Journal of the Korean Nuclear Society
Volume 9, Number 1, March, 1977

M. O. Studies of Configuration and Conformation (Part II) Configuration and Conformation of Ketimine isomers

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(Received December 17, 1976)

Abstract

The configuration and conformation of N-methyl-C-phenylalkyl-ketimine isomers, Ph—CR=NCH_3 (R=H, CH_3, CH_3CH_2), have been studied from extended Hückel molecular orbital calculations.

The result shows that the E-configuration of the C=N double bond is favored compared with that of the Z-configuration. The most preferable conformation of the phenyl ring rotamer in N-methyl-C-phenylaldimine and N-methyl-C-phenylmethylketimine are the coplanar forms with regard to the C=N plane, but the conformation of the CH_3CH_2-rotamer, in N-methyl-C-phenylethyl-ketimine, the gauche form (dihedral angle between C=N and CH_3 CH_2- plane=90°) is favored.

要 約

N-methyl-C-phenylalkyl ketimine 異性質體, Ph—CR=NCH_3 (R=H, CH_3, CH_3CH_2)의 配置와 形態를 EHT 分子軌道函數法으로 연구하였다.

計算結果는 C=N 二重結合에 對하여 E-型의 配置가 Z-型의 配置보다 安定함을 나타내고 있다.

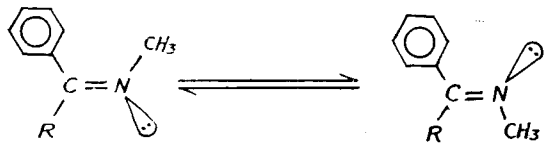
N-methyl-C-phenylaldimine과 N-methyl-C-phenylmethylketimine에서는 phenyl 고리 回轉子가 C=N 平面과 同一平面에 있는 形態가 안정하다.

N-methyl-C-phenylethylketimine에서는 phenyl 고리와 C=N결합이 同一平面에 있고 回轉子 CH_3CH_2-가 C=N 平面과 90°인 gauche形이 가장 안정하다.

1. Introduction

Information on the stereochemistry of the N-methyl-C-phenyl-alkylketimine, Ph—CR=NCH_3 (R=H, CH_3 CH_3CH_2), may be o fimportance both in connection with mechanistic studies and with configurational and conformational problems in related systems. The stereochemical problem of the N-methyl-

C-phenylalkylketimine is quite complex since in addition to the configuration of the C=N double bond (structure (A) or (B)), the conformation of the phenyl group and C-alkyl group rotamers[1,2,3].



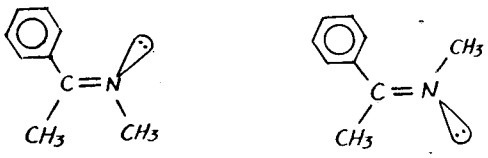
E-configuration (A) **Z-configuration** (B)

Comparatively little work has been done on the configuration and conformation of N-methyl-C-phenylalkylketimine[4,5]. Bjφrgo et al[5] have employed the infrared and nuclear magnetic resonance spectroscopy which gives information on the partial structure and population of individual forms, but no conclusive evidence has been presented as to the preferred conformation of this compounds.

The spatial arrangement of the phenyl ring and C-alkyl group rotamers are defined by the conformation of the dihedral angle between phenyl ring (or C-alkyl group) and $C=NCH_3$ molecular plane.

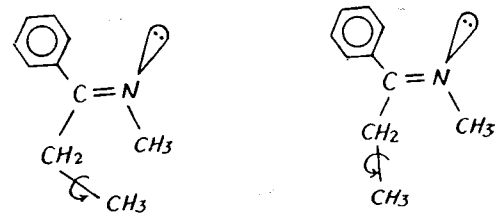
In the N-methyl-C-phenylaldimine, the conformers of the dihedral angle (β), between phenyl ring and $C=NCH_3$ molecular plane, are 0°, 45°, and 90° designated E-Ⅰ, E-Ⅱ, and E-Ⅲ in the E-form and Z-Ⅰ, Z-Ⅱ, Z-Ⅲ in the Z-form, respectively (Fig 2).

But for the N-methyl-C-phenylmethylketimine, only the conformers of the dihedral angle, 0°, between phenyl ring and $C=NCH_3$ molecular plane, designated E-Ⅰ and Z-Ⅰ were considered.

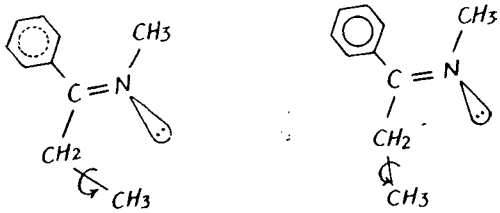


E-I **Z-I**

For N-methyl-C-phenylethylketimine, the conformers considered were of the dihedral angle(α), between ethyl group and $Ph-C=NCH_3$ molecular plane, 0° and 90° (gauc he form) designated E-Ⅰ, E-Ⅱ in the E-form. and Z-Ⅰ, Z-Ⅱ in the Z-form.



E-I (α=0°) **E-II** (α=90°)



Z-I (α-0°) **coplaner-form** **Z-II** (α-90°) **gauche-form**

In order to investigate the various posibilities reported by Bjφrgo et al[5] using molecular orbital method, we have undertaken the extended Hückel theory (EHT)[6] calculation on N-methyl-C-phenylalkylketimine, $Ph-CR=NCH_3$ (R=H, CH_3, CH_3CH_2). The EHT calculations have been successfully employed in determining configulation and conformation of organic compounds[7]. Martin et al[8], also pointed out that in conformational analysis, using various theoretical

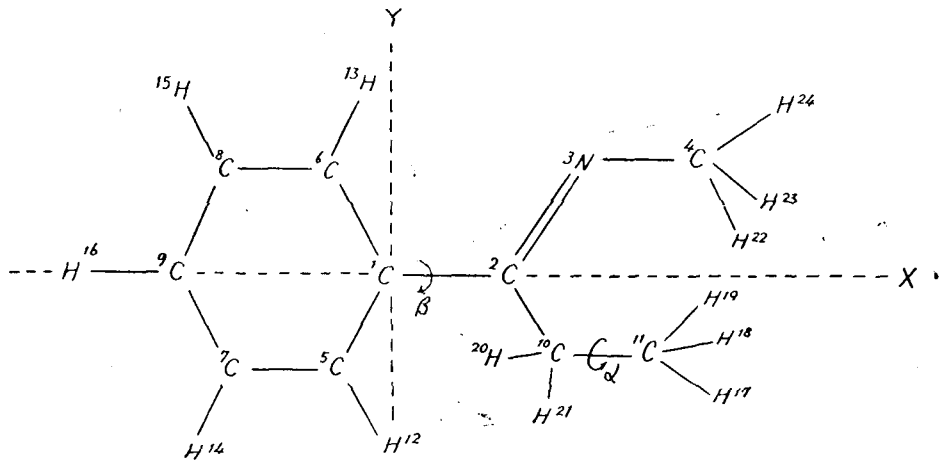


Fig. 1. Coordinate system and numbering scheme of N-methyl-C-phenylethyl ketimine

Table 1. Bond parameters used in atomic coordinate calculation.

bond length (A°)[a]	bond angle[b]
$d(C^{c)}_{ar}-C_{ar})=1.39$	$C_{ar}-\hat{C}_{ar}-C=120°$
$d(C_{ar}-C)=1.45$	$C-\hat{C}=N=125°$
$d(C_{ar}-H)=1.08$	$C=\hat{N}-C=114°$
$d(C_2-H_{16})=1.07$	$N-\hat{C}-H=109.5°$
$d(C_4-H)=1.09$	$C_{ar}-\hat{C}_{ar}-H=120°$
$d(N_3-C_4)=1.45$	$C_{ar}-\hat{C}-H=108°$
$d(C=N)=1.31$	$C_{ar}-\hat{C}-C=112°$
$d(C_2-C)\parallel 1.49$	$C-\hat{C}-C=109.5°$
$d(C-C)=1.54$	$C-\hat{C}-H=109.5°$

a) from reference (9). b) from reference (10).
c) C_{ar} show aromatic carbon atom.

Table 2. The Orbital Exponents, Z and -VSIP used.

AO	Z	−VSIP (eV)
H 1s	1.00	−13.60
C 2s	1.59	−21.01
2p		−11.27
N 2s	1.92	−26.90
2p		−14.42

(from R. Hoffmann, J. Chem. Phys., **39**, 1397 (1963).)

method (EHT, CNDO, INDO, PCILO and "ab initio" STO-3G), EHT provides the results most equivalent to the "ab initio" ones, and both methods also give the best fit with experimental conformations. This method is particularly suitable for our purpose since it does not require excessive computational expenses but still gives correct prediction of relative energies involved in the configurational and conformational analysis.

2. Calculation

1) Molecular geometry

The calculation of atomic cartesian coordinates of the molecular system for the input of the EHT program was carried out with an aid of a modified version of Quantum Chemistry Program Exchange (QCPE) at Indiana University No 226 program by means of IBM 1130 computer.

A typical coordinate system and numbering scheme is shown in Fig. 1. The bond length and bond angles used in these calculations are listed in Table 1.

2) EHT calculations

The computer program for EHT calculation was obtained from QCPE No 64. Input data

Table 3. Summary of the total energies for six conformation of N-methyl-C-phenylaldimine.

form	E (eV)	ε^{LU}(eV)	ε^{HO}(eV)	ΔE (kcal mole^{-1})	order of stability
E-I	−811.86	−9.64	−12.32	0.000 (Standard)	1
E-II	−811.84	−9.30	−12.24	0.363	2
E-III	−811.80	−8.73	−12.15	1.312	3
Z-I	−807.28	−9.53	−10.83	105.6	6
Z-II	−810.28	−9.24	−11.79	36.35	5
Z-III	−811.63	−8.68	−12.00	5.122	4

Table 4. Summary of the total energies for two configuration of N-methyl-C-phenylmethylketimine.

form	E (eV)	ε^{LU}(eV)	ε^{HO}(eV)	ΔE (kcal·mole^{-1})	order ofst ability
E-I	−914.21	−9.31	−12.08	0.000 (standard)	1
Z-I	−910.22	−9.24	−10.84	92.00	2

Table 5. Summary of the total energies for four conformation of N-methyl-C-phenylethylketimine.

form	E (eV)	ε^{LU}(eV)	ε^{HO}(eV)	ΔE (kcal·mole^{-1})	order of stability
E-I	−1008.76	−9.32	−9.74	191.5	4
E-II	−1017.06	−9.30	−11.93	0.000(standard)	1
Z-I	−1013.32	−9.24	−10.83	86.37	2
Z-II	−1013.00	−9.27	−10.83	93.58	3

in this program are the orbital exponents Z, valence state ionization potential (-VSIP) of AO's and cartesian coordinates of atom in the molecule.

Z and -VSIP used in this work are summarized in Table 2.

3. Results and Discussion

The results of the calculated total energies for various configuration and conformation of N-methyl-C-phenylalkyl ketimine isomers, Ph−CR=NCH_3 (R=H, CH_3, CH_2CH_3), are summarized in Table 3, Table 4 and Table 5.

1) N-methyl-C-phenylaldimine.

According to the energies calculated (Table 3), E-configuration of the C=N bond are more stable than those of Z-configuration in N-methyl-C-phenylaldimine. The mostst able form is E-I and the most unstable form is Z-I with the energy difference of about 105.6 kcal·mole^{-1}.

The molecular orbital energies of the lowest unoccupied (ε^{LU}) and highest occupied (ε^{HO}) MOs also are compatible with trend in the configuration of C=N bond.

It has previously been assumed that the bulkier group on the imine carbon atom prefers to be trans to the nitrogen substituent[11]. Bjφrgo et al[5] also suggested that the ratio of E-Z-imine isomers is dominantly influenced by the classical steric interactions between the N-alkyl group and proximate

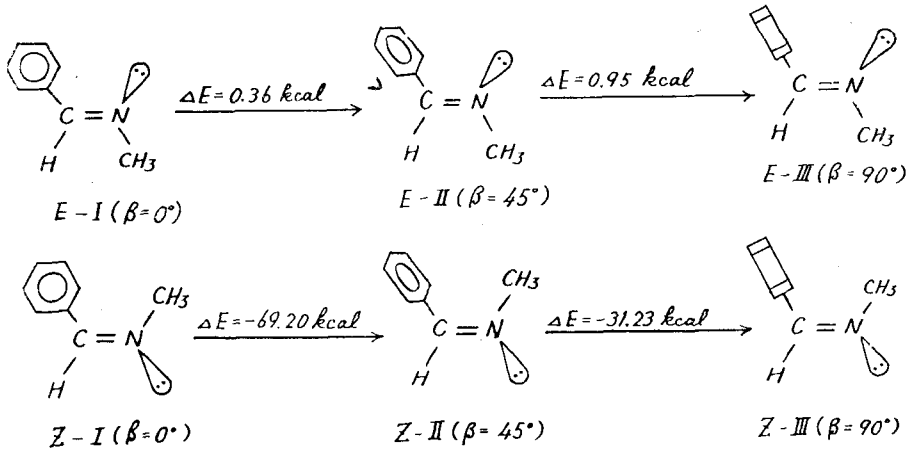


Fig. 2. Conformational change of N-methyl-C-phenylaldimine.

C-phenyl or C-alkyl groups. Thus the strong preference for the E-isomer in the aldimine may be attributed to adverse repulsive interaction between the phenyl ring and the N-methyl group in the Z-configuration.

Increasing the dihedral angle (β), (0°, 45°, 90°) of the phenyl ring rotamer destabilized the E-isomer, but stabilizes the Z-isomer (Table 3). It seems that the effect of the delocalization (resonance) energy favors the coplanar conformation (E-I), but the steric interactions between the ortho-hydrogen atom of the phenylring and cis-N-methyl group in the Z-isomer may force the phenyl ring out of the C=N molecular plane as depicted in Fig 2.

It has been reported that the net result gives a ground state conformation where the ring is slightly twisted out of the imine plane (C-phenyl ring in benzylideneaniline, PhCH=NPh, in the crystalline state, is twisted from C=N plane by ca. 10° in the E-configuration[12]). In this calculation, not the twisted form but a coplanar conformation (E-I) is favored in the E-isomers. It means that the ortho-hydrogen effect does not matter in E-isomers, but influences to a large degree in conformational terms in Z-isomers.

2) N-methyl-C-phenylmethylketimine

Table 4 shows that the E-configuration of the C=N double bond is favored compared with that of Z-configuration with the same conformation of the phenyl ring rotamers.

The energy difference is about 92.0 kcal·mole^{-1}. In contrast to the high sensitivity of the configurational change to C=N bond, only minor change (Ca. 10kcal mole^{-1}) were observed for C-methyl group.

3) N-methyl-C-phenylethylketimine

Table 5 shows that the order of stability is

E-II>Z-I>Z-II>E-I

It is clear that the repulsive interaction between the ortho-hydrogen atom of the phenyl ring and the cis-N-methyl group in the Z-isomer destabilizes the Z-configuration and therefore E-configuration appeared to be favored, but in E-I form the strong repulsive interaction between the trans-N-methyl group and C-ethyl group destabilizes the E-I conformation.

Increase of dihedral angle between C-ethyl group and C=N molecular plane will tend to reduce the attractive interaction between N atom and C-ethyl group, thus Z-II form

is destabilized compared with that of Z-I conformation.

In conclusion, the EHT calculations result that the E-configuration of the C=N double bond is favored compared with that of the Z-configuration in N-methyl-C-phenylketimine isomers.

The most prefererable conformation of the phenyl ring rotamer in N-methyl-C-phenylaldimine and N-methyl-C-phenylmethylketimine are the coplanar forms with regard to the C=N plane, but the conformation of the CH_3CH_2-rotamer, in N-methyl-C-phenylethylketimine, the gauche form (dihedral angle between C=N and CH_3CH_2—plane=90°) is favored.

Acknowledgement

We express our gratitude to the Euisuk Research Foundation for the support of this work.

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