Supplementary information of the paper

Aminophenol isomers unraveled by conformer-specific far-IR action spectroscopy

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Table S1. The experimental and calculated wavenumbers of vibrational transitions of 4-aminophenol in the range of 220-800 cm^{-1}. The theoretical results were obtained with B3LYP functional and aug-pc-2 basis set, within harmonic and anharmonic VPT2 [1] approaches. The assignments in bold are given according to Varsaniy's notation [2]. List of abbreviations used: i.p. – in plane, o.p. – out of plane.

		Experiment		B3LYP/aug-pc-2			
Mode	Assignment	ν_{exp}, cm^{-1}	Relative Intensity, %	harmonic wavenumber, cm^{-1}	anharmonic wavenumber, cm^{-1}	I_{harm}, km/mol***	Potential Energy Distribution
26(1)	C-H o.p. wagging, **10a**	792.0	58.8	810.0	796.1	5.9	HCCC torsion (87%)
27(1)	C-C-C i.p. bending, **12**	759.5	100.0	773.0	757.4	16.8	CCC bend i.p. (36%), OC stretch (16%), CC stretch (11%)
	Comb. 33(1)+36(1)*	735.0	21.3	768.8	767.3	1.1	
	NH_2 wagging overtone 0-3	711.0	37.5				
28(1)	Ring puckering, **4**	676.5	56.3	727.3	712.1	5.8	CCCC, CCCN o.p. torsion (67%)
29(1)	C-C-C i.p. bending, **6b**	645.5	6.3	662.2	654.8	0.3	CCC, CCO, CCN bend i.p. (79%), CC stretch (16%)
	Comb. 32(1)+30(1)*,**	532.0	22.5				
30(1)	NH_2 wagging fundamental**	-	-	616.2	484.8	268.3	HNCC torsion o.p. (73%), HNH bend (11%)
31(1)	C-C-C o.p. bending, **16b**	502.0	81.3	517.7	506.0	56.7	NCCC, OCCC bend o.p. (82%)
	OH rock overtone 0-2	478.0	42.5				
32(1)	C-C-C i.p. bending, **6a**	472.0	12.5	474.4	469.4	0.3	CCC bend i.p. (70%), CC stretch (16%)
	NH_2 wagging overtone 0-2	467.0	42.5				
	NH_2 torsion overtone 0-2	462.0	53.8				
33(1)	C-O , C-N i.p. bending, **9b**	370.0	30.0	439.3	437.9	6.5	CCO, CCN bend i.p. (91%)
34(1)	C-C-C o.p. bending, **16a**	422.0	45.0	426.5	418.0	1.3	CCCC torsion o.p. (83%)
35(1)	C-O, C-N o.p. bending, **10b**	350.0	23.8	358.2	351.3	7.0	CCCN torsion o.p. (88%), CCCC torsion o.p. (13%)
36(1)	C-O , C-N i.p. bending, **15**	326.5	18.8	329.5	328.8	3.4	CCO,CCN i.p. bend (82%)
37(1)	OH wagging	254.5	76.3	294.9	254.3	93.9	HOCC torsion (96%)
38(1)	NH_2 torsion	237.0	53.8	245.8	244.6	18.5	HNCC torsion (97%)
39(1)	C-C-C o.p. bending, **11**	-	-	150.2	147.3	2.5	CCCC torsion (77%)

* Tentative assignment of the observed experimental bands

** NH_2 wagging fundamental 30(1) is expected to have the value of 30-60 cm^{-1} according to aniline and halosubstituted anilines studies [3,4]

*** Theoretical intensities of overtone and combination bands were taken when available from anharmonic VPT2 treatment.

Table S2. The experimental and calculated wavenumbers of vibrational transitions of *trans* 2-aminophenol in the range of 220-800 cm^{-1}. The theoretical results were obtained with B3LYP functional and aug-pc-2 basis set, within harmonic and anharmonic VPT2 [1] approaches. The assignments in bold are given according to Varsaniy's notation [2]. List of abbreviations used: i.p. – in plane, o.p. – out of plane.

		Experiment		B3LYP/aug-pc-2			
Mode	Assignment	ν_{exp}, cm^{-1}	Relative Intensity, %	harmonic wavenumber, cm^{-1}	anharmonic wavenumber, cm^{-1}	I_{harm}, km/mol***	Potential Energy Distribution
26(1)	ring breathing, **1**	767	14.3	778.3	768.0	5.7	HOC bend i.p. (20%), CC stretch (16%, 16%), CCC bend i.p. (16%)
27(1)	C-H o.p. in phase, **11**	737.5	100.0	751.0	737.3	44.2	HCCC torsion (55%), CCCC torsion o.p. (25%)
28(1)	Ring puckering, **4**	748.5	49.3	747.0	730.6	42.0	CCCC torsion o.p. (48%), HCCC torsion (33%)
	NH_2 wagging overtone 0-3*	696	17.1				
	NH_2 torsion overtone 0-2*	653	15.0	693.7	664.8	1.0	
29(1)	C-C-C i.p. bending, **6a**	542	9.3	596.8	590.5	3.9	CCC bend i.p. (51%)
30(1)	NH_2 wagging fundamental**	-	-	586.4	526.6	58.3	HNCC torsion, CCN,CCO o.p. bend (66%)
31(1)	C-C-C o.p. bending, **16a**	501.0	15.0	561.3	477.0	129.2	HNCC torsion, CCN,CCO o.p. bend (54%), CCC bend o.p. (10%)
32(1)	C-C-C in plane bending, **6b**	486	11.8	538.3	491.1	57.7	HNCC torsion (22%), CCC bend i.p. (19%)
		453	9.3				
33(1)	C-C-C out of plane bending, **16b**	445.5	57.1	457.1	446.2	22.8	CCCC, CCCN, CCCO torsion o.p. (66%, 18%)
	NH_2 wagging overtone 0-2*	437.0	10.0				
34(1)	C-N, C-O in plane bending, **9b**	351.0	18.6	446.0	441.1	2.7	CCO, CCN bend i.p. (68%)
35(1)	NH_2 torsion	323	28.6	346.8	339.3	21.5	HNCC torsion (83%)
36(1)	C-N, C-O i.p. bending, **15**	303	20.0	314.6	317.3	10.9	CCO,CCN,CCC bend i.p. (79%)
37(1)	OH wagging	286.5	17.9	310.7	291.5	55.8	HOCC torsion (75%), CCCC torsion o.p. (13%)
38(1)	C-N, C-O o.p. wagging, **10a**	256	32.1	278.1	274.0	48.0	CCCC,CCCO,CCCN torsion o.p. (59%, 17%), HOCC torsion (17%)
39(1)	C-C-C o.p. bending, **10b**	-	-	184.2	184.2	1.6	CCCC torsion o.p. (80%)

* Tentative assignment of the observed experimental bands

** NH_2 wagging fundamental 30(1) is expected to have the value of 30-60 cm^{-1} according to aniline and halosubstituted anilines studies [3,4]

*** Theoretical intensities of overtone and combination bands were taken when available from anharmonic VPT2 treatment

Table S3. The experimental and calculated wavenumbers of vibrational transitions of *trans* 3-aminophenol in the range of 220-800 cm^{-1}. The theoretical results were obtained with B3LYP functional and aug-pc-2 basis set, within harmonic and anharmonic VPT2 [1] approaches. The assignments in bold are given according to Varsaniy's notation [2]. List of abbreviations used: i.p. – in plane, o.p. – out of plane.

		Experiment		B3LYP/aug-pc-2			
Mode	Assignment	ν_{exp}, cm^{-1}	Relative Intensity, %	harmonic wavenumber, cm^{-1}	anharmonic wavenumber, cm^{-1}	I_{harm}, km/mol***	Potential Energy Distribution
26(1)	C-H o.p. in phase, **11**	755	100.0	768.7	753.8	35.7	HCCO,HCCN,HCCC torsion o.p. (82%)
27(1)	ring breathing, **1**	745	24.3	759.4	748.8	2.9	CC stretch (45%), CCC bend (22%,12%)
	NH_2 wagging overtone 0-3*	715	24.3				
	Comb. 39(1)+30(1)*	698	20.3				
28(1)	Ring puckering, **4**	678	55.4	698.7	685.3	29.2	CCCC torsion o.p. (76%)
29(1)	C-C-N, C-C-O o.p. bending, **16a**	612	10.8	636.2	607.4	18.1	CCCN,CCCO o.p. bend (82%)
	Comb. 37(1)+36(1)*	602	23.0	640.2	633.7	11.2	
	Comb. 37(1)+38(1)*	542	10.8	543.0	537.4	3.7	
30(1)	C-C-C i.p. bending, **6a**	432	9.5	555.0	517.3	44.7	CCC bend i.p. (40%), HNCC torsion (19%)
31(1)	C-C-C i.p. bending, **6b**	427	29.7	535.4	484.4	66.0	CCC bend i.p. (56%), HNCC torsion (18%)
	NH_2 wagging overtone 0-2*	419	67.6				
32(1)	NH_2 wagging**	-	-	525.9	426.3	156.8	HNCC torsion (43%), CCC bend (15%), NC,OC stretch (10%)
33(1)	C-C-C out of plane bending, **16b**	459	24.3	465.4	463.8	4.1	CCCC torsion o.p. (64%), CCC,CCN,CCO bend (17%)
34(1)	C-N, C-O in plane bending, **15**	449	12.2	462.3	449.8	19.8	CCC,CCN,CCO bend i.p. (68%), CCCC torsion o.p. (11%)
	39(2), **10b** overtone*	409	5.4				
	37(1)+32(1)*,**	385	6.8				
35(1)	OH wagging	316	74.3	355.9	328.1	88.9	HOCC torsion (95%)
36(1)	C-N, C-O i.p. bending, **9a**	325	14.9	328.1	324.3	2.0	CCN,CCO bend i.p. (49%), HNCC torsion (31%)
37(1)	NH_2 torsion	329	21.6	312.1	312.8	19.8	HNCC torsion (59%), CCN,CCO bend i.p. (27%)
	37(1)-32(1)*,**	274	10.3				
	35(1)-32(1)*,**	262	14.8				
38(1)	C-C-C o.p. bending, **10a**	-	-	230.8	224.7	0.6	CCCC torsion o.p. (80%)
39(1)	C-C-C o.p. bending, **10b**	-	-	217.9	212.9	12.9	CCCC,CCCN,CCCO torsion o.p. (79%,10%)

* Tentative assignment of the observed experimental bands

** NH_2 wagging fundamental 32(1) is expected to have the value of 30-60 cm^{-1} according to aniline and halosubstituted anilines studies [3,4]. Our estimation for *trans* 3-aminophenol is ~55 cm^{-1} obtained from the tentatively assigned combination bands 262, 274 and 385 cm^{-1} (sum and difference frequency)

*** Theoretical intensities of overtone and combination bands were taken when available from anharmonic VPT2 treatment

Table S4. The experimental and calculated wavenumbers of vibrational transitions of *cis* 3-aminophenol in the range of 220-800 cm^{-1}. . The theoretical results were obtained with B3LYP functional and aug-pc-2 basis set, within harmonic and anharmonic VPT2 [1] approaches. The assignments in bold are given according to Varsaniy's notation [2]. List of abbreviations used: i.p. – in plane, o.p. – out of plane.

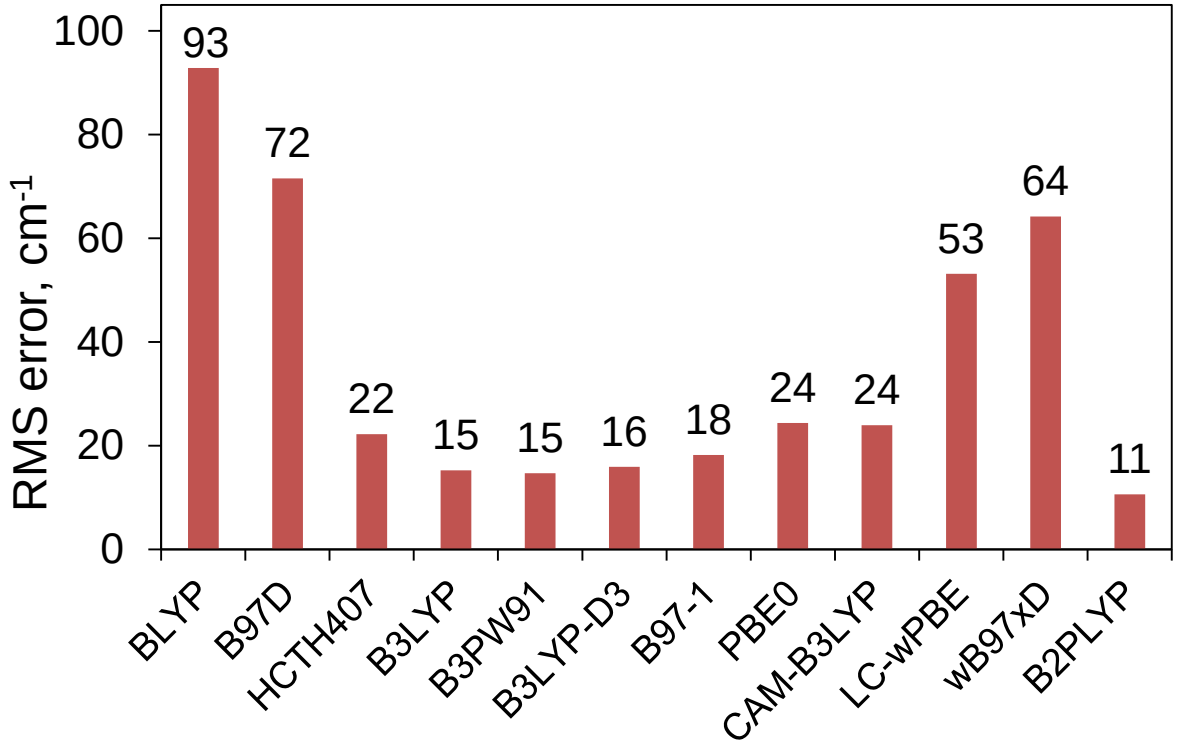
		Experiment		B3LYP/aug-pc-2			
Mode	Assignment	ν_{exp}, cm^{-1}	Relative Intensity, %	harmonic wavenumber, cm^{-1}	anharmonic wavenumber, cm^{-1}	I_{harm}, km/mol***	Potential Energy Distribution
26(1)	C-H o.p. in phase, **11**	766	100.0	776.7	760.5	20.8	HCCN,HCCO,HCCC torsion o.p. (91%)
27(1)	ring breathing, **1**	748	43.1	762.0	750.0	5.3	CCC bend (41%,17%), CC stretch (18%), NC,OC stretch (10%)
	NH_2 wagging overtone 0-3*	717	37.9				
	Comb. 38(1)+33(1)*	700	44.8				
28(1)	Ring puckering, **4**	679.5	72.4	698.7	685.6	25.1	CCCC torsion o.p. (71%), HCCN torsion (15%)
29(1)	C-C-N, C-C-O o.p. bending, **16a**	604	17.2	635.8	604.3	17.5	CCCN,CCCO torsion o.p. (86%)
	Comb. 37(1)+36(1)*	580	31.9				
30(1)	NH_2 wagging*	-	-	557.4	481.0	112.6	HNCC torsion (40%), CCC bend (13%,10%)
31(1)	C-C-C i.p. bending, **6a**	434	32.8	540.4	468.2	98.5	CCC bend i.p. (12%,13%), NC,OC stretch (11%), HNCC torsion (30%)
32(1)	C-C-C i.p. bending, **6b**	430	50.0	529.4	500.2	51.7	CCC bend i.p. (59%), NC,OC stretch (13%)
	NH_2 wagging overtone 0-2*	422	84.5				
33(1)	C-N, C-O in plane bending, **15**	461	27.6	467.2	465.6	13.8	CCC,CCN,CCO bend i.p. (83%)
34(1)	C-C-C out of plane bending, **16b**	446	43.1	460.2	451.1	28.1	CCCC,CCCN,CCCO torsion o.p. (75%)
	35(1)+32(1)*,**	348	17.2				
35(1)	OH wagging	307	124.1	348.3	317.2	90.0	HOCC torsion (95%)
36(1)	C-N, C-O i.p. bending, **9a**	312	20.7	323.9	321.2	4.8	CCN,CCO bend i.p. (66%), CC stretch (11%)
37(1)	NH_2 torsion	318.5	29.3	301.7	299.7	14.0	HNCC torsion 86%)
	37(1)-32(1)*,**	268	19.0				
	35(1)-32(1)*,**	256	23.4				
38(1)	C-C-C o.p. bending, **10a**	-	-	230.0	223.8	1.3	CCCC torsion o.p. (84%)
39(1)	C-C-C o.p. bending, **10b**	-	-	218.9	214.0	4.5	CCCC,CCCN,CCCO torsion o.p. (83%)

* Tentative assignment of the observed experimental bands

** NH_2 wagging fundamental 30(1) is expected to have the value of 30-60 cm^{-1} according to aniline and halosubstituted anilines studies [3,4]. Our estimation for *cis* 3-aminophenol is ~50 cm-1, and was obtained from the tentatively assigned combination bands 256, 268 and 348 cm^{-1} (sum and difference frequency)

*** Theoretical intensities of overtone and combination bands were taken when available from anharmonic VPT2 treatment

Fig. FS1. Comparison between the accuracy of calculated fundamental transitions in the high wavenumber region (800-4000 cm^{-1}) with respect to experimental data, achieved by different GGA and hybrid functionals with 6-311+G(d,p) basis set. The root mean square (RMS) errors were calculated based on 50 unequivocally assigned mid-IR fundamental transitions from literature data for the studied aminophenol isomers.



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