First Principle Gas Phase Study of the Trans and Gauche Rotamers of 1,2-Diisocyanoethane, 1,2-Diisocyanodisilane and Isocyano(isocyanomethyl)silane

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Abstract. The trans and gauche rotamers of 1,2-diisocyanoethane, 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane have been studied in the gas phase. A transition state has also been obtained for the interconversion of these rotamers. The methods used are MP2 and DFT/B3LYP and the basis sets used for all atoms are 6-311++G(d,p). The optimised geometries, dipole moments, moment of inertia, energies, energy differences and rotational barriers are reported. Vibrational frequencies of the rotamers are presented with appropriate assignments. The results indicate that the trans rotamer is more stable and the G2MP2 rotational energy differences are 2.97 kJ/mol (1,2-diisocyanoethane), 3.02 kJ/mol (isocyano(isocyanomethyl)silane) and 2.12 kJ/mol (1,2-diisocyanodisilane). The rotational barrier for 1,2-diisocyanoethane is larger than its energy difference but the barrier becomes comparable to the energy difference for isocyano(isocyanomethyl)silane.

Keywords: 1, 2-diisocyanoethane, 1, 2-diisocyanodisilane and isocyano (isocyanomethyl)silane, MP2, DFT/B3LYP, energy difference, rotational barrier.

1 Introduction

1,2-Diisocyanoethane is a symmetrical 1,2-disubstituted ethane and therefore exists as two rotamers namely the trans and gauche rotamers which are in equilibrium [1-5]. 1,2-Dicyanoethane has been the subject of experimental [6] and theoretical conformational studies [7-11]. However 1,2-diisocyanoethane has not been comparably studied although the isocyano group is one of the most polar neutral substituents.

Schrumpf and Martin [12] reported the conformation and vibrational spectra of 1,2-diisocyanoethane by measuring its infrared spectra in the vapour, liquid crystalline solid and several solvents. They also carried out semiempirical computations at the INDO level and concluded that the two forms are of about equal stabilities with the gauche form being slightly favoured. However they pointed about the shortcomings of semi empirical computation, which can be remedied by more refined ab initio level. Schrumpf *et al.* [13] reported the molecular structure of 1,2-diisocyanoethane obtained using the gas electron-diffraction method. They identified two distinct rotamers namely the trans and gauche forms. They concluded that the trans form is

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more stable with a percentage of 56.9 in the equilibrium mixture. In a previous communication [11], a theoretical gas phase study of trans and gauche rotamers of 1,2-dicyanoethane and structurally analogous compounds, 1,2-dicyanodisilane and cyano(cyanomethyl)silane, was reported in terms of molecular structures, energies and infrared frequencies. The results indicate that in general, the energy difference between the trans and gauche rotamers is in the order: 1,2-dicyanoethane > cyano(cyanomethyl)silane > 1,2-dicyanodisilane.

Thus although 1,2-diisocyanoethane has received attention, to the best of our knowledge there have not been studies involving 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane although they are structurally related to 1,2-diisocyanoethane. Some of the motivations of this work are derived from the limited literature of 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane and more importantly, isocyano compounds are widely used as ligands [14] and occur naturally in marine organisms [15].

In this paper, the molecular structures, energy difference (ΔE) between the gauche and trans rotamers, rotational barrier, rotational thermodynamics, and vibrational spectra of the trans and gauche rotamers have been obtained for the title compounds using MP2 and DFT/B3LYP methods. Some of the results obtained are compared with the reported parameters of their isomeric dicyano compounds [11]. The findings of this work are hereby reported.

2 Methods

MP2 and DFT/B3LYP computations have been carried out for molecular geometry optimisation of the trans and gauche rotamers of the title compounds. The trans rotamers of 1,2-diisocyanoethane and 1,2-diisocyanodisilane have been studied in C_{2h} symmetry but the trans rotamer of isocyano(isocyanomethyl)silane has been considered in C_s symmetry. The gauche rotamers of 1,2-diisocyanoethane and 1,2-diisocyanodisilane have been studied in C_2 symmetry but the gauche rotamer of isocyano(isocyanomethyl)silane has been considered in C_1 symmetry. A transition state has also been obtained for the interconversion of these rotamers. The basis sets used for all atoms are 6-311++G(d,p). G2/MP2 computations have also been carried out. Frequency computations have been carried out using the optimised structures. All computations have been done using Gaussian 03W [16] program suite and Gauss View [17] has been used for visualising the rotamers.

3 Results and Discussion

The relevant structural optimised structures of the trans and gauche rotamers of the title compounds are reported in Table 1. Several conclusions can be drawn from Table 1. Firstly, there is little difference between the values of the different parameters obtained using the two methods of theory. Secondly, there is a good comparison between some of the calculated parameters and available literature data 1,2-diisocyanoethane. To be more precise, the reported bond lengths (Å) of C-H, N≡C, C-C and C-N are 1.123. 1.172, 1.529 and 1.424 respectively [13]. Further the torsional angle N-C-C-N for the gauche conformer is reported to be 56.9° [13]. Thirdly, the torsional angles calculated for the gauche rotamers are generally greater from DFT than MP2 computations. Lastly, the moment of inertias calculated for the rotamers follow the order $I_A >> I_B \approx I_C$. Apart from these, the effect of substituting the cyano group by the isocyano group can be found by comparing the results obtained with those reported [11]. It is found that substitution affects mainly the bond length between carbon and nitrogen with the bond being shorter in case of the dicyano compounds. The transition state modeled corresponds to the isocyano group eclipsing

Table 1. Optimised parameters of the trans and gauche rotamers of 1,2-diisocyanoethane, 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane

	MP2		DFT	
	CNCH$_2$CH$_2$NC			
Parameter	Trans	Gauche	Trans	Gauche
r (C-H)/ Å	1.092	1.093	1.092	1.093
r (N≡C)/ Å	1.186	1.187	1.171	1.171
r (C-C)/ Å	1.534	1.529	1.540	1.535
r (C-N)/ Å	1.423	1.423	1.423	1.422
τ (N-C-C-N)/ °	180.0	64.2	180.0	67.6
μ/ Debye	0	5.239	0	5.554
I_A/ GHz	24.689	7.110	25.465	7.579
I_B/ GHz	1.649	2.690	1.633	2.508
I_C/ GHz	1.576	2.110	1.564	2.029
	CNSiH$_2$SiH$_2$NC			
r (Si-H)/ Å	1.470	1.472	1.479	1.479
r (N≡C)/ Å	1.191	1.191	1.178	1.178
r (Si-Si)/ Å	2.349	2.348	2.360	2.360
r (Si-N)/ Å	1.762	1.758	1.758	1.754
τ (N-Si-Si-N)/ °	180.0	64.1	180.0	69.5
μ/ Debye	0	4.584	0	4.836
I_A/ GHz	7.647	3.441	7.833	3.716
I_B/ GHz	1.059	1.494	1.045	1.360
I_C/ GHz	0.951	1.186	0.942	1.126
	CNSiH$_2$CH$_2$NC			
r (Si-H)/ Å	1.446	1.469	1.475	1.478
r (C-H)/ Å	1.094	1.095	1.094	1.095
r ($_{C}$N≡C)/ Å	1.187	1.187	1.172	1.172
r ($_{Si}$N≡C)/ Å	1.191	1.190	1.178	1.178
r (Si-C)/ Å	1.894	1.893	1.905	1.903
r (Si-N)/ Å	1.756	1.750	1.753	1.748
r (C-N)/ Å	1.426	1.424	1.424	1.421
τ (N-Si-C-N)/ °	180.0	63.9	180.0	68.0
μ/ Debye	0.642	6.192	0.451	5.236
I_A/ GHz	12.994	4.299	13.273	5.028
I_B/ GHz	1.347	1.900	1.331	1.911
I_C/ GHz	1.248	1.440	1.237	1.517

Table 2. Energies of the trans and gauche rotamers of 1,2-diisocyanoethane, 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane

			ΔE/ kJ/mol	ΔH/ kJ/mol	ΔH/ kJ/mol	ΔG/ kJ/mol	ΔS J/mol
Level	Trans/Hartrees	Gauche/Hartrees		0 K	298.15 K	298.15 K	298.15 K
1,2-Diisocyanoethane							
MP2/6-311++G(d,p)	-263.553797 (0.073121)*	-263.553770 (0.073350)	0.07		0.20	0.99 (42.7)**	2.64
DFT/B3LYP/ 6-311++G(d,p)	-264.308002 (0.072546)	-264.306678 (0.072599)	3.48		3.33	3.50 (67.2)	0.55
MP2/ 6-311+G(3df,2p)	-263.703031	-263.702261	2.02				
G2MP2	-263.785502 (0.070277)	-263.784369 (0.070364)		2.97	2.70	2.84 (61.1)	0.48
1,2-Diisocyanodisilane							
MP2/6-311++G(d,p)	-765.643099 (0.051346)	-765.642636 (0.051513)	1.22		5.49	5.89 (58.4)	1.36
DFT/B3LYP/ 6-311++G(d,p)	-767.175861 (0.050625)	-767.174855 (0.050591)	2.64		6.09	6.49 (68.2)	1.34
MP2/ 6-311+G(3df,2p)	-765.793665	-765.792823	2.21				
G2MP2	-765.905662 (0.049055)	-765.904854 (0.049077)		2.12	2.34	2.09 (62.0)	-0.50
Isocyano(isocyanomethyl)silane							
MP2/6-311++G(d,p)	-514.604265 (0.061471)	-514.603668 (0.061624)	1.57		1.63	2.56 (60.4)	3.12
DFT/B3LYP/ 6-311++G(d,p)	-515.745887 (0.060865)	-515.744528 (0.060880)	3.57		3.43	3.61 (58.4)	0.60
MP2/ 6-311+G(3df,2p)	-514.754754	-514.753655	2.88				
G2MP2	-514.851786 (0.058859)	-514.850637 (0.058900)		3.02	2.84	2.94 (52.3)	0.32

* Values in bracket are zero point energies in Hartrees; ** Values in bracket are percentage of trans rotamers in the equilibrium mixture at 298.15K.

hydrogen atom. Further, the bond lengths of the transition state structures are comparable to those of the trans and gauche rotamers.

Table 2 summarises the energies of the trans and gauche rotamers, ΔE and related thermodynamical parameters. Some conclusions can be drawn from Table 2. Firstly, for all the three molecules, the trans rotamer has lower energy than the gauche form. Secondly, ΔE is generally larger from DFT than MP2 computations when the same basis set is used. Lastly, the percentage of the trans rotamer can be calculated using the free energy difference (ΔG) between the trans and gauche rotamers and the fact that there are two equivalent gauche forms. It is found that at 298.15 K, in general, the equilibrium mixture is more populated with the trans conformer and this is in agreement with literature for 1,2-diisocyanoethane [13]. The rotational barriers, the energy difference between the gauche rotamer and transition state, for 1,2-diisocyanoethane, 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane are 16.32, 6.59 and 2.32 kJ/mol (MP2) and 11.35, 4.46 and 1.77 kJ/mol (DFT) respectively. It can be found that the rotational barrier decreases and it becomes comparable to the energy difference for isocyano(isocyanomethyl)silane. Apart from these, for a given method, the relative energy indicates that a dicyano compound has lower energy than its isomeric diisocyano compound [11].

Table 3. Vibrational analysis of the trans and gauche rotamers 1,2-diisocyanoethane

		Trans					Gauche			
Vibration	MP2	DFT	Experimental	Mode	Assignment	MP2	DFT	Experimental	Mode	Assignmen
ν_1	3115.4 (0)	3058.2 (0)	2990	A_g	C-H stretch	3170.9 (1.9)	3095.4 (4.2)	2990	A	C-H stretch
ν_2	2134.4 (0)	2219.9 (0)	2155		N≡C stretch	3113.0 (15.5)	3057.5 (18.5)	2958		C-H stretch
ν_3	1513.1 (0)	1494.4 (0)	1445		CH$_2$ scissors	2134.0 (122.9)	2219.9 (184.5)	2155		N≡C stretch
ν_4	1428.5 (0)	1403.7 (0)			CH$_2$ wag	1508.1 (0.05)	1486.7 (0.1)	1445		CH$_2$ scissors
ν_5	1079.4 (0)	1036.5 (0)			C-C stretch	1415.3 (12.4)	1388.4 (12.7)	1358		CH$_2$ wag
ν_6	1017.1 (0)	996.7 (0)	1002		C-NC stretch	1316.8 (0.7)	1308.3 (0.5)	1275		CH$_2$ twist
ν_7	469.4 (0)	459.1 (0)	520		C-CN bend	1112.7 (0.02)	1086.6 (0.5)	1073		C-C stretch
ν_8	186.0 (0)	196.3 (0)	209		C-N-C bend	1066.9 (8.6)	1037.3 (7.7)	1002		CH$_2$ rock
ν_9	3192.2 (1.8)	3117.5 (5.3)	2998	A_u	C-H stretch	851.8 (11.1)	821.1 (8.6)	823		C-NC stretch
ν_{10}	1268.5 (4.1)	1258.0 (3.1)	1231		CH$_2$ twist	395.6 (0.4)	389.3 (0.3)	395		C-C-N bend
ν_{11}	804.5 (0.03)	794.6 (2.8)	778		CH$_2$ rock	304.4 (0.6)	299.7 (0.9)	308		C-N-C bend
ν_{12}	280.6 (2.8)	297.9 (4.1)	306		C-N-C bend	167.7 (0.6)	173.4 (0.6)	184		C-N-C bend
ν_{13}	82.5 (23.1)	84.1 (20.4)			torsion	86.2 (4.4)	82.2 (4.6)	108		torsion
ν_{14}	3154.0 (0)	3096.1 (0)	2958	B_g	C-H stretch	3180.9 (2.8)	3106.1 (6.1)	2990	B	C-H stretch
ν_{15}	1326.9 (0)	1323.8 (0)	1022		CH$_2$ twist	3111.3 (2.7)	3054.1 (2.9)	2958		C-H stretch
ν_{16}	1043.1 (0)	1108.5 (0)			CH$_2$ rock	2136.5 (100.5)	2217.6 (183.3)	2180		N≡C stretch
ν_{17}	336.1 (0)	265.1 (0)	274		C-N-C bend	1508.5 (18.0)	1487.2 (19.6)	1445		CH$_2$ scissors
ν_{18}	3123.7 (12.7)	3067.2 (14.4)	2958	B_u	C-H stretch	1402.2 (19.4)	1390.1 (22.2	1344		CH$_2$ wag
ν_{19}	2137.2 (242.4)	2217.6 (396.7)	2155		N≡C stretch	1285.3 (3.4)	1270.8 (2.5)	1248		CH$_2$ twist
ν_{20}	1517.8 (10.8)	1503.3 (11.9)	1459		CH$_2$ scissors	1047.7 (4.6)	1029.1 (5.0)	1022		C-C stretch
ν_{21}	1334.8 (21.5)	1336.6 (22.1)	1344		CH$_2$ wag	868.5 (12.2)	855.9 (12.7)	834		CH$_2$ rock
ν_{22}	986.0 (43.7)	965.6 (38.2)	945		C-NC stretch	565.2 (18.7)	550.7 (20.1)	558		C-C-N bend
ν_{23}	416.2 (13.5)	416.9 (16.1)	520		C-CN bend	255.5 (0.5)	263.4 (1.0)	274		C-N-C bend
ν_{24}	118.9 (19.5)	126.4 (16.1)	187		C-N-C bend	191.5 (3.6)	196.3 (2.1)	207		C-N-C bend

Frequencies are in (cm^{-1}), values in bracket are intensities in (km mol^{-1}), experimental frequencies are from Ref [12]

Table 4. Vibrational analysis of the trans and gauche rotamers of 1,2-diisocyanodisilane

		Trans				Gauche		
Vibration	MP2	DFT	Mode	Assignment	MP2	DFT	Mode	Assignment
ν_1	2345.5 (0)	2260.4 (0)	A_g	Si-H stretch	2351.9 (14.5)	2264.6 (12.6)	A	Si-H stretch
ν_2	2083.9 (0)	2148.9 (0)		N≡C stretch	2341.0 (88.2)	2254.5 (71.8)		Si-H stretch
ν_3	983.8 (0)	947.7 (0)		SiH_2 scissors	2084.4 (292.5)	2149.4 (406.7)		N≡C stretch
ν_4	894.3 (0)	870.1 (0)		SiH_2 wag	986.8 (76.1)	949.4 (74.8)		SiH_2 scissors
ν_5	659.4 (0)	655.5 (0)		Si-N stretch	889.8 (125.0)	861.9 (83.4)		SiH_2 wag
ν_6	473.6 (0)	454.3 (0)		Si-Si stretch	755.0 (7.3)	739.4 (8.8)		SiH_2 twist
ν_7	266.1 (0)	268.7 (0)		Si-Si-N bend	674.1 (73.8)	669.8 (57.6)		Si-N stretch
ν_8	112.8 (0)	122.2 (0)		Si-N≡C bend	570.3 (13.4)	543.0 (9.7)		SiH_2 rock
ν_9	2361.9 (131.1)	2275.5 (128.9	A_u	Si-H stretch	431.5 (13.9)	401.1 (12.7)		Si-Si stretch
ν_{10}	735.1 (48.3)	726.0 (43.0)		SiH_2 twist	222.1 (1.8)	235.1 (1.4)		Si-Si-N bend
ν_{11}	376.2 (27.3)	368.1 (22.7)		SiH_2 rock	186.7 (0.1)	201.7 (0.1)		Si-N≡C bend
ν_{12}	180.2 (0.4)	201.7 (0.1)		Si-N≡C bend	77.3 (0.08	82.0 (0.3)		Si-N≡C bend
ν_{13}	25.8 (12.0)	32.9 (10.0)		torsion	36.6 (3.3)	33.9 (3.2)		torsion
ν_{14}	2354.3 (0)	2267.1 (0)	B_g	Si-H stretch	2356.3 (115.4)	2269.1 (109.6)	B	Si-H stretch
ν_{15}	754.0 (0)	740.2 (0)		SiH_2 twist	2333.9 (48.2)	2245.3 (46.5)		Si-H stretch
ν_{16}	608.0 (0)	592.3 (0)		SiH_2 rock	2082.2 (187.8)	2144.5 (321.0)		N≡C stretch
ν_{17}	176.3 (0)	197.1 (0)		Si-N≡C bend	963.8 (115.6)	928.6 (85.3)		SiH_2 scissors
ν_{18}	2342.8 (99.9)	2256.8 (91.6)	B_u	Si-H stretch	837.5 (487.9)	811.1 (479.3)		SiH_2 wag
ν_{19}	2082.0 (506.2)	2144.5 (747.0)		N≡C stretch	744.2 (31.2)	731.1 (29.7)		SiH_2 twist
ν_{20}	972.0 (220.6)	943.4 (182.8)		SiH_2 scissors	659.9 (64.7)	656.5 (72.2)		Si-N stretch
ν_{21}	802.6 (594.3)	784.2 (527.5)		SiH_2 wag	431.5 (13.9)	453.6 (42.8)		SiH_2 rock
ν_{22}	658.7 (233.1)	654.2 (215.9)		Si-N stretch	222.1 (1.8)	269.2 (9.1)		Si-Si-N bend
ν_{23}	227.4 (3.7)	242.8 (3.9)		Si-Si-N bend	186.7 (0.1)	195.7 (0.3)		Si-N≡C bend
ν_{24}	61.5 (16.1)	67.4 (13.3)		Si-N≡C bend	111.5 (9.9	116.5 (8.1)		Si-N≡C bend

Frequencies are in (cm^{-1}), values in bracket are intensities in (km mol^{-1})

The calculated infrared raw vibrational frequencies, their intensities and assignments of the trans and gauche rotamers of the title compounds are reported in Tables 3-5 respectively. The experimental infrared vibrational frequencies of the trans and gauche

Table 5. Vibrational analysis of the trans and gauche rotamers of isocyano(isocyanomethyl)silane

		Trans				Gauche		
Vibration	MP2	DFT	Mode	Assignment	MP2	DFT	Mode	Assignment
ν_1	3165.6 (0.004)	3091.7 (0.4)	A''	C-H stretch	3154.3 (0.3)	3078.1 (1.1)	A	C-H stretch
ν_2	2380.8 (74.8)	2292.1 (74.1)		Si-H stretch	3093.6 (7.0)	3033.7 (8.3)		C-H stretch
ν_3	1251.3 (8.0)	1242.7 (6.6)		CH$_2$ twist	2376.4 (67.8)	2290.0 (64.7)		Si-H stretch
ν_4	869.9 (22.4)	855.0 (21.3)		CH$_2$ rock	2355.2 (78.7)	2268.2 (69.7)		Si-H stretch
ν_5	724.6 (32.1)	713.0 (30.1)		SiH$_2$ twist	2127.6 (80.3)	2211.8 (152.4)		$_{\mathrm{C}}$N≡C stretch
ν_6	507.0 (14.9)	502.7 (13.4)		SiH$_2$ rock	2087.4 (246.5)	2150.1 (363.3)		$_{\mathrm{Si}}$N≡C stretch
ν_7	268.9 (0.9)	279.7 (1.5)		C-N≡C bend	1474.6 (13.1)	1460.3 (13.3)		CH$_2$ scissors
ν_8	177.8 (0.05)	198.7 (0.005)		Si-N≡C bend	1292.1 (2.2)	1271.5 (1.2)		CH$_2$ wag
ν_9	52.7 (18.3)	55.1 (16.5)		torsion	1258.9 (14.7)	1250.8 (12.4)		CH$_2$ twist
ν_{10}	3103.6 (5.8)	3046.6 (5.9	A'	C-H stretch	993.1 (13.1)	976.7 (2.3)		C-N stretch
ν_{11}	2366.5 (43.6)	2279.2 (41.3		Si-H stretch	985.1 (125.4)	950.4 (113.1)		SiH$_2$ scissors
ν_{12}	2125.3 (83.7)	2209.2 (137.0)		$_{\mathrm{C}}$N≡C stretch	921.6 (278.5)	900.4 (261.3)		SiH$_2$ wag
ν_{13}	2087.0 (268.4)	2150.2 (405.5)		$_{\mathrm{Si}}$N≡C stretch	814.0 (24.8)	794.1 (22.3)		SiH$_2$ twist
ν_{14}	1476.2 (9.8)	1465.3 (9.9)		CH$_2$ scissors	742.1 (26.4)	729.4 (24.7)		SiH$_2$ twist
ν_{15}	1285.2 (6.8)	1265.3 (4.3)		CH$_2$ wag	714.0 (24.6)	701.7 (28.3)		Si-C stretch
ν_{16}	993.3 (83.6)	968.4 (30.8)		SiH$_2$ scissors	547.5 (72.0)	635.8 (62.4)		Si-N stretch
ν_{17}	978.8 (28.1)	956.7 (64.4)		SiH$_2$ scissors	575.5 (42.9)	556.9 (35.6)		SiH$_2$ rock
ν_{18}	880.8 (335.7)	864.6 (301.2)		SiH$_2$ wag	380.8 (11.7)	378.4 (12.1)		S-C-N bend
ν_{19}	737.8 (19.8)	711.6 (18.3)		Si-C stretch	282.5 (0.9)	283.1 (0.9)		C-N≡C bend
ν_{20}	669.4 (100.0)	664.4 (87.0)		Si-N stretch	267.7 (2.1)	273.1 (2.5)		C-N≡C bend
ν_{21}	375.3 (1.3)	375.2 (2.1)		C-N≡C bend	186.2 (0.4)	198.2 (0.1)		Si-N≡C bend
ν_{22}	275.0 (5.5)	281.6 (6.1)		Si-N≡C bend	149.6 (7.3)	156.8 (5.6)		C-N≡C bend
ν_{23}	148.0 (0.7)	158.6 (0.5)		C-N≡C bend	114.2 (0.6)	120.7 (0.5)		Si-N≡C bend
ν_{24}	81.9 (18.7)	89.2 (15.9)		Si-N≡C bend	57.8 (4.6)	53.2 (4.8)		torsion

Frequencies are in (cm^{-1}), values in bracket are intensities in (km mol^{-1})

rotamers of 1,2-diisocyanoethane obtained in the liquid phase are also included in Table 3. The 24 modes of vibrations account for the irreducible representations $\Gamma_v = 8A_g + 5A_u + 4B_g + 7B_u$ of the C_{2h} point group of the trans rotamer of1,2-diisocyanoethane and

1,2-diisocyanodisilane and $\Gamma_v = 13A + 11B$ of the C_2 point group of the gauche rotamer of 1,2-diisocyanoethane and 1,2-diisocyanodisilane. Further, the 24 modes of vibrations account for the irreducible representations $\Gamma_v = 9A'' + 15A'$ of the C_s point group of the trans rotamer of isocyano(isocyanomethyl)silane and $\Gamma_v = 24A$ of the C_1 point group of the gauche rotamer of isocyano(isocyanomethyl)silane. These infrared vibrational frequencies are dominated by the high intensity of the N≡C stretching frequency. It is interesting to note the close agreement of the calculated infrared raw vibrational frequencies (gas phase) and experimental literature data (liquid phase) [12] for 1,2-diisocyanoethane. Apart from these, it can be found that substitution of the cyano groups by the isocyano groups affects mainly the vibrational frequencies where the cyano groups are attached [11].

4 Conclusion

This paper reports the gas phase theoretical study of the trans and gauche rotamers of 1,2-diisocyanoethane, novel 1,2-diisocyanodisilane and isocyano(isocyanomethyl)-silane in terms of optimised molecular structures and infrared raw vibrational frequencies. The rotational barrier and related thermodynamic parameters are also given. The trans rotamer is more stable than gauche rotamer. An interesting outcome of this work is that some of the calculated parameters for 1,2-diisocyanoethane compare satisfactorily with experimental literature data. More interestingly, although the changes in structure and energy are relatively small when carbon is substituted by silicon, data for the trans and gauche rotamers for the novel 1,2-diisocyanodisilane and isocyano(isocyanomethyl)silane could serve as a reliable set of reference as their literature is limited.

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