Relaxation during Internal Rotation
Ethane and Hydrogen Peroxyde*

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An *ab initio* SCF-LCAO-MO study of the relaxation process during internal rotation has been performed for ethane and hydrogen peroxyde. A large gaussian basis set has been used, with polarization functions. The total energy has been optimized with respect to the bond lengths and bond angles. The computed barrier for the ethane molecule is 3.07 kcal/mole with the optimized geometry (experimental 2.93 kcal/mole). For hydrogen peroxyde, this yields a cis-barrier of 10.9 kcal/mole (experimental 7.0 kcal/mole) and a trans barrier of 0.6 kcal/mole (experimental 1.1 kcal/mole), with a dihedral angle equal to 123° (experimental 111°—120°). The eclipsed or cis conformations are found to have more "open" structures than the staggered or equilibrium conformations.

Une étude des phénomènes de relaxation liés à la rotation interne a été effectuée pour l'ethane et l'eau oxygénée par la méthode *ab initio* SCF-LCAO-MO. Avec une base étendue de fonctions gaussiennes comprenant des fonctions de polarisation, on minimise l'énergie par rapport aux longueurs et aux angles des liaisons. La barrière calculée pour l'ethane est de 3,07 kcal/mole (valeur expérimentale 2,93 kcal/mole). Pour l'eau oxygénée, on trouve pour les barrières cis 10,9 kcal/mole, trans 0,6 kcal/mole et pour l'angle dièdre 123° (values expérimentales 7,0 et 1,1 kcal/mole et 111°—120°). Les conformations éclipsée ou cis possèdent des structures plus « ouvertes » que les conformations en étoile ou trans.

Der Relaxationsprozeß während der inneren Rotation wurde für Äthan und Wasserstoffperoxid mit Hilfe einer *ab initio* SCF-LCAO-MO-Rechnung untersucht. Dabei wurde eine große Basis von Gaußfunktionen mit Polarisationsfunktionen benutzt. Die Gesamtenergie wurde unter Variation der Bindungslänge und Bindungswinkel optimiert. Die berechnete Rotationsbarriere mit der optimalen Geometrie beträgt 3,07 kcal/Mol für Äthan (experimentell 2,93 kcal/Mol). Für Wasserstoffperoxid ergibt sich eine cis-Barriere von 10,9 kcal/Mol (experimentell 7,0 kcal/Mol) und eine trans-Barriere von 0,6 kcal/Mol (experimentell 1,1 kcal/Mol) sowie ein Verdrillungswinkel von 123° (experimentell 111°—120°). Die verdeckten oder *cis*-Konformationen besitzen mehr „offene" Strukturen als die gestaffelten oder die Gleichgewichtskonformationen.

1. Introduction

Barriers to internal rotation have been the subject of many "ab-initio" treatments in recent years. In most cases the computations were done within the Hartree-Fock approximation, under the tacit assumption that the correlation energy does not change when the rotation takes place. To date, all the calculations also assumed a fixed geometry for the various conformations, except for the change in the rotation angle.

Within this framework, the *ab-initio* calculation of barriers to rotation has been very successfull in some cases, less successfull in a few other cases. Two among

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* Quantum Mechanical Calculations on Barriers to Internal Rotation. Part VI. Preceding paper, Ref. [35].

Table 1. *Summary of the previous calculations of the barrier to internal rotation in ethane*

Basis set	Energy[a] in a.u.	Barrier in kcal/mole	Reference
STO (2,1/1)	− 79.09797	3.3 − 3.5	[1, 2]
GTF (10,6/5)	− 79.10824	3.6	[3]
GLF (10,5/4)	− 79.14778	2.51	[4]
GTF (5,2/2)	− 78.50898	2.88	[5]
GTF (5,2/2,1)	− 78.57040	3.45	[5]
GTF (7,3/3)	− 79.09725	3.04	[6]
GTF (7,3/3)[b]	− 79.09305	2.40	[6]
STO (2,1/1)[c]	− 79.0999	3.3	[7]

[a] For the staggered conformation.
[b] Bond orbital calculation.
[c] Exponents and geometry optimized.

Table 2. *Summary of the previous calculations of the barrier to internal rotation in hydrogen peroxyde*

Basis set	Energy[a] in a.u.	Barrier (kcal/mole)		Reference
		cis	trans	
STO (2,1/1)	− 150.1565	11.8	2.2	[11]
GLF (11,6/4)	− 150.7374	13.6	0.0	[4]
GLF (10,5/4,1)	− 150.7228	13.2	0.1	[4]
STO (2,1/1)	− 150.2232	13.0	0.0	[12]
GTF (5,2/2)	− 149.2640	15.9	0.0	[5]
GTF (5,2/2,1)	− 149.2884	—	0.1	[5]
STO (2,1/1)[b]	− 150.2353	9.4	0.0	[7]

[a] For the conformation of lower energy.
[b] Exponents and geometry optimized.

the most investigated molecules have been the ethane molecule C_2H_6 and the hydrogen peroxyde molecule H_2O_2. A summary of the previous calculations of the rotation barriers in these two molecules is given in Tables 1 and 2. For ethane the computed barriers are in the range 2.5 − 3.6 kcal/mole, in moderately good agreement with the experimental result of 2.93 kcal/mole. Within the Hartree-Fock scheme, all calculations predict the staggered conformation to be the more stable, in agreement with the experimental and intuitive evidence[1]. On the opposite, results have not been so satisfactory for the hydrogen peroxyde molecule, although it is the simplest molecule to exhibit a rotation barrier. The first calculation by Kaldor and Shavitt [11] found an equilibrium dihedral angle of 120° in good agreement with the experimental values of 111° [13] and 120° [38]. However, nearly all subsequent calculations [4, 5. 12] failed to reproduce this result and they predicted the molecule to be trans-planar in the equilibrium conformation, with only a cis-barrier. This is indeed the case for the best reported calculation, energy speaking [4]. Another calculation by Fink and Allen, with a smaller basis set but

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[1] Calculations have also been performed for the rotation barrier of ethane with the group function method [8]. Two independant calculations found the eclipsed conformation to be more stable than the staggered conformation [9, 10].

including *p*-polarization functions on the hydrogen atoms, produced a slight minimum of the total energy for a dihedral angle close to 150° [4]. This is still far from the experimental value of 111° – 120° and, according to the authors, "the absolute value of the trans-barrier is so small as to be of questionable significance". Also the computed cis-barrier is about twice as high as the experimental value.

Lowe has shown that the discrepancy in quality of barrier prediction is probably not as great as it first appears [14]. The high symmetry of the methyl group may force a great deal of error cancellation whereas the errors will be still highly evident in the case of the hydrogen peroxide. Calculation of the barrier for this last molecule appears as a much more rigorous test that a calculation for the barrier of ethane.

So far, all of these *ab-initio* calculations of the rotational barriers have suffered from two limitations. First, none of these calculations has reached the Hartree-Fock limit or get close enough to it that the corresponding results (total energy and height of the barrier) can be viewed as the Hartree-Fock values. From the presently available results for ethane, it is not possible to infer what will be the Hartree-Fock value for the barrier height, except that it will be probably in the range 2.5 – 3.5 kcal/mole. The knowledge of the Hartree-Fock limit for some barrier heights would make possible to infer, from a comparison with the experimental values, how much the correlation energy contributes to the barrier. Up to now, there is no information on this point, except for the reasonable assumption that this contribution should be very small. Most of the reported calculations suffer from the lack of polarization functions (*d*-functions on the first-row atoms and mainly *p*-functions on the hydrogen atoms) together with a lack of flexibility in the basis set describing the valence shells: this is especially true of most of the calculations using Slater orbitals with only one Slater orbital to describe each valence shell (even when the orbital exponents are optimized). A similar situation is encountered with gaussian orbitals when a severe contraction has been used. These neglected polarization effects together with the lack of flexibility in the valence shell orbitals have been quoted as likely source of errors mainly in the description of non-bonding electron pairs [14].

The other limitation has been in the neglect of the structural changes accompanying the internal rotation. All the previously quoted calculations assume that, except for the torsional angle, the bond lengths and bond angles remain unchanged during the process of internal rotation. Simple estimates based on force constants indicate that, if small deformations of the bond lengths and bond angles actually occur, they bring in a variation of the energy which is of the order of magnitude of the computed barriers [14]. This means that one has to minimize the energy with respect to the bond angles and bond lengths for each torsional angle. Sovers and Karplus investigated the effect of structural changes on the magnitude of the barrier for ethane, however through simplified model calculations using a wide range of empirical non-bonded potentials [15]. They found an eclipsed structure more open than the staggered form, with an HCC angle increased by a few tenths of a degree and a carbon-carbon bond elongated by a few hundredths of an angstrom. However the quantitative results were found very sensitive to the form of the non bonded potentials.

We report here *ab-initio* LCAO-MO-SCF calculations for the barriers to rotation of the ethane and hydrogen peroxyde molecules. Our purpose was to achieve calculations close enough to the Hartree-Fock limit so as to be significant and to perform simultaneously a geometry optimization for each rotational angle. We believe that these requirements have to be satisfied simultaneously. As stated above, a refined calculation without geometry optimization does not appear satisfactory, while optimizing the geometry with a crude wavefunction could lead to dubious results.

After a preliminary report of this work had been published [16, 17] a paper by Monkhorst dealed also with the geometrical changes during the internal rotation in ethane [18, 19]. This author used a minimal basis set of Slater orbitals with only the valence electrons explicitly treated and most of the integrals approximated. Although some of his results regarding the geometrical changes are qualitatively in agreement with ours, his computed barrier, 6.16 kcal/mole, appears rather poor and the optimized geometry departs severely from the experimental one.

Another paper by Stevens [7] deals also with the geometry optimization in the computation of the barriers of ethane and hydrogen peroxyde, using a minimum basis set of Slater orbitals with optimized exponents. Due probably to the lack of polarization functions, this calculation as the previous ones is unable to reproduce the trans barrier of hydrogen peroxyde. This substantiates our previous statement as to the need of performing the geometry optimization with a refined wavefunction.

2. Computations and Results

The present calculations are of the SCF-LCAO-MO type using Gaussian functions. The Gaussian basis set is built from an $11s$, $7p$ atomic set for the C and O atoms [20] and a $6s$ set for the H atom [21]. Using this basis set, the total energy for the ground states of the first-row atoms is very close to the Hartree-Fock energy (for instance -37.6874 a.u. for the C atom versus -37.6886 a.u.). Moreover, this basis set has one additional Gaussian function to describe the tail of the valence orbitals: this function does not contribute much to the atomic ground state, but could be of importance to describe the molecular wavefunction. These atomic sets are incremented with one $2p$ polarization function on the H atom (namely $2p_x$, $2p_y$, $2p_z$) of exponent 1.0 and one $3d_{xz}$ and $3d_{yz}$ polarization function on the C and O atoms of exponent 1.5 (the z axis is chosen as the central bond axis). The atomic sets are then contracted to a $5s$, $3p$ sets for the C and O atoms and a $3s$ set for the H atom. We used the contractions labelled No. 10 (s orbitals), No. 1 (p orbitals) and No. 5 (s orbitals of H atoms) in a previous paper devoted to a comparison of different contractions [22]. This leaves uncontracted the Gaussian functions used for describing the tail of the orbitals. It reduces the basis of 122 Gaussians for ethane and 86 Gaussians for hydrogene peroxyde to, respectively, 68 and 44 contracted Gaussians.

The computations were carried out using the program IBMOL [23, 24]. Since the geometry optimization requires to compute the energy for many con-

formations with relatively minor changes in the geometry, we took advantage of the feature of the program which allows to recompute only the changed integrals. Also, since the final SCF vectors for one geometry are usually a very good starting point for other geometries which do not differ appreciably, we used in some case a version of IBMOL modified to avoid the explicit integral transformation [25].

The procedure of geometry optimization was repeated for the staggered and eclipsed conformations of the ethane molecule and for four conformations (dihedral angle equal to 0°, 60°, 120° and 180°) of the hydrogen peroxyde molecule. A first calculation was performed with the experimental geometry. For the ethane molecule, the experimental values of the C–C and C–H bond lengths and of the HCH angle are 1.543 Å, 1.102 Å and 109.3° [26]. For the hydrogen peroxyde, the values obtained from the infrared spectrum for the O–O and O–H bond lengths and the OOH bond angle are 1.475 Å, 0.950 Å and 94.8° [27]. Next a set of calculations minimizes the total energy with respect to the C–C or O–O bond length, keeping the experimental values for the other parameters. Then another set of calculations minimizes the total energy with respect to the HCH or the OOH bond angle, with the experimental C–H or O–H bond length and the previously optimized value for the central bond length. No attempt was made to

Table 3. *Total energy in a.u. for the eclipsed and staggered conformations of ethane*

	Staggered	Eclipsed
r_{exp}, Θ_{exp}	− 79.23770	− 79.23188
$r_{exp} - 0.15$ a.u.	− 79.23369	− 79.22588
$r_{exp} + 0.15$ a.u.	− 79.23507	− 79.23076
r_{optim}	− 79.23769	− 79.23217
$\Theta_{exp} - 5°$	− 79.23599	− 79.23158
$\Theta_{exp} + 5°$	− 79.22284	− 79.21499
Θ_{optim}	− 79.23899 [a]	− 79.23410 [a]

[a] Interpolated values.

Table 4. *Total energy in a.u. for the four conformations* $\varphi = 0°$, 60°, 120°, 180° *of hydrogen peroxyde*

	0°	60°	120°	180°
r_{exp}, Θ_{exp}	− 150.77256 (− 150.73252) [a]	− 150.78550 (− 150.74685) [a]	− 150.79574 (− 150.76044) [a]	− 150.79566 (− 150.76290) [a]
$r_{exp} - 0.15$ a.u.	− 150.76534	− 150.78052	− 150.79173	− 150.79149
$r_{exp} + 0.15$ a.u.	− 150.77098	− 150.78207	− 150.79144	− 150.79146
r_{optim}	− 150.77287	(− 150.78550) [b]	(− 150.79574) [b]	(− 150.79566) [b]
$\Theta_{exp} - 4°$	—	—	− 150.79013	− 150.79030
$\Theta_{exp} + 4°$	—	− 150.78992	− 150.79871	− 150.79811
$\Theta_{exp} + 8°$	− 150.78129	− 150.79185	− 150.79902	− 150.79772
$\Theta_{exp} + 12°$	− 150.78178	—	—	—
Θ_{optim}	− 150.78190	− 150.79202	− 150.79922	− 150.79832

[a] Without polarization functions.
[b] r_{optim} equal to r_{exp}.

optimize the C–H or O–H bond length. The values of the total energy for the various geometries are reported in Table 3 for the ethane molecule and in Table 4 for the hydrogen peroxyde molecule.

Due to the high symmetry of the molecule, the rotation barrier for ethane is the difference of the total energy obtained for the staggered and eclipsed conformations. For the hydrogen peroxyde molecule, one has to find the more stable conformation. This is done by fitting the optimized values of the total energy by a function of the torsional angle φ

$$E(\varphi) = a + b \cos\varphi + c \cos 2\varphi + d \cos 3\varphi .$$

The following values are found for the four parameters (in a.u.):

$$a = -150.7938, \quad b = 0.0079, \quad c = 0.0037, \quad d = 0.0003 .$$

From this expression, the minimum of the total energy is predicted to occur for a dihedral angle $\varphi = 123°$ with an energy value of -150.7993 a.u. Since this minimum energy conformation is very close to the one with $\varphi = 120°$, we found unnecessary to perform a separate calculation for the value $\varphi = 123°$. The total energy as a function of the dihedral angle is displayed in Fig. 1.

The various components of the total energy (kinetic energy T, nuclear repulsion energy V_{nn}, nuclear-electron attraction energy V_{ne}, electron-electron repulsion energy V_{ee}, repulsive energy $T + V_{nn} + V_{ee}$) are given in Table 5 for the four conformations with an optimized geometry.

To assess the importance of geometry optimization, we also report some results obtained for the four conformations with the experimental geometry. In
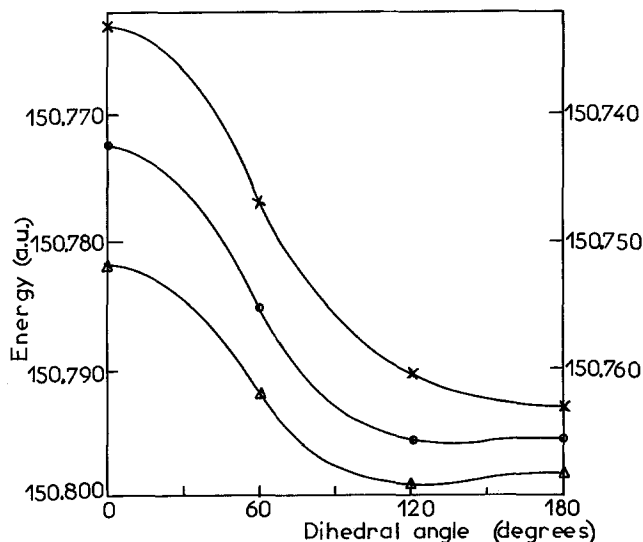

Fig. 1. Total energy as a function of the dihedral angle. × Experimental geometry without polarization function (right hand energy scale). ○ Experimental geometry with polarization function (left hand energy scale). Δ Optimized geometry with polarization function (left hand energy scale)

this case the following values are found for the four parameters

$$a = -150.7884, \quad b = 0.0111, \quad c = 0.0043, \quad d = 0.0004.$$

The minimum of the total energy is then predicted to occur for a dihedral angle $\varphi = 136°$ with an energy value of -150.7960 a.u. The total energy obtained as a function of the dihedral angle when the experimental geometry is used is also displayed in Fig. 1. The corresponding energy components are also given in Table 5.

To assess the effect of polarization functions, we took advantage of the program ability to perform separate SCF calculations with some orbitals deleted. In Table 4, we report also the energy values obtained for the four conformations with the experimental geometry when all the polarization functions have been deleted from the calculation. One then finds the following values for the four parameters

$$a = -150.7516, \quad b = 0.0146, \quad c = 0.0039, \quad d = 0.0005,$$

and the minimum of the total energy is predicted to occur for the dihedral angle $\varphi = 180°$. The corresponding results for the ethane molecule are given in Table 6.

The optimized geometries for the ethane and hydrogen peroxyde molecules are reported in Tables 7 and 8. We also report in Table 9 the results of a population analysis [36] for the four conformations of the hydrogen peroxyde molecule, with the experimental geometry and the optimized geometry.

Table 5. *Energy components for the four conformations of hydrogen peroxyde (experimental geometry and optimized geometry)*

	Optimized geometry				Experimental geometry			
	0°	60°	120°	180°	0°	60°	120°	180°
T	150.614	150.650	150.650	150.651	150.724	150.706	150.692	150.691
V_{nn}	36.023	36.492	36.535	36.553	36.848	36.805	36.753	36.736
V_{ee}	92.691	93.151	93.237	93.278	93.374	93.384	93.410	93.420
V_{ne}	−430.110	−431.085	−431.222	−431.281	−431.719	−431.681	−431.651	−431.643
$T + V_{nn} + V_{ee}$	279.328	280.293	280.422	280.482	280.946	280.895	280.855	280.847

Table 6. *Effect of the polarization functions on the total energy and the rotation barrier for the eclipsed and staggered conformations of ethane (experimental geometry)*

	Energy (in a.u.)		Rotation barrier
	staggered	eclipsed	(in kcal/mole)
No polarization functions	−79.20983	−79.20439	3.42
with d functions	−79.21509	−79.20966	3.41
with p functions on the H atoms	−79.23458	−79.22867	3.71
with d and p (H) functions	−79.23770	−79.23188	3.65

Table 7. *Optimized geometries of* C_2H_6

	Eclipsed	Staggered	Exp.
r_{C-C}(Å)	1.570	1.551	1.543
HCH	107.0°	107.3°	109.3°

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Table 8. *Optimized geometries of* H_2O_2 *as a function of the dihedral angle*

	0°	60°	120°	180°	Exp. (111°)
r_{O-O}(Å)	1.500	1.475	1.475	1.475	1.475
OOH	105.6°	103.9°	101.3°	100.2°	94.8°

Table 9. *Gross atomic populations and overlap populations for the four conformations of hydrogen peroxyde (experimental geometry and optimized geometry)*

	Optimized geometry				Experimental geometry			
	180°	120°	60°	0°	180°	120°	60°	0°
O	8.31	8.32	8.29	8.28	8.30	8.32	8.29	8.26
H	0.69	0.68	0.71	0.72	0.70	0.68	0.71	0.74
O–O	−0.062	−0.022	−0.080	−0.083	−0.068	−0.026	−0.070	−0.074
O–H	0.573	0.540	0.518	0.503	0.572	0.544	0.524	0.506
H–H	−0.003	−0.014	−0.027	−0.034	−0.007	−0.013	−0.028	−0.062

3. Discussion

3.1. The Rotation Barrier in Ethane

The lower energy computed for the staggered conformation of ethane is −79.2377 a.u. (the energy value interpolated for an optimized HCH angle is −79.2390 a.u.). This result is 0.055 a.u. lower than the best value reported previously −79.1825 a.u. [28]. Since the same calculation gave an energy value of −79.2098 a.u. when all the polarization functions are deleted (Table 6), one can see that half of the improvement comes from the use of a larger s, p basis set together with a more flexible contraction and that the other half comes from the introduction of polarization functions. We believe that our best total energy is within 0.02−0.03 a.u. of the Hartree-Fock limit. We expect the Hartree-Fock energy of the ethane molecule to be in the range −79.26/−79.27 a.u. on the following basis. Using a similar basis set, we computed a total energy for the ammonia molecule of −56.210 a.u., while a recent calculation gave a value of −56.222 a.u. which is claimed to be within 2 kcal/mole (0.003 a.u.) of the Hartree-Fock limit [29].

When the experimental geometry is used for the eclipsed and staggered conformations, one finds for the rotation barrier a value of 0.00582 a.u. = 3.65 kcal/mole (Table 6). The corresponding values when the polarization functions are deleted is 3.42 kcal/mole (Table 6). In fact most of the increase in the rotation barrier upon introduction of the polarization functions comes from the $2p$ functions on the hydrogen atoms. This is not surprising in view of the theory given by Wyatt and Parr of the origin of the barrier [37]. These authors concluded that the electronic component of the barrier arises from threefold components which are most important near the protons. The above value of the barrier, 3.65 kcal/mole, should be very close to the Hartree-Fock value when the experimental geometry is assumed for the two conformations.

However, geometry optimization affects markedly this result. When optimal C–C bond lengths are used for each conformation together with the experimental angle of 109.3°, the rotation barrier is decreased to 0.00552 a.u. = 3.47 kcal/mole. When optimal C–C bond lengths and optimal HCH bond angles are used (namely the interpolated values corresponding in Table 3 to the minimum of the total energy), the rotation barrier is now found to be 0.00489 a.u. = 3.07 kcal/mole. We believe that this value is very close to the Hartree-Fock value when the geometry is optimized for each conformation. This is in very close agreement with the experimental determination of 2.928 kcal/mole obtained from the infrared torsional spectrum [30]. It should be emphasized that this very satisfactory agreement (5% discrepancy) is obtained as the result of a two-steps process, namely the introduction of polarization functions followed by a geometry opti- mization. While the first step makes the agreement worst by increasing the barrier, the second one brings it close to the experimental result. We conclude that most previous calculations which neglected simultaneously the polarization functions and the geometry optimization benefited from some at least partial cancellation of errors. We also conclude a posteriori from the good agreement obtained that correlation energy should be relatively unimportant for the calculation of rotation barriers[2].

The optimized values for the CC bond length and the HCH bond angle in the staggered conformation are in very good agreement with the experimental results (1.551 Å versus 1.543 Å and 107.3° versus 109.3°, discrepancies 0.5% and 2%). This is expected in view of the ability of the Hartree-Fock method to give accurate bond lengths and bond angles [29, 31]. For the eclipsed conformation, the optimized values are 1.570 Å for the CC distance and 107.0° for the HCH angle. In agreement with the simplified model calculations of Sovers and Karplus [15], the eclipsed conformation has a more "open" structure with smaller HCH angles and a longer C–C bond than the staggered conformation. The corresponding variations are 0.019 Å for the C–C bond length and 0.34° for the HCH angle, the relative variations being 1% for the CC bond and 0.3% for the HCH angle. It should be emphasized that, despite a smaller relative variation, the optimization of the bond angle produces a greater change in the barrier than the optimization of the CC distance, the corresponding values being 0.40 kcal/mole and 0.19 kcal/mole. From the analysis given by Kivelson for the microwave spectrum of methylsilane [32], Monkhorst attempted to make an estimate of the central bond stretching during rotation [18]. From the change in the moment of inertia, he concluded that the central bond lengths will differ by at least 0.5% for the staggered and eclipsed conformations of methylsilane. Since one will expect a relatively larger stretching for ethane than for methyl-silane due to the shorter H–H distances, there is a qualitative agreement with our calculation.

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[2] From a configuration interaction calculation, Pipano et al. have recently concluded that as much as half the inversion barrier in ammonia may be due to correlation effects [40]. This is at variance with the findings of Rauk et al. [29], who found that the ammonia inversion barrier is quantitatively predicted within the Hartree-Fock approximation. However, Rauk et al. pointed to the fact that d functions on nitrogen are almost solely responsible for the barrier. Since the basis set used by Pipano et al. has no d functions, it is not surprising that the SCF calculation by these authors accounts for only half of the barrier.

Finally, it should be mentioned that, from the various empirical potentials used by Sovers and Karplus, the Hill potential seems to reproduce best our results. It predicts an HCC distortion of 0.34° and a C–C bond distortion of 0.0054 Å giving rise to relative changes in the barrier of 13% and 5%, while our calculation leads to relative changes of 11% and 5%.

3.2. The Rotation Barrier in Hydrogen Peroxyde

The lower energy computed for the hydrogen peroxyde molecule is -150.7992 a.u. and this value is 0.062 a.u. lower than the best result reported previously -150.737 a.u. [4]. As for ethane, one can see from the results of Table 4 that about half of the improvement comes from the additional flexibility in the s, p basis set and that the other half is linked to the use of polarization functions. On the same basis as the one used for the ethane molecule, we estimate the Hartree-Fock energy for the hydrogen peroxyde molecule to be in the range $-150.82/-150.83$ a.u.

When the experimental geometry is used, one finds a value of 0.0235 a.u. $= 14.7$ kcal/mole for the cis barrier and a value of 0.00038 a.u. $= 0.2$ kcal/mole for the trans barrier (Table 4). The corresponding values when the polarization functions are deleted is 0.0304 a.u. $= 19.1$ kcal/mole for the cis barrier and 0.0 for the trans barrier, the trans conformation becoming the more stable conformation. However, the geometry optimization has a pronounced effect on the barriers. When optimized geometries are used for each conformation, the cis barrier is decreased to 0.01737 a.u. $= 10.9$ kcal/mole, while the trans barrier is raised to 0.00095 a.u. $= 0.6$ kcal/mole. This is in much better agreement with the experimental determination of 7.0 and 1.1 kcal/mole obtained from the infrared torsional spectrum [13]. It should be noted that, in contrast to the ethane situation, the two steps of the improvement work in the same way for the hydrogen peroxyde molecule. Both the introduction of polarization functions and the process of geometry optimization decrease the cis barrier while increasing the trans barrier. One satisfactory result is that it is possible to account for the trans barrier of hydrogen peroxyde within the Hartree-Fock scheme.

The optimized values for the OO bond length and the OOH bond angle are in good agreement with the experimental determinations (1.475 Å versus 1.475 Å and 101.3° versus 94.8°). The most important result is the good agreement now obtained for the dihedral angle, 123° versus an experimental value of 111° [13] or 120° [38]. This is a definite improvement with respect to previous calculations which usually found the trans conformation to be the more stable, except for the work of Fink and Allen [4] which gave a dihedral angle close to 150°. For the cis conformation, the optimized values are 1.500 Å for the OO distance and 105.6° for the OOH angle. This conformation can be looked as the analogous of the eclipsed conformation of ethane and has also a more open structure. With respect to the most stable conformation, the variations are 0.025 Å for the O–O bond length and 4.3° for the OOH angle, the relative variations being 1.5% for the OO bond and 4% for the OOH angle. One will notice that the absolute and relative changes in the bond angle are much larger in the hydrogen peroxyde molecule than in the ethane molecule.

From the results in Table 9, one can see that the gross atomic populations and the overlap populations are very close for the experimental and optimized geometries. There is a marked increase in the value -0.022 of the O–O overlap population for the near equilibrium conformation $\varphi = 120°$ with respect to the values -0.062 and -0.083 for the trans and cis conformations. This is the result of some hyperconjugative interaction between the O–H σ bond and the electron pair on the other oxygen, which contributes a π-bond character to the O–O bond. This situation is similar to the one encountered for the hydrogen persulfide molecule [35], although the amount of π-bonding appears lesser for the hydrogen peroxyde. One will also notice that the H–H antibonding character increases from the trans to the cis conformations, while the O–H bonding character decreases at the same time. The cis barrier appears then as the result of three unfavourable situations, at the level of the O–O, O–H and H–H bondings. On the contrary, the trans barrier would result of a balance between a decreased O–O bonding, an increased O–H bonding and a decreased H–H antibonding.

An energy component analysis of rotational barriers has been proposed recently by Allen [33]. This author separates the total energy into two components:

$$E_T = (T + V_{nn} + V_{ee}) + (V_{ne}) = V_{\text{repulsive}} + V_{\text{attractive}}.$$

As a reason for this particular decomposition, Allen claims that it is the only component combination that retains an adequate stability under two perturbations which must be dealt with when constructing *ab initio* wave functions. These are the small displacements due to uncertainties in the experimental specification of the molecular geometry and the differences in the degree of completeness of the wave function basis sets. According to Allen, although ΔV_{att} and ΔV_{rep} are definitely changed by these two perturbations, it turns out in practice that there is an inherent similarity in the changes produced in ΔV_{att} and in ΔV_{rep} and that modifications in these do not alter qualitative conclusions. From this energy partition, Allen concluded that in hydrogen peroxide the cis barrier is attractive dominant and that most likely the trans barrier should be repulsive dominant. We have performed a similar analysis from the data reported in Table 5.

From our results obtained with the experimental geometry, the cis barrier appears to be repulsive dominant and this conclusion is at variance with the one by Allen. This points to the fact that the changes in ΔV_{att} and ΔV_{rep} brought about by the difference in the basis sets are such as to alter qualitative conclusions. A similar situation is encountered for the hydrogen persulfide molecule. Two studies of the barriers to internal rotation in this molecule have been reported recently [34, 35]. In the first paper, both barriers are found to be repulsive dominant [34]. From our work [35], we conclude that the cis barrier is repulsive dominant and the trans barrier attractive dominant. Since the same geometrical parameters were used in both calculations, this difference as to the energy partitioning should be traced to differences in the basis sets used.

If one turns now to the results obtained for the hydrogene peroxyde molecule with an optimized geometry, it is found that the cis barrier is attractive dominant while the trans barrier is repulsive dominant. This would seem to support the conclusions by Allen. However, it should be noticed that the process of geometry

optimization has changed our conclusions as to the nature of the cis barrier. We thus conclude that the energy decomposition proposed by Allen does not exhibit an adequate stability with respect to geometry optimization and to differences in the basis sets used [3].

4. Conclusion

The calculations reported here might be improved by using more polarization functions and by optimizing the energy with respect to the C–H and O–H bond lengths. Despite these limitations, the computed values for the rotations barriers are probably close to the Hartree-Fock values. We have found that improvement in the wavefunction and optimization of the geometry are equally important to achieve satisfactory results. For the ethane molecule, the computed rotation barrier is 3.42 kcal/mole when the experimental geometry is used for the two con-formations without polarization functions. The introduction of polarization func-tions raises the barrier to 3.65 kcal/mole. When the geometry is optimized for each conformation the computed barrier is decreased to 3.07 kcal/mole. For the hydrogen peroxyde molecule, use of the experimental geometry without polariza-tion functions yields a cis barrier of 19.1 kcal/mole with the trans conformation being the more stable conformation. When the polarization functions are intro-duced, the cis barrier is decreased to 14.7 kcal/mole and the computed trans barrier is 0.2 kcal/mole, the equilibrium angle being 136°. Geometry optimization brings the cis barrier to 10.9 kcal/mole, the trans barrier to 0.6 kcal/mole and the equilibrium angle to 123°. To summarize, the use of polarization functions together with geometry optimization brings the cis barrier to one half of the initial value, while the equilibrium angle is shifted from 180° to 123°.

The eclipsed conformation of ethane and the cis conformation of hydrogen peroxyde are found to have more "open" structures than the staggered or equi-librium conformations. The computed bond length variation during internal rotation is 0.019 Å for the C–C bond and 0.025 Å for the O–O bond. The bond angle change is 0.34° for the HCH angle and 4.3° for the OOH angle.

From the good agreement between the computed and experimental barriers, we conclude *a posteriori* that correlation energy should be relatively unimportant for the calculation of rotation barriers.

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