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Comparative study on the vibrational IR spectra of N-aryl imidazoline-2-(thio) one derivatives by various semi-empirical methods

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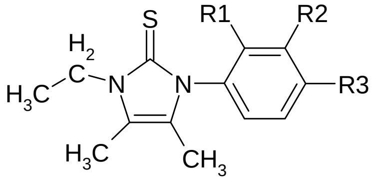
Abstract- The vibrational IR spectra of several derivatives of imidazoline and their dipole moment have been calculated using the MNDO , AM1 and PM3 methods , using Jaguar software and the results are compared with those calculated from ab initio and density functional theory (DFT) calculation. The ability of the semi empirical methods to predict the vibrational frequencies has been probed.

Key Words: Imidazoline; IR spectra; DFT; MNDO; AM1; PM3

INTRODUCTION

Because of the importance of imidazole derivatives for living bodies, we carry on working on these molecules both at experimental and theoretical levels. To determine the physical and chemical properties of the molecule studied: Di Me -4,5 Δ^4 N-Ethyl N-Phenyl Imidazoline-thione-2 (**1**) as well as its derivatives, we conducts the theoretical calculations with the software of molecular simulation (Jaguar) by using some semi empirical methods (AM1,PM3 and MNDO) and of the ab initio methods (HF and B3LYP). This calculation will be validated by the results of the infrared spectroscopy. The result of the comparison will be to find the theoretical method that interprets best the physical and chemical experimental properties of the molecule studied ie that it gives the results with the weakest mistakes. Thus, we can project , with the found method, the calculation for the no determined parameters by the experimental (Table 1).



MATERIALS AND METHODS

Theoretical calculations were carried out with both semi empirical (AM1, PM3, MNDO) , ab initio (3-21 G) and DFT B3LYP (6-31 +G*) methods with Jaguar software. We are going to study the vibrational parameters with a separated way. For every case, we are going to study the molecule **1** then we pass to the set of the derivatives to verify the substituting effect.

RESULTS AND DISCUSSION

The analysis done for the set of imidazoline in strong state by the initialization of the tablets prepared from KBr gives the following values :

Table 1. Experimental results of Infra red spectra of imidazoline derivatives (KBr)

	R1	*R2*	*R3*	*Frequence band RI (KBr) cm^{-1}*
1	H	H	H	3094,3022,2920,1602,1578,1506,1482,1419,1332, 1311,1275, 1254, 912, 801,765,714,696, 674, 573
2	Me	H	H	3100,3016,2926,1578,1506,1479,1416,1323,1290,1251,1146, 1101, 1089, 912,795,777,720,684, 585
3	OMe	H	H	3148,3106,3022,1605,1575,1509,1473,1446,1422,1320,1278, 1254,1198, 1152, 1101, 1020, 912,771, 732, 684
4	OEt	H	H	2997,1605,1551,1425,1335,1245,1150,675, 575
5	H	Cl	H	3160,1605,1590,1488,1458,1437, 1323, 1257, 1233, 1077, 774, 705, 687 and 669
6	H	H	Cl	3154, 3112, 3028, 1578, 1500, 1476, 1419, 1320, 1284, 1269, 1251, 1089, 912, 873,756, 741, 573

To understand the physical and chemical properties and in order to interpret the specters of imidazoline and its derivatives, the IR specters give very interesting information on the types of the functions that exist within molecules and especially that constructs the functional groups. The frequencies of vibrations calculated by PM3, MNDO, AM1 that are near and belong to the zone of the characteristic vibrations of the molecule and these derivatives (Experimental) are presented in the Tables 3,4 and 5.

Table 2. Comparison of the theoretical results IR with the experimental

EXP	PM3	B3LYP(DFT)	HF	N°
	42.58	51.43	34.13	1
	485.88	509.47	502.56	2
573	571.92	578.05	552.66	3
	583.22	622.11	618.5	4
	611.30	623.85		5
	629.38			6
	665.17			7
678	679.55	668.11		8
696		687.88	683.45	9
714		714.86	706.03	10
765		765.76	774.26	11
801	782.51	783.66	806.91	12
	821.94	823.12	817.57	13
	849.63	842.43	846.54	14

			896.13	15
	944.89	937.23	917.17	16
912	950.36	980.71	988.25	17
		957.49	1237.89	18
	1223.03	1205.04		19
	1267.18	1239.21	1250.25	20
1254	1292.94		1285.80	21
1275	1314.40	1321.61	1317.33	22
1311	1332.76	1337.96	1322.39	23
1332	1377.37	1360.83	1349.43	24
	1402.61	1403.71		25
	1406.61	1424.76	1425.93	26
1419	1429.81	1462.33	1469.46	27
	1456.93	1499.43	1496.81	28
1482	1472.54	1504.93		29
	1540.50	1506.60	1505.43	30
1506	1559.96	1547.63	1573.31	31
1578	1605.32	1645.61	1599.53	32
1602			1623.17	33
	2896.87	3041.01		34
	2966.65	3050..90		35
2920	3011.91	3088.29		36
	3046.23	3099.13		37
	3047.67	3117.83		38
3094	3049.99	3203.73		39
	3067.20	3229.68	3205.57	40
	3083.54		3207.85	
	3138.32		3301.72	
	3144.63		3398.27	
	3177.77			

The Tables 2 summarize the frequencies of the strips of vibration feature of this molecule. The calculated values are those of the maximal vibration that characterize the position of the absorption strip in IR

We present first the theoretical calculation of the frequencies of vibration of the molecule 1, with the AM1 methods, PM3 and MNDO, compared to the experimental results (Table 2). The specters of vibration of the molecule 1 have been calculated using the AM1, PM3 and MNDO methods. The results are compared with the frequencies of vibration feature of the experimental specters of these molecules, so the best method pulled from this comparison will be compared again to the ab initio and DFT methods.

Table 3. Comparison of the molecule 1 vibration frequencies calculations

N°	AM1	PM3	MNDO	Experiment
1	40.57	42.58	37.70	
2	500.03	485.88	531.29	
3	541.33	571.92	585.75	573
4	615.84	583.22	597.93	
5	625.11	611.30	604.00	
6		629.38	621.82	
7	656.96	665.17	640.40	

8	684.49	679.55	696.17	678
9				696
10	728.16		714.09	714
11				765
12	814.80	782.51	841.02	801
13	853.93	821.94	873.58	
14		849.63	897.34	
15	890.26	944.89	920.65	912
16	954.09	950.36	967.54	
17				
18	1203.58	1223.03	1223.93	
19	1251.12	1267.18	1257.63	1254
20	1273.35	1292.94	1270.92	1275
21			1276.41	
22	1327.70	1314.40	1340.33	1311
23	1341.30	1332.76	1366.47	1332
24	1376.58	1377.37	1381.80	
25				
26	1393.71	1402.61		
27	1425.61	1406.61	1426.88	
28	1430.74	1429.81	1429.94	1419
29	1435.27	1456.93	1432.08	
30			1443.01	
31	1445.32	1472.54	1480.63	
32			1491.96	1482
33			1508.21	
34	1525.83	1540.50	1554.01	1506
35	1548.43		1591.73	
36	1572.21	1559.96	1602.10	1578
37	1588.01	1605.32		1602
38	1636.51			
39		2896.87		
40	2954.18	2966.65		2920
41		3011.91		
42				
43	3021.14	3046.23		
44	3048.17	3047.67		3022
45	3053.73	3049.99		
46	3067.46	3067.20		
47	3068.08	3083.54	3202.43	
48	3139.32	3138.32		3094
49	3142.79	3144.63	3342.45	
	3179.41	3177.77	3408.19	

The comparison with the ab initio and DFT methods succeeds to the most precise method that presents the most complete specter. The geometries of different bases are considered from the standards values of bases. The frequencies of vibration are calculated for the whole set of the frequencies of the imidazoline derivatives.

The values of vibration frequencies compared are only those that belong to the same scale (same zone of vibration): according to the type and mode of vibration with the characteristic values. Others comparison between the methods in the zones non mentioned in the experimental specter.

Table 4. Results of the Molecule 1 vibration frequencies calculations

EXP	PM3	B3LYP(DFT)	HF	N°
	42.58	51.43	34.13	1
	485.88	509.47	502.56	2
573	571.92	578.05		3
	583.22	622.11	552.66	4
	611.30	623.85		5
	629.38		618.5	6
	665.17			7
678	679.55	668.11		8
696		687.88		9
714		714.86		10
765		765.76	683.45	11
801	782.51	783.66		12
	821.94	823.12	706.03	13
	849.63	842.43		14
			774.26	15
	944.89	937.23		16
912	950.36	980.71	806.91	17
		957.49		18
	1223.03	1205.04	817.57	19
	1267.18	1239.21		20
1254	1292.94		846.54	21
1275	1314.40	1321.61		22
1311	1332.76	1337.96	896.13	23
1332	1377.37	1360.83		24
	1402.61	1403.71	917.17	25
	1406.61	1424.76		26
1419	1429.81	1462.33	988.25	27
	1456.93	1499.43		28
1482	1472.54	1504.93	1237.89	29
	1540.50	1506.60		30
1506	1559.96	1547.63		31
1578	1605.32	1645.61	1250.25	32
1602				33
	2896.87	3041.01	1285.80	34
2920	2966.65	3050..90		35
	3011.91	3088.29	1317.33	36
	3046.23	3099.13		37
3094	3047.67	3117.83	1322.39	38
	3049.99	3203.73		39
	3067.20	3229.68	1349.43	40
	3083.54			
	3138.32			
	3144.63		1425.93	
	3177.77			
			1469.46	
			1496.81	

1505.43
1573.31
1599.53
1623.17
3205.57
3207.85
3301.72
3398.27

According to the Table 1, the PM3 method gives good nearest results to the experimental in relation to AM1 and PM3. According to works already done on the heterocyclic, the DFT determines better the structure and the relative energies of the molecule. In the same way the ab initio method has been introduced in large biologically active molecule domains that are difficult and very long for the macromolecules that contain some heterocyclic . Therefore, it is necessary to compare the results already calculated by the semi empirical method : PM3 (interpreting the physical and chemical parameters of this class of bioactive compound better). In this study , we notice that the DFT method is nearer to the experimental result. The zone of distortion DFT is better than the PM3 . The study of the IR matrix of this molecule shows the existence of the vibrations N-H, even we not really finds them as covalent link chemical in the molecule, it can be Van der Waals 's link as hydrogen links N-H are the weak links that vibrate toward 3100-3250 cm 1. The results of DFT are bad

in the region 3000-3400 cm^{-1}, on the other hand for the other regions present a considerable approach with the experimental results and that the DFT also represents the totality of the specter as the case of the PM3. For example the strips respective 1114,1044 cm^{-1} calculated by the DFT and ab initio are of frequency that belongs to the vibration safe C-N by the molecules that contains the oxygen because are characteristic of the C-O link which is an intense strip. In the contrary the C-N and C-C strips are weak strips. The comparison of the PM3 method with the ab initio methods shows that for the totality of the IR matrixes, the DFT is more believable, but without excluding the PM3 in zones of calculations that are not presented agreement well with the experimental in the strips of very elevated vibrations, these characteristic strips of all aromatic organic compounds, So, the PM3 finds a very important place to be complement to the ab initio method. Generally we can conclude from the results that the frequencies calculated by the PM3 method are the nearest to the experimental values except that the MNDO especially presents an important agreement in the zone of the distortion vibrations 500-1000 cm-$_1$ that concerns the vibration of distortion = C-H that appear to 696 cm-$_1$ in the experimental specter and to 696,17 cm-$_1$ in the MNDO spectra (Table 3) , the MNDO is rightly after the PM3 method concerning the totality of the characteristic frequencies (37 for PM3 and 34 for MNDO). We notice in the MNDO specters and AM1 the absence of the frequencies of vibration of groupings CH elongation, CH2 and CH3 in the zone 2800-3000 cm-1 which are determinist values of functional 5 groupings in this molecule. In the zone 1000 to 1800 cm-1, the AM1 method gives nearer calculations for the vibration of the aromatic connection C=C that appears to 1578 cm-1 ,1506 cm-1 in the experimental spectra and to 1572,21 cm-1, 1525,83 cm-1 in the AM1 spectra (Table 3) and distortion of CH3 that appears to 1419 cm-1 in the experimental spectra and to 1425,61 cm-1 in the spectra AM1(Table 3). In the zone of the most elevated frequencies of vibration that characterizes the vibrations aromatic CH between 3000-3100 cm-1 and the vibrations N-H (3100-3400cm-1) the calculation by the PM3 method gives good results that agree well with the experimental. For example the vibrations C-HS aromatic appear to 3016 cm 1, 3100 cm 1 in the experimental specter and to 3044,27 cm 1, 3100,21 cm 1 in the PM3 specter (Table 3).In the case of OEt phenyl and OMe phenyl we finds the C-O aromatic vibration and aliphatic C-O whrer the calculations done by the PM3 method are nearer to the results of spectroscopic analysis. For example the C-O aromatic vibrations and aliphatic appear to 1020 cm 1 and 1101 cm-1 in the experimental specter and to 1014,66 cm 1, 1097,33 cm 1, in the PM3 specter (Table 4) also the molecule 4 present a C-O vibration to 1089 cm-1 in the experimental specter and 1083,10 cm 1 in the PM3 specter (Table 4).

Table 5. Results of the Molecule 2 vibration frequencies calculations

Exp	MNDO	PM3	AM1		N°
	37.61	60.22	25.11		1
	501.24	522.71	500.84		2
585	574.92	579.39	580.91		3
	591.92	590.71	658.85		4
684	644.02	668.35	690.19	δ (=CH arom)	5
720	709.93	734.81	705.38	δ (-CH_2)	6
		758.96	738.26		7
777	783.51	784.00	766.17	δ (=CH arom)	8
795	848.02	870.41	897.05	δ (C=C arom)	9
		887.85			10
912	913.14	930.29	916.97	δ (C_4=C_5 heterocycle)	11
	1025.80	1001.13	1007.5		12
1089	1087.91	1087.20	1078.87		13
	1097.29	1094.42			14
1101	1106.74	1098.16			15
		1114.42	1122.09		16
1146	1168.79	1137.85	1164.33		17
			1215.93		18
	1224.88	1269.40	1280.76		19
1251	1285.92	1294.17	1289.98		20
1290	1335.28	1338.37	1323.92	υ(C=S)	21
1323			1330.70		22
	1416.33	1407.33	1403.59		23
1416	1480.64	1448.19	1461.03	δ (-CH_2)	24
1479	1487.43			δ (-CH_3)	25
	1496.28			υ(C=C aroma)	26
	1506.78	1535.76	1495.48		27
1506	1548.93			υ(C=C aroma)	28
	1593.19	1576.19	1569.63		29
1578	1600.5	1603.90	1605.65	υ(C=C heterocycle)	30
				υ(CH_2 , CH_3)	31
2926		3044.27		υ(=C-H aroma)	32
3016		3100.21		υ(=C-H aroma)	33
3100		3157.80	3194.29		34

					35
	3202.59	3208.32	3209.50		36
	3302.61	3215.74	3325.36		37
	3400.55		3330.30		38
	3418.42				

We observe in the theoretical specters of the values of vibration frequency raised between 3100-3500 cm 1 that represents the harmonic weak vibrations and non harmonic that are not present in the experimental specters It remains the vibration to weak absorption. For example the zone of vibration 3362,49 to 3457,51 for the MNDO specter (Table 5) . The strips calculated between 1650-1900 don't represent really experimental vibration, but very weak vibrations of the C=C to different substitutions . For example the absorption to 1674,05 cm 1 in the AM1 specter (Table 6). The vibrations 500-900 represent the zone of distortion vibration in the plan and outside of the plan. The vibrations inferior to 500 cm^{-1} due to the vibration of conformation (distortion) the molecule due to the rotation around the C-N link between the C hybridizes sp2 of the aryl in a gate of very determined rotation that gives to this molecule an atrophic chirality.
Here is a comparison therefore between the characteristic strips of valences for the set of the derivatives imidazole for the experimental IR specters : According to the Tables 10 and 11 the frequencies _ =C-H arom generally appears between 3000 and 3150 cm-1 the strip of absorption of the double heterocyclic link appears toward 1600 cm-1. We can differentiate between this six imidazoline derivatives by IR spectroscopy according to the characteristic vibrations of the substituting so the additive effect on the other links. The presence of vibration in the domain 1000 -1150 cm-1 for the molecules 4 and 5 show the vibrations of the aliphatic C-O link and aromatic = C-O .(Table 7 and 8)

Table 6. Results of the Molecule 3 vibration frequencies calculations

exp	MNDO	PM3	AM1		N°
	97.92	60.19	14.67		1
	504.63	521.04	515.37		2
684	623.65	668.16	699.29	δ (=CH arom)	3
732	703.46	737.56	733.40	δ (=CH arom)	4
771	765.62	759.97	773.18	δ (-CH$_2$)	5
		784.27			6
912	919.26	929.74	911.09	δ (C$_4$=C$_5$ heterocycle)	7
		1006.57	1007.00		8
1020	1011.06	1014.66	1013.89	υ(CH$_2$, CH$_3$)	9
1101	1145.41	1097.33	1120.79		10
		1104.39			11
1152	1171.62	1137.63	1160.92	υ(=C-O)	12
1198	1196.52	1189.12	1198.41		13
	1233.67	1224.37	1226.88		14
1254	1259.34	1269.08			15
1278		1293.23	1275.23	υ(C=S)	16
1320	1318.59	1338.27	1325.60		17
	1418.41				18
1422	1420.47	1407.49	1421.96		19
1446	1452.02	1447.72	1453.94		20
1473	1471.94		1484.56		21
1509	1507.70	1537.10	1494.80	υ(C=C aroma)	22

	1540.11			υ(C=C aroma)	23
1575	1596.37	1578.97	1588.80		24
1605				υ(C=C aroma)	25
3022		3044.28	3194.20	υ(C=C)	26
		3100.38	3219.16	υ(=C-H aroma)	27
3106		3109.12	3325.41		28
3148		3145.90	3330.40	υ(=C-H aroma)	29
		3208.52			30
		3216.02			31
	3362.82				32
	3430.70				33
	3457.98				34

Generally, we can conclude from the results that the calculated frequencies by the PM3 method are the nearest to the experimental values except that the MNDO method especially presents an important agreement in the zone of the distortion vibrations 500-1000 cm^{-1} which concerns the = C-H distortion vibration that appear to 696 cm^{-1} in the experimental specter and to 696,17 cm^{-1} in the MNDO spectra (Table2) , the MNDO is rightly after the PM3 method concerning the totality of the characteristic frequencies (37 for PM3 and 34 for MNDO). We notice in the MNDO and AM1 specters, the absence of the CH elongation groupings vibration frequencies, CH2 and CH3 in the zone 2800-3000 cm^{-1} which are determinist values of five functional groupings in this molecule. In the zone 1000 to 1800 cm^{-1}, the AM1 method gives nearer calculations for the vibration of the aromatic bond C=C that appears to 1578 cm^{-1} ,1506 cm^{-1} in the experimental spectra and to 1572,21 cm^{-1}, 1525,83 cm^{-1} in the AM1 spectra (Table 2) and distortion of CH3 that appears to 1419 cm^{-1} in the experimental spectra and to 1425,61 cm^{-1} in the spectra AM1(Table 2). In the zone of the most elevated vibration frequencies that characterizes the aromatic vibrations CH between 3000-3100 cm^{-1} and the vibrations N-H (3100-3400cm^{-1}) the calculation by the PM3 method gives good results that agree well with the experimental. For example the aromatic vibrations C-HS appear to 3016 cm^{-1}, 3100 cm^{-1} in the experimental specter and to 3044,27 cm^{-1}, 3100,21 cm^{-1} in the PM3 specter (Table 3).

In the case of OEt phenyl and OMe phenyl, we finds the C-O aromatic vibration and aliphatic C-O (CH3-O or And Oh) the calculations done by the PM3 method are nearer to the results of spectroscopic analysis. For example the C-O aromatic vibrations and aliphatic appear to 1020 cm^{-1} and 1101 cm^{-1} in the experimental specter and to 1014,66 cm^{-1}, 1097,33 cm^{-1}, in the PM3 specter (Table 5) also the molecule 4 present a C-O vibration to 1089 cm^{-1} in the experimental specter and 1083,10 cm^{-1} in the PM3 specter (Table 5). We observe in the theoretical specters of the vibration frequency values raised between 3100-3500 cm^{-1} that represents the harmonic weak vibrations and non harmonic which are not present in the experimental specters It remains the vibration to weak absorption. For example the vibration zone 3362,49 to 3457,51 for the MNDO specter (Table 7). The strips calculated between 1650-1900 don't represent really experimental vibration, but very weak C=C vibrations to different substitutions. For example the absorption to 1674,05 cm^{-1} in the AM1 specter (Table 8), The vibrations 500-900 represent the vibration distortion zone in the plan and outside of the plan. The vibrations inferior to 500 cm^{-1} due to the conformation vibration (distortion) caused by the rotation around the C-N bond between the C hybridizes sp^2 of the aryl in a gate of very determined rotation that gives to this molecule an atrophic chirality. Here is a comparison between the characteristic strips of valences for the Imidazole derivatives set which concern the experimental IR specters

According to the Tables 9 and 10 the frequencies ν =C-H arom generally appears between

3000 and 3150 cm^{-1} the strip of absorption of the double heterocyclic bond appears toward 1600 cm^{-1}.

We can differentiate between this six imidazolines derivatives by IR spectroscopy according to the vibrations characteristic of the substituting so the additive effect on the other bonds. The presence of vibration in the domain 1000 -1150 cm^{-1} for the molecules 4 and 5 show the aliphatic C-O bond vibrations and aromatic = C-O one.

Table 7. Results of the Molecule 4 vibration frequencies calculations

exp	MNDO	PM3	AM1		N°
	56.32	9.69	12.20		1
	502.25	510.90	513.85		2
	518.73				3
	561.80				4
575	586.17	574.40	584.14		5
	607.53	618.22	614.96		6
	629.13				7
675	703.96	668.67	659.98	δ (=CH arom) δ (-CH_2)	8
	925.62	740.53	745.05		9
	1001.29	939.95	932.64		10
	1079.56	1005.67	1006.00		11
		1099.21	1101.76		12
	1145.56	1144.52	1150.94		13
1150		1224.22			14
	1246.94	1269.39	1224.70	υ(=C-O)	15
1245			1274.76		16
	1328.35	1338.22	1334.77	υ(C=S)	17
1335	1345.64		1399.81		18
	1420.62	1412.58	1450.86	δ (-CH_2) , δ (-CH_3)	19
1425		1447.98	1494.51		20
	1540.27	1538.27	1589.97	δ (-CH_3)	21
1551		1580.13	1657.57		22
	1596.76	1604.75		υ(C=C arom)	23
1605	1665.16				24
2997		3015.07		υ(C=C)	25
		3100.38		υ(=C-H arom)	26
					27
			3194.19		28
		3202.06	3202.35		29
		3216.10	3322.27		30
			3330.37		31
	3356.89				32
	3412.56				33
	3457.96				

Table 8. Results of the Molecule 5 vibration frequencies calculations

exp	MNDO	PM3	AM1		N°

	33.84	64.40	55.01		1
	527.13	530.31	539.55		2
669	639.29	661.39	658.82		3
687	689.11			δ (=C-H)	4
705	700.90	715.55	700.20	δ (-CH$_2$)	5
774	809.51	776.30	789.37	δ (=C-H)	6
	966.29	909.14	914.70		7
	1005.68	1006.56	1008.64		8
1077	1077.19	1070.22	1076.68		9
	1106.64	1130.69	1201.33		10
	1223.20		1207.15		11
1233	1240.30	1238.40	1252.10		12
1254	1276.96	1272.27			13
1323	1340.74	1339.76	1327.02	υ(C=S)	14
	1426.71	1401.33	1330.59	δ (-CH$_2$)	15
	1431.38	1407.63	1401.63		16
	1442.39	1444.86	1461.19		17
1437				δ (-CH$_2$)	18
1458	1480.31	1508.24	1494.05	δ (-CH$_3$)	19
1488	1491.92	1535.55	1553.97	υ(C=C arom)	20
	1507.82				21
	1592.62				22
1590	1601.07	1605.83	1595.54		23
1605			1674.29	υ(C=C arom)	24
				υ(C=C)	25
		3044.52			26
		3108.85			27
3160	3202.85	3142.47	3194.07	υ(=C-H arom)	28
		3208.57			29
		3216.35	3217.41		30
	3343.49		3325.20		31
	3401.12		3330.08		32
	3414.61				33

Table 9. Results of the Molecule 6 vibration frequencies calculations

exp	MNDO	PM3	AM1		N°
	127.51	64.59	57.76		1
	504.80	501.95	553.59		2
573	567.23	565.63	561.51		3
	592.15	580.39	588.29		4
741	676.15	709.59	738.10	δ (-CH$_2$)	5
756	802.38	782.77	779.02	δ (=C-H arom)	6
837	809.16	837.94	840.27	δ (C=C)	7
912	931.03	931.11	919.22	δ (C=C)	8
	1021.32	1006.59	1008.79		9
1089	1067.39	1083.10	1076.86		10
	1118.59	1094.75	1110.53		11
		1100.35			12
1251	1246.10	1237.60	1258.09		13
1269	1288.46	1271.67	1275.74	υ(C=S)	14
1284		1295.87	1290.24		15
1320	1316.31	1339.77	1316.82	δ (-CH$_3$)	16

	1325.52				17
1419	1419.64	1407.73	1401.04	δ (-CH_2)	18
1476	1471.60	1446.88	1459.59	δ (-CH_3),υ(C=C arom)	19
1500	1488.67	1498.63	1496.81		20
	1515.66	1535.61		υ(C=C arom)	21
1578	1543.51	1606.24	1598.74		22
	1618.88		1674.05	υ(C=C)	23
					24
3028		3044.51			25
3112		3112.91		υ(=C-H arom)	26
3154		3142.07		υ(=C-H arom)	27
			3194.07		28
		3209.93			29
		3216.39			30
			3217.31		31
			3325.21		32
			3330.08		33
	3362.49				
	3430.90				
	3457.51				

Table 10. Comparison between methods and characteristic bands

	Méthodes	*Molécule1*	*Molécule2*	*Molécule3*	*Molécule4*	*Molécule5*	*Molécule6*
$\nu_{c=c}$	AM1	1588.01	1569.63	1588.80	1589.97	1595.54	1598.74
	PM3	1605.32	1576.19	1578.97	1604.75	1605.83	1606.24
	MNDO	1602.10	1593.19	1596.37	1596.76	1601.07	1543.51
	HF	1599.53					
	B3LYP	1645.61					
	Experim	1602	1578	1605	1605	1605	1578
ν_{CH2} et ν_{CH3}	AM1	2954.18	-				
	PM3	2966.65	-				
	MNDO						
	HF						
	B3LYP	3041.01					
	Experim	2920	2926	-	-	-	-
$\nu_{c=c\ arom}$	AM1	1525.83	1461.03	1484.56,	1589.97	1494.05	1459.59
		1572.21	1495.48	1494.80			1496.81
	PM3	1540.50	1448.19	1573.10	1538.27	1508.24	1446.88
		1559.96	1535.76				1498.63
	MNDO	1508.21	1480.64	1471.94	1540.27	1480.31	1471.60
		1591.73	1506.78	1507.70		1592.62	1488.67
	HF	1505.43					
	B3LYP	1506.60					
	Experim	1506	1479	1473	1551	1590	1500
		1578	1506	1509		1488	1476
				1575			
$\nu_{=c-o}$	AM1			1160.92	1150.94		
	PM3			1137.63	1144.52		
	MNDO			1171.62	1145.56		
	HF						

	Experim	1152	1150

Tableau 11. The characteristic valence bands:

	Mol1	Mol2	Mol3	Mol4	Mol5	Mol6
$\nu_{c=c}$	1602	1578	1605	1605	1605	1578
$\nu_{\mathrm{CH2\ et}}\ \nu_{\mathrm{CH3}}$	2920	2926				
$\nu_{c=c}$ arom	1482	1479	1473	1551	1590	1500
	1506	1506	1509		1488	1476
	1578		1575			
$\nu_{=c\text{-}H}$ arom	3022	3016	3022	2997	3160	3028
	3094	3100	3106			3112
$\nu_{c=s}$	1254	1251	1254	1245	1257	1251
$\nu_{=c\text{-}o}$			1152	1150		
$\nu_{\mathrm{CH3\text{-}0\ ou\ CH2\text{-}0}}$			1020			

Conclusion

However, the ab intio and DFT methods have given us the better results of IR spectra calculations, the ability of the semi empirical methods and especially PM3 method to predict the vibrational frequencies has been probed.

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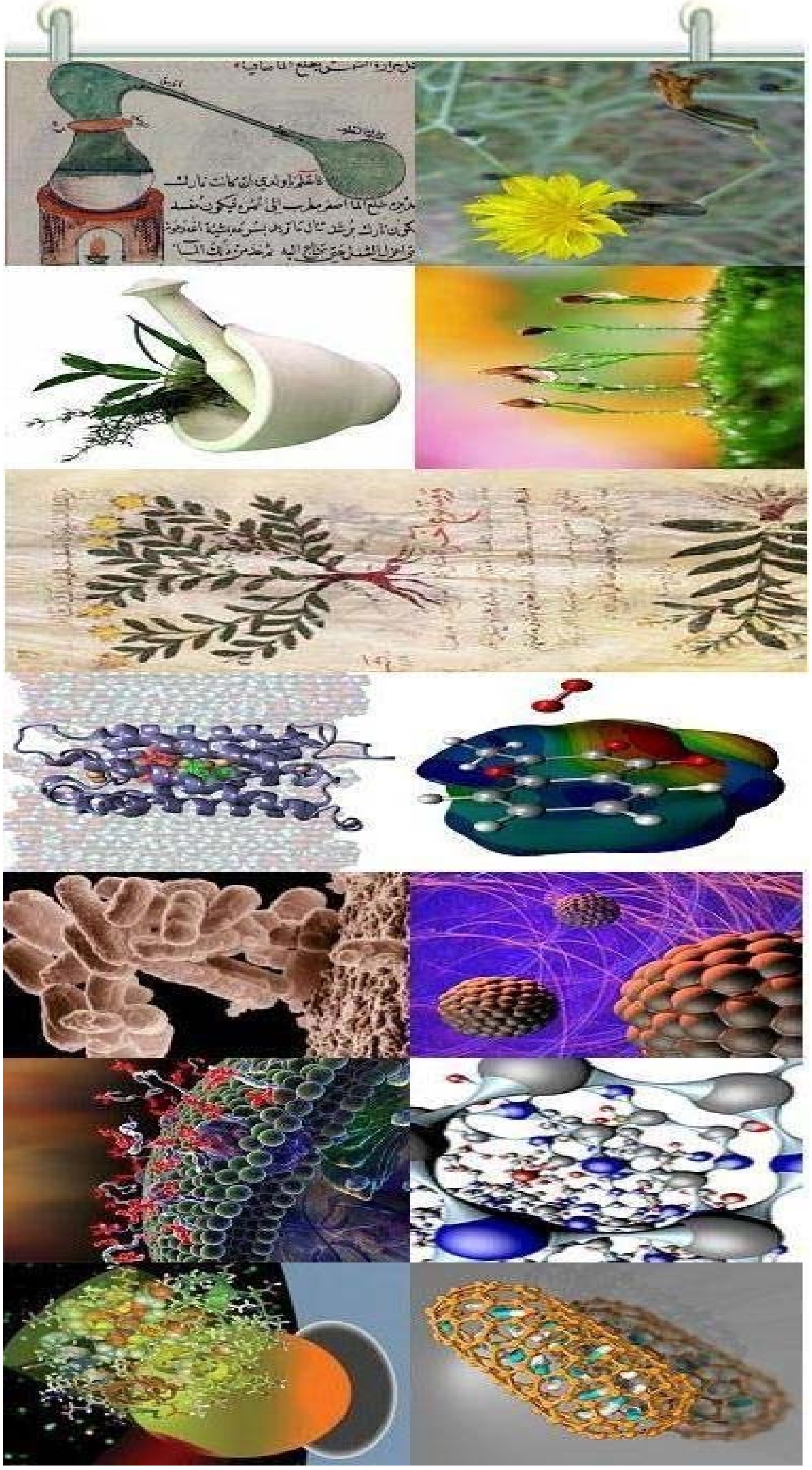

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