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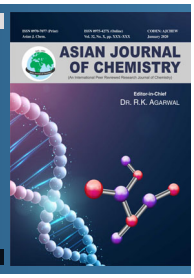

Comparative Studies of Infrared Spectral Simulation of Some Benzoyl Derivatives of *N*-Heterocyclic Compounds Using Semi-Empirical Methods

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Simulation studies based on *ab initio*, semi-empirical or density functional (DFT) calculations are now becoming common among the researchers who are pursuing their intereset in theoretical chemistry. These studies are based on quantum chemical softwares. These studies provide better insight for the structural and other parameters of the compounds. The present paper includes the studies on synthesis or procurement along with the simulated IR spectra of some benzoyl derivatives of *N*-heterocyclic compounds *viz*. 2-aminopyridine, 4-aminoantipyrine, 2-aminopyrimidine or 3-aminopyridine using four different AM1, PM3, MNDO and ZINDO1 semi-empirical methods. Among the methods used for the study, AM1 method is more reliable and more accurate so far as the prediction of spectral results is concerned.

Keywords: Semi-empirical, Simulation, Heterocyclic compounds.

INTRODUCTION

Semi-empirical methods modify Hartree-Fock calculations by introducing functions with empirical parameters. These methods are extremely demanding, especially in large systems. On the basis of experiments, and not of chemical interaction parameters two-electron integrals, this approximation is introduced, which increases the computational speed. The modified neglect of differential overlap (MNDO) method is the basis for all the modern semi-empirical techniques [1]. In this method, different parameters are assigned to various atomic types and fitted to recreate the properties such as dipole moments, the heat of formation, the first ionization energy, and geometrical variables. AM1 and PM3 are the state-of-the-art MNDO methods [2-4].

Infrared (IR) spectroscopy is one of the fundamental techniques for the determination of structure of organic compounds. This technique is a highly suitable tool for the qualitative analysis of the organic compounds. Furthermore, the peak size of IR spectra is used to determine the amount of an element or a molecule present in the compound; thus, IR spectroscopy facilitates the quantitative analysis of substances. Currently, modern software-based algorithms are used for such analyses and these algorithms render the technique an outstanding approach to quantitative and qualitative analyses [5-10].

Nuclear magnetic resonance and IR spectral simulations and studies related to these methods have emerged as a novel investigation field in chemical sciences. Currently, these methods are receiving attention from various scientists [11]. The simulated IR spectra acquired through quantum calculations are employed to discuss the structure, while the results are used to determine the relationship between the bond vibrations and the responses of the related IR peaks of the compounds [12]. These simulated spectra may be compatible with the spectra observed during experiments with a small error.

Some of the most commonly used software are MOPAC, HYPERCHEM, GAMESS and Gaussian. Simulation studies related to the structure of various organic compounds are reported by several researchers [12-15]. In this work, a comparative studies of experimental and simulated IR spectral values using semi-empirical methods *viz*. AM1, PM3, MNDO and ZINDO1 of some benzoyl derivatives of heterocyclic compounds were evaluated.

EXPERIMENTAL

All chemicals purchased were of laboratory grade and used as such. The FT-IR spectra of benzoyl derivatives of amino compounds were recorded in 4000-400 cm^{-1} region at room

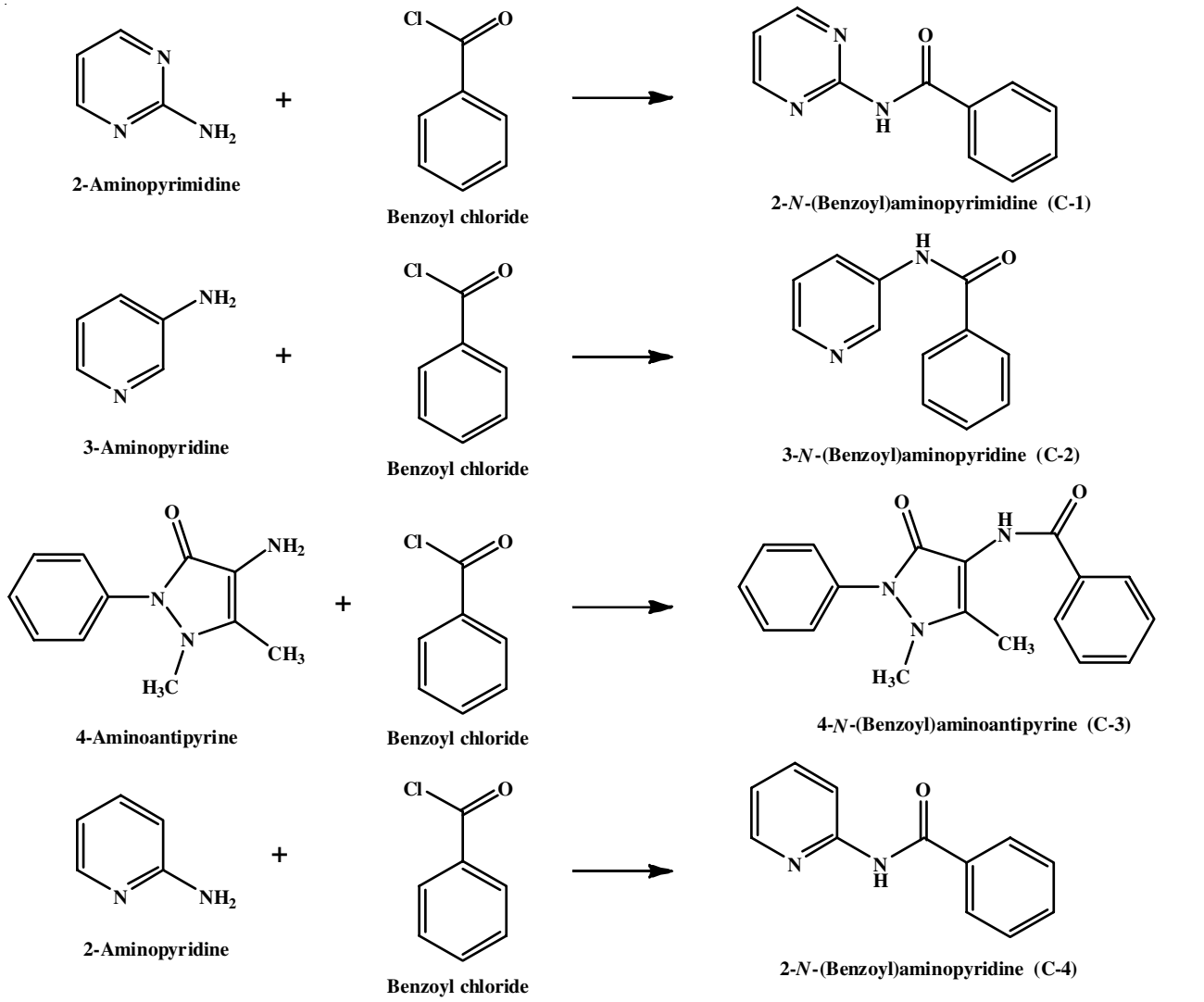
temperature, using KBr pellet, on a Fourier-transform infrared spectrometer in the solid phase at at SAIF, Jiwaji University, Gwalior, India.

The simulated infrared spectrum adopted standard quantum chemical program-HYPERCHEM [16] and all the quantum chemical computation work was carried on the Intel based Pentium Core-2 duo machine with configuration Intel® core™2 Duo Processor, T5450@1.66 GHz, 2 GB RAM.

Synthesis of benzoyl derivatives of *N*-heterocyclic compounds: An appropriate *N*-heterocyclic compound *viz*. 2-aminopyridine, 4-aminoantipyrine, 2-aminopyrimidine or 3-aminopyridine (1M, 15 mL) in ice-cold water was added to a solution of benzoyl chloride (10 mL) and stirred the reaction mixture vigorously for some period. A white precipitate formed was collected using vacuum filtration and washed thoroughly with cold ethanol (**Scheme-I**). The analytical data of the synthesized benzoyl derivatives of *N*-heterocyclic compounds are presented in Table-1.

RESULTS AND DISCUSSION

Mass analysis: Mass spectra of three compounds *viz*. C-1, C-3 and C-4 are shown in Fig. 1, which revealed that the parent ion peak in the spectra of these compounds appear at the *m/e* values where these are expected.



Scheme-I

TABLE-1
ANALYTICAL DATA FOR THE COMPOUNDS UNDER STUDY

Code	m.p. (°C)	m.w.	Colour	Elemental analysis (%)		
				C	H	N
C-1	120-125	198	White	56.89	5.44	1.89
C-2	115-120	198	Pinkish white	57.31	5.50	1.90
C-3	105-110	307	Yellowish white	56.79	5.84	5.25
C-4	100-105	198	Pinkish white	57.02	5.43	1.07

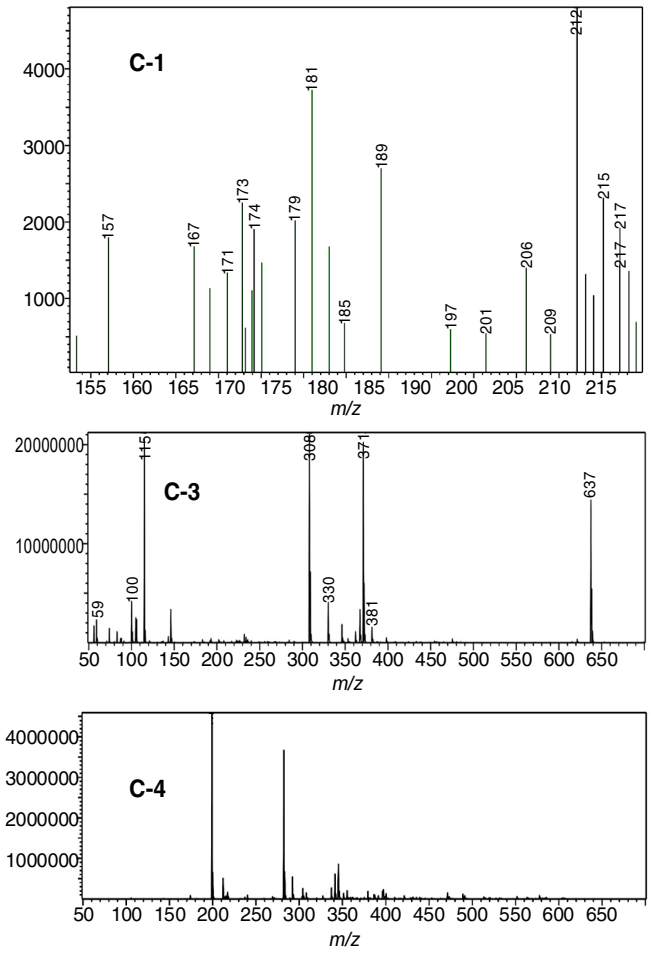


Fig. 1. Mass spectra of 2-*N*-(benzoyl)aminopyrimidine (**C-1**), 4-*N*-(benzoyl)-aminoantipyrine (**C-3**) and 2-*N*-(benzoyl)aminopyrimidine and 2-*N*-(benzoyl)aminopyridine (**C-4**)

Computational studies: All the parameters *viz*. zero point energy (ZPE), heat of formation (HF), dipole moment (DM), highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), total energy (TE), binding energy (BE) of the synthesized compounds were computed on the basis of AM1, PM3, MNDO and ZINDO1 semi-empirical methods and their values are reported in Table-2. Generally, energy values of HOMO and LUMO, as well as their energy gaps indicate the chemical activity of a molecule. Smaller HOMO-LUMO energy gaps (DE) correspond to an easier excitability HOMO electrons [17].

Simulated infrared spectra compared with experimental infrared spectra: The experimental IR spectra of the synthesized benzoyl derivatives of heterocyclic compounds are shown in Fig. 2. The AM1, PM3, MNDO and ZINDO1 computed results of benzoyl derivatives of N-heterocyclic compounds along with the experimentally observed bands and assignment peaks are presented in Table-3. The simulated infrared spectra reproduces position and intensity of major peaks and corresponds well with the experimental IR spectra. However, the spectra data obtained from experimental and simulated methods are not absolutely same after all. Owing to the absence of intermolecular hydrogen bonds in simulated system, some difference emerges at high-frequency region. Considering compound 2-*N*-(benzoyl)-aminopyrimidine (**C-1**) into the account, some of the major peaks of obtained and simulated IR spectrum are disscussed as follows:

AM1: Using AM1 semi-emperical method, a peak at 3138.43 cm^{-1} has been assigned to C-H symmetric stretching mode of vibration while the band at 1437.77 cm^{-1} is the symmetric mode of vibration due to C-CH_3. The band at 1946.94 cm^{-1} to symmetric mode of vibration is due to C-NH_2 and the band at 1669.43 cm^{-1} has been assigned to C=O stretching vibration. The peaks at 1629.65, 1592.44, 1320.40 and 1275.74 cm^{-1} are assigned to the stretching, scissoring and bending modes to the C=C, NH_2, C-C and C-N bands.

PM3: A band at 3063.77 cm^{-1} is assigned as C-H symmetric stretching mode of vibration. The peaks at 2936.34 and 1404.89 cm^{-1} are the symmetric mode of vibration due to C-CH_3. The other major peaks at 1718.29, 1594.06, 1538.38, 1360.60 and 1285.64 cm^{-1} are assigned to the stretching, scissoring and bending modes to the C=O, C=C, NH_2, C-C and C-N modes, respectively

TABLE-2
COMPUTED PARAMETERS FOR **C-1** to **C-4**

	AM1	PM3	MNDO	ZINDO1	AM1	PM3	MNDO	ZINDO1
	2-*N*-{Benzoyl}amino pyrimidine (**C-1**)				3-*N*-{Benzoyl}amino pyridine (**C-2**)			
TE (Kcal/mol)	-56993.09	-51221.79	-57088.08	-79306.04	-55495.33	-50560.35	-55571.82	-77328.70
BE (Kcal/mol)	-2687.58	-2715.95	-2704.90	-8021.18	-2808.60	-2822.69	-2806.57	-8623.16
DM (Debye)	4.14	4.00	3.86	5.44	3.98	4.03	4.24	8.22
ZPE (Kcal/mol)	118.56	113.14	121.11	160.26	125.89	119.89	128.36	175.20
HOMO (eV)	-0.19	-0.58	-0.20	-7.17	-0.03	-0.05	-0.0004	-4.56
LUMO (eV)	0.42	0.32	0.17	5.87	0.11	0.84	1.34	4.85
HF (Kcal/mol)	59.68	31.31	42.36	-5273.91	48.65	34.56	50.68	-5765.90
	4-*N*-{Benzoyl}amino antipyrine (**C-3**)				2-*N*-{Benzoyl}amino pyridine (**C-4**)			
TE (Kcal/mol)	-87443.32	-79832.20	-87634.22	-122065.14	-55508.61	-50575.94	-55601.37	-77202.80
BE (Kcal/mol)	-4242.83	-4286.51	-4272.03	-13169.39	-2821.88	-2838.29	-2836.12	-8497.25
DM (Debye)	5.39	5.18	4.01	10.28	4.60	4.54	4.86	4.92
ZPE (Kcal/mol)	202.12	194.95	207.62	281.38	126.53	121.30	129.36	172.11
HOMO (eV)	-0.22	-0.33	-0.80	-3.98	-0.08	-0.02	-0.17	-6.96
LUMO (eV)	0.13	0.01	0.05	4.72	0.16	0.87	0.09	6.78
HF (Kcal/mol)	177.03	133.36	147.84	-8749.52	35.37	18.96	21.13	-5639.99

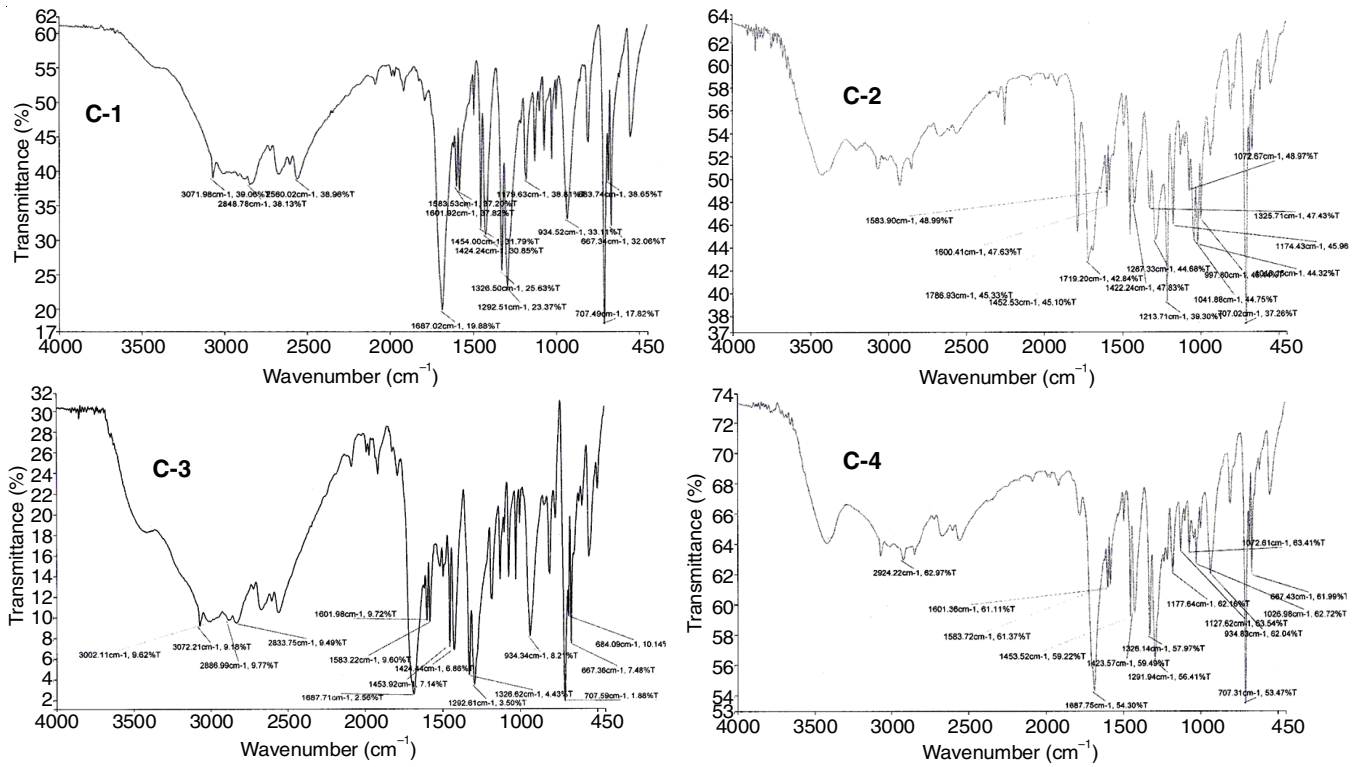


Fig. 2. IR spectra of 2-*N*-(benzoyl)aminopyrimidine (**C-1**), 3-*N*-(benzoyl)aminopyridine (**C-2**), 4-*N*-(benzoyl)aminoantipyrine (**C-3**) and 2-*N*-(benzoyl)aminopyrimidine and 2-*N*-(benzoyl)aminopyridine (**C-4**)

MNDO: A simulated band at 3386.42 cm^{-1} has been assigned to C-H symmetric stretching mode of vibration while the peak at 2044.63 cm^{-1} is assigned to symmetric mode of vibration due to C-NH_2. The other key peaks at 1626.57, 1595.23, 1563.65, 1495.78, 1320.51 and 1272.32 cm^{-1} are assigned to the stretching, scissoring and bending modes to the C=O, C=C, NH_2, C-C and C-N modes, respectively.

ZINDO1: Using ZINDO1 semi-emperical methods, the peaks at 2684.07 and 1420.91 cm^{-1} are due to symmetric vibrational mode of C-CH_3, while the peak at 2544.90 cm^{-1} is due to symmetric vibrational mode of C-NH_2. The other key peaks at 1790.59, 1581.27, 1435.91, 1326.47 and 1301.56 cm^{-1} are assigned to the stretching, scissoring and bending modes to the C=O, NH_2, C=C, C-C and C-N bands.

Due to the limitation of calculation in the computational methods, the bonds vibration affect the frequency of relevant peaks in experimental infrared spectrum. It is suspected that existing computational method in dealing with such a system

TABLE-3
COMPARATIVE STUDY OF EXPERIMENTAL AND COMPUTED (AM1, PM3, MNDO, ZINDO1) GROUP FREQUENCIES (cm^{-1}) FOR **C-1** TO **C-4**

Experimental group frequency (cm^{-1})	AM1 computed group frequency (cm^{-1})	PM3 compound group frequency (cm^{-1})	MNDO computed group frequency (cm^{-1})	ZINDO1 computed group frequency (cm^{-1})	Assignment
2-*N*-{Benzoyl}amino pyrimidine (**C-1**)					
3072.98	3138.43	3063.77	3386.42	4426.37	ν_s(C–H)
2849.78	–	2936.34	–	2684.07	ν_{as}(C–H) in CH_3
2561.02	1946.94	–	2044.63	2544.90	ν_{as}(C–NH_2)
1687.92	1669.43	1718.29	1626.57	1790.59	ν(C=O)
1601.92	1629.65	1594.06	1595.23	–	ν(C=C)
1582.53	1592.44	1538.38	1563.65	1581.27	NH_2(Sci)
1455.00	–	1514.34	1495.78	1435.91	ν(C=C)
1424.94	1434.77	1404.89	1430.81	1420.91	ν_{as}(C–CH_3)
1326.90	1320.40	1360.60	1320.51	1326.47	ν(C–C)
1293.51	1275.74	1285.64	1272.32	1301.56	ν(C–N)
1179.33	1172.45	1198.88	1166.32	1130.66	δ(C–H)
933.22	959.17	955.63	952.45	932.27	δ(C–H)
708.49	711.38	697.38	701.96	716.40	δ(N–N)
682.74	–	674.23	–	–	δ(CCC)

3-*N*-{Benzoyl}amino pyridine (**C-2**)					
1787.93	1787.45	1761.75	1762.75	1809.29	ν(C=O)
1717.20	1741.37	1755.74	1728.15	1693.12	ν(C=O)
1600.11	1634.42	1596.91	1600.26	1601.03	ν(C=C)
1583.92	1589.47	1577.46	1548.72	1528.82	NH_2(Sci)
1452.33	1461.43	1442.28	1492.49	1442.53	ν(C=C)
1422.44	–	1384.05	1424.80	1424.74	ν_{as}(C–CH_3)
1325.11	1321.42	1315.23	1309.09	1313.36	ν(C–N)
1287.33	1290.94	1290.22	1285.42	1269.99	–CH_2Cl
1212.71	1201.21	1222.23	1212.28	1207.60	δ(C–H)
1175.43	1185.30	1178.21	1177.75	1193.31	δ(C–H)
1072.77	1071.26	1088.38	1082.89	1056.22	δ(C=O)
1042.88	–	1050.38	1039.71	1034.21	(NH_2) Twi
1017.16	1011.98	1011.79	1008.34	1010.62	δ(C–N)
997.82	988.39	980.48	981.87	975.74	δ(C–H)
707.22	685.33	673.16	724.08	688.81	δ(N–N)
4-*N*-{Benzoyl}amino antipyrine (**C-3**)					
3072.24	3086.54	3077.90	3240.94	3804.60	ν_s(C–H)
3002.22	3012.71	3009.11	–	–	ν_s(C–H)
2887.99	–	–	–	–	ν_s(C–H)
2834.75	–	2751.02	2155.11	2843.03	ν_{as}(C–H) in CH_3
1688.71	1749.46	1773.04	1639.35	1693.54	ν(C=O)
1602.98	1638.40	–	1619.00	1595.34	ν(C=C)
1584.22	1575.88	1588.22	1544.50	1540.84	NH_2(Sci)
1453.22	1457.18	1457.01	1456.87	1452.88	ν(C=C)
1425.44	1425.20	1416.40	1412.41	1429.98	ν_{as}(C–CH_3)
1327.62	1334.01	1315.74	1331.36	1315.71	ν(C–C)
1292.16	1294.50	1282.38	1297.67	1299.10	δ(C–N)
934.44	907.02	938.47	916.74	967.91	δ(C–H)
707.99	721.66	707.06	696.55	727.74	δ(N–N)
2-*N*-{Benzoyl}amino pyridine (**C-4**)					
2924.32	3180.40	3037.12	3388.82	2723.69	ν_{as}(C–H) in CH_3
1687.55	1672.38	1746.58	1675.75	1653.75	ν(C=O)
1602.36	1635.50	1598.66	1599.84	–	NH_2(Sci)
1583.22	1576.30	1559.46	1568.62	1550.13	NH_2(Sci)
1453.32	1458.93	1529.40	1484.19	1453.37	ν(C=C)
1423.77	–	1418.95	1434.81	1410.84	ν_{as}(C–CH_3)
1326.44	1349.75	1333.30	1335.27	1340.54	ν(C–N)
1292.94	1289.61	1303.38	1283.92	1298.29	ν(C–C)
1177.34	1180.97	1169.37	1182.41	1173.44	δ(C=O)
1127.62	1108.24	1119.01	1159.91	1108.80	δ(C=O)
1072.11	1082.21	1088.83	1070.56	–	δ(C=O)
1026.98	1009.98	1022.76	1025.91	1037.76	δ(C–H)
934.33	918.87	944.25	940.06	939.89	δ(C–H)
707.32	696.22	706.51	698.70	726.71	δ(N–N)

which may have flaw that may be the main cause of the deviation of calculated results. Besides, there are some shifts between the simulated IR peaks and experimental ones. For example, in synthesized compound **C-1**, the simulated IR peak of C=O stretching vibrations, revealed a weak red shift (by AM1 method) (about 18 nm, compared to the experimental IR spectrum). It may be due to partial absence of compound's inter-molecular short contact in the simulated system. By comparing the other semi-empirical methods (PM3, MNDO and ZINDO1), AM1 semi-empirical method is more reliable and more accurate so far as the prediction of spectral results is concerned.

Conclusion

In this work, a comparative studies of infrared spectral simulation of some benzoyl derivatives of *N*-heterocyclic compounds using semi-empirical methods *viz*. AM1, PM3, MNDO, ZINDO1 was applied to calculate the normal modes frequencies of vibrations. The normal modes frequencies of vibration are in a good agreement with the experimental one. Among all these methods, AM1 method is reasonably good & closed to the experimental values as compared to others.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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