with a number of variables. Calculation of the potential energy of hexahelicene (13 variables) takes ca 0·3 sec, one iteration 2 min, and 15 iterations, permitted to find a minimum, 30 min.

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