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Calculation of Molecular Geometry with the PCILO-Method

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Comparison of calculations on the geometry of a group of four related molecules by a perturbation method shows qualitative agreement with the experimental trends.

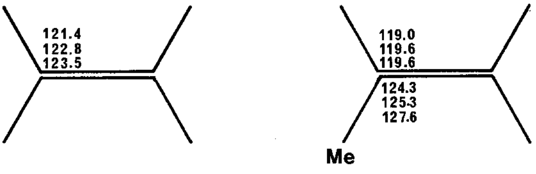
1. Introduction

As a relatively fast method to calculate the electronic energy of a given configuration of atoms the PCILO-method has been used recently to calculate minimum energy conformations of complex molecules [1, 2]. The PCILO-method is, in contrast with other approximate methods like SCF-variation methods, essentially a perturbation method. It is based on the concept of bond orbitals instead of atomatic orbitals, thereby establishing a connection with chemical sense. The method is extensively described by Diner, Malrieu and others [3, 4] and this description does not need to be repeated here. One feature of the method worth mentioning is the handling of atoms with lone pairs like oxygen. They are treated by adding fictitious atoms in the direction of the lone pairs and polarizing the bonds with these completely on the atom carrying the lone pairs. In the calculations described below the perturbation treatment is carried through to the second and third order. The values of the basic integrals are those given by Pople and Segal [5].

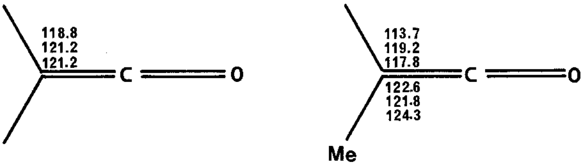
An impression of the power of an approximate method to provide useful predictions of a molecular quantity like geometry can be obtained by calculations on a series of related molecules and comparing the calculated with the observed trends in the property studied. For this purpose we chose the molecules ethylene, propylene, ketene and methylketene for the following reasons. The molecules are related by a simple substitution of $-CH_3$ for $-H$ and/or $=C=O$ for CH_2. The experimental structures were determined in the gasphase, so that packing effects which may be present in the results of crystal structure determinations are absent. Finally similar calculations in the extended Hückel scheme [6] allow comparison with a less sophisticated method.

2. Results

In Fig. 1 the results of the calculations are summarized. The upper value denotes the experimental results; obtained from [7–10] for ethylene, propylene, ketene and methylketene, respectively. The value in the middle represents the energy minimum in the second order approximation and the lower value that in the third order.



ETHYLENE PROPYLENE



KETENE METHYLKETENE

Fig. 1. Experimental (top) and calculated structures (2nd order middle, 3rd order below)

It is clear that there is no good agreement between the experimental and calculated values of the terminal angles. However, the calculations reproduce qualitatively the effects of both the methylation and the substitution of a CH_2 group by a C=O group. On replacing a hydrogen atom by a methyl group, we observe in both experimental and theoretical results (a) an opening of the angle enclosed by the double bond and the substituted atom (CCH and CCMe respectively); (b) a decrease of the adjacent C=C–H angle. These effects are summarized in the Table. Effect (a) is more pronounced in the third order results. This effect is approximately correct in the second order for the couple ethylene-propylene and in the third order for the couple ketene-methylketene. Effect (b) is exaggerated in both second and third order for the couple ethylene-propylene and it is too weak in both second and third order for couple ketene-methylketene. On replacing the CH_2 group by a C=O group we observe a decrease in the two angles adjacent to the double bond, in both experimental and theoretical results but like the extended Hückel method [6] the calculations do not reproduce the drastic reduction of CCH angle for the pair propylene-methylketene. For this angle we observe a reduction of 0.4° in the second order and 2° in the third order instead of the experimental value of 5.3°.

Table. *Effect on valence angles of replacement of* H *by a methyl group*

		Δ^a	Δ^b
Ethylene-Propylene	exp.	2.9°	2.4°
	2nd order	2.5°	3.2°
	3rd order	4.1°	3.9°
Ketene-Methylketene	exp.	3.8°	5.1°
	2nd order	0.6°	2.0°
	3rd order	3.1°	3.4°

[a] Δ increase of the angle CCMe, in degrees.
[b] Δ decrease of the angle H−C=C.

The barriers to internal rotation of the methyl group calculated in second and third order for the experimental geometry are (all values in kcal/mole):

propylene 1.31 and 1.22 (exp. 1.98),
methylketene 1.54 and 1.31 (exp. 1.18).

Clearly calculated and observed quantities are not in line.

Our conclusion can be that the PCILO-method is well able to represent the geometrical effects of intramolecular interactions, but that a careful calibration of the parameters, i.c. the values of the basic integrals, would add much to its usefulness.

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