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Simulation of the Adiabatic Potentials α- and β-Substituted Gamma Yrone

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Abstract: Within the framework of the Density Functional theory DFT/b3LYP implemented model quantum calculations of the geometric structure and vibrational spectra of α- and β-substituted gamma pyrone. The signs of the spectral identification of compounds are identified. The possibility of the use of information technology (Gaussian) in predictive calculations of the structure and spectra of the investigated class of compounds are formulated and stated.

Key words: Gamma pyrone, vibrational spectra, spectral identification, adiabatic potential, investigated

INTRODUCTION

The main physical and chemical properties of molecular objects, according to modern scientific views are defined by a form of their adiabatic potential, possibly to estimate which parameters a solution of the quantum equation for an electronic subsystem of a molecule.

Justification of reliability of estimates of such parameters of adiabatic potential which it is accepted to call harmonic and anharmonic force constants is considered good coincidence of results of theoretical and experimental interpretation of oscillatory ranges of molecular systems.

Earlier such estimates were obtained from the solution of inverse problems of the theory of molecular vibrations using a scheme transfer of harmonic force constants related to the electronic structure of molecular fragments (Heneczkowski *et al*., 2001). Despite the known shortcomings of this approach, accumulated an extensive database on the harmonic force constants of compounds of different classes and a number of known molecular fragments. This database is often used to justify the validity of the results in the predictive model calculations of quantum adiabatic potential parameters that have become dominant in modern theoretical spectroscopy (Erdogdi *et al*., 2009; Sundaraganesan *et al*., 2012). As additional arguments involved data on the characteristic vibrations of the individual molecular fragments, results of physical assumptions about the influence of substituents on the force fields of basic molecular fragments (Corredor *et al*., 2009).

MATERIALS AND METHODS

Such approach has been used in publications for the construction of structural and dynamic models of a number of flavonoids (hydroxy substituted flavone and isoflavone) a naturally occurring biomolecules, scientific interest which involves the study of the impact of their biochemical and pharmacological effects on the cellular structures of a living organism. However presented by Elkin, the results should be considered preliminary and therefore, require additional justification. Such in our opinion is the approach of parameter estimation of the adiabatic potential of individual molecular fragments observed molecular object.

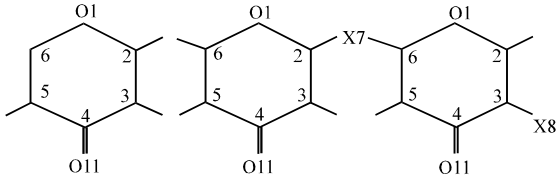

Fig. 1: The numbering of the atoms in the gamma pyrone, α and β-gamma pyrone

The purpose of this message is a theoretical analysis of the results of model calculations of the structure and range of a number of α- and β-substituted molecule gamma pyrone (Fig. 1) as one of the basic molecular fragments benzo-gamma-pyrone, α- and β-phenyl substituted which result, respectively, molecules flavone and isoflavones.

RESULTS AND DISCUSSION

Model quantum calculations of geometry and parameters of adiabatic potential of a molecule of the Gamma Pirona (GP) and row it α- and β-replaced (X = CH3, F, NO2, Cl, OH, COH, COOH, S6N5) are carried out within a method of functionality of density of DFT/b3LYP. Ranges of change of lengths of valent communications

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and values of valent corners are specified in Table 1. Not represented geometric parameters differ from those in benzene on the value of ~0.01Å and 1°, respectively. Values of lengths of communications of C-X (X = CH3, F, Cl, C6H5) will well be coordinated with the data of microwave and electron diffraction experiment given by Sverdlov and Kovner for toluene, galoidobenzolov, definila. Shown in Table 1 results suggest that the effect of substitution on the force field six-membered ring GP has a local character.

Initial criterion of reliability of model quantum calculations is reproduction of frequency of torsional vibration for fragments of CH3, NO2, OH, COOH, C6H5.

According to quantum calculations of such a result is achieved under the assumption of a non-planar original geometry (symmetry C1) for α- and β-phenyl substituted GP (C6H5 fragment) and 3b conformer nitro GP. For other replaced GP calculations indicate that they belong to the group of symmetry Cs. Geometry optimization yields the following values of the dihedral angles in the α- and β-phenyl substituted GP: D (1, 2, 7, 12)~17°; D (2, 3, 8, 12) = 39°, respectively. For such an assessment is diphenyl ~41°, for flavone and isoflavone ~19° and 40°.

Accounting diffuse basis of calculation parameters in the evaluation of molecular geometry principle does not matter. This conclusion applies to the results of the theoretical interpretation of the spectrum of fundamental GP and its substituted analogs shown in Table 2. The fringe shift (ν_{thr}) does not exceed the value of ~10 cm^{-1}, which will dispense a single column for the frequencies of the fundamental vibrations (ν_{thr}). Qualitative assessment of the intensity is maintained. However, excluded from consideration bands of low intensity not of interest to the problems of the spectral identification of compounds. These bands are attributed to deformation vibrations of the angles (γ) GP six-membered ring, the bond angle CC = O ($\beta_{C=O}$), a number of non-planar deformation vibrations of CH bonds (ρ) and links six-membered cycle (χ).

The good agreement between the available experimental (ν_{emp}) and theoretical (ν_{thr}). The strips given by situation (Fausto *et al*., 2001) gives the grounds to speak about of the results of model calculations of the parameters of quantum adiabatic potential.

The theoretical interpretation of the fundamental vibrations GP core, based on the results of model calculations of quantum adiabatic potential parameters are presented in Table 3 and 4. Table 3 interpretation for those fragments substituent assignment of the bands which is not difficult because they are separated by a large gap from the bands of fundamental vibrations six-membered cycle GP. Delocalization occurring forms of the normal vibrations does not preclude the classification procedure. Here, we have a complete analogy with such fluctuations in monoreplaced benzene. This applies particularly to the halogenated GP that can uniquely interpret fluctuations six-membered cycle GP.

This fact is considered when forming Table 4 where fragments deputies contain Hydroxyl group (OH) which deformation fluctuations are shown in the same area of a

Table 1: Assessment of geometrical parameters of gamma pyrone substituted

Parameters	2-GP	2X-GP	3-GP	3X-GP	Parameters	2-GP	2X-GP	3-GP	3X-GP
R(1,2)	1.36	1.34-1.36	1.36	1.34-1.36	A(2,3,4)	121	120-121	123	120-122
R(1,6)	1.36	1.35-1.37	1.35	1.36-1.37	A(2,3,8)	120	119-121	119	115-120
R(2,3)	1.34	1.34-1.35	1.34	1.35	A(4,3,8)	119	119-120	118	119-126
R(3,4)	1.47	1.47	1.47	1.48-1.49	A(3,4,5)	113	113	111	111-112
R(4,5)	1.47	1.47-1.48	1.47	1.47	A(3,4,11)	124	123-124	124	124-125
R(4,11)	1.22	1.22	1.22	1.22	A(5,4,11)	124	123-124	125	122-124
R(5,6)	1.34	1.34	1.34	1.34	A(4,5,6)	121	121	122	122
A(2,1,6)	118	117-118	118	118	A(4,5,9)	119	119	118	118
A(1,2,3)	124	123-126	123	123-125	A(1,6,5)	124	123-124	124	123-124
A(1,2,7)	111	110-115	113	112	A(1,6,10)	111	110-111	111	111
A(3,2,7)	125	122-126	124	124-125	A(5,6,10)	125	125-126	125	125-126

The bond lengths R (i, j) in Å, the values of bond angles A (I, j, k) in degrees)

Table 2: Interpretation of the fundamental vibrations of gamma pyrone

			6-311G**		6-311+G**					6-311G**		6-311+G**	
FK	*N_{norm}	N_{calc}	IR	IR	IR	KP	FK	*N_{norm}	N_{calc}	IR	IR	IR	KP
$Q_{C=O}$	1694	1702	438	47	545	84	β,Q	1029	1007	6	3	7	2
Q,β,γ	1637	1635	12	19	2	28	γ,β	1008	1000	4	11	3	13
Q,β	1610	1572	1	5	2	9	γ,Q	924	918	89	6	96	7
β,Q	1399	1376	60	1	60	0	γ,Q	790	794	0	14	0	17
β,Q	1314	1300	121	1	117	2	ρ	852	856	78	0	77	0
β	1197	1194	11	11	16	11	χ	430	435	16	2	16	1

The oscillation frequency ν in cm^{-1}; the intensity of the IR spectra in km mol^{-1} in CD ranges in Å4/aem; *Fausto *et al*. (2001)

Table 3: Interpretation of oscillations in the cyclic skeleton and α-substituted β-gamma pyrone

Mode			2-CH_3		2-F		2-NO_2		2-Cl	
shape	*N_{norm}	N_{calc}	IR	KP	IR	KP	IR	KP	IR	KP
$Q_{C=O}$	1694	1686-1702	499	62	499	47	376	85	454	52
Q,β,γ	1610	1624-1664	18	18	141	15	0	54	85	20
Q,β	1593	1558-1586	1	11	20	6	22	19	46	9
β	1399	1374-1397	14	2	11	2	10	2	20	2
β,Q,γ	1314	1313-1357	140	2	320	0	114	12	297	0
β	1212	1221-1259	1	0	1	3	30	4	27	6
β	1187	1177-1197	8	5	18	0	0	0	1	1
β,Q,γ	1029	1005-1048	12	14	6	8	9	14	10	11
γ,Q	960	914-930	53	1	73	4	74	4	74	7
γ,Q	924	838-912	16	2	1	3	44	2	6	2
γ,Q	790	683-748	1	16	7	16	3	4	12	11
ρ,χ	924	847-900	40	1	76	1	32	2	51	1
ρ	852	811-831	22	2	3	2	34	2	17	2
			3-CH_3		3-F		3-NO_2		2-Cl	
FK	N_{norm}	N_{calc}	IR	KP	IR	KP	IR	KP	IR	KP
$Q_{C=O}$,γ	1694	1682-1706	388	45	388	54	398	45	338	38
Q,β,γ	1610	1625-1645	1	24	18	25	46	42	35	41
Q,β	1593	1559-1584	4	5	21	10	71	6	0	6
β,Q	1399	1374-1412	16	4	15	0	9	3	13	2
β,Q	1314	1333-1357	14	8	13	4	6	16	25	5
β,Q	1314	1291-1319	83	1	48	2	234	4	101	2
β	1187	1136-1191	38	3	99	4	4	6	8	6
Q,β,γ	1029	1055-1103	26	1	6	2	19	2	4	2
Q,β,γ	924	943-947	20	13	34	12	41	5	82	8
γ	852	827-862	22	4	38	4	59	4	9	12
Q,γ	790	654-734	6	12	8	11	6	3	11	6
ρ	924	861-932	25	1	40	1	10	2	20	1
ρ	852	829-835	38	2	35	2	54	1	49	1

Table 4: Interpretation of fluctuations in the cyclic skeleton conformers (a, b) α-and β-substituted gamma pyrone

Mode			2a-OH		2b-OH		2a_COH		2b-COH		2a-COOH		2b-COOH	
Shape	*N_{norm}	N_{calc}	IR	KP	IR	KP	IR	KP	IR	KP	IR	KP	IR	KP
$Q_{C=O}$,γ	1694	1692-1696	620	55	524	45	401	94	376	90	433	78	408	91
Q,β	1610	1624-1673	30	10	154	13	11	50	34	103	23	47	11	70
Q,β	1593	1575-1595	28	7	114	7	17	38	34	37	12	26	27	26
β,Q	1399	1384-1424	346	1	123	1	1	4	16	2	28	4	61	4
β,Q	1314	1319-1370	118	3	37	2	30	4	113	5	4	8	47	4
β	1212	1227-1258	22	3	115	2	89	2	13	6	65	2	18	6
β	1187	1129-1196	16	4	22	2	28	25	40	13	1	1	6	1
β,Q	1029	1019-1036	16	6	2	7	15	15	5	13	4	10	7	14
γ	960	925-935	34	0	17	0	93	2	48	4	82	3	101	3
γ	852	868-913	52	5	30	8	14	1	71	1	10	1	4	2
γ	790	732-775	4	19	7	18	33	11	23	11	17	17	23	16
ρ	924	903-939	0	0	0	0	37	1	29	1	22	2	22	2
ρ	852-	832-855	75	2	81	0	24	1	29	2	42	78	39	2
			3a		3b		3a		3b		3a		3b	
		N_{calc}	IR	KP	IR	KP	IR	KP	IR	KP	IR	KP	IR	KP
$Q_{C=O}$,γ	1694	1662-1706	371	48	248	16	400	45	150	17	257	46	138	19
Q,β,γ	1610	1626-1655	41	39	157	76	52	62	55	49	40	50	40	42
Q,β,γ	1593	1556-1585	33	9	7	15	105	17	40	5	79	11	35	4
β,Q	1399	1375-1417	33	1	115	2	22	4	77	5	79	6	111	4
β,Q	1314	1338-1387	2	3	44	2	36	3	64	5	36	5	57	4
β,Q	1212	1290-1314	19	3	66	4	167	3	213	2	164	1	125	0
β,Q	1187	1153-1210	211	8	23	4	1	3	2	10	54	4	14	10
β,Q	1029	1030-1092	3	0	52	1	3	2	11	1	127	4	147	8
Q,β,γ	960	944-980	31	12	28	14	41	6	45	7	55	5	42	4
γ	852	842-864	40	5	50	5	23	12	58	11	32	11	20	10
γ	790	708-789	7	13	8	13	77	10	10	12	39	12	18	14
ρ	924	936-942	0	2	0	0	10	1	14	1	-	2	-	1
ρ, χ	852	829-847	62	1	89	0	49	1	48	1	63	3	65	1

Frequencies of fluctuations ν in cm^{-1}; intensity in IR ranges in km mol^{-1} in CD ranges in Å4/aem; *Fausto *et al.* (2001)

Table 5: Interpretation of cyclical fluctuations of the core in β- and α-phenyl-substituted gamma pyrone

Mode	GP	MB	Diphenyl				2-C6H5			3-C6H5		
shape	(N_{norm})	(N_{norm} *)	N_{norm} *	N_{calc}	IR	KP	N_{calc}	IR	KP	N_{calc}	IR	KP
Q,β,γ	1637	-	1611	1603	12	2	1630	26	206	1628	7	144
Q,β,γ	1610	1605	1611	1601	0	463	1603	1	346	1602	0	187
Q,β,γ	-	1585	1595	1584	0	4	1582	2	92	1579	3	13
Q,β,γ	-	-		1569	5	1	1570	32	235	1560	10	54
β,Q	-	1500	1504	1499	33	51	1489	14	9	1489	10	12
β,Q	-	1445	-	-	-	-	1443	21	13	1440	7	4
β,Q	1399	-	1452	1425	9	1	1384	57	9	1387	44	27
β,Q	-	-	-	-	-	-	1342	201	52	1352	19	5
β,Q	1314	1315	1326	1324	1	2	1324	11	3	1324	14	8
β,Q	-	1280	1300	1294	0	3	1294	47	5	1312	99	28
β,Q_{CC}	-	-	1280	1271	0	243	1248	2	115	1255	90	81
β,Q	1220	-		1266	2	0	1225	29	133	1283	6	1
β,Q	1197	1180	1185	1181	0	12	1180	5	15	1180[d]	21	12
β,Q	1148	1156	1155	1155	0	13	1157	0	9	1155	0	6
β,Q	-	1070	1092	1078	9	0	1038	5	4	1076	10	1
β,Q	1029	1028	1032	1035	3	28	1029	8	32	1034	1	3
β,γ,Q	1008	1000	1003	998	7	98	998[d]	13	59	998[d]	17	77
γ	960	-	-	-	-	-	917	47	9	942	72	7
γ	852	-	-	-	-	-	858	5	1	840	13	16
γ	790	-	-	-	-	-	725	1	17	705	3	11
ρ	852	838	838	839	0	13	871	17	2	841	43	2
ρ	790	-	780	780	6	0	819	20	3	770	11	2
ρ,χ	-	740	740	740	72	0	772	27	1	741	21	2
ρ,χ	734	-	699	700	73	1	690	42	2	695	39	1

Frequencies of fluctuations ν in cm^{-1}; intensity in IR ranges in km mol^{-1} in CD ranges in Å4/aem

range as deformation fluctuations of communications of CH (β). Delocalization of a form of normal fluctuations becomes a known hindrance of unambiguous reference of strips by this criterion. Besides, data on intensity of strips (Table 4) can be used at the solution of problems of spectroscopic identification conformers hydroxy, carboxy and aldehyde GP.

Strips, weak on intensity are excluded from consideration. They are carried to the same fluctuations as in GP molecule. The remained strips (Table 3 and 4) on frequency well will be coordinated with experimental data for GP. This fact suggests that influence of monosubstituted with a force field of six-membered cycle GP has local character and is shown in shift of the strips carried to deformation fluctuations of corners of a six-membered cycle (γ) in long-wave range. The dominating contribution carries kinematic effect (increase in mass of the deputy and length of communication of C-X) which is visually shown for the first group of deputies (Table 3).

The above assumption about the local impact monosubstitution in the GP on the force field of its cyclic fragment is confirmed in the case when as deputy acts Phenyl Moiety (C6H5). This is confirmed by the information provided in Table 5. There is a good agreement between the results of model calculations of the spectrum of fundamental oscillations with real data experiment for GP (Fausto *et al*., 2001), mono-substituted benzene and biphenyl. On the other hand, it is possible to consider gamma pyrone as a substituent on the benzene monosubstituted representatives. The fact that the local impact of such substitution on the benzene cycle force field is known. Suffice it to refer to the monograph.

We emphasize that we are talking about the spectral range above 600 cm^{-1} which are arranged and the band assigned to the fundamental vibrations of cyclic α- and β-fragments substituted gamma-pyrone. In this case, the difference in the position of the bands assigned to the deformation vibrations of the valence angles of six-membered cycles, determined by the kinematics of the substituent.

CONCLUSION

The presented results of creation of the structural and dynamic models replaced gamma-pyrone, comparison of the obtained data of theoretical and experimental interpretation of a range of fundamental fluctuations give the grounds to approve the following:

- The method of functionality of density allows to receive reliable predictive estimates of parameters of adiabatic potential of the studied class of connections

- The estimated fact of the local influence of the substituents on the force field six-membered cycle of gamma-pyrone with monosubstituted, observed exhibit specific fundamental vibrations of this cycle in the range of 1600-1000 cm^{-1}. This fact should be taken into account when constructing the structural-dynamic model of substituted benzo-gamma pyrone, including flavone and isoflavones

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