

## Rotational isomerism and barriers to internal rotation in 3-halopropenes by SCF-MO methods

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**Abstract.** Electronic structures of 3 halopropenes have been investigated through semi-empirical SCF-MO calculations using valence basis sets of atomic orbitals (AO) constructed from Slater type orbitals (STO). The electronic structures of stable conformers have been predicted and the corresponding calculated dipole moments show good agreement with experimental data. The considerable differences between the dipole moments of various conformers confirm the hindrance to internal rotation about the C–C bond, i.e., the existence of a definite potential barrier to rotation. The barrier heights hindering the internal rotation in each system are also estimated.

**Keywords.** CNDO/2 and INDO methods; 3-halopropenes; barrier heights; internal rotation; dipole moment.

### 1. Introduction

In the last few years, there has been a great deal of interest in understanding the structural features of 3-halopropenes and most of the attempts in this direction are based on experimental methods such as electron diffraction in the gas phase (Schei and Shon 1982) proton magnetic resonance spectral studies (Bothner-by *et al* 1965, 1966), microwave spectral studies (Hirota 1965, 1970), etc. Theoretical investigations on the conformations of these systems are very much limited mainly because of the large computation time involved in such calculations. The structural features of 3-fluoropropene (3FP) have been reported following the full *ab initio* SCF-MO calculations using minimal basis sets of atomic orbitals  $7s$ ,  $3p$  (for C, O and F) and  $3s$  (for H) Gaussian functions (Cadioli and Pincelli 1972). In the present theoretical study, SCF-MO calculations at INDO (intermediate neglect of differential overlap) and CNDO (complete neglect of differential overlap) levels of approximations have been performed for 3-chloropropene (3ClP), 3-bromopropene (3BrP) and 3-iodopropene (3IP), using both *spd* ( $s$ ,  $p$  and  $d$  valence functions) and *sp* ( $s$  and  $p$  valence functions only) basis sets. The reason for resorting to semi-empirical methods rather than full *ab initio* calculations, is to save computation time, which would normally be very high for *ab initio* type calculations, especially when heavy atoms such as bromine and iodine are involved. Calculations on 3FP have also been performed at the same levels of approximation and the results have been compared with both the experimental values and the predictions of full *ab initio* calculations to ascertain the accuracy of the semi-empirical methods adopted in the present investigations. Thus the aim of the present study is two-fold:

(a) to identify the stable conformers and to estimate the barrier heights to internal rotation about the C–C bond;

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(b) to establish the validity and the applicability of INDO and CNDO semi-empirical methods in these calculations.

## 2. Method of calculation

The calculations have been performed following Roothan's SCF scheme based on the Hartree-Fock equation for a many electron system. Valence basis sets, comprising just those orbitals of the valence shell of each atom in the molecule are adopted in the present calculations and to construct such AO basis set, Slater type orbitals (STO) are used. Of all the semi-empirical schemes available in the literature for running MO calculations, the SCF-MO method developed by Pople and Beveridge (1970) in the approximations of INDO and CNDO are considerably more accurate. Thanks to the possibility of calculating the electronic populations of all the valence atomic orbitals, one can calculate all the components of the total molecular dipole moment and achieve very good agreement between the calculated and the experimental values of dipole moments. The earlier computer program based on Pople and Beveridge's CNDO/2 and INDO methods allow all-valence electron calculations for molecules containing only simple atoms such as hydrogen and the elements of the first and second rows of the periodic table. Subsequently the formula for calculating molecular dipole moment by CNDO/2 method has been extended (Hase and Schweig 1973) to cover molecules containing elements of the third row of the periodic table. In the earlier work (Santhanam and Sobhanadri 1985) the authors have succeeded in extending the scheme to cover molecules containing elements of the fourth row as well and the same programme has been adopted for performing calculations on 3IP.

## 3. Computations, results and discussion

In calculations performed for 3FP, 3CIP, 3BrP and 3IP, experimental bond distances and bond angles of the *cis* form (figure 1) are used (refer table 1) (Sutton 1965). SCF total energies and the dipole moments have been calculated for selected values of the torsional angle  $\alpha$  and the results collected in tables 2-6. The values of the dipole moments for various conformers in each system differ substantially from each other, indicating that all the possible isomers produced by internal rotation are not

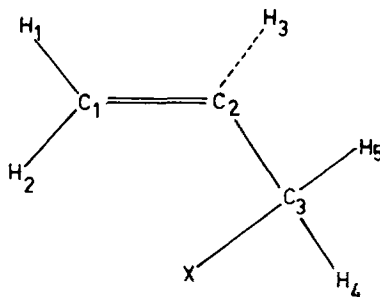


Figure 1. *s*-Cis-3-halopropene ( $\alpha = 0^\circ$ ); X = F, Cl, Br, I.

**Table 1.** Bond distances for the *cis* form in Å.

C(1)=C(2) = 1.34	C(3)-H(5) = 1.09
C(2)-C(3) = 1.52	C(3)-F = 1.36
C(1)-H(1) = 1.08	C(3)-C1 = 1.795
C(1)-H(2) = 1.08	C(3)-Br = 2.00
C(2)-H(3) = 1.08	C(3)-I = 2.18
C(3)-H(4) = 1.09	

**Table 2.** INDO and CNDO total energies ( $E/a.u.$ ) and dipole moments ( $\mu/D$ ) for 3FP for selected values of the torsional angle (*spd* basis set).

Method	Torsional angle, $\alpha$				
	0°	60°	120°	180°	
INDO	$E$	-50.67982	-50.67610	-50.67689	-50.67749
	$\mu$	1.84	1.83	1.91	1.79
CNDO	$E$	-52.74805	-52.74389	-52.74447	-52.74533
	$\mu$	1.82	1.76	1.79	1.64

**Table 3.** INDO and CNDO total energies ( $E/a.u.$ ) and dipole moments ( $\mu/D$ ) for 3CIP for selected values of the torsional angle (*spd* basis set).

Method	Torsional angle, $\alpha$				
	0°	60°	120°	180°	
INDO	$E$	-39.51736	-39.51222	-39.51363	-39.51124
	$\mu$	2.04	1.97	2.02	1.96
CNDO	$E$	-41.17606	-41.17065	-41.17175	-41.16942
	$\mu$	1.86	1.72	1.68	1.64

**Table 4.** INDO and CNDO total energies ( $E/a.u.$ ) and dipole moments ( $\mu/D$ ) for 3BrP for selected values of the torsional angle (*spd* basis set).

Method	Torsional angle, $\alpha$				
	0°	60°	120°	180°	
INDO	$E$	-36.79063	-36.77415	-36.77477	-36.77126
	$\mu$	2.31	2.02	2.00	2.02
CNDO	$E$	-38.35380	-38.33735	-38.33762	-38.33398
	$\mu$	2.08	1.75	1.61	1.66

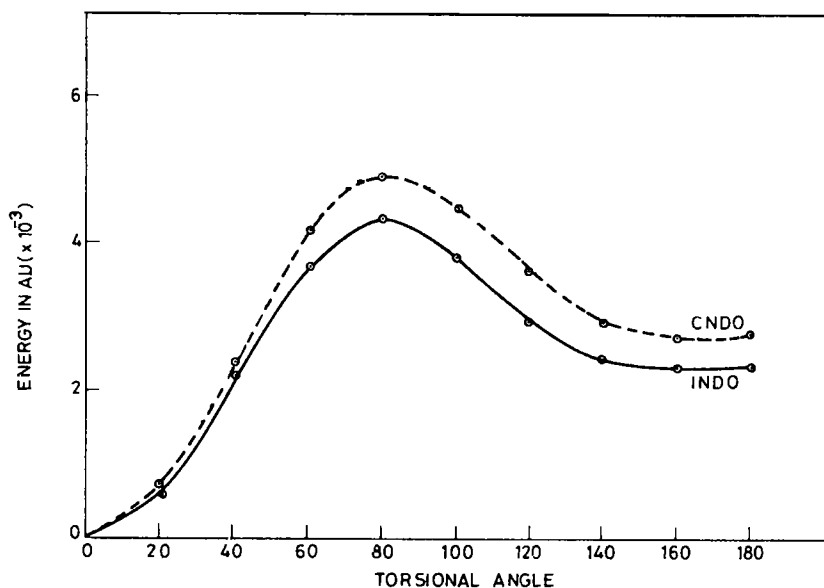
**Table 5.** INDO and CNDO total energies ( $E/a.u.$ ) and dipole moments ( $\mu/D$ ) for 3IP for selected values of the torsional angle ( $spd$  basis set).

Method	Torsional angle, $\alpha$				
	$0^\circ$	$60^\circ$	$120^\circ$	$180^\circ$	
INDO	$E$	-36.23769	-36.22922	-36.23098	-36.22683
	$\mu$	0.51	0.25	0.25	0.22
CNDO	$E$	-37.68140	-37.67283	-37.67421	-37.67003
	$\mu$	0.01	0.39	0.53	0.44

**Table 6.** INDO and CNDO total energies ( $E/a.u.$ ) and dipole moments ( $\mu/D$ ) for 3IP for selected values of the torsional angle ( $sp$  basis set).

Method	Torsional angle, $\alpha$				
	$0^\circ$	$60^\circ$	$120^\circ$	$180^\circ$	
INDO	$E$	-36.14842	-36.14888	-36.15217	-36.14765
	$\mu$	1.86	1.74	1.78	1.79
CNDO	$E$	-37.58692	-37.58733	-37.59035	-37.58579
	$\mu$	1.47	1.23	1.15	1.20

energetically equivalent and hence, the necessity for taking into account the potential energy of internal rotation in calculations of the mean dipole moment for each temperature. Results of the full *ab initio* calculations (Cadioli and Pincelli 1972) indicate the existence of two stable conformers for 3FP, one at  $\alpha = 0$  and the other at  $\alpha = 130^\circ$  with an energy difference of 1.17 kcal/mole between them. Experimental study predicts the same trend, but the second conformer corresponds to an  $\alpha$  value of  $127^\circ$  and the energy difference between the two stable conformers is as low as 0.31 kcal/mole. In the present study, the INDO potential curve for 3FP, as shown in figure 2, predicts the existence of two stable conformers one at  $\alpha = 0^\circ$  and the other at  $\alpha = 160^\circ$  with an energy separation of 1.45 kcal/mole between them. Two distinct barriers to internal rotation, a *cis-gauche* barrier at  $\alpha = 68^\circ$  with a height of 2.89 kcal/mole and a *gauche-trans-gauche* barrier at a height 0.82 kcal/mole above the  $130^\circ$  energy have been reported for 3FP by full *ab initio* calculation. The present INDO calculations on 3FP lead to a value of 2.7 kcal/mole for the first potential barrier and the second *gauche-trans-gauche* barrier is not well defined at this level of approximation (figure 2). Experimental observation (Meakin *et al* 1969) indicated the existence of a first potential barrier at 3.11 kcal/mole and the second at 1.46 kcal/mole. As regards the dipole moment, the calculated INDO values agree quite well with the experimental figures. For example, the INDO values of dipole moment of 3FP in the *cis* and  $120^\circ$  *gauche* forms are 1.84D and 1.91D which compare favourably with the stark effect values of 1.77D and 1.94D respectively. The corresponding values from the *ab initio* calculations are 1.91D and 2.12D respectively. It appears therefore that SCF-MO formalism working within the



**Figure 2.** Energy versus torsional angle curves for 3FP (zero reference corresponds to the *cis*-form).

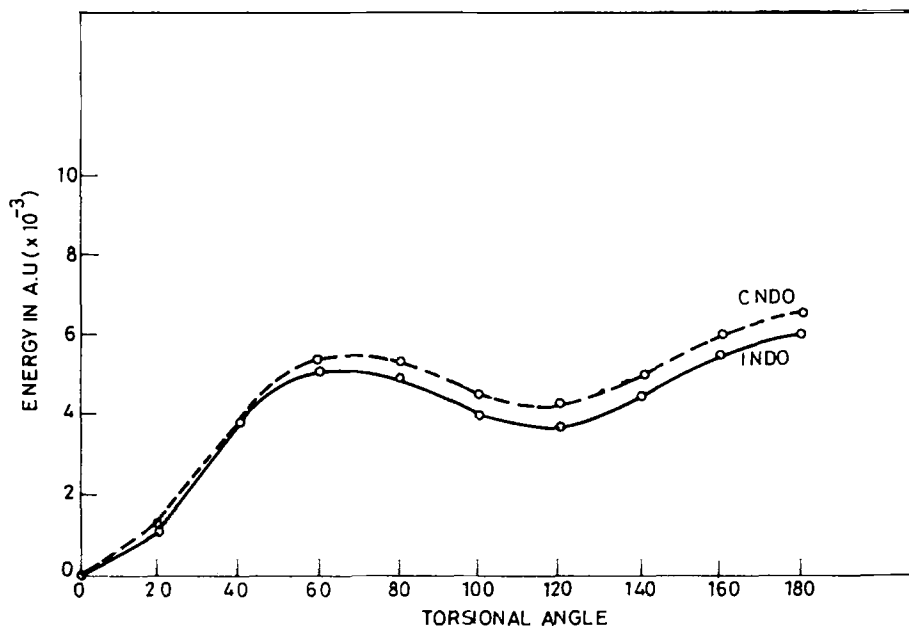
framework of INDO level approximation along with the chosen basis set can give reliable results in molecular calculations.

Similar analysis has been carried out from the results of the calculations performed for 3CIP, 3BrP and 3IP and stable isomers have been identified in terms of the total molecular energy.

In the case of 3CIP, stable conformers have been found at  $\alpha$  values  $0^\circ$  and  $120^\circ$  with an energy difference 2.35 kcal/mole by the INDO method and 2.37 kcal/mole by the CNDO method (figure 3). The *cis*-gauche and gauche-*trans*-gauche barriers to internal rotation have been found with peak heights 3.23 kcal/mole and 3.85 kcal/mole respectively by the INDO method. Calculated dipole moments for various conformers of 3CIP by the INDO method range from 1.96D to 2.04D (table 3) which compare reasonably well with the experimental range of 1.90D and 2.40D (Hannay and Smyth 1946; Trinh 1949). Dipole moments obtained from CNDO calculations have also been given for the sake of comparison.

For 3BrP also two stable conformers with  $\alpha$  values  $0^\circ$  and  $120^\circ$  have been identified but the energy difference between them is pretty high (9.9 kcal/mole). Here again two distinct barriers with peak values 10.7 kcal/mole and 12.2 kcal/mole have been observed (figure 4). The range of the dipole moments for various conformers is found to be 1.99D to 2.31D which falls a little away from the experimental value of 1.82D cited in the literature (Rogers and Panish 1955).

Calculations on 3IP revealed almost the same trend as in other halopropenes but the dipole moments for all the conformers are very poorly estimated. Two stable conformers, one at  $\alpha = 0^\circ$  and the other at  $\alpha = 100^\circ$  with an energy difference of 4.33 kcal/mole (CNDO) and 4.14 kcal/mole (INDO) have been observed (figure 5). Both INDO and CNDO methods show the *cis*-gauche barrier at  $\alpha = 60^\circ$  with a height of 5.34 kcal/mole. The gauche-*trans*-gauche barrier has been determined as 2.7 kcal/mole



**Figure 3.** Energy versus torsional angle curves for 3 CIP (zero reference corresponds to the *cis*-form).

and 2.82 kcal/mole above 100° energy by INDO and CNDO methods respectively. The calculated dipole moments for various conformers are as low as 0.5D, which is very small compared to the experimental value of 1.62D (Rogers and Panish 1955). The above results are obtained from calculations using *spd* valence basis set. On the other hand, when the calculations are repeated using only *s* and *p* valence orbitals (*sp* basis set) the dipole moments for various conformers improve very nicely but the profile of the energy versus torsional angle curve is completely reversed (figure 6).

This graph clearly indicates that in the case of 3IP, the *gauche* form is more stable than the *cis* form. Energy versus torsional angle curves shown in figures 2–5 have been drawn using energy values calculated using *spd* basis set. From all these curves, it is clear that for all halides, the *cis* form is energetically more favourable than the *gauche* form. But the high resolution proton NMR spectral studies (Bothner-by and Gunther 1962; Govil 1966) show that in 3CIP itself, there is some preference for the *gauche* form rather than the *cis* form and this tendency is much pronounced in the case of 3BrP and 3IP. This fact has been confirmed quite recently from electron diffraction study in the gas phase on 3BrP (Schei and Shen 1982) wherein it is reported that the population of the *gauche* form is as high as 95%. In the present study, the MO calculations carried out with the *sp* basis set on 3IP reveals this experimental trend unambiguously.

Inclusion of *d*-orbitals in the basis set should generally improve the accuracy of the calculation of molecular properties at the loss of simple pictorial description of the molecular orbitals (Galasso 1974) and several authors (Svendsen and Stroyer-Hansen 1978; Teixeira-Dias and Mursell 1970; Teixeira-Dias and Saree 1975; Facelli and Contreras 1980) have realized the need to introduce such polarization functions into

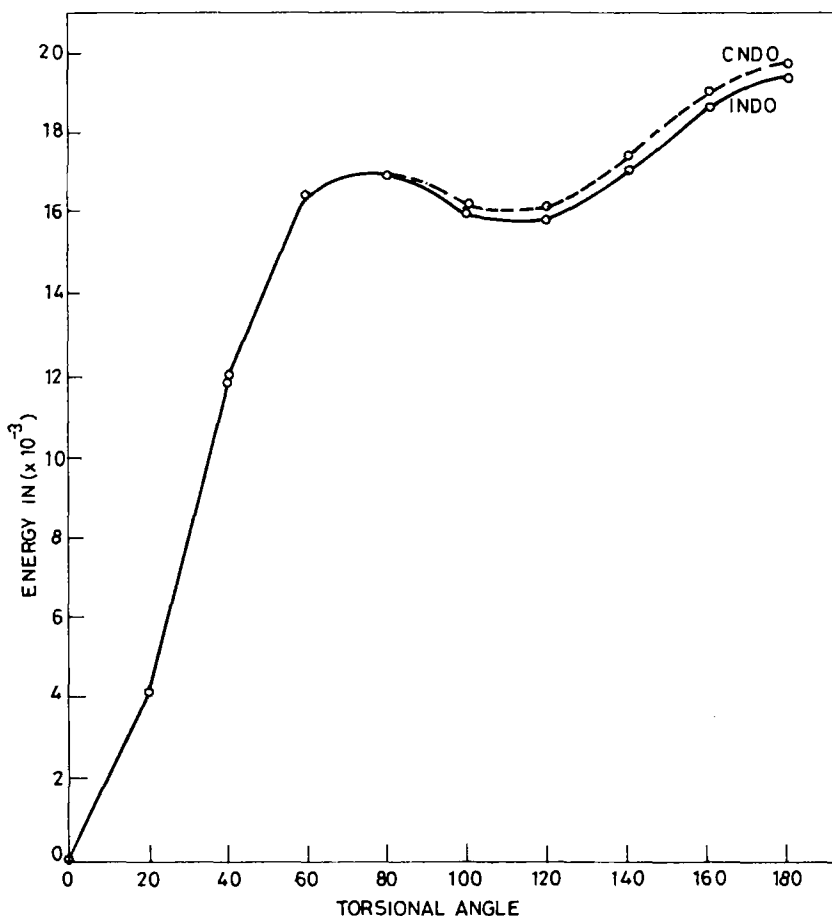


Figure 4. Energy versus torsional angle curves for 3 BrP (zero reference corresponds to the *cis*-form).

the basis set to improve the calculation. The reason for the very poor performance of the *d* orbitals in the present calculation could be that the energy gap between the *p* and *d* valence orbitals in the case of heavy elements is very large and hence if one could make a provision to include the intermediate orbitals (lying between *p* and *d* valence orbitals) also in the calculation, the results might improve satisfactorily (Santhanam and Sobhanadri 1985). This requires some provision for the mixing of orbitals with different principal quantum numbers. Also the lack of a better parameterization scheme, especially for heavy elements, could be another reason for such a poor show of the *d* orbitals in the present investigation.

On the other hand, the experimental findings of the most stable conformers for 3FP are replicated by the present calculations. Most of the main features of the potential energy curves drawn between the total energy and the torsional angle for all the halides have been satisfactorily reproduced even though the barrier heights in the case of 3 BrP and 3IP are slightly overestimated. In particular, the calculated values of dipole moments in all cases closely match with the experimental range, thus establishing the

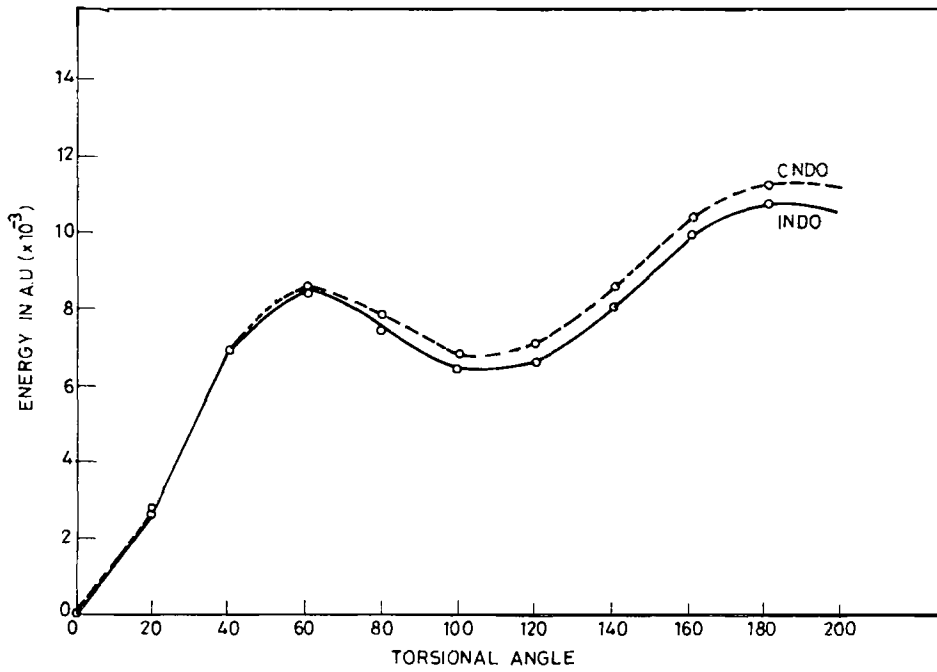


Figure 5. Energy versus torsional angle curves for 3IP (zero reference corresponds to the *cis*-form).

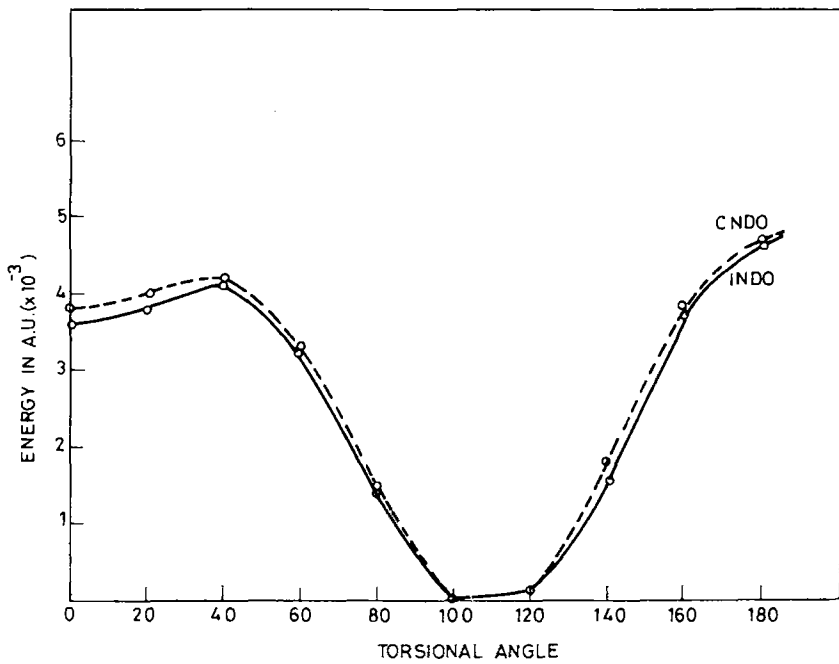


Figure 6. Energy versus torsional angle curves for 3IP (*sp* basis set).



validity of the approximations that are inherent in the INDO and CNDO semi-empirical SCF-MO schemes. It must also be realised at this point that the results presented here are obtained by a rigid rotation of the CH<sub>2</sub>X group, without allowing for any geometrical relaxation with respect to the bond parameters of the *cis* form. The importance of such geometric relaxation has been felt and stressed by many authors (Veillard 1970). Also it should be mentioned that even though the independent particle model (Veillard 1970; Fink and Allen 1967; Allen 1968) could satisfactorily account for the most hindered internal rotations about pure single bonds one should explicitly include the electron correlation effects for reducing the SCF energy separation between the two stable conformers of the molecules.

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