Quantum Chemical Conformational Analysis on Isotactic Polyacrylonitrile Using Molecular Model Compounds

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ABSTRACT: An attempt was made to decide the most stable structure for isotactic polyacrylonitrile using dimer and trimer model compounds with aids of semi-empirical quantum chemical methods (*i.e.*, CNDO/2 and MINDO/3 methods) where possible conformations were considered by rotating main chain bond and bending nitrile triple bond from ordinary C–C–N straight bond at side chain. The results show that two adjacent nitrile groups have mutual attractive interactions and bend to get near to each other by assuming the prolonged CN bond length which reflects the tendency of double bond for CN groups in *meso* arrangement. This conclusion supports Kamide *et al.*'s proposal deduced from the systematic experimental results on chain stiffness and NMR peak assignment for stereoregular polyacrylonitrile. The bending nitrile bond structure of PAN was obtained for the first time from the view point of molecular orbital interactions in low molecular model compound.

KEY WORDS Polyacrylonitrile / Model Compounds / Conformational Analysis / Modified Intermediate Neglect of Differential Overlap/3 (MINDO/3) / Complete Neglect of Differential Overlap/2 (CNDO/2) /

Polyacrylonitrile (PAN) is one of the well-known polymers which have been produced very widely in the world. All of PAN, however, commercially available today, have no stereoregularity in the sense of molecular arrangement. Stereoregular PAN (*i.e.*, highly isotactic PAN) was first reported by White¹ in 1960 employing irradiation with a beam from X-ray type resonant transformer on acrylonitrile-urea canal complex. Matsuzaki *et al.*² synthesized highly isotactic PAN using γ -ray irradiation method in 1968, and very recently anionic synthesis method using organomagnesium compounds has proved to give PAN with high isotacticity.^{3–7} In this situation, one may tend to distinguish the highly stereoregular PAN from atactic PAN, if any, from both industrial and scientific view points. But there are few systematic studies on the property of stereoregular PAN molecules except for ones by Kamide *et al.*,⁸ who investigated the dilute solution properties.

As basic knowledge, it is very important to reveal the conformational nature of PAN for predicting the properties of PAN either in its solid state or in its solution state. First conformational study of PAN has been carried out by Krigbaum and Tokita⁹ by using model compounds (*meso*- and *racemo*-dicyanopentane, that is isotactic and syndiotactic dimer model compounds for PAN, respectively), regarding a nitrile group as an electric dipole. They proposed that isotactic and syndiotactic PAN had a possibility of some types of helical conformation with three monomer units per repeat distance, in which structure two adjacent nitrile groups were moderately separated from each other. Röttger *et al.*¹⁰ calculated energetical state of *mm*, *mr*, and *rr* trimer model compounds of PAN using MNDO (Modified Neglect of differential Diatomic Overlap) method to get a result that a simple repulsion structure was stable for *mm* model compound. Applying PCILO (Perturbative Configuration Interaction using Localized Orbitals, an advanced molecular conformational energy method) to dimer model compound of PAN,

Ganster and Lochmann¹¹ concluded that two neighboring nitrile carbons were apt to approach each other to an extent of *ca.* 2.2 Å.

All these studies, however, have assumed that nitrile group is attached to methine carbon in main chain straightforwardly, in other words, three atoms of methine carbon, nitrile carbon and nitrogen are aligned in a straight line. On the contrary, Kamide *et al.*⁸ have considered that neighboring nitrile groups in *meso* arrangement of PAN bend toward adjacent nitrile group and have nearly conjugate double bond structure at the side chain of PAN molecules with a little large length between nitrile carbon and nitrogen, which leads to somewhat ladder-like chain and enables us to convert easily PAN strand to carbon fiber. The notion of conjugate double bond of nitrile group has been proposed by Kamide *et al.*^{8,12–15} from the following experimental facts:

- 1) PAN in solution has comparatively large conformation parameter σ defined as the ratio of unperturbed chain dimension to that of a chain rotated freely, compared with σ for other vinyl type polymers with almost same molecular weight.⁸

- 2) Consideration of electric and magnetic environments around nitrile groups on the basis that nitrile groups in *meso* arrangement of PAN have almost conjugate double bond made Kamide *et al.*¹² possible to give the full assignments for ¹³C NMR spectra in nitrile and methine carbon region.

- 3) The characteristic ratio of PAN increases abruptly when triad isotacticity passes 50–60%,¹³ which is far lower region observed for isotactic polypropylene calculated by Flory.¹⁴

- 4) The melting point of PAN under the coexistence of water also rises steeply in not so particularly high triad isotacticity region.¹⁵

Note that in Kamide *et al.*'s proposal the word "double bond nature" for nitrile group means that bond length for the nitrile group is inevitably somewhat larger than

ordinary nitrile triple bond. These experimental results may be a least necessary condition for considering the bent and the tendency of double bond of nitrile group in *meso* arrangement, but not be a sufficient condition to conclude the above conformation. In the present article it has been tried to decide the conclusive structure for *meso*-type nitrile groups, whether they are bending or not, directly from the standpoint of molecular chemical calculation for dimer and trimer model compounds of isotactic PAN. The different optimal structures decided from two typical semi-empirical molecular orbital methods have been compared from the view of the characteristic feature of these two methods.

CALCULATION

A *meso* dimer and a *meso-meso* trimer were employed for model compounds as isotactic PAN, and a *racemo* dimer was used as that of syndiotactic PAN as reference. The former two model compounds were *meso*-2,4-dicyanopentane (*m*-DCP, see Figure 1) and *meso-meso*-2,4,6-tricyanoheptane (*mm*-TCH, see Figure 2), respectively, and the latter one was *racemo*-2,4-dicyanopentane (*r*-DCP). Two semi-empirical molecular orbital basis sets were used to carry out the quantum chemical calculations. One of them is CNDO/2 method (Complete Neglect of Differential Overlap), established by Segal and Pople,¹⁶ and the other, MINDO/3 method (Modified Intermediate Neglect of Differential Overlap), modified by Dewar *et al.*¹⁷

Gaussian 88 by Gaussian, Inc.¹⁸ and a program package offered by Tokita and Tominaga¹⁹ were utilized for CNDO/2 calculations, and the package by TORAY SYSTEMS CENTER²⁰ was used for MINDO/3 calculation, using the electronic computers (Alliant FX/8 for Gaussian 88 and PC-9801RA and PC-9801UX for other calculations).

RESULTS AND DISCUSSION

CNDO/2 Calculation for Dimer Model Compound

Figure 1 shows the structure of *m*-DCP which has methyl groups at both ends of molecule. Bond angles of carbon atoms on the main chain are given so as to form a tetrahedral angle. Here, the angles for two C–C–N bonds (*i.e.*, angles $\angle$ C–C–N) are given as ψ_1 and ψ_2 , torsional angles of main chains in question are given as ϕ_1 and ϕ_2 as illustrated in Figure 1.

The second column in Table I shows the interatomic bond lengths optimized by CNDO/2 keeping $\psi_1 = \psi_2 =$

Figure 1. *meso*-2,4-Dicyanopentane.

180° and $\phi_1 = \phi_2 = 60^\circ$ to arrange the model compound in *trans-trans* conformation. This case basically corresponds to the case used by Krigbaum and Tokita.⁹ Here, all carbon-carbon bonds constituting the main chain of polymer are assumed to have same lengths, and they are referred to as main chain bond in the present article. The lengths of carbon-hydrogen bonds are assumed to be constant in each methyl, methylene, and methine groups. The optimizing calculation using CNDO/2 gave -80.470 a.u. (-50462 kcal mol⁻¹) as the total energy of *m*-DCP, and this value expressed as kcal mol⁻¹ unit was adopted as a standard for comparison with the energy values calculated for other conformational varieties.

Figure 3 shows a contour map of energy calculated by quantum chemical conformational study with constant ψ_1 and ψ_2 ($=180^\circ$, that is, C–C–N is aligned straight) by varying ϕ_1 and ϕ_2 in the range of 0 to 360° . Here, the bond length was taken as constant. Obviously, there exist two minimum points near $\phi_1 = 0^\circ$ and $\phi_2 = 120^\circ$, giving the value of total energy about -47.1 kcal mol⁻¹. The ϕ_1 and ϕ_2 values renders two nitrile groups in *m*-DCP to approach toward each other without bending in view of molecular model. The results of CNDO/2 calculation for *m*-DCP strongly suggest that the energetically stable structure of this model compound is not necessarily repulsive one.

Next, the Kamide *et al.*'s proposal on a conformation for two neighboring nitrile groups in *meso* arrangement will be discussed. They assumed that neighboring nitrile groups in *meso* arrangement have mutual interactions. First, we examined the cases where two nitrile nitrogen atoms are arranged in bent manner making a particular plane but keeping the same constant nitrile carbon-nitrogen bond lengths (referred to as nitrile lengths), as the case discussed above. Figure 4 portrays a contour map of total energy for *m*-DCP, in which ψ_1 and ψ_2

Table I. Optimized bond length for *meso*-2,4-dicyanopentane

Bond	Optimal bond length/Å	
	Basis set	
	CNDO/2	MINDO/3
C–C ^a	1.487	1.585
C–C ^b	1.487	1.530
C–C ^c	1.425	1.485
C–N	1.192	1.161
C–H ^d	1.129	1.120
C–H ^e	1.125	1.113
C–H ^f	1.119	1.109

^a between methine and methylene carbon; ^b between methine and methyl carbon; ^c between methine and nitrile carbon; ^d in methine group; ^e in methylene group; ^f in methyl group.

Figure 2. *meso-meso*-2,4,6-Tricyanoheptane.

Figure 3. Contour map of rotational potential energy [kcal mol^{-1}] calculated by using CNDO/2 for *meso*-2,4-dicyanopentane.

Figure 4. Contour map of CN bond bending potential energy [kcal mol^{-1}] calculated by using CNDO/2 for *meso*-2,4-dicyanopentane.

shown in Figure 1 varied from 60° to 300° keeping two dihedral angles defined by the set of the bonds C_1C_2 , C_2C_6 , and C_6N_1 and by that of the bonds C_3C_4 , C_4C_7 , and C_7N_2 as 210° . The two minimum points in Figure 4 exist near $\psi_1 = 120^\circ$, $\psi_2 = 190^\circ$, and $\psi_1 = 170^\circ$, $\psi_2 = 250^\circ$, and both of the values of total energy at these two points are about $-85.9 \text{ kcal mol}^{-1}$. Since those values are far lower than that of the minimum in Figure 3, it can be understood that the structure of bending nitrile–nitrile interaction is more stable than that of the most stable rotational conformation with straight alignment for C–C–N. This result fairly contradicts with those obtained by Krigbaum and Tokita⁹ who pointed out that neighboring nitriles existed in a manner of helical molecular conformation on the basis that each nitrile group did not bend and was regarded as an electric dipole.

CNDO/2 Calculation for Trimer Model Compound

To examine a possibility that the interaction between neighboring nitriles exists for trimer model with *meso-meso* structure (*mm*-TCH, see Figure 2), CNDO/2 method was also employed under the condition that three nitrile groups bend in a same plane keeping main chain bonds *trans-trans* conformation. Variable parameters are ψ_1 , ψ_2 , and ψ_3 , as shown in Figure 2. The bond angles except nitrile carbons have also been kept as tetrahedral. The values of all interatomic bond lengths of *m*-DCP have been employed for *mm*-TCH, assuming that all methine carbon–methylene carbon bond lengths have almost same value for convenience's sake. The value of total energy (-115.581 a.u. , *i.e.*, $-72480 \text{ kcal mol}^{-1}$) calculated by CNDO/2 for *mm*-TCH with $\psi_1 = \psi_2 = \psi_3 = 180^\circ$ and $\phi_1 = \phi_2 = 60^\circ$ has been employed for a standard value of total energy. Since the energy minimum for *m*-DCP proved to appear near $\phi_1 = 120^\circ$ and $\phi_2 = 190^\circ$, the calculation for *mm*-TCH was made by keeping one of ϕ around 120° .

Figure 5(a) shows the total energy against ψ_3 with variable parameter ψ_2 keeping $\psi_1 = 130^\circ$. The minimum exists near $\psi_2 = 120^\circ$ and $\psi_3 = 191^\circ$, with the minimum value of total energy $-65 \text{ kcal mol}^{-1}$, which is larger than the standard value. Another graph of total energy against ψ_3 with variable parameter ψ_2 keeping $\psi_1 = 120^\circ$ is shown in Figure 5(b). Minimum point exists near $\psi_2 = 120^\circ$, $\psi_3 = 190^\circ$, showing minimum value of total energy is about $-82 \text{ kcal mol}^{-1}$ which is more stable than that in Figure 5(a). Figure 5(c) shows the relation between total energy and ψ_3 with variable parameter ψ_1 keeping $\psi_2 = 120^\circ$. The minimum value in Figure 5(c) is about $-70 \text{ kcal mol}^{-1}$ near $\psi_2 = 120^\circ$, $\psi_3 = 192^\circ$.

The above results demonstrated for the first time that bent type of nitrile group in *meso* arrangement for PAN might be quite possible energetically, showing that the total minimum point exists near $\psi_1 = 120^\circ$, $\psi_2 = 120^\circ$, and $\psi_3 = 190^\circ$, with total energy of about $-82 \text{ kcal mol}^{-1}$. Thus CNDO/2 study on *meso-meso* type trimer model compound lead to the most stable structure, in which a nitrile group at one end of trimer bends about 10° toward the other two nitrile groups, and the other two groups bend about 60° approaching toward the former one. This result for trimer model compound is consistent with that for dimer.

MINDO/3 Calculation for Dimer Model Compound (I)

In order to confirm the results obtained by using CNDO/2 method more precisely, MINDO/3 method, an advanced semi-empirical basis set, has been used for dimer model compound of PAN. The patterns of calculations are similar to the cases in Figures 3 and 4. As the bond angles the tetrahedral values are also used in the present case except for nitrile carbons, and the bond lengths were newly optimized using MINDO/3 (see the third column in Table I). The values of total energy are expressed in kcal mol^{-1} on a basis energy value (-1418.75 eV , *i.e.*, $-32695 \text{ kcal mol}^{-1}$) calculated for *m*-DCP using MINDO/3 with $\phi_1 = \phi_2 = 60^\circ$ and $\psi_1 = \psi_2 = 180^\circ$.

Figure 6 shows a total energy contour map calculated by using MINDO/3 as basis set for *m*-DCP with keeping ψ_1 and ψ_2 as 180° and with rotating ϕ_1 and ϕ_2 from the

Figure 5. CN bond bending potential energy [kcal mol^{-1}] calculated by using CNDO/2 for *meso-meso*-2,4,6-tricyanoheptane: (a), $\psi_1 = 130^\circ$; (b), $\psi_1 = 120^\circ$; (c), $\psi_2 = 120^\circ$.

trans-trans position ($\phi_1 = \phi_2 = 60^\circ$). In the figure, the minimum point is found near $\phi_1 = 90^\circ$ and $\phi_2 = 330^\circ$, where the conformational structure corresponds to a completely repulsive state of two nitrile groups. The value of total energy is about $-9.0 \text{ kcal mol}^{-1}$.

Figure 7 illustrates also a total energy contour map obtained from calculations varying ψ_1 and ψ_2 and keeping $\phi_1 = \phi_2 = 60^\circ$. The minimum point exists near $\psi_1 = 190^\circ$ and $\psi_2 = 170^\circ$, and the value of total energy is $-1.6 \text{ kcal mol}^{-1}$. This structure corresponds to nitrile arrangement in slightly repulsive manner. This structure, however, should not realize in polymer molecule, because all the repeating units cannot take repulsive forms at the same time as far as *trans-trans* conformation is concerned. The condition for repeating unit in *trans-trans* conformation must be

$$\psi_1 + (360^\circ - \psi_2) < 360^\circ,$$

namely $\psi_1 < \psi_2$. Under this condition, the actually probable structure in Figure 7 has the relation $\psi_1 = 180^\circ$

and $\psi_2 = 180^\circ$, which means straight form of nitrile groups from methine carbon.

Summarizing these results shown in Figures 6 and 7, calculations for *m*-DCP using MINDO/3 suggest that optimal structure is repulsive one and do not lead to bending nitrile groups against Kamide *et al.*'s proposal.⁸ Note that these conclusion was drawn under the assumption that nitrile bond length is equal to that of standard nitrile triple bond.

MINDO/3 Calculation for Dimer Model Compound (II)

Compared with CNDO/2 method, the principal feature of MINDO/3 method lies in 1) employing the differential overlaps, which is completely neglected in CNDO/2 method, and 2) consideration of one centered exchange integrals and two centered repulsion integrals between nuclei.²¹ Thus, MINDO/3 is generally regarded to be more precise and reliable method than CNDO/2 from the standpoint of the interaction between two nuclei. As discussed above, MINDO/3 calculation gave straight

Figure 6. Contour map of rotational potential energy [kcal mol^{-1}] calculated by using MINDO/3 for *meso*-2,4-dicyanopentane with standard CN bond length.

Figure 7. Contour map of CN bond bending potential energy [kcal mol^{-1}] calculated by using MINDO/3 for *meso*-2,4-dicyanopentane with standard CN bond length.

C–C–N conformation as stable one. The above results, however, were derived by assuming that the nitrile length is that for standard nitrile triple bond.

The most characteristic feature of the Kamide *et al.*'s proposal is that nitrile groups in *meso* arrangement have tendency of double bond. As described before, this means that the nitrile length in *meso* arrangement must be somewhat larger than that for ordinary nitrile triple bond length.

Thus, further calculations have been carried out in which nitrile lengths are 10%-lengthened (*i.e.*, $1.2771 \text{ \AA}$) in order to depress the interatomic repulsions. This assumption concerning the nitrile length might be supported by other experimental fact that the values of ν_{CN} , the wave number of nitrile stretching vibration, for *m*-rich and *r*-rich mixture of DCP obtained from our infrared measurements²² are 2228.7 and 2239.2 cm^{-1} , respectively, showing that less value of wave number of *m*-DCP than *r*-DCP means that double bond nature of *m*-DCP is stronger, in other word, its nitrile length is longer than that of *r*-DCP. The double bond nature (that is, prolongation of CN length) of nitrile groups in any

Figure 8. Contour map of rotational potential energy [kcal mol^{-1}] calculated by using MINDO/3 for *meso*-2,4-dicyanopentane with 10%-lengthened CN bond.

Figure 9. Contour map of CN bond bending potential energy [kcal mol^{-1}] calculated by using MINDO/3 for *meso*-2,4-dicyanopentane with 10%-lengthened CN bond.

conformation could be realized by polymer–polymer interaction and polymer–solvent interactions. The result described above indicates that *meso* configuration of CN brings about the lengthening of the CN without such interactions. The extent of prolongation (*i.e.*, 10%) in the study is only tentative but can be referred to the results that the lengths of hydrogen bond for aggregate molecules of ammonium, water, or hydrogen fluoride have been reported to be lengthened as 10–20%²³ from standard lengths for pure species.

Molecular calculations have been carried out using same values of bond lengths and angles as used in the case 3) except nitrile lengths. The basis of total energy has also been taken as same value as case 3).

Figure 8 shows a contour map of rotational conformation around the bonds C_2C_3 and C_3C_4 as axes. The minimum point of total energy in Figure 8 is found to be close to $\phi_1 = 90^\circ$ and $\phi_2 = 330^\circ$, and its value is about $23.0 \text{ kcal mol}^{-1}$. This structure corresponds to a repulsive state of two nitrile groups, being completely the same to that of Figure 6.

Figure 9 also illustrates a contour map obtained from

Table II. Results of quantum chemical calculations for low molecular model compounds of PAN with standard and prolonged CN bond length

Figure	Model compound	CN bond length	Holding condition	Molecular orbital basis	Minimum energy point	Minimum energy/ kcal mol ⁻¹	Stable structure
3	<i>m</i> -DCP	Standard	$\psi_1 = \psi_2 = 180^\circ$	CNDO/2	$\phi_1 \equiv 0^\circ$ $\phi_2 \equiv 120^\circ$	-47.1 ^a	—
4	<i>m</i> -DCP	Standard	$\phi_1 = \phi_2 = 60^\circ$	CNDO/2	$\psi_1 \equiv 120^\circ$ $\psi_2 \equiv 190^\circ$	-85.9 ^a	stable
5	<i>mm</i> -TCH	Standard	$\phi_1 = \phi_2 = \phi_3 = 60^\circ$	CNDO/2	$\psi_1 \equiv 120^\circ$ $\psi_2 \equiv 120^\circ$ $\psi_3 \equiv 190^\circ$	-82.0 ^b	(stable) ^c
6	<i>m</i> -DCP	Standard	$\psi_1 = \psi_2 = 180^\circ$	MINDO/3	$\phi_1 \equiv 90^\circ$ $\phi_2 \equiv 330^\circ$	-9.0 ^d	stable
7	<i>m</i> -DCP	Standard	$\phi_1 = \phi_2 = 60^\circ$	MINDO/3	$\psi_1 \equiv 120^\circ$ $\psi_2 \equiv 120^\circ$	-1.6 ^d	—
8	<i>m</i> -DCP	10%-prolonged	$\psi_1 = \psi_2 = 180^\circ$	MINDO/3	$\phi_1 \equiv 90^\circ$ $\phi_2 \equiv 330^\circ$	23.0 ^d	—
9	<i>m</i> -DCP	10%-prolonged	$\phi_1 = \phi_2 = 60^\circ$	MINDO/3	$\psi_1 \equiv 140^\circ$ $\psi_2 \equiv 200^\circ$	21.1 ^d	stable
—	<i>r</i> -DCP	Standard	$\psi_1 = \psi_2 = 180^\circ$	MINDO/3	$\phi_1 \equiv 90^\circ$ $\phi_2 \equiv 90^\circ$	-2.5 ^d	stable
—	<i>r</i> -DCP	Standard	$\phi_1 = \phi_2 = 60^\circ$	MINDO/3	$\psi_1 \equiv 180^\circ$ $\psi_2 \equiv 180^\circ$	11.7 ^d	—
—	<i>r</i> -DCP	10%-prolonged	$\psi_1 = \psi_2 = 180^\circ$	MINDO/3	$\phi_1 \equiv 90^\circ$ $\phi_2 \equiv 90^\circ$	29.3 ^d	stable
—	<i>r</i> -DCP	10%-prolonged	$\phi_1 = \phi_2 = 60^\circ$	MINDO/3	$\psi_1 \equiv 150^\circ$ $\psi_2 \equiv 210^\circ$	36.5 ^d	—

^a Zero level, at the structure with normal CN length, $\phi_1 = \phi_2 = 60^\circ$ and $\psi_1 = \psi_2 = 180^\circ$ by CNDO/2. ^b Zero level, at the structure with normal CN length, $\phi_1 = \phi_2 = \phi_3 = 60^\circ$ and $\psi_1 = \psi_2 = \psi_3 = 180^\circ$ by CNDO/2. ^c Rotating optimization was not carried out. ^d Zero level, at the structure with normal CN length, $\phi_1 = \phi_2 = 60^\circ$ and $\psi_1 = \psi_2 = 180^\circ$ by MINDO/3.

similar calculations as Figures 4 and 7, and in this case nitrile nitrogens are located variably keeping nitrile bond 10%-lengthened from standard length. The minimum point is found near $\psi_1 = 140^\circ$, $\psi_2 = 200^\circ$, and the value of total energy is about 21.1 kcal mol⁻¹.

Through the results from Figures 8 and 9, the most stable structure has been concluded as nitrile bending one in which nitrile bonds approach toward neighbor if nitrile bond is a little longer than standard state.

Table II summarizes the results of quantum chemical calculations corresponding to Figures 3—9, and Table II also contains the results obtained from the calculations carried out for *r*-DCP (*racemo* dimer model compound for syndiotactic PAN). Table II suggests that a *meso*-type bond tends to have a “ladder” structure in nature. Table II also shows that syndiotactic PAN tends to maintain straight nitrile group forms as stable ones for both ordinary CN triple bond strength and prolonged CN bond strength.

Using an advanced molecular orbital method of PCIO conformational calculation, Ganster and Lochmann¹¹ reported that energy minima of *m*-DCP were characterized by a relatively close approach of nitrile groups accompanied by a charge shift in the triple bonds increasing the bond dipole moment. Although their results are based upon straight nitrile group, they have something in common with our results in the present study concerning an aspect of mutual attractive interaction of two adjacent nitrile groups.

CONCLUSION

Quantum chemical calculations using CNDO/2 and MINDO/3 on *m*-DCP (dicyanopentane) and *mm*-TCH (tricyanoheptane) have suggested that two adjacent nitrile groups in *meso* arrangement of PAN molecules have mutual interactions and get near to each other with prolonged carbon-nitrogen bond length. The calculations employing the prolonged carbon-nitrogen bond length were carried out in order to examine the cases of nitrile group solvation with arbitrary solvent which solvated to lone pair electrons of nitrile nitrogen. This conclusion demonstrates for the first time that the rough conformation proposed by Kamide *et al.* could be realized in view of energetic stabilization. The existence of bent type cyano group has not been anticipated from studies due to the assumption such as simple polar groups or electric dipoles for nitrile groups. It has been also suggested in another way that a *meso*-type bond tends to have a “ladder” structure in its nature.

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