Vibrational Study and Electronic Parameters of "2-Diphenylphosphanyl-6-fluoro-pyridine"using First Principle

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Abstract

Vibrational investigations along with theoretical quantum chemical studies on "2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)" have been carried out. The quantum chemical density functional method at B3LYP/3-21Glevel is used to obtain the equilibrium geometries of the title compound. We have also performed vibrational analysis of the title compound at their equilibrium geometries and established the complete assignments of the significant vibrational modes. Electronic parameters such as HOMO, LUMO and frontier orbital energy band gap, has been calculated. Besides it the thermodynamical parameters like internal thermal energy, entropy and constant volume specific heat capacity have been calculated.

1. INTRODUCTION

The aim of the present study is to investigate in detail the vibrational spectra of the title molecule "2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)", a derivative of pyridine due to its biologically active properties. Pyridine is a heterocyclic aromatic tertiary amine, also called azabenzene and azine, is characterized by a six member ring composed of five carbon atoms and a nitrogen atom which replace one carbon-hydrogen unit in the benzene ring (C_5H_5N). Pyridine is a base with chemical properties similar to tertiary amines. Pyridine and its derivatives are used as solvents and starting material for the synthesis of target compounds for instance insecticides, herbicides, medicines, vitamins, food flavorings, feed additives, dyes, rubber chemicals, explosives, disinfectants, and adhesives. It is also used as a denaturant for antifreeze mixtures, as a dyeing assistant in textiles and in fungicides [1, 2].

2. MATERIALS AND METHODS

The model molecular structure of the title compound is shown fig 1. The title molecule is an asymmetric top with rotational symmetry number equal to 1 and 93 degrees of freedom. The theoretical IR spectra plotted is shown in fig 2.

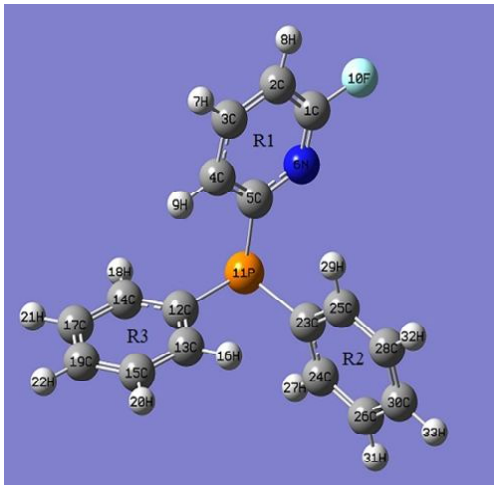

Fig.1: Model Molecular Structure of 2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$) as seen by Gaussview 5.0.8

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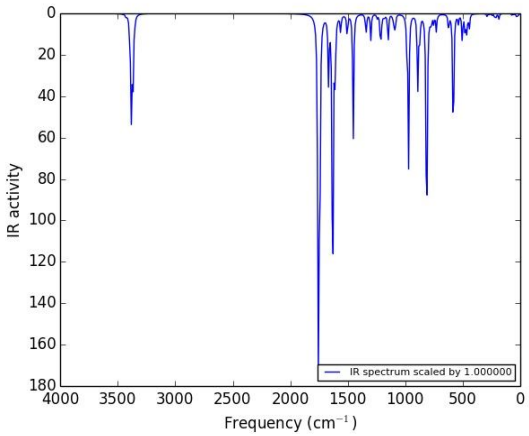

Fig.2: Theoretical IR spectra of 2-Diphenylphosphanyl-6-fluoro-pyridine

3. RESULT AND DISCUSSION

All the calculations were performed on an AMD dual core/2.71 GHz personal computer by the B3LYP [3, 4] method using the 6-31+g(d,p) level basis set of density functional theory. All computations were carried out with the Gaussian 09 package [5] by combining the results of the Gaussview 5.0.8 program package [6] with symmetry considerations and the VEDA 4 program to calculate the PED values [7].

3.1 Geometry Optimization

The optimized geometrical parameters of the title molecule 2-Diphenylphosphanyl-6-fluoro-pyridine are listed in table 1, showing bond lengths and bond angles only. The out of plane and torsional vibrations are not shown for the sake of space and are with the corresponding author. The optimized geometry parameters of the title compound are calculated by the DFT-B3LYP method. The calculations converged to optimized geometries by allowing the relaxation of all the parameters, which also correspond to true energy minima. This is revealed by the absence of any imaginary frequencies in the vibrational spectra calculations. Subsequently the zero point vibrations energy obtained for structure optimization of the title molecule is calculated as 172.99 Kcal/mol.

Table-1: Optimized Parametrs of 2-Diphenylphosphanyl-6-fluoro-pyridine (C17H14NFP)

S.No	Parameters	Bond Length (Å)	S.No	Parameters	Bond Angles (Deg)
1	R(1,2)	1.3822	46	A(5,4,9)	120.4392
2	R(1,6)	1.2964	47	A(4,5,6)	121.1044
3	R(1,10)	1.3466	48	A(4,5,11)	125.3575
4	R(2,3)	1.3754	49	A(6,5,11)	113.4681
5	R(2,8)	1.0676	50	A(1,6,5)	119.535
6	R(3,4)	1.3921	51	A(5,11,12)	101.0055
7	R(3,7)	1.0712	52	A(5,11,23)	101.844
8	R(4,5)	1.3777	53	A(12,11,23)	101.8554
9	R(4,9)	1.0674	54	A(11,12,13)	123.7258
10	R(5,6)	1.8782	55	A(11,12,14)	117.2473
11	R(5,11)	1.8782	56	A(13,12,14)	119.0239
12	R(11,12)	1.881	57	A(12,13,15)	120.4121
13	R(11,23)	1.8759	58	A(12,13,16)	119.8261
14	R(12,13)	1.3871	59	A(15,13,16)	119.7598
15	R(12,14)	1.3888	60	A(12,14,17)	120.6793
16	R(13,15)	1.3841	61	A(12,14,18)	119.5354
17	R(13,16)	1.0706	62	A(17,14,18)	119.7835
18	R(14,17)	1.384	63	A(13,15,19)	120.1713
19	R(14,18)	1.0728	64	A(13,15,20)	119.7762
20	R(15,19)	1.3843	65	A(19,15,20)	120.0523
21	R(15,20)	1.0721	66	A(14,17,19)	119.8829
22	R(17,19)	1.3837	67	A(14,17,21)	119.9119
23	R(17,21)	1.072	68	A(15,19,17)	119.8257
24	R(19,22)	1.072	69	A(15,19,22)	120.0891
25	R(23,24)	1.3886	70	A(17,19,22)	120.0839
26	R(23,25)	1.386	71	A(11,23,24)	116.7929
27	R(24,26)	1.3828	72	A(11,23,25)	124.1735
28	R(24,27)	1.0726	73	A(24,23,25)	119.0336
29	R(25,28)	1.3847	74	A(23,24,26)	120.6552
30	R(25,29)	1.0699	75	A(23,24,27)	119.6583
31	R(26,30)	1.384	76	A(26,24,27)	119.6853
32	R(26,31)	1.0719	77	A(23,25,28)	120.4019
33	R(28,30)	1.3831	78	A(23,25,29)	120.1809
34	R(28,32)	1.072	79	A(28,25,29)	119.4144
35	R(30,33)	1.0719	80	A(24,26,30)	119.9514
	Angle Bending		81	A(24,26,31)	119.8475
36	A(2,1,6)	124.1166	82	A(30,26,31)	120.1993
37	A(2,1,10)	118.4941	83	A(25,28,30)	120.1998
38	A(6,1,10)	117.3892	84	A(25,28,32)	119.7076
39	A(1,2,3)	116.9298	85	A(30,28,32)	120.0921
40	A(1,2,8)	120.2367	86	A(26,30,28)	119.7531
41	A(3,2,8)	122.8333	87	A(26,30,33)	120.1188
42	A(2,3,4)	119.7956	88	A(28,30,33)	120.1268
43	A(2,3,7)	120.0355			
44	A(3,4,5)	118.5167			
45	A(3,4,9)	121.0441			

3.2 Thermodynamic and Electronic Parameters

The thermodynamic functions like internal thermal energy (E), specific heat capacity at constant volume (C_v) and entropy (S) are shown in table 2. It is evident from the table 2 that of the total values of E and C_v, major contributions are due to the vibrational part. Whereas in the entropy calculated value the contributions of all three parts i.e. translational, rotational and vibrational motions of the atoms in the title molecule are comparable

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with again the vibrational part got the maximum contribution. This shows the importance of the study of vibrational nature of the molecule.

The frontier molecular orbitals participate in chemical reactions or interactions with other species and their energy gap helps to quantify the chemical reactivity of the molecule. HOMO primarily acts as an electron donor and LUMO acts as an electron acceptor, whereas the HOMO-LUMO energy gap is an important measure of the stability of the compound. Molecule with small values of frontier orbital gap, are more polarizable, with high chemical reactivity and low kinetic stability and is called a soft molecule [8, 9] and vice versa. In our calculations the orbital gap of 2-Diphenylphosphanyl-6-fluoro-pyridine is calculated as 11.26 eV. This shows that table molecule is at higher value of band gap and so less polarizable, less chemical reactivity and high kinetic stability. In the present DFT study the plots of LUMO and HUMO are shown in Fig 3 and Fig 4 respectively and their values are given Table 2. From 2d plot of HOMO (-8.563 eV), it is clear that most of the HOMO is distributed over ring R3 and most of the LUMO (2.755 eV) is distributed over ring R1. The rotational constants are calculated are calculated as 0.35554, 0.277289 and 0.1798 GHz respectively.

Table-2: Thermodynamic and Electronic Parameters of 2-Diphenylphosphanyl-6-fluoro-pyridine

Parameters	(Thermal)	C_V	S
	KCal/Mol	Cal/Mol-Kel	Cal/Mol-Kel
Total	182.489	57.621	131.498
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.799
Rotational	0.889	2.981	34.158
Vibrational	180.711	51.660	54.541
Zero-point vibrational energy		172.99051 (Kcal/Mol)	
Rotational constants (GHZ):	0.35554	0.27789	0.17980
HOMO = -0.31368*27.3 eV=-8.563 eV			
LUMO = 0.10093* 27.3 eV=2.755 eV			
Energy Band Gap= 11.26 eV			

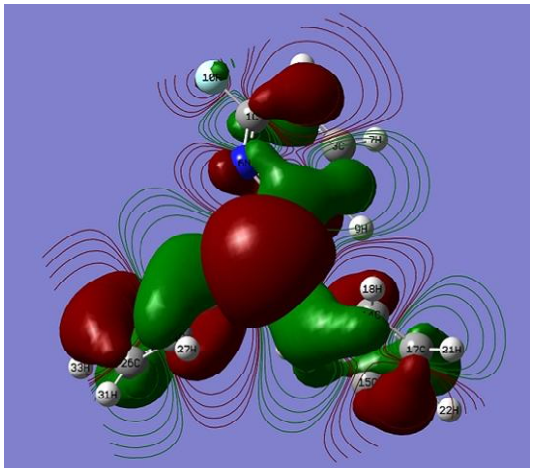

Fig.3: Plot of HOMO of 2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)

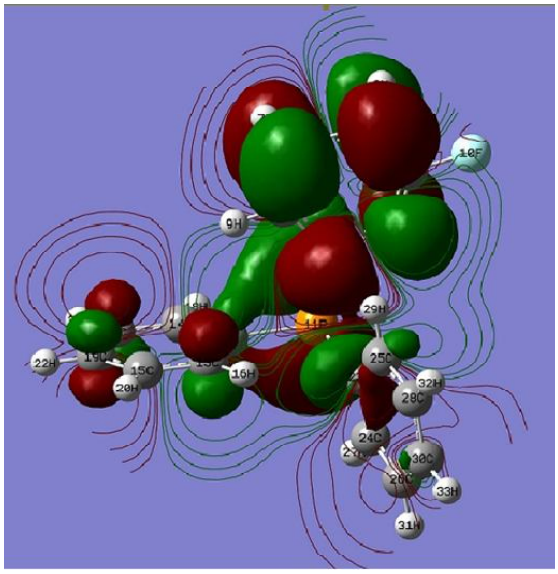

Fig.4: Plot of LUMO of 2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)

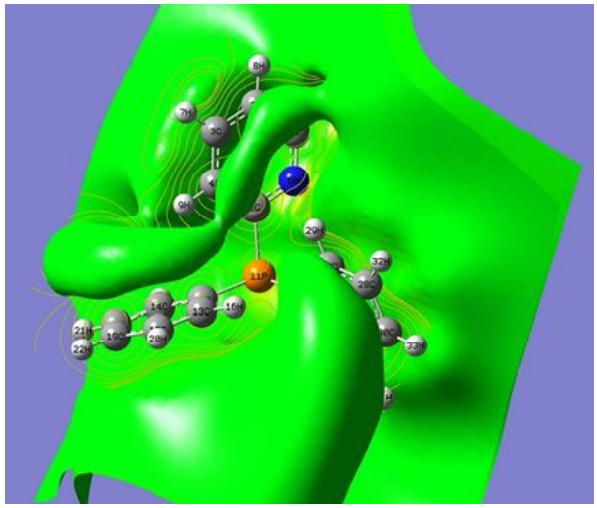

Fig.5: MESP plot of 2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)

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3.3 *Vibrational Analysis*

The maximum number of potentially active observable fundamentals of a nonlinear compound containing N-atoms is equal to (3N-6) [10]. The title compound "2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)" contains 34 atoms and hence exhibits 96 normal modes of vibrations. The assignment of the calculated frequency, are supported by the animation of Gauss View 5.0.8, which gives a 3D-view of the vibrational modes. The potential energy distribution (PED) is calculated by VEDA 4 software program. To correct overestimations at the calculated harmonic frequencies an empirical uniform scaling factor of 0.983 up to 1700 cm^{-1} and 0.958 for above 1700 cm^{-1} were used [11]. All the vibrational assignments are presented in table 3.

3.3.1 (C-H) stretch

The aromatic structure rings R1, R2 and of the title compound show the presence of C-H stretching vibration in the region 3300- 3200 cm^{-1} which is the a bit higher than the characteristic region for the ready identification of C-H stretching vibration [12]. These vibrations are found to be affected due to the position of the substitution. **(Table-3 Annexure-1)**

3.3.2 C-C stretch

Ring Vibrations. The C–C aromatic stretch known as semi-circle stretching, are calculated at 1689, 1682, 1640, 1603, 1277 and 1224 cm^{-1}. They are in good agreement with the reported frequencies with appropriate PED. The theoretically calculated C–C–C bending and C–C torsional modes have been found to be consistent with the reported values [12].

3.3.3 C-N stretch

The C-N vibrational mode is not easily identified due to the mixing of vibrations of other modes in this region. In the title molecule, the C-N stretching vibrations are calculated at 1277, 1157 and 1069 cm^{-1}. Various bending and torsional vibrations assigned to the ν(C-N) stretching mode are also supported by the literature [13].

3.3.4 C-F Stretch

The C-F stretching vibrations are calculated at frequencies 1603, 1427, 969 and 611 cm^{-1}. The corresponding in plane bending and torsional modes are reported in the literature [14, 15].

3.3.5 P- C stretch

The calculated values of P-C stretching mode is obtained at frequencies values 1277, 969, 768, 759, 739,454 and 435 cm^{-1} with max PED value at 768 cm^{-1}. The frequency range of P-C stretching, in plane bending, out of plane wag and torsional Vibrational modes are reported in the literature [16].

3.3.6 Lower region vibrational modes

The study of low frequency vibrations is of great importance because it provides the information for weak intermolecular interactions, which occurs in enzyme reactions [17]. Study of low frequency modes is also useful for the interpretation of the effect of electromagnetic radiation on biological systems [18]. In the present study, some important calculated lower order vibrational mode are 701, 574 and 569 with assignment R3 puckering, ω(P-C-C-C) out of plane bending with 71%, 16% and 23% PED values. These mode seems to be one of the characteristic modes of the title compound.

In lower range discrepancies are observed in the experimental and theoretical intensity in lower range of frequencies which are due to the impurity of the sample used, intermolecular interactions, anharmonicity and mixing of different modes of vibrations.

4. CONCLUSION

Present study reports a comprehensive theoretical quantum chemical study on "2-Diphenylphosphanyl-6-fluoro-pyridine ($C_{17}H_{14}NFP$)". The molecular geometry, vibrational wave numbers, infrared intensities, electronic and thermodynamic

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electronic properties of the title molecule have been calculated using DFT (B3LYP) method adopting at 6-31+g(d,p) basis set. Normal modes analysis provides detailed description of the Vibrational spectra of the molecules in question. A good agreement between reported and calculated normal modes of vibrations has been achieved. The aim of this paper is to obtain direct information on lower and higher frequency vibrations of such biological molecule. In the absence of experimental vibrational spectra of the title compound, the theoretically calculated spectra should provide an important path for experimentalists. All the measurements were made for the gas phase.

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(Annexure-1)

Table-3 : Frequency assignments for 2-DiphenylPohospanyl-6-Fluoro-Pyridine at B3LYP/6-311G(d,p) in cm-1, with PED % in Square Brackets

S. No.	Calc Freq Unscaled	Calc Freq Scaled	Theo. Freq FTIR	Assignment Modes[PED]
1	3430	3286	3891(w)	ν(C4-H9)[72]+ν(C2-H8)sym[22]
2	3425	3281		ν(C2-H8)asym-[74]+ ν(C4-H9)sym[25]
3	3397	3254	3345(s)	ν(C25-H29)sym[83]+ν(C28-H32)sym[12]
4	3392	3250	3308(vs)	ν(C13-H16)sym[73]+ν(C15-H20)sym[16]
5	3382	3240	3183(s)	ν(C25-H29)[10]+ν(C26-H31)asym[38]+ν(C26-H31)sym[27]
6	3368	3227		ν(C24-H27)[31]+ν(C26-H31)[27]
7	3356	3215		ν(C14-H18)[34]+ν(C15-H20)[38]
8	3349	3208	2849(m)	ν(C14-H18)asym[38]+ν(C19-H22)[20]+ν(C15-H20)[10]
9	1763	1689	1725(vs)	ν(C24=C26)sym[24]
10	1746	1673		ν(C30=C28)[23]+ν(C23=C25)asym[15]
11	1668	1640	1599(m)	φ(H27-C24-C26)[21]+φ(H29-C25-C28)[19]+ν(C=C)[17]
12	1631	1603	1507(vs)	ν(C4=C5)[10]+ν(F10-C1)[10]
13	1609	1582	1469(wsh)	φ(H22-C19-C15)[31]+φ(H31-C26-C30)[21]φ(H20-C15-C19)[20]+φ(H21-C17-C19)[21]
14	1561	1534	1444(s)	ν(N6-C5)[19]+φ(C4=C5-N6)[16]
15	1506	1480	1408(s)	φ(H27-C24-C26)[33]+φ(H29-C25-C28)[35]
16	1452	1427	1378(m)	ν(F10-C1)[33]+φ(H8-C2-C1)[19]+ν(C2-C3)[11]
17	1342	1319		ν(C1-N6)[10] +ν(C5-N6)[14]
18	1338	1315	1314(wsh)	φ(H21-C17-C19)[17]+φ(H20-C15-C19)[14]+φ(H18-C14-C17)[18]
19	1299	1277	1309(wsh)	ν(C4-C5)[35]+φ(H9-C4-C3)[13]+ν(P11-C5)[10]+φ(C4-C5-N6)[12]
20	1248	1227	1267(s)	ν(C26-C30)[35] +ν(C17-C19)[12] +ν(C23-C25)[14]
21	1218	1197	1234(s)	φ(C12-P11-C5)[15] + ν(N6-C5)[11]+ φ(C1-C2-C3)[18]
22	1202	1182		τ(H8-C2-C1-N6)[10]+τ(H7-C3-C4-C5)[32]+τ(H9-C4-C5-P11)[19]+τ(H20-C15-C19-C17)[18]
23	1198	1178	1182(s)	τ(H31-C26-C30-C28)[18]+τ(H33-C30-C28-C25)[28]+τ(H32-C28-C30-C26)[17]
24	1188	1168		R3-ROCK[13]
25	1177	1157	1148(s)	φ(C1-N6-C5)[25] +τ(H21-C17-C19-C15)[25]+τ(H18-C14-C17-C19)[20]
26	1167	1147		τ(H29-C25-C28-H30)[20]+ τ(H27-C24-C26-H31[28]
27	1149	1129	1106(vs)	φ(C19-C15-C13)[15]+φ(C12-C14-C17)[13]
28	1113	1094		τ(H22-C19-C17-C14)[38]+τ(H16-C13-C15-C19[22]
29	1104	1085	1058(wsh)	τ(H33-C30-C28-C25)[13]
30	1098	1079	1013(m)	τ(H9-C4-C5-P11)[48]
31	1087	1069		φ(C2-C1-N6)[15]+φ(C1-N6-C5)[12]
32	1008	991	984(wsh)	τ(H18-C14-C17-C19)[21]+τ(H20-C15-C19-C17)[29]+τ(H16-C13-C15-C19)[19]
33	998	981		τ(H29-C25-C28-C30)[24]+τ(H27-C24-C26-C30)[22]+τ(H31-C26-C30-C28)[26]
34	986	969	957(m)	ν(C1-C2)[30]+ν(C1-F10)[21]+ν(P11-C5)[10]
35	970	954	893(s)	τ(H9-C4-C5-P11)[15]+ω(F12-C1-N6-C2)[17]
36	893	878		τ(H20-C15-C19-C17)[14]+τ(C19-C15-C13-C11)[22]+τ(C19-C15-C13-C11)[22]
37	888	873		τ(C23-C25-C28-C30)[21]
38	872	857	802(w)	τ(C2-C1-N6-C5)[15]+ω(F10-C1-N6-C2)[23]+τ(H8-C2-C1-N6)[19]
39	817	803	772(s)	τ(H22-C19-C15-C17)[14]+τ(H18-C14-C12-C17)[15]+τ(C19-C15-C13-C12)[23]
40	810	796		τ(C23-C25-C28-C30)[24]+τ(H33-C30-C28-C25)[18]+τ(H29-C25-C28-C30)[14]
41	781	768		R2-PUCK[43] + ν(P11-C12)asym[10]+ ν(P11-C23)asym[14]
42	772	759	699(s)	R3-PUCK[27] + ν(P11-C12)[13]
43	752	739	668(wsh)	ν(P11-C5)[10]+ ν(C1-C2)[12]+φ(C1-C2-C3)[34]
44	729	717		ω(F10-C2-N6-C1)[35]+ ω(C4-P11-N6-C5)[28]+τ(H8-C2-C1-N6)[12]
45	713	701	613(vs)	R3-PUCK[71]
46	622	611		φ(C6-C1-F10)[13]+φ(C2-C1-N6)[28]+ν(F10-C1)[19]
47	584	574		ω(P11-C24-C25-C23)[16]+ φ(C12-P11-C23)[13]
48	579	569	522(wsh)	ω(P11-C23-C12-C5)[10] + ω(P11-C24-C25-C23)[13]
49	537	528		ω(C4-P11-N6-C5)[12]+τ(C3-C2-C1-N6)[17]+τ(C2-C1-N6-C5)[29]
50	503	494	505(s)	φ(N6-C1-F10)[27]+τ(F10-C2-N6-C1)[24]
51	478	470	449(s)	ν(P11-C23)[26]+φ(C23-C25-C28)[10]+φ(C5-P11-C23)[13]
52	469	461		τ(C17-C19-C15-C13)[23]+τ(C14-C17-C19-C15)[27]
53	462	454	400(msh)	ν(P11-C5)[21]+τ(C24-C26-C30-C28)[16]
54	443	435		ν(P11-C12)[29]+φ(F10-C1-N6)[14]+ω(H27-C24-C26-C30)[13]
55	68	67		τ(C13-C12-P11-C23)[68]

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