Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The photoinduced isomerisation and its implication in the photo-dynamical processes in two simple Schiff bases isolated in solid argon.

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Supporting Material

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Table S3. The comparison of the DFT/B3LYP/6-311++G(2d,2p) calculated harmonic frequencies (cm^{-1}) and intensities ($kmmol^{-1}$) for all optimized enol conformers of the 2-(1-(methylimino)methyl)-phenol.

Table S4. The selected, DFT/B3LYP/6-311++G(2d,2p) calculated geometrical parameters of the I_E and II_E conformers of 2-(1-(methylimino)methyl)-phenol (r in Å, angle values in degrees).

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Table S6. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for I_{CE} conformer of the 2-(1-(methylimino)methyl)-6-chlorophenol.

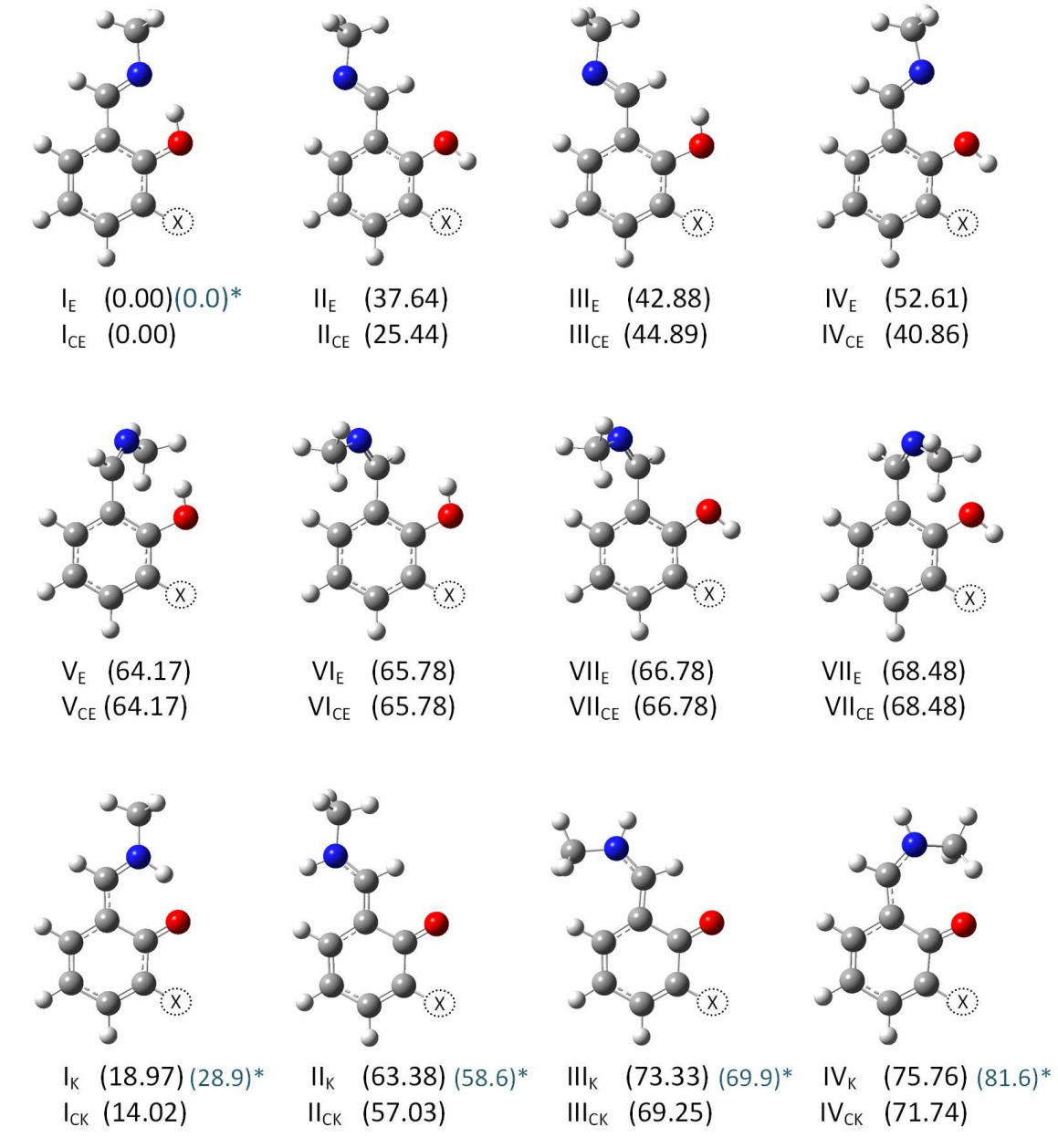
Table S7. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for II_{CE} conformer of the 2-(1-(methylimino)methyl)-6-chlorphenol.

Table S9. The comparison of the DFT/B3LYP/6-311++G(2d,2p) calculated harmonic frequencies (cm^{-1}) and intensities ($kmmol^{-1}$) for all optimized enol conformers of 2-(1-(methylimino)methyl)-6-chlorophenol.

Table S10. The comparison of the DFT/B3LYP/6-311++G(2d,2p) calculated harmonic frequencies (cm^{-1}) and intensities ($kmmol^{-1}$) for all optimized keto conformers of 2-(1-(methylimino)methyl)-6-chlorophenol.

Table S11. The selected, DFT/B3LYP/6-311++G(2d,2p) calculated geometrical parameters of the I_{CE}, II_{CE} and II_{CK} conformers of 2-(1-(methylimino)methyl)-6-chlorophenol (r in Å, angle values in degrees).

Figure S1. The DFT/B3LYP/3-311G++(2d,2p) optimized structures of
2-(1-(methylimino)methyl)phenol (X = H) and
2-(1-(methylimino)methyl)-6-chlorphenol (X = Cl).
The relative energies (ΔE_{ZPE}, kJ/mol) are given in the parantheses.



* M.Z.Zgierski; A.Grabowska *J. Chem. Phys.* **2000,** *113*, 7845-7852

Figure S2. The comparison of the experimental spectrum and theoretical spectra of the I_E, II_E, III_E and IV_E SMA conformers in the CH stretching region.

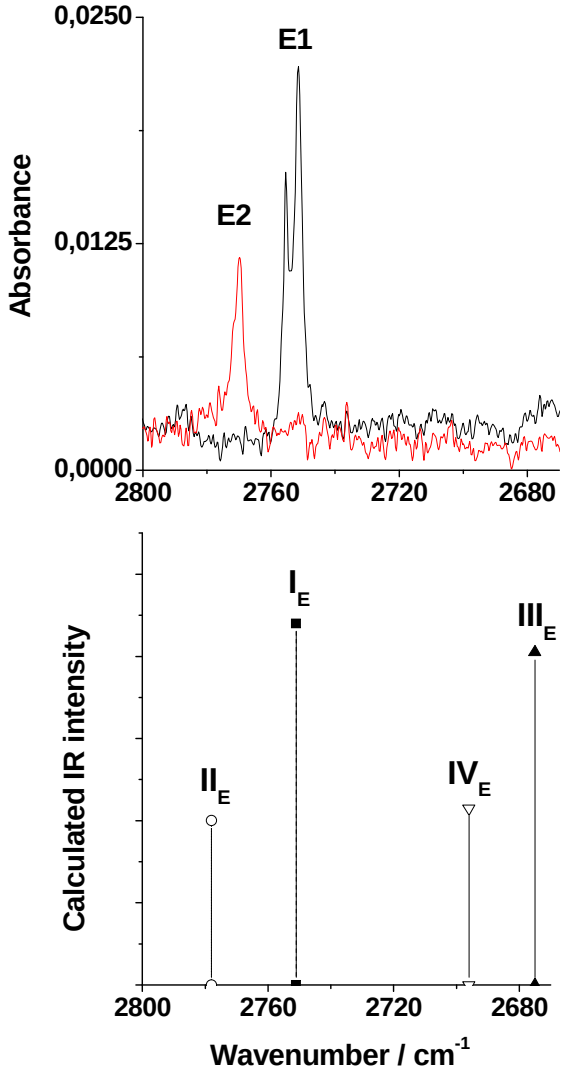
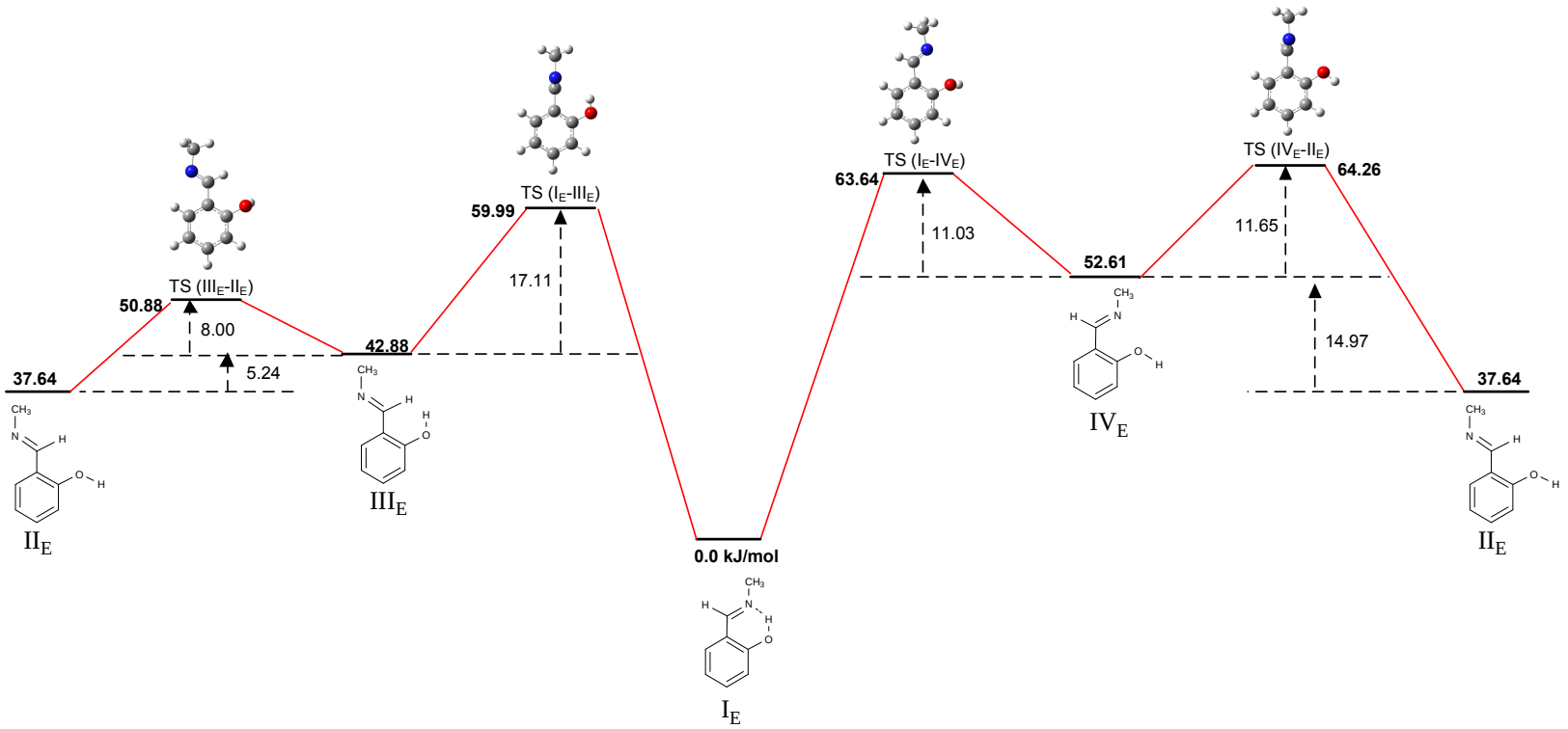


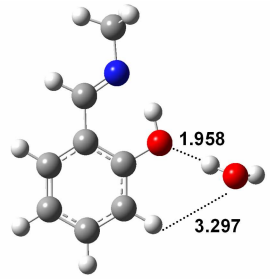
Figure S3 The schematic energy diagram for the possible mechanisms of conversion of I_E conformer into II_E one, in the ground electronic SMA state (energy in kJ/mol). [a]



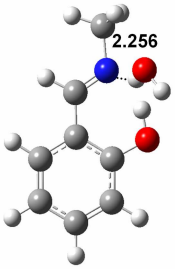
[a]The DFT/B3LYP/6-311++G(2d,2p) calculations were done to optimize the structures and to calculate the frequencies. For all energies the zero point energy values have been considered. All the stationary points were unambigously characterized as minima or transition states by their vibrational spectra. To confirm that a given transition state links proper reactant and product, IRC calculations were performed. These examine the intrinsic reaction path leading down from a transition structure on a potential energy surface.

Two possible mechanisms of conversion of I_E conformer into II_E one were considered:
1. The rotation of the OH group around C-O bond is followed by rotation of the $C(H)NCH_3$ group around C-C bond.
2. The rotation of the $C(H)NCH_3$ group around C-C bond is followed by the rotation of the OH group around C-O bond.
We have not considered the simultaneous rotation of the OH and $C(H)NCH_3$ groups

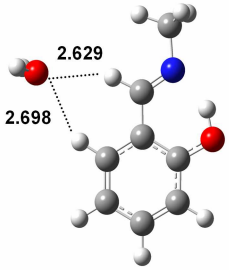
Figure S4. The DFT/B3LYP/3-311G++(2d,2p) optimized structures of 2-(1-(methylimino)methyl)phenol complexes with water: SMA–H_2O; SMA–$(H_2O)_2$. The interaction energies (ΔE_{ZPE}, $kJmol^{-1}$) are given in the parantheses.



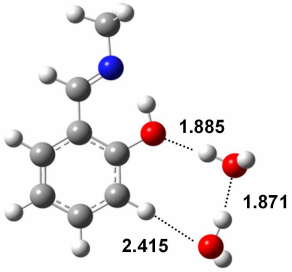
I_{EW1} (-10.45)



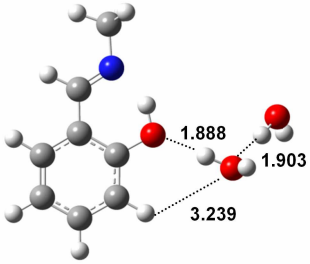
I_{EW2} (-4.35)



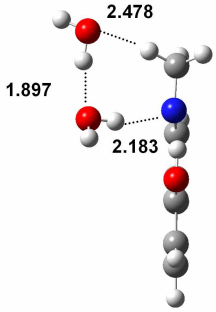
I_{EW3}(-2.94)



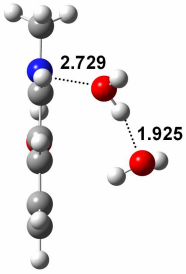
II_{EW1} (-63.09)



II_{EW2} (-57.19)



II_{EW3} (-50.10)



II_{EW4} (-50.07)

Figure S5. The infrared spectra of SMAC/Ar matrix in the 1710-1240 region: (a) the spectrum recorded after matrix deposition and (b,c) after matrix exposure to λ>320 nm radiation for 25 and 190 min, respectively.

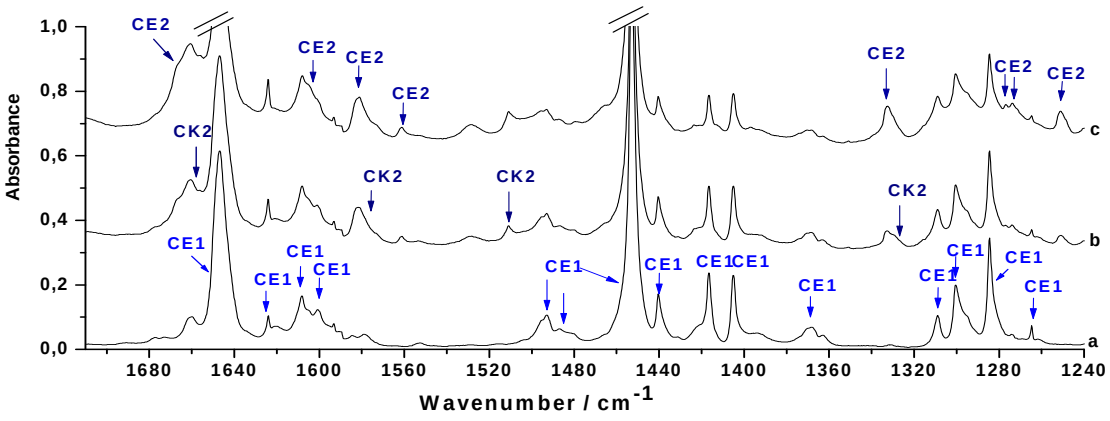


Table S1. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for I_E conformer of the 2-(1-(methylimino)methyl)phenol. The relative experimental intensities and the calculated intensities ($kmmol^{-1}$) corresponding to harmonic frequencies are also given. The potential energy distribution of the normal modes is presented.

IR[1] liquid phase	IR[2] gas phase	Experimental Ar matrix		Experimental N_2 matrix		Calculated			PED[c] %
$\nu_{obs.}$ cm^{-1}	$\nu_{obs.}$ cm^{-1}	$\nu_{obs.}$[a] cm^{-1}	I[b]	ν_{obs} cm^{-1}	I	$\nu_{harm.}$ cm^{-1}	I	$\nu_{anh.}$ cm^{-1}	
	3179					3202	14	3063	97νCH$_{ring}$
3057.0	3076					3196	19	3081	95νCH$_{ring}$
3009.1	3053					3175	26	3042	98νCH$_{ring}$
	3013					3162	4	3013	96νCH$_{ring}$
~2750	2990	3250-3050	s	3200-3000		3189	408	2784	96νOH
2951.1	2903	2883-2850	vw	2862-2855	vw	3083	14	2931	100νCH$_3$
2890.7	2867					3072	24	2926	100νCH$_3$
2782.3	2741					2995	78	2890	96νCH$_3$
2857.9	2790	2751.6	vw	2762.2	vw	3007	88	2856	96νCH
		1674.5, 1673.1		1673.8					
1637.5	1648	1650.1, 1648.7	s	1652.7, 1651.5, 1648.9	s	1691	188	1653	60νC=N+11δ(NCH+CCH)+7δCCC+7νCC
1613.3		1627.3, 1625.9	m	1625.1, 1623.3	m	1663	103	1614	44νCC$_{ring}$+20δCOH+7δCCO+7δCCC$_{ring}$
1584.3	1589	1586.6	m	1584.7	m	1620	52	1577	45νCC$_{ring}$+20δCOH+7δCCH$_{ring.}$+7δCCC$_{ring}$
1497.7	1494	1499.0-1488.2	w	1496.2-1485.3	w	1540	48	1499	27δCOH+23δCCH$_{ring}$+21νCC$_{ring}$
1464.9	1457					1508	6	1464	57δCH$_3$
1452.9	1465	1465.6	vs	1467.9, 1465.8	s	1496	60	1455	20δCH$_3$+24νCC$_{ring}$+13δCCH$_{ring}$+11δCCC$_{ring.}$+7νCO
	1405					1482	6	1475	98δCH$_3$
1418.9	1412	1386.5	m	1393.2, 1391.3, 1389.6	w	1462	42	1423	41δCOH+26δCCH$_{ring}$+15νCC$_{ring}$
1401.8	1405			1387.6	vw	1446	21	1428	86δCH$_3$
1368.5	1373	1338.7	vw	1346.4	w	1400	15	1384	58δ(NCH+CCH)+7νCC+7νC=N
1316.2	1318	1325.0	w	1325.7,1324.2	w	1347	4	1317	67νCC$_{ring}$+7δCCH$_{ring}$+7δ(CCN+NCH+CCH)+7δCCC
1280.5	1283	~1287	vs	1289.6, 1283.8, 1280.4	vs	1316	95	1289	37νCO+13δCCC$_{ring}$+9δCCH$_{ring}$

Table S1, cd

1212.6	1242	1231.8, 1229.1	w	1235.0-1225.8	m	1268	2	1246	37δCCH$_{ring.}$+14νCC$_{ring}$+9δCCO+7νCC+7νCO
1198.1?	1210	1206.2, 1203.3,	m	1206.0, 1190.0	s	1233	36	1207	51νCC$_{ring}$+15δCCH$_{ring}$+9δ(NCH+CCH)
1151.8	1147	1148.9	m	1149.8, 1151.4	m	1179	20	1164	72δCCH$_{ring}$+9νCC$_{ring}$
						1164	16	1141	60δCH$_3$+11νC-N
						1140	0	1116	89δCH$_3$
1139.8		1116.3	m	1115.8	vw	1134	3	1117	21δCCH$_{ring}$+15δCH$_3$+13νCO+10δCCC$_{ring}$+8δCCC+7δCCO
1036.9	1036	1029.3	vw	1031.4, 1029.1	w	1056	9	1038	34νCC$_{ring}$+17δCCH$_{ring}$+10νC-N
1006.5	1008					1024	25	999	53νC-N+14δ(CCN+NCH+CCH)+7δCH$_3$
965.5	966					998	6	979	47γCCH+27γCCH$_{ring}$+9τCCC$_{ring}$
						994	3	987	69γCCH$_{ring}$+15γCCH+7τCCC$_{ring}$
						955	0	943	81γCCH$_{ring}$+8γCCH
895.5	895	885.3	s	885.5	vs	909	14	905	58δCCC$_{ring}$+17δCCN+7νCO+7νCC
844.8	797	744.0	m	749.8, 747.2	m	884	31	855	63γCOH+22γCCH$_{ring.}$
756.5	753	757.1, 758.8	m	766.1, 763.8	vs	872	35	855	42γCCH$_{ring}$+13γCCO+13τCCC$_{ring.}$+12γCOH
782.9	782	768.2	w	770.3	m	795	8	790	46νCC$_{ring}$+12νCO+10δ(CCN+NCH+CCH)+7δCCC$_{ring}$
736.2		718.2	s	723.5	m	767	47	754	38γCCH$_{ring}$+25τCCC$_{ring}$+22γCCO
		721.4	m	725.5	w	755	27	747	43τCCC$_{ring}$+19γCCH$_{ring}$+18γCCN+10γCCO
647.4	646			667.4	w	663	11	656	52δCCC$_{ring}$+22δ(CCN+NCH+CCH)

[1] M. Matusiak, W. Wrzeszcz, T. Dziembowska, J.P. Hawranek, *J. Mol. Struct.*,2004, **704**, 223-227.
[2] A. Filarowski, A. Koll , A. Karpfen and P. Wolschann, *Chem. Phys.*, 2004**, 297,** 323-332

[a] - in the case of the bands that show multiple components the frequency of the most intense component is underlined.
[b] - vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad
[c] - only the components of PED that contribute more than 7% are taken into account

Table S2. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for II_E conformer of the 2-(1-(methylimino)methyl)phenol. The relative experimental intensities and the calculated intensities ($kmmol^{-1}$) corresponding to harmonic frequencies are also given. The potential energy distribution of the normal modes is presented.

Experimental Ar matrix		**Calculated**			
$\nu_{obs.}$ [a] cm^{-1}	**I [b]**	**$\nu_{harm.}$ cm^{-1}**	**I**	**$\nu_{anh.}$ cm^{-1}**	**PED [c] %**
3632.1	vs	3838	70	3669	100νOH
~ 2966	vw	3206	7	3070	96νCH_{ring}
		3193	10	3054	97νCH_{ring}
		3178	7	3063	95νCH_{ring}
		3155	13	3012	99νCH_{ring}
~ 2883	vw	3073	18	2922	100νCH_3
		3060	30	2941	100νCH_3
		2975	95	2873	100νCH_3
2770.2	vw	3036	40	2878	99νCH
1703.4, <u>1700.6</u>	vs	1708	89	1671	57νC=N+25δ(NCH+CCH)
1615.3	s	1645	43	1605	55νCC_{ring} +8δCCH_{ring}+8δCCC_{ring}
		1625	21	1587	62νCC_{ring}9δCCH_{ring}+8δCCC_{ring}
1495.2	w	1532	11	1497	47δCCH_{ring}+29νCC_{ring}
1464.2	vs	1503	16	1460	78δCH_3+7δ(NCH+CCH)
1464.2	vs	1490	72	1459	39δCCH_{ring}+27νCC_{ring}
		1480	5	1501	97δCH_3
		1442	15	1423	85δCH_3
1401.1	vw	1410	12	1392	90δ(NCH+CCH)
1323.5	m	1358	52	1330	48νCC_{ring}+24δCCH_{ring}+20δCOH
1308.8, <u>1302.0</u>	vs	1329	73	1301	31νCC_{ring} + 30δCCH_{ring}+11δCCC
<u>1251.0</u>, 1244.2	w	1265	74	1239	40νCO+25νCC_{ring}+8νCC
1210.9	w	1240	26	1220	38δ(NCH+CCH)+17νCC+16νCC_{ring} +12δCOH+8δCCC_{ring}
1165.6	w	1191	46	1175	30δCOH+40δCCC_{ring}+15νCC_{ring}
1158.3, 1155.4	vw	1183	14	1171	77δCCH_{ring}+16νCC_{ring}
		1154	7	1126	69δCH_3+9νC-N+7δCCH
1092.5	vw	1114	38	1099	25νCC_{ring} +22δCCC_{ring}+9δCOH+7δCCH_{ring}
		1019	12	994	68νC-N+11δ(CCN+NCH+CCH)+7δCCC_{ring}
845.7	m	876	19	865	39δCCH_{ring}+14νCC+ 12δ(CCN+NCH+CCH)+9νCC_{ring}
804.9	w	827	14	819	30νCC_{ring} +21νCO+21δCCH_{ring} + 13δ(CCN+NCH+CCH)
758.5, 757.2	m	766	62	769	29γCCH_{ring}+28γCCO+26τCCC_{ring}
760.1	m	743	8	773	44τCCC_{ring}+34γCCN+14γCCO
632.1	vw	643	6	637	67δCCC_{ring}+9δ(CCN+NCH+CCH)+9νCC_{ring}

[a] - in the case of the bands that show multiple components the frequency of the most intense component is underlined.
[b] - vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad
[c] - only the components of PED that contribute more than 7% are taken into account

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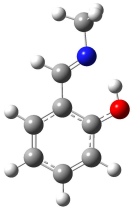
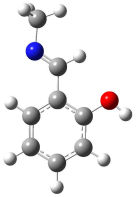
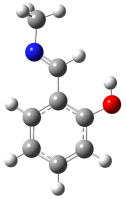
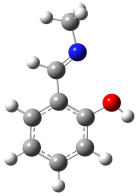
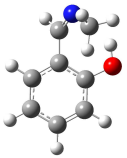
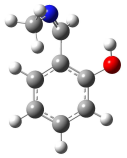
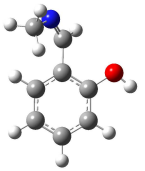
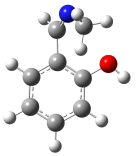
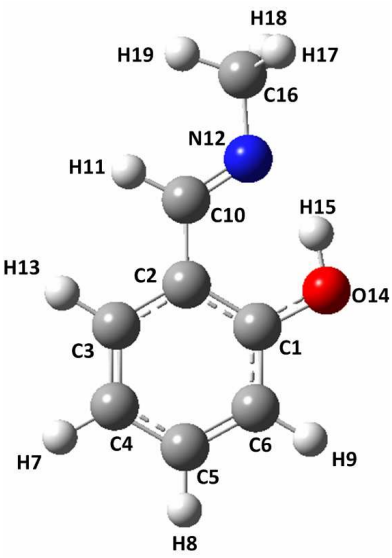
															
I_E (0 kJ/mol)		II_E (ΔE=37.64)		III_E (ΔE=42.88)		IV_E (ΔE=52.61)		V_E (ΔE=64.17)		VI_E (ΔE=65.78)		VII_E (ΔE=66.78)		$VIII_E$ (ΔE=68.48)	
$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I	$\nu_{harm.}$	I
3202	14	3838	70	3843	54	3819	54	3802	71	3825	72	3837	73	3836	67
3196	19	3206	7	3207	7	3199	14	3202	8	3204	7	3204	8	3199	13
3189	408	3193	10	3201	6	3182	12	3195	12	3197	11	3192	11	3183	10
3175	26	3178	7	3190	10	3168	3	3179	6	3186	6	3180	3	3168	2
3162	4	3155	13	3175	2	3152	13	3168	3	3176	1	3156	12	3154	11
3083	14	3073	18	3078	15	3075	17	3089	18	3089	23	3093	15	3089	15
3072	24	3060	30	3062	29	3059	31	3078	14	3074	17	3084	28	3080	29
3007	88	3036	40	2968	111	2963	133	3067	22	3032	18	3066	22	3063	25
2995	78	2975	95	2923	81	2946	43	3018	31	3014	42	3009	38	3014	43
1691	188	1708	89	1709	109	1714	104	1693	102	1698	83	1703	90	1711	89
1663	103	1645	43	1653	56	1642	53	1650	23	1651	38	1642	46	1642	33
1620	52	1625	21	1616	38	1620	24	1614	26	1614	33	1623	16	1623	15
1540	48	1532	11	1519	33	1537	14	1520	49	1516	54	1532	15	1535	15
1508	6	1503	16	1505	20	1504	10	1506	5	1505	6	1510	4	1507	5
1496	60	1490	72	1497	65	1483	54	1496	17	1495	38	1490	20	1487	27
1482	6	1480	5	1478	5	1479	4	1482	14	1487	9	1486	43	1476	31
1462	42	1442	15	1446	17	1441	17	1441	3	1436	8	1437	9	1435	4
1446	21	1410	12	1437	10	1418	12	1408	15	1423	8	1429	7	1415	16
1400	15	1358	52	1355	20	1365	51	1368	20	1363	22	1359	58	1360	45
1347	4	1329	73	1332	49	1329	57	1319	15	1322	42	1323	44	1317	34
1316	95	1265	74	1267	28	1295	31	1264	29	1269	27	1272	57	1273	35
1268	2	1240	26	1238	82	1240	27	1238	107	1223	132	1216	44	1224	41
1233	36	1191	46	1189	74	1196	30	1192	25	1193	33	1194	37	1190	21
1179	20	1183	14	1177	59	1186	7	1176	33	1177	39	1184	7	1183	8
1164	16	1154	7	1154	8	1154	12	1160	2	1161	0	1160	6	1163	4

Table S3 cd.

1140	0	1140	0	1136	0	1137	0	1138	3	1136	4	1134	7	1133	3
1134	3	1114	38	1111	11	1125	57	1120	1	1111	1	1111	49	1119	58
1056	9	1061	3	1056	12	1071	4	1055	11	1056	11	1064	2	1063	3
1024	25	1019	12	1020	15	1014	18	997	0	997	0	993	1	992	0
998	6	1007	2	1005	0	992	3	968	3	972	5	969	11	966	14
994	3	987	4	983	4	982	3	955	15	960	10	958	10	960	7
955	0	964	0	952	2	949	0	928	8	935	9	930	7	922	6
909	14	876	19	880	2	905	20	891	14	879	6	866	8	885	31
884	31	861	1	875	11	856	2	867	6	853	12	851	18	853	4
872	35	827	14	824	10	787	7	804	9	836	9	833	8	800	9
795	8	766	62	773	59	762	59	768	55	767	57	765	54	764	59
767	47	743	8	747	0	744	15	735	7	736	5	735	15	731	10
755	27	643	6	641	6	663	9	677	12	674	15	673	12	679	12
663	11	555	4	554	8	574	3	578	2	575	2	575	1	579	1

Table S4. The selected, DFT/B3LYP/6-311++G(2d,2p) calculated geometrical parameters of the I_E and II_E conformers of 2-(1-(methylimino)methyl)phenol (r in Å, angle values in degrees).



	I_E	II_E
r C_1-O_{14}	1.342	1.370
r C_2-C_{10}	1.454	1.472
r C_{10}=N_{12}	1.278	1.269
r C_{10}-H_{11}	1.097	1.094
r N_{12}-C_{16}	1.449	1.448
r O_{14}-H_{15}	0.993	0.962
R N_{12}···H_{15}	1.734	
θ H_{19}-C_{16}-N_{12}	112.8	113.6
θ C_{16}-N_{12}=C_{10}	119.4	118.1
θ N_{12}=C_{10}-H_{11}	120.7	121.5
θ H_{11}-C_{10}-C_2	116.4	116.2
θ C_1-O_{14}-H_{15}	107.3	109.5
θ N_{12}···H_{15}-O_{14}	147.9	
φ H_{19}-C_{16}-N_{12}=C_{10}	0.0	0.0
φ C_{16}-N_{12}=C_{10}-H_{11}	0.0	0.0
φ H_{11}-C_{10}-C_2-C_1	-180.0	0.0
φ C_6-C_1-O_{14}-H_{15}	-180.0	0.0

Table S5. The experimental (E1) and calculated frequencies of I_E conformer and the identified frequencies of I_E–H_2O (E1W1) and I_E–$(H_2O)_n$ (E1W2) complexes. The observed and calculated frequency shifts ($\Delta\nu = \nu_{compl} - \nu_{mon}$) for the 1:1 complexes are also presented.

SMA		**SMA-H_2O**				**SMA-$(H_2O)_n$**
E1	**I_E**	**E1W1**		**I_{EW1}**	**Assignment**	**E1W2**
$\nu_{obs.}$	**$\nu_{harm.}$**	**$\nu_{obs.}$**	**$\Delta\nu_{obs.}$**	**$\Delta\nu_{harm.}$**		**$\nu_{obs.}$**
1650.1	1691	1655.7	+5.6	+4	νC=N+δCCH	1667.3
1586.6	1620				νCC_{ring}+δCOH	1583.8
1499-1488	1540	1493.9	0.0	+8	δCOH+δCCH_{ring}+νCC_{ring}	1491.8
1465.6	1496	1467.7	+2.1	0	δCH_3+νCC_{ring}+δCCH_{ring}	
1386.5	1462	1390.1	+3.6	+7	δCCH+νCC	1397.3
1338.7	1400	1341.5	+2.8	+2	δ(NCH+CCH)	
1325.0	1347	1327.9	+2.9	-2	νCC_{ring}	
~1287	1316				νCO+δCCC_{ring}	1289.3, 1285.5
1231.8	1268	1234.6	+2.8	0	δCCH_{ring}+νCC_{ring}	1230.6
1203.3	1233	1206.3	+3.0	+5	νCC_{ring}+δCCH_{ring}	
1148.9	1179	1151.2, 1155.7	+2.3, +6.8	+3	δCCH_{ring}+νCC_{ring}	1150.3, 1153.6
1029.3	1056	1032.4	+3.1	+2	νCC_{ring}+δCCH_{ring}+νC-N	
885.3	909	886.7	+1.4	0	δCCC_{ring}+δCCN	887.9
768.2	795	773.3	+5.1	+1	νCC_{ring}+νCO	
718.2	767	720.9	+2.7	+2	γCCH_{ring}+τCCC_{ring}+γCCO	715.2
744.0	884	759.0	+15.0	+19	γCOH+γCCH_{ring}	738.6
667.9	663	667.9	0.0	0	δCCC_{ring}+δ(CCN+NCH+CCH)	
H_2O						
$\nu_{obs.}$	**$\nu_{harm.}$**	**$\nu_{obs.}$**	**$\Delta\nu_{obs.}$**	**$\Delta\nu_{harm.}$**	**Assignment**	
3733.0	3823	3622.7	-110.3	-109	ν_{asym} H_2O	3715.3
3638.0	3925	3586.0	-52.0	-32	$\nu_{sym.}$ H_2O	3559.8

Table S6. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for I_{CE} conformer of the 2-(1-(methylimino)methyl)-6-chlorphenol. The relative experimental intensities and the calculated intensities ($kmmol^{-1}$) corresponding to harmonic frequencies are also given. The potential energy distribution of the normal modes is presented.

Experimental Ar matrix		Calculated			
$\nu_{obs.}$	I[a]	$\nu_{harm.}$	I	$\nu_{anh.}$	PED[b] %
		3209	5	3040	97νCH_{ring}
		3196	5	3051	99νCH_{ring}
		3172	9	3048	99νCH_{ring}
2800-2600	b	3129	492	2690	96νOH_{HB}
2968.4		3086	12	2945	99νCH_3
2921.4		3075	21	2939	100νCH_3
2898.7		2998	100	2892	97νCH_3
2866.3		3015	87	2854	98νCH
1646.9	m	1692	177	1652	64νC=N+11δ(NCH+CCH)+7δCCC+7νCC
1600.1	vw	1655	66	1605	40νCC_{ring}+19δCOH+8δCCO+7δCCH_{ring}+7δCCC_{ring}
1552.8	vw	1610	6	1545	49νCC_{ring}+14δCOH+10δCCH_{ring}+7δCCC_{ring}
1492.7	vw	1535	29	1496	28δCOH+25νCC_{ring}+20δCCH_{ring}
1440.5	vw	1505	6	1431	72δCH_3+9δCOH
~1484	vw	1482	6	1470	97δCH_3
1452.9	vs	1476	152	1446	21νCO+24νCC_{ring}+16δCCH_{ring}+9δCH_3+7δCCC
1405.2	w	1461	18	1419	39δCOH+26δCCH_{ring}+10νCC_{ring}+7νCC
1416.6	w	1445	23	1424	86δCH_3
1363.1, 1369.2	vw	1400	34	1378	56δ(NCH+CCH)+9νCC+7δ(CCN+NCH+CCH)+7νC=N
1308.9, 1301.3	vw	1328	24	1300	72νCC_{ring}+7δ(CCN+NCH+CCH)
1284.8	w	1314	31	1290	43νCO+14νCC_{ring}+13δCCH_{ring}+11δCCC_{ring}
1233.4	vw	1253	22	1231	21νCC_{ring}+20νCC+17δCCH_{ring}+9δ(NCH+CCH)
1190.0	m	1213	49	1191	38δCCH_{ring}+11δCOH+10νCC_{ring}+8δCCO+7δCCC_{ring}
1150.3, 1152.5	w	1172	59	1148	38δCH_3+24δCCH_{ring}+13νCC_{ring}+7νC-N
1136.2	vw	1154	15	1127	47δCH_3+8δCCH_{ring}+8δCCC_{ring}+7νCCl+7νC-N
		1141	0	1114	66δCH_3+10γNCH
1078.4	vw	1101	14	1081	54νCC_{ring}+27δCCH_{ring}
1013.3	m	1027	28	999	55νC-N+14δ(CCN+NCH+CCH)+7δCH_3
965.1	vw	998	9	972	49γNCH +18γCCH_{ring}+9δCH_3+8γCCN+8τCCC_{ring}
		982	0	953	68γCCH_{ring}+12γNCH+9τCCC_{ring}
940.1	vw	947	10	934	24δCCC_{ring}+15δ(CCN+NCH+CCH)+10νCC+ 8δCOH+6νCC_{ring}
		928	0	906	82γCCH_{ring}+7τCCC_{ring}
842.6	vw	902	62	847	96γCOH
836.9	w	848	11	837	21δCCC_{ring}+22νCC_{ring}+17νCO+9νCCl
		814	6	738	42τCCC_{ring}+18γCCO+14δCCC+8γCCCl+7γCCH_{ring}
739.5	m	760	49	735	56γCCH_{ring}+17τCCC_{ring}+17γCCO
692.1, 681.5	vw	694	37	690	52δCCC_{ring}+27δ(CCN+NCH+CCH)+12νCCl+7νCC_{ring}
		612	6	607	32δCCC_{ring}+14δCCC+11νCC_{ring}+9νCCl

[a] - vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad
[b] - only the components of PED that contribute more than 7% are taken into account

Table S7. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for II_{CE} conformer of the 2-(1-(methylimino)methyl)-6-chlorphenol. The relative experimental intensities and the calculated intensities ($kmmol^{-1}$) corresponding to harmonic frequencies are also given. The potential energy distribution of the normal modes is presented.

Experimental Ar matrix		Calculated			
$\nu_{obs.}$	I[a]	$\nu_{harm.}$	I	$\nu_{anh.}$	PED[b] %
3552.6	vs	3750	119	3540	100νOH
		3213	5	3069	99νCH_{ring}
		3207	0	3053	99νCH_{ring}
		3189	4	3034	99νCH_{ring}
2967.6		3076	16	2936	100νCH_3
2927.8		3063	27	2930	100νCH_3
2865.5		2979	90	2867	99νCH_3
2893.8		3043	35	2876	99νCH
1661.2	vs	1708	78	1670	55νC=N+28δ(NCH+CCH)
1581.5	m	1636	34	1598	60νCC_{ring}+8δCCH_{ring}+8δCCC_{ring}
1561.3	vw	1609	8	1554	64νCC_{ring}+9δCCH_{ring}+8δCCC_{ring}
		1507	2	1475	42δCCH_{ring}+28νCC_{ring}+7νCC
		1503	14	1450	83δCH_3+7δ(NCH+CCH)
		1480	5	1487	90δCH_3
1452.9		1478	143	1443	34νCC_{ring}+24δCCH_{ring}+16νCO+7δCCC
1423.8	vw	1442	14	1426	83δCH_3
1396.9	vw	1410	16	1387	93δ(NCH+CCH)
1332.8	m	1369	52	1337	40νCC_{ring}+30δCOH+19δCCH_{ring}
1276.9, 1273.9	m	1294	79	1267	43νCC_{ring}+16δCCH_{ring}+10νCC+7δ(CCN+NCH+CCH)
1251.0	m	1273	64	1248	39νCO+18δCCH_{ring}+14νCC_{ring}+7δCCC_{ring}
1209.5	vw	1244	42	1220	33δ(NCH+CCH)+20νCC_{ring}+16δCOH+14νCC+7δCCC_{ring}
1169.4	vw	1191	13	1176	66δCCH_{ring}+9δCOH+7νCC_{ring}
1136.6	w	1156	14	1131	61δCH_3+19δ(NCH+CCH)+7νC-N
1129.4	w	1146	35	1127	24νCC_{ring}+21δCCC_{ring}+12νCCl+12δCCH_{ring}
		1140	0	1114	72δCH_3+21γNCH
~1071	w	1094	10	1071	49νCC_{ring}+30δCCH_{ring}+7δCCC_{ring}
		1023	11	998	69νC-N+10δ(CCN+NCH+CCH)
		1007	3	982	44γCCH_{ring}+21τCCC_{ring}+14γCCN+14γNCH
		986	3	962	56γNCH+12γCCN+8γCCH_{ring}+7τCCC_{ring}
		937	0	915	66γCCH_{ring}+11τCCC_{ring}
893.3	w	895	29	881	20δCCC_{ring}+18νCC+19δ(CCN+NCH+CCH)+11νCC_{ring} +10νCCl
		844	8	828	43δCCC_{ring}+23νCO+17νCC_{ring}
		803	17	789	38τCCC_{ring}+24γCCN+15γCCO+11γCCH_{ring}
752.9	m	753	34	754	36τCCC_{ring}+26γCCO+19γCCN+7γCCH_{ring}
~715	v	721	48	711	27δCCH_{ring}+25νCCl+15δ(CCN+NCH+CCH)+24δCCC

[a] - vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad
[b] - only the components of PED that contribute more than 7% are taken into account.

Table S8. The comparison of the experimental and DFT/B3LYP/6-311++G(2d,2p) calculated anharmonic and harmonic frequencies (cm^{-1}) for II_{CK} conformer of the 2-(1-(methylimino)methyl)-6-chlorphenol. The relative experimental intensities and the calculated intensities ($kmmol^{-1}$) corresponding to harmonic frequencies are also given. The potential energy distribution of the normal modes is presented.

Experimental Ar matrix		Calculated			
$\nu_{obs.}$	I[a]	$\nu_{harm.}$	I	$\nu_{anh.}$	PED[b] %
3439.7	vw	3608	45	3449	99νNH
		3202	10	3069	97νCH$_{ring}$
		3186	8	3037	98νCH$_{ring}$
		3142	13	3012	95νCH$_{ring}$
		3141	5	2998	97νCH$_3$
		3089	16	2942	100νCH$_3$
		3039	68	2876	99νCH$_3$
		3171	1	3014	98νCH
1656.2	vs	1694	567	1655	31νC=O+17νC=C+13νCN+7νC=C$_{ring}$+8δ(NCH+CNH)+7δ(NCH+CCH)
		1646	16	1607	51νC=C$_{ring}$+18νCN+17δCCH$_{ring}$
1581.6		1618	508	1581	44νC=O+11νCN+10δ(NCH+CNH)+7νC=C$_{ring}$
1510.8	m	1539	67	1502	46νC=C$_{ring}$+20νC-C+11δCCH$_{ring}$+7δCCC$_{ring}$
		1521	43	1478	79δCH$_3$
1465.8	m	1498	33	1469	39δCCH$_{ring}$+20νC-C+7δCH$_3$+7νC=C
		1491	8	1463	95δCH$_3$
		1480	16	1460	78δCH$_3$ +13δ(NCH+CNH)
		1445	107	1410	31δCH$_3$+18δ(NCH+CNH)+15νC=C+13δ(C=CH+NCH)+7νC-C$_{ring}$
		1381	7	1353	27δCCH$_{ring}$+16δ(C=CH+NCH)+8δCCC+7δ(NCH+CNH)+7νC-C$_{ring}$+7νCN
1329.4		1351	274	1329	30νCN+22δ(C=CH+NCH)+17δ(NCH+CNH)+7δCH$_3$
1308.9, 1301.3		1333	121	1308	38δCCH$_{ring}$+18νC-C$_{ring}$+10νC=C+10νC=C$_{ring}$
		1268	19	1240	33νC-C$_{ring}$+12δ(C=CH+NCH)+11δCCH$_{ring}$+8νC=C$_{ring}$
		1190	0	1177	58δCCH$_{ring}$+9νC-C+7δCH$_3$
		1154	29	1129	33δCH$_3$+16νNC(H$_3$)+10νC-C
		1148	0	1120	93δCH$_3$
1115.5	s	1131	100	1108	16δCH$_3$+13δCCC$_{ring}$+17νC-C$_{ring}$+8νCCl+7δCCO+7δCCC
		1064	23	1046	60νC-C$_{ring}$+17δCCH$_{ring}$+7νC=C$_{ring}$
		1022	1	1001	39νNC(H$_3$)+18δCH$_3$+9δCCO
		1021	12	982	92γCNH
		964	1	951	85γCCH$_{ring}$+11τCCC$_{ring}$
		927	4	915	90γCCH$_{ring}$+7τCCC$_{ring}$
893.4	m	904	68	890	20δCCC$_{ring}$+23δ(CCN+NCH+CCH)+10νC-C$_{ring}$+9νCCl+7νC=C(N)+7δCH$_3$
825.6	m	833	84	821	39νC-C$_{ring}$+32δCCC$_{ring}$+10νCCl
		811	4	769	39τCCC$_{ring}$+26γCCO+15γCCN+10γCCCl
730.6	w	744	50	735	78γCCH$_{ring}$+8γCCO
		717	25	707	21δ(C=CH+C=CN)+17νCCl+13δCCC$_{ring}$+10δCCC+7δCCO+7νC-C$_{ring}$
		642	67	629	69γCNH+10γCCN+9δCH$_3$

[a] - vs – very strong, s – strong, m – medium, w – weak, vw – very weak, b – broad

[b] - only the components of PED that contribute more than 7% are taken into account

Table S9. The selected, DFT/B3LYP/6-311++G(2d,2p) calculated geometrical parameters of the I_{CE}, II_{CE} and II_{CK} conformers of 2-(1-(methylimino)methyl)-6-chlorphenol (r in Å, angle values in degrees).

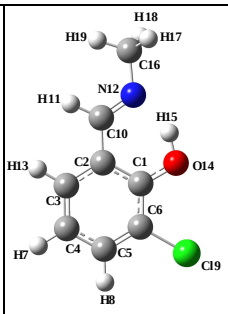
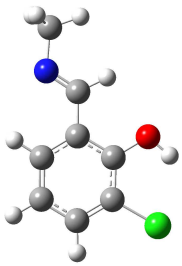
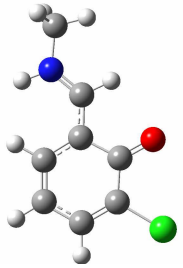
			
Parametr	**I_{CE}**	**II_{CE}**	**II_{CK}**
r C_1-O_{14} (r C_1=O_{14})	1.334	1.357	1.231
r C_2-C_{10} (r C_2=C_{10})	1.456	1.474	1.382
r C_{10}=N_{12} (r C_{10}-N_{12})	1.277	1.268	1.333
r C_{10}-H_{11}	1.096	1.093	1.084
r N_{12}-C_{16}	1.449	1.448	1.454
r O_{14}-H_{15}	0.997	0.966	
r N_{12}-H_{15}			1.007
r C_6-Cl_9	1.749	1.763	1.746
R N_{12}···H_{15}	1.713		
R Cl_9···H_{15}		2.358	
θ H_{19}-C_{16}-N_{12}	112.8	113.6	109.0
θ C_{16}-N_{12}=C_{10} (θ C_{16}-N_{12}-C_{10})	119.6	118.1	124.5
θ N_{12}=C_{10}-H_{11} (θ N_{12}-C_{10}-H_{11})	120.9	121.7	115.9
θ H_{11}-C_{10}-C_2 (θ H_{11}-C_{10}=C_2)	116.2	116.2	116.3
θ C_1-O_{14}-H_{15}	107.1	108.8	
θ C_1-C_6-Cl_9	119.0	118.0	116.9
θ O-H···N	148.4		
θ O-H···Cl		120.9	
φ H_{19}-C_{16}-N_{12}=C_{10} (φ H_{19}-C_{16}-N_{12}-C_{10})	0.0	0.0	0.0
φ C_{16}-N_{12}=C_{10}-H_{11} (φ C_{16}-N_{12}-C_{10}-H_{11})	0.0	0.0	0.0
φ H_{11}-C_{10}-C_2-C_1 (φ H_{11}-C_{10}=C_2-C_1)	-180.0	0.1	0.0
φ C_6-C_1-O_{14}-H_{15}	-180.0	0.0	
φ C_2-C_1-C_6-Cl_9	180.0	180.0	180.0

Table S10. The comparison of the DFT/B3LYP/6-311++G(2d,2p) calculated harmonic frequencies (cm^{-1}) and intensities ($kmmol^{-1}$) for all optimized enol conformers of 2-(1-(methylimino)methyl)-6-chlorphenol. The relative energies (ΔE_{ZPE}, $kJmol^{-1}$) are also given.

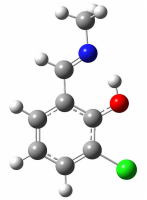
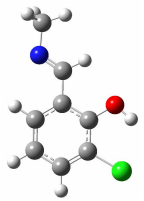
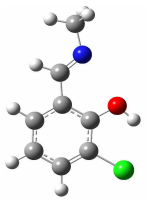
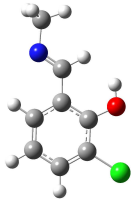
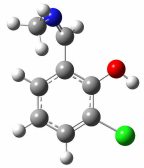
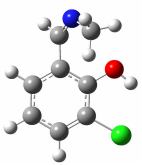
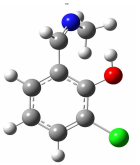
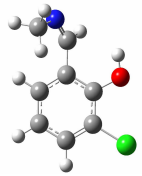
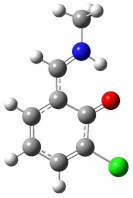
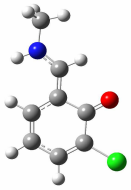
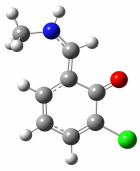
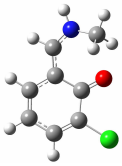
							
I_{CE} 0 kJ/mol	II_{CE} (ΔE=25.44)	III_{CE} (ΔE=40.86)	IV_{CE} (ΔE=44.98)	V_{CE} (ΔE=54.86)	VI_{CE} (ΔE=56.35)	VII_{CE} (ΔE=65.46)	$VIII_{CE}$ (ΔE=67.22)
$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I	$\nu_{harm.}$ I
3210 4	3750 119	3735 105	3842 64	3753 115	3751 107	3797 84	3820 84
3196 5	3213 5	3212 3	3214 5	3213 3	3212 3	3211 3	3213 3
3172 10	3207 0	3197 6	3208 0	3205 3	3196 6	3196 6	3200 5
3129 492	3190 4	3176 5	3190 4	3190 2	3176 3	3176 2	3187 1
3086 12	3076 16	3078 15	3080 13	3095 13	3092 14	3091 18	3091 21
3075 21	3063 27	3062 27	3065 26	3086 26	3083 28	3082 12	3077 15
3015 87	3043 35	2965 132	2972 103	3068 21	3068 23	3071 20	3037 16
2998 100	2979 90	2953 42	2932 73	3010 36	3014 39	3020 28	3016 37
1692 177	1708 78	1715 95	1710 100	1705 85	1712 85	1694 92	1699 79
1655 66	1636 34	1634 34	1641 29	1633 37	1633 24	1639 9	1639 17
1610 6	1609 8	1605 6	1603 15	1608 5	1608 1	1602 7	1603 15
1535 29	1507 2	1508 5	1507 9	1508 4	1506 8	1507 2	1504 11
1505 6	1503 15	1503 8	1506 13	1505 1	1505 0	1501 11	1503 1
1482 6	1480 5	1479 117	1478 5	1488 12	1486 46	1488 36	1488 11
1476 152	1478 143	1478 5	1476 107	1477 124	1472 78	1476 52	1474 95
1461 18	1442 14	1439 14	1445 26	1436 8	1434 4	1441 2	1436 6
1445 22	1410 16	1417 39	1438 11	1426 14	1408 24	1404 16	1420 15
1400 34	1369 52	1379 52	1344 51	1368 47	1371 39	1357 47	1352 61
1328 24	1294 78	1307 7	1296 12	1293 53	1288 16	1292 5	1290 10
1314 31	1273 63	1284 59	1273 60	1277 68	1275 63	1267 55	1277 55
1253 22	1244 42	1244 22	1236 83	1224 43	1229 27	1232 69	1220 103
1213 49	1191 13	1196 19	1186 32	1193 10	1191 15	1190 19	1191 19
1172 59	1156 14	1162 58	1155 4	1161 7	1162 6	1160 3	1161 7
1154 14	1146 35	1146 8	1137 136	1143 38	1149 56	1145 97	1142 79
1141 0	1140 0	1137 0	1136 0	1134 6	1134 3	1138 3	1135 18
1101 14	1094 10	1108 16	1099 14	1098 13	1097 17	1098 17	1099 15

Table S9 cd.

1027 38	1023 11	1015 24	1025 23	993 2	989 1	989 1	993 1
998 8	1007 3	993 5	1004 1	969 22	966 18	960 9	971 7
982 0	986 3	976 1	959 3	945 4	940 1	939 4	946 5
947 10	937 0	928 33	938 2	921 8	916 16	925 6	924 11
928 0	895 30	925 0	897 8	865 10	894 29	899 4	869 0
902 65	844 8	835 2	842 13	849 14	837 2	840 14	847 12
848 11	803 17	802 10	811 15	802 27	796 21	801 19	807 27
814 6	753 34	755 45	758 32	765 48	758 43	760 43	767 47
761 49	721 46	694 38	725 29	736 32	707 30	711 27	739 25
694 37	587 3	607 10	584 14	606 4	617 8	618 7	607 7
612 6	559 0	567 0	565 1	569 3	572 1	573 9	569 11
570 0	557 14	552 1	554 1	561 1	558 1	557 3	560 1
546 0	548 0	532 11	545 0	533 11	505 7	507 5	531 1

Table S11. The comparison of the DFT/B3LYP/6-311++G(2d,2p) calculated harmonic frequencies (cm^{-1}) and intensities ($kmmol^{-1}$) for all optimized keto conformers of 2-(1-(methylimino)methyl)-6-chlorphenol. The relative energies (ΔE_{ZPE}, $kJmol^{-1}$) are also given.

							
I_{CK} (ΔE=14.02)		II_{CK} (ΔE=57.03)		III_{CK} (ΔE=69.25)		IV_{CK} (ΔE=71.74)	
ν_{harm}, cm^{-1}	I	ν_{harm}, cm^{-1}	I	ν_{harm}, cm^{-1}	I	ν_{harm}, cm^{-1}	I
3205	9	3608	45	3644	118	3636	116
3188	5	3202	9	3226	10	3203	10
3159	7	3187	8	3197	5	3187	7
3146	0	3171	1	3184	6	3158	10
3122	4	3142	12	3160	3	3150	4
3096	11	3141	5	3136	16	3141	7
3070	137	3089	16	3098	11	3113	18
3038	93	3039	69	3042	24	3046	41
1692	665	1693	567	1689	421	1669	564
1649	127	1646	16	1641	13	1644	27
1585	127	1617	505	1592	572	1592	175
1540	75	1538	67	1570	28	1577	43
1519	26	1521	43	1536	201	1534	142
1488	5	1498	34	1518	3	1505	23
1488	7	1491	8	1496	12	1478	38
1470	43	1480	16	1487	23	1471	5
1409	45	1445	106	1463	119	1442	23
1374	1	1381	7	1393	150	1416	111
1369	30	1351	273	1360	125	1357	38
1312	65	1333	122	1305	2	1322	43
1262	62	1268	19	1263	9	1249	34
1193	8	1190	0	1192	10	1192	15
1151	31	1154	29	1172	3	1171	11
1150	131	1148	0	1148	0	1150	13
1146	0	1131	99	1128	51	1144	36
1079	25	1064	23	1067	24	1070	36
1025	51	1022	1	1015	1	986	6
1013	26	1021	12	989	29	974	12
973	0	964	1	970	1	960	7
943	22	927	4	935	3	932	2
941	14	905	67	862	19	903	20
918	13	833	83	832	73	831	63
845	48	811	4	813	0	812	12
816	0	744	50	766	51	750	52
755	53	718	25	751	50	699	25
667	26	642	67	606	19	623	15
600	6	591	17	596	0	614	21
568	1	549	10	546	2	563	8
547	1	548	4	538	19	527	15