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Semiempirical versus *ab initio* Calculations of Molecular Properties.

II. Comparative Study of Interatomic Distances and Bond Angles in Some Strained Medium Size Hydrocarbons as Obtained by the STO-3G, MINDO/3 and IMOA Methods

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A comparative study of the structural parameters in some strained spirohydrocarbons is presented. The theoretical values provided by the STO-3G, MINDO/3 and IMOA methods are in reasonable agreement with each other and with available experimental data offering thus a posteriori justification of the employed approximate schemes.

Key words: Interatomic distances – Bond angles – Hybrid orbitals.

Quantum chemistry has developed in last five decades a wide spectrum of theories of chemical bonding ranging from simple intuitive models to rigorous a priori treatments which require advanced computational procedures. Various methods, differing in their levels of sophistication and scopes, serve usually different purposes. Comparative studies of molecular properties by distinct methods are useful because they may shed some light on the merits of particular approach suggesting sometimes remedy of its shortcomings. Lipscomb et al. [1] were recently examined a number of contemporary semiempirical methods regarding their speed and accuracy as judged by the ab initio STO-3G method. We studied

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several semiempirical theories by calculating some one-electron molecular properties [2, 3] which provide sensitive probes of electron charge distribution in molecules. Here we consider the structural characteristics of some strained spiro-compounds and their parent molecules employing the results obtained by the minimal basis set STO-3G, MINDO/3 and IMOA[1] methods. The STO-3G approach [4-7] is one of the simplest *ab initio* methods which can be applied to larger systems at moderate costs, MINDO/3 method [8] is known as one of the most successful current semiempirical theories while IMO approximation [9–11] exhibits an utmost conceptual simplicity yet providing a fairly good description of covalent bonding in hydrocarbons. The MINDO/3 and IMOA calculation on spiro-compounds were executed by using standard procedures [8–10]. The STO-3G results and the computed structural parameters by MINDO/3 and IMOA methods for small parent molecules were taken from the literature [4–10] in order to enlarge the set of related compounds. The results are presented in Table 1. It is interesting to observe the changes in geometrical parameters of smaller molecules which serve as building blocks for constructing larger compounds. The changes in interatomic distances are most pronounced in bonds which emanate from the common atom connecting two or more fused fragments. The influence of the perturbation quickly falls off in the more remote bonds. Spiro[2.4]hepta-4,6-diene, spiro[2.4]heptatriene and spiro[4.4]nonatetraene provide good illustrative examples of the transferability of certain structural groups. The $C_2C_3C_4C_5$ moieties of the cyclopentadiene fragment (including cyclopentadiene itself) in the above mentioned system possess practically geometrical characteristics of 1,3-butadiene as far as interatomic distances are concerned. The interatomic distances C_6C_7 in spiro[2.4]hepta-4,6-diene and spiro[2.4]heptatriene are very close to those in cyclopropane and cyclopropene, respectively. The effect of ring fusion is augmented if all carbon atoms are involved in the formation of new bonds as in tetrahedrane and cubane. The quantitative changes are easily deduced from the data displayed in Table 1. The influence of the use of more flexible (4 –31 G) basis set on the C—C and C—H distances is illustrated by tetrahedrane [12]. This interesting molecule exhibiting high electron charge deformation is still not synthetized and comparison with experiment is impossible. However, the calculated interatomic distances for the related Platonic polyhedron, cubane, are in fairly good agreement with the measured values.

To summarize, survey of the results shows that the geometric parameters provided by STO-3G, MINDO/3 and IMOA methods are, apart a few exceptions, in reasonable accordance with the available experimental data. Better estimates could be obtained by employing very flexible basis sets involving polarization functions and multiconfigurational [14, 15] ab initio technique but at the expense of the considerably increased computational complexities. Thus, each of the methods examined in this work has its own *raison d'etre* being feasible for compounds increasing in size. It is interesting to note that simple concepts like hybridization and effective overlapping have far reaching consequences as evidenced by the good performance of the IMOA method. This finding indicates that

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[1] IMOA is acronym for the iterative maximum overlap approximation.

Table 1. Comparison between the interatomic distances and bond angles as calculated by the STO-3G, MINDO/3 and IMOA methods with available experimental data for some medium size strained hydrocarbons (distances in Å, angles in degrees)

Structural Parameters^{v}

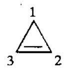
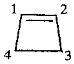
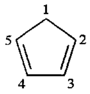
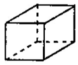
Molecule		STO-3G	MINDO/3	IMOA	EXPTL.
	d(C—C)	$=1.502^{a}$	1.504^{b}	1.516^{c}	1.510^{d}
	d(C—H)	=1.081	1.103	1.088	1.089
	∡HCH	=113.8	108.7	113.5	115.1
	d(C_1—C_2)	$=1.493^{a}$	1.481^{b}	1.471	1.509^{f}
	d(C_2—C_3)	=1.277	1.317	1.304	1.296
	d(C_1—H)	=1.087	1.114	1.089	1.088
	d(C_2—H)	=1.075	1.084	1.065	1.072
	∡HC_1H	=112.5	105.2		114.6
	∡HC_2C_3	=150.3	153.1		149.9
	d(C—C)	$=1.554^{g}$	1.525^{b}	1.552^{c}	1.548^{h}
	d(C—H)	=1.087	1.110	1.097	1.092
	∡HCH	=108.7	—	111.9	110.0
	d(C_1—C_2)	$=1.314^{g}$	1.345^{b}	1.343^{c}	1.342^{i}
	d(C_2—C_3)	=1.526	1.512	1.521	1.517
	d(C_3—C_4)	=1.565	1.535	1.559	1.566
	d(C_1—H)	=1.082	1.099	1.077	1.083
	d(C_3—H)	=1.089	1.116	1.096	1.094
	∡HC_1C_2	=134.2	134.7	136.6	133.5
	∡HC_3H	=109.0	—	112.0	109.5
	d(C_1—C_2)	$=1.313^{g}$	1.330	1.340^{j}	1.337^{k}(1.341)^{l}
	d(C_2—C_3)	=1.488	1.464	1.470	1.483 (1.463)
	d(C_1—H)	=1.081	1.099	1.081	1.083 (1.090)
	d(C_2—H)	=1.085	1.099	1.081	1.083 (1.090)
	∡$C_1C_2C_3$	=124.2	131.0	121.3	122.4 (123.4)
	∡HC_1C_2	=121.9	—	121.4	119.8 (120.9)
	∡HC_2C_1	=120.2	—	121.6	119.8 (120.9)
	d(C_1—C_2)	$=1.522^{m}$	1.515^{b}	1.508^{j}	1.506^{n}
	d(C_2—C_3)	=1.319	1.352	1.341	1.345
	d(C_3—C_4)	=1.490	1.492	1.466	1.468
	d(C_1—H)	=1.091	1.116	1.100	1.099
	d(C_2—H)	=1.080	1.103	1.081	1.078
	d(C_3—H)	=1.081	1.102	1.081	1.080
	d(C—C)	$=1.561^{p}$	1.568^{p}	1.552^{c}	1.550^{r}
	d(C—H)	=1.081	1.105	1.089	1.11
	d(C—C)	$=1.473^{g}$ (1.48)^{o}	1.504	1.491	—
	d(C—H)	=1.069 (1.05)	1.083	1.065	—

Table 1. (cont.)

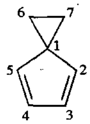
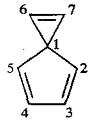
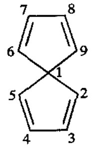
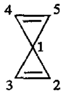
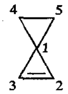
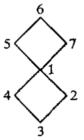
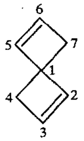
Molecule		Structural Parameters STO-3G	MINDO/3	IMOA	EXPTL.
	$d(C_6-C_7)$	$=1.495^m$	1.475^u	1.517	1.510^s
	$d(C_1-C_2)$	$=1.506$	1.520	1.498	1.509
	$d(C_2-C_3)$	$=1.321$	1.359	1.334	1.341
	$d(C_3-C_4)$	$=1.488$	1.474	1.484	1.460
	$d(C_1-C_6)$	$=1.518$	1.532	1.516	1.510
	$d(C_2-H)$	$=1.081$	1.100	1.076	1.100
	$d(C_3-H)$	$=1.081$	1.100	1.075	1.100
	$d(C_6-H)$	$=1.081$	1.106	1.089	1.120
	$\measuredangle HC_2C_1$	$=123.0$	122.3	122.3	119.2
	$\measuredangle HC_3C_2$	$=127.1$	127.5	127.8	131.2
	$d(C_1-C_2)$	$=1.512^m$	1.519^u	1.501	
	$d(C_2-C_3)$	$=1.321$	1.360	1.333	
	$d(C_3-C_4)$	$=1.488$	1.474	1.482	
	$d(C_1-C_6)$	$=1.505$	1.527	1.466	
	$d(C_6-C_7)$	$=1.275$	1.302	1.304	
	$d(C_2-H)$	$=1.081$	1.100	1.075	
	$d(C_3-H)$	$=1.081$	1.101	1.077	
	$d(C_6-H)$	$=1.075$	1.085	1.065	
	$\measuredangle C_2C_1C_5$	$=103.0$	101.5	103.5	
	$\measuredangle HC_6C_1$	$=144.1$	141.4	145.3	
	$\measuredangle HC_2C_1$	$=123.2$	122.4	122.4	
	$\measuredangle HC_3C_2$	$=127.2$	127.5	127.7	
	$d(C_1-C_2)$	$=1.534^m$	1.542	1.509	
	$d(C_2-C_3)$	$=1.318$	1.356	1.336	
	$d(C_3-C_4)$	$=1.491$	1.477	1.482	
	$d(C_2-H)$	$=1.081$	1.100	1.076	
	$d(C_3-H)$	$=1.081$	1.100	1.077	
	$\measuredangle C_2C_1C_5$	$=100.8$	99.4	101.8	
	$\measuredangle HC_2C_1$	$=122.0$	121.5	121.6	
	$\measuredangle HC_3C_2$	$=127.0$		128.0	
	$d(C_1-C_2)$	$=1.473^m$	1.493	1.444	
	$d(C_2-C_3)$	$=1.296$	1.321	1.305	
	$d(C_2-H)$	$=1.077$	1.090	1.066	
	$\measuredangle HC_2C_3$	$=147.0$	146.6	151.4	
	$d(C_1-C_2)$	$=1.475^m$	1.497	1.443	
	$d(C_2-C_3)$	$=1.287$	1.313	1.304	
	$d(C_1-C_4)$	$=1.485$	1.500	1.494	
	$d(C_4-C_5)$	$=1.527$	1.500	1.479	
	$d(C_2-H)$	$=1.076$	1.087	1.066	
	$d(C_4-H)$	$=1.082$	1.107	1.091	
	$\measuredangle HC_2C_3$	$=146.5$		151.4	
	$\measuredangle HC_4H$	$=113.5$		113.1	

Table 1. (cont.)

Structural Parameters

Molecule		STO-3G	MINDO/3	IMOA	EXPTL.
	d(C_1—C_2)	=1.549[t]	1.556	1.541	
	d(C_2—C_3)	=1.550	1.520	1.555	
	d(C_2—H)	=1.087	1.114	1.093	
	d(C_3—H)	=1.087	1.113	1.093	
	$\measuredangle C_2C_1C_4$	=90.0	86.56	91.00	
	$\measuredangle HC_2H$	=108.7	103.6	112.1	
	$\measuredangle HC_3H$	=108.7	103.8	112.1	
	d(C_1—C_2)	=1.526[t]	1.535	1.509	
	d(C_2—C_3)	=1.318	1.346	1.343	
	d(C_1—C_4)	=1.567	1.567	1.548	
	d(C_3—C_4)	=1.524	1.502	1.527	
	d(C_2—H)	=1.082	1.100	1.071	
	d(C_3—H)	=1.082	1.100	1.071	
	d(C_4—H)	=1.089	1.115	1.092	
	$\measuredangle HC_2C_3$	=134.4	135.1	135.6	
	$\measuredangle HC_3C_2$	=134.2	136.1	134.3	
	$\measuredangle C_2C_1C_4$	= 85.4	83.64	86.9	
	$\measuredangle HC_4H$	=109.0	103.9	112.4	

[a] Ref. [4]. [b] Ref. [8]. [c] Ref. [9]. [d] Bastiansen, O., Fritsch, F. N., Hedberg, K.: Acta Crystallogr. **17**, 538 (1964). [e] Eckert-Maksić, M., Maksić, Z. B. (unpublished results). [f] Stigliani, W. M., Laurie, V. W., Li, J. C.: J. Chem. Phys. **62**, 1890 (1975). [g] Ref. [5]. [h] Almeningen, A., Bastiansen, O., Skancke, P. N.: Acta Chem. Scand. **15**, 711 (1961). [i] Bak, B., Led., J. J., Nygaard, L., Rastrup-Anderson, J., Sorensen, J. O.: J. Mol. Structure **3**, 369 (1969). [j] Ref. [10]. [k] Almeningen, A., Bastiansen, O., Traetteberg, M.: Acta Chem. Sand. **12**, 1221 (1958). [l] Kuchitsu, K., Fukuyama, T., Morino, Y.: J. Mol. Struct. **1**, 463 (1967–8). [m] Ref. [6]. [n] Damiani, D., Ferretti, L., Gallinella, E.: Chem. Phys. Letters **37**, 265 (1976). [o] Ref. [12]. [p] Ref. [13]. [r] Fleischer, E. B.: J. Am. Chem. Soc. **86**, 3889 (1964). [s] Chiang, J. F., Wilcox, C. F., Jr.: J. Am. Chem. Soc. **95**, 2885 (1973). [t] Ref. [7]. [u] Our results are essentially in agreement with those given in Ref. [16] but they are presented here in some more detail. [v] The maximal possible symmetry is supposed in each molecule in order to diminish computational efforts.

pictorial models of covalent bonding based hybrid orbitals are worth of further development and exploitation.

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