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Normal coordinate analyses of 3,5-dichlorophenylcyanamide

Abstract The structure of 3,5-dichlorophenylcyanamide $c\text{-}C_6H_3Cl_2\text{–}NHCN$ was investigated by DFT-B3LYP and ab initio MP2 calculations with the 6-311+G** basis set. The planar to perpendicular rotational barrier was calculated to be of about 5 kcal mol^{-1} at both levels of calculation. The stability of the planar structure of the molecule was explained on the basis of conjugation effects between the cyanamide–NHCN moiety and the phenyl $c\text{-}C_6H_5$ ring in agreement with earlier NMR results. The CNC and the HNC bond angles were calculated to be about 120° especially by MP2 calculation, which is consistent with sp^2 (planar –NH–CN group) and not sp^3 (pyramidal –NH–CN group) structure. The vibrational frequencies of the d_0, d_1 and d_3 species of 3,5-dichlorophenylcyanamide and the potential energy distributions among symmetry coordinates of the normal modes of the parent molecule were computed at the DFT-B3LYP level. The calculated infrared and Raman spectra of the molecule were plotted. Complete vibrational assignments were made on the basis of isotopic substitution and normal coordinate calculations.

**Keywords** Vibrational spectra and assignments · Rotational barrier · 3,5-Dichlorophenylcyanamide

Introduction

The interesting electronic structure of cyanamide $H_2N\text{–}C\equiv N$ and its chemical importance have attracted attention over the years. [1, 2, 3, 4, 5] The molecule was reported to have a large amplitude inversion motion caused by a double-minimum potential and the equilibrium configuration is pyramidal where the potential barrier corresponds to a planar configuration. [1, 3] Brown et al.

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determined the barrier height as 510 cm^{-1} (1.45 kcal mol^{-1}). [2]

Recently, vinyl cyanamide $CH_2=CH\text{–}NHCN$ was predicted to adopt a planar configuration with the *cis* and the *trans* conformations being the equilibrium minima for the molecule. The *cis* to *trans* rotational barrier was predicted to be of about 6 kcal mol^{-1}. [6] Furthermore, the CNC and the HNC bond angles were calculated to be of about 120° by both levels of calculations, which is clearly consistent with sp^2 (planar –NH–CN group) and not sp^3 (pyramidal –NH–CN group) bonding and hence with a planar configuration of vinyl cyanamide.

The planar structure of the cyanamide –NHCN moiety in vinyl cyanamide [6] could be best explained on the basis of the following resonance structures:

$$CH_2 = CH - NH - C \equiv N \leftrightarrow CH_2 = CH - \overset{+}{N}H = C = \overset{-}{N}$$
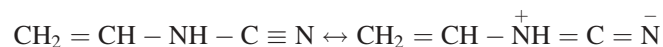
The conjugation between the vinyl $CH_2=CH\text{–}$ and the cyanamide –NHCN groups leads to significant π character of the C–N bond [6] that explains the predicted high rotational barrier (6 kcal mol^{-1}) for the molecule in a very similar way to vinyl ketene $CH_2=CH\text{–}CHCO$ (6 kcal mol^{-1}). [7]

In the present study, we investigated the structure of 3,5-dichlorophenylcyanamide $c\text{-}C_6H_3Cl_2\text{–}NHCN$ by DFT-B3LYP and ab initio MP2 calculations. The energies of the molecule in its possible structures were optimized at the DFT-B3LYP/6-311+G** and MP2/6-311+G** levels. The vibrational frequencies were computed at the DFT-B3LYP/6-311+G** level. Then we carried out normal coordinate analyses and calculated the potential energy distributions (PEDs) among symmetry coordinates for the molecule. The vibrational assignments of the normal modes were provided on the basis of the calculated PED values and the results are presented herein.

Ab initio calculations

The Gaussian 98 program, [8] running on an IBM RS/6000 43P model 260 workstation, was used to carry out
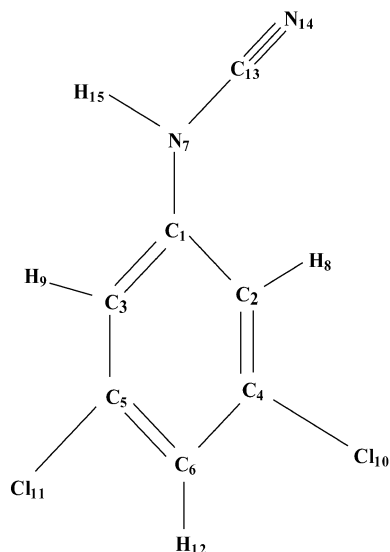
Fig. 1 Atom numbering for 3,5-dichlorophenylcyanamide in the planar form

DFT-B3LYP and ab initio MP2 calculations. The 6-311+G** basis set was employed to optimize the structures and predict the energies and dipole moments of 3,5-dichlorophenylcyanamide c-$C_6H_3Cl_2$–NHCN in the planar (Fig. 1) and perpendicular structures. The optimized energies and structural parameters of the molecule in the stable planar conformation at both levels of calculation are shown in Tables 1 and 2, respectively.

Asymmetric torsional potential function

The potential scan for the internal rotation about the C–N single bond in 3,5-dichlorophenylcyanamide was obtained by allowing the CCNC dihedral angles (φ) to vary from 0° (planar position) to 90° (perpendicular position). Full geometry optimizations at each of the fixed dihedral angles (φ) of 0°, 15°, 30°, 45°, 60°, 75° and 90° were carried out at DFT-B3LYP/6-311+G** and MP2/6-311+G** levels of calculation. The calculated potential functional scans at the two levels in 3,5-dichlorophenylcyanamide are shown in Fig. 2.

Table 1 Calculated structural parameters (Å and degrees), total dipole moment (Debye), and rotational constants of the planar 3,5-dichlorophenylcyanamide

| Parameter	B3LYP/6-311+G**	MP2/6-311+G**
r (C_1–C_2=C_1–C_3)	1.388	1.393
r (C_2–C_4=C_3–C_5)	1.389	1.396
r (C_6–C_4=C_6–C_5)	1.400	1.405
r (C_1–N_7)	1.411	1.407
r (N_7–C_{13})	1.332	1.339
r ($C_{13}\equiv N_{14}$)	1.159	1.179
r (N_7–H_{15})	1.010	1.001
r (C_2–H_8)	1.083	1.087
r (C_3–H_9)	1.084	1.087
r (C_4–Cl_{10})	1.746	1.727
r (C_5–Cl_{11})	1.748	1.729
r (C_6–H_{12})	1.081	1.085
Bond angle		
($C_3C_1C_2$)	120.1	120.3
($C_1C_2C_4$=$C_1C_3C_5$)	120.0	119.8
($C_2C_4C_6$=$C_3C_5C_6$)	120.8	120.7
($C_4C_6C_5$)	118.4	118.6
($C_2C_1N_7$)	121.1	120.7
($C_3C_1N_7$)	118.8	119.0
($C_1N_7C_{13}$)	124.2	122.6
($N_7C_{13}N_{14}$)	179.5	178.5
($C_1C_2H_8$)	120.3	120.4
($C_1C_3H_9$)	120.6	120.7
($C_2C_4Cl_{10}$)	119.7	119.5
($C_3C_5Cl_{11}$)	119.6	119.5
($C_4C_6H_{12}$)	120.8	120.7
($C_1N_7H_{15}$)	118.3	119.2
($C_2C_1N_7C_{13}$)	0.0	0.0
($H_{15}N_7C_1C_{13}$)	180.0	180.0
Dipole moment		
(μ_t)	3.50	3.76
Rotational constants		
A	918	930
B	578	580
C	354	357

Vibrational frequencies and normal coordinate analyses

The optimized structural parameters were used to compute the vibrational frequencies of d_0, d_1, and d_3 species of 3,5-dichlorophenylcyanamide at the DFT-B3LYP/6-311+G** level. 3,5-Dichlorophenylcyanamide in the planar conformation has C_s symmetry. In the planar molecule, the 39 vibrational modes span the irreducible representations: 27 A' and 12 A". The A' modes should be polarized and the A" modes depolarized in the Raman spectra of the liquid. Normal coordinate analyses were carried out for the stable planar structure of the molecule as described previously. [9, 10] The internal and symmetry coordinates of the molecule are listed in Tables 3 and

Table 2 Computed total energies (hartree) and relative energies (kcal mol^{-1}) for the possible structures of 3,5-dichlorophenylcyanamide

Structure	B3LYP/6-311+G**			MP2/6-311+G**		
	(φ)[a] (°)	Total energy	Relative energy	(φ) (°)	Total energy	Relative energy
Planar	0.0	−1299.179861	0.0	0.0	−1296.952025	0.0
Perpendicular	90.0	−1299.171696	5.1	90.0	−1296.944356	4.8

[a] φ is the CCNC dihedral angle
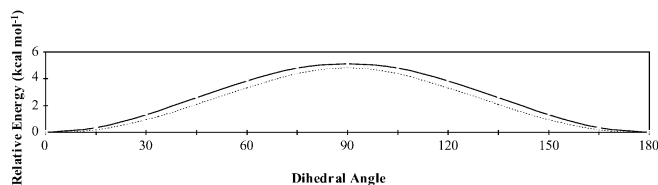
Fig. 2 Potential curves for the internal rotation in 3,5-dichlorophenylcyanamide as determined by DFT-B3LYP/6-311+G** (*solid*) and MP2/6-311+G** (*dotted*) calculations

4. The PEDs for each normal mode among the symmetry coordinates of the molecule were calculated and are given in Table 5. A complete assignment of the fundamentals was proposed based on the calculated PED values, infrared band intensities, Raman line activities, and depolarization ratios. The data of the vibrational assignments are listed in Tables 5 and 6.

The vibrational infrared and Raman spectra were calculated using the computational methods previously described. [10, 11] To calculate the Raman spectra, the frequencies v_j, the scattering activities S_j, and the depolarization ratios ρ_j were obtained from DFT-B3LYP/6-311+G** calculation. The calculated vibrational infrared and Raman spectra of the molecule are shown in Figs. 3 and 4.

Discussion

The chemistry of phenylcyanamide and its derivatives has attracted attention due to the active role of their ligands in inorganic chemistry. [12, 13, 14, 15, 16, 17, 18, 19, 20, 21] On the basis of ^{15}N NMR chemical shifts of phenylcyanamide and the shielding changes of the amino nitrogen –N–C (relative to ammonia NH_3) and the cyano nitrogen –C≡N (relative to methyl cyanide CH_3CN), a substantial build-up of positive charge at the amino N atom was suggested. [12] This build-up is a result of significant π-character in the aryl–N bond that arises from the contribution of two resonance structures. [12] The aromatic substituent effect on the ^{15}N resonance of 3,5-dichlorophenylcynamide was reported to be minor and less than 4 ppm relative to phenylcyanamide. [12]

From energy optimization at DFT-B3LYP and ab initio MP2 levels (Fig. 2) an energy difference of about 5 kcal mol^{-1} was predicted between the planar and the perpendicular structures of 3,5-dichlorophenylcyanamide. Similar to vinylcyanamide, [12] the CNC and the HNC bond angles were calculated to be of about 120°, especially at the MP2 level, which supports the sp^2 (planar – NH–CN group) and not sp^3 (pyramidal –NH–CN group) bonding in 3,5-dichlorophenylcyanamides (Table 1). Furthermore, the increase in the C–N barrier in going from 3,5-dichlorophenylcyanamide (5 kcal mol^{-1}) to vinyl-

Table 3 Internal coordinate definitions[a] for 3,5-dichloro-phenylcyanamide

No.	Coordinate	Definition		No.	Coordinate	Definition	
1	C_1–C_3	Stretch	R_1	32	$N_7C_1C_2$	Bend	β_1
2	C_1–C_2	Stretch	R_2	33	$N_7C_1C_3$	BEND	β_2
3	C_2–C_4	Stretch	R_3	34	$C_{13}N_7C_1$	Bend	γ
4	C_4–C_6	Stretch	R_4	35	$H_{15}N_7C_1$	Bend	δ_1
5	C_5–C_6	Stretch	R_5	36	$H_{15}N_7C_{13}$	Bend	δ_2
6	C_3–C_5	Stretch	R_6	37	$N_{14}C_{13}N_7$	Bend	σ
7	C_1–N_7	Stretch	A	38	$H_8C_2C_1N_7+H_9C_3C_1N_7$	Torsion	λ_1
8	C_2–H_8	Stretch	r_3	39	$H_8C_2C_1N_7-H_9C_3C_1N_7$	Torsion	λ_2
9	C_4–Cl_{10}	Stretch	r_5	40	$Cl_{10}C_4C_6H_{12}+Cl_{11}C_5C_6H_{12}$	Torsion	λ_3
10	C_6–H_{12}	Stretch	r_7	41	$Cl_{10}C_4C_6H_{12}-Cl_{11}C_5C_6H_{12}$	Torsion	λ_4
11	C_5–Cl_{11}	Stretch	r_9	42	$H_{12}C_6C_4C_5$	Wag	η_1
12	C_3–H_9	Stretch	r_{11}	43	$H_{15}N_7C_1C_{13}$	Wag	ϖ
13	N_7–C_{13}	Stretch	B	44	$N_7C_1C_3C_2$	Wag	η_2
14	C_{13}–N_{14}	Stretch	C	45	$N_{14}C_{13}N_7C_1$	Torsion	χ
15	N_7–H_{15}	Stretch	D	46	$(C_2C_1N_7C_{13}, C_2C_1N_7N_{14},$	Torsion	τ
16	$C_2C_1C_3$	Bend	α_1		$C_2C_1N_7H_{15})$		
17	$C_4C_2C_1$	Bend	α_2				
18	$C_6C_4C_2$	Bend	α_3	47	$C_3C_1C_2C_4$	Torsion	κ_1
19	$C_5C_6C_4$	Bend	α_4	48	$C_1C_2C_4C_6$	Torsion	κ_2
20	$C_6C_5C_3$	Bend	α_5	49	$C_2C_4C_6C_5$	Torsion	κ_3
21	$C_5C_3C_1$	Bend	α_6	50	$C_4C_6C_5C_3$	Torsion	κ_4
22	$C_1C_2H_8$	Bend	v_1	51	$C_6C_5C_3C_1$	Torsion	κ_5
23	$C_4C_2H_8$	Bend	v_2	52	$C_5C_3C_1C_2$	Torsion	κ_6
24	$C_1C_3H_9$	Bend	v_3				
25	$C_5C_3H_9$	Bend	v_4				
26	$C_2C_4Cl_{10}$	Bend	v_5				
27	$C_6C_4Cl_{10}$	Bend	v_6				
28	$C_3C_5Cl_{11}$	Bend	v_7				
29	$C_6C_5Cl_{11}$	Bend	v_8				
30	$C_4C_6H_{12}$	Bend	v_9				
31	$C_5C_6H_{12}$	Bend	v_{10}				

[a] For atom denotation see Fig. 1

Table 4 Symmetry coordinates for 3,5-dichlorophenylcyanamide

Species	Description	Symmetry coordinate[a,b]
A'	β-CH antisymmetric stretch	$S_1 = r_3 - r_{11}$
	β-CH symmetric stretch	$S_2 = r_3 + r_{11}$
	γ-CCl antisymmetric stretch	$S_3 = r_5 - r_9$
	γ-CCl symmetric stretch	$S_4 = r_5 + r_9$
	δ-CH stretch	$S_5 = r_7$
	N–H stretch	$S_6 = D$
	Ring–N stretch	$S_7 = A$
	NCN antisymmetric stretch	$S_8 = B - C$
	NCN symmetric stretch	$S_9 = B + C$
	β-CH bend (in-plane)	$S_{10} = \nu_1 - \nu_2 + \nu_3 - \nu_4$
	β-CH bend (in-plane)	$S_{11} = \nu_1 - \nu_2 - \nu_3 + \nu_4$
	γ-CCl bend (in-plane)	$S_{12} = \nu_5 - \nu_6 + \nu_7 - \nu_8$
	γ-CCl bend (in-plane)	$S_{13} = \nu_5 - \nu_6 - \nu_7 + \nu_8$
	δ-CH bend (in-plane)	$S_{14} = \nu_9 - \nu_{10}$
	N–H bend (in-plane)	$S_{15} = \delta_1 - \delta_2$
	NCN bend (in-plane)	$S_{16} = \sigma$
	Ring–NCN bend (in-plane)	$S_{17} = \beta_1 - \beta_2$
	CNC bend (in-plane)	$S_{18} = \gamma$
	Ring breathing	$S_{19} = R_1 + R_2 + R_3 + R_4 + R_5 + R_6$
	Ring deformation	$S_{20} = R_1 + R_2 - 2R_3 + R_4 + R_5 - 2R_6$
	Ring deformation	$S_{21} = R_1 + R_2 - R_4 - R_5$
	Ring deformation	$S_{22} = R_1 - R_2 + R_3 - R_4 + R_5 - R_6$
	Ring deformation	$S_{23} = R_1 - R_2 + R_4 - R_5$
	Ring deformation	$S_{24} = R_1 - R_2 - 2R_3 - R_4 + R_5 + 2R_6$
	Ring deformation	$S_{25} = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$
	Ring deformation	$S_{26} = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$
	Ring deformation	$S_{27} = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$
A"	β-CH deformation	$S_{28} = \lambda_1$
	β-CH and ring-NCN deformation	$S_{29} = \lambda_2 \cos \Phi + \eta_2 \sin \Phi$
	β-CH and ring-NCN deformation	$S_{30} = -\lambda_2 \sin \Phi + \eta_2 \cos \Phi$
	γ-CCl deformation	$S_{31} = \lambda_3$
	γ-CCl and δ-CH deformation	$S_{32} = \lambda_4 \cos \Omega + \eta_1 \sin \Omega$
	γ-CCl and δ-CH deformation	$S_{33} = -\lambda_4 \sin \Omega + \eta_1 \cos \Omega$
	N–H bend (out-of-plane)	$S_{34} = \varpi$
	Ring deformation	$S_{35} = \kappa_1 - \kappa_2 + \kappa_3 - \kappa_4 + \kappa_5 - \kappa_6$
	Ring deformation	$S_{36} = \kappa_1 - \kappa_3 + \kappa_4 - \kappa_6$
	Ring deformation	$S_{37} = \kappa_1 - 2\kappa_2 + \kappa_3 + \kappa_4 - 2\kappa_5 + \kappa_6$
	NCN bend (out-of-plane)	$S_{38} = \chi$
	HNCN asymmetric torsion	$S_{39} = \tau$

[a] Not normalized
[b] $\Phi = -15°$ and $\Omega = +20°$

Fig. 3 Calculated vibrational infrared spectrum of d_0- (*upper*), d_1- (*middle*) and d_3- (*lower*) 3,5-dichlorophenylcyanamide at 300 K by the DFT-B3LYP/6-311+G** calculation
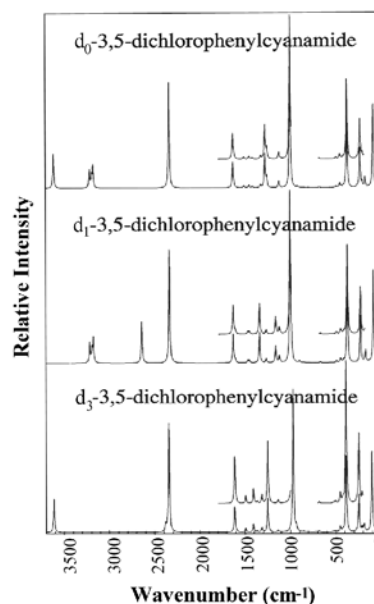
Fig. 4 Calculated vibrational Raman spectrum of d_0- (*upper*), d_1- (*middle*) and d_3- (*lower*) 3,5-dichlorophenylcyanamide at 300 K by the DFT-B3LYP/6-311+G** calculation

cyanamide (6 kcal mol^{-1}) is due to the difference in the bond π-character in both molecules.

Therefore, we calculated in the present work the vibrational wavenumbers of only the planar 3,5-dichlorophenylcyanamide and plotted its vibrational infrared and Raman spectra (Figs. 3 and 4). The vibrational assignments of several fundamental vibrations of the molecule were straightforward based on the calculated PED but many were predicted to mix strongly with other modes, as shown in Table 5, especially bending modes.

There are three stretches that are associated with the C–H modes (S_2–S_6) of the phenyl group and one N–H stretch (S_1) of the cyanamide group. Only the N–H stretch was predicted to have no mixing with other vibrations (100% PED as given in Table 5). This mode was predicted at 3,614 cm^{-1} and 2,647 cm^{-1} in the spectra of the d_1 species (Table 6). The three C–H stretches were calculated at 3,199, 3,189, 3,180, 3,173 and 3,157 cm^{-1} in

Table 5 Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311+G** level for planar 3,5-dichlorophenylcyanamide

Sym.	No.	B3LYP				PED
		Freq.	IR Int.	Raman Act.	Depol. Ratio	
A'	ν_1	3614	74.2	112.7	0.1	99% S$_6$ (N–H str.)
	ν_2	3219	1.7	63.4	0.3	100% S$_5$ (δ-CH str.)
	ν_3	3194	1.7	39.2	0.2	51% S$_1$ (β-CH antisym. str.), 49% S$_2$ (β-CH sym. str.)
	ν_4	3180	2.2	75.5	0.3	51% S$_2$ (β-CH sym. str.), 49% S$_1$ (β-CH antisym. str.)
	ν_5	2342	230.9	219.9	0.3	91% S$_8$ (NCN antisym. str.)
	ν_6	1639	330.5	65.9	0.6	63% S$_{20}$ (ring def.), 19% S$_{10}$ (β-CH in-plane bend)
	ν_7	1626	101.5	17.3	0.7	66% S$_{23}$ (ring def.), 10% S$_{15}$ (N–H in-plane bend)
	ν_8	1519	93.4	2.7	0.3	40% S$_{15}$ (N–H in-plane bend), 16% S$_{24}$ (ring def.), 13% S$_{11}$ (β-CH in-plane bend), 10% S$_{14}$ (δ-CH in-plane bend)
	ν_9	1462	83.6	2.6	0.2	34% S$_{21}$ (ring def.), 17% S$_{10}$ (β-CH in-plane bend), 16% S$_{20}$ (ring def.), 11% S$_7$ (ring-N str.)
	ν_{10}	1425	37.3	3.3	0.6	29% S$_{15}$ (NH in-plane bend), 22% S$_{24}$ (ring def.)
	ν_{11}	1334	15.4	2.3	0.1	57% S$_{22}$ (ring def.), 21% S$_{14}$ (δ-CH in-plane bend), 20% S$_{11}$ (β-CH in-plane bend)
	ν_{12}	1287	26.4	22.7	0.1	21% S$_7$ (ring-N str.), 16% S$_{11}$ (β-CH in-plane bend), 11% S$_{22}$ (ring def.)
	ν_{13}	1266	7.5	7.5	0.1	29% S$_{22}$ (ring def.), 25% S$_{11}$ (β-CH in-plane bend), 10% S$_7$ (ring-N str.)
	ν_{14}	1142	15.7	0.9	0.3	43% S$_9$ (NCN sym. str.)
	ν_{15}	1134	25.6	3.5	0.1	38% S$_{10}$ (β-CH in-plane bend), 37% S$_{21}$ (ring def.)
	ν_{16}	1119	41.5	0.5	0.2	30% S$_{24}$ (ring def.), 26% S$_{14}$ (δ-CH in-plane bend), 15% S$_9$ (NCN sym. str.)
	ν_{17}	1011	1.5	64.2	0.1	59% S$_{25}$ (ring def.), 39% S$_{19}$ (ring breathing)
	ν_{18}	934	47.9	2.4	0.6	25% S$_7$ (ring-N str.), 17% S$_4$ (γ-CCl sym. str.), 11% S$_{26}$ (ring def.)
	ν_{19}	813	86.9	0.4	0.7	53% S$_3$ (γ-CCl antisym. str.), 30% S$_{27}$ (ring def.)
	ν_{20}	695	10.7	1.3	0.7	34% S$_{18}$ (CNC in-plane bend), 20% S$_{26}$ (ring def.), 17% S$_{16}$ (NCN in-plane bend)
	ν_{21}	466	3.2	0.9	0.2	39% S$_{26}$ (ring def.,) 18% S$_{13}$ (γ-CCl in-plane bend), 12% S$_7$ (ring-N str.), 11% S$_{17}$ (ring-NCN in-plane bend)
	ν_{22}	452	2.6	0.6	0.7	35% S$_{13}$ (γ-CCl in-plane bend), 22% S$_{16}$ (NCN in-plane bend), 18% S$_{17}$ (ring-NCN in-plane bend)
	ν_{23}	429	3.2	1.5	0.7	50% S$_{27}$ (ring def.), 30% S$_3$ (γ-CCl antisym. str.)
	ν_{24}	389	2.6	11.5	0.1	54% S$_4$ (γ-CCl sym. str.), 18% S$_{19}$ (ring breathing), 12% S$_{25}$ (ring def.)
	ν_{25}	247	2.8	7.0	0.5	30% S$_{13}$ (γ-CCl in-plane bend), 23% S$_{16}$ (NCN in-plane bend), 15% S$_{17}$ (ring-NCN in-plane bend), 10% S$_{18}$ (CNC in-plane bend)
	ν_{26}	189	0.5	1.8	0.7	88% S$_{12}$ (γ-CCl in-plane bend)
	ν_{27}	103	6.4	4.2	0.6	36% S$_{18}$ (CNC in-plane bend), 31% S$_{17}$ (ring-NCN in-plane bend), 21% S$_{16}$ (NCN in-plane bend)

Table 5 (continued)

Sym.	No.	B3LYP				PED
		Freq.	IR Int.	Raman Act.	Depol. Ratio	
A"	v_{28}	888	15.2	0.1	0.8	43% S_{28} (β-CH def), 34% S_{29} (β-CH and ring-NCN def.)
	v_{29}	867	7.2	0.3	0.8	77% S_{32} (γ-CCl and δ-CH def.), 12% S_{28} (β-CH def)
	v_{30}	860	37.6	0.4	0.88	39% S_{28} (β-CH def), 28% S_{29} (β-CH and ring-NCN def.), 16% S_{35} (ring def.), 13% S_{32} (γ-CCl and δ-CH def.)
	v_{31}	686	14.1	0.2	0.8	63% S_{35} (ring def.), 36% S_{30} (β-CH and ring-NCN def.)
	v_{32}	576	0.4	0.2	0.8	53% S_{30} (β-CH and ring-NCN def.), 34% S_{36} (ring def.), 14% S_{29} (β-CH and ring-NCN def.)
	v_{33}	549	0.4	0.1	0.7	52% S_{37} (ring def.), 39% S_{31} (γ-CCl def.)
	v_{34}	508	4.3	2.0	0.8	99% S_{38} (NCN out-of-plane bend)
	v_{35}	277	80.0	0.8	0.8	75% S_{34} (N–H out-of-plane bend), 16% S_{39} (HNCN asym. torsion)
	v_{36}	223	12.1	1.8	0.8	59% S_{36} (ring def.), 20% (β-CH and ring-NCN def.)
	v_{37}	192	0.5	0.9	0.8	54% S_{31} (γ-CCl def.), 43% S_{37} (ring def.)
	v_{38}	151	2.3	0.1	0.8	91% S_{33} (γ-CCl and δ-CH def.)
	v_{39}	51	6.8	0.5	0.8	72% S_{39} (HNCN asym. torsion), 24% S_{34} (N–H out-of-plane bend)

[a] IR intensities and Raman activities are calculated in km mol^{-1} and A^4 amu^{-1} respectively

Table 6 Calculated vibrational frequencies (cm^{-1}) at B3LYP/6-311+G** level of d_0-, d_1- and d_3-3,5-dichlorophenylcyanamide

Sym.	No.	Wavenumbers			Assignments[a]
		c-C$_6$H$_3$Cl$_2$-NHCN	c-C$_6$H$_3$Cl$_2$-NDCN	c-C$_6$D$_3$Cl$_2$-NHCN	
A'	v_1	3614	2646	3613	N–H stretch
	v_2	3219	3219	2381	*γ-CH symmetric*
	v_3	3194	3194	2362	*β-CH antisymmetric and symmetric stretches*
	v_4	3180	3179	2351	*β-CH symmetric, δ-CH and γ-CH antisymmetric stretches*
	v_5	2342	2342	2343	NCN antisymmetric stretch
	v_6	1639	1639	1615	Ring deformation
	v_7	1626	1616	1610	Ring deformation
	v_8	1519	1478	1493	*N–H in-plane bend*
	v_9	1462	1350	1406	*Ring deformation*
	v_{10}	1425	1528	1367	*N–H in-plane bend and ring deformation*
	v_{11}	1334	1333	1313	*Ring deformation*
	v_{12}	1287	1278	1249	*Ring-N stretch*
	v_{13}	1266	1174	1136	*Ring deformation and β-CH in-plane bend*
	v_{14}	1142	1134	1000	*NCN symmetric stretch*
	v_{15}	1134	1204	970	*β-CH in-plane bend and ring deformation*
	v_{16}	1119	1123	934	*Ring deformation and δ-CH in-plane bend*
	v_{17}	1011	1015	855	*Ring deformation and ring breathing*
	v_{18}	934	913	852	*Ring-N stretch and γ-C–Cl symmetric stretch*
	v_{19}	813	812	682	γ-C–Cl antisymmetric stretch and ring deformation
	v_{20}	695	681	452	CNC in-plane bend and ring deformation
	v_{21}	466	462	431	*Ring deformation and γ-C–Cl in-plane bend*
	v_{22}	452	449	452	*γ-C–Cl and NCN in-plane bends*
	v_{23}	429	428	419	Ring deformation and γ-C–Cl antisymmetric stretch
	v_{24}	389	389	388	γ-C–Cl symmetric stretch
	v_{25}	247	245	246	γ-C–Cl in-plane bend and NCN in-plane bend
	v_{26}	189	189	189	γ-C–Cl in-plane bend
	v_{27}	103	103	103	*CNC and ring-NCN in-plane bends*
A"	v_{28}	888	888	804	*β-CH and (β-CH and ring-NCN) deformations*
	v_{29}	867	867	791	(γ-CCl and δ-CH deformation)
	v_{30}	860	860	728	*β-CH and (β-CH and ring-NCN) deformations*
	v_{31}	686	686	715	Ring deformation
	v_{32}	576	576	543	(β-CH and ring-NCN deformation) and ring deformation
	v_{33}	549	548	531	Ring and γ-C–Cl deformations
	v_{34}	508	506	503	NCN out-of-plane bend
	v_{35}	277	239	276	N–H out-of-plane bend
	v_{36}	223	196	209	Ring deformation
	v_{37}	192	188	179	γ-C–Cl and ring deformations
	v_{38}	151	147	149	(γ-CCl and δ-CH deformation)
	v_{39}	50	50	50	HNCN asymmetric torsion

[a] Italic denotes vibrational modes with PED values lower than 45% in Table 5

the spectrum of the d_0 species and at 2,372, 2,361, 2,350, 2,341 and 2,330 cm^{-1} in the spectrum of the d_3 dichloride (Tables 5 and 6).

The antisymmetric NCN stretch with high infrared intensity and Raman activity could be assigned with confidence to the calculated wavenumber at 2,337 cm^{-1} (91% S_8) in the spectrum of 3,5-dichlorophenyl-cyanamide. This was not the case for the assignments of the corresponding symmetric stretch (S_9), two C–Cl (S_3 and S_4) stretches, the ring–N stretch (S_7) and the ring breathing (S_{19}) modes, which were all predicted to couple strongly with other vibrations, as shown in Table 5. However, the ring breathing is very characteristic and has the highest Raman activity below 1,200 cm^{-1} in the Raman spectra of cyclic compounds. Therefore, this mode could be assigned to the calculated wavenumber at 1,014 cm^{-1} (Table 5). The two C–Cl stretches were predicted to have PED value of about 53% (Table 5).

Similarly, many of the skeletal modes associated with bendings of the heavy atoms were calculated to mix considerably with other vibrations and hence they could not be assigned clearly. The lowest HNCN torsional mode in the spectrum of 3,5-dichlorophenylcyanamide was calculated at 57 cm^{-1} with a PED value of 74% S_{21}.

In conclusion, we optimized the structure of 3,5-dichlorophenylcyanamide at DFT-B3LYP/6-311+G** and MP2/6-311+G** levels to include diffuse and polarization functions in the calculations. The calculated C–N rotational barrier of about 5 kcal mol^{-1} in 3,5-dichlorophenylcyanamide supports the stability of the molecule in the planar conformation as a result of pronounced conjugation between the cyanamide and the phenyl groups. We carried out normal coordinate analyses for such relatively large molecule. We then calculated the PEDs among the symmetry coordinates of the normal modes of the molecule and provided reliable vibrational assignments on the basis of the calculated PED values and isotopic substitution.

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