

## Brønsted Acidity of Protic Ionic Liquids: a Modern *ab initio* Valence Bond Theory Perspective

Amol Baliram Patil and Bhalchandra Mahadeo Bhanage\*

Geometry co-ordinates of the structures of PILs optimized at B3LYP-D3/6-31+G\* level of theory using COSMO salvation model.

### [BAmm][Ac]

C 0.160317 -0.166476 0.668020  
C -0.603840 -1.135237 -0.226340  
C -0.784705 0.827171 1.355395  
H -1.512977 0.275029 1.965174  
H -1.359320 1.368762 0.590861  
C -0.026601 1.828248 2.234782  
H -0.716398 2.519502 2.733450  
H 0.674768 2.421814 1.634146  
H 0.550194 1.308071 3.010291  
H 0.897678 0.379591 0.065510  
H -1.291389 -1.758810 0.350373  
H -1.164222 -0.605402 -0.999614  
H -0.165242 -2.712820 -1.538833  
H 0.905623 -2.596102 -0.296219  
H 0.717873 -0.731236 1.428439  
H 0.991805 -1.478034 -1.577787  
N 0.340620 -2.046696 -0.949618  
O 1.900058 -0.383730 -2.418383  
C 1.105372 0.362265 -3.093353  
O -0.066526 0.028067 -3.418145

C 1.608053 1.754262 -3.472579  
H 2.688866 1.753445 -3.646036  
H 1.403796 2.435919 -2.636415  
H 1.087697 2.136542 -4.354551

**[HBAm][Ac]**

C 0.178766 -1.446903 -0.079787  
C -0.589550 -2.401359 -0.985412  
C -0.767998 -0.469666 0.629315  
H -1.495541 -1.034665 1.229514  
H -1.343997 0.089466 -0.122230  
C -0.016961 0.516470 1.533105  
C -0.942882 1.485335 2.276217  
H -1.534228 2.058027 1.545681  
C -0.182589 2.458321 3.186834  
H -1.661857 0.911335 2.880116  
H 0.699192 1.089495 0.925480  
H 0.577202 -0.048227 2.267028  
H 0.911364 -0.888624 -0.676584  
H -1.281202 -3.026835 -0.415737  
H -1.146767 -1.859478 -1.752707  
H -0.161024 -3.967832 -2.314113  
H 0.910469 -3.870251 -1.070251  
H 0.740811 -2.023961 0.667742  
N 0.349128 -3.310957 -1.718370  
H 1.004097 -2.740273 -2.341049  
O 1.922046 -1.650914 -3.175190

C 1.133970 -0.910253 -3.863689  
O -0.037485 -1.244112 -4.190697  
C 1.645476 0.474196 -4.258258  
H 2.725009 0.462117 -4.439486  
H 1.453739 1.164465 -3.426281  
H 1.122629 0.853396 -5.140037  
C -1.109389 3.420035 3.940190  
H 0.533025 3.033871 2.581555  
H 0.412844 1.881714 3.909695  
H -0.538797 4.098081 4.587206  
H -1.816904 2.866160 4.571116  
H -1.692589 4.031828 3.239093

**[MBAmm][Ac]**

C 0.184048 0.517086 0.747845  
C -0.576363 -0.524013 -0.069470  
C -0.783076 1.541540 1.360591  
H -1.493544 1.022129 2.018070  
H -1.375689 2.006754 0.560614  
C -0.045623 2.627401 2.152194  
H -0.750466 3.333565 2.606839  
H 0.631028 3.194723 1.500000  
H 0.555590 2.185545 2.957151  
H 0.904576 1.030525 0.099316  
H -1.202580 -1.160141 0.564140  
H -1.208770 -0.029361 -0.809577  
C -0.478319 -2.281842 -1.790920

C 1.189505 -2.285644 0.012578  
H 0.550493 -2.901299 0.649803  
H 1.828176 -1.649967 0.624087  
H 1.805242 -2.919532 -0.626603  
H 0.204929 -2.915181 -2.358875  
H -1.019896 -1.618120 -2.464430  
H -1.166179 -2.897774 -1.207908  
H 0.754177 0.041012 1.554317  
N 0.323381 -1.437392 -0.856817  
H 0.948341 -0.813346 -1.456160  
O 1.864153 0.296534 -2.286139  
C 1.055775 1.082267 -2.897522  
O -0.132165 0.779538 -3.189251  
C 1.563379 2.483381 -3.236431  
H 2.641048 2.484697 -3.428328  
H 1.375570 3.136622 -2.373689  
H 1.030135 2.900469 -4.094701

**[Et<sub>3</sub>Amm][Ac]**

C -0.017333 1.662929 1.012038  
C -0.780492 0.563152 0.285971  
H -0.741250 2.411638 1.350227  
H 0.704149 2.153568 0.352208  
H -1.443707 0.031669 0.970715  
H -1.371680 0.981325 -0.530650  
C -0.654095 -1.388767 -1.260431  
C 0.977387 -1.219197 0.637198

H 0.506692 1.285671 1.894706  
H 0.465967 -1.184967 1.601784  
C 2.404373 -0.696390 0.735941  
H 0.996593 -2.259491 0.309563  
H 0.096087 -1.999143 -1.770349  
H -1.132541 -0.745751 -2.001933  
C -1.664134 -2.266203 -0.532212  
H -2.120171 -2.939628 -1.265839  
H -2.466950 -1.682867 -0.072454  
H -1.192719 -2.883213 0.239342  
H 2.914130 -0.759643 -0.230471  
H 2.948301 -1.323163 1.450156  
H 2.449336 0.337047 1.088166  
N 0.122984 -0.459978 -0.355824  
H 0.751874 0.087974 -1.014497  
O 1.606073 1.158699 -1.989742  
C 0.789668 1.974126 -2.543436  
O -0.396972 1.683741 -2.858187  
C 1.278038 3.403562 -2.778668  
H 2.369794 3.466125 -2.764615  
H 0.887125 4.040384 -1.974281  
H 0.890352 3.796976 -3.723724

**[NMP][Ac]**

C -1.239601 -0.997392 -0.733140  
C -1.589148 -0.322726 0.605521  
C -1.091777 1.149941 0.473338

C -0.631942 1.285386 -0.982460  
C 0.039925 -0.321282 -2.793559  
H -0.823339 -2.001072 -0.640278  
H -2.088480 -1.010725 -1.421062  
H -2.666253 -0.376584 0.780490  
H -1.093318 -0.829236 1.436876  
H -0.253889 1.336278 1.149873  
H -1.875528 1.875585 0.700625  
H -1.452666 1.547549 -1.655246  
H 0.201251 1.971036 -1.140673  
H 0.816604 0.365182 -3.131683  
H 0.362415 -1.352575 -2.947692  
H -0.889284 -0.131224 -3.335109  
N -0.192681 -0.104951 -1.343514  
H 0.710887 -0.294337 -0.827572  
O 1.989769 -0.494723 0.225933  
C 1.711223 -1.390079 1.101746  
C 1.735393 -0.941259 2.562080  
O 1.408229 -2.580906 0.828488  
H 1.412889 -1.742208 3.232296  
H 2.748630 -0.622079 2.834211  
H 1.080339 -0.072592 2.691912