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X-ray crystallographic, spectroscopic and quantum chemical studies on ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate

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Abstract

Structural and spectral characteristics of ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate have been studied by methods of X-ray crystallography, infrared spectroscopy and quantum chemistry. The compound crystallizes in monoclinic space group $P2_1/n$ with unit cell parameters a = 4.26(1) Å, b = 11.16(1) Å, c = 19.63(3) Å and $\beta = 95.5(1)^\circ$. The X-ray based three-dimensional structure analysis has been carried out by direct methods and fully refined. Density functional theory calculations for potential energy curves, optimized geometries and vibrational spectra have been carried out using 6-31G and 6-31G** basis sets and B3LYP functionals. These suggest the possibility of existence of two structural isomers for the molecule—a more stable s-*cis* and a less stable s-*trans* isomer, having enthalpy difference of 2.85 kcal/mol. The optimized molecular geometry is in agreement with experimental geometry from X-ray analysis and suggests a preferential s-*cis* conformation for the molecule in the solid state. Based on experimental and theoretical studies, it may be concluded that the molecule has an almost planar conformation with the cyanide group also lying in the molecular plane; the deviation from planarity does not exceed 3°. The structure is stabilized by the presence of intra-molecular and inter-molecular interactions.

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1. Introduction

2-Cyanoacrylates and their derivatives have received considerable attention recently [1–5] because of their versatile biological activity and the possibility of application in agrochemistry. Some of the 2-cyanoacrylates are also known to exhibit Hill inhibitory activity [3]. Song et al. [1] have reported anti-cancer bioactivity in some 2-cyano-3,3-dimethyl thioacrylates for which they carried out detailed spectroscopic and structural studies using methods of infrared spectroscopy, NMR and X-ray crystallography. It is inferred that molecules like ethyl 2-cyano-3,3-dimethyl thio acrylate maintain a planar structure due to strong hydrogen bonding. In the present communication, we are reporting a detailed study of the three-dimensional structure, physico-chemical properties and spectral characteristics of an analogous molecule ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate by experimental and theoretical methods of X-ray crystallography, infrared spectroscopy and quantum chemistry. A complete analysis of the vibrational spectra using density functional theory (DFT) is also being provided.

2. Methodology

2.1. Experimental methods

The synthesis of ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate has been carried out by making an equimolar mixture of ethylcyanoacetate and *N*,*N*-dimethyl formamide dimethylacetate, which was refluxed in methanol for about 2–5 h and cooled. The solvent was removed by rotatory evaporation. The semi-solid mass was obtained and recrystallized from *n*-hexane.

Transparent needle shaped crystal (dimensions: $0.30 \text{ mm} \times 0.15 \text{ mm} \times 0.10 \text{ mm}$) of grown material was mounted on the goniometer of the CAD4 single crystal diffractometer. The three-dimensional data has been collected by using Mo K α radiation

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Fig. 1. Numbering scheme of atoms of ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate with displacement ellipsoids drawn at 50% probability level.

 $(\lambda = 0.71073)$ in the θ range of 2.10–24.99° by using $\omega/2\theta$ scan mode. A total of 1747 reflections were recorded, out of which 1545 were found unique (index range: $0 \le h \le 5$, $0 \le k \le 13$, $-23 \le l \le 23$) and 889 were treated as observed $[F_0 > 4\sigma(F_0)]$. Two standard reflections (1, -2, -1) and (1, -3, 3), measured after every 100 reflections, showed no significant variation in the intensity data. The data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied.

The structure determination of the title compound has been carried out by direct methods using SHELXS software [6]. Full-matrix least-squares refinement were carried out by using SHELXL software [7]. Refinement of the positional and isotropic thermal parameters of non-hydrogen atoms led to the reliability-factor of 0.215. Few more cycles of refinement with anisotropic thermal parameters reduced the *R*-factor. The final cycles of refinement with stereo-chemical fixation of hydrogen atoms converged the *R*-factor at 0.095. The maximum and minimum value for the residual electron density is 0.32 and -0.35, respectively. The goodness-of-fit on F^2 was 1.0516. The infrared spectrum of the sample in the 4000–400 cm⁻¹ range was recorded in the KBr pellet on FT-IR spectrophotometer Bruker Vector 22.

2.2. Computational methods

In order to verify the possibility of rotational isomerism in ethyl 2-cyano-3-N,N-dimethyl amino acrylate (CAAC), potential energy curve for asymmetric torsion about C1-C2 bond (Fig. 1) was obtained by calculating the variation in the total energy of the molecule with change in dihedral angle φ (O1C1C2C3) in intervals of 20° in the range of 0–360° by DFT/6-31G method. Geometries of the stable conformers of the molecule were optimized by density functional theory (DFT) using 6-31G** basis set and Becke's three parameter (local, non-local, Hartree-Fock) hybrid exchange functionals with Lee-Yang-Parr correlational functional (B3LYP). The vibrational spectra of the two stable conformers of CAAC were calculated by DFT/6-31G**, using the optimized geometries obtained by the same method and basis set. Since the DFT vibrational frequencies are known to be higher than the experimental frequencies due to neglect of anharmonicity effects, they were scaled down by wavenumber linear scaling (WLS) procedure

Table 1 Crystal data and structure refinement for ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate

C ₈ H ₁₂ N ₂ O ₂ 168.20 293(2) K 0.71073 Å
Monoclinic, $P2_1/n$
$a = 4.258(5) \text{ Å}, \alpha = 90^{\circ}$ $b = 11.163(12) \text{ Å}, \beta = 95.50(11)^{\circ}$ $c = 19.632(30) \text{ Å}, \gamma = 90^{\circ}$
928.8(21) Å ³ 4, 1.203 Mg/m ³ 360 2.10–24.99° $0 \le h \le 5, 0 \le k \le 13, -23 \le l \le 23$
1807/1595 Full-matrix least-squares on F^2 1573/0/140 1.069 R1 = 0.0938, wR2 = 0.2357 R1 = 0.1475, wR2 = 0.3933 0.327 and -0.318 einstein Å ⁻³

suggested by Yoshida et al. [8] using the expression:

 $v_{\text{obs.}} = (1.0087 - 0.0000163v_{\text{calc.}}) v_{\text{calc.}}$

All calculations were performed by using computer software Gaussian 98W [9] and the vibrational modes were analyzed by using the software GaussView [10].

3. Results and discussion

3.1. Structural studies

The crystallographic data for ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate (CAAC) are summarized in Table 1. The final fractional coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are presented in Table 2.

Potential energy curve (Fig. 2) for internal rotation of the molecule about C1–C2 bond, as obtained from DFT/6-31G quantum chemical calculations, shows two energy minima at

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms in ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate

Atom	X	у	z	U (equiv.)
01	5414(10)	6569(3)	4704(2)	0.084(1)
O2	5555(8)	7866(3)	3846(2)	0.069(1)
N1	-138(9)	4202(3)	3560(2)	0.055(1)
N2	1869(11)	6841(4)	2385(3)	0.083(1)
C1	4666(11)	6825(4)	4120(3)	0.058(1)
C2	2762(10)	6101(4)	3626(2)	0.052(1)
C3	1638(10)	5030(4)	3869(2)	0.052(1)
C4	-1385(11)	4251(4)	2853(2)	0.065(1)
C5	-910(17)	3127(5)	3932(3)	0.074(2)
C6	2219(10)	6502(4)	2944(3)	0.057(1)
C7	7399(16)	8649(5)	4322(3)	0.085(2)
C8	8082(29)	9755(7)	3945(5)	0.127(3)

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Fig. 2. Potential energy curve of ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate for rotation about C1–C2 bond. The abscissa is the angle of rotation about C1–C2 bond relative to the s-*cis* conformer for which the dihedral angle φ (O1C1C2C3)=0°. The ordinate represents total energy relative to the s-*cis* conformation.

 $\varphi(O1C1C2C3) = 0^\circ$ and 180° . These correspond to the s-*cis* and s-trans conformations of the molecule in which the C1=O1 and C2=C3 bonds are either on the same side or on opposite sides of the C1–C2 bond (Fig. 1). It may thus be inferred that the molecule can exist in two rotameric conformations s-cis and s-trans; with the former being more stable than the latter. More accurate DFT calculations using 6-31G** basis set show after complete geometry optimization that the total energies of the s-cis and s-trans conformers are -572.03280344 and -572.02826294 Hartree, respectively. The s-cis conformer is, therefore, more stable than s-trans by 2.850 kcal/mol. Further, it is found that the s-cis conformer has to overcome a rotational barrier of 19.496 kcal/mol to change into the s-trans conformer. A rotational barrier of 17.638 kcal/mol has to be overcome for the reverse process. Due to high barrier to internal rotation, the molecule therefore prefers the lower energy s-cis conformation. This result is confirmed by X-ray crystallographic data which indicates the presence of only the more stable s-cis conformer in the crystalline state. A similar observation about preference for a s-cis conformation has been made by Song et al. [1] in some other 2-cyanoacrylates.

The results of X-ray single crystal analysis and the optimized geometries of the s-cis and s-trans conformers of CAAC are given in Tables 3 and 4. Table 5 contains the optimized values of the dihedral angles involving hydrogen atoms. It follows from these tables that there is no significant difference in the molecular geometries of the s-cis and s-trans conformers; the maximum difference in bond lengths and bond angles being 0.01 Å and 5° , respectively. The experimental values of these parameters agree with the optimized values within 0.03 Å and 2° , respectively, for bonds between non-hydrogen atoms. The experimental values of the dihedral angles between non-hydrogen atoms agree with the optimized values for the s-*cis* conformer within 3° and show that in the crystalline state the molecule exists in the scis form. The optimized as well as experimental values of the dihedral angles between non-hydrogen atoms have values close to 0° or 180° and suggest an almost planar conformation of the molecule with the cyanide group also lying in the molecu-

Table 5
Bond lengths (Å) and bond angles (°) of ethyl 2-cyano-3-N,N-dimethyl amino
acrylate

	Experimental	Calculated	
		s-Cis	s-Trans
01–C1	1.1948(63)	1.2207	1.2148
O2-C1	1.3499(56)	1.3486	1.3629
O2-C7	1.4537(69)	1.4449	1.4444
N1-C3	1.3062(56)	1.3416	1.3448
N1-C4	1.4398(62)	1.4598	1.4599
N1-C5	1.4583(74)	1.4589	1.4585
N2-C6	1.1559(70)	1.1667	1.1658
C1-C2	1.4491(62)	1.4812	1.4792
C2-C3	1.3886(62)	1.3803	1.3806
C2-C6	1.4113(66)	1.4212	1.4244
C7–C8	1.4830(109)	1.5163	1.5166
С3—Н3	0.9967(507)	1.0871	1.0843
C4—H4A	0.9600(64)	1.0860	1.0856
C4—H4B	0.9601(72)	1.0964	1.0965
C4-H4C	0.9600(65)	1.0964	1.0965
С5—Н5А	0.9095(849)	1.0908	1.0968
C5-H5B	0.9567(793)	1.0966	1.0966
C5-H5C	0.9975(794)	1.0966	1.0906
C7-H7A	0.9700(89)	1.0946	1.0943
C7—H7B	0.9699(97)	1.0946	1.0942
C8-H8A	1.0515(653)	1.0945	1.0943
C8-H8B	0.8981(719)	1 0935	1 0940
C8-H8C	1.0338(1698)	1.0935	1.0940
C1 - 02 - C7	114 58(37)	116.00	115 31
$C_{3}-N_{1}-C_{4}$	124 38(39)	125.82	126.12
C3-N1-C5	119 86(41)	119.81	119 75
C4-N1-C5	115.36(11) 115.74(41)	114 37	114.12
01 - C1 - 02	121.97(43)	123 50	122.88
01 - C1 - C2	121.97(45) 126.09(45)	124.70	122.00
$01 \ C1 \ C2$ $02 \ C1 \ C2$	120.09(43) 111.04(37)	111 78	112 83
$C_1 - C_2 - C_3$	116.05(38)	114.80	112.85
C1 - C2 - C6	110.05(30)	110.00	117.77
$C_1 C_2 C_0$	119.20(40) 124.67(40)	126.11	114.74
$1 - C^2 - C^2$	124.07(40) 120.72(41)	120.11	123.47
N1 - C5 - C2 N2 - C6 - C2	130.73(41)	132.97	132.03
$N_2 - C_0 - C_2$	177.92(52) 107.45(52)	1/9.49	1/9.49
$U_2 - U_7 - U_8$	107.43(32)	107.49	107.49
$NI = C_3 = H_3$	112.35(2.82)	114.20	113.18
С2-С3-Н3	110.90(2.89)	112.62	114.17
NI-C4-H4A	109.48(0.50)	111.27	111.30
NI-C4-H4B	109.48(0.50)	109.73	109.73
NI-C4-H4C	109.48(0.50)	109.69	109.58
NI-C5-H5A	111./3(5.27)	110.20	110.47
NI-C5-H5B	116.05(4.74)	110.42	110.41
NI-CS-H5C	108.88(4.64)	110.40	110.32
02-C/-H/A	110.23(0.67)	108.87	108.93
02-C/-H7B	110.23(0.63)	108.85	108.92
C/-C8-H8A	101.46(3.80)	109.79	109.81
C/C8H8B	115.54(5.11)	110.91	111.04
C7–C8–H8C	81.90(9.69)	110.91	111.02

E.s.d. values are given in parenthesis.

lar plane. Further, it is observed that significant changes occur in the lengths of bonds C1–O1, C1–C2, C2–C3, C3–N1 and C1–O2 with respect to their normal values as covalent single and double bonds. This indicates delocalization of electron density along the chain N1–C3–C2–C1–O1, which is confirmed by Mulliken population analysis given in Table 6. A similar observation has been reported by Song et al. [1] in the case of other 2-cyanoacrylates.

Table 4 Dihedral angles for non-hydrogen atoms in ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate

Table 6

Atomic population density and dipole moments of s-cis and s-trans conformers of ethyl 2-cyano-3-N,N-dimethyl amino acrylate

	Experimental	Calculated	
		s-Cis	s-Trans
C7-02-C1-01	-1.61(0.66)	0.02	0.00
C7-02-C1-C2	178.29(0.40)	-179.97	180.00
C1O2C7C8	-178.27(0.55)	-179.82	179.34
C4-N1-C3-C2	-0.48(0.76)	0.12	0.05
C5-N1-C3-C2	178.02(0.50)	179.89	179.44
01	2.17(0.71)	0.00	179.84
O1-C1-C2-C6	-176.71(0.47)	180.00	-0.10
O2-C1-C2-C3	-177.73(0.38)	180.00	-0.15
O2-C1-C2-C6	3.39(0.59)	-0.01	179.90
C1-C2-C3-N1	179.12(0.46)	-180.00	179.88
C6-C2-C3-N1	-2.07(0.79)	0.00	-0.18

3.2. Atomic population density, dipole moment and hydrogen bonding

The atomic population densities for the s-*cis* and s-*trans* conformers of CAAC based on Mulliken analysis are given in Table 6, which also contains the calculated dipole moments of the two conformers. It may be noted that the oxygen atoms O1 and O2 have large net negative charge -0.524 and -0.489 and the adjoining carbon atom C1 has a large net positive charge 0.642. Similarly, the nitrogen atoms N1 and N2 also have large negative charge -0.414 and -0.537, respectively. Being attached to more electronegative carbon atoms, all the hydrogen atoms H3, H4A and H5A have significantly large net positive charge 0.150, 0.137 and 0.167. The presence of large amounts of negative charge on O1, O2 and N2 atoms and net positive charge

Table 5

Dihedral angles for hydrogen atoms in ethyl 2-cyano-3-N,N-dimethyl amino acrylate

	s-Cis	s-Trans
С1—02—С7—Н7А	58.60	-59.08
C1-O2-C7-H7B	-58.24	57.74
C4-N1-C3-H3	-179.89	-180.00
C5-N1-C3-H3	-0.12	-0.61
C3-N1-C4-H4A	-0.50	-1.26
C3-N1-C4-H4B	120.11	119.40
C3-N1-C4-H4C	121.08	-121.87
C5-N1-C4-H4A	179.72	179.33
C5-N1-C4-H4B	-59.67	-60.01
C5-N1-C4-H4C	59.13	58.71
C3-N1-C5-H5A	0.21	0.95
C3-N1-C5-H5B	-120.00	119.27
C3-N1-C5-H5C	120.40	121.15
C4-N1-C5-H5A	-179.98	-179.59
C4-N1-C5-H5B	59.81	60.18
C4-N1-C5-H5C	-59.79	-59.40
С1-С2-С3-Н3	0.01	-0.07
С6-С2-С3-Н3	-179.99	179.87
O2-C7-C8-H8A	-179.89	180.00
O2-C7-C8-H8B	60.27	60.35
O2-C7-C8-H8C	-60.05	-60.35

Atom no.	s-Cis		s-Trans	
	Total charge	Net atomic charge	Total charge	Net atomic charge
01	8.524	-0.524	8.494	-0.494
O2	8.849	-0.489	8.514	-0.514
N1	7.414	-0.414	7.414	-0.414
N2	7.537	-0.537	7.529	-0.529
C1	5.356	0.642	5.363	0.637
C2	6.036	-0.036	6.045	-0.045
C3	5.829	0.171	5.832	0.168
C4	6.178	-0.178	6.176	-0.176
C5	6.199	-0.199	6.199	-0.199
C6	5.726	0.274	5.712	0.288
C7	5.942	0.058	5.936	0.064
C8	6.339	-0.339	6.342	-0.342
H3	0.850	0.150	0.857	0.143
H4A	0.863	0.137	0.869	0.131
H4B	0.869	0.131	0.868	0.132
H4C	0.869	0.131	0.868	0.132
H5A	0.833	0.167	0.831	0.169
H5B	0.871	0.129	0.871	0.129
H5C	0.870	0.130	0.871	0.129
H7A	0.883	0.117	0.879	0.121
H7B	0.883	0.117	0.878	0.122
H8A	0.893	0.107	0.886	0.114
H8B	0.874	0.126	0.883	0.117
H8C	0.874	0.126	0.833	0.117
Dipole moment (Debye)	4.655		8.106	

on H3, H4A and H5A atoms may suggest the presence of both inter-molecular as well as intra-molecular hydrogen bonding in the crystalline phase.

The analysis of inter-molecular hydrogen interactions is shown in Fig. 3. In agreement with the quantum chemical predictions, the X-ray diffraction study suggests that atom O1 is related



Fig. 3. Inter-molecular hydrogen interactions in ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate.

Table 7
Inter- and intra-molecular hydrogen bonds in ethyl 2-cyano-3-N,N-dimethyl amino acrylate

Donor—H	Donor···acceptor	H···acceptor	Donor—H···acceptor
(a) Inter-molecular ^a			
C5–H5A	$C5 \cdots O1: 3.40(1)$ (weak)	H5A···O1: 2.54(1) (weak)	C5–H5A···O1 ^b : 160(7) (moderate)
С3—Н3	$C3 \cdots O1: 3.45(1)$ (weak)	H3···O1: 2.54(5) (weak)	$C3-H3 \cdots O1^{b}$: 153(4) (moderate)
C4—H4A	C4…N2: 3.56(1) (weak)	H4AN2: 2.62(1) (weak)	C4—H4A···N2 ^c : 167(1) (moderate)
(b) Intra-molecular ^d			
s-Cis			
С3—Н3	C3···O1: 2.768	H3···O1: 2.282	C3-H3···O1: 104.38
C4—H4B	C4···N2: 3.543	$H4B\cdots N2$	C4—H4B····N2: 158.27
s-Trans			
С3—Н3	C3···O2: 2.694	H3···O2: 2.213	С3—Н3…О2: 104.33
C4—H4B	C4···N2: 3.543	H4B····N2: 2.511	C4—H4B····N2: 158.27

^a Based on X-ray crystallographic analysis.

^b -x+1, -y+1, -z+1.

^c -x - 1/2, +y - 1/2, -z + 1/2.

^d Based on quantum chemical studies.

to atoms C3 and C5 through two inter-molecular hydrogen interactions. Thus, O1 acts as bifurcated acceptor. There also exists one weak C–H···N hydrogen inter-molecular interaction. The details of inter-molecular and intra-molecular hydrogen interactions are presented in Table 7. Using compiled data for a large number of C–H···O and C–H···N contacts, Desiraju et al. [11] find significant statistical directionality even as far out as 3.0 Å, and conclude that these are to be legitimately viewed as 'weak' hydrogen bonds with a greater contribution to packing forces than simple van der Waals attractions. Table 7 also reveals that in the isolated molecule of the s-*cis* isomer of CAAC, there exists the possibility of weak intra-molecular hydrogen bonding between atoms O1 and H3 and N2 and H4B, having inter-atomic distances of 2.282 and 2.511 Å, respectively. In the case of the s-*trans* conformer, there also exists the possibility of a much stronger intra-molecular hydrogen bond C3–H3···O2 owing to a smaller distance of 2.213 Å between atoms H3 and O2.

4. Vibrational analysis

The infrared spectrum of ethyl 2-cyano-3-*N*,*N*-dimethyl amino acrylate (CAAC) in the 4000–400 cm⁻¹ region in KBr pellet is given in Fig. 4. The fundamental frequencies of its *s*-*cis* and *s*-*trans* conformers, as calculated by Density Functional Theory using 6-31G** basis set and B3LYP functionals, are given in Table 8

, which also contains the experimental infrared frequencies and spectral assignments. The atomic numbering used in this table is based on Fig. 1. It may be noted from Table 8 that, with the presently used scaling factors, the observed and calcu-



Fig. 4. Infrared spectrum of ethyl 2-cyano-3-N,N-dimethyl amino acrylate.

Table 8

Experimental and calculated vibrational frequencies, intensities and assignments for s-cis and s-trans conformers of ethyl 2-cyano-3-N,N-dimethyl amino acrylate

S. no.	$v_{\text{expt.}}$ (cm ⁻¹)	(cm ⁻¹) s-Cis s-Trans		Assignments ^a			
			$v_{\text{calc.}}$ (cm ⁻¹)	Intensity (kM/mol)	$\overline{\nu_{\text{calc.}} (\text{cm}^{-1})}$	Intensity (kM/mol)	
1		24	2.30	42	0.00	O2–C7 torsion	
2		55	0.15	53	0.53	C3–N1 torsion	
3		62	3.27	67	0.78	N1-C4 torsion	
4		82	1.51	82	0.35	N1-C5 torsion, C7-C8 torsion	
5		94	3.21	96	1.53	i.p. skeletal bend	
6		110	0.02	102	0.31	C1–C2 torsion	
7		143	0.00	139	0.01	N1-C4 torsion, N1-C5 torsion	
8		159	5.09	161	5.69	C6≡N2 bend	
9		202	1.76	193	2.12	o.p. skeletal bend	
10		222	7.94	219	2.04	i.p. skeletal bend	
11		263	0.08	267	0.16	i.p. skeletal bend	
12		285	0.36	287	9.16	C3–N1–C5 bend	
13		291	9.00	294	1.34	o.p. skeletal bend	
14		352	9.11	364	13.86	C1O2C7 bend	
15	424 (w)	395	8.32	399	1.35	i.p. skeletal bend	
16		404	1.80	393	2.69	$C2 \equiv C6 - N2 \text{ o.p. bend}$	
17		460	0.05	446	0.80	$C2 \equiv C6 - N2$ i.p. bend	
18	484 (vw)	475	1.34	486	1.27	C5N1C4 i.p. bend	
19		549	2.52	511	4.23	C1C2C6 i.p. bend	
20	568 (w)	592	4.77	590	4.46	C6≡N2 o.p. bend	
21	759(m)	751	23.43	748	21.98	C2C1O2 i.p. bend	
22		783	4.30	795	5.46	O1C1O2 i.p. bend	
23		808	0.09	811	0.11	CH ₂ rock	
24	813 (w)	828	3.87	824	10.89	N1C3C2 bend, C2–C6 str., N1–C5 str.	
25	850(w)	866	10.37	889	2.08	C1O2C7 bend	
26	894 (w)	916	0.26	893	5.83	N1C4 str., C7C8 str.	
27	950(w)	989	2.18	962	2.14	C1H3 o.p. def.	
28	1025 (w)	1037	9.41	1031	0.35	C7C8 str., O2C7 str.	
29		1075	20.13	1076	18.80	CH ₃ asym. def. (N1–C5)	
30	1092 (s)	1111	358.2	1100	333.68	CH ₃ asym. def. (N1–C4)	
31		1121	0.56	1120	0.41	CH_3 asym. def. (N1–C5)	
32		1130	13.64	1128	11.81	CH_3 asym. def. (C7–C8)	
33	1148 (m)	1152	54.24	1142	89.65	C2C6 str., C3N1C4 def.	
34		1165	1.88	1165	1.80	CH ₃ asym. def. (N1–C5), CH ₃ asym. def. (N1–C4)	
35		1172	4.13	1174	3.91	CH ₂ asym. def.	
36	1222 (s)	1242	219.57	1223	230.09	N1C4 str., N1C5 str., C1O2 str.	
37		1279	0.54	1281	0.44	CH ₂ twist	
38	1289 (s)	1293	711.02	1295	484.57	C1O2 str., C1C2 str.	
39	1365 (m)	1384	35.53	1387	23.95	CH ₃ sym. def. (C7–C8)	
40		1398	19.31	1401	3.74	C3H3 i.p. bend	
41	1437 (m)	1417	6.34	1419	10.68	CH_2 sym. def., CH_3 asym. def. (N1-C5)	
42		1432	1.80	1428	94.90	C1–C2, N1–C3 str.	
43		1446	8.38	1447	24.29	CH_3 sym. def. (N1–C5)	
44	1460	1460	69.88	1464	33.40	CH_3 sym. def. (N1–C4)	
45		1466	2.62	1466	5.14	CH_3 asym. def. (N1–C5)	
46	1480(b)	1476	4.88	1478	5.52	CH ₃ asym. def. (C7–C8)	
47		1484	16.98	1484	16.06	CH ₃ asym. def. (N1–C5), CH ₃ asym. def. (N1–C4)	
48		1487	2.57	1489	2.82	CH ₃ asym. def. (C7–C8), CH ₂ asym. def.	
49		1491	12.29	1492	14.06	CH ₃ asym. def. (N1–C5)	
50		1508	5.79	1510	5.00	CH ₃ asym. def. (C7–C8), CH ₂ asym. def.	
51		1516	6.26	1517	6.44	CH ₃ asym. def. (N1 $-$ C5), CH ₃ asym. def. (N1 $-$ C4)	
52	1622 (vs)	1649	602.94	1655	573.95	C2=C3 str., N1-C5 str.	
53	1700 (s)	1747	276.74	1758	278.82	C1=01 str.	
54	2204 (s)	2251	69.50	2259	60.50	N2≡C6 str.	
55		2907	35.81	2906	36.09	CH ₃ sym. str. (N1–C6)	

Table 8 ((Continued)
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S. no.	$v_{\text{expt.}}$ (cm ⁻¹)	s-Cis		s-Trans		Assignments ^a	
			$\nu_{\text{calc.}} (\text{cm}^{-1})$	Intensity (kM/mol)	$v_{\text{calc.}}$ (cm ⁻¹)	Intensity (kM/mol)	
56	2898(m)	2915	96.53	2914	93.96	CH ₃ sym. str. (N1–C5)	
57	2934 (m)	2931	16.59	2929	16.31	CH ₃ sym. str. (C7–C8)	
58		2937	21.42	2941	19.38	CH ₂ str.	
59	2982(s)	2957	37.52	2956	35.96	CH ₃ asym. str. (N1–C4)	
60		2962	11.07	2960	12.77	CH ₃ asym. str. (N1-C5)	
61		2974	11.99	2976	4.62	CH ₂ asym. str.	
62	2982(s)	2999	25.30	2997	26.15	CH ₃ asym. str. (C7–C8)	
63		3008	31.87	3003	41.45	CH ₃ asym. str. (C7–C8)	
64	3018(w)	3026	10.61	3021	11.76	CH ₃ asym. str. (N1-C4)	
65		3053	1.87	3073	3.98	C1H3 str.	
66		3070	2.96	3080	0.25	CH ₃ asym. str. (N1–C5)	

Abbreviations: w weak, vw very weak, m medium, s strong, vs very strong, b broad, i.p. in-plane, o.p. out-of-plane. ^a Atom numbering as per Fig. 1.

lated frequencies agree on an average within 20 cm^{-1} and the observed intensities are fairly reproduced by the calculations.

Despite the fact that both in the s-cis and s-trans conformations, the CAAC molecule is almost planar (deviations from planarity not exceeding 3°), for the purpose of vibrational analysis, it was taken as belonging to C_1 symmetry group. In this case, the vibrational frequencies of the heavy atom skeleton may be broadly divided into in-plane and out-of-plane modes (Table 8), with very small interaction between them. This results in the appearance of a large number of calculated frequencies, both stretch and deformation, for the three methyl groups with very few corresponding experimental frequencies. It is also noted that the attachment of the methyl group to a nitrogen atom, which is more polar than a carbon atom, shifts the frequency of its symmetric deformation mode by about $100 \,\mathrm{cm}^{-1}$ from $1365 \,\mathrm{cm}^{-1}$ (v_{39}) in C–CH₃ to 1460 cm⁻¹ (v_{44}) in N–CH₃, i.e. to a region close to that for asymmetric deformation modes. The very strong absorption band at $1622 \,\mathrm{cm}^{-1}$ and a strong band at $1700 \,\mathrm{cm}^{-1}$ may be assigned to the stretch modes of C=C and C=O bonds. The strong band at $2204 \,\mathrm{cm}^{-1}$ may be assigned to the stretch mode of the nitrile group. Some other prominent absorption bands in the spectrum at 1092 (s) cm^{-1} , 1222 (s) cm^{-1} , 1289 (s) cm^{-1} and 2982 (s) cm^{-1} may be assigned to methyl asymmetric deformation (v_{30}) and N1–C4 (v_{36}) , C1–O2 (v_{38}) and methyl asymmetric stretch modes, respectively. It is also found that while the calculated frequencies of almost all the bands of the s-cis and s-trans conformers are very close to each other, their intensities are significantly different, particularly for bands corresponding to the skeletal modes such as in-plane skeletal bend (v_{15}) , C1–O2–C7 bend (v_{25}) , C1–O2 stretch (v_{38}) , C1–C2 stretch (v_{42}) and C=C stretch (v_{52}) . Finally, a comparison of the calculated vibrational frequencies and intensities of the two stable isomers of CAAC with the corresponding experimental values lead to the conclusion that in the solid state the molecule is primarily in the s-cis conformation. This is in agreement with the findings based on X-ray crystallographic studies.

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References

- [1] B. Song, S. Yang, H. Zhong, L. Jin, D. Hu, G. Liu, J. Fluor. Chem. 126 (2005) 87–92.
- [2] H.-K. Sun, Q.-M. Wang, R.-Q. Huang, H. Li, Y.-H. Li, J. Organomet. Chem. 655 (2002) 182–185.
- [3] Q.M. Wang, H.K. Sun, R.Q. Huang, Heteroatom Chem. 15 (2004) 67-70.
- [4] Z.J. Wang, R. Neidlein, C. Krieger, Heterocyclic Commun. 5 (3) (1999) 203.
- [5] Z. Denchev, M. Tomanova, Materials 2005—III International Materials Symposium and XII Portuguese Materials Society Meeting, University of Aveiro, Aveiro, Portugal, 2005.
- [6] G.M. Sheldrick, Program for Solution of Crystal Structures, University of Gottingen, Germany, 1997.
- [7] G.M. Sheldrick, Program for Refinement of Crystal Structures, University of Gottingen, Germany, 1997.
- [8] H. Yoshida, K. Takeda, J. Okamura, A. Ehara, H. Matsurra, J. Phys. Chem. A 106 (2002) 3580–3586.
- [9] Computer Program Gaussian98W, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Computer Program Gaussian98, Gaussian Inc., Pittsburgh, PA, 2001.
- [10] Computer Program GaussView Ver. 2, Gaussian Inc., Pittsburgh, PA, USA.
- [11] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond, Oxford University Press, New York, USA, 1999, p. 13.