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STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Vibrational Spectra and Stable Conformations of Methyl 6-Methoxy-2,3,4,9-Tetrahydro-1H-1,4-Ethanocarbazole-3-Carboxylate

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Abstract—A study is performed of IR absorption and Raman spectra of methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3-carboxylate. Optimized structures and the harmonic force fields of stable conformers are calculated using the density functional theory (the B3LYP, M062X, and BVP86 functionals combined with basis sets of different completeness). A detailed explanation of the spectra is proposed based on calculations, and the characteristic frequencies of the most stable forms of a given compound are identified. The theoretical spectra are analyzed relative to experimental data.

Keywords: conformation, vibrational spectrum, vibrational frequencies, melatonin, methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3-carboxylate

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INTRODUCTION

Melatonin (*N*-acetyl-5-methoxytryptamine) (Fig. 1) is a neurohormone with chronobiotic, anticancer, and immunostimulating activities. It also participates in the regulation of blood pressure, body temperature, and the cardiovascular system [1]. Melatonin has been found in unicellular algae, plants [2], invertebrates, and vertebrates (including humans). The pineal gland of the brain is the main source of melatonin in vertebrate animals. Changes in melatonin production following those in daylight hours lead to daily and seasonal changes in the bodies of humans and animals. In addition, all endogenous rhythms are subordinated to melatonin production rhythms [3].

The use of melatonin in treating various diseases is limited because of its relatively short half-life in the body (about thirty minutes) [4]. One way of modifying the structure of melatonin is to limit the conformational mobility of its molecule through the condensation of an indole core with a rigid bicyclic framework [5]. The spatial structure of functional groups plays a key role in interactions with receptors, to which vibrational IR absorption and Raman spectra are strongly sensitive. They contain much more information and are comparatively easy to use. Finally, Raman spectroscopy is of special importance when studying melatonin analogs in aqueous solutions. Reliable spectral means for the identification of new compounds are needed to study the mechanisms of their action in real conditions. As a result, it is important to obtain as much information as possible on the structure of molecules of conformationally constrained melatonin analogs.

In this work, we studied and interpret IR absorption and Raman spectra of methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3-carboxylate (**A**), allowing for possible rotational isomerism (Fig. 2).

Our test substance was synthesized at the Department of Chemistry, Moscow State University as a part of the program to find substances that act on melatonin receptors. Compound **A** is an intermediate in the synthesis of a conformationally constrained analog of melatonin *N*-(*exo*-6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazol-3-yl)acetamide [6]. The BVP86/TZVP level of theory [7–12] was used as the basis for explaining the experimental spectra [7–12]. It proved to be highly efficient, due to its low computa-

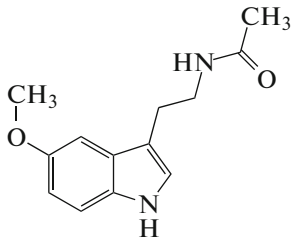

Fig. 1. Structure of melatonin.

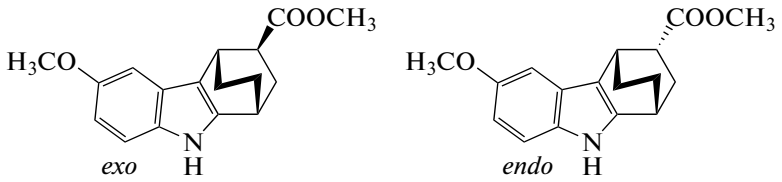

Fig. 2. Structures of *exo*-isomers and *endo*-isomers of **A**.

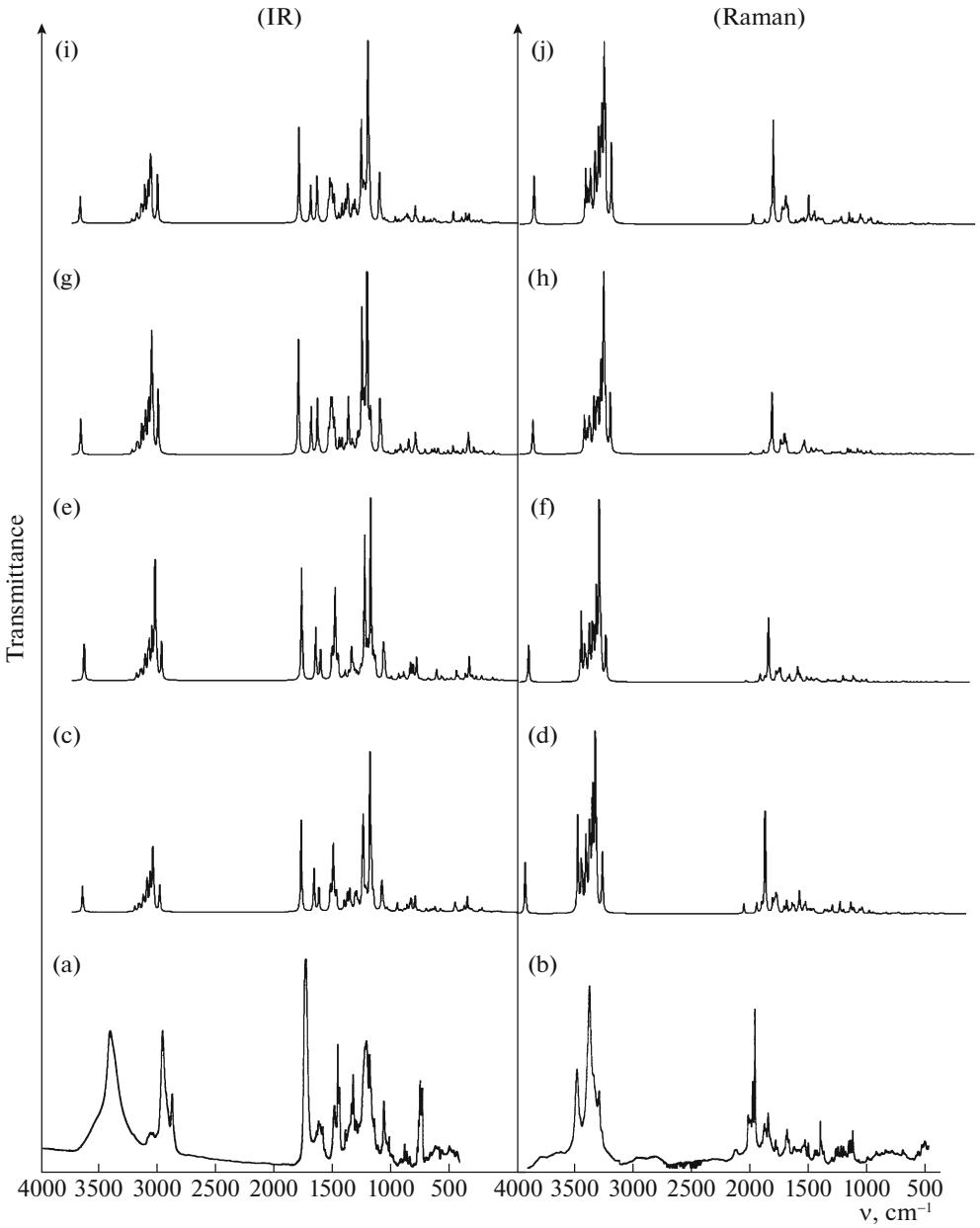

Fig. 3. Comparison of the experimental (a) IR absorption and (b) Raman spectra of a mixture of isomers **A** to ones calculated (BVP86/TZVP) for conformers (c, d) *exo*-1, (e, f) *endo*-1, (g, h) *endo*-2, and (i, j) *exo*-2.

tional costs in performing calculations for polycyclic organic compounds [13, 14]. The theoretical spectra were analyzed relative to experimental ones obtained in the 400–3600 (IR) and 50–3600 cm^{-1} (Raman) wavenumber ranges.

EXPERIMENTAL

Methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3-carboxylate **A** is a mixture of *endo*- and *exo*-isomers in an approximately 1 : 1 ratio. The

Table 1. Internal coordinates for the methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3-carboxylate molecule

No.	Coordinates	Atoms	No.	Coordinates	Atoms	No.	Coordinates	Atoms
1	qNH-1	1 19	52	a9	2 7 6	103	a60	15 32 9
2	qCH-1	17 34	53	a10	3 20 8	104	a61	15 32 13
3	qCH-2	16 33	54	a11	3 20 2	105	a62	15 31 9
4	qCH-3	12 25	55	a12	3 8 2	106	a63	15 31 13
5	qCH-4	14 30	56	a13	4 10 1	107	a64	15 9 13
6	qCH-5	37 40	57	a14	4 10 9	108	a65	16 33 18
7	qCH-6	6 21	58	a15	4 1 9	109	a66	16 33 11
8	qCH-7	14 28	59	a16	5 12 1	110	a67	16 18 11
9	qCH-8	14 29	60	a17	5 12 11	111	a68	17 34 12
10	qCH-9	2 35	61	a18	5 1 11	112	a69	17 34 18
11	qCH-10	13 27	62	a19	6 21 10	113	a70	17 12 18
12	qCH-11	7 22	63	a20	6 21 13	114	a71	18 36 16
13	qCH-12	15 32	64	a21	6 21 2	115	a72	18 36 17
14	qCH-13	9 24	65	a22	6 10 13	116	a73	18 16 17
15	qCH-14	7 23	66	a23	6 10 2	117	a74	36 18 37
16	qCH-15	13 26	67	a24	6 13 2	118	a75	37 40 39
17	qCH-16	15 31	68	a25	7 22 23	119	a76	37 40 38
18	qCH-17	37 39	69	a26	7 22 2	120	a77	37 40 36
19	qCH-18	37 38	70	a27	7 22 9	121	a78	37 39 38
20	qCO-1	3 20	71	a28	7 23 2	122	a79	37 39 36
21	qCO-2	3 8	72	a29	7 23 9	123	a80	37 38 36
22	qCC-1	4 10	73	a30	7 2 9	124	X1a	33 16 11 18
23	qCN-1	1 4	74	a31	8 3 14	125	Xmox	36 18 16 17
24	qCO-3	18 36	75	a32	9 24 4	126	X2a	34 17 12 18
25	qCC-2	5 12	76	a33	9 24 7	127	X3a	25 12 17 5
26	qCN-2	1 5	77	a34	9 24 15	128	XNH	19 1 4 5
27	qCC-3	16 18	78	a35	9 4 7	129	XCO	20 3 2 8
28	qCC-4	12 17	79	a36	9 4 15	130	T1a	10 5 0 33 18 0 11 16
29	qCC-5	11 16	80	a37	9 7 15	131	T2a	11 33 0 36 17 0 16 18
30	qCC-6	17 18	81	a38	10 4 11	132	T3a	16 36 0 12 34 0 18 17
31	qCO-4	36 37	82	a39	10 4 6	133	T4a	18 34 0 25 5 0 17 12
32	qCC-7	10 11	83	a40	10 11 6	134	T5a	25 17 0 11 1 0 12 5
33	qCC-8	5 11	84	a41	11 16 10	135	Tmox1	38 39 40 18 0 0 37 36
34	qCO-5	8 14	85	a42	11 16 5	136	Tmox2	37 0 0 16 17 0 36 18
35	qCC-9	4 9	86	a43	11 10 5	137	Tab	12 1 0 10 16 0 5 11
36	qCC-10	6 10	87	a44	12 25 5	138	T1b	10 9 0 5 19 0 4 1
37	qCC-11	2 3	88	a45	12 25 17	139	T2b	11 12 0 4 19 0 5 1
38	qCC-12	6 13	89	a46	12 5 17	140	T3b	5 16 0 6 4 0 11 10
39	qCC-13	2 7	90	a47	13 27 26	141	Tbc	1 9 0 6 11 0 4 10
40	qCC-14	7 9	91	a48	13 27 6	142	Tc1	2 13 21 4 11 0 6 10
41	qCC-15	9 15	92	a49	13 27 15	143	Tc2	7 15 24 1 10 0 9 4
42	qCC-16	13 15	93	a50	13 26 6	144	Tcd1	2 21 10 15 26 27 6 13
43	qCC-17	2 6	94	a51	13 26 15	145	Tcd2	6 26 27 9 31 32 13 15
44	a1	1 19 4	95	a52	13 6 15	146	Tcd3	13 31 32 4 7 24 15 9
45	a2	1 19 5	96	a53	14 30 28	147	Td1	10 13 21 3 7 35 6 2
46	a3	1 4 5	97	a54	14 30 29	148	Td2	6 3 35 22 23 9 2 7
47	a4	2 35 3	98	a55	14 30 8	149	Td3	2 22 23 4 15 24 7 9
48	a5	2 35 7	99	a56	14 28 29	150	Tac1	6 7 35 8 20 0 2 3
49	a6	2 35 6	100	a57	14 28 8	151	Tac2	2 20 0 14 0 0 3 8
50	a7	2 3 7	101	a58	14 29 8	152	Tac3	3 0 0 28 29 30 8 14
51	a8	2 3 6	102	a59	15 32 31			

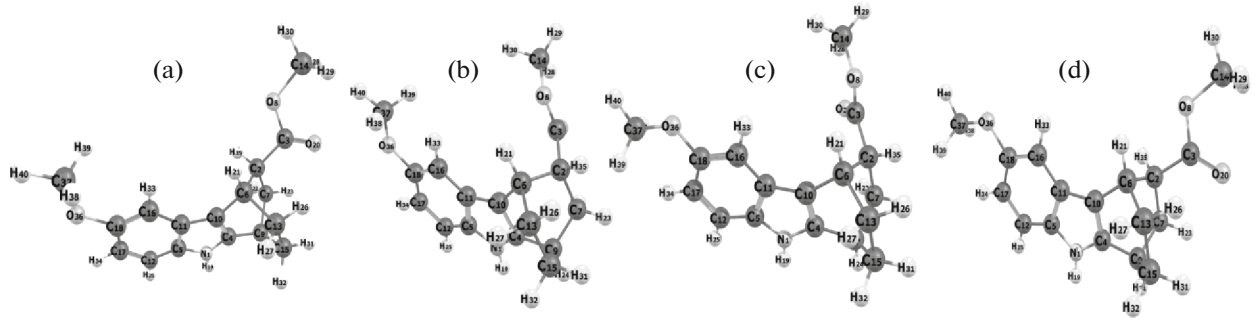

Fig. 4. Structures of the stable conformations of isomers **A**: (a) *exo*-1, (b) *endo*-1, (c) *endo*-2, and (d) *exo*-2.

sample of the studied compound is a brown resin at room temperature. The purity of the substance was ~95%. The IR absorption spectrum of the substance pressed into a pellet with potassium bromide was recorded on a Bruker Tensor-27 Fourier spectrometer (Germany) with a resolution of 1 cm^{-1}. The Fourier transform Raman spectrum of the solid compound was obtained on a Bruker EQINOX 55 spectrometer equipped with an FRA-106 attachment (Germany). The excitation source was a Nd:YAG laser (1064 nm) with a power of 500 mW. The resolution was 2 cm^{-1}. The signal was averaged over a thousand scans. Figures 3a and 3b show the resulting spectra.

CALCULATIONS

Quantum-mechanical calculations were performed using the density functional theory and the Gaussian 09 software (version D.01) [15]. Quantum-chemical calculations of the stable conformations of molecules were performed with B3LYP [16], M062X [17], and BVP86 hybrid functionals [11–14], coupled with the 6-31G**, 6-31+G** [18–20], and TZVP basis sets [11, 12], respectively. Optimized geometries were obtained for all possible conformers (with no symmetry restrictions), and their harmonic force fields, the vibration frequencies, the intensities of IR absorption bands in the gas phase, and the activities in Raman spectra were calculated. In addition, the vibration frequencies in an anharmonic approximation were calculated for all conformers. All energy differences given below were calculated with allowance for corrections for the zero vibrational level. The Chemcraft program was used to visualize the results from quantum-mechanical calculations [21]. The quantum-chemical matrices of the force constants were converted from Cartesian coordinates to a dependent system of internal coordinates, the normal vibrations were analyzed, and the distribution of potential energy over vibrations of the conformers was calculated with the SPEKTR program [22, 23]. Table 1 presents the internal coordinates.

RESULTS AND DISCUSSION

A number of conformations were possible for the test compound that had different orientations of the methoxy and methoxycarbonyl groups. Eight conformations of the test compound that arose for the *syn*- and *anti*-positions of a methyl group with fixed *syn*- or *anti*-orientations relative to the C=O bond of a five-membered cycle and a methoxy group bound directly to an indole core were considered for the *exo*- and *endo*-isomers of **A**.

The structures were optimized and the harmonic force fields were calculated along with the vibration frequencies of sixteen stable structures at the B3LYP/6-31G**, B3LYP/6-31+G**, M062X/6-31+G**, and RBVP86/TZVP levels of theory.

The results from calculations show that the *anti-syn-syn*-conformations of (a) *exo*-1 and (b) *endo*-1 isomers were the ones most stable (Fig. 4). The energy difference between them was only ~0.04 kcal/mol (RBVP86/TZVP). The energy difference between the ones most stable and the *syn-syn-syn* conformers of *exo*-2 and *endo*-2 was ~0.6 kcal/mol for the *exo*-isomer and ~0.5 kcal/mol for the *endo*-isomer, which corresponds to the relative amount in mixtures of 3 : 1 and 7 : 3, respectively. A detailed explanation of the vibrational spectrum is proposed for the most stable conformations, based on an analysis of normal vibrations (Table 2).

CONCLUSIONS

A comparison of our theoretical and experimental vibration frequencies (Fig. 3 and Table 2) shows that the BVP86/TZVP level satisfactorily reproduces both the structural and spectral data for the considered compound, which confirms the possibility of using this approximation.

A comparison of theoretical spectra of the isomers shows there are slight differences between the vibrational frequencies in the 1700–3000 and 500–630 cm^{-1} ranges. Minor differences in the fingerprint region are apparent mainly in the relative intensity of the bands.

Table 2. Experimental and calculated normal vibration frequencies (in cm^{-1}) of the two most stable conformers of *exo* and *endo* isomers of methyl 6-methoxy-2,3,4,9-tetrahydro-1H-1,4-ethanocarbazole-3 carboxylate

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
3397 (very intense)		3576 (54.6); (146.8)	100(qNH-1)	3577 (54.2); (136.7)	100(qNH-1)
		3133 (6.4); (46.2)	100(qCH-1)	3134 (6.4); (46)	100(qCH-1)
		3131 (5.5); (217.6)	92(qCH-2)7(qCH-3)	3131 (5.5); (208.2)	92(qCH-2)7(qCH-3)
		3102 (12.8); (116.5)	92(qCH-3)7(qCH-2)	3102 (12.3); (111.6)	92(qCH-3)8(qCH-2)
		3092 (12.5); (71)	82(qCH-4) 10(qCH-7)9(qCH-8)	3091 (13.1); (65.8)	80(qCH-4) 12(qCH-7)8(qCH-9)
		3064 (27.5); (178.9)	93(qCH-5)4(qCH-17)4(qCH-18)	3063 (27.4); (176.8)	93(qCH-5)4(qCH-17)3(qCH-18)
		3054 (19.1); (60.3)	51(qCH-7) 49(qCH-8)	3056 (18.8); (47)	51(qCH-7) 49(qCH-9)
3051 (low)	3055 (45%)	3033 (21.4); (146.3)	34(qCH-11) 30(qCH-14) 10(qCH-10)8(qCH-9)	3036 (15.9); (69)	94(qCH-6)3(qCH-8)
3030 (low)		3031 (38.5); (60.7)	27(qCH-10) 18(qCH-12) 16(qCH-15) 14(qCH-11)	3035 (10); (88.4)	75(qCH-8) 19(qCH-13)4(qCH-6)
		3024 (15.6); (91.2)	94(qCH-6)	3026 (48.1); (131.7)	40(qCH-10) 33(qCH-11) 12(qCH-14) 12(qCH-15)
		3011 (1.3); (47.9)	36(qCH-12) 26(qCH-10) 21(qCH-16) 16(qCH-15)	3007 (7); (45.5)	41(qCH-11) 37(qCH-10) 10(qCH-14)7(qCH-15)
		3008 (3.6); (61.6)	85(qCH-9) 10(qCH-14)	3003 (61.8); (273)	88(qCH-12)5(qCH-14)3(qCH-13)
	2950 (100%)	3003 (63.9); (240.4)	88(qCH-13) 4(qCH-16)	2981 (33.4); (139.1)	43(qCH-9) 37(qCH-7) 19(qCH-4)
		2985 (55.7); (168.6)	45(qCH-15) 27(qCH-10) 13(qCH-16)9(qCH-12)	2979 (55.9); (320.6)	58(qCH-13) 18(qCH-8) 17(qCH-16)5(qCH-12)
		2983 (14.3); (156.3)	45(qCH-11) 43(qCH-14)6(qCH-13)	2976 (44.3); (51.2)	51(qCH-17) 49(qCH-18)
		2981 (36.2); (138.5)	42(qCH-8) 39(qCH-7) 18(qCH-4)	2975 (65.2); (236.8)	40(qCH-14) 31(qCH-15) 16(qCH-11) 8(qCH-10)
2948 (very intense)		2978 (42.6); (51.1)	51(qCH-17) 50(qCH-18)	2964 (18.9); (71.4)	79(qCH-16) 16(qCH-13)
		2974 (24.3); (76.4)	45(qCH-16) 29(qCH-12) 14(qCH-15)8(qCH-10)	2962 (18.7); (54)	49(qCH-15) 31(qCH-14) 10(qCH-10)8(qCH-11)
2866 (intense)	2868 (17%)	2923 (55.8); (169.4)	47(qCH-18) 46(qCH-17)7(qCH-5)	2922 (56.3); (166)	48(qCH-18) 45(qCH-17)7(qCH-5)
1725 (very intense)		1719 (178.8); (27.9)	88(qCO-1)4(qCC-11)	1729 (161.8); (8.1)	88(qCO-1)4(qCC-11)

Table 2. (Contd.)

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
1616 (intense)	1617 (7%)	1610 (83.3); (28.5)	22(qCC-4) 14(qCC-3) 13(qCC-5) 12(qCC-2)	1610 (75.1); (29.8)	22(qCC-4) 14(qCC-3) 13(qCC-5) 12(qCC-2)
1580 (intense)	1579 (11%)	1569 (49.5); (24.7)	15(qCC-6) 10(qCC-2)9(qCC-5)7(qCC-7)	1570 (46.3); (19.2)	15(qCC-6) 10(qCC-2)9(qCC-5)7(qCC-7)
	1560 (19%)	1539 (1.1); (283.2)	29(qCC-1) 11(qCC-4)7(qCC-9)6(a15)	1538 (0.8); (227.7)	29(qCC-1) 11(qCC-4)7(qCC-9)6(a15)
1479 (intense)	1480 (8%)	1475 (19.6); (33.2)	16(qCC-8)7(a69)6 (qCC-2)5(qCC-10)	1475 (19.9); (31.3)	17(qCC-8)8(a69) 7(qCC-2)6(qCC-3)
		1469 (36.4); (7.3)	15(qCN-1) 10(a59)8(a25)6(a2)	1469 (31.8); (10.5)	16(qCN-1) 11(a59)7(a25)7(a2)
		1461 (2.3); (4.5)	48(a78) 11(a47)6(a59)5(a76)	1461 (2.1); (4.3)	54(a78)7(a47)6(a59) 5(a80)
1449 (very intense)		1458 (3.4); (20.2)	30(a47) 17(a78) 13(a59)3(qCC-3)	1458 (2.4); (16)	29(a47) 20(a59) 12(a78)
		1450 (10.4); (10.4)	71(a56)7(a57)7(a58) 7(a54)	1452 (9.4); (7.1)	71(a56)7(a53)7(a58) 7(a57)
	1449 (10%)	1447 (116.6); (30.5)	11(qCC-2)9(a45) 6(qCC-3)6(a65)	1447 (113.2); (29.1)	11(qCC-2)9(a45) 7(qCC-3)6(a65)
1435 (intense)		1445 (9.4); (5.7)	53(a25) 19(a47)4(a29)3(a28)	1444 (11.9); (5.4)	57(a25) 18(a47)4(a27)3(a26)
		1438 (8); (17.1)	48(a75) 47(a76)3(a80)	1438 (5); (25.5)	46(a75) 36(a76)6(a59)3(a79)
		1435 (4.1); (17.6)	31(a54) 28(a53) 18(a59)6(a47)	1438 (4.4); (3.4)	37(a59) 22(a47) 10(a25)6(a76)
		1435 (5.7); (5.7)	31(a59) 19(a54) 15(a53) 11(a47)	1435 (7.9); (12.2)	49(a54) 44(a53)4(a58)3(a57)
		1421 (25.5); (2.9)	19(a75) 17(a76) 15(a77) 11(a79)	1421 (22.7); (2.1)	23(a76) 15(a77) 14(a75) 11(a80)
		1419 (14.3); (0.6)	28(a53) 22(a55) 20(a54) 12(a57)	1419 (10.6); (1.2)	26(a53) 22(a55) 22(a54) 12(a57)
1385 (low)	1387 (3%)	1377 (2.7);(18.8)	15(qCC-6)6(qCC-5) 6(qCC-7)6(qCC-9)	1378 (4.4); (15.9)	16(qCC-6)7(qCC-7) 6(qCC-5)6(qCC-9)
		1355 (21.4);(35.6)	11(qCC-10)6(qCC-5)6(qCC-2)6(a50)	1360 (12.5); (27.8)	12(qCC-10)7(qCC-5)7(a19)6(qCC-2)
1332 (intense)		1328 (35.9); (7.3)	20(a5) 17(a4)9(a28)6(a21)	1330 (10.9); (2.3)	21(a4) 16(a26) 14(a5) 11(a27)
1319 (very intense)		1311 (13.8); (21.5)	14(a26) 12(a27)8(a48)7(a49)	1308 (40); (9.6)	8(a29)7(a28)7(a1)5(a 32)
1309 (low)		1306 (31.9); (3.8)	10(a62)9(a63)8(a34) 7(a65)	1302 (12.9); (6.8)	16(a48) 11(a49)8(a4)5(a20)
1299 (low)		1301 (1.8); (8)	14(a60) 12(a61)6 (qCN-2)4(a6)	1297 (3); (7.2)	22(a60) 17(a61)7(a63)6(a62)
	1290 (4%)	1292 (9.1); (20.1)	11(a26) 11(a27)8(a50)7(a51)	1290 (16.2); (48.5)	8(a50)8(qCC-8)6(a28)5(a51)
1274 (low)		1266 (10.8); (3.8)	7(a68)7(a44)6(a6)5 (a65)	1275 (10.4); (24.3)	11(a6) 10(a48) 10(a21)7(a49)
		1261 (24.9); (2.6)	28(a6) 18(a21)7(a4)5(a20)	1260 (9.8); (14)	11(a27)8(a62)6(a60)6 (a26)

Table 2. (Contd.)

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
		1249 (33.4); (61.2)	11(a60) 11(a48)9 (a27)6(qCN-2)	1236 (9.5); (1.3)	14(a51)9(a63)8(a20)6 (a34)
		1235 (12.5); (8.1)	13(a51)9(a63)8(a49)6 (a50)	1225 (12.4); (1.5)	8(a45)8(qCC-5)8(a6)7(qCN-2)
		1214 (1.6); (2)	16(a19) 10(qCN-2)5(a21)5(a63)	1214 (1.3); (17.5)	10(a19) 10(a21) 7(qCN-2)7(a32)
1209 (very intense)		1209 (2.6); (15.1)	11(a33) 10(a29)9(a28)7(a1)	1205 (15.4); (5.6)	15(a49) 11(a20)9(a4)6(a6)
		1198 (101); (24.1)	13(qCO-3) 10(a66)6(a33)5(a61)	1195 (197.3); (5.3)	24(qCO-3) 15(a66) 6(qCO-4)5(a77)
		1193 (120.8); (9.2)	12(qCO-3)8(a28) 6(a21)6(a29)	1177 (5.5); (15.3)	15(a1) 11(a2)6(qCN-1)6(a77)
1178 (very intense)		1174 (26.6); (7.3)	11(a1)8(a77)8(a2)5 (a51)	1172 (34.4); (1.5)	9(a55)7(qCO-2)6(a50)6(a26)
		1165 (13.1); (6.5)	48(a55) 13(a57) 13(a58)6(a56)	1164 (0.6); (3.6)	40(a55) 10(a58)9(a57)5(a56)
		1163 (7.5); (1.6)	38(a77)7(a80)6(a79) 4(a78)	1162 (11.7); (1.5)	39(a77)7(a79)6(a80) 4(qCO-3)
		1149 (5.7); (10.3)	13(a32) 11(a50) 10(a63) 10(a62)	1147 (16.9); (5.9)	16(a34)9(a26)8(a21)7 (a33)
1138 (intense)	1139 (3%)	1135 (280.9); (7.1)	31(qCO-2) 11(qCC-11) 10(a4)9(a10)	1144 (248.5); (2.3)	33(qCO-2) 11(qCC-11) 10(a10)8(a5)
		1129 (30); (3.8)	44(a58) 40(a57)4(a53)	1136 (1.1); (5.7)	15(a19)7(a28)7(a5) 6(a32)
		1127 (0.2); (4.7)	47(a79) 46(a80)	1131 (0.8); (3.7)	45(a57) 44(a58)3(a54)3(a53)
		1124 (32.7); (2.9)	7(qCC-9)5(qCC-7)5(a68)5(qCC-10)	1127 (0.1); (4.6)	48(a80) 46(a79)
		1121 (19.2); (2)	9(a34)9(a20)8(a6)7 (a61)	1119 (25.8); (6.5)	10(a68) 10(a32)9 (a44)6(qCC-7)
1109 (very low)	1111 (3%)	1106 (27.8); (3.1)	18(a68) 15(a44) 14(a69)9(qCC-2)	1106 (27.7); (5.2)	15(a68)12(a44) 12(a69)7(qCC-2)
1056 (intense)		1038 (37); (5.2)	13(qCO-5) 10(qCC-13)8(a60)5(a62)	1037 (37.5); (8.2)	17(qCC-12)14(qCO-5) 10(qCC-16)5(qCC-17)
1037 (low)		1032 (41.8); (9.6)	39(qCO-4)9(qCC-13) 6(qCO-5)4(qCC-11)	1035 (11.1); (2.7)	15(qCO-4)5(a62) 5(qCO-5)5(a48)
		1021 (10.5); (0.5)	32(qCO-4)6(qCC-6)6(qCC-13)3(a48)	1026 (28.7); (1.4)	50(qCO-4)6(qCC-6) 5(qCC-16)4(qCC-15)
1010 (low)	1010 (3%)	1013 (1.8); (10.7)	20(qCC-15) 20(qCC-16)8(qCC-12)8(qCC-14)	1017 (3.4); (4.6)	14(qCC-14) 11(qCC-15)9(qCC-12)7(a48)
997 (very low)		992 (4.2); (4)	13(qCC-12) 11(a27)6(a34)5(a22)	996 (0.7); (6.3)	18(qCC-13) 12(qCC-17)9(qCC-16)8(a27)
993 (very low)		988 (5); (3.8)	8(qCC-16)7(a70)6 (a65)6(a41)	988 (1); (2.8)	9(a70)8(a65)7(a41)7(a45)
960 (much low)		970 (2.4); (22.9)	41(qCO-5) 14(qCC-17) 10(qCC-11)6(qCC-13)	968 (5.7); (10)	52(qCO-5)8(qCC-14) 5(qCC-11)5(qCC-17)

Table 2. (Contd.)

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
		941 (1.1); (3.5)	16(qCC-14) 10(a29)9 (qCO-5)6(a7)	908 (9.9); (24.8)	8(a9)7(a3)6(qCO-5) 4(a52)
		904 (18.1); (33.4)	8(a3)7(a52)6(qCO-5)5(a64)	907 (0.7); (0.7)	10(qCC-13)9(qCC-15) 9(a29)8(qCC-17)
879 (low)		875 (4.2); (11.2)	9(qCO-2)8(qCO-5) 6(qCC-11)5(qCC-14)	882 (4.6); (10.8)	7(qCC-17)7(qCC-13)5(a36)4(XCO)
861 (low)		852 (0.4); (0.5)	41(T4a) 26(X3a) 22(X2a)9(T5a)	865 (12.1); (5)	16(qCC-14) 12 (qCC-16)9(qCC-12) 8(qCO-5)
835 (low)		847 (3.9); (3)	12(qCC-16) 12(qCC-14) 10(qCC-13)9 (qCC-12)	854 (0.1); (0.3)	40(T4a) 25(X3a) 24(X2a) 10(T5a)
	835 (3%)	841 (3.2); (2)	19(qCC-15) 10(qCC-12)9(XCO)8(qCC-17)	850 (2.3); (3.6)	7(a51)5(qCC-15)5(qCC-11)4(qCO-2)
		822 (13.5); (3.8)	8(qCO-2)8(qCC-16)4(qCC-11)4(qCO-3)	821 (2.6); (23.9)	12(qCC-15)7(qCC-16)5(qCN-2)4(qCO-2)
800 (low)		812 (0.4); (30.3)	10(qCN-2)6(qCC-5)6(qCC-4)5(a73)	808 (1.2); (2.9)	15(qCC-15) 13(qCC-16)7(qCC-14)6(qCC-4)
		797 (14.3); (2.2)	6(Tcd1)6(qCO-3)6(a63)6(a61)	806 (25); (7)	11(qCO-3)6(a18)5(a71)4(a17)
		788 (7.2); (14.6)	14(qCC-15) 12(qCC-14) 10(qCC-12)8(XCO)	784 (19.4); (0.3)	60(X1a) 18(T1a)4(Xmox)4(T2a)
772 (low)	772 (2%)	787 (16.7); (0.4)	70(X1a) 20(T1a) 5(Xmox)3(T2a)	783 (1.1); (5.5)	9(X1a)9(Tcd3)8(Tcd1)7(qCC-14)
753 (intense)	759 (2%)	754 (32.3); (0.6)	45(X2a) 40(X3a) 9(Xmox)5(T5a)	756 (32.7); (0.7)	42(X2a) 40(X3a) 9(Xmox)6(T5a)
745 (very intense)	737 (5%)	740 (1.3); (12.2)	15(XCO) 14(qCC-17)9(a10)5(a31)	748 (4.6); (11.7)	16(XCO) 11(a23) 8(qCC-13)8(a10)
728 (very intense)		726 (0.8); (6.1)	14(T2a) 12(a23) 11(a36) 10(XCO)	723 (1.5); (2.4)	16(a35) 12(a22) 12(T2a) 12(T2b)
696 (low)		715 (4); (16.7)	8(a46)5(qCO-3)5(qCC-6)5(a3)	710 (1.5); (11.5)	7(a46)5(qCO-3)4(XCO)4(a36)
		662 (4.5); (1.1)	19(T1b) 13(Tc1) 13(T2a)9(X3a)	660 (3.6); (0.7)	18(T1b) 14(T2a) 14(Tc1) 10(XNH)
660 (very low)		655 (4.3); (9)	11(a10) 10(qCC-11)9(a11)8(XCO)	645 (1.5); (2.1)	6(XCO)5(qCC-11)5(a10)5(a24)
617 (low)		624 (5.4); (5.8)	7(qCC-17)5(a67) 5(a46)4(a41)	615 (1.5); (3.2)	11(XCO)8(qCC-17)5(qCC-11)4(a67)
		603 (5.8); (0.2)	10(XCO)7(qCC-9)6(Td2)5(a24)	587 (7.1); (0.5)	7(qCC-9)5(a64) 5(a52)4(a73)
587 (low)		585 (11.3); (0.8)	59(Xmox) 20(T3a) 7(X3a)4(T1a)	585 (10.5); (0.4)	57(Xmox) 18(T3a) 6(X3a)3(T1a)
566 (very low)		539 (6.3); (1.2)	8(a74)6(a64)6(a30) 4(a12)	546 (6.5); (0.8)	11(a30)9(a64)9(a52)8 (T2b)

Table 2. (Contd.)

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
		532 (2.4); (1.2)	12(a16)7(a72)7(a74)6(a42)	534 (3.7); (1.4)	17(a74) 12(a16) 10(a71)7(a18)
497 (low)		514 (2.6); (4.5)	7(a73)7(a74)5(a52) 4(a43)	496 (3.3); (4.7)	8(qCC-10) 7(a73)6(a43)5(a72)
461 (very low)		463 (0.6); (2.6)	17(a74)9(a15)8(a36)5(T1b)	465 (3.8); (1)	12(a74) 10(a35)7(a22)5(a15)
436 (very low)		448 (1.1); (1)	15(a35) 12(a22) 11(a36)9(T1b)	459 (0.9); (1.2)	15(a36)9(a74)8(a23)8(T1b)
410 (very low)		416 (18.9); (3.7)	9(T2a)9(T1b)8(T4a) 6(Tc2)	416 (15.3); (0.7)	14(T1b)9(T2a) 8(T4a)7(T3b)
		405 (5.3); (3.2)	12(T4a) 10(X2a)6(T2a)6(a72)	403 (2.6); (1.5)	13(X2a) 13(T4a)8(Xmox)5(T2a)
		398 (2.9); (0.9)	13(T5a)9(Xmox)9(X2a)8(T1b)	396 (3.3); (6.1)	7(T5a)6(T1b)5(a37)5(a72)
		365 (4.1); (1.1)	19(a31) 14(a11)6(a12)5(T1b)	374 (2.1); (2.6)	11(a31) 10(T1b) 10(a11) 10(Tab)
		337 (12.5); (0.6)	20(a7) 12(a31)8(a10)7(Td3)	342 (9.7); (1.9)	21(a7) 13(a31) 10(a10)7(a11)
		309 (30.7); (1.6)	40(XNH) 35(T2b) 7(T3a)4(T2a)	310 (35.5); (1.5)	43(T2b) 41(XNH) 8(T3a)4(Tmox1)
		286 (5.5); (0.5)	22(a31) 10(Td3) 8(Tcd3)7(a74)	286 (2.8); (1)	23(a31) 10(qCC-11)8(a8)8(a24)
		271 (6.7); (4.6)	10(qCC-11)9(XNH) 7(a23)6(a37)	281 (5.4); (1.6)	14(a37)9(a31)8(a24)7(Td3)
		251 (1); (0.3)	70(Tmox1)4(T2b) 4(Tc1)4(T5a)	252 (1.8); (1.6)	29(Tmox1) 15(a74)8(a71)6(a72)
		240 (0.4); (1.5)	19(a74) 12(a71) 11(a31)7(a72)	249 (4.7); (1)	36(Tmox1) 13(a74)7(a71)4(Tbc)
		210 (5.1); (0.3)	26(Tac2) 16(Tcd2) 14(a8) 12(Tcd1)	211 (2.1); (1.8)	19(Tcd1) 15(Tcd3) 10(Tmox1)7(Tc1)
		202 (0.1); (2)	14(Tmox1) 10(Tac2) 9(T3a)8(T2a)	202 (6.7); (1.4)	27(XNH) 14(T3a) 9(Tmox1)9(Tc2)
		186 (9.3); (1.8)	25(XNH) 16(Tab) 11(T1a)6(T3a)	178 (1.2); (0.5)	16(Tcd3) 13(Tcd1) 13(a7) 12(a12)
		165 (1.9); (1.7)	16(T1a) 15(XNH) 6(Tcd3)6(Tab)	166 (2.1); (1.2)	34(Tac2) 14(T1a) 13(XNH)8(Tab)
		135 (0.7); (1.3)	39(Tac3)7(Tac2) 5(a42)5(XCO)	137 (0.2); (0.6)	87(Tac3)3(a8)
		127 (0.7); (0.6)	32(Tac3) 12(Tmox2) 7(T3b)4(a42)	132 (0); (0.9)	22(Tmox2) 12(T3b)8(T5a)4(Tc2)
		119 (0.3); (2)	25(Tmox2) 22(Tac3) 16(Tac2) 11(T3b)	122 (0.8); (1.9)	11(a42)9(a40)7(a72)7(Tac2)
		90 (1.9); (0.4)	27(Tmox2) 18(Tac2) 16(a8)8(XCO)	110 (5.4); (1.4)	25(Tac2) 22(Tmox2) 14(a8)7(Tc2)
		62 (0.3); (1.5)	15(Tc2) 11(Tmox2) 9(Td1)7(a7)	78 (2); (0.4)	38(Tmox2) 11(Td2) 7(Td1)7(Tac1)

Table 2. (Contd.)

Experiment		*Anti-syn-syn-exo*-1	PED, %	*Anti-syn-syn-endo*-1	PED, %
IR	Raman				
		56 (2.8); (0.7)	20(Tmox2) 17(Tac1) 10(Tc1)7(T5a)	47 (0.3); (1.8)	32(Tac1) 13(T3b) 10(Tmox2)9(Td2)
		37 (0.3); (2.4)	28(Tc1) 16(Tc2) 13(T1b) 10(Td1)	36 (0.7); (2.1)	37(Tc1) 16(T1b) 12(Tc2)7(T5a)
		28 (0.9); (0.4)	74(Tac1)9(Td2)8 (Td1)	22 (0.6); (1.9)	56(Tac1) 19(Td2) 16(Td1)

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