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Anionic Polymerization of an Acrylonitrile Trimer Studied by Photoelectron Spectroscopy

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A photoelectron spectrum of an acrylonitrile (AN:CH₂=CHCN) trimer anion, (AN)₃[−], produced by electron impact on an acrylonitrile cluster was measured, and was compared with that of a molecular anion of 1,3,5-cyclohexanetricarbonitrile (*c*-HTCN) in the triequatorial form, which was first synthesized in the present experiment. A comparison of the vertical detachment energies of (AN)₃[−] and the molecular anion lead us to conclude that (AN)₃[−] is assigned as one of the stereoisomers (diaxial form) of *c*-HTCN (−) on the basis of our previous studies refs 13, 14, and 20–22 [Tsukuda, T.; Kondow, T. *J. Chem. Phys.* **1991**, 95, 6989. Tsukuda, T.; Kondow, T. *J. Am. Chem. Soc.* **1994**, 116, 9555. Ichihashi, M.; Tsukuda, T.; Nonose, S.; Kondow, T. *J. Phys. Chem.* **1995**, 99, 17354. Fukuda, Y.; Tsukuda, T.; Terasaki, A.; Kondow, T. *Chem. Phys. Lett.* **1995**, 242, 121. Fukuda, Y.; Tsukuda, T.; Terasaki, A.; Kondow, T. *Chem. Phys. Lett.* **1996**, 260, 423.].

1. Introduction

Chemical reactions in cluster media have attracted much attention because they are expected to provide unique reaction products that are very different from those obtained in the usual condensed media. Intracuster polymerization is a typical example of such reactions. Several groups have so far investigated cationic polymerization in clusters followed by ionization.^{1–12} The mass spectra of cluster cations exhibit characteristic distributions in intensity. They have analyzed in such a manner that intracuster polymerization takes place when the neutral clusters are ionized. For instance, Garvey et al.^{1–6} have reported the enhancement in the intensity distributions of (CH₂=R)_n⁺ (R=CH₂, CF₂, and CHCH₃) produced by electron impact ionization of van der Waals clusters of (CH₂=R)_m and interpreted the intensity enhancement in terms of formation of six membered cyclic ions because of a kinetic bottleneck in the chain propagation sequences. El-Shall et al.^{7–9} have observed the cationic polymerization in van der Waals clusters of vinyl chloride and isoprene. El-Sayed et al.¹⁰ have reported dissociative ionization of acrylate clusters with releasing carboxy groups under irradiation of a laser light and suggested that intracuster polymerization proceeds.

On the other hand, Tsukuda et al.^{13,14} have investigated Rydberg electron attachment onto an acrylonitrile (AN:CH₂=CHCN) cluster, (AN)_m, and observed intensity enhancements in the mass spectra of (AN)_n[−] and [(AN)_n−X][−] (X = H, H₂, HCN, and H₂ + HCN) at *n* = 3, 6, and 9, where [(AN)_n−X][−] represents an anion produced by eliminating a neutral species, X, from (AN)_n[−]; no intensity enhancements are observed in the

mass spectra of the cluster cation of (AN)_n⁺. They have concluded that three AN molecules are hydrogen-bonded in a ring geometry in (AN)_m and undergo anionic polymerization by the electron attachment. Similar intensity enhancement at *n* = 3, 6, and 9 were also observed in the mass spectra of the cluster anions of olefin molecules such as 2-chloroacrylonitrile,^{15–18} methyl acrylate,¹⁹ methacrylonitrile,^{14,19} and styrene.¹⁴

To elucidate the mechanism of the intracuster anionic polymerization in (AN)_m by the electron attachment, systematic studies have been conducted by using techniques of collision-induced dissociation, photodissociation, and photoelectron detachment. Ichihashi et al.²⁰ have shown that a neutral AN trimer unit, (AN)₃, is released dominantly from a parent cluster anion (AN)_n[−] by Kr-atom impact. They have interpreted this result in such a manner that (AN)₃ is present in (AN)_n[−] as a stable trimer unit. Fukuda et al.²¹ have undertaken the photodissociation measurement of (AN)_n[−] (2 ≤ *n* ≤ 9) at photon energies of 1.17 and 2.33 eV and have observed (AN)₃[−] and (AN)₆[−] as the main products. They concluded that the parent anion (AN)_n[−] (*n* ≥ 3) consists of an anionic trimer unit, (AN)₃[−], a neutral trimer unit, (AN)₃, and AN molecule(s). They²² have also measured the vertical detachment energies of (AN)_n[−] (2 ≤ *n* ≤ 11) and showed that the core ion of (AN)_n[−] (*n* ≥ 3) is an anionic trimer unit, (AN)₃[−], in a ring geometry. In summary, previous studies have revealed that (AN)_n[−] (*n* ≥ 3) consists of a polymerized cyclic trimer core ion, (AN)₃[−], solvated with a polymerized cyclic neutral trimer unit, (AN)₃, and AN molecule(s). The polymerized cyclic trimer core ion, (AN)₃[−], is regarded to be one of the four stereoisomers of the molecular anion of 1,3,5-cyclohexanetricarbonitrile (*c*-HTCN; see Table 1). The final goal of this series of studies is to identify the isomeric structure of (AN)₃[−]. In the present study, a photoelectron spectrum of (AN)₃[−] was measured and compared with that of the molecular anion of *c*-HTCN in a triequatorial form, which was first synthesized in the present study. An ab initio MO method based on Gaussian 94²³ was employed to calculate the

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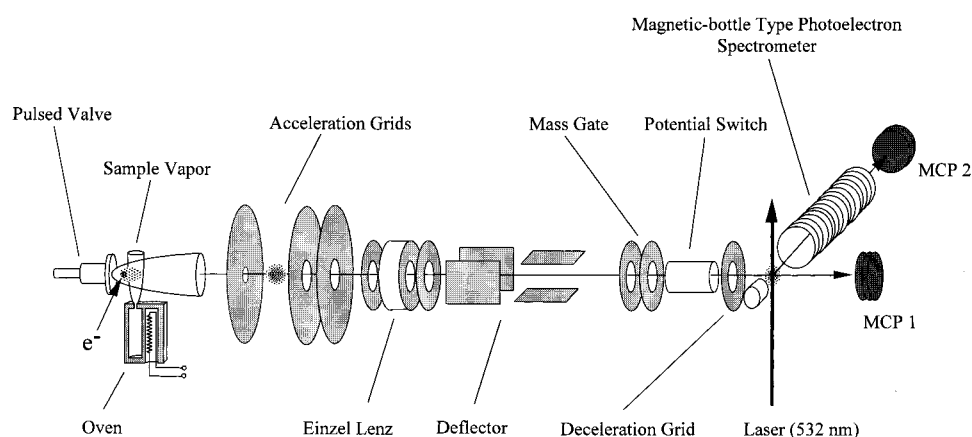
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TABLE 1: Relative Energies and Vertical Detachment Energies for Four Stereoisomers of 1,3,5-Cyclohexanetricarbonitrile (–) Calculated with HF/6-31+G//MP2/6-31++G(d,p)^a

	Stereoisomers of 1,3,5-cyclohexanetricarbonitrile (–)			
	(a)	(b)	(c)	(d)
Relative energy ^b , ΔE_{anion} (eV)	0.00 (0.00)	0.91 (0.75)	0.97 (0.86)	1.60 (1.50)
Relative vertical detachment energy ^c , ΔV_{cal} (eV)	-0.29 (-0.46)	0.05 (0.04)	0.00 (0.00)	-0.39 (-0.42)

^a The values shown in parentheses were calculated with HF/6-31+G//MP2/3-21+G. ^b Relative energy with respect to the stereoisomer a which has the most stable structure. ^c Relative energy with respect to the stereoisomer c which has the structure of the synthesized sample.

**Figure 1.** Schematic diagram of the experimental apparatus equipped with a magnetic-bottle-type TOF photoelectron spectrometer.

vertical detachment energies of the four stereoisomers of *c*-HTCN (–) for the sake of comparison with the vertical detachment energy of (AN)₃[–].

2. Experimental Section

Figure 1 shows a schematic diagram of the experimental setup employed for the measurements of both the mass and the photoelectron spectra. The apparatus consists of a pulsed cluster ion source, a time-of-flight (TOF) mass spectrometer, and a magnetic-bottle type TOF photoelectron spectrometer.

Helium gas of 4–8 atm was expanded from a pulsed nozzle of 0.8 mm in diameter. Electrons having a kinetic energy of ~300 eV were introduced at the distance of 2 mm downstream from the nozzle. The diameter of the electron beam was 1 mm. A powder sample of *c*-HTCN in the triequatorial form (see the Appendix for its synthesis) was heated in a stainless steel oven at 160 °C, and *c*-HTCN vapor was effused into the vacuum through a 0.5 mm orifice on a lid of the oven. The supersonic expansion from the nozzle was allowed to mix with the effusive beam of the sample vapor at the distance of 7 mm downstream from the nozzle. The anions produced in the expansion region were extracted by applying a pulsed electric field and accelerated up to 1500 eV in a field-free path of 2.7 m. After passing through the ion optics, the anions were detected by a tandem microchannel plate (Hamamatsu F2223-21S), and the mass spectrum of the product anions was obtained.

The photoelectron spectrum of *c*-HTCN (–) was measured as follows: The anions were extracted by applying a pulsed

electric field and accelerated up to 500 eV in a field-free path of 2.7 m. The anion, *c*-HTCN (–), was selected out from spatially separated ion bunches by using a mass gate and was decelerated down to 50 eV by a potential switch located in front of the magnetic-bottle-type TOF photoelectron spectrometer. Then, at the photodetachment region, *c*-HTCN (–) was irradiated by the output of unfocused second harmonics of a Nd:YAG laser (Quanta Ray DCR-11). Laser fluence was maintained in the range of 50 mJ cm^{–2} pulse^{–1}. Photoelectrons, created in a strong inhomogeneous magnetic field (~1000 G) generated by a pulsed electromagnet located outside the vacuum chamber, were guided in a 2 m drift tube applied with a weak magnetic field (~10 G) and detected by a tandem microchannel plate (Hamamatsu F2223-21S). The signal was recorded by a 1 GHz time-to-digital converter (LeCroy TDC4208) interfaced with a personal computer (NEC PC-9801 VX). The data were accumulated for 30 000–60 000 laser shots so as to obtain one photoelectron spectrum of *c*-HTCN (–) with a good signal-to-noise ratio. Energy calibration was performed by measuring the known photoelectron spectra of O[–] and O₂[–].^{24–27} The resolution of this photoelectron spectrometer was determined to be 30 and 150 meV fwhm (full width at half-maximum) at $E_{c.m.} = 1.148$ and 2.79 eV, respectively, from the measurement of the photoelectron spectrum of Cu[–].

The photoelectron spectrum of (AN)₃[–] was also measured under the same experimental condition by using the same procedure as stated above. A detailed description of the

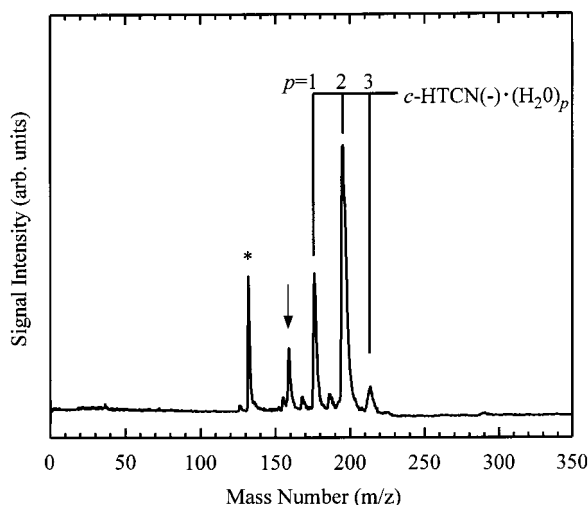


Figure 2. Mass spectrum of anionic species produced by electron impact on *c*-HTCN. The peak indicated by a vertical arrow ($m/z = 159$) was assigned to *c*-HTCN ($-$). Peaks with $m/z = 177$, 195, and 213 were assigned to *c*-HTCN ($-$) solvated with H_2O molecule(s). The peak indicated by an asterisk ($m/z = 132$) was assigned to an anion produced by eliminating one HCN unit from *c*-HTCN ($-$).

measurement of a photoelectron spectrum of $(\text{AN})_3^-$ was shown in one of our previous papers.²²

3. Results

3.1. Anionic Products by Electron Impact on *c*-HTCN.

Figure 2 shows a typical TOF mass spectrum of anions produced by electron attachment on *c*-HTCN (1,3,5-cyclohexanetricarbonitrile). The peak indicated by a vertical arrow ($m/z = 159$) was assigned to *c*-HTCN ($-$). The peaks with $m/z = 177$, 195, and 213 were assigned to *c*-HTCN ($-$) solvated with H_2O molecule(s). On the other hand, the peak indicated by an asterisk ($m/z = 132$) was assigned to an anion produced by eliminating one HCN unit from *c*-HTCN ($-$). This anion is regarded as $[(\text{AN})_3\text{-HCN}]^-$, which was also produced by electron attachment on $(\text{AN})_m$.^{13,14} The production of the anion ($m/z = 132$) lends a further support that $(\text{AN})_3^-$ is one of the stereoisomer of *c*-HTCN ($-$), because the product anions from $(\text{AN})_3^-$ and *c*-HTCN ($-$) are same.

3.2. Vertical Detachment Energies of $(\text{AN})_3^-$ and *c*-HTCN ($-$). Figure 3 shows typical photoelectron spectra of $(\text{AN})_3^-$ and *c*-HTCN ($-$) measured at the photon energy of 2.33 eV under the same experimental conditions, where the abscissa represents the electron binding energy. The small hump at ~ 0.2 eV is an artifact caused by a multiphoton process. The peak energy of $(\text{AN})_3^-$ is smaller than that of *c*-HTCN ($-$), whereas the spectral width of both the spectra is almost the same; a slight difference in spectral width is explained by a difference in internal energy between $(\text{AN})_3^-$ and *c*-HTCN ($-$).

The vertical detachment energy, V_{exp} , of an anion, is derived from the peak energy of the photoelectron spectrum of the anion by using the relation

$$I(E_b) = C \exp \left\{ - \left(\frac{E_b - V_{\text{exp}}}{\delta} \right)^2 \right\} \quad (1)$$

where $2\delta\sqrt{\ln 2}$ is the full width at a half-maximum of the spectrum, E_b is the electron binding energy, and C is a constant. The parameters V_{exp} and δ were obtained by a least-squares fitting of the rising portions of the $(\text{AN})_3^-$ and *c*-HTCN ($-$) spectra with the Gaussian function given by eq 1. The vertical

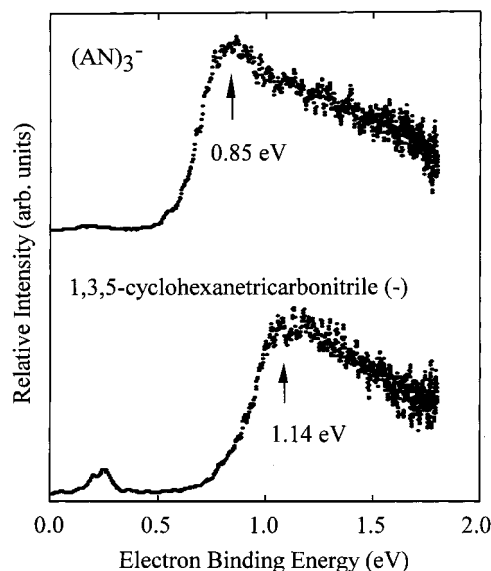


Figure 3. Photoelectron spectra of $(\text{AN})_3^-$ (upper trace) and 1,3,5-cyclohexanetricarbonitrile ($-$) in the triequatorial form (lower trace) at a photon energy of 2.33 eV. The vertical arrows represent the vertical detachment energies of both anionic species.

detachment energies of $(\text{AN})_3^-$ and *c*-HTCN ($-$) were determined to be 0.85(3) and 1.14(3) eV, respectively; the vertical detachment energy of $(\text{AN})_3^-$ is smaller by 0.29(6) eV than that of *c*-HTCN ($-$) in the triequatorial form.

3.3. Ab Initio MO Calculation. Previous studies^{13,14,20–22} have shown that $(\text{AN})_3^-$ is one of the stereoisomers of *c*-HTCN ($-$) as described in section 1. This conclusion is actually supported by the photoelectron spectra of $(\text{AN})_3^-$ and *c*-HTCN ($-$) in the triequatorial form; the spectral profile is almost same but only the peak energy is different by 0.29(6) eV. The molecular anion, *c*-HTCN ($-$), is known to have four stereoisomers as listed in Table 1: They are (a) the diaxial form in which two $-\text{CN}$ groups are oriented axially and the other one equatorially with respect to the average plane of the chair-form cyclohexane ring, (b) the diequatorial form in which two $-\text{CN}$ groups are oriented equatorially and the other one axially, (c) the triequatorial form in which all of the three $-\text{CN}$ groups are oriented equatorially, and (d) the triaxial form in which all of the three $-\text{CN}$ groups are oriented axially.

To identify the isomeric structure of $(\text{AN})_3^-$, the vertical detachment energies of these stereoisomers were calculated as shown below:

(1) Geometry optimization was carried out for a given isomer of *c*-HTCN ($-$) possessing a predetermined $-\text{CN}$ conformation by using the 6-31+G basis set at the Hartree–Fock level.

(2) The energies of *c*-HTCN ($-$) and *c*-HTCN (defined as E_{anion} and E_{neutral} , respectively) were calculated at the second-order Møller–Plesset (MP2) level with the 6-31++G(d,p) basis set on the premise that both *c*-HTCN ($-$) and *c*-HTCN have the same geometrical structure calculated in procedure 1.

(3) The vertical detachment energy, V_{cal} , for the isomer was obtained as

$$V_{\text{cal}} = E_{\text{neutral}} - E_{\text{anion}} \quad (2)$$

In the calculation, the spin-restricted Hartree–Fock (RHF) and the spin-unrestricted Hartree–Fock (UHF) methods were employed for the closed-shell and the open-shell systems, respectively. Let us define the relative energy ΔE_{anion} for a given isomer anion with respect to the energy of isomer a which is the most stable structure of *c*-HTCN ($-$). On the other hand,

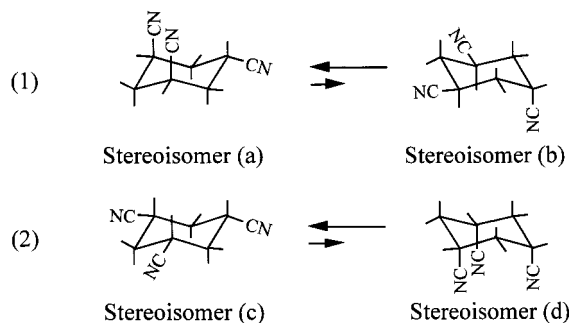


Figure 4. Conformational inversion in 1,3,5-cyclohexanetricarbonitrile (—). The topomerization gives rise to the interconversion of two diastereomers.

the relative vertical detachment energy, ΔV_{cal} , is defined with respect to the vertical detachment energy of isomer c, because the synthesized *c*-HTCN (—) corresponds to isomer c. The methods and the basis sets employed in the present calculation are reliable enough to predict the relative energy, ΔE_{anion} , and the relative vertical detachment energy, ΔV_{cal} , but not sufficiently accurate to reproduce the absolute energy and the observed vertical detachment energy. The ΔE_{anion} and ΔV_{cal} obtained from the calculations are listed in Table 1. As shown in Table 1, the order of the magnitudes of ΔE_{anion} and ΔV_{cal} does not change by reducing the number of the basis functions, although ΔE_{anion} and ΔV_{cal} themselves change slightly.

4. Discussion

4.1. Identification of $(\text{AN})_3^-$ Structure. In *c*-HTCN (—), the pair of isomers a and b and that of c and d are mutually invertible (see Figure 4 parts 1 and 2),^{28,29} whereas all of the other two pairs are not mutually invertible in a thermal condition because of a high energy barrier for the conformational change, which involves the rupture of chemical bonds. According to the calculation, the energy differences between the pair of isomers a and b and that between c and d are found to be sufficiently large (0.91 and 0.63 eV, respectively) that the equilibrium favors formation of isomer a through the interconversion reaction between isomers a and b and isomer c through that between isomers c and d. Furthermore, the calculation shows that the vertical detachment energy of isomer a is smaller by 0.29 eV than that of isomer c (see Table 1). In summary, *c*-HTCN (—) has stable isomers a and c, where the vertical detachment energy of isomer a is calculated to be smaller by 0.29 eV than that of isomer c.

Note the experimental result that the vertical detachment energy of $(\text{AN})_3^-$ is smaller by 0.29(6) eV than that of *c*-HTCN (—) having the structure of isomer c. In comparison with the calculation described above, it is concluded that $(\text{AN})_3^-$ holds the structure of isomer a, whereas the synthesized *c*-HTCN (—) holds the structure of isomer c.

4.2. Preferential Stereoisomer Formation. The formation of $(\text{AN})_3^-$ in isomer a by intracuster polymerization in $(\text{AN})_m$ initiated by electron attachment can be explained as follows: As discussed in our previous paper,^{13–22} prealigned hydrogen-bonded three AN molecules in $(\text{AN})_m$ are polymerized into the six-membered ring molecule, *c*-HTCN (—), when one electron attached to it. In the intracuster polymerization, chain propagation is likely to proceed so as to seek a product having the most stable structure among the four stereoisomers. As mentioned previously, the most stable structure is isomer a, so that the product of the intracuster polymerization must be isomer a as a natural consequence on the basis of the energetics. On the

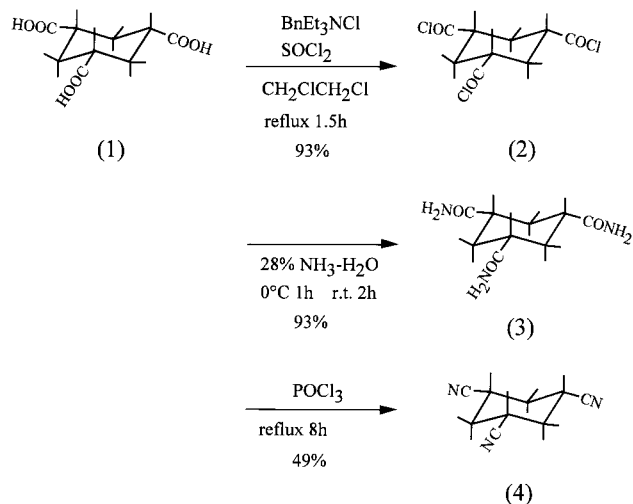


Figure 5. Synthetic scheme for 1,3,5-cyclohexanetricarbonitrile.

other hand, the preferential formation of isomer a can also be predicted by an argument based on an entropy point of view. As each $-\text{CN}$ group can be oriented either equatorially or axially, there exist eight possible combinations for three $-\text{CN}$ groups. Two combinations out of the eight give rise to triequatorial (isomer c) or triaxial (isomer d) stereoisomers, and the rest provide diaxial (isomer a) and diequatorial ones (isomer b). This implies that a probability for producing isomer a or b is three times larger than that for producing isomer c or d. In addition, isomer b is readily inverted to isomer a as discussed above. These considerations lead us to conclude that the intracuster anionic polymerization favors the formation of stereoisomer a on the basis of the energetics and the entropy requirement.

5. Conclusion

A characteristic feature of intracuster polymerization reactions was investigated by using such a bench mark system that three acrylonitrile molecules assembled in a ring form undergo anionic polymerization by electron attachment. The formation of the most preferable stereoisomer was found to be determined by the energetics and the entropy requirement of the reaction system.

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Appendix

Synthesis of 1,3,5-Cyclohexanetricarbonitrile. The compound 1,3,5-cyclohexanetricarbonitrile was synthesized by the following procedures and was examined by ^1H NMR, ^{13}C NMR, and IR spectroscopy. The synthetic scheme is shown in Figure 5.

1,3,5-Cyclohexanetricarbonyl Chloride (2). A solution of a triequatorial 1,3,5-cyclohexanetricarboxylic acid (**1**; 737 mg, 3.41 mmol) and benzyltriethylammonium chloride (23.3 mg, 0.102 mmol) in 1,2-dichloroethane (5 mL) was refluxed while

dropping thionyle chloride (5 mL) at 100 °C for 1.5 h under argon atmosphere. After cooling to room temperature, the solvent was distilled out under reduced pressure. The solid thus obtained was washed twice by tetrahydrofuran (THF; 1 mL) and dried off under reduced pressure, and then 1,3,5-cyclohexanetricarbonyl chloride (**2**; 859 mg, 3.16 mmol, 93%) was obtained.

1,3,5-Cyclohexanetriamide (3). A solution of 1,3,5-cyclohexanetricarbonyl chloride (**2**; 859 mg, 3.16 mmol) in 28% aqueous ammonia (50 mL) was stirred at 0 °C for 1 h and was allowed to react at room temperature for 2 h. The solvent was filtered out. The solid thus obtained was washed by acetone and dried off under reduced pressure. Then 1,3,5-cyclohexanetriamide (**3**; 626 mg, 2.93 mmol, 93%) was obtained.

The physical properties of product **3** are given below:

¹H NMR (*d*₆-DMSO) δ = 1.30–1.33 (1H, dd), 1.73–1.76 (1H, d, *J* = 11.4 Hz), 2.11 (1H, dd), 6.69 (1H, s), 7.18 (1H, s).

¹³C NMR (*d*₆-DMSO) δ = 176.3, 42.5, 31.5.

IR (KBr): 3346, 3180, 1676, 1620, 1480 cm⁻¹.

1,3,5-Cyclohexanetricarbonitrile (4). A solution of 1,3,5-cyclohexanetriamide (**3**; 626 mg, 2.93 mmol) in chloride phosphate in excess was refluxed for 8 h under argon atmosphere. The reaction was terminated by adding a saturated aqueous solution of sodium hydrogencarbonate. The organic portion of the solution was extracted, washed by a saturated aqueous solution of sodium chloride, and dehydrated by sodium sulfate anhydride. The solvent was distilled out under reduced pressure. The solid thus obtained was refined by thin chromatography (ethyl acetate) to prepare 1,3,5-cyclohexanetricarbonitrile (**4**; 230 mg, 1.45 mmol, 49%).

The physical properties of product **4** are given below:

White-colored solid at room temperature.

Melting point = 156.0–156.5 °C.

¹H NMR (CDCl₃) δ = 1.80–1.87 (1H, dd, *J* = 25.9, 13.0 Hz), 2.45–2.48 (1H, m), 2.53–2.59 (1H, dddd, *J* = 12.6, 12.6, 3.5, 3.5 Hz).

¹³C NMR (CDCl₃) δ = 118.5, 30.9, 26.2.

IR (KBr): 2250 cm⁻¹.

The NMR spectra show that product **4** has a triequatorial form; all of the three –CN groups are oriented equatorially with respect to the average plane of chair-form cyclohexane ring.

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