Geometries , Vibration Frequencies , Normal Coordinates and IR Absorption Intensities of Newly Azo Imidazoles : 3,5-DMPID and 2,4-DMPID Molecules

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Key words:-MINDO/3-FORCES version 6.00 1996 program , 3,5-DMPID and 2,4-DMPID Molecules

(NJC)

(Recevied on 30/3/2010) (Accepted for publication 12/5/2010)

Abstract

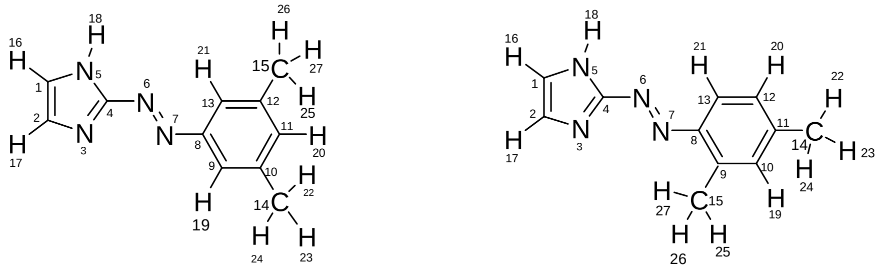
MINDO/3-FORCES calculations had been done after complete optimization of geometry on two newly azo imidazoles: 3,5-DMPID and 2,4-DMPID molecules. The dipole moments , geometric parameters, heats of formation, orbital energies, ionization energies and the electron densities were reported. The (3N-6) fundamental vibration frequencies along with their assignments and the corresponding IR absorption intensities for each one of the two molecules were , also, listed. It was shown that the 2,4-DMPID molecule is the more stable one and it has the lower dipole moment and the higher frequency value for the -N=N- stretch fundamental vibration mode.

الخلاصة

أجريت حسابات الميندو/ 3-فورسيز المتضمنة الحصول على الشكل الهندسي ذي الطاقة الأقل لاثنتين من جزيئات ألأوزو غير المحضرة سابقا وهما 3,5-DMPID و 2,4-DMPID . وتم تدوين الأبعاد الهندسية , حرارات التكوين , الطاقات المدارية وطاقات التاين وكذلك الكثافات ألالكترونية. وتم أيضا حساب ترددات الأنماط الاهتزاز الأساسية (3N-6) و شدد امتصاص الأشعة تحت الحمراء المقابلة لها . إضافة إلى تصنيف كل نمط من هذه الأنماط في هاتين الجريئتين . وجد إن الجريئة 2,4- DMPID هي ألأكثر استقرارا وإنها تمتلك العزم الثنائي القطب ألأقل وكذلك التردد الأعلى لمط ألاهتزاز ألأساسي -N=N-.

Introduction

Azo compounds are highly colored and have been used as dyes and pigments for a long time. A large number of (N,N$^-$)-donar ligands in azo imine family have been prepared in the last few years(1-2). One of this family is the aryl azo imidazoles(3).This type of molecules are used as analytical reagents(4)and as a staining agents(5). However, two newly aryl azo imidazoles : 3,5-Dimethyl-phenyl -(1H-imidazol-2-yl)-diazene (3,5-DMPID) and 2,4 -Dimethyl- phenyl-(1H-imidazol-2-yl)-diazene (2,4-DMPID) molecules have been synthesis(6), Fig.1



3,5-DMPID 2,4-DMPID

Fig.1: 3,5-DMPID and 2,4-DMPID molecules

The molecular energy of each one of the 3,5-DMPID and 2,4-DMPID molecules, obtained from the semi emperical MINDO/3 method(15), was completely minimized according to the Murtagh- Sargent minimization technique(16) .The derivative of the energy was calculated , analytically, according to Pulay's Force method(17) .The numerically evaluated force constants of molecules are introduced then to the Wilson Secular equation of the following form(18) ,

$$\sum_j L_j (F_{ij} - M_{ij}\lambda) = 0$$

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients , L_j.These coefficients are utilized in evaluating the atomic partial participation values (APP) (the partial contribution of each atom to the molecular vibration), the IR absorption intensities and in doing the graphical representation of each of vibration mode.(10-11).

The aim of present work is to report the optimized geometries , heats of formation, dipole moments, HOMO-LUMO energies, ionization energies, charge and electron densities , and the IR characteristic (the 3N-6 fundamental frequencies along with their assignments and intensities) for these two newly imidazole molecules by calculation based on the MINDO/3-FORCES model(7,8). The calculation method was developed and applied to the treatment of organic molecules (9-14). Such treatment yields the equilibrium geometry and energy values of the molecules in addition to their fundamental vibration frequencies (3N-6) and IR absorption intensities.

Results and Discussion

For the 3,5-DMPID and 2,4-DMPID molecules , the calculated geometric parameters(bond lengths and bond angles) along with some physical properties; heat of formation, ΛH_f , kcal mol^{-1}, Dipole moment, (μ in Debye), energies (eV) of the High Occupied Molecular Orbital (HOMO) and the Lower Unoccupied Molecular Orbital (LUMO), and the ionization energies , eV, were listed , Table 1

Compared with other molecule, it was shown that 2,4-DMPID molecule has the lower ΛH_f and lower dipole moment , higher $\Delta_{HOMO-LUMO}$, eV , Table 1, and, in turn , it is the more stable one. Also, This molecule has the higher value of $\angle N_3C_4N_6$ and $\angle C_4N_6N_7$, Table 1.This may be attributed to the steric effect causes by the CH_3 group which is in the ortho position with respect to the N=N group. On the other hand, the 3,5-DMPID molecule, posses the lower values for the $\angle C_{13}C_{12}C_{11}$ and $\angle C_9C_{10}C_{11}$, Table 1 .The reason may be attributed to the fact that the substituent produces some decrease in the bond angle to which it is attached. For the same reason, the 2,4-DMPID molecule has the lower value for each of the $\angle C_{10}C_{11}C_{12}$ and $\angle C_8C_9C_{10}$ angle . In addition to, Table 1 shows that the 2,4-DMPID molecule has the shorter N=N bond length. This may be attributed to the presence of the methyl electron-donating group in the ortho position with respect to the N=N group.

3,5-DMPID and 2,4-DMPID molecules belong to the C_1 symmetry point group and each of them has 3N-6 (=75) fundamental vibration modes. From the character table, it is shown that all the modes have the A_1 symmetry. The frequency values for all of these modes along with their assignments and the corresponding IR absorption intensities for the 3,5-DMPID and 2,4-DMPID molecules were listed in Tables 3 and 4 respectively. From these two Tables it was shown that the frequency with the higher value is that of v_1; N_5-H st.; calculated with about the same value for the two molecules. The next higher frequency values were these of the 11, C-H stretch fundamental vibrations localized at the C-H bonds . Two of them v_2 and v_3 are for the imidazole ring with the as symmetric stretch mode , v_3, is of the lower frequency values;3497 and 3492 cm^{-1} against 3521 and 3522 cm^{-1} for 3,5-DMPID and 2,4-DMPID molecules respectively, Tables 3 and 4. The next lower C-H frequency values are the 3 modes of the phenyl ring and the 6 modes of the two CH_3 groups. The 2,4-DMPID molecule has the higher frequency value for the -N=N- stretch vibration mode, v_{13}, Tables 3 and 4. The reason may be due to the shortage of the N=N bond length as it was mentioned before .The shorter bond length means the higher bond order and consequently the more energy is needed for the vibration mode localized at this bond to be occurred. In addition to, the 2,4-DMPID molecule, also , has v_{22}, stretch vibration mode with the higher frequency and the lower intensity values, Tables 3 and 4. The reason may be due to the shrinkage of the C_4-N_5 and N_3-C_4 bonds , Table 1 . So, the bond order of these bonds will be increased and , in turn, the energy needed for occurring the vibration is increased. The reduction in the intensity value may be attributed to the fact that the 2, 4-DMPID molecule is the more stable one so, the electronic motion during the vibration will be the more restricted. Further more, the v_{14} and v_{15} , C=C stretch normal modes , have the higher frequency values for 2,4-DMPID molecule, Tables 3 and 4. The reason may be is the same as that mentioned before.

Finally , due to the anharmonicity , the stretch vibration frequencies modes have the larger deviation from the observed ones. In order to reduce these differences, scaling factors may be applied (19). Some of the scaled frequencies were , also, shown in Tables 3 and 4. .

Acknowledgments

Thanks to Prof. Dr. M. Shanshal for providing the MINDO/3 Forces program and to Prof. Dr. Abid Allah. M. Ali, College of Education for Women , University of Kufa, for his assistance.

Table -1: The geometric parameters for3,5-DMPID and 2,4-DMPID molecules. Bond lengths in angstrom and bond angle in degree.

Geometric parameter	MINDO/3-FORCES*	
	3,5-DMPID	2,4-DMPID
$C_1 – C_2$	1.383	1.384
C_2- N_3	1.377	1.376
N_3- C_4	1.335	1.332
C_4- N_5	1.370	1.368
N_5- C_1	1.373	1.372
$C_4 – N_6$	1.382	1.401
$N_6 – N_7$	1.191	1.164
$N_7 – C_8$	1.371	1.404
$C_8 – C_9$	1.426	1.443
$C_9 –C_{10}$	1.419	1.424
C_{10}-C_{11}	1.424	1.420
C_{11}-C_{12}	1.421	1.423
C_{12}-C_{13}	1.421	1.399
C_{13}-C_8	1.424	1.424
C_{12}-C_{15}	1.492	1.399
C_{10}-C_{14}(C_{10}-H_{19})	1.492	1.111
C_1-H_{16}	1.102	1.101
C_2-H_{17}	1.104	1.104
N_5-H_{18}	1.026	1.026
C_9-H_{19}(C_9-C_{15})	1.108	1.493
C_{11}-H_{20}(C_{11}-C_{14})	1.108	1.490
C_{13}-H_{21}	1.108	1.107
C_{14}-H_{22}	1.112	1.111
C_{14}-H_{23}	1.112	1.112
C_{14}-H_{24}	1.111	1.112
C_{15}-H_{25}	1.112	1.112
C_{15}-H_{26}	1.111	1.113
C_{15}-H_{27}	1.112	1.113
$\angle C_1 N_5 C_4$	110.1	110.4
$\angle N_5 C_4 C_3$	108.6	108.2
$\angle C_4 N_3 C_2$	106.9	107.6
$\angle N_3 C_2 C_1$	110.5	110.0
$\angle C_2 C_1N_5$	104.1	104.1
$\angle N_3C_4N_6$	118.7	133.3

$\angle C_4N_6N_7$	123.5	137.0
$\angle C_2C_1H_{16}$	133.8	134.2
$\angle C_1C_2H_{17}$	128.3	127.9
$\angle C_4N_5H_{18}$	128.8	128.2
$\angle C_9C_8C_{13}$	118.1	119.0
$\angle C_8C_{13}C_{12}$	122.4	121.7
$\angle C_{13}C_{12}C_{11}$	116.5	122.3
$\angle C_{10}C_{11}C_{12}$	124.2	114.7
$\angle C_9C_{10}C_{11}$	116.5	126.2
$\angle C_8C_9C_{10}$	122.4	116.4
$\angle C_{12}C_{15}H_{25}(\angle C_9C_{15}H_{25})$	112.8	113.6
$\angle C_{12}C_{15}H_{26}(\angle C_9C_{15}H_{26})$	114.3	114.1
$\angle C_{12}C_{15}H_{27}$ $(\angle C_9C_{15}H_{27})$	113.4	114.2
$\angle C_{10}C_{14}H_{22}(\angle C_{11}C_{14}H_{22})$	113.2	114.4
$\angle C_{10}C_{14}H_{23}(\angle C_{11}C_{14}H_{23})$	112.8	113.2
$\angle C_{10}C_{14}H_{24}\angle C_{11}C_{14}H_{24}$	114.5	113.0
$\angle C_9C_{10}C_{14}$ $(\angle C_9C_{10}H_{19})$	122.0	116.9
$\angle C_{10}C_{11}H_{20}(\angle C_{10}C_{11}C_{14})$	117.9	123.0
$\angle C_{10}C_9H_{19}(\angle C_{10}C_9C_{15})$	122.0	116.5
$\angle C_9C_{10}C_{11}$	122.0	126.2
$\angle C_{11}C_{12}C_{15}$ $(\angle C_{11}C_{12}H_{20})$	122.2	119.5
$\angle C_{12}C_{13}H_{21}$	118.0	117.7
$\angle N_7C_8C_{13}$	120.7	118.9
ΛH_f, kcal mol^{-1}	36.257	26.782
Dipole moment, (μ in Debye)	2.154	1.843
$E_{HOMO\ ,\ LUMO}$, eV	-7.1680 , 0.7898	-7.4813, 0.6200
$\Delta_{HOMO-LUMO}$, eV	-7.9578	-8.1013
Ionization energy, eV	7.1680	7.4813

* calculated in this work

Table-2: The Charge and electron densities for 3,5-DMPID and 2,4-DMPID molecules*.

atom	MINDO/3-FORCES*	
	Charge(electron density)	
	3,5-DMPID	2,4-DMPID
C_1	-0.056(4.056)	-0.061(4.061)
C_2	0.015(3.985)	0.016(3.984)
N_3	-0.182(5.182)	-0.182(5.182)
C_4	0.132(3.868)	0.070(3.930)
N_5	0.017(4.983)	0.040(4.960)
N_6	0.022(4.978)	0.031(4.969)
N_7	-0.046(5.046)	0.039(4,961)
C_8	0.149(3.851)	0.031(3.969)
C_9	-0.090(4.090)	-0.022(4.022)
C_{10}	0.064(3.936)	0.018(3.982)
C_{11}	-0.067(4.067)	-0.009(4.009)
C_{12}	0.065(3.935)	0.026(3.974)
C_{13}	-0.092(4.092)	-0.031(4.031)
C_{14}	0.080(3.920)	0.094(3.906)
C_{15}	0.080(3.920)	0.095(3.905)
H_{16}	0.030(0.970)	0.030(0.970)
H_{17}	0.017(0.983)	0.012(0.988)
H_{18}	0.035(0.965)	0.028(0.972)
H_{19}	-0.004(1.004)	-0.021(1.021)
H_{20}	-0.011(1.011)	-0.015(1.015)
H_{21}	-0.003(1.003)	-0.004(1.004)
H_{22}	-0.025(1.025)	-0.030(1.030)
H_{23}	-0.024(1.024)	-0.029(1.029)
H_{24}	-0.028(1.028)	-0.031(1.031)
H_{25}	-0.025(1.025)	-0.029(1.029)
H_{26}	-0.027(1.027)	-0.036(1.036)
H_{27}	-0.026(1.026)	-0.030(1.030)

* calculated in this work

Table 3: Theoretical data of vibration frequencies (v in cm^{-1}) and infrared absorption intensities (ir intensities in $km.\ mol^{-1}$) for 3,5-DMPID molecule.

No	Sym$ A	MINDO/3-FORCES*		Assignments
		$$Freq, cm^{-1};	IR intensity, $km.mol^{-1}$	
v_1		3592(3111)	52.82	Imidazole ring(N_5-H st.)
v_2		3521(3049)	47.56	Imidazole ring [(C_1+C_2)H s.st].
v_3		3497(3028)	30.36	Imidazole ring [(C_1+C_2)H as.st].
v_4		3463(2999)	2.26	Benzene ring[(C_9+C_{13})H st].
v_5		3461(2997)	84.39	Benzene ring[(C_9+C_{13})H st].
v_6		3459(2995)	133.97	Benzene ring[(C_{11}+C_9)H st].
v_7		3456(2993)	5.37	C_{14}-H st
v_8		3455(2992)	18.04	C_{14}-H st
v_9		3449(3037)	56.79	C_{15}-H st
v_{10}		3448(2986)	35.40	C_{15}-H st
v_{11}		3445(2983)	75.81	C_{14}-H st
v_{12}		3444 (2983)	46.07	C_{15}-H st
v_{13}		1925	43.93	N_6-N_7 st.
v_{14}		1682(1475)	1.67	Benzene ring(CCC) st.
v_{15}		1649 (1446)	66.40	Benzene ring[(C_9+C_{10}) st].
v_{16}		1597	0.51	(C_1+C_2) st.+$N_3C_4N_5$ st.
v_{17}		1531	2.63	C_4-N_6 st + Imidazole ring(C_1-C_2) st.
v_{18}		1516	11.43	Benzene ring[($C_{10}C_{11}C_{12}$) st].
v_{19}		1513	5.40	Benzene ring (CCC)st+ C- $_{14}CH_3$ st.
v_{20}		1452	82.32	$N_6N_7C_8$ st.+ Benzene ring(CC)st
v_{21}		1432	20.39	Imidazole ring(C_1-N_5+C_2-N_3) as.st
v_{22}		1377	24.97	Imidazole ring($C_1N_5C_4$+C_4-N_3)st
v_{23}		1367	45.49	$\delta_{s\ 14}CH_3$
v_{24}		1350	8.88	δ as $C_{15}H_3$+C-$_{14}CH_3$ st
v_{25}		1313	5.03	δ as $C_{15}H_3$
v_{26}		1313	2.39	δ as $C_{14}H_3$
v_{27}		1304	4.18	δ as $C_{14}H_3$
v_{28}		1303	3.18	δ as $C_{14}H_3$
v_{29}		1263	25.29	Imidazole ring(C_1-N_5+C_2-N_3) s.st
v_{30}		1211	1.15	Benzene ring(C_{10}-C_{11})st
v_{31}		1192	26.13	Benzene ring δ (C_9-C_{11})H+C_8-N_7 st.
v_{32}		1189	13.08	Benzene ring(δ CH)
v_{33}		1171	5.31	Imidazole ring(δ N_5-H)
v_{34}		1148	7.30	Benzene ring(C=C)st
v_{35}		1106	0.23	Imidazole ring(δ [C_1+C_2]H)
v_{36}		1082	0.11	δ (Imidazole+ Benzene) ring
v_{37}		1063	0.24	Imidazole ring(δ [C_1+C_2]H)
v_{38}		1047	3.77	Imidazole ring(δ [C_1+C_2]H)
V_{39}		976	0.99	Benzene ring elongation (δ C C C)
V_{40}		942	0.32	$\rho\ _{14}CH_3$

V_{41}	941	14.66	δ $N_7N_6C_4$
V_{42}	937	4.56	ω $_{15}CH_3$
V_{43}	929	4.23	ω $_{14}CH_3$
V_{44}	914	10.83	ρ $_{15}CH_3$
V_{45}	807	0.02	Benzene ring(δ [C_1-H+C_2-H]
V_{46}	803	0.07	Benzene ring(δ C-H)
V_{47}	758	7.74	Benzene ring(δ C-H)
V_{48}	749	3.86	Imidazole ring(γ C_1-H+ γ C_2-H)
V_{49}	722	3.74	Imidazole (ring elongation)
V_{50}	695	2.18	Imidazole ring(γ N_5-H)
V_{51}	659	1.17	Imidazole ring(γ C_1-H+ γ C_2-H)
V_{52}	617	23.33	δ ($C_4N_6N_7$)
V_{53}	609	0.15	δ (midazole+ Benzene) ring
V_{54}	599	4.45	Benzene ring (δ CCC)
V_{55}	529	0.82	Imidazole ring(δ $N_3C_4N_5$)
V_{56}	525	2.35	Benzene ring (δ CCC)
V_{57}	510	0.63	Imidazole ring(γ C_1-H+ γ C_2-H)
V_{58}	506	0.00	Benzene ring(δ $C_{10}C_{11}C_{12}$)
V_{59}	497	0.18	Benzene ring elongation(δ CCC)
V_{60}	485	0.33	Benzene ring elongation(δ CCC)
V_{61}	462	0.04.	Benzene ring(clock-anti clock wise) δ C-H
V_{62}	338	0.11	motion of Benzene ring is against that of N_7
V_{63}	305	0.51	motion of Imidazole is against that of N_7
V_{64}	255	0.88	δ CH_3
V_{65}	236	0,22	δ $N_7N_6C_4$
V_{66}	210	0.82	δ $C_8N_7N_6$
V_{67}	197	0.05	Benzene ring (δ $C_{13}C_8C_9$)
V_{68}	182	0.54	τ $_{14}CH_3$
V_{69}	144	0.74	motion of Benzene ring is against that of CH_3 group
V_{70}	101	0.03	δ $C_4N_6N_7$
V_{71}	46	0.01	τ $_{15}CH_3$
V_{72}	35	0.01	δ ring(Imidazole+ Benzene)
V_{73}	15	1.44	δ Imidazole ring
V_{74}	10	0.31	δ $_{14}CH_3$
V_{75}	9	0.01	δ $_{15}CH_3$

*calculated in this work , $:under C_1 symmetry point group, $$: values in parentheses are for the scaled frequencies, reference 19, s: symmetric, st: stretching, δ : in plane bending, s: symmetric, as: anti symmetric, γ : out of plane, τ : torsion, ρ :rock, ω :wag,

Table.4: Theoretical data of vibration frequencies (v in cm^{-1}) and infrared absorption intensities (ir intensities in km. mol^{-1}) for 2,4-DMPID molecule.

No	Sym$^{\$}$ A	MINDO/3-FORCES		. Assignments
		$^{\$\$}$Freq, cm^{-1};	IR intensity, km.mol^{-1}	
v_{1}		3590(3389)	77.67	Imidazole ring(N_5-H st.)
v_{2}		3522(3050)	38.99	Imidazole ring [(C_1+C_2)H s.st].
v_{3}		3492(3024)	33.51	Imidazole ring [(C_1+C_2)H as.st].
v_{4}		3476(3010)	56.54	Benzene ring[(C_{12}+C_{13})H st].
v_{5}		3459(2995)	35.28	Benzene ring[(C_{12}+C_{13})H st].
v_{6}		3456(2993)	92.42	C_{14}-H st.
v_{7}		3449(3037)	67.35	C_{15}-H st.
v_{8}		3443(2982)	64.24	C_{14}-H st.
v_{9}		3440(2979)	77.62	C_{14}-H st.
v_{10}		3439(2978)	38.95	C_{15}-H st..
v_{11}		3435(2975)	36.63	Benzene ring [(C_{10}+C_{12})H st].
v_{12}		3432(2972)	58.05	C_{15}-H st.
v_{13}		1968	55.82	N_6-N_7 st.
v_{14}		1704(1494)	20.07	Benzene ring(CCC) st.
v_{15}		1621(1422)	6.60	Benzene ring(CC) st.+C_{11}-C_{14} st.
v_{16}		1602	42.59	Imidazole ring ($N_3C_4N_5$)st+(C_1-C_2) st.
v_{17}		1548	1.71	Benzene ring(CCC) st.
v_{18}		1526	31.78	Imidazole ring (C_1-C2) st+(C_4-N_6)st.
v_{19}		1502	0.82	Benzene ring($C_{11}C_{10}C_9$) st.
v_{20}		1430	30.96	Imidazole ring (C_1-N_5 +C_2-N_3) as.st.
v_{21}		1405	16.90	Benzene ring(CCC) st
v_{22}		1383	16.54	Imidazole ring ($C_1N_5C_4$+N_3-C_4)st.
v_{23}		1376	34.56	$\delta_{s\ 15}CH_3$
v_{24}		1346	29.75	$\delta_{s\ 14}CH_3$

v_{25}	1321	3.22	$\delta_{as}\,{}_{15}CH_3$
v_{26}	1313	4.00	$\delta_{s}\,{}_{14}CH_3$
v_{27}	1309	4.51	$\delta_{as}\,{}_{15}CH_3$
v_{28}	1306	2.95	$\delta_{s}\,{}_{14}CH_3$
v_{29}	1255	27.09	Imidazole ring(C_1-N_5+C_2-N_3) s. st.
v_{30}	1215	2.83	Benzene ring($\delta\,C_8C_9C_{10}$)
V_{31}	1204	7.03	Benzene ring [$\delta\,(C_{12}+C_{13})H$]
V_{32}	1202	6.08	Benzene ring($\delta\,C_{10}$-H)
V_{33}	1178	0.56	Imidazole ring ($\delta\,N_5$-H)
V_{34}	1155	4.77	Benzene ring(C=C+C=C+C=C) st.
V_{35}	1104	1.50	Benzene ring($\delta\,[C_{10}$-H+C_{12}-H])
V_{36}	1083	1.41	Imidazole ring $\delta\,[C_1$-H+C_2-H]+$\delta\,C_4N_3N_5$
V_{37}	1046	3.05	Imidazole ring $\delta\,[C_1$-H+C_2-H]
V_{38}	1028	1.07	$\rho\,{}_{15}CH_3+\delta_{s}\,{}_{14}CH_3+\delta$ Benzene ring
V_{39}	946	0.01	$\rho\,{}_{14}CH_3+\rho\,{}_{15}CH_3$
V_{40}	943	6.91	$\omega\,{}_{14}CH_3+\omega\,{}_{15}CH_3$
V_{41}	934	5.56	$\rho\,{}_{15}CH_3+\ \delta$ Imidazole ring..
V_{42}	928	4.39	$\rho\,{}_{15}CH_3+\delta\,C_4N_3N_5$
V_{43}	923	8.73	$\rho\,{}_{14}CH_3+\delta\,C_4N_3N_5$
V_{44}	862	0.19	Benzene ring ($\gamma C_{12}+C_{13})H$
V_{45}	830	0.08	Benzene ring ($\gamma\,C_{13}$-H+ $\gamma\,C_{10}$-H)
V_{46}	807	2.57	Benzene ring(δ CCC)
V_{47}	769	2.26	Benzene ring ($\gamma\,C_{10}$-H+$\gamma\,C_{13}$-H+$\gamma\,C_{12}$-H)
V_{48}	754	3.56	Imidazole ring($\gamma\,C_1$-H+$\gamma\,C_2$-H)
V_{49}	721	1.52	Imidazole ring elongation
V_{50}	694	1.97	Imidazole ring($\gamma\,N_5$-H)
V_{51}	680	4.10	Benzene ring($\delta\,C_{12}C_{13}C_8$)
V_{52}	662	0.94	Imidazole ring $\delta\,[C_1$-H+C_2-H]

V_{53}	660	0.58	$\delta N_6N_7C_8+\delta$ Imidazole ring [$\delta (C_1$-H+C_2-H)]
V_{54}	610	0.24	$\delta C_4N_6N_7$
V_{55}	594	12.46	Imidazole ring elongation+ $\delta C_4N_6N_7$
V_{56}	546	2.32	Benzene ring(γC-C+ γC_8-N_7)
V_{57}	528	0.10	δ Benzene ring + δ Imidazole ring
V_{58}	520	1.03	δ Imidazole ring
V_{59}	493	3.94	δ Imidazole ring+ δ Benzene ring
V_{60}	482	1.09	δ Imidazole ring
V_{61}	438	2.46	δ Benzene ring
V_{62}	404	0.62	δ Benzene ring
V_{63}	386	0.11	δ Benzene ring
V_{64}	287	0.56	δ Benzene ring+ δ Imidazole ring
V_{65}	259	0.13	δCH_3
V_{66}	235	0.70	$\delta C_4N_6N_7$
V_{67}	200	0.83	δ Imidazole ring
V_{68}	186	0.02	δ Benzene ring
V_{69}	140	0.02	δ Imidazole ring
V_{70}	100	0.27	δ (Benzene+ Imidazole) ring
V_{71}	98	0.01	$\delta\ _{15}CH_3$
V_{72}	38	0.04	δ (Benzene+ Imidazole) ring
V_{73}	33	0.02	$\tau\ _{14}CH_3$
V_{74}	17	1.52	δ Imidazole ring
V_{75}	11	0.06	$\tau\ _{15}CH_3$

For abbreviations and symbols, see Table 3.

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