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Intramolecular hydrogen bonding and molecular structure of 2-iminomethyl-phenol and molecular structure of iminomethyl-benzene from ab initio MO calculations

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Abstract

Ab initio calculations, including electron correlation (MP2), have been performed for iminomethyl-benzene and 2-iminomethyl-phenol. They indicate the existence of two (syn and anti) stable conformers of 2-iminomethyl-phenol. The principal syn conformer is characterized by considerable hydrogen bonding between the iminomethyl and hydroxy groups, accompanied by pronounced structural changes in the rest of the molecule, as compared with phenol and iminomethyl-benzene calculated at the same theoretical level. These structural changes are consistent with the notion of resonance-assisted hydrogen bonding, also observed in a series of nitrophenols and similar molecules. The anti conformer of 2-iminomethyl-phenol has 41.8 kJ mol^{-1} higher energy than the syn conformer. The internal rotation of iminomethyl group in 2-iminomethyl-phenol is hindered by a considerably higher barrier, 55.9 kJ mol^{-1}, due to intramolecular hydrogen bond formation, than that in iminomethyl-benzene, 27.6 kJ mol^{-1}, according to the calculations at the HF/6-31G* level. The amino tautomer form of 2-iminomethyl-phenol has 25.0 kJ mol^{-1} (HF/6-31G*) or 30.6 kJ mol^{-1} (MP2(FC)/6-31G*) higher energy than the imino form. The energy of the structural changes as compared to iminomethyl-benzene and phenol and the energy of the intramolecular hydrogen bond formation in 2-iminomethyl-phenol was estimated to be −28.8 kJ mol^{-1} at the HF/6-31G* level and −36.8 kJ mol^{-1} at the MP2(FC)/6-31G* level of theory.

Keywords: Ab initio MO calculations; Iminomethyl-benzene; 2-Iminomethyl-phenol; Intramolecular hydrogen bonding; Molecular structure

1. Introduction

Our previous investigations on the molecular structure and internal rotation in o-nitrophenols [1–5] and salicylaldehyde [6] by electron diffraction and ab initio calculations have shown that the intramolecular hydrogen bonding in these molecules is assisted by pronounced structural changes in the rest of the molecule as compared with the structures of phenol and nitrobenzene or benzaldehyde. The internal rotation of the nitro group in the o-nitrophenols [5] is hindered by a higher barrier than that of nitrobenzene, and the same applies to the formyl group torsion in salicylaldehyde as compared to that of benzaldehyde

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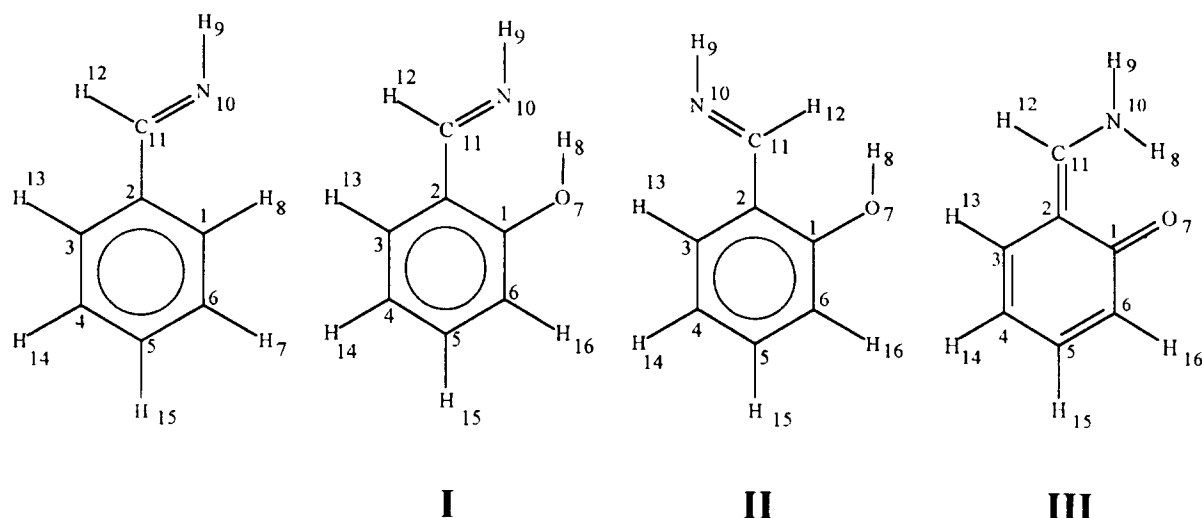
Fig. 1. Iminomethyl-benzene, syn (I) and anti (II) conformers of 2-iminomethyl-phenol, its amino tautomer form (III), and the numbering of atoms.

[6]. As a continuation of our research into the structural consequences of the intramolecular ydrogen bond formation, we report here the results of ab initio calculations on 2-iminomethyl-phenol and iminomethyl-benzene. The structure of the latter, and that of phenol [2] serve as references for comparison.

2. Computation details

The ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 series of programs [7]. The standard 6-31G basis set [8], augmented by the polarization function, was used throughout. Initially, RHF/6-31G* optimizations, as well as frequency analyses were performed for iminomethyl-benzene in its planar and orthogonal conformations, for planar conformer of 2-iminomethyl-phenol (syn (I), see Fig. 1), and for the amino tautomer form of 2-iminomethyl-phenol (III, Fig. 1). The potential energy curve corresponding to rotation of the iminomethyl group in 2-iminomethyl-phenol was calculated at the HF/6-31G* level. In these calculations all parameters were optimized except the angle of the iminomethyl group torsion, which was assumed at 10 degrees steps in the 0–180° interval. The geometry of the anti (II) (Fig. 1) conformer of 2-imino-methyl-phenol in the vicinity of the second minimum

of the potential energy curve (Fig. 2) was then fully optimized at the same level of theory, followed by vibrational frequency analysis. The calculations for the planar conformation of iminomethyl-benzene, for the lowest-energy stable conformer of 2-imino-methyl-phenol (I), and for the amino tautomer (III) were followed by second-order Møller–Plesset (MP2(FC)/6-31G*) optimizations [9] to include the effect of electron correlation in the calculations. Data on phenol used here for reference had been obtained previously [2] from calculations at the same level of theory.
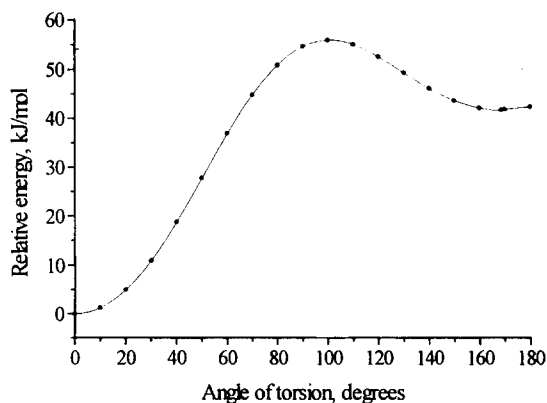

Fig. 2. Potential energy curve describing the rotation of the iminomethyl group in 2-iminomethyl-phenol.

3. Results and discussion

The computed geometries for the planar and ortho-gonal conformation of iminomethyl-benzene and for the two stable conformers, (I) and (II), of 2-imino-methyl-phenol are presented in Tables 1 and 2, respectively. The results of the calculations on the amino tautomer of 2-iminomethyl-phenol (III) are compiled in Table 3. The numbering of atoms is presented in Fig. 1. The potential energy curve describing the rotation of the iminomethyl group in 2-iminomethyl-phenol is presented in Fig. 2 and the corresponding data are compiled in Table 4. The potential energy function in the form

$V(\phi) = \sum_{i=1}^{n} \frac{1}{2}V_i(1 - \cos\phi)$ was fitted to the calculated points. While the contributions of the three first terms are essential ($V_1 = 38.1$, $V_2 = 34.0$, $V_3 = 3.4$ kJ mol^{-1}), higher terms should also be considered to adequately describe the behaviour of the potential function.

The orthogonal conformer of iminomethyl-benzene and the anti conformer of 2-iminomethyl-phenol proved to be first order rotational transition states by frequency analyses. Concerning the other computed species, they are stable states. The imino (I) and amino (III) tautomers of 2-iminomethyl-phenol repre-sent the minima on a double-minimum potential energy well of the proton transfer with the imino form having the lowest energy. The difference of

Table 1
Iminomethyl-benzene: computed geometries[a]

Parameter	Planar conformation		Orthogonal conformation
	HF/6-31G*	MP2(FC)/6-31G*	HF/6-31G*
C_1-C_2	1.3933	1.4031	1.3887
C_2-C_3	1.3881	1.4008	1.3884
C_3-C_4	1.3866	1.3955	1.3854
C_4-C_5	1.3834	1.3960	1.3853
C_5-C_6	1.3896	1.3996	1.3855
C_1-C_6	1.3809	1.3922	1.3851
C_3-H_{13}	1.0768	1.0893	1.0756
C_4-H_{14}	1.0753	1.0874	1.0754
C_5-H_{15}	1.0756	1.0875	1.0753
C_6-H_7	1.0754	1.0875	1.0754
C_1-H_8	1.0734	1.0867	1.0756
$\angle C_1-C_2-C_3$	119.32	119.59	119.30
$\angle C_2-C_3-C_4$	120.60	120.36	120.35
$\angle C_3-C_4-C_5$	119.74	119.88	120.12
$\angle C_4-C_5-C_6$	120.00	119.90	119.75
$\angle C_5-C_6-C_1$	120.22	120.36	120.13
$\angle C_6-C_1-C_2$	120.12	119.90	120.35
$\angle C_2-C_3-H_{13}$	119.76	119.64	119.76
$\angle C_3-C_4-H_{14}$	120.02	119.98	119.77
$\angle C_4-C_5-H_{15}$	120.02	120.04	120.13
$\angle C_5-C_6-H_7$	119.93	119.87	120.09
$\angle C_6-C_1-H_8$	120.91	121.41	119.90
C_2-C_{11}	1.4806	1.4725	1.4950
$C_{11}-N_{10}$	1.2546	1.2874	1.2522
$C_{11}-H_{12}$	1.0860	1.0997	1.0865
$N_{10}-H_9$	1.0042	1.0258	1.0060
$\angle C_1-C_2-C_{11}$	121.15	120.86	120.34
$\angle C_2-C_{11}-N_{10}$	122.75	121.51	121.81
$\angle H_{12}-C_{11}-N_{10}$	122.52	123.26	122.50
$\angle C_{11}-N_{10}-H_9$	111.49	109.82	111.03
$N_{10}...H_8$	2.5770	2.5387	3.3166
Energy (a.u.)	−323.5896873	−324.6299108	−323.5791618

[a] "r_e" equilibrium bond lengths (Å) and angles (deg).

25.0 kJ mol^{-1} was calculated at the HF/6-31G* level and 30.6 kJ mol^{-1} was obtained when the electron correlation was included into calculations.

The relatively short $N_{10}\cdots H_8$ and $N_{10}\cdots O_7$ distances (see Table 2) directly indicate the presence of intramolecular hydrogen bonding in the syn (I)

conformer of 2-iminomethyl-phenol. In addition, the following pronounced changes, as compared to iminomethyl-benzene and phenol, are observed, as summarized in Table 5. When going from imino-methyl-benzene to 2-iminomethyl-phenol the C_1–C_2 bond lengthens, the C_2–C_{11} bond shortens and the

Table 2
2-Iminomethyl-phenol: computed geometries[a]

Parameter	Syn (I) conformation		Anti (II) conformation
	HF/6-31G*	MP2(FC)/6-31G*	HF/6-31G*
C_1–C_2	1.4026	1.4160	1.3929
C_2–C_3	1.3970	1.4066	1.3971
C_3–C_4	1.3759	1.3882	1.3768
C_4–C_5	1.3925	1.4013	1.3912
C_5–C_6	1.3773	1.3902	1.3785
C_1–C_6	1.3935	1.4019	1.3891
C_3–H_{13}	1.0768	1.0895	1.0732
C_4–H_{14}	1.0742	1.0863	1.0746
C_5–H_{15}	1.0756	1.0876	1.0754
C_6–H_{16}	1.0739	1.0864	1.0739
$\angle C_1$–C_2–C_3	118.82	119.14	118.46
$\angle C_2$–C_3–C_4	121.76	121.21	121.28
$\angle C_3$–C_4–C_5	118.63	119.17	119.34
$\angle C_4$–C_5–C_6	121.02	120.70	120.48
$\angle C_5$–C_6–C_1	120.31	120.44	119.88
$\angle C_6$–C_1–C_2	119.47	119.34	120.55
$\angle C_2$–C_3–H_{13}	118.61	118.71	117.94
$\angle C_3$–C_4–H_{14}	120.69	120.39	120.28
$\angle C_4$–C_5–H_{15}	119.77	119.95	120.05
$\angle C_5$–C_6–H_{16}	121.49	121.58	121.61
C_2–C_{11}	1.4682	1.4579	1.4796
C_{11}–N_{10}	1.2607	1.2938	1.2556
C_{11}–H_{12}	1.0846	1.0979	1.0849
N_{10}–H_9	1.0026	1.0230	1.0041
$\angle C_1$–C_2–C_{11}	122.23	121.73	121.60
$\angle C_2$–C_{11}–N_{10}	123.30	121.75	122.46
$\angle H_{12}$–C_{11}–N_{10}	121.81	122.33	121.55
$\angle C_{11}$–N_{10}–H_9	112.80	111.89	111.47
C_1–O_7	1.3311	1.3525	1.3593
O_7–H_8	0.9590	0.9955	0.9454
$\angle C_2$–C_1–O_7	123.06	123.00	123.13
$\angle C_1$–O_7–H_8	110.12	107.29	111.67
$N_{10}\cdots H_8$	1.8840	1.7765	—
$N_{10}\cdots O_7$	2.7078	2.6605	—
$\angle C_{11}$–$N_{10}\cdots H_8$	98.89	100.26	—
$\angle O_7$–$H_8\cdots N_{10}$	142.40	145.98	—
C_1–C_2–C_{11}–N_{10}	0.0	0.0	168.6
C_2–C_{11}–N_{10}–H_9	180.0	180.0	178.2
C_2–C_1–O_7–H_8	0.0	0.0	326.9
Energy (a.u.)	−398.4555867	−399.6771951	−398.4396755

[a] "r_e" equilibrium bond lengths (Å) and angles (deg).

Table 3

Amino tautomer form of 2-iminomethyl-phenol: computed geometries[a]

Parameter	HF/6-31G*	MP2(FC)/6-31G*
C_1-C_2	1.4628	1.4615
C_2-C_3	1.4407	1.4296
C_3-C_4	1.3414	1.3686
C_4-C_5	1.4432	1.4277
C_5-C_6	1.3430	1.3707
C_1-C_6	1.4587	1.4460
C_3-H_{13}	1.0777	1.0904
C_4-H_{14}	1.0740	1.0862
C_5-H_{15}	1.0768	1.0888
C_6-H_{16}	1.0743	1.0869
$\angle C_1-C_2-C_3$	120.15	121.04
$\angle C_2-C_3-C_4$	121.51	120.63
$\angle C_3-C_4-C_5$	118.92	119.39
$\angle C_4-C_5-C_6$	122.57	121.84
$\angle C_5-C_6-C_1$	121.36	121.59
$\angle C_6-C_1-C_2$	115.49	115.52
$\angle C_2-C_3-H_{13}$	118.25	118.78
$\angle C_3-C_4-H_{14}$	121.45	120.68
$\angle C_4-C_5-H_{15}$	118.18	118.90
$\angle C_5-C_6-H_{16}$	122.01	121.66
C_2-C_{11}	1.3744	1.3943
$C_{11}-N_{10}$	1.3203	1.3280
$C_{11}-H_{12}$	1.0773	1.0907
$N_{10}-H_8$	1.0018	1.0361
$N_{10}-H_9$	0.9927	1.0105
$\angle C_1-C_2-C_{11}$	120.30	119.44
$\angle C_2-C_{11}-N_{10}$	126.18	123.00
$\angle H_{12}-C_{11}-N_{10}$	115.17	116.96
$\angle C_{11}-N_{10}-H_8$	117.90	114.69
$\angle C_{11}-N_{10}-H_9$	121.18	121.61
C_1-O_7	1.2240	1.2698
$\angle C_2-C_1-O_7$	122.66	122.78
$O_7...H_8$	1.9369	1.7386
$N_{10}...O_7$	2.6666	2.5848
$\angle N_{10}-H_8...O_7$	127.43	135.84
$\angle C_1-O_7...H_8$	105.54	104.25
Energy (a.u.)	–398.4460564	–399.6655529

[a] "r_e" equilibrium bond lengths (Å) and angles (deg).
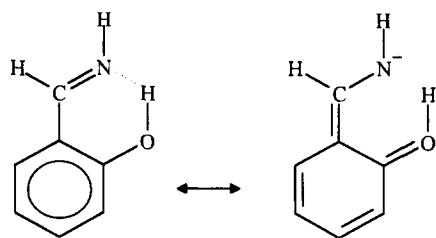
Scheme 1.

$C_{11}-N_{10}$ bond lengthens. When going from phenol to 2-iminomethyl-phenol, again, the C_1-C_2 bond lengthens, the C–O bond shortens and the O–H bond lengthens. All these changes are consistent with the notion of resonance-assisted hydrogen bonding in 2-iminomethyl-phenol, similarly to o-nitrophenols [1–5] and salicylaldehyde [6]. Resonance structures implying these changes are presented in Scheme 1. Note that these changes become even more pronounced in the amino form of the 2-iminomethyl-phenol (Table 3), but diminish in the anti (II) conformer (Table 2).

The barrier height to internal rotation of the iminomethyl group in iminomethyl-benzene was determined as energy difference, 27.6 kJ mol^{-1}, between the stable state and the first order rotational transition state, calculated at the HF/6-31G* level. The barrier to internal rotation of 2-iminomethyl-phenol is 55.9 kJ mol^{-1}, calculated at the same theoretical level, and it is 28.3 kJ mol^{-1} higher than that of iminomethyl-benzene. The increase is due to the restraining influence of the intramolecular hydrogen bond, in agreement with observations on o-nitrophenols as compared with nitrobenzene [5], and salicylaldehyde as compared with benzaldehyde [6], for which the increases were 12 and 10 kJ mol^{-1}, respectively.

The energy accompanying the structural changes and the formation of the intramolecular hydrogen bond in 2-iminomethyl-phenol may be estimated as the energy of the isodesmic reaction [10] presented in Scheme 2. It is –28.8 kJ mol^{-1} from the calculations

Table 4

Relative energies as a function of the angle of the iminomethyl group torsion (ϕ, degrees) in 2-iminomethyl-phenol from ab initio calculations[a]

ϕ	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
E	0.0	1.3	5.0	10.9	18.8	27.7	36.8	44.8	50.9	54.6	55.9	55.0	52.6	49.4	46.2	43.7	42.2	41.9	42.4

[a] Computed at HF/6-31G* level, kJ mol^{-1}.
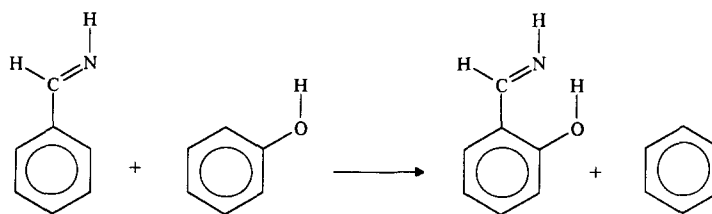
Scheme 2.

Table 5
Comparison of phenol, iminomethyl-benzene and 2-iminomethyl-phenol geometrical parameters from *ab initio* calculations[a]

Parameter	Phenol[b]	Iminomethyl-benzene	2-Iminomethyl-phenol(I)
C_1-C_2	1.397	1.403	1.416
C_2-C_{11}	–	1.473	1.458
$C_{11}-N_{10}$	–	1.287	1.294
$\angle C_1-C_2-C_{11}$	–	120.9	121.7
$\angle C_2-C_{11}-N_{10}$	–	121.5	121.8
C–O	1.375	–	1.353
O–H	0.973	–	0.996
$\angle C_C-C_O-O$	122.8	–	123.0
$\angle C-O-H$	108.3	–	107.3
CO, tilt[c]	+3.0	–	+2.7
CC, tilt[d]	–	+0.7	+1.3

[a] "r_e"equilibrium bond lengths (Å) and angles (deg) computed at MP(FC)/6-31G* level, present work.
[b] Ref [2].
[c] Positive when the C–C–O angle is opening.
[d] Positive when the $C_1-C_2-C_{11}$ angle is opening.

using the Hartree–Fock approximation and -36.8 kJ mol^{-1} with electron correlation effects included.

4. Conclusions

There is considerable resonance assisted intramolecular hydrogen bonding in the principal syn conformer of 2-iminomethyl-phenol. This can be recognized not only in the short N...H and N...O distances, but also in the structural changes in the rest of the molecule as compared with iminomethyl-benzene and phenol.

The internal rotation of the iminomethyl group in 2-iminomethyl-phenol is hindered by a higher barrier than that in iminomethyl-benzene.

There is a second stable anti conformer of 2-iminomethyl-phenol, having 41.8 kJ mol^{-1} higher energy than the hydrogen-bonded syn conformer.

Acknowledgements

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