Force Field Calculation with a Top Desk Calculator

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A modified "Consistent Force Field" method is described in which the energy minimization is carried out according to the Murtagh-Sargent method rather than the Newton-Raphson method and the number of non-bonded interactions is reduced to interactions between atoms separated by three bonds at the most. The smaller number of interaction terms allowed the programming of the method for a desk top calculator (HP-9810). Calculations are reported for a number of aliphatic molecules.

Force field calculations of molecular conformations and conformation energies gain an increasing importance for chemists generally and organic chemists particularly [1–22]. Compared to the existing quantum mechanical methods the force field method is simpler in the choice of the mathematical functions used in the calculation and allows much more efficiently the introduction of empirical data to its model. Among the many different force field models which had been used is that of Ermer and Lifson (El model) [22]. It was applied successfully to aliphatic and olefinic organic molecules. The model was based on a harmonic energy function of the type;

$$E = (1/2)\, c_i (b_i - b_{0,i})^2 ,$$

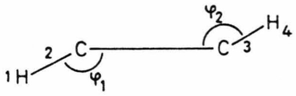
where c_i is the force constant, $b_{0,i}$ and b_i are the equilibrium and the actual values of the internal coordinate i. The equation was modified such as to consider the energies of the different internal coordinates, i.e. valence bonds, bond angles, rotation angles and out of plane deformation angles. The nonbonded interaction between all atoms was also considered using a function of the type

$$E_{\text{nonbonded}} = \sum \varepsilon [2 (r^*/r)^9 - 3 (r^*/r)^6] ,$$

where r is the distance between the two corresponding atoms, r^* is the distance at which the nonbonded interaction vanishes and ε is an energy constant for this type of interaction.

The values of the empirical parameters were obtained from a least squares fit to obtain experimental energies of a certain set of molecules. The model allows the minimization of the energy according to the Newton-Raphson method, in which the second derivatives of the energy over the coordinates were used [14]. Its calculated conformation energies and geometries agreed well with the existing experimental data. In an attempt to reduce the time of computation and apply a top desk calculator we introduced the following modifications to the model;

- Decreasing the number of nonbondel terms to interactions between atoms separated by three bonds only (1–4),



The distance between atoms 1 and 4 was calculated then according to the formula

$$r_{1-4} = \sqrt{[r_{34} \cos \varphi_2 \cos d - \{r_{12} \cos (180 - \varphi_1) + r_{23}\}] + [r_{34} \cos d \sin \varphi_2 - r_{12} \cos \varphi_1]^2 + [r_{34} \sin d]^2} ,$$

where d is the dihedral angle.

- The minimization of energy was carried out according to the Murtagh-Sargent technique [23] using first order derivatives of energy over the coordinates in a similar manner to that applied by us in the MINDO-FORCES method [24]. The derivatives were evaluated analytically and the new coordinates Q' were calculated from the old coordinates according to the equation

$$Q' = Q - \alpha F ,$$

where α is a constant and F is the forces matrix.

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- The program was written using the machine language for a HP-9810 top desk calculator with an extra casette memory (HP-9895A).

All other features of the model were retained. The calculations were carried out iteratively till the energy difference between two successive iterations was ≦0.5 kcal/mol.

Results

In order to compare our results with those of Ermer and Lifson [22] we calculated the conformation energies for a number of molecules for which calculations were done by them. We shall limit our discussion to a comparison with their theoretical findings, since they made an extensive discussion of their results comparing them with the experimental results and found remarkable agreement. The first molecule in the serie was ethylene for which we chose an initial geometry which deviated strongly from the expected equilibrium geometry. The initial bond distances were 1.2 Å(C—H), 1.5 Å(C=C) and the bond angle was 130° (H—C=C). The calculation required eight iterations to reach the energy boundary as defined before. The change in the internal coordinates was smooth and continuous (Fig. 1) and the calculated conformation energy decreased smoothly along the iterations. The calculated final geometry of the molecule (1.339 Å for C=C and 1.09 Å for C—H) compares well with the EL as well as with the experimental values (Table 1).

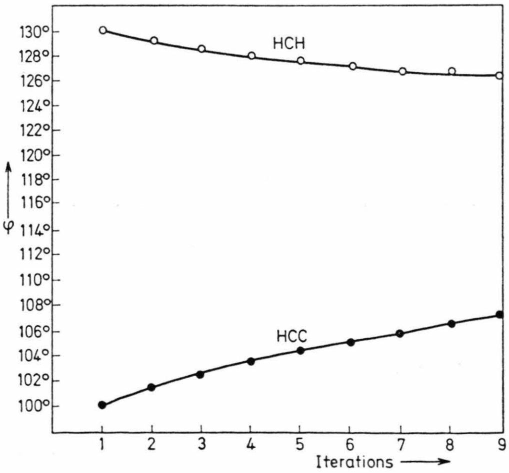


Fig. 1. Calculated bondangle values of ethylene resulting from different iterations.

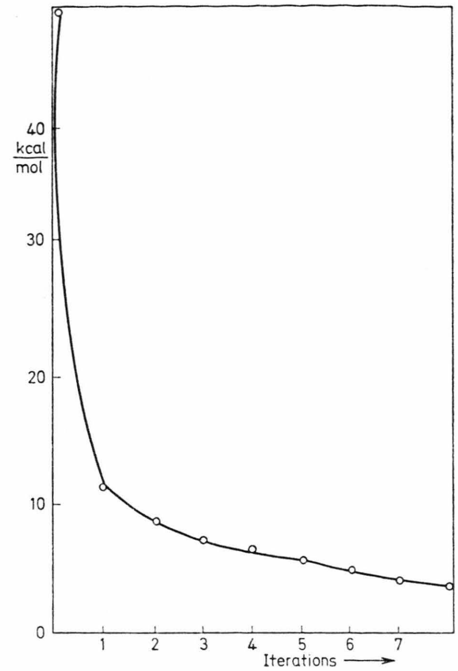
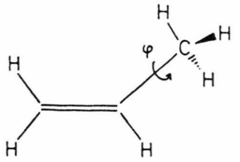


Fig. 2. Calculated energy values of ethylene resulting from different iterations.

Table 1. Calculated bond distances and angles of ethylene compared with those of Ermer and Lifson.

	This calculation	Ermer and Lifson [22]
C—H	1.090 Å	1.089 Å
C=C	1.339 Å	1.333 Å
∢HCC	122.72	121.4
∢HCH	114.42	117.2

The second molecule for which the conformation energy was calculated was propene. The calculations were done with different rotation angles of the methyl group relative to the plane described by the olefinic double bond. The so calculated rotation barrier was 2.57 kcal/mol, compared with the microwave value 1.98 kcal/mol [25]. The resulting most stable conformation was that with a methyl hydrogen atom eclipsed to the double bond (Figure 3). The resulting bond distances and angles compare well with the EL values (Table 2). Figure 4 shows the iterative energy change of propene.



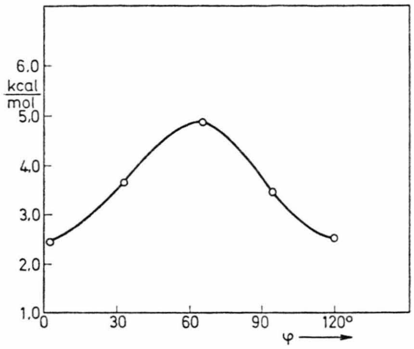


Fig. 3. Calculated rotation barrier of the methyl group in propene.

Table 2. Calculated bond distances and angles of propene.

	This calculation	Ermer and Lifson [22]
$C_{sp^2}-H$	1.089 Å	1.089 Å
$C_{sp^3}-H$	1.108 Å	1.105 Å
$C=C$	1.328	1.334
$C-C$	1.509	1.504
$\sphericalangle_{\mathrm{CCC}}$	123.53	123.9

We also carried out the calculations for the molecules 2-butene, trans and C_{2v}-cis, cyclopentene and 1,4-cyclohexadien, all of which were considered in the original EL calculation. Table 3 includes the calculated internal coordinates for the molecules.

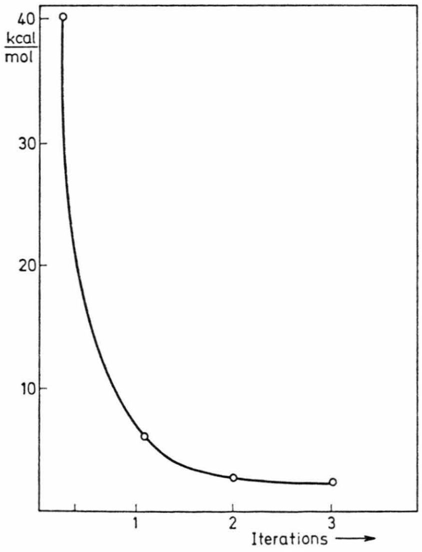


Fig. 4. Energy change of propene as calculated iteratively.

Table 3*. Calculated internal coordinates and conformation energies.

	This calculation	Ermer and Lifson [22]
cis, 2-butene		
$C_{sp^3}-C$	1.505	1.500
$C=C$	1.333	1.333
$C_{sp^3}-H$	1.105	1.105
$C_{sp^2}-H$	1.089	1.089
$\sphericalangle_{\mathrm{CCC}}$	127.32	127.6
$\sphericalangle_{\mathrm{HC=C}}$	119.55	118.2
$\sphericalangle_{\mathrm{HCC}}$	115.26	115.3
$\sphericalangle_{\mathrm{HCH}}$[1]	112.66	111.8
$\sphericalangle_{\mathrm{HCH}}$	106.55	105.8
Energy 2.97 kcal/mol		
trans, 2-butene		
$C_{sp^3}-C$	1.505	1.505
$C=C$	1.332	1.334
$C_{sp^3}-H$	1.108	1.105
$C_{sp^2}-H$	1.089	1.089
$\sphericalangle_{\mathrm{CCC}}$	123.23	123.5
$\sphericalangle_{\mathrm{HC=C}}$	121.83	121.20
$\sphericalangle_{\mathrm{HCC}}$	112.96	112.20
$\sphericalangle_{\mathrm{HCH}}$[1]	114.05	113.60
$\sphericalangle_{\mathrm{HCH}}$	106.84	106.10
Energy 1.22 kcal/mol		
Cyclopentene		
$C=C$	1.333	1.340
$C_{sp^2}-C$	1.501	1.521
$C-C$	1.526	1.548
$C_{sp^2}-H$	1.089	1.089
$C-H$	1.105	1.105
$\sphericalangle_{\mathrm{C=CC}}$	115.82	111.80
$\sphericalangle_{\mathrm{CCC}}$	105.97	105.80
$\sphericalangle_{\mathrm{CCC_{sp^2}}}$	108.08	103.0
$\sphericalangle_{\mathrm{HC=C}}$	127.04	127.4
Energy 7.14 kcal/mol		
Cyclohexadien		
$C=C$	1.331	1.334
$C-C$	1.505	1.503
$\sphericalangle_{\mathrm{C=CC}}$	123.7	124.0
$\sphericalangle_{\mathrm{CCC}}$	112.6	113.56
$\sphericalangle_{\mathrm{HC_{sp^2}H}}$	109.6	110.06
Energy 9.48 kcal/mol		

* Bondlengths in Å and angles in degrees.

[1] H in the plane of the double bond.

As for 2-butene, our method correctly yields the relative stability of the trans structure over the C_{2v}-cis structure. The resulting energy difference 1.75 kcal/mol compares well with 1.31 kcal/mol of EL. Also the C_{2v}-cis is calculated more stable than the C_2-cis isomer. The calculated most stable conformation for cyclopentene is the out of plane deformed conformation. The deformation angle is 20.1°, compared with 21.4° of El. The energy difference is 1.56 kcal/mol; $E_{EL} = 0.36$ kcal/mol. The experimental energy difference is 0.66 kcal/mol.

The calculation for 1,4-cyclohexadien yielded the expected relative stability of the D_{2h} over the C_{2v} symmetry in agreement with the theoretical results of Ref. [22] and with the experimental results cited therein. Our calculated energy difference for both structures was 4.65 kcal/mol.

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