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配置와 形態에 關한 分子軌道論的 硏究(第1報). Methyl Benzamidoxime의 配置와 形態

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MO Studies of Configuration and Conformation(I). Configuration and Conformation of Methyl Benzamidoxime

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요 약. Methyl benzamidoxime의 C=N결합에 의한 configuration과 N--O 및 C—N결합에 대한 conformation에 관하여 확장 Hückel 분자궤도법 계산을 실시하였다. 계산 결과는 C—N결합의 conformation이 *sp*-형이면 *E*-configuration이 *Z*-configuration보다 더 안정하나, *ap*-형이면 *Z*-configuration이 더 안정하다. C=N결합의 configuration과 N-O의 conformation이 같은 경우에는 C—N의 conformation이 *sp*-형인 것이 더 안정하고, C=N결합의 configuration과 C-N의 conformation이 같으면 N-O의 conformation이 *ap*-형인 것이 더 안정하다. 이 안정화 에너지의 대부분은 정전기적인 원자간에 힘에 기인하는 것임을 밝혔다.

ABSTRACT. The configuration and conformation of methyl benzamidoxime have been studied from extended Hückel molecular orbital calculations.

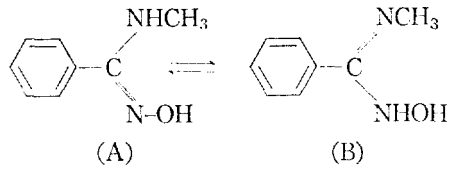
The results show that the *E*-configuration of the C=N double bond is favored compared with that of *Z*-configuration with the *sp*-conformation of the C—N bond rotamers, but *Z*-configuration is more stable with the *ap*-conformation of the C—N bond rotamers. The conformation of C—N bond with equal configuration of C=N bond and equal conformation of N—O bond, *sp*-form is favored, but the conformation of N—O bond with equal configuration and equal conformation of C—N bond *ap*-form is more stable.

The major part of the stabilization energies can be accounted for by the electrostatic energies between the atoms involved.

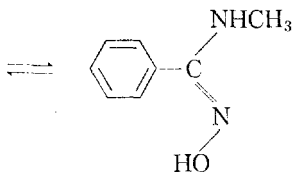
1. INTRODUCTION

Information on the stereochemistry of the methyl benzamidoximes may be of importance both in connection with mechanistic studies and with configurational problems in related systems. The stereochemical problem of the methyl benzamidoximes is quite complex since in addition to

the configuration of the C=N double bond (structure (A) or (C), the conformation of the formally single bonds N-O and C-N also have to be considered (Structure (D)-(L)); finally, there is the possibility of tautomerism ((A) ⇌ (B) or (B) ⇌ (C))



(A) (B)



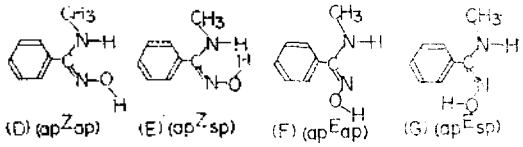
(C)

Comparatively little work has been done on the configuration and conformation of methyl benzamidoxime. Exner and Jehlička[1] have employed two independent and complementary experimental approaches, namely the dipole moment method[2] which requires examination of the molecule as a whole and takes into consideration all possible forms, and nmr spectroscopy which gives information on the partial structure and population of individual forms, but no conclusive evidence has been presented as to the preferred configuration and conformation of this compound.

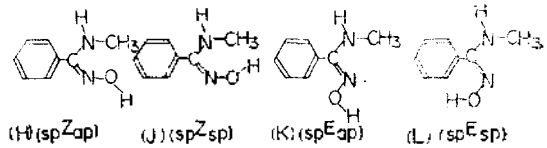
From the electric dipole moments with related data in benzene and the nmr spectral data in ($^2H_6$) dimethyl sulphoxide (($^2H_6$) DMSO) of benzamidoximes, the problem of tautomerism in unsubstituded methyl benzamidoxime has been solved in favour of the hydroxyimino form (A) or (C) in both the solid state and in solution.[3,4] The nmr. also support the hydroxyiminoform for methyl benzamidoxime.[1]

The spatial arrangement of the C=NOH group is defined by the configuration of the C=N bond and by the conformation of the N—O bond; the latter has been attributed partial double bond character.[3a] For oximes in the gas phase[5] as well as in solution[6] the whole C=NOH group is planar with O—H antiperiplanar (ap) to C=N bond. This conformation is consistent with dipole moment data of more complex compounds.[3a,7,8]

The conformational problem of the C-N bond in the methyl benzamidoxime the planarity of the NH·CH_3 group is supported particularly by the results on formamidoxime[3b] and amidines.[9] Hence we consider primarily the eight planar conformation (D)-(L), namely the sequence from the form ap^2ap to sp^Esp.



(D) (ap^Zap) (E) (ap^Zsp) (F) (ap^Eap) (G) (ap^Esp)



(H) (sp^Zap) (J) (sp^Zsp) (K) (sp^Eap) (L) (sp^Esp)

In order to investigate the various posibilities reported by Exner *et al.*[1] using molecular orbital method, we have undertaken the extended Hückel theory (EHT)[10] calculation on methyl benzamidoxime. The EHT calculations have been successfully employed in determing configuration and conformation of organic compds.[11] Martin *et al.* also pointed out that in conformational analysis, using various theoretical 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.[12] 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. CALCULATIONS

1) Molecular Geometry. The geometries of the methyl benzamidoxime molecules were assumed to be planar and were constructed from the probable bond angles and lengths, and dihedral angles. 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.

The coordinate system and numbering scheme are shown in *Fig.* 1, and bond lengths 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 in this program are the orbital exponents Z, valence state ionization potential(VSIP), -I of AO's and cartesian coordinates of atom in molecule. Z and -I values used in this work are summarized in *Table* 2.

In the EHT method, MO Ψ_i are constructed as a linear combination of Slater type atomic orbitals ϕ_i

$$\Psi_i = \sum_{j=1}^{n} C_{ij}\phi_i \qquad (1)$$

where n is the number of VAO. The Slater atomic orbital is in turn given as

$$\phi_i = Nr^{n-1}\exp(-rZ)\ Y_{lm}(\theta,\varphi) \qquad (2)$$

where Z is the orbital exponent for the atom and other terms have their usual significances. The summation in (1) is over all valence orbitals thought to be of importance, namely the 1s orbital for hydrogen, $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals for the second row elements. Theusual secular equation (3) is then solved with approximations

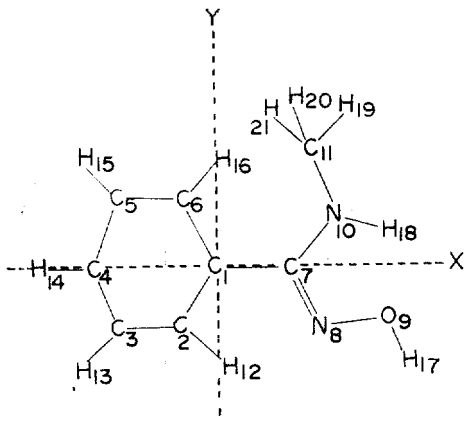


Fig. 1. Coordinate system and numbering scheme.

Table 1. Bond parameters used in atomic coordinate calculation.

bond length (A°)[a]	bond angle[b]
$d(C^{\circ}_{ar}—C_{ar})=1.39$	C—Ĉ—C=120°
$d(C_{ar}—C)=1.45$	C—N̂—C=120°
$d(C_{ar}—H)=1.08$	C—N̂—H=120°
$d(C—H)=1.09$	C—Ĉ=N=125°
$d(C=N)=1.31$	N=Ĉ—N=125°
$d(C_7—N_{10})=1.33$	N—Ô—H=105°
$d(N_{10}—C_{11})=1.45$	C=N̂—O=114°
$d(N—O)=1.36$	(*Z*-form)
$d(O—H)=0.96$	C=N̂—O=118°
$d(N—H)=1.01$	(*E*-form)

[a] from reference (13), [b] from reference (1), [c] C_{ar} show aromatic carbon atom.

Table 2. The orbital exponents, Z and -VSIP used.

AO	Z	−VSIP (eV)
H 1*s*	1.00	−13.60
C 2*s*	1.59	−21.01
2*p*		−11.27
N 2*s*	1.92	−26.90
2*p*		−14.42
O 2*s*	2.24	−36.07
2*p*		−18.53

$$\sum_{i=1}^{j}(H_{ij}-ES_{ij})C_{ij}=0, \quad i=1,2,\cdots\cdots \qquad (3)$$

that the Coulomb integral H_{ii} is equal to the negative of valence state ionization potential (-VSIP) and the off-diagonal matrix element H_{ij} is given by

$$H_{ij}=0.5K(H_{ii}+H_{jj})S_{ij} \qquad (4)$$

with $K=1.75$. The Mulliken population analysis has been carried out and the following MO quantities have been calculated.

Atomic orbital population

$$N_r=2\sum_{i}^{occ}\sum_{s}C_{ri}C_{si}S_{rs}$$

Atomic orbrital bond population

$$N_{rs}=4\sum_{i}^{occ}C_{ri}C_{si}S_{rs}$$

Gross atomic population

$$M_A=\sum_{r}^{A}N_r$$

Atomic bond population

$$M_{AB}=\sum_{r}^{A}\sum_{s}^{B}N_{rs}$$

Total electron Energy

$$E=2\sum_{i}^{occ}\varepsilon_i$$

Formal change

$$Q_A=n_A-M_A$$

where C_{ri} is the coefficient of AO r in the i-th MO, $\sum^{A}$ signifies the summation over all the AOs of atom A, and n_A is the number of electron in atom A. ε_i is the MO energies.

3. RESULTS and DISCUSSION

The results of the calculated total energies for various configuration and conformation of methyl benzamidoxime are summarized in *Table* 3.

1) Conformational Change of C—N Bond Rotamer. According to the energies calculated, synperiplanar (*sp*) forms of the C—N bond ((H), (J), (K) and (L)) are more stable than those of antiperiplanar (*ap*) forms ((D), (E), (F) and (G)) with the energy difference of about 200 kcal·mole^{-1}. This finding is not in harmony with the experimental results from the dipole moment and nmr data in solution, which implied (D) as the most preferred and (K) as the next.

Table 3 shows that the most stable form is (K), while (D) is far less stable.[1] The dipole moment method has been proved reliable less for conformational problems[14] and nmr data again do not constitute conclusive evidence since the spectra are taken in solution of highly polar solvent. We therefore consider these experimental findings disputable.

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

2) Configurational Change of C=N Bond.

Table 3. Summary of the total energies for eight planar conformation of methyl benzamidoxime.

form	E(eV)	ε^{LU}(eV)	ε^{HO}(eV)	ΔE(kcal·mole^{-1})	order of stability
D(ap^Zap)	−1070.7312	−7.8267	−8.7535	204.332	6
E(ap^Zsp)	−1070.9132	−7.8267	−8.7535	200.131	5
F(ap^Eap)	−1069.7504	−7.8265	−8.7465	226.958	7
G(ap^Esp)	−1069.3329	−7.8265	−8.7465	236.591	8
H(sp^Zap)	−1070.4544	−8.8879	−12.4202	3.087	3
J(sp^Zsp)	−1079.0529	−8.8879	−12.4212	12.349	4
K(sp^Eap)	−1079.5882	−8.8698	−12.1229	0.000 (standars)	1
L(sp^Esp)	−1079.1700	−8.8698	−12.1220	9.643	2

Table 4 shows the configurational energy differences of C=N bond with equal conformation of C—N and N—O bonds.

From the *Table* 4 it may be concluded that the *E*-configuration of the C=N double bond is favored compared with that of *Z*-configuration with the *sp*-conformation of the C—N bond rotamers, but *Z*-configuration is more stable with the *ap*-conformation of the C—N bond rotamers.

Table 4. The configurational energy differences of C=N bond.

Comparable form	E(kcal·mole^{-1})
D(ap^Zap)—F(ap^Eap)	−22.6
E(ap^Zsp)—G(ap^Esp)	−36.5
H(sp^Zap)—K(sp^Eap)	+3.1
J(sp^Zsp)—L(sp^Esp)	+2.7

Table 5. The conformational energy differences of N—O bond.

Conparable form	ΔE(kcal·mole^{-1})
D(ap^Zap)—E(ap^Zsp)	+4.2
F(ap^Eap)—G(ap^Esp)	−9.6
H(sp^Zap)—J(sp^Zsp)	−9.3
K(sp^Eap)—L(sp^Esp)	−9.6

3) Conformational Change of N—O Bond. *Table* 5 shows the conformational energy differences of N—O bond with equal configuration of C=N bond and equal conformation of C—N bond.

The *ap*-conformation of N—O bond, with equal conformation of C—N bond and equal configuration of C=N bond, is more stable than that of *sp*-conformation except the D(ap^Zap) from. It means the stability of the molecule is affected by the repulsion energies of the proton in OH group. In D(ap^Zap) form, the decrease in the repulsion energy of the proton in OH group are compensated for by the decrease of the attraction energy between the N atom in NH group and the proton in OH group(*Fig.* 2).

4) Electrostatic Interactions. Wennerstrom *et al.*[15], suggested that the electrostatic effects

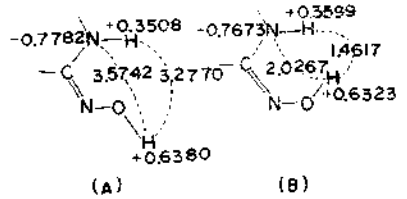


Fig. 2. Formal charge and atomic distance((D) and(E)). (charges are electronic charge unit, ····· indicates distance in Å)

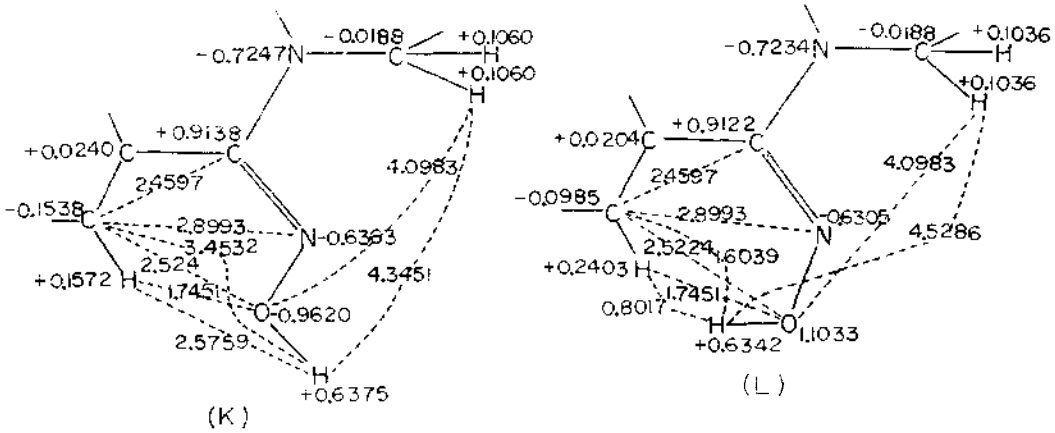


Fig. 3. Formal charge and atomic distance ((K) and (L)). (charges are electronic charge unit, ·····indicates distance in A°)

are of major importance in determining the most stable conformation. We have therefore been examined the similar calculation of electrostatic energy, which is given by $\sum_{i>j} q_i q_j / r_{ij}$, with the conformational change of N—O bond. Typical value of formal charge q and atomic distance r used are shown in *Fig.* 2, & *Fig.* 3, and calculated electrostatic energies are listed in *Table* 6.

The calculated electrostatic energy differences, ΔE_e (D-E) and ΔE_e (K-L) agrees very closely with the total conformational energy difference, but the ΔE_e (F-G) and ΔE_e (H-J) show relatively large deviation from total energy differences. In case of ΔE_e (D-E) and ΔE_e (K-L), there are comparatively simple electrostatic interaction between NH, OH group and C_2—H_{12} in phenyl group, but in case of ΔE_e(F-G) and ΔE_e (H-J), there are complex interaction between C=N—OH group and C_2—H_{12}, N—CH_3 group. Therefore this type of simple electrostatic calculation may not reflect the true interaction.

In conclusion, the *E*-configuration of the C=N bond is favored compared with that of *Z*-configuration with the *sp*-conformation of C—N bond, but *Z*-configuration is more stable with the *ap*-conformation of the C—N bond. The conformation of C—N bond with equal configuration of C=N bond and equal conformation of N—O bond, *sp*-form is favored, but the conformation of N—O bond with equal configuration and equal conformation of C—N bond, *ap*-form is more stable. The most stable form is K (sp^E *ap*) and the most unstable form is the G (ap^E *sp*). The major part of the stabilization energies can be accounted for by the electrostatic energies between the atoms involved.

Table 6. The electrostatic energy difference calculated from formal charge and atomic distance.

	ΔE_e(kcal·mole^{-1})
D-E	+4.3
F-G	−16.3
H-J	−13.4
K-L	−10.1

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