Supplementary Material

Mechanisms of the formation of imines in aqueous solution and the effect of the pH: a theoretical analysis

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Coordinates of the optimized structures, obtained with the X3LYP functional and the def2-SVP basis set for C and H, and ma-def2-SVP basis set for O and N. Solvent effect obtained with the continuum SMD method in water.

MS1

N  -5.26401235692409   0.91593659814520   0.35683571776014
C  -6.56273604653515   0.38120743444600  -0.06020356853919
H  -4.81362887472060  1.38499691255716  -0.43023861348805
H  -4.64270743912648  0.14721450288601   0.61286546055630
H  -7.23837768610955  1.20538062589453  -0.33359799634405
H  -7.03192546943695 -0.16026126283105   0.7756753953788
H  -6.51724212714717 -0.31115481109786  -0.92133639348303

MS2

C  -7.31062737115367  2.42800733671458   0.00001106115704
O  -7.37379390996936  3.64769892925866   0.0000915825348
H  -8.25259952170799  1.83126692629228  -0.0011174923897
C  -6.04628940591867  1.64463862993460  -0.0009262748713
H  -5.16236977912815  2.29652581191849  -0.00011003611831
H  -6.0389650444979   0.97983350820800  -0.88159576957270
H  -6.0394805069918   0.98004885767340   0.88158403988366

H2O

O  -3.603639499444461  1.19013489923631  -0.01540395682791
H  -2.63580610204266  1.16306703451380   0.02084240860864
H  -3.88309439851273  0.63549806624989   0.72732154821927
N  -4.79276453033164  1.21154311427186  -0.23056174071627
C  -5.14575692177053  -0.20002313771775  -0.42433311794586
H  -5.08075067501989  1.77707087619296  -1.03350477064228
H  -3.7125269821028  1.51417743357605  0.33355782442297
H  -6.23589649449229  -0.33845170471490  -0.47931386377874
H  -4.74518591633134  -0.79429913183617  0.40778592371816
H  -4.69494670716993  -0.56266321845328  -1.35786723155608
C  -5.14927755416097  1.86564840737943  1.08629155213345
O  -3.82357118205065  2.07293780739081  1.51691250113522
C  -5.96835541138644  3.12705946610304  0.90978733643008
H  -5.45312114230274  3.83133117364330  0.23667848021478
H  -6.10267720721689  3.61921338587755  1.88485640982247
H  -6.96497515377828  2.90066167691906  0.4974049421788
H  -5.69188410577811  1.12869376036804  1.70783120254422

N  -5.23686261450975  0.84471483761051  0.11213340824991
C  -6.57238083330550  0.29508902819564  -0.20693819369395
H  -4.91588880231340  1.54149376508975  -0.61706278344362
H  -4.53805956841097  0.09099316328754  0.12397636515616
H  -7.30499100015185  1.1150619778387  -0.19325681534971
H  -6.84966173143051  -0.46907822636503  0.5283999116442
H  -6.54187575654847  -0.15791339370168  -1.20596200861661
C  -5.12307824729864  1.62692528041077  1.42557081622569
O  -3.95767429114078  2.37274921230080  1.35721833819129
H  -6.02802944551757  2.26541685346144  1.42312813444646
C  -5.14296103231532  0.68880662183242  2.61428183144464
O  -3.94227313836957  2.93787391257347 -0.99204053241151
H  -3.8961537050345  2.77546400388251  0.2793178256650
H  -4.39907110331712  3.76823574896504 -1.1863491368248
H  -4.26814591674002  0.01813285584684  2.59375324056723
H  -6.05912418030448  0.07962550634910  2.64460234930068
H  -5.10291896782259  1.28519063247702  3.53741191629950

N  -5.39301477296586  1.23847582511870 -0.0128036554496
C  -6.53625633159800  0.3126903937946 -0.19408018061748
H  -5.56184989049164  2.10663267315960 -0.53566600037044
H  -4.53863258708197  0.78735084119318 -0.42749680133635
H  -6.57497684377945 -0.00197539148123 -1.2443626204151
H  -7.47320305535170  0.8165038437781  0.06696218021775
H  -6.38710107837421 -0.56854420056828  0.44235706543338
C  -5.04905101122556  1.62955874825650  1.43573692821679
O  -4.00359673967658  2.52224460130011  1.41541378650399
C  -6.27129184468890  2.22358815441159  2.11300770951609
H  -4.77327030083928  0.6647494495862  1.90409171491945
O  -3.06596649077067  0.0250532531628 -0.97643728499712
H  -2.92939575970561 -0.90363964453968 -0.73725951801439
H  -2.48100264147621  0.56915607026523 -0.34262732951272
H  -2.99263723628126  2.07166614028071  1.0878320329994
O  -1.87596642361060  1.5774983057780  0.7083635204778
H  -1.39862401503349  2.28227579157969  0.24875383527130
H  -6.63246919971706  3.10122469328156  1.5533241325580
H  -5.98102923355751  2.55266370646733  3.12062051677527
H  -7.09070454377747  1.49893914110498  2.21492531607469
N -5.52514337185785 1.56168679939380 -0.20664081743269
C -6.72106676127694 0.69296243925327 -0.32022535181593
H -5.67340588331396 2.42607972848293 -0.74223246078862
H -4.70111884227126 1.06922340927767 -0.64438808067058
H -6.82084433892515 0.36234513774702 -1.36127304331880
H -7.61813972178544 1.24970835530834 -0.02804573263071
H -6.58737847142616 -0.18173379317487 0.32841912897742
C -5.11866711978200 1.96013101261597 1.21250019018581
O -3.96522497918823 2.72229910753392 1.12852713895586
C -6.23695098504142 2.72158768086806 1.8930435034674
H -4.93397074901794 0.99796891410744 1.72248549592474
O -3.24231260191460 0.30459134360725 -1.20300690067501
H -3.24264825576742 -0.66184481164282 -1.25606464135261
H -2.68416000092183 0.55211934848451 -0.36635955345012
H -3.12301798009844 2.07287273648282 1.05214746321441
O -2.09230105932965 1.08726244035959 0.92083248413040
H -1.25217692563032 1.52620232041004 0.72750732711352
H -6.51778160178387 3.61194238782578 1.30791647889187
H -5.87870473831709 3.05285631979916 2.87782277866170
H -7.12681561235043 2.09685913609464 2.04844459264261
Table 1: Selected Geometric Parameters for MS4H^+ and MS5H^+

| Atom | C  | H   | C  | H   |
|------|----|-----|----|-----|
|      |    |     |    |     |
| MS4H^+ | C  | -6.99142261811526 | 3.11771190191638 | 1.19407665259960 |
|       | H  | -7.2240961358897  | 2.11357534363381 | -0.69746731762994 |
|       | H  | -6.40261912739297 | 0.11792128794503 | 0.20760685550238 |
|       | C  | -9.67631542895325 | 1.88113809522165 | -0.04103972217805 |
|       | H  | -8.71696219364676 | 1.23978509654308 | 1.63475984892274 |
|       | H  | -9.78032871321015 | 2.96074137953371 | 0.18504852982911 |
|       | H  | -10.60874668076544 | 1.38720781939570 | 0.2669054599036 |
|       | H  | -9.58743946339665 | 1.76968767637333 | -1.13362774256720 |
|       | H  | -6.00347258695003 | 3.53971502844436 | 0.95292182845370 |
|       | H  | -7.02385187559828 | 2.88408591848062 | 2.27183331532449 |
|       | H  | -7.74709683324856 | 3.88765066310227 | 0.97764797918780 |

| Atom | C  | H   | C  | H   |
|------|----|-----|----|-----|
|      |    |     |    |     |
| MS5H^+ | C  | -6.89167826707524 | 2.03744024590900 | -0.05751238402216 |
|       | N  | -7.90736321314775 | 1.39715090448686 | -0.52197801032025 |
|       | H  | -6.46097332171341 | 1.6198434790796  | 0.85826493227547 |
|       | C  | -6.27457762972347 | 3.24590280939228 | -0.6211139375833 |
|       | H  | -6.73758382470374 | 3.61832530732309 | -1.5405072014390 |
|       | H  | -5.20559315106655 | 3.03385346698307 | -0.79507742048618 |
|       | H  | -6.30673379731837 | 4.02738973589851 | 0.15823818593673 |
|       | C  | -8.69234451510649 | 1.67893419964460 | -1.71702973966895 |
|       | H  | -8.25757586143625 | 2.5059880265921  | -2.28396026209355 |
|       | H  | -9.71822271504664 | 1.93227965930896 | -1.41544105373303 |
|       | H  | -8.71628069887212 | 0.77378933884479 | -2.33868015177926 |
|       | H  | -8.21276300478998 | 0.57859618164167 | 0.01103456499342 |
H  -8.19177567003981  -0.04547130770492  0.94700631530559
H  -8.64259039911173  -0.61938737517396  -0.69616007656849
H  -9.75250527641715  0.45375220884602  0.20871027755759
H  -6.90817690785364  3.46456881936890  -1.68776265517656
H  -5.35201300763054  2.9562257260307  -0.92521723351787
H  -6.44435350854352  4.01603375478642  -0.03123437594172
H  -8.46642838650573  1.72524612852310  -1.45654965876942

OH^-

O  -3.60381467095367  1.18978075977902  -0.01492585257951
H  -3.88291532904633  0.63584924022098  0.72684585257951

MS3-cluster

C  -6.85436798777789  2.38577437876243  -0.24217138383505
O  -6.67508739142301  3.58314743689223  -0.99536818865435
N  -8.02563634369791  1.71975176715059  -0.81797440722760
C  -7.02781108104515  2.68227595440822  1.24058609921324
H  -5.95327213457606  1.75384880562021  -0.39137745295513
H  -5.90526528345093  4.08046409900401  -0.62983075220216
C  -8.07348340433355  0.28234868098116  -0.53701777453298
H  -7.96209506575951  1.84671778754413  -1.82991673507773
H  -8.21480109681132  0.10313893601215  0.53912945336640
H  -7.15657027543135  -0.24933814374000  -0.85530658036369
H  -8.92696852752782  -0.16542719607528  -1.06435469289052
H  -7.23587801962044  1.76279489608192  1.80720851726408
H  -7.85765383109311  3.38839599793258  1.39900648281515
H  -6.11121715557723  3.12765123804675  1.65653584034491
O  -4.54633420238985  5.02576740573336  0.03605896225256
H  -4.32914713117373  4.84506192181629  0.96355742393976
H  -4.77884476989214  5.96767722361157  0.02697880835752
O  -8.83273313045728  5.25918469544492  -1.30899719373726
H  -8.03071928246858  4.68994733354762  -1.21490149607132
H  -8.50296489674980  6.13938628393622  -1.54003876530124
| Atom | X1 | Y1 | Z1 | X2 | Y2 | Z2 |
|------|----|----|----|----|----|----|
| O    | -10.41614388430552 | 5.00386387036542 | 0.89280851630618 | H  | -9.79526532482238 | 5.19913482834214 | 0.14822790163948 |
| H    | -9.93262372595489  | 5.24141731921821 | 1.69764620340931 | O  | -10.57825816070802 | 2.25758159441353 | 0.28275347891205 |
| H    | -10.58966254745128 | 3.19316173451072 | 0.57610697932511  | H  | -9.66565534550026  | 2.13528115043878 | -0.09000606662848 |
| C    | 6.99836948316842   | 2.08915791682175 | 0.03039846754361  |
| N    | -7.99245691097021  | 1.43757869319059 | -0.46094201477410 |
| H    | -6.66598177735971  | 1.76265539961878 | 1.02132349261147  |
| C    | -6.27915497459342  | 3.17847340706848 | -0.65181761862323 |
| H    | -6.92023096387644  | 3.75627837437206 | -1.33187375515102 |
| H    | -5.47184050721857  | 2.72057067282630 | -1.25482885450267 |
| H    | -5.8016193188980   | 3.83828045030976 | 0.08473475577048  |
| C    | -8.57913828753048  | 1.65341360458540 | -1.7821274244437  |
| H    | -8.91366427825771  | 2.69455322413909 | -1.89026953626291 |
| H    | -9.43812055436680  | 0.98477193513651 | -1.89456574951225 |
| H    | -7.83861044378313  | 1.42780953097200 | -2.56230610719385 |
| H    | -8.38014169585126  | 0.67366661168992 | 0.13806901834213  |
| O    | -8.78613138404282  | -0.45359641921975 | 1.39992768352007  |
| H    | -8.76769269612688  | -1.36572520212762 | 1.0691937097188  |
| H    | -9.68846672396430  | -0.33915819938331 | 1.73692827170479  |

MS4H⁺-cluster

| Atom | X1 | Y1 | Z1 | X2 | Y2 | Z2 |
|------|----|----|----|----|----|----|
| C    | -6.99836948316842 | 2.08915791682175 | 0.03039846754361 |
| N    | -7.99245691097021 | 1.43757869319059 | -0.46094201477410 |
| H    | -6.66598177735971 | 1.76265539961878 | 1.02132349261147 |
| C    | -6.27915497459342 | 3.17847340706848 | -0.65181761862323 |
| H    | -6.92023096387644 | 3.75627837437206 | -1.33187375515102 |
| H    | -5.47184050721857 | 2.72057067282630 | -1.25482885450267 |
| H    | -5.8016193188980  | 3.83828045030976 | 0.08473475577048 |
| C    | -8.57913828753048 | 1.65341360458540 | -1.7821274244437 |
| H    | -8.91366427825771 | 2.69455322413909 | -1.89026953626291 |
| H    | -9.43812055436680 | 0.98477193513651 | -1.89456574951225 |
| H    | -7.83861044378313 | 1.42780953097200 | -2.56230610719385 |
| H    | -8.38014169585126 | 0.67366661168992 | 0.13806901834213 |
| O    | -8.78613138404282 | -0.45359641921975 | 1.39992768352007 |
| H    | -8.76769269612688 | -1.36572520212762 | 1.0691937097188 |
| H    | -9.68846672396430 | -0.33915819938331 | 1.73692827170479 |

MS5H⁺-cluster
C -8.64244852082759  0.14204363377494  0.09873863313503
H -8.21209621679001  0.01929057966956  1.09936061436912
H -8.48266361213535  -0.76935050729123  -0.49375692079762
H -9.72309166906375  0.32829366603317  0.17652516015644
H -6.91351639259399  3.31311245870048  -1.7894793800459
H -5.39154652869086  2.9457168790643  -0.8936335014300
H -6.57479914041780  4.04189553200376  -0.17408828718226
H -8.34633119116805  1.46825947996378  -1.54968674510045
O -8.91694914026089  1.66992267067077  -3.20906009555013
H -8.29791818339904  2.06363681911889  -3.84343624981995
H -9.71148563470199  2.22292640802424  -3.27181942272776

OH-cluster

O -3.94060499622666  1.23110304913552  0.21070292272186
H -4.75000871818598  1.70592384202131  -0.02576123578365
O -4.3593409525508  -0.67514372196435  1.96580371221892
H -4.23679090468130  0.07106613217783  1.28594346830522
H -5.20386563971290  -1.08587372803963  1.73431445305110
O -3.15048855585745  -0.20082414369423  -1.83147931036684
H -3.4886803277339  0.35324522114229  -1.04641215844217
H -3.91655592268456  -0.71544770077137  -2.12115126107321
O -2.13120164438510  2.94867506224449  0.94045583727589
H -2.84871576203568  2.29285151312879  0.62863647500808
H -1.77894882820195  3.33793447461934  0.12779709708482

Pyridine

C -10.44284436674023  4.90327076200995  0.00021710273203
C -9.19886237296036  5.53700329715143  0.00008780254449
C -10.47943783565055  3.50806958687788  0.00007661069285
H -11.37190677994311  5.47622938133689  -0.00004215425212

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| Element | X  | Y  | Z   |
|---------|----|----|-----|
| C       | -8.04666063641891 | 4.74918935375683 | -0.00012735808797 |
| H       | -9.12584207011121  | 6.62759128238044  | 0.00003972971730 |
| C       | -8.18902302448812  | 3.36086719317896  | -0.00011574374898 |
| H       | -7.05203380308522  | 5.19914367438430  | -0.00017441065107 |
| N       | -9.37811009590932  | 2.74209318253854  | -0.00002454687480 |
| H       | -11.43959929322736 | 2.98311435129653  | -0.00019262465262 |
| H       | -7.30456972146560  | 2.71692793508825  | 0.00025559258451 |

PyridineH+

| Element | X  | Y  | Z    |
|---------|----|----|------|
| C       | -10.44985538069542 | 4.90155043666397 | -0.00042173333900 |
| C       | -9.19850718377402  | 5.52559128419317  | 0.00270443278024 |
| C       | -10.50820291693143 | 3.51785057346555  | -0.00717601048152 |
| H       | -11.37388444552511 | 5.47907640387158  | 0.00202266992489 |
| C       | -8.03142365085546  | 4.75582245110503  | -0.00071422716482 |
| H       | -9.13036671063350  | 6.61560222410053  | 0.00798179720564 |
| C       | -8.13993720148193  | 3.37539802094007  | -0.00751620902310 |
| H       | -7.04471663457354  | 5.21867705969440  | 0.0020177607401 |
| N       | -9.36220877103876  | 2.80937624602120  | -0.01091654373825 |
| H       | -11.43502014966864 | 2.94470305246839  | -0.01093673963827 |
| H       | -7.28836777213156  | 2.69596072855235  | -0.00947642234891 |
| H       | -9.42460918269063  | 1.78879151864278  | -0.01613881025090 |

MS4

| Element | X  | Y  | Z    |
|---------|----|----|------|
| C       | -7.04832767966448 | 2.02943608850922 | -0.32731290908620 |
| N       | -7.99423957083117 | 1.38949253047210 | -0.9020397730521 |
| C       | -6.47055097512466 | 1.82774592164347 | 1.03750792634403 |
| H       | -6.59284257673867 | 2.84588266662730 | -0.91040256846133 |
| C       | -8.64894710787218 | 0.29716876285284 | -0.1905580167868 |
| H       | -7.93508219610853 | -0.42293520171039 | 0.24262472417713 |
| H       | -9.30404207274126 | -0.25319024094982 | -0.87991047834974 |
| H       | -9.27954637864099 | 0.67795486952210  | 0.62979295593490 |
H  -6.94898145686808  1.02407526246827  1.60967416244674
H  -6.5553189912226  2.76879060692481  1.60815433310753
H  -5.39095108628774  1.61164873364009  0.95155803287084

C  -7.09756553122744  1.98480071940775  -0.14381948794781
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Propanone

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PropanoneH+

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C  -5.98588033040631  1.73192342545071  0.12613006567774
H  -5.11384930799698  2.34057661368704  0.39478960693929
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H3O+

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