

《Original》 An MO Theoretical Studies on Conformations of
Methyl and Ethyl Cyanoacetates

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Abstract

The extended Hückel molecular orbital calculations have been carried out on rotamers of methyl and ethyl cyanoacetates. Results show that cis orientation of C≡N group is favored while for CH₃ group trans orientation is favored.

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

요 약

메틸 및 에틸 시아노 아세테이트의 각종 회전체에 대하여 확장 Hückel 분자 궤도법 계산을 실시 하였다. 결과로 C≡N 기는 cis 배치가 안정하고 CH₃ 기는 trans 배치가 안정함을 알았다.

또 안정화 에너지의 대부분은 정전기적인 원자간의 인력에 기인되는 것임을 밝혔다

1. Introduction

Comparatively little work has been done on the conformation of methyl and ethyl cyanoacetates. Brown and Krishna *et al*¹⁾, measured the dipole moment of ethyl cyanoacetate but no conclusion has been reached as to the preferred conformations of this compound. Owen *et al*²⁾, have examined the infra-red

absorption spectra of liquid and solid methyl and ethyl cyanoacetates. They found evidence of rotational isomerism arising from internal rotation about the NCH₂C-C bond while for ethyl cyanoacetate the infra-red spectrum suggested the presence of several rotamers brought about by rotation about both the NCH₂C-C and the O-C₂H₅ bonds.

In order to investigate the various possibili-

ties reported by Owen *et al*²⁾. using molecular orbital (MO) method, we have undertaken the extended Hückel theory (EHT)³⁾ calculations on methyl and ethyl cyanoacetates. The EHT calculations have been successfully employed in determining conformations of organic compounds⁴⁾. 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 conformational analysis.

1) Calculations

The method of calculations is the same as described previously⁵⁾. The new parameters⁶⁾ used in the calculation of molecular geometries are as follows.

$$dC \equiv N = 1.16 \text{ \AA}$$

$$\angle CCN = 180^\circ$$

Formal atomic charges are obtained from population analysis included in the program.

2. Results and Discussion

1) Methyl cyanoacetate

The rotameric forms of methyl cyanoacetate are given in Fig. 1 with the energies calculated in this work. The basic ester skeleton for this compound is assumed to retain a planar s-cis conformation⁷⁾. According to the energies calculated, the cis form is more stable than the gauche although admittedly the energy difference of 0.1 kcal mol⁻¹ is very small

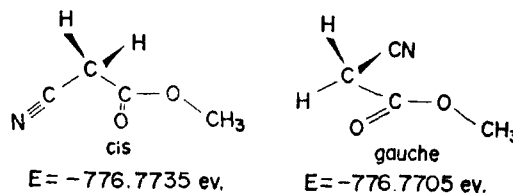
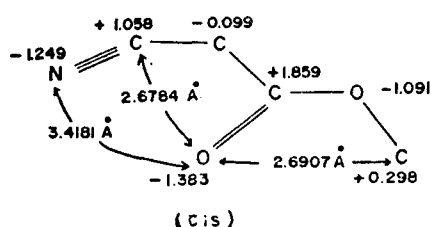


Fig. 1. Rotameric Forms of Methyl Cyanoacetates

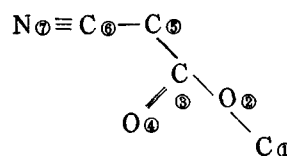
indeed.

The experimental value for the enthalpy difference between the two rotamers in the liquid was found to be ≈ 1.0 kcal mol⁻¹²⁾

None of the two energy differences can be considered to be sufficient for the preferential existence of any one rotamer. Thus two forms must be present in liquid phase as reported by Owen *et al*²⁾. We have given relevant atomic charges (in electronic charge unit) and distances (in Å unit) in Fig. 2.

As usual for an EHT calculation, rather exaggerated charge alternations⁸⁾ can be seen for both forms. Hydrogens are omitted since their charge densities are very small as compared with those of atoms in the main skeleton (I).

Wennerström *et al*⁹⁾., suggested that the



energy difference between s-trans and s-cis

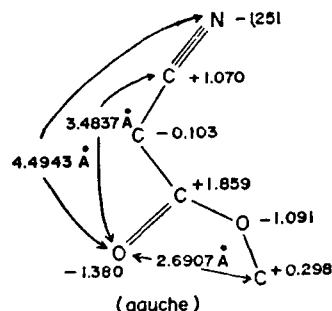


Fig. 2. Charge densities and Distances for Methyl Cyanoacetate

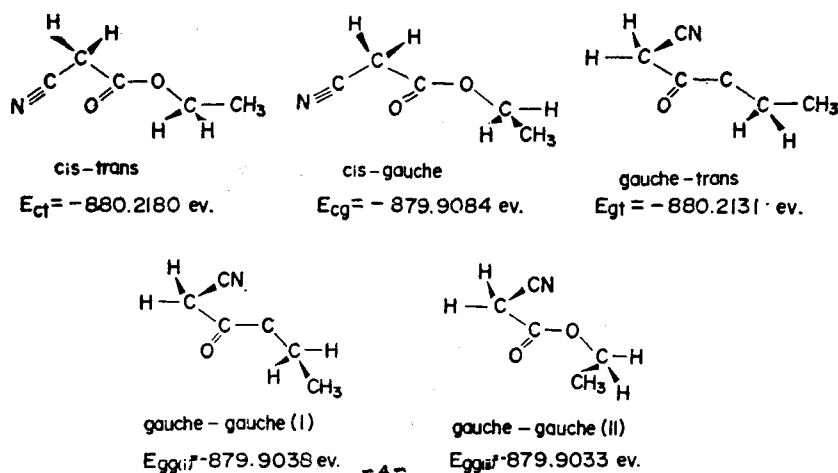


Fig. 3. Rotameric Forms of Ethyl Cyanoacetate

conformers of methyl formate can be accounted for by electrostatic interactions between point charges placed at the nuclei.

They have shown using *ab initio* self-consistent-field MO calculation that the electrostatic effects are of major importance in determining the most stable conformation. We have therefore performed the similar calculations of electrostatic energy, which is given by $\sum_{i>j} q_i q_j / r_{ij}$. Since the main difference between the cis and gauche forms of methyl cyanoacetates is in the relative position of $\text{C}\equiv\text{N}$ group to $\text{C}=\text{O}$, electrostatic energy calculations were confined to interactions between atoms in these two groups using the formal charges and distances shown in Fig. 2. Results of calculation showed that interaction energies are stabilizing *i.e.*, attractive in both forms, but the cis form was more stabilizing by $0.1 \text{ kcal mol}^{-1}$ than that for the gauche form. This shows that the entire energy difference ($\approx 0.1 \text{ kcal mol}^{-1}$) of the two conformers can be accounted for by the electrostatic energy difference. Energetically $\text{C}\equiv\text{N}$ group situated nearest to the O atom is the most favored and this is the planar cis form.

Table 1. Energies of Various Rotameric Forms of Ethyl Cyanoacetate

	E (ev)	$\Delta E = E - E_{ct}$ (Kcal mol^{-1})
cis-trans	-880.2180	
gauche-trans	-880.2131	0.1
cis-gauche	-879.9084	7.1
gauche-gauche (i)	-879.9038	7.2
gauche-gauche (ii)	-879.933	7.3

2) Ethyl Cyanoacetate

For this compound five rotameric forms are possible and these are illustrated in Fig. 3. with the calculated EHT energies. Energetics are summarized in Table 1. It can be seen from this table that the most stable form predicted is the cis-trans form while the most unstable form is the gauche-gauche(ii) form. The cis-trans and gauche-trans forms have energy difference of only $0.1 \text{ kcal mol}^{-1}$ which is the same as that of cis and gauche methyl cyanoacetate. Thus it looks that this energy difference of $0.1 \text{ kcal mol}^{-1}$ is characteristic of the two (*i.e.*, cis and gauche) orientations of $\text{C}\equiv\text{N}$ with respect to the carbonyl group in cyanoacetates. The energy difference between

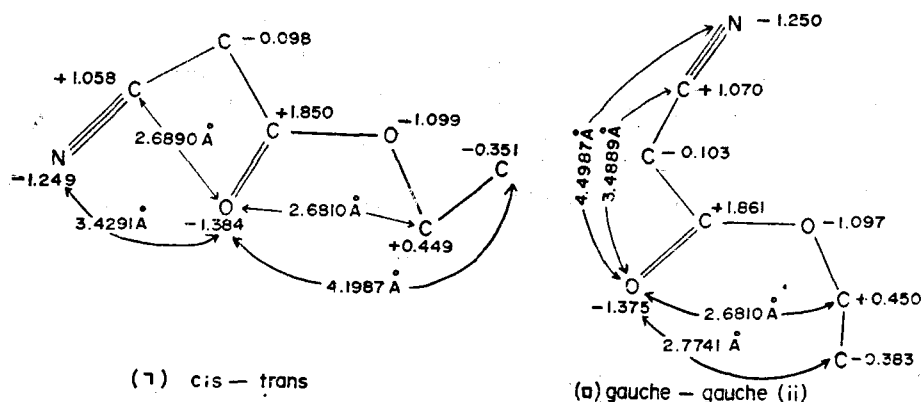
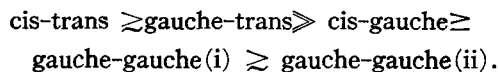


Fig. 4. Charge densities and Distances for Ethyl Cyanoacetate

the two conformers, trans and gauche, caused by internal rotation about the O-C₂H₅ bond is large. In this case trans orientation of CH₃ group to C=O is strongly favored as compared with the gauche orientation, the energy difference being ≈ 7 kcal mol⁻¹. The stability of conformers based on energetics decreases in the order:



This is consistent with the experimental findings of Owen *et al*²⁾. They reported that the cis-trans form with a planar heavy atom framework is the conformation exclusively present in the crystalline solid state while other conformers are also present in liquid state. On the other hand dipole moment of ethyl cyanoacetate¹⁰⁾ lies approximately midway between the predicted values for cis-trans and gauche-trans conformers, suggesting that these two are the main forms existing in conformational equilibrium.

For ethyl cyanoacetate the relevant formal atomic charges and distances are given only for the two forms in Fig. 4. Electrostatic energy difference calculated for cis and gauche orientations of C \equiv N group to C=O gave 0.1 kcal mol⁻¹, which is the same as the value obtained for methyl cyanoacetate. This supports

the contention that the energy difference of 0.1 kcal mol⁻¹ is characteristic of the difference between cis and gauche orientations of C \equiv N to C=O in alkyl cyanoacetate.

The similar electrostatic energy calculation shows that trans orientation of CH₃ group to C=O is more stabilizing by 6.2 kcal mol⁻¹ as compared with gauche orientation. Since the total EHT energy differences shown in table 1. between trans and gauche forms of CH₃ to C=O are ≈ 7 kcal mol⁻¹, the electrostatic attraction energy accounts for the major part of the total energy difference. The energy difference due to the two different orientations of CH₃ group to C=O (≈ 7 kcal mol⁻¹) is much greater than that due to the different orientations of C \equiv N group to C=O (0.1 kcal mol⁻¹). Thus the net stability of five conformers of ethyl cyanoacetate is primarily determined by the orientation of CH₃ group with respect to C=O, and the orientation effect of C \equiv N to C=O is very small as it was in the case of methyl cyanoacetate.

In conclusion, for C \equiv N group the cis orientation is mildly favored compared with gauche, while for CH₃ group the trans orientation is strongly favored compared with gauche. Relative stabilities of conformers predicted by EHT calculation agree with the experimental

findings and the major part of the stabilization energies can be accounted for by the electrostatic energies between the groups concerned.

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