

THE INFLUENCE OF THE MOLECULAR GEOMETRY ON THE BARRIERS TO INTERNAL ROTATION

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ABSTRACT

A systematic study of the barriers to internal rotation (BIR) for 50 molecules was performed. It is shown that the methods CNDO/2 and INDO with the original parametrization are adequate tools for obtaining BIR only for atoms of the first row of the periodic table. The results are not reliable when the axial bond which participates in the rotation is saturated with fluorine, chlorine or oxygen.

1. INTRODUCTION

Barriers to internal rotation are determined by the variation of the potential energy with the dihedral angle, when restricted to rotations around a single bond (axial bond). This barrier can be ignored if it is much smaller than kT (*c.a.* 5 cal/mole), in which case the problem reduces to the free internal rotation. The most usual situation is found when the barrier is in the range of 0.5 – 10 kcal/mole. This is an intermediate situation between the two extreme conditions, that is, a free internal rotation as above and a hindered rotation (restrictive potential much higher than kT , *c.a.* 20 kcal/mole).

The orthodox way of utilizing quantum-mechanical methods for conformational analysis requires the knowledge of several geometrical parameters. Experimental and/or data are needed for this purpose. However, a systematic study of the influence of the geometrical parameters on the magnitude of the internal rotational barriers has not yet been performed. This sistematization is extremely necessary in order to establish accurately the applicability of each method and to allow for the choice of the most advantageous criteria to solve the problem under investigation.

Within this frame, this work describes and discusses the calculations of rotational barriers for various molecules by utilizing the CNDO/2 and INDO methods. The results obtained with the two methods have been compared among themselves as well as with experimental data found in the literature.

2. METHODOLOGY

The semi-empirical methods CNDO/2 (Complete Neglect of Differential Overlap) and INDO (Intermediate Neglect of Differential Overlap) with the original para-

metrization have been used for the conformational analysis [1–4].

The internal rotational barriers calculated by utilizing the experimental geometry have been compared to those calculated for the standard geometry (Table 4.16 of ref. 4). In addition, the axial bond has been optimized while the remaining structural parameters have not been altered.

In order to compare the theoretical results to the experimental ones, the following priority order of confidence in the experimental results has been obeyed, where the percentages refer to the experimental errors associated to the methods: microwave splitting method, 8% [5]; infrared and Raman methods, 10% [6]; thermodynamic method, 10–20% [7, 8]; electron diffraction method, 5–30% [9, 10]; microwave intensity method [5, 6]; neutron scattering method [11]; NMR method [12] and dipole moment method [13]. The last four methods have shown poor precision, but on the other hand, IR and Raman methods provide precise results only for gaseous molecules with well-characterized centers of the torsional band.

3. RESULTS

There are several examples in the literature of failure of the methods CNDO/2 and INDO for the calculation of the barriers to internal rotation (BIR) as, for example, for conjugated molecules [14–16]. However, a systematic study of BIR for saturated molecules and the influence of the substituents directly bonded or near to the atoms of the rotational axis is missing.

In order to overcome this difficulty, we have studied 50 molecules involving rotations around C-C, C-N and C-O bonds. Tables 1, 2 and 3 present the BIR for these molecules, calculated for the experimental and optimized geometries, together with experimental results. In Figures 1 and 2, the distribution of frequency of the percentages of error for the molecules containing atoms of the first row of the periodic table is plotted.

We have neglected the molecules of hexachloroethane and hydrogen peroxide in the discussion of the results, because the *ab initio* (minimal basis set) and semi-empirical methods do not provide the most stable conformation (*anti*) for the latter, while for the former the experimental results of Morito and Hirota [10] are not precise. It would be noted that the C-C bond distance for the hexachloro-

thane molecule varies too much when passing from the most (1.40 Å) to the least (1.44 Å) stable conformation,

which is not the normal behaviour for ethane and hexafluoroethane.

TABLE 1

Barriers to Internal Rotation (BIR) calculated for the experimental and optimized geometries and experimental results for molecules containing atoms of the first row of the Periodic Table.

Molecules	BIR experimental (a)	BIR geom. exper. CNDO INDO (b)	ERROR CNDO INDO (%) (d)	BIR geom. optim. CNDO INDO (c)	ERROR CNDO INDO (%) (d)
CH ₃ CH ₃	3.03 (21) (e)	2.18	-25.6	2.82	-3.75
	<u>2.93 (22) (f)</u>				
	2.75 (23) (g)				
	2.72 (24) (f)				
CH ₃ CH ₂ F	4.26 (25) (e)	2.01	-39.3	2.60	-21.5
	3.96 (24) (f)				
	<u>3.31 (26) (e)</u>				
CH ₃ CHF ₂	3.95 (24) (f)	1.84	-42.1	2.40	-24.5
	3.58 (27) (h)				
	<u>3.18 (26) (e)</u>				
CH ₃ CF ₃	3.66 (28) (f)	2.66	-19.2	2.28	-30.7
	3.48 (29) (h)				
	3.45 (30) (f)				
	<u>3.29 (31) (f)</u>				
CH ₂ FCF ₃	3.29 (6) (i)	1.45	-65.5	1.94	-55.5
	3.25 (32) (g)				
CHF ₂ CF ₃	<u>4.20 (33) (f)</u>	1.42	-66.2	1.87	-58.8
	CF ₃ CF ₃	<u>3.50 (34) (f)</u>	1.37	-60.9	1.57
CH ₃ CH ₂ Cl		1.42	1.42	-59.4	1.59
	CH ₃ CHCl ₂	<u>4.35 (35) (g)</u>	1.87	-57.0	1.39
CH ₃ CH ₂ Cl		2.04	2.04	-53.1	1.54
	4.70 (36) (g)	2.09	-43.4	2.85	-22.8
	<u>3.69 (37) (e)</u>				
	3.69 (6) (f)				
	3.69 (38) (f)				
3.67 (39) (f)					
3.56 (40) (e)	----	-----	-----	-----	
3.40 (41) (h)					
CH ₃ CHCl ₂	3.75 (42) (g)	2.28	-34.9	3.00	-14.3
	3.55 (43) (g)				
	<u>3.50 (6) (f)</u>				
	3.49 (32) (g)				

continuation of the TABLE 1

CH ₃ CCl ₃	5.80 (11) (j)	2.24	-26.6	2.98	-2.30
	5.70 (12) (k)				
	5.49 (6) (i)	----	-----	----	-----
	3.05 (28) (f)				
	2.97 (44) (g)				
	2.70 (45) (g)				
CCl ₃ CCl ₃	<u>10.8 (10) (1)</u>	25.8	+150	29.4	+185
		----	-----	----	-----
CH ₃ CF ₂ Cl	<u>3.71 (28) (f)</u>	1.77	-52.3	2.39	-35.6
		----	-----	----	-----
CH ₃ CFCCl ₂	<u>3.47 (28) (f)</u>	2.06	-40.6	2.76	-20.5
		----	-----	----	-----
CH ₃ CH ₂ CH ₃	<u>3.56 (46) (e)</u>	2.38	-33.2	2.98	-16.3
	3.20 (47) (g)	2.32	-34.8	2.91	-18.3
	> 2.70 (48) (e)				
gauche- CH ₃ CH ₂ CH ₂ F	<u>2.87 (49) (e)</u>	2.38	-17.1	2.95	+2.79
		2.35	-18.1	2.88	-0.35
anti- CH ₃ CH ₂ CH ₂ F	<u>2.69 (49) (e)</u>	2.18	-19.0	2.71	+0.74
		2.07	-23.1	2.53	-5.95
CH ₃ CHClCH ₃	<u>4.32 (39) (f)</u>	2.64	-38.9	3.14	-27.3
	> 3.45 (50) (e)	----	-----	----	-----
(CH ₃) ₃ CH	3.94 (51) (i)	2.97	-17.8	3.50	-3.31
	3.90 (51) (f)				
	3.90 (52) (h)				
	3.87 (53) (g)				
	<u>3.62 (53) (g)</u>	2.84	-21.6	3.28	-9.34
(CH ₃) ₃ CF	<u>4.30 (52) (h)</u>	2.47	-42.6	2.95	-31.4
	> 3.00 (39) (f)	2.22	-48.4	2.60	-39.5
(CH ₃) ₃ CCl	3.70 (12) (k)	3.05	-4.69	3.70	+15.6
	<u>3.20 (39) (i)</u>	----	-----	----	-----
CH ₃ NH ₂	<u>1.98 (54) (e)</u>	1.27	-35.8	1.61	-18.6
	1.98 (55) (e)	1.27	-35.8	1.60	-19.1
	1.80 (56) (e)				
(CH ₃) ₂ NH	3.62 (39) (f)	1.86	-42.2	2.27	-29.5
	3.62 (57) (e)				
	3.46 (7) (g)				
	<u>3.22 (58) (e)</u>				
	1.83	-43.2	2.22	-31.1	

Continuation of the TABLE 1

(CH ₃) ₃ N	5.75 (59) (k)				
	5.19 (60) (i)				
	4.73 (60) (i)				
	4.41 (38) (f)				
	4.40 (61) (h)				
	4.38 (39) (f)	2.64	-27.3	2.96	-18.5
	4.35 (51) (i)	2.56	-29.5	2.87	-19.4
	4.27 (62) (f)				
	4.08 (39) (f)				
	4.03 (60) (i)				
	3.77 (60) (i)				
<u>3.63 (51) (f)</u>					
CH ₃ NF ₂	<u>4.17 (63) (e)</u>	2.22	-46.8	2.59	-37.9
		2.04	-51.2	2.35	-32.4
CH ₃ OH	1.11 (64) (e)	0.95	-13.6	1.21	+10.0
	1.07 (65) (e)	0.95	-13.6	1.18	+7.27
CH ₃ OC ₂	<u>3.06 (66) (e)</u>	0.71	-76.8	0.77	-74.8
		----	-----	-----	-----
(CH ₃) ₂ O	3.00 (67) (g)				
	<u>2.72 (67) (e)</u>	3.62	+33.1	4.43	+62.9
	2.70 (68) (g)	3.45	+26.8	4.21	+57.8
	2.50 (69) (g)				
> 3.12 (39) (f)					
HOOH	<u>7.04 (70) (f)</u>	5.27	-25.1	11.5	+63.9
		5.75	-18.3	11.4	+62.9

- (a) – in kcal/mole
 (b) – Barrier to Internal Rotation (BIR) calculated with experimental and/or standard geometry quoted in the literature and referring to specific molecules in the table (BIR in kcal/mole)
 (c) – Barrier to Internal Rotation (BIR) calculated with axial bond optimized through identified method. The angles correspond to the most stable position and the most instable position. (BIR in kcal/mole)
 (d) – (% ERROR) – Percentage of error of the theoretical result compared to the particular experimental result underlined
 (e) – Microwave Splitting Method
 (f) – Infrared and Raman Method
 (g) – Thermodynamic Method
 (h) – Microwave Intensity Method
 (i) – Infrared and Raman Method – Solid State
 (j) – Neutron Scattering Method
 (k) – NMR Method
 (l) – Electron Diffraction Method

TABLE 2
Barriers to Internal Rotation (BIR) for double and triple rotors.

Molecules	Simultaneous Optimization of the bonds between rotors				Optimization of the axial bond only			
	CNDO/2		INDO		CNDO/2		INDO	
	BIR	%	BIR	%	BIR	%	BIR	%
	(a)	ERROR	(a)	ERROR	(a)	ERROR	(a)	ERROR
CH ₃ CH ₂ CH ₃	2.89	-9.69	2.82	-11.9	2.98	-6.88	2.91	-9.06
gauche- CH ₃ CH ₂ CH ₂ F	2.85	-0.70	2.81	-2.09	2.95	+2.79	2.88	+0.35
anti- CH ₃ CH ₂ CH ₂ F	2.49	-3.72	2.46	-8.55	2.71	+1.49	2.54	-5.58
CH ₃ CHC≡CH ₃	3.15	-4.85	----	----	3.14	-4.55	----	----
(CH ₃) ₃ CH	3.44	-4.97	3.14	-12.2	3.50	-3.31	3.28	-9.39
(CH ₃) ₃ CF	2.88	-33.0	2.50	-41.9	2.95	-31.4	2.60	-39.5
(CH ₃) ₃ CCl	3.63	+13.4	----	----	2.70	+15.6	----	----
(CH ₃) ₂ NH	2.20	-31.7	2.16	-32.9	2.27	-29.5	2.22	-20.4
(CH ₃) ₃ N	2.96	-18.5	2.87	-20.4	2.96	-18.5	2.87	-20.4

(a) - In kcal/mole

(b) - (% ERROR) - Percentage of error of the theoretical result compared to the experimental result (underlined) from Table 1.

TABLE 3
Barriers to Internal Rotation (BIR) calculated for the experimental and optimized results for molecules containing atoms of the second row of the Periodic Table.

Molecules	BIR Experimental (a)	BIR geom. exper. CNDO/2 (b)	% ERROR (c)	BIR geom. optim. CNDO/2 (b)	% ERROR (c)
CH ₃ SH	1.46 (71) (g) <u>1.275 (72) (e)</u> 1.06 (73) (e)	1.57	+32.1	2.75	+115
(CH ₃) ₂ S	<u>2.132 (74) (e)</u> 1.267 (72) (e)	4.05	+90.5	7.10	+230
CH ₃ PH	<u>1.96 (75) (e)</u>	3.57	+80.2	5.19	+165
(CH ₃) ₃ P	3.58 (51) (i) <u>2.60 (52) (h)</u> > 1.5 (76) (i)	3.18	-11.1	4.44	+24.5
CH ₃ SiH ₃	<u>1.700 (77) (e)</u> 1.665 (78) (e)	3.90	+129	4.70	+176
CH ₃ SiH ₂ F	<u>1.559 (79) (e)</u>	3.23	+157	3.56	+184
CH ₃ SiF ₃	<u>1.200 (29) (e)</u> 1.200 (80) (h)	2.72	+126	3.47	+189

Continuation of the TABLE 3

$\text{CH}_3\text{SiHCl}_2$	<u>2.90 (81) (g)</u> 2.09 (81) (i)	3.76	+23.4	4.83	+66.1
$(\text{CH}_3)_2\text{SiH}_2$	<u>1.647 (82) (e)</u>	3.73	+126	4.40	+167
$(\text{CH}_3)_2\text{SiHF}$	<u>2.39 (83) (i)</u>	3.29	+38.0	4.24	+77.3
$(\text{CH}_3)_2\text{SiF}_2$	<u>1.70 (83) (i)</u>	2.99	+76.6	3.75	+120
$(\text{CH}_3)_2\text{SiHCl}$	<u>2.56 (83) (i)</u>	4.46	+74.3	4.85	+89.2
$(\text{CH}_3)_3\text{SiH}$	<u>2.49 (51) (i)</u>	3.92	+57.4	4.50	+81.3
$(\text{CH}_3)_3\text{SiF}$	<u>2.25 (51) (i)</u>	3.84	+71.1	3.84	+71.1

(a); (b); (c); (d); (e); (f); (g); (h); (i); (j); (k) and (l), see Table 1.

DISCUSSION

Figure 1 summarizes the results that we have obtained by comparing those calculated for the experimental geometry with those for the optimized geometry. As justified above, hexachloethane and hydrogen peroxide have not been included in the figure.

It is shown that the average error diminishes of 10% when passing from the experimental and/or standard geometry to an optimized one with respect of the axial bond. However, the distribution of frequency for the experimental and/or standard geometry shows a slight positive

assimetry (mean value > median > mode). On the other hand, this positive assimetry is much more pronounced (mean value > median >> mode) for the optimized geometry. This result suggests that anomalous results may lead to the pronounced positive assimetry and to an increase of the barrier.

In an attempt to identify the origin of the anomalous results, it has been verified that the fluorine atom(s), when directly bound to the atom(s) of the axial bond, is the responsible for this problem. In a previous work [16], it was shown that the contribution to the energy which gives rise to the BIR was over-stressed for the non-bonded atoms

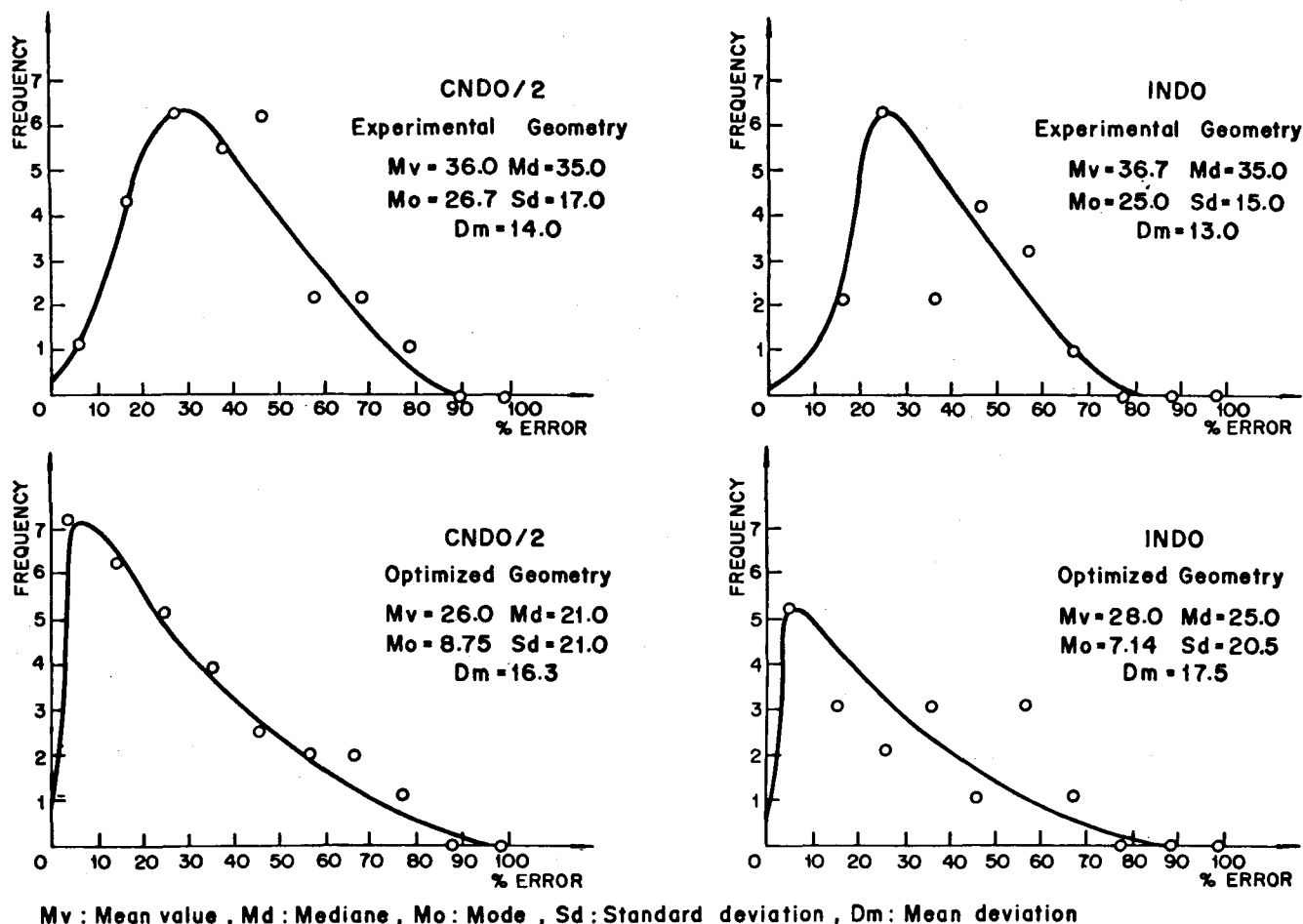
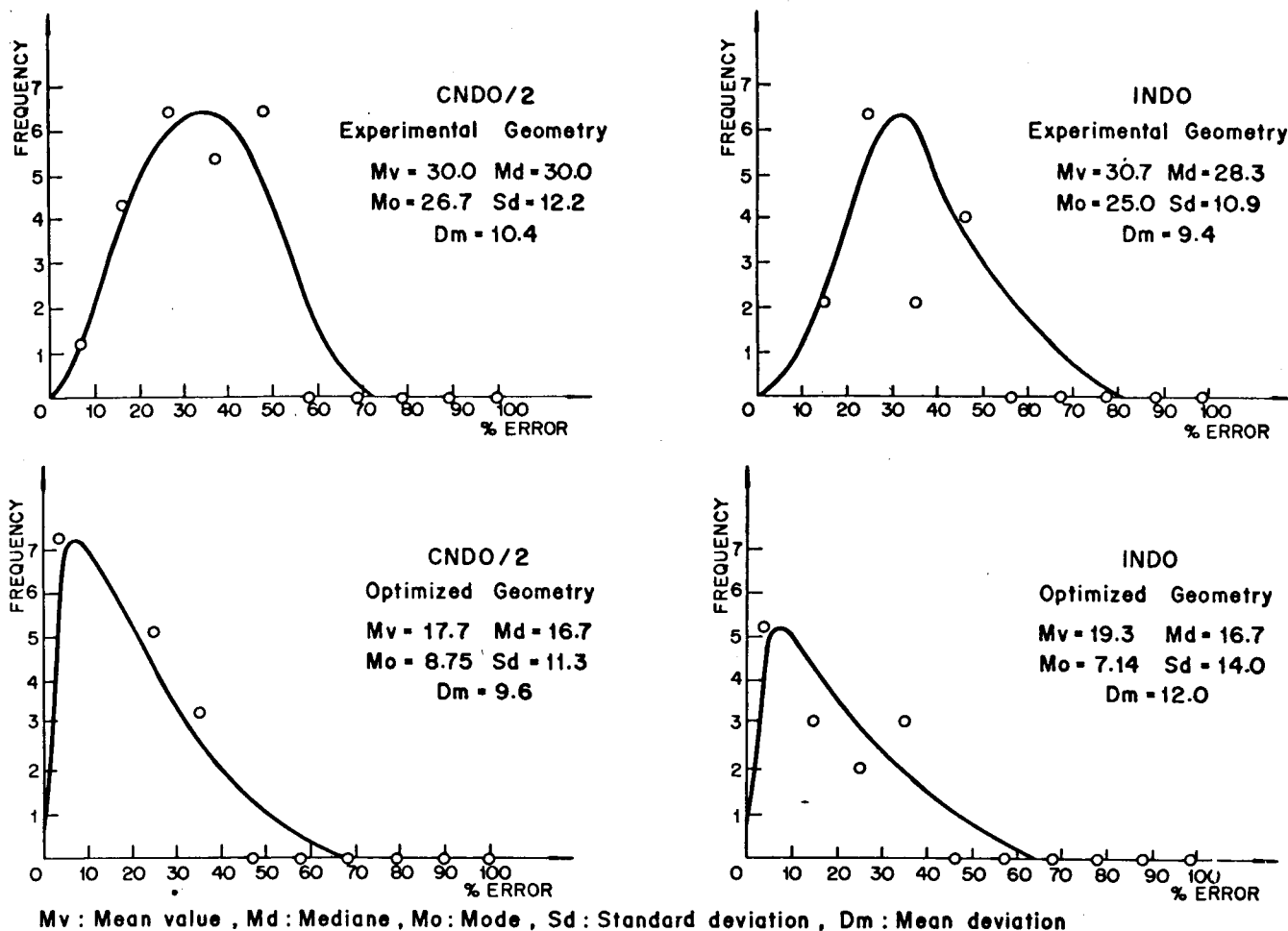


Fig. 1 - Distribution of frequency of the percentages of error for molecules containing atoms of the first row of the periodic table.



Mv : Mean value , Md : Mediane , Mo : Mode , Sd : Standard deviation , Dm : Mean deviation

Fig. 2 - Distribution of frequency of the percentage of error for molecules containing atoms of the first row of the periodic table, neglecting the results with errors higher than 50%.

(atoms attached to the axial bond) F, Cl, N and O. A possible explanation for this result is that the contribution to the energy depends on the relative instantaneous positions of the electrons. Even in the Hartree-Fock method [17] this effect is not taken into account properly. There are two ways to overcome this problem: re-parametrizing the monocentric [18] and bicentric integrals [19] or modifying the empirical parameter β_F^0 , β_{Cl}^0 , β_N^0 , and β_O^0 . In the former case, there is a theoretical justification. The same does not hold for the second case.

However, by neglecting the results with errors > 50%, we have obtained Figure 2, which shows a pronounced reduction of the asymmetry and of the dispersion value. The mean error has diminished considerably, showing that the increased value is due to the presence of the atoms of fluorine and oxygen directly bonded to the atoms of the axial bond. The high positive asymmetry in the distribution of frequencies of Figure 1 and the reduction of this asymmetry in Figure 2 corroborates this fact. It is important to emphasize that, by optimizing the axial bond, the most usual value of the percentage of error (mode) (8%) is within the order of magnitude of experimental error of the most accurate methods.

Table 2 shows that the methods CNDO/2 and INDO with the original parametrization are not sensitive to variations of bond distances of adjacent atoms. It is seen that,

either by optimizing simultaneously the rotors or by optimizing only the axial bond, the bond distance of axial bonds is the same if the remaining structural parameters are not altered.

It is important to emphasize that the atoms which give rise to anomalous results, as the fluorine atom, only show this trend if directly bonded to the atoms of the axial bond. The molecules *gauche*-1-fluoropropane and *anti*-1-fluoropropane are good examples of this fact.

It is also seen that nearly the same BIR are obtained by optimizing the rotors simultaneously or by optimizing only the axial bond (Table 2). This fact is a support to the hypothesis of Bach-Chevaldonnet *et al.* [20], who have postulated that the BIR are related almost exclusively to the atoms of the bond around which the rotation is done.

The results show that the methods CNDO/2 and INDO with the original parametrization are adequate tools to determine BIR for the atoms of the first row of the periodic table. The calculations for C-C bonds reproduce experimental results with a very small percentage of error. The same does not hold for C-N, C-O and O-O bonds. However, the results for these bonds are within the order of magnitude of the experimental errors of the least precise methods, thus performing a good evaluation of the magnitude of the BIR. Fluorine, chlorine and oxygen, when directly bonded to the atoms of the axial bond, give rise

to repulsion and attraction effects that disturb the calculated BIR.

In the other hand, the method CNDO/2 with the original parametrization does not reproduce quantitatively or qualitatively the experimental results of BIR for axial bonds composed of atoms of the second row of the periodic table (Table 3). The optimization of the axial bond leads to a percentage of error larger than the results obtained for the experimental geometry, thus characterizing a failure in the original parametrization for obtaining BIR. However, there are other parametrizations of the method which may allow for good results of BIR for atoms of the second row.

In summary, the results obtained through the optimization of the axial bond justify the use of such procedure, even when the experimental geometry is employed. The anomalies presented by fluorine, chlorine and oxygen suggest that both CNDO/2 and INDO methods should be reparametrized for these atoms.

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