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SCALED QUAMTUM MECHANICAL (SQM) FORCE FIELD FOR AMINO-OXO TAUTOMER OF 1, 5 DIMETHYLCYTOSINE

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SUMMARY

We have performed a force field calculation for the amino-oxo tautomer of 1, 5-dimethylcytosine at B3LYP/6-31G* level following the refinement and the scaling methodologies. Quantum mechanical calculations were carried out by using Density Functional Theory (DFT/B3LYP) methods with 6-31G* basis set. The force constants were scaled using the transferable scale factors of Rauhut and Pulay. The refined force constants obtained in terms of independent symmetry coordinates have been expressed in terms of simple valence internal coordinates.

Keywords 1, 5- dimethylcytosine, DFT, vibrational spectra, molecular geometry, force field.

1. INTRODUCTION

The study of the methylated derivatives of the nucleic acids is very important for a better understanding of the role of DNA methylation in important biological processes [1-14], including the regulation of the genome expression during the embryonic development [13-16]. Many previous studies in relation to the vibrational properties of methylated nucleic acid bases (DNA and RNA) have been published [17, 18]. Moreover, the force field of the nucleic acid bases like uracil, cytosine and guanine, have been studied by several authors [19-24] including the force field of tautomers of cytosine [25] and thiocytosine [26], 1-Methylcytosine [27] and 5-Methylcytosine [28,29], but not the one of the 1,5-Dimethylcytosine (DMC). We have reported recently a theoretical-experimental structural and vibrational analysis of this compound and we have proposed the existence of four tautomers, the most stable being the amino-oxo tautomer. In this case we have presented an assignment for the IR and Raman bands of the amino-oxo tautomer of 1, 5- dimethylcytosine using the DFT/BLYP method and 6-31G* basis set [30].
Now, a theoretical study is carried out for the amino-oxo tautomer of this compound with the methods of quantum chemistry in order to have a better understanding of its

vibrational properties by determining the force field and assessing vibrational assignments through B3LYP/6-31G* calculations. In the present paper, we report the results of the DFT calculation for force field for the amino-oxo tautomer of 1, 5-dimethylcytosine and compare the results with the assignment we realized previously [30]. The optimized geometry and wavenumbers for the normal modes of vibration were calculated at B3LYP/6-31G* level. The harmonic force constants given by these calculations were subsequently scaled using transferable scale factors to reproduce the experimental frequencies as well as possible and thus obtain an enhanced assignment.

2. RESULTS AND DISCUSSION

2.1. Geometry

Table 1 shows the optimized geometrical parameters for amino-oxo tautomer of 1,5-dimethylcytosine at B3LYP/6-31G* level compared with theoretical parameters obtained by us for this compound at BLYP/6-31G* level [30], with experimental parameters determinated by X-ray diffraction for 1-Methylcytosine [24, 31] and for 5-Methyl-cytosine [32] and also with theoretical parameters obtained for 1-methylcytosine [24] and aniline. The geometrical parameters for 1- methylcytosine [24] were obtained by SCF/MO method with STO-3G basis set and were corrected using 4-31G basis set. In the aniline the parameters were obtained at Hartree Fock level using 4-21G basis set augmented with d functions for the nitrogen atoms [33]. As can be seen the best results for bond distances and angles are obtained with the BLYP/6-31G* method. The geometry of the amino-oxo tautomer of 1, 5-dimethylcytosine predicts that the amino group does not lie in the plane of the ring (Figure 1) according to the above calculations [30]. Also, the results show that the C4-N8 bond length is longer with DFT methods (1.384 Å with BLYP method and 1.370 Å with B3LYP method) than experimental values but smaller than the other theoretical methods (1.374 Å for 1- methylcytosine [24] and 1.401 Å for aniline [33]). For amino-oxo tautomer of 1, 5- dimethylcytosine, the C11-C5 (C-CH_3) and C16-N1 (N-CH_3) bonds length obtained with DFT method are close to the experimental values reported for 1- methylcytosine [31] and 5- methylcytosine [32].

2.2. Force field calculation

Simple or uniform scaling (i.e., the use of a single scale factor) has become a common practice in quantum chemistry. This method involves a simple multiplication of the theoretical vibrational frequencies by a factor (its value is 0.963 in conjunction with the B3-LYP/6-31G* level [34]). Still this approach is very attractive for large-scale studies (avoiding the complex procedure of defining the internal coordinates, etc.), however, it is not quite capable to correct each individual frequency appropriately. The Scaled Quantum Mechanical (SQM) force field method [35] is a more complex procedure than the uniform scaling. This method applies selective scaling for different classes of internal coordinates which possess a common physical meaning and thus allows to extract all the quantum mechanical information from the computations. The SQM method is very successful at the B3-LYP/6-31G* level [34], and we refer to the literature [34, 36] for further details. In this work we use the density functional derived SQM force field method in its original form [34]. This means that we scale the

quadratic force constant matrix (evaluated in terms of the natural internal coordinates [37]) using the scaling procedure and the transferable scale factors of Rauhut and Pulay (see column A of B3-LYP values in Table 4 of Ref. [34]). Since the SQM force field and the calculated harmonic frequencies of the 1, 5-dimethylcytosine do not contain any empirical parameters coming from the target molecule itself, they can be considered of "a priori" quality. Table 2 summarizes the description of the natural internal coordinates used for the amino-oxo tautomer of 1, 5-dimethylcitosine. Table 3 used for 1-methylcytosine [27] and also with scale factors of other molecules that have similar groups such aniline [33] and toluene [38]. In all cases the scale factors were obtained by their transferability between related molecules. In 1-methylcytosine a planar geometry was assumed for the amino group in order to simplify the normal coordinate analysis and the scale factor values were transferred from maleimide, uracil, formamide and methanol [24]. The scale factors from benzene have been used in aniline and toluene. In both cases, the force fields have been computed at the Hartree Fock level using the 4-21G basis set augmented with d functions for the nitrogen atoms in the aniline case. Thus, the results predict correctly that the amino group does not lie in the plane of the ring in aniline. Table 3 shows that the scale factor values for the stretching of 1-methylcytosine are lower than the corresponding to 1, 5 dimethylcytosine and to the other compared molecules. Although the smaller scale factor (0.395) corresponding to the inversion mode (γNH_2) and the higher scale factor (1.292) for the NH_2 torsion fundamental of aniline present a highly anharmonic character reflected in the observed frequencies but not in the calculated force constants, as seen later [33], Table 4 shows the unscaled (theoretical) and SQM values of the vibrational frequencies of 1, 5-dimethylcytosine. We also give the calculated absolute infrared intensities at the SQM level and the TED values (see above) for a qualitative assignment. In Table 5 the scaled force constants are presented for amino-oxo tautomer of 1, 5- dimethylcytosine compared with force constants for 1-methylcytosine [27], cytosine [24], aniline [33] and toluene [38]. In 1-methylcytosine the force constants were scaled using the CNDO/2 calculations while in cytosine *ab initio* calculations were performed by the STO-3G/4-31G basis sets. In aniline and toluene *ab initio* calculations were performed by the Hartree Fock method using 4-21G basis set. In the case of aniline, augmented with d functions having orbital exponents of 0.8 on the nitrogen atom to give a better representation of the electron distribution in this region of the molecule. The CNDO/2 method predicts lower values for the force constants of the C-N and C=O bonds than for the STO-3G/4-31G and B3LYP/6-31G* methods. When the experimental value with the out of plane angle set at 37.5° was used in aniline, the inversion force constant changed markedly from 0.336 to 0.082 mdyn Å rad $^{-2}$, closer to 1,5 -dimethylcytosine value (0.051 mdyn Å rad $^{-2}$). This difference is probably observed because the out of plane angle in 1, 5- dimethylcytosine is lower (11.9º with B3LYP/6-31G* and 13.8º with BLYP/6-31G* [30]) than the corresponding to the aniline value. Moreover, the values of force constants of the ring torsion obtained for the aniline and toluene are very different from the 1, 5-dimethylcytosine values. These differences can be attributed indistinctly to the different calculations or to the nature of the ring (aromatic for the aniline and toluene). Note that for 1,5- dimethylcytosine the obtained scaled force constants with DFT B3LYP/6-31G* method are very close to values found for 1-methylcytosine with CNDO/2 method while the exception are the force constants related to stretching (f_{16}) and the plane deformation (F_{26}) of the C16-N1 bond. The

calculated force constant values for the amino-oxo tautomer of 1, 5- dimethylcytosine, with the B3LYP/6-31G* method are approximately similar to the 1-methylcytosine, as is expected, because both molecules have CH_3 groups in its structures. The force constant values are greater in cytosine than 1-methylcytosine and 1, 5-dimethylcytosine as can be seen in Table 5.

2.3. Spectroscopic analysis

In Table 6 the experimental wavenumbers and the assignments of the infrared and Raman bands for the amino-oxo tautomer of 1, 5-dimethylcytosine can be seen. The calculated vibrational wavenumbers lead to a rectification of the previously proposed assignment of bands observed with the exception of bands marked with asterisk in Table 6 (see row six). The calculations combining the hybrid functional B3LYP method with 6-31G* basis set gives somewhat better results than the BLYP/6-31G* method. These calculations determine the best theoretical approximation to predict the vibrational frequencies. All the density functional methods explored, systematically overestimate the higher vibrational frequencies. The inverse situation can be observed for the lower frequencies. These effects are essentially due to the neglect of the anharmonicity of the vibrations in the calculations, especially for NH and CH modes and the basis set deficiencies even taking into account the electronic correlation corrections. The hybrid B3LYP method gives somewhat better results than the BLYP method.

Band assignments

The assignment of the experimental bands to the normal modes of vibration of the molecule was based on the existing vibrational analysis [30], the results obtained from the theoretical calculations and the total energy distribution (TED) [39, 40]. In the following discussion, results obtained using the B3LYP/6-31G* method will be referred to. All the observed bands in the vibrational spectra are shown in Table 6 along with their relative intensities and the proposed assignments. Only 12 of the 51 normal vibration modes are completely pure modes as can be seen in Table 4. The remaining normal vibration modes are strongly coupled among them. In some cases however the relative intensity bands predicted by the B3LYP/6-31G* method, are very different from the experimental ones, i. e. the intensities of NH_2 and C6-H15 stretching bands, as well as the O7=C2 and C6=C5 stretching bands, show a reversal of the observed intensity ratio. The calculated intensities are not reliable but they may be employed as auxiliary information.

4000- 2000 cm^{-1} region. In this region the previous assignment is confirmed [30]. The ν_1 and ν_2 modes are assigned to the shoulder and the band recorded in the infrared spectrum at room temperature at 3546 and 3391 cm^{-1} respectively, and both are associated to NH_2 stretchings (N8-H10 and N8-H9, respectively). The ν_3 mode is clearly assigned to the medium intensity band in the room temperature infrared spectrum located at 3112.4 cm^{-1} and associated with the C6-H15 stretching mode because it is calculated as a pure mode (99% TED). The modes from ν_4 to ν_9 are calculated strongly coupled among them and can be assigned to the infrared and Raman bands at 3043, 2990, 2964.4, 2951, 2933 and 2924 cm^{-1} as in our above calculations [30]. All these modes are associated to the C-H stretching, being the ν_4,

ν_5 and ν_7 modes related to N-CH_3 group while the ν_6, ν_8 and ν_9 modes are associated to C-CH_3 (See Table 6).
1700- 1500 cm^{-1} region. Newly here, the above assignment is confirmed, its are, the ν_{10} mode is assigned to strong IR band at 1670.3 cm^{-1} and is associated to the C2=O7 stretching mode; the ν_{11} mode is assigned to the shoulder in infrared band at 1660 cm^{-1} (C5 = C6 stretching) while the ν_{12} mode is assigned to the strong band at 1615.6 cm^{-1} (NH_2 deformation) and finally, the ν_{13} mode is assigned to the medium intensity IR band at 1520 cm^{-1} (N3=C4 stretching).
1500- 1000 cm^{-1} region. In this zone the theoretical calculations predict the frequencies and the intensities of the bands accurately for some modes which permit to carry out a reliable assignment compared with the experimental spectrum (see Figure 2). The ν_{14}, ν_{16} and ν_{20} modes could be assigned to the IR bands at 1482.5, 1464.4 and 1364.7 cm^{-1} related to the C-CH_3 deformation, where the two first of them are associated to antisymmetric modes and the remain to symmetric mode. The ν_{15}, ν_{18} and ν_{19} modes are assigned to the bands at 1475.7, 1427.9 and 1395.4 cm^{-1} and are associated to the N-CH_3 deformation modes. In this case, the two first of them associated to antisymmetric modes while the last band to symmetric mode. Here, there is a little difference in reference to above assignment [30]. The mode associated to C4-N8 stretching mode, the ν_{17} mode, is assigned to the band at 1445 cm^{-1} because is calculated using B3LYP/6-31G method with higher TED value (31%). In this case, the ν_{21}, ν_{22}, and ν_{23} modes are in agreement with the above assignment (associated to C6-N1 stretching, βC6-H15 and C5-C11 stretching, respectively as in Table 6 is indicated), only the ν_{24} and ν_{25} modes are assigned to the IR band at 1163.3 cm^{-1} and 1147.9 cm^{-1}, respectively instead of 1224.7 cm^{-1} and 1045.5 cm^{-1} as in Ref. [30]. In this case, these modes are associated respectively, to N3-C2 and C16-N1 stretchings instead of the N-CH_3 rocking modes. The ν_{26} and ν_{29} modes are easily assigned to the bands at 1106.9 and 1022 cm^{-1} and related with the N-CH_3 rocking modes while the NH_2 rocking, associated to ν_{27} mode, is assigned to the very weak band located at 1066 cm^{-1} instead of 1163.3 cm^{-1} as in BLYP/6-31G* calculations. The ν_{28} and ν_{30} modes are assigned to the bands at 1045.5 and 910.7 cm^{-1} and are related to two C-CH_3 rocking modes.
1000- 100 cm^{-1} region. The assignments in this region are less reliable due to the large number of vibrations expected and, for this, some modes such as, ν_{31}, ν_{32}, ν_{33}, ν_{34}, ν_{38}, ν_{39}, ν_{41}, ν_{42}, ν_{43} and ν_{47} modes appear inverted with B3LYP/6-31G* calculations in relation to BLYP method [30]. The assignments are confirmed for the ν_{35}, ν_{36}, ν_{37}, ν_{40}, and the modes from ν_{44} to ν_{51} modes. In Table 6 can be seeing the mentioned modes associated to the groups of the amino-oxo tautomer and its corresponding wavenumbers. Is important to note that, during the scaling process some bands change notably of intensity i.e. the bands located at 775, 541 and 360 cm^{-1} increase its intensities while the intense band at 552 cm^{-1} decrease it intensity. The band observed at 541 cm^{-1} is assigned to ν_{39} mode associated with the NH_2 twisting vibration. The present calculation also predicts this mode coupled with the inversion mode (ν_{43}) of the amino group. The NH_2 twisting vibration of the amino-oxo form of cytosine is calculated using HF/6-31G** method with higher TED value (37%) at 501 cm^{-1} and observed in the Ar matrix spectrum at 507 cm^{-1} [25]. The out of plane vibration (or inversion mode) of the amino-oxo form of cytosine is calculated at 224 cm^{-1} (53% TED) [25] and experimentally not observed while is very different than the

amino-oxo tautomer of 1, 5- dimethylcytosine (ν_{43}), that it is observed at 400 cm^{-1}. In aniline [48], the inversion mode of the amino group is calculated at 567.4 cm^{-1} and observed at 541.6 cm^{-1} while the NH_2 twisting vibration is calculated at 235.2 cm^{-1} and observed at 210 cm^{-1}. The difference observed in these values could be attributed to the different scale factor because they are strongly affected by the anharmonicity of the combined torsion-inversion motion and, also for the method of calculations.

3. Conclusions

The present study confirms most of the assignments realized for us using the BLYP/6-31G* method with some modifications indicated by the "A priori" force field developed in the present study at B3LYP/6-31G*.

We demonstrate that a DFT/B3LYP molecular force field for the amino-oxo tautomer of 1, 5- dimethylcytosine, computed using 6-31G* basis set are well represented.

An SQM force field was obtained for the amino-oxo tautomer of 1, 5- dimethylcytosine after adjusting the theoretically obtained force constants in order to minimize the difference between observed and calculated frequencies.

The complete force field for the amino-oxo tautomer of 1, 5-dimethylcytosine have been determined, as well as the force constants for stretching and deformations modes and the coupling force constants more significant.

4. Experimental

The infrared spectra of 1,5-dimethylcytosine, $C_4HN_2(NH_2)(CH_3)_2$, at room and low temperatures in KBr pellets and the Raman spectra at room temperature were taken from our previous study [30].

5. Computational Details

Ground-state equilibrium geometries, analytic Cartesian derivatives (first derivative of the dipole moment and second derivative of the energy) have been determined at the DFT level [41] using Becke's non local three-parameter exchange functional [42] and the Lee-Yang-Parr correlation functional (B3-LYP) [43] supplemented by the 6-31G* basis set. The aforementioned calculations were made by the Gaussian 98 [44] suite of programs. The system of natural internal coordinates has been determined by the INTC program [37]. The Cartesian quadratic force constants and the dipole moment derivatives have been transformed to the system of the natural internal coordinates, then the force constants were scaled according to the SQM force field method of Pulay [45] using the transferable scale factors of Rauhut and Pulay [34] with the help of the SCALE2 program [35] written by one of us (Gabor Pongor). The atomic masses used for the generation of the G matrix [46] were as follows: C 12.011; H 1.00794; O 15.9994; and N 14.0067 (in a. u. units). We have used a UNIX-script (originated from Pulay's group) in a somewhat modified form [47] for the manipulations mentioned in this paragraph. The script uses the archive site of the Gaussian 98 [44] output as its input. The form of the normal modes was characterized by the Total Energy Distribution (TED) values [39, 40]. The computed IR spectrum (in harmonic approximation) was considered as the sum of individual Lorentzian bands using an empirical mean of the halfwidths (12 cm^{-1}). Details are given in Ref. [48]. The IR spectrum was visualized by the GNUPLOT program [49].

Details not given in the present work can be asked from the authors upon request (see the [36] references below).

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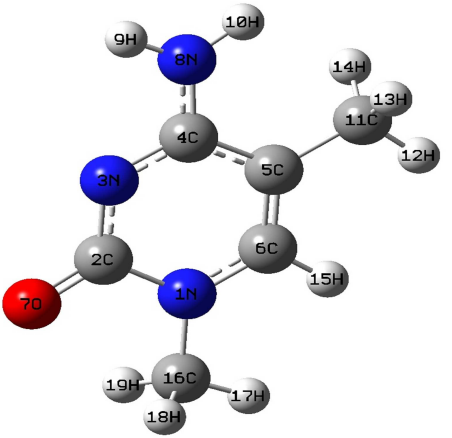

Fig. 1. Molecular structure of 1,5 Dimethylcytosine with labeling of atoms.

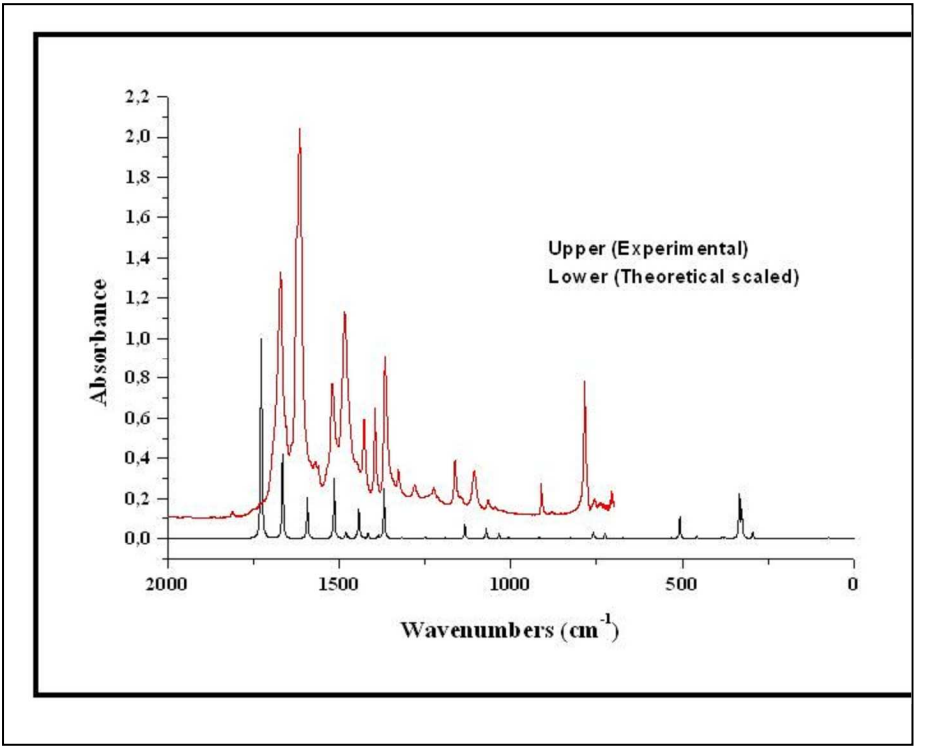

Fig. 2. Comparison between: Upper, the experimental infrared spectrum of the solid 1,5 Dimethylcytosine from Ref [30] with, lower, the corresponding theoretical at B3LYP/6-31G* theory level.

Table 1 : optimised geometrical parameters (distances in Å and bond and dihedral angles in degrees) for amino-oxo tautomer of 1,5 Dimethylcytosine compared with others parameters of related molecules.

Parameters	BLYP 6-31G* [30]	B3LYP 6-31G* This work	1-Methyl-cytosine [46]	1-Methyl-cytosine [24]	5-Methyl-cytosine [47]	Aniline [48]
R(1,2)	1.459	1.434	1.395	1.398	1.376	
R(1,6)	1.367	1.357	1.357	1.370	1.365	
R(1,16)	1.472	1.460	1.464	1.409		
R(2,3)	1.380	1.370	1.358	1.369	1.354	
R(2,7)	1.235	1.223	1.234	1.284	1.252	
R(3,4)	1.332	1.318	1.332	1.334	1.338	
R(4,5)	1.450	1.443	1.422	1.422	1.438	1.401
R(4,8)	1.384	1.370	1.336	1.374	1.337	1.415
R(5,6)	1.377	1.364	1.334	1.352	1.350	1.392
R(5,11)	1.514	1.504			1.508	
R(6,15)	1.094	1.087		1.119		1.079
R(8,9)	1.020	1.011		1.061		1.007
R(8,10)	1.018	1.009		1.061		1.007
R(11,12)	1.102	1.095				
R(11,13)	1.108	1.100				
R(11,14)	1.106	1.099				
R(16,17)	1.099	1.093				
R(16,18)	1.101	1.093				
R(16,19)	1.101	1.093				
A(2,1,6)	121.2	121.2	120.1	120.0	121.3	119.0
A(2,1,16)	116.6	116.6	118.5	117.6		
A(6,1,16)	122.3	122.2	121.5	122.4		120.5
A(1,2,3)	116.6	116.8	118	120.0	119.2	
A(1,2,7)	117.9	118.0	118.6	117.3	119.0	
A(3,2,7)	125.4	125.1	122.4	122.7	121.8	
A(2,3,4)	120.6	120.7	120.0	117.8	119.5	
A(3,4,5)	124.5	124.3	121.8	124.6	123.1	118.7
A(3,4,8)	116.3	116.7	117.8	115.8	117.1	120.6

A(5,4,8)	119.1	118.9	120.4	119.6	119.9	120.6
A(4,5,6)	114.7	114.5	117.2	115.8	115.2	120.5
A(4,5,11)	122.8	122.7		121.6	122.6	
A(6,5,11)	122.4	122.7		122.6	122.2	
A(1,6,5)	122.2	122.3	121.8	121.6	121.7	120.7
A(1,6,15)	116.2	116.1		115.4		120.0
A(5,6,15)	121.6	121.6		123.0		120.1
A(4,8,9)	114.4	115.2		122.4		111.2
A(4,8,10)	118.9	119.8		123.2		111.2
A(9,8,10)	115.9	116.7		114.4		108.1
A(5,11,12)	110.9	110.9				
A(5,11,13)	112.3	112.3				
A(5,11,14)	111.8	111.8				
A(12,11,13)	106.9	106.9				
A(12,11,14)	107.5	107.4				
A(13,11,14)	107.0	107.2				
A(1,16,17)	109.1	109.1		112.0		
A(1,16,18)	109.9	110.0		111.5		
A(1,16,19)	109.9	110.0		111.4		
A(17,16,18)	110.0	109.9		107.2		
A(17,16,19)	110.0	109.9		107.3		
A(18,16,19)	107.7	107.7		107.2		
D(3,4,8,9)	13.5	11.9				
D(3,4,8,10)	156.3	159.3				
D(8,4,5,11)	1.9	1.6				
D(7,2,1,16)	0.0036	0.0511				

Table 2. Description of the natural internal coordinates for the amino-oxo tautomer of 1,5-Dimethylcytosine.

S_1= R(2-1)	ν N1-C2	C 2 - N 1
S_2= R(3-2)	ν N3-C2	N 3 -C 2
S_3=R(4-3)	ν C4-N3	C 4 -, N 3
S_4=R(5-4)	ν C5-C4	C 5 - C 4
S_5=R(6-1)	ν C6-N1	C 6 - N 1
S_6=R(6-5)	ν C6=C5	C 6 = C 5
S_7=R(7-2)	ν O7=C2	O 7 = C 2
S_8=R(8-4)	ν N8-C4	N 8 - C 4
S_9=R(9-8)	ν H9-N8	H 9 - N 8
S_{10}=R(10-8)	ν H10-N8	H10 - N 8
S_{11}=R(11-5)	ν C11-C5	C11 - C 5
S_{12}=R(12-11)	ν H12-C11	H12 - C11
S_{13}=R(13-11)	ν H13-C11	H13 - C11
S_{14}=R(14-11)	ν H14-C11	H14 - C11
S_{15}=R(15-6)	ν H15-C6	H15 - C 6
S_{16}=R(16-1)	ν C16-N1	C16 - N 1
S_{17}=R(17-16)	ν H17-C16	H17 - C16
S_{18}=R(18-16)	ν H18-C16	H18 - C16
S_{19}=R(19-16)	ν H19-C16	H19 - C16
S_{20}=2 $\beta_{6,2,1}$- $\beta_{1,3,2}$- $\beta_{2,4,3}$ + 2 $\beta_{3,5,4}$- $\beta_{4,6,5}$- $\beta_{5,1,6}$	β R3	6-membered ring
S_{21}= $\beta_{1,3,2}$- $\beta_{2,4,3}$+ $\beta_{4,6,5}$- $\beta_{5,1,6}$	β R2	6-membered ring
S_{22}= $\beta_{6,2,1}$+ $\beta_{1,3,2}$ + $\beta_{2,4,3}$- $\beta_{3,5,4}$ + $\beta_{4,6,5}$ - $\beta_{5,1,6}$	β R1	6-membered ring
S_{23}= $\tau_{6,1,2,3}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{5,6,1,2}$	τ R2	6-membered ring
S_{24}= -$\tau_{6,1,2,3}$ + 2 $\tau_{1,2,3,4}$ - $\tau_{2,3,4,5}$ - $\tau_{3,4,5,6}$ + 2 $\tau_{4,5,6,1}$- $\tau_{5,6,1,2}$	τ R3	6-membered ring
S_{25}= -$\tau_{6,1,2,3}$ + $\tau_{1,2,3,4}$ - $\tau_{2,3,4,5}$ + $\tau_{3,4,5,6}$ - $\tau_{4,5,6,1}$ + $\tau_{5,6,1,2}$	τ R1	6-membered ring
S_{26}= $\beta_{6,16,1}$- $\beta_{2,16,1}$	β C16-N1	Ring tXY C16- N1
S_{27}= $\gamma_{16,6,2,1}$	γ C16-N1	Ring tXY C16-N1
S_{28}= $\beta_{1,7,2}$- $\beta_{3,7,2}$	β C2=O7	Ring sXY C 2-O7
S_{29}= $\gamma_{7,1,3,2}$	γ C2=O7	Ring sXY C 2-O7
S_{30}= $\beta_{5,8,4}$- $\beta_{3,8,4}$	β N8-C4	Ring tXY N 8-C4

$S_{31} = \gamma_{8,5,3,4}$	γ N8-C4	Ring tXY N 8-C4
$S_{32} = \beta_{6,11,5} - \beta_{4,11,5}$	β C11-C5	Ring tXY C11-C5
$S_{33} = \gamma_{11,6,4,5}$	γ C11-C5	Ring tXY C11-C5
$S_{34} = \beta_{1,15,6} - \beta_{5,15,6}$	β C6-H15	Ring sXY C 6-H11
$S_{35} = \gamma_{15,1,5,6}$	γ C6-H15	Ring sXY C 6-H15
$S_{36} = 2\,\beta_{9,10,8} - \beta_{4,9,8} - \beta_{4,10,8}$	δNH_2	PXY2,2-1-1,X= N8
$S_{37} = \beta_{4,9,8} - \beta_{4,10,8}$	ρ NH_2	PXY2, 1-1, X= N8
$S_{38} = \gamma_{4,9,10,8}$	γ NH_2	PXY2, oop, X= N8
$S_{39} = \beta_{13,14,11} + \beta_{12,14,11} + \beta_{12,13,11} - \beta_{5,12,11} - \beta_{5,13,11} - \beta_{5,14,11}$	δ_s C11-H_3	Prim XY3 , X= C11
$S_{40} = 2\,\beta_{13,14,11} - \beta_{12,14,11} - \beta_{12,13,11}$	δ_a C11-H_3	Prim XY3 , X= C11
$S_{41} = \beta_{12,14,11} - \beta_{12,13,11}$	δ_a C11-H_3	Prim XY3 , X= C11
$S_{42} = 2\,\beta_{5,12,11} - \beta_{5,13,11} - \beta_{5,14,11}$	ρ C11-H_3	Prim XY3 , X= C11
$S_{43} = \beta_{5,13,11} - \beta_{5,14,11}$	ρ C11-H_3	Prim XY3 , X= C11
$S_{44} = \beta_{18,19,16} + \beta_{17,19,16} + \beta_{17,18,16} - \beta_{1,17,16} - \beta_{1,18,16} - \beta_{1,19,16}$	δ_s C16-H_3	Prim XY3 , X= C16
$S_{45} = 2\beta_{18,19,16} - \beta_{17,19,16} - \beta_{17,18,16}$	δ_a C16-H_3	Prim XY3 , X= C16
$S_{46} = \beta_{17,19,16} - \beta_{17,18,16}$	δ_a C16-H_3	Prim XY3 , X= C16
$S_{47} = 2\beta_{1,17,16} - \beta_{1,18,16} - \beta_{1,19,16}$	ρ C16-H_3	Prim XY3 , X= C16
$S_{48} = \beta_{1,18,16} - \beta_{1,19,16}$	ρ C16-H_3	Prim XY3 , X= C16
$S_{49} = \tau_{9,8,4,3} + \tau_{10,8,4,3} + \tau_{9,8,4,5} + \tau_{10,8,4,5}$	τ_{wist} NH_2	Torsion N 8- C4
$S_{50} = \tau_{12,11,5,4} + \tau_{13,11,5,4} + \tau_{14,11,5,4} + \tau_{12,11,5,6} + \tau_{13,11,5,6} + \tau_{14,11,5,6}$	T_{wist} C11-C5	Torsion C11- C5
$S_{51} = \tau_{17,16,1,2} + \tau_{18,16,1,2} + \tau_{19,16,1,2} + \tau_{17,16,1,6} + \tau_{18,16,1,6} + \tau_{19,16,1,6}$	T_{wist} C16-N1	Torsion C16- N1

(a) See text and Fig. 1 for details. p, s, and t refer to primary, secondary and tertiary centers X, respectively., to which the atom(s) Y are attached. -, - and = mean single, partial double and double bonds, respectively.

Abbreviations: ν, stretching; δ, deformation; ρ, rocking or deformation in the plane; βR, ring deformation; γ, out of plane deformation or wagging; τ, twisting; τR, ring torsion. a: antisymmetric, s: symmetric.

Table 3. SQM scale factors assigned for amino-oxo tautomer of 1,5-Dimethylcytosine.

N°	Scale factor*#	C_6H_7N[a]	C_7H_8[b]	1-methylcytosine[c]
1	0.922	0.919		
2	0.922	0.919		
3	0.922	0.919		
4	0.922	0.919	0.911	0.316
5	0.922	0.919		0.314
6	0.922	0.919	0.911	0.391
7	0.922			0.350
8	0.922	0.919		
9	0.920	0.863		0.462
10	0.920	0.863		0.462
11	0.922		0.873	
12	0.920		0.863	
13	0.920		0.863	
14	0.920		0.863	
15	0.920	0.863	0.863	0.424
16	0.922			0.314
17	0.920			0.410
18	0.920			0.410
19	0.920			0.410
20	0.990	0.794	0.808	1.420
21	0.990	0.794	0.808	1.420
22	0.990	0.794	0.808	1.420
23	0.831	0.768	0.768	
24	0.831	0.768	0.768	
25	0.831	0.768	0.768	
26	0.990			1.000
27	0.976			
28	0.990			1.020
29	0.976			
30	0.990	0.940		
31	0.976	0.794		
32	0.990		0.842	
33	0.976		0.739	
34	0.950	0.794	0.797	0.641
35	0.976	0.739	0.739	
36	0.915	0.794		0.923
37	0.950	0.794		1.390
38	0.806	0.395		
39	0.915		0.765	
40	0.915		0.765	
41	0.915		0.765	
42	0.950			
43	0.950			
44	0.915			0.770
45	0.915			0.770
46	0.915			0.770
47	0.950			
48	0.950			
49	0.831	1.292		
50	0.831			
51	0.831			

*At B3-LYP level.
#Ref. [37],
[a] [48], [b] [49], [c] [27]

Table 4. Theoretical (unscaled) and SQM scaled vibrational frequencies (cm^{-1}), SQM infrared intensities (km/mol) and TED values for 1,5-Dimethylcytosine

Modes	IR Experimental.	Theoretical Unscaled	Intensity unscaled	SQM	Intensity scaled	TED values (a)
ν_1	3546 sh	3708	31.57	3556	31.58	62 S_{10}+ 38 S_9
ν_2	3391 s	3587	52.54	3440	52.38	62 S_9 +38 S_{10}
ν_3	3112.4 m	3198	11.88	3068	11.89	99 S_{15}
ν_4	3043 m	3160	11.55	3031	11.59	64 S_{17} + 19 S_{19} +18 S_{17}
ν_5	2990 vw	3146	10.83	3018	10.84	51 S_{18} + 49 S_{19}
ν_6	2964.4 vw	3119	15.32	2991	15.36	86S_{12}+ 10S_{14}
ν_7	2951 m	3074	37.10	2949	37.07	35 S_{17} +.33 S_{17} + 32 S_{19}
ν_8	2933.1	3069	24.58	2944	24.55	66 S_{14} + 32 S_{13}
ν_9	2924 s	3021	48.19	2898	48.21	66S_{13}+ 24 S_{14} + 10 S_{12}
ν_{10}	1670.3 s	1791	647.53	1726	662.12	72 S_7
ν_{11}	1660 sh	1723	303.19	1664	276.21	35 S_6.+13 S_3 + 11 S_{34}
ν_{12}	1615.6 vs	1662	116.21	1592	136.71	81 S_{36}
ν_{13}	1520 m	1568	189.45	1514	197.18	27.S_3 + 17 S_4 + 14 S_6
ν_{14}	1482.5 s	1540	19.35	1480	21.13	29 S_{40} + 16 S_{45} + 15 S_3
ν_{15}	1475.7 w	1536	3.41	1473	6.93	53 S_{45}+ .26 S_{40}
ν_{16}	1464.4 sh	1512	7.00	1449	7.36	92 S_{41}
ν_{17}	1445 sh	1499	105.26	1442	97.25	31 S_{40} + 14 S_8 + 13 S_4
ν_{18}	1427.9 m	1496	5.500	1433	5.51	91 S_{46}
ν_{19}	1395.4 m	1477	16.53	1415	18.57	81 S_{44}
ν_{20}	1364.7 m	1448	8.54	1386	11.07	86 S_{39}
ν_{21}	1328.9 w	1418	177.89	1369	162.69	26 S_5 + 11 S_{44}
ν_{22}	1281 vw	1357	5.99	1317	4.42	56 S_{34}
ν_{23}	1274 sh	1288	8.75	1249	6.89	20 S_{22} + 15 S_{11} + 14 S_8
ν_{24}	1163.3 w	1232	2.86	1192	3.22	34 S_2 + 17 S_{37} + 11 S_{16}
ν_{25}	1147.9 sh	1169	45.89	1133	47.63	28 S_7 + 16 S_{16} + 14 S_{34}
ν_{26}	1106.9 w	1160	0.03	1131	0.01	89 S_{48}
ν_{27}	1066 vvw	1100	34.48	1071	34.53	48 S_{37} + 14 S_2 + 11 S_{28}

ν_{28}	1045.5vvw	1081	1.24	1057	1.53	81 S_{43}
ν_{29}	1022 vw	1070	17.32	1034	17.47	29 S_{47} + 20 S_5 + 18 S_{16}
ν_{30}	910.7 w	1035	3.23	1007	4.72	65 S_{42} + 10 S_6
ν_{31}	878sh	922	8.20	917	7.36	100 S_{35}
ν_{32}	786 m	855	6.37	826	5.43	23 S_1 + 22 S_4 + 10 S_{11}
ν_{33}	775	773	13.10	759	21.28	97 S_{29}
ν_{34}	758.7 vvw	770	22.08	753	4.71	35 S_{22} + 16 S_1 + 13 S_8
ν_{35}	741.7 vvw	742	10.29	725	19.00	79 S_{31} + 12 S_{25}
ν_{36}	705.8 vvw	689	3.47	672	3.52	17 S_{21} + 15 S_4 + 13 S_{22} + 12 S_1 + 11 S_{11}
ν_{37}	624 w	625	0.45	617	0.33	31 S_{28} + 14 S_{30} + 11 S_{26} + 10 S_{32}
ν_{38}	552 vs	558	76.22	531	2.94	35 S_{21} + 11 S_{11}
ν_{39}	541 sh	540	6.17	507	71.13	64 S_{49} + 21 S_{38}
ν_{40}	470 w	464	5.47	458	8.14	62 S_{20} + 15 S_{21}
ν_{41}	457 vw	421	4.84	384	6.99	45 S_{24} + 28 S_{25} + 16S_{23}
ν_{42}	427 w	383	29.32	376	5.97	28 S_{30} + 27 S_{28}
ν_{43}	400 vw	362	214.75	333	140.43	38 S_{38} + 26 S_{26}
ν_{44}	360 vw	332	5.50	326	89.46	28 S_{38} + 26 S_{26} + 17 S_{30}
ν_{45}	326 w	299	5.69	294	19.77	42 S_{33} + 33 S_{27}.
ν_{46}	304 w	282	0.32	280	1.46	63 S_{32} + 11 S_{26}
ν_{47}	209	234	1.74	219	2.46	60 S_{25} + 17 S_{33} + 16 S_{27}
ν_{48}	183	197	1.35	181	1.12	89 S_{50}
ν_{49}	165	162	1.51	155	1.95	36 S_{27} + 28 S_{24} + 13 S_{33}
ν_{50}	139	113	1.65	104	1.53	81S_{51} + 12 S_{27}.
ν_{51}	90	83	4.48	74	4.57	71 S_{23} + 37 S_{24} + 11 S_{51}

(a) See text

Table 5.- Scaled force constants for amino-oxo tautomer of 1,5 Dimethylcytosine and comparison with force constants for others related molecules.

Force Constant	Description	unscaled	scaled	$C_6H_7N^a$	$C_7H_8^b$	1-Methylcytosine[c]	Cytosine[d]
F_1	ν N1-C2	4.759322	4.3881			5.720	6.629
F_2	ν N3-C2	6.516765	6.0085			6.184	6.275
F_3	ν C4-N3	8.762175	8.0787			7.068	9.572
F_4	ν C5-C4	5.848912	5.3927		6.470	5.277	6.532
F_5	ν C6-N1	7.468285	6.8858			6.344	8.473
F_6	ν C6=C5	8.414510	7.7582		6.600	8.216	10.225
F_7	ν O7=C2	12.456581	11.485			9.387	13.347
F_8	ν N8-C4	7.166466	6.6075	5.814		6.275	8.483
F_9	ν H9-N8	7.336687	6.7498	6.599		6.821	8.435
F_{10}	ν H10-N8	7.446552	6.8508	6.599		6.842	8.483
F_{11}	ν C11-C5	4.814733	4.4392		4.470		
F_{12}	ν C12-C11	5.326558	4.9004		4.940		
F_{13}	ν C13-C11	5.10448	4.6961		4.770		
F_{14}	ν C14-C11	5.182104	4.7675		4.830		
F_{15}	ν H15-C6	5.611885	5.1629	5.085	5.170	4.923	6.173
F_{16}	ν C16-N1	5.237578	4.829			6.072	
F_{17}	ν H17-C16	5.408658	4.976			4.752	
F_{18}	ν H18-C16	5.385205	4.9544			4.946	
F_{19}	ν H19-C16	5.38794	4.9569			4.752	
F_{20}	β R3	1.502955	1.4879	1.280	1.300	1.725	1.729
F_{21}	β R2	1.39662	1.3827	1.216	1.260	1.653	1.740
F_{22}	β R1	1.437019	1.4226	1.239	1.270	1.671	0.843
F_{23}	τ R2	0.189731	0.1577	0.294	0.300		
F_{24}	τ R3	0.240218	0.1996	0.320	0.310		
F_{25}	τ R1	0.245316	0.2039	0.356	0.370		
F_{26}	β C16-N1	1.050852	1.0403			0.542	
F_{27}	γ C16-N1	0.310007	0.3026				

F_{28}	β C2=O7	1.288069	1.2752			1.070		1.336
F_{29}	γ C2=O7	0.819998	0.8003					
F_{30}	β N8-C4	1.225659	1.2134	1.014		0.910		1.352
F_{31}	γ N8-C4	0.716207	0.699	0.648				
F_{32}	β C11-C5	0.846921	0.8385		0.830			
F_{33}	γ C11-C5	0.469156	0.4579		0.520			
F_{34}	β C6-H15	0.597831	0.5679	0.509	0.520	0.465		0.635
F_{35}	γ C6-H15	0.462818	0.4517	0.442	0.430			
F_{36}	δNH_2	0.536944	0.4913	0.651		0.510		0.574
F_{37}	ρ NH_2	0.624762	0.5935	0.732		0.782		0.693
F_{38}	γ NH_2	0.063336	0.051	0.133				
F_{39}	δ_s C11-H_3	0.601345	0.5502		0.560			
F_{40}	δ_a C11-H_3	0.633954	0.5801		0.540			
F_{41}	δ_a C11-H_3	0.611125	0.5592		0.550			
F_{42}	ρ C11-H_3	0.70977	0.6743		0.620			
F_{43}	ρ C11-H_3	0.700349	0.6653		0.660			
F_{44}	δ_s C16-H_3	0.682233	0.6242			0.640		
F_{45}	δ_a C16-H_3	0.587022	0.5371			0.605		
F_{46}	δ_a C16-H_3	0.578625	0.5294			0.605		
F_{47}	ρ C16-H_3	0.855083	0.8123			0.805		
F_{48}	ρ C16-H_3	0.841872	0.7998			0.818		
F_{49}	τ_{wist} NH_2	0.239771	0.1992	0.016				
F50	T_{wist} C11-C5	0.07581	0.063		0.000			
F_{51}	T_{wist} C16-N1	0.033509	0.0278					

Units in mdyn $Å^{-1}$ for stretching and mdyn Å rad^{-2} for angle deformations.

[a] [48]
[b] [49]
[c] [27]
[d] [24]

Table 6. Experimental wavenumbers (cm^{-1}) and assignments of the infrared and Raman bands of 1,5 Dimethylcytosine on the basis of the vibrations of the amino-oxo tautomer.

IR Room Temperature	IR Low Temperature	IR Deuterated	RAMAN	Assignments B3LYP/6-31G* Ref. [30]	Assignments B3LYP/6-31G* This work
3546 sh	3418 sh		3539 vw	$\nu_a NH_2$	ν N8-H10
3391 vs	3374.1 vs	3385.5 vs	3371 m	$\nu_S NH_2$	ν N8-H9
3305.8 w	3302.9 w	3305.8 sh	3300 vvw	2x 919.7 + 1482.5=3304	2x 919.7 + 1482.5=3304
			3267 vw	2x 1274 + 703= 3251	2x 1274 + 703= 3251
3229 vw	3231.8 w		3252 vvw	2x 1615.6= 3231.2	2x 1615.6= 3231.2
	3140 sh			4x 786= 3144	4x 786= 3144
3112.4 m	3103.8 s	3112.4 s	3114 vw	ν C6-H15	ν C6-H15
			3043 m	$\nu_a C16H_3$	ν_a C16H17
2990 vw	2990 vw	2987.2 vw	3004 w	$\nu_a C16H_3$	$\nu_a C16H_3$
2964.4 vw	2967.3 vw	2967.3 vw	2978 m	$\nu_a C11H_3$	$\nu_a C11H_3$
			2951 m	$\nu_s C16H_3$	$\nu_s C16H_3$
2933.1	2935.9	2933.1 vw	2943 m	$\nu_a C11H_3$	$\nu_a C11H_3$
			2924 s	$\nu_s C11H_3$	$\nu_s C11H_3$
2862.0 vvw	2864.0 vvw	2865.6 w	2866	2x 1428= 2856	2x 1428= 2856
			2829	2x 703+1425=2831	2x 703+1425=2831
2765.3	2773.8 vvw			1670.3 + 2x 552= 2774.3	1670.3 + 2x 552= 2774.3
	2756.7 vvw	2769.8 w		2x 703 + 1364.7= 2770.7	2x 703 + 1364.7= 2770.7
		2607.7 vvw			
		2534.8 s			
		2455.1 w			
		2427.2			
		2355.6 sh			
		2327.2 s			
		2312.9 sh			
		2221.9 vw			
1813 vvw				1274 + 552= 1826	1274 + 552= 1826

1670.3 s	1677.1 sh	1673.9 s		ν C2=O7		ν C2=O7
	1671.9 s					
1660 sh	1660 m	1650 sh	1656 vw	ν C5=C6		ν C5=C6
1620.8 sh	1622.5 s					
1615.6 vs	1612.2 vs	1619.1 vs		δ NH_2		δ NH_2
1590 sh	1590 sh		1592 m	?		?
1571.3 vw	1571.3 w			2x 786= 1572		2x 786= 1572
	1564.4 w	1566.8 w				
1559.3 vw	1550 vw			2x 775= 1550		2x 775= 1550
1520 m	1523.5 m	1522 w		ν N3=C4		ν N3=C4
		1504.6 m	1513 w			
1482.5 s	1489.3 s	1487.2 w		δ_a C11H_3		δ_a C11H_3
	1475.7 w			δ_a C11H_3		δ_a C16H_3
1464.4 sh	1460.3 w	1462.3 sh	1460 w	δ_a C11H_3		δ_a C11H_3
	1451vvw			?		?
1445 sh	1445 vw			δ_a C16H_3		ν C4 -N8 (*)
	1434.7 vvw			?		?
1427.9 m	1427.8 w	1427.5 w	1425 w	ν C4 -N8		δ_a C16H_3 (*)
1395.4 m	1397.1 s	1397.6 w	1391 m	δ_s C16H_3		δ_s C16H_3
1364.7 m	1368.1 s	1365.2 m	1357 w	δ_s C11H_3		δ_s C11H_3
	1349.4 sh			?		?
1328.9 w	1328.9 vw	1330.4 vw	1325 w	ν N1-C6		ν N1-C6
1281 vw	1284.5 sh	1283.1 vw		β C6H15		β C6H15
1274 sh	1274.2 vw		1274 s	ν C5-C11		ν C5-C11
	1245.2 vw			703 + 552= 1255		703 + 552= 1255
1224.7 vw	1224.7 vw	1225.8 vvw	1222 m	ν C2-N3		
		1213.4 vvw				
		1188.5 vvw				
1163.3 w	1170.1 w	1163.6 w		ρ C16H_3		ν C2-N3 (*)
1147.9 sh	1147.9 w		1169 w	ρ C16H_3		ν N1-C16 (*)
		1136.2 vvw				
1106.9 w	1113.8 sh					

	1110.4 w	1108.8 w		ρ NH_2	ρ $C16H_3$ (*)
1066 vvw	1071.1 w	1071.5 w	1060 w	ρC11H_3	ρ NH_2 (*)
1045.5vvw	1045.5 vvw	1049 vvw		ν N1-C16	ρ $C11H_3$ (*)
	1026.7 vvw		1022 vw	ρ $C11H_3$	ρ $C16H_3$ (*)
		949.5 vw			
910.7 w	915.8 w	912.1 w	907 vw	γ C6H15	ρ $C11H_3$ (*)
878sh	883.3 vvw	882.3 vvw	867 m	ν N1-C2	γ C6H15 (*)
		827.5 vvw			
786 m	786.1 m	787.7 m	786 w	βR_1	ν N1-C2 (*)
	779.2 w		775 vs		γ C2 =O7 (*)
		765.3 vvw			
758.7 vvw	755.3 w	756.6 vvw	750 w	γ C2 =O7	βR_1 (*)
741.7 vvw	736.5 w	745.4 vvw		γ C4 -N8	γ C4 -N8
705.8 vvw	707.5 w	705.6 vvw	703 s	ν C4-C5	ν C4-C5
		670.7 vvw			
		638.3 w			
		623.4 vvw	624 w	βC2 =O7	βC2 =O7
		608.5 vvw			
		553.7 vvw	552 vs	τ N8H9	βR_2 (*)
		537 vvw	541 sh	βR_2	τwist. NH_2 (*)
		466.6 w	470 w	βR_3	βR_3
		462 sh	457 vw	τR_1	τR_3 (*)
		428 vvw	427 w	τ N8H10	β C4 -N8 (*)
		421 vvw			
		406.4 vvw	400 vw	β C4 -N8	γ NH_2 (*)
			360 vw	β N1C16	β N1C16
			326 w	γ C5 C11	γ C5 C11
			304 w	β C5 C11	β C5 C11
			209	τR_3	τR_1 (*)
			183	Twis $C11H_3$	Twis $C11H_3$
			165	γ N1C16	γ N1-C16
			139	Twis $C16H_3$	Twis $C16H_3$
			90	τR_2	τR_2

Abbreviations: ν: stretching, δ: bending;. ρ:rocking, γ: wagging or out the plane deformation, τ: torsion. β: in the plane deformation. β_R deformation of the ring; τ_R, torsion of the ring; τ_{twist} twisting, a: antisymmetric, s: symmetric. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; sh, shoulder.
(*) See text.

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