Theoret. chim. Acta (Berl.) 5, 413—421 (1966)

Quantum Mechanical Calculations on Barriers to Internal Rotation

I. Self-Consistent-Field Wave Functions and Theoretical Potential Energy Curves for the Hydrazine Molecule, in the Gaussian Approximation

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Received June 3, 1966

The barrier to internal rotation in hydrazine has been studied by the non empirical SCF-LCAO method, in the gaussian approximation. Calculations have been performed for values 0°, 60°, 120°, 180° and 94° (equilibrium conformation) of the dihedral angle, with all other bond angles and bond lengths fixed. The gaussian basis set used consisted of $9s + 3p$ for nitrogen and $3s$ for hydrogen. The calculated total molecular energy for the equilibrium conformation, −111.030 a.u., is 0.865 a.u. higher than the experimental value. The theoretical dihedral angle 94° is in good agreement with experimental indications of 90—95°. The computed rotation barriers are 11.5 kcal/mole for the cis position and 4.7 kcal/mole for the trans.

La barrière de rotation interne de l'hydrazine a été étudiée par la méthode LCAO-SCF dans l'approximation des orbitales gaussiennes. Les calculs ont été effectués pour des valeurs de l'angle dièdre de 0°, 60°, 120°, 180° et 94° (valeur correspondant à l'équilibre), tout en gardant constants les autres angles et les longueurs des liaisons. On obtient pour la position d'équilibre une énergie moléculaire totale de −111.030 u.a., l'écart avec l'énergie expérimentale étant de 0.865 u.a.. La valeur obtenue pour l'angle dièdre, 94°, est en bon accord avec les indications expérimentales de 90—95°. Les barrières de rotation théoriques sont de 11.5 kcal/mole pour la position cis et de 4.7 kcal/mole pour la position trans.

Die Rotationsbarriere von Hydrazin wurde mit Gaußfunktionen nach einer nicht-empirischen SCF-LCAO-Methode studiert. Rechnungen wurden für die Werte 0°, 60°, 120°, 180°, 94° (Gleichgewichtslage) des Diederwinkels durchgeführt, wobei alle übrigen Bindungswinkel und -längen festgehalten wurden. Der Basissatz von Gaußfunktionen bestand aus $9s$- und $3p$-Funktionen für Stickstoff und $3s$-Funktionen für Wasserstoff. Die berechnete Gesamtenergie der Gleichgewichtskonformation, −111,030 at. E. liegt um 0,865 at. E. höher als der experimentelle Wert. Der theoretische Diederwinkel von 94° stimmt gut mit den experimentellen Daten von 90—95° überein. Die berechneten Rotationsbarrieren sind 11,5 kcal/mol für die cis- und 4,7 kcal/mol für die trans-Lage.

1. Introduction

The LCAO-MO-SCF method [*28*] has been successfully used for studying the geometry of simple compounds. In diatomic molecules the bond length can be accurately known from near Hartree-Fock wavefunctions and energies [*11*]. Equilibrium angle and bond length for AH_n molecules have been accurately computed as well in the gaussian approximation [*18, 24*] as in the one-center approximation [*13, 20*]. A different problem relative to molecular shape is encountered with compounds of the type $H_mA - BH_n$: molecular energy varies when rotation about the $A - B$ bond takes place; one conformation is energetically favoured and free rotation is more or less hindered. Theoretical study of the barrier to internal rotation has been presently restricted to ethane: a calculation by Pitzer and Lipscomb of the energy difference for the eclipsed and staggered forms gave a theoretical estimate of 3.3 Kcal/mole for the barrier to internal rotation, versus an experimental value close to 3.0 Kcal/mole [*27*]. This agreement appeared satisfactory despite the fact that the basis set used was a minimal Slater one with no exponent optimization. More recently Clementi reinvestigated this problem using gaussian basis sets of different sizes [*6*]: the improvement of the total energy and wave functions with respect to Pitzer's results did not affect seriously the theoretical value for the barrier to internal rotation. Clearly ethane corresponds to the most simple situation with respect to a barrier to internal rotation: due to molecular symmetry energy extrema belong necessarily to the eclipsed and staggered forms, i.e. to dihedral angles 0° and 60°. The situation should appear quite different in compounds $AH_m - BH_n$ where A and/or B is no longer a carbon atom, but for instance a nitrogen or oxygen atom like in hydrazine (N_2H_4), hydrogen peroxyde H_2O_2, hydroxylamine NH_2OH, etc. First there is no longer any reason why the equilibrium conformation should correspond to a simple value of the dihedral angle: in fact the experimental value of the equilibrium angle is rather uncertain in N_2H_4 and spread over a large range from 90° to 120° for H_2O_2 (see Ref. [*2*]). Moreover the presence of lone pairs on atoms A and B might affect strongly the barrier of internal rotation. For instance it is often claimed that no free rotation can take place in hydrazine [*9*], but in fact the barrier height is unknown experimentally. For H_2O_2 the situation is rather conflicting: the values of the barrier of rotation differ by one order of magnitude [*2*], although the last experimental results [*10*] seem to indicate a cis barrier of 7.03 Kcal/mole considerably higher than in ethane, implying that free rotation should be seriously hindered in H_2O_2. The rotation barrier in hydrogen peroxyde has been theoretically studied by Kaldor and Shavitt [*14*].

At present there is not yet available a general computer program which can give good SCF functions for molecules $AH_m - BH_n$ when Slater-type orbitals are used as basis functions: such calculations with Slater-type orbitals have been carried only with a minimal basis [*27, 14*] and gave a total energy rather far from the Hartree-Fock limit. The one-center method was inherently restricted to AH_n compounds. Instead, the use of gaussian orbitals seems appropriate for compounds $AH_m - BH_n$: ground state calculations for ethylene C_2H_4 [*24, 25*] and diborane B_2H_6 [*3*] gave a total energy probably not too far from the Hartree-Focklimit, while the other molecular properties were in relatively fair agreement with experiment.

Using the gaussian approximation, a study of the barrier of internal rotation in hydrazine N_2H_4 seems of interest: as stated previously, the equilibrium conformation is rather uncertain experimentally, while the rotation barrier, and even its order of magnitude, are practically unknown. Moreover, no theoretical study of hydrazine has been undertaken previously.

2. Mode of Approach and Calculations

The Roothaan's SCF method [*28*] has been applied to the molecule, making use of the Polyatom system of programs written at MIT [*7*] and slightly modified for CDC 3600 computer.

A series of calculations has been performed for different molecular conformations: the various bond lengths and bond angles were kept constant except for the dihedral angle, defined as the angle of the two planes going through the N–N axis (z axis) and bisectors of the H–N–H angles (Fig. 1). Four conformations have been considered first: they are represented on Fig. 2 through the atomic projections on the plane $X\ 0\ Y$. The various bond lengths and bond angles were taken from the electron diffraction work by MORINO et al. [*22*] for N–N = 1.499 Å, N–H = 1.022 Å, angle N–N–H = 112° and from ABE et al. [*1*] for the angle H–N–H = 106°. Due to the fact that the bond angles at nitrogen are not tetrahedral, the dihedral angles for conformations 2 and 3 depart slightly from 60° and 120°, the exact values being 61° 4′ and 118° 56′.

The molecule is of symmetry C_{2v} for conformation 1, C_2 for conformations 2 and 3, C_{2h} for conformation 4. The symmetry orbitals are shown in Tab. 1 along with their irreducible representations. The electronic structure of the ground state ^1A_g was represented as arising from the filling of nine delocalized molecular orbitals, according to the following configurations:

Table 1. *The symmetry orbitals for the different conformations of hydrazine*

Symmetry orbitals	C_{2v}	C_2	C_{2h}
$s_1 + s_2$	a_1	a	a_g
$z_1 - z_2$	a_1	a	a_g
$h_1 + h_2 + h_3 + h_4$	a_1		a_g
$h_1 + h_3, h_2 + h_4$		a	
$s_1 - s_2$	b_2	b	b_u
$z_1 + z_2$	b_2	b	b_u
$h_1 + h_2 - h_3 - h_4$	b_2		b_u
$h_1 - h_3, h_2 - h_4$		b	
$x_1 - x_2$	b_1	b	b_u
$x_1 + x_2$	a_2	a	a_g
$y_1 + y_2$	a_1	a	a_u
$y_1 - y_2$	b_2	b	b_g
$h_1 - h_2 + h_3 - h_4$	b_1		a_u
$h_1 - h_2 - h_3 + h_4$	a_2		b_g

Conformation 1: $(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(2b_2)^2\,(1b_1)^2\,(3a_1)^2\,(1a_2)^2\,(4a_1)^2\,(3b_2)^2$.

Conformation 2, 3 and 5: $(1a)^2\,(1b)^2\,(2a)^2\,(2b)^2\,[(3b)^2\,(3a)^2/(3a)^2\,(3b)^2]\,(4a)^2\,[(5a)^2\,(4b)^2/(4b)^2\,(5a)^2]$.

Conformation 4: $(1a_g)^2\,(1b_u)^2\,(2a_g)^2\,(2b_u)^2\,(1a_u)^2\,(3a_g)^2\,(1b_g)^2\,(3b_u)^2\,(4a_g)^2$.

The choice of the gaussian basis set is the main difficulty in the gaussian approximation. From HUZINAGA's results for atoms of the first row [*12*], a gaussian basis of $9(s) + 5(p)$ give an energy close to the one obtained with a double zeta Slater basis set, the difference being 2.10^{-3} a.u. for nitrogen in the ground state ^4S (while the energy difference for the (9,5) gaussian basis and the Hartree-Fock limit is 6.10^{-3} a.u. for N^4S). On the other hand, $3s$-type gaussians on hydrogen

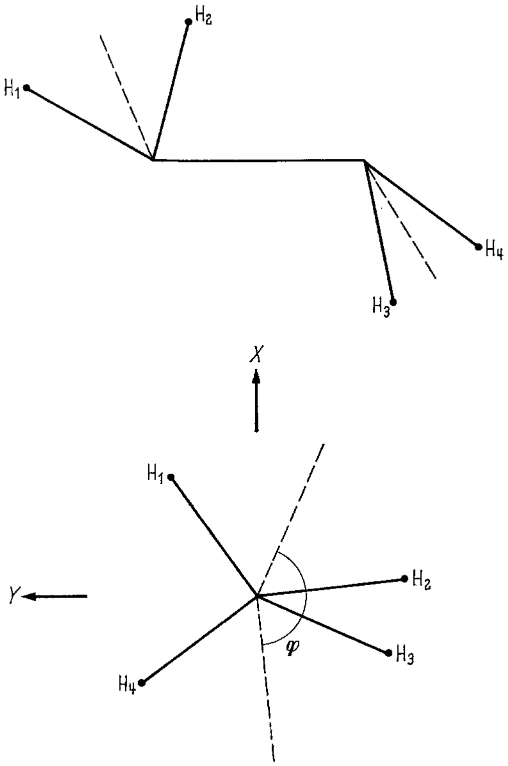
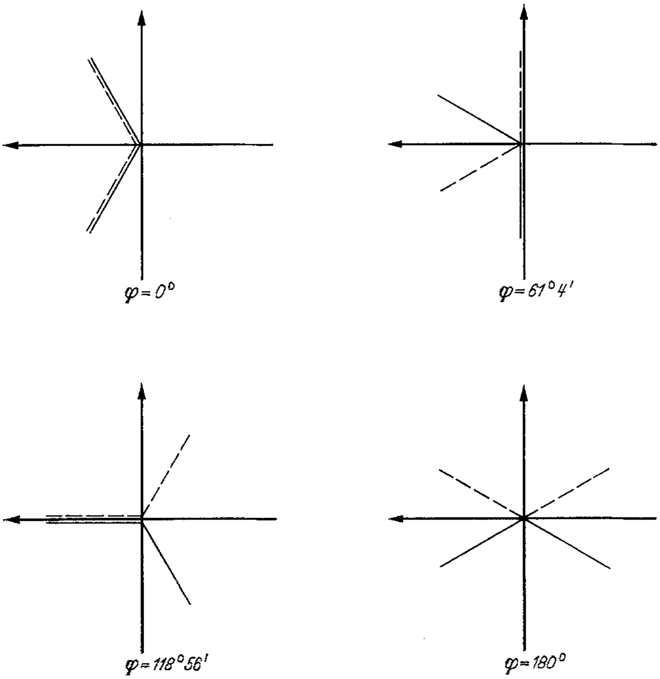


Fig. 1



$\varphi = 0°$ $\varphi = 61° 4'$

$\varphi = 118° 56'$ $\varphi = 180°$

Fig. 2

atom have been found to constitute an adequate set for molecular calculations [*23*]. But such a basis set (9,5,3) for hydrazine would consist of 60 functions: the necessity of performing several calculations in order to study the energy curve as a function of rotation angle ruled out this basis set for time factors. We used in fact a gaussian basis (9,3,3), which thus involved for N_2H_4 a total of 48 gaussians. Similar basis (9,3,3) have been previously used for ethylene [*25*] and for diborane [*3*]. Results for the molecule BH [*3*] indicated that the use of a basis set (9,3,3) instead of (9,5,3) does not affect seriously the value of the energy (-5.10^{-3} a.u. for a total energy of -25.114 a.u.).

Exponents of the gaussian function have been chosen in the following manner. Extensive optimization of the orbital exponents in the atomic case has been done by HUZINAGA for basis (9,5) [*12*]. For nitrogen basis (9,3) we retained the exponent values given by HUZINAGA for the 9 orbitals *s* and we carried out an exponent optimization for the 3 orbitals *p*. Final values of the exponents used in the calculation for nitrogen atom are given in Tab. 2, together with the hydrogen atom exponents (taken from HUZINAGA's work [*12*]) and the corresponding atomic energies.

Table 2. *Gaussian orbital exponents and corresponding atomic energies (in* a.u.*)*

Atom	Energy	Type	Exponents
N (^4S)	−54.3535	*s*	7.1927, 59.8376, 204.749, 887.451, 2.6860, 0.7000, 19.9981, 5909.44, 0.2133
		p	0.3112, 1.3643, 6.6642
H	−0.4970	*s*	0.1514, 0.6813, 4.5004

3. Numerical Results

The primary purpose of the present work was to calculate the potential energy curve as a function of the dihedral angle. Results for the four conformations described above are summarized in Tab. 3. The corresponding values of the total energy were fitted by a function of the dihedral angle φ:

Table 3. *Final* SCF *results for the five conformations*

Conformation	Dihedral angle	Total Energy (a.u.)	Orbital energy of the highest occupied orbital (a.u.)	Dipole moment (Debye)
1	0°	−111.011 67	−0.324	3.635
2	61° 4′	−111.025 85	−0.361	2.958
3	118° 56′	−111.028 37	−0.348	1.773
4	180°	−111.022 62	−0.313	0.
5	94°	−111.030 06	−0.378	2.333

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

with the following values for a, b, c, d:

$a = 111.023\,65 \qquad b = 0.00454 \qquad c = 0.00651 \qquad d = 0.00093$

(in atomic units).

With such an analytical expression for the total energy, the minimum of the potential energy curve was predicted to occur for a value of the dihedral angle

$\varphi = 94°$. Therefore another SCF calculation has been performed for this conformation 5: the results are equally reported in Tab. 3. Using this new point, a term $e \cos 4\varphi$ was added to the analytical development: the corresponding value of e was found very small, 0.00009, while parameters a, b, c, d remained practically unchanged. This indicated that the first expression was a satisfactory representation of the potential energy curve and that the minimum should be very close to the value 94° for the dihedral angle. The minimum energy derived from the analytical fitting is -111.03022 a.u. while the result of the SCF calculation for a dihedral angle of 94° is -111.03006 a.u.. The potential energy curve as a function of the dihedral angle is presented in Fig. 3.

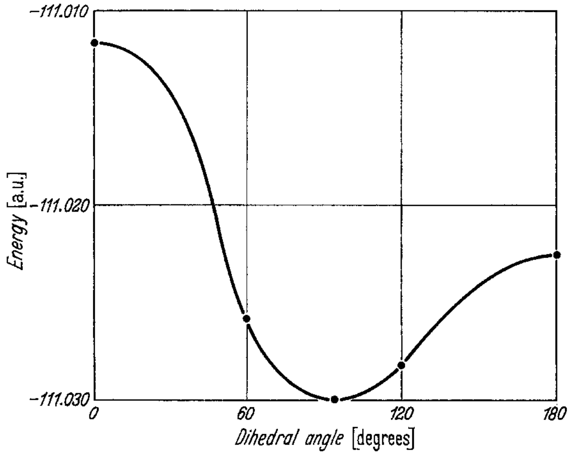


Fig. 3. Total energy as a function of the dihedral angle

It is also possible to fit the dipole moment values for conformations 1 to 4 by a function:

$$\mu = a \cos\frac{\varphi}{2} + b \cos\frac{3\varphi}{2} + c \cos\frac{5\varphi}{2}$$

with the following values for a, b and c:

$$a = 3.512 \qquad b = 0.046 \qquad c = 0.077$$

(in Debyes).

4. Discussion

Tab. 4 summarizes the computed molecular properties and the experimental ones when known. Theoretical values are given for the configuration with a 94° dihedral angle. The energy obtained -111.03006 a.u. is 0.865 a.u. higher than the experimental value -111.895 a.u.. The experimental energy of the hydrazine molecule has been obtained from the atomic ionization potentials [*21*] and the experimental binding energy of hydrazine molecule [*29*] corrected for the zero-point vibrational energy [*33*]. Our result appears satisfactory when compared with similar calculations [*3, 25*]: for diborane the difference ($E_{\text{calc}} - E_{\text{exp}}$) was 0.468 a.u. with an experimental energy -53.22 a.u., and for ethylene 0.667 a.u. with an experimental energy -78.617 a.u.. It seems even possible to give a rough discussion of correlation energy in hydrazine along the lines used by Moskowitz for ethylene and acetylene [*25*]. Details of the energy partitioning are given in Tab. 5.

This indicates an upper limit to the correlation energy of 0.715 a.u.. This result can be checked against the corresponding values of the isoelectronic atom and diatomic molecule: the correlation energy is 0.791 a.u. in argon [*5*] and can be estimated to 0.750 a.u. in fluorine molecule from values given by Wahl [*31*] (assuming a relativistic correction of 0.150 a.u. [*4*]).

Tab. 3 and Fig. 3 show the existence of two barriers to internal rotation. The cis barrier height is 0.01839 a.u. or 11.5 Kcal/mole, while the trans barrier has a smaller value of 0.00744 a.u. or 4.7 Kcal/mole. The value 94° obtained for the dihedral angle at equilibrium conformation is in good agreement with experimental indications of 90° [*17*] and 90°—95° [*32*]. Unfortunately, little reliance can be placed on the only available value 3.14 Kcal/mole of the barrier height, which was derived from microwave spectrum by assuming the equality of the two barriers cis and trans [*15*]. Nevertheless it is probable that our theoretical values are too high: using a minimal Slater basis, Kaldor and Shavitt obtained for hydrogen peroxyde theoretical barrier heights which are about twice the experimental ones [*14*]. Moreover, from results obtained for ethane with different gaussian basis sets and from those of Ref. [*27*], Clementi concluded that better is the total computed energy, higher are the theoretical barrier heights [*6*]. Therefore it does not seem that the results of Kaldor and Shavitt would improve through the use of a larger basis set. So we might expect a similar error for hydrazine. The obtention of relatively accurate rotation barriers from near Hartree-Fock wave functions is based on the assumption that correlation energy is approximately invariant for

Table 4. *Computed and experimental properties*

	Computed	Experimental
Molecular energy	−111.03006	−111.895[a]
Energy of separate atoms	−110.69484	−111.1975[b]
Binding energy	0.3352 a.u. = 210 Kcal/mole	406 Kcal/mole[c]
Equilibrium dihedral angle	94°	90° – 95°[d]
Cis barrier	11.5 Kcal/mole	—
Trans barrier	4.7 Kcal/mole	—
Dipole moment	2.33 D	(1.9 D)[e]
First ionization potential	10.29 eV	9.56 – 9.00 eV[f]

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[a] See text.
[b] Ref. [*21*].
[c] Ref. [*29*].
[d] Ref. [*17*, *32*].
[e] For benzene solution, Ref. [*19*].
[f] Ref. [*8*, *30*].

Table 5. *Correlation energy of hydrazine in* a.u.

Experimental + zero point	−111.895		
SCF (9,3,3)	−111.030		
Relativistic[a]	0.050		
Molecular correction		0.815	
(*sp*) Error due to basis truncation		0.100	
Estimated correction			0.715
Atomic correction[a]			0.376
Estimated molecular extra correction			0.339

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[a] Ref. [*4*].

the different conformations: some justification has been found in the fact that correlation energy appears roughly invariant in isoelectronic compounds and would depend only on the number of electron pairs [*27*]. Discrepancies for H_2O_2 might well cast some doubt on these assumptions. However, it should be pointed that a near Hartree-Fock calculation should include *d*-like polarization functions [*24*]: results obtained by MOSKOWITZ for H_2O [*24*] seem to indicate that inclusion of *d*-orbitals is not very important energetically but we cannot assess presently what effect it would have on the barrier heights.

Nevertheless, from our results and from those of Ref. [*27*] and [*14*], it is clear that the rotation barrier increases markedly when going from ethane to hydrazine and hydrogen peroxyde. This is not an unexpected result and it has often been claimed that rotation in compounds like hydrazine and hydrogen peroxyde are hindered by the repulsion between the lone pairs. In fact this point requires a further analysis: it is not clear if the increase is due mainly to the lone pairs or to a quantitative modification of the repulsion between A–H bonds. Gross atomic populations [*26*] are 7.56 for N atoms, 0.71 and 0.73 for H atoms (for equilibrium conformation): they indicate that the N–H bond is strongly polar in hydrazine.

No experimental value has been reported for the dipole moment of hydrazine in the gaseous state; our theoretical result 2.33 D is in relatively good agreement with value 1.9 D for benzene solution [*19*]. It is noticeable that the dipole moment varies in a nearly linear manner with the cosinus of the dihedral angle: by extension, this would be an *a*-posteriori justification of the one term development used in Ref. [*10*] for the analysis of the Stark effect in hydrogen peroxyde.

If one assumes KOOPMANS' approximation [*16*] to be valid, the first ionization potential of hydrazine is found 10.29 eV while the experimental reported values are 9.56 eV and 9.00 eV [*30, 8*]. The involved orbital has a strong nitrogen *p*-orbital character, thus corresponding to the usual idea of a lone pair.

As a conclusion, treatment of the hydrazine molecule through the gaussian approximation seems to give reasonable results. Total energy, ionization potential and dipole moment appear satisfactory. With respect to our primary purpose, the study of the barrier to internal rotation, one goal seems attained, namely the prediction of the equilibrium dihedral angle. The lack of experimental data for barrier heights prevents any comparison, but theoretical values appear probably to be overestimated although in a reasonable range.

Acknowledgements. We thank Dr. G. BERTHIER and Prof. A. RASSAT who called to our attention the problem of internal rotation in hydrazine. The Polyatom program was made avalaible to us through the Quantum Chemistry Program Exchange. We are indebted to Prof. L. BURNELLE for informations about the use of the program and to Prof. E. CLEMENTI for numerous talks about gaussian orbitals. Calculations were performed on the CDC 3600 computer of the Institut Blaise Pascal du C.N.R.S.

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