Supporting information: Photoisomerization of Protonated Azobenzenes in the Gas Phase

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Typical experimental timings

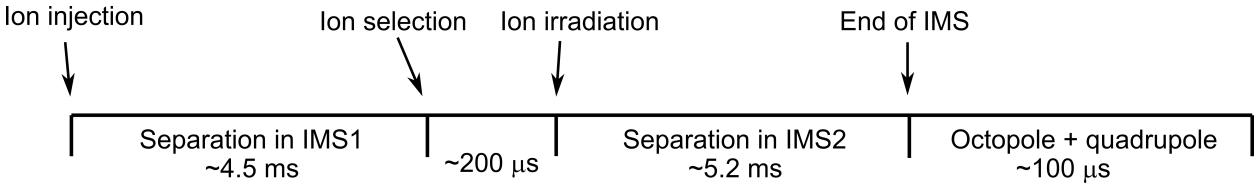

Figure S1: Schematic illustration showing ordering and typical durations of stages in the present experiment.

ABH^+ equilibrium geometry

Feráud *et al.* used the RI-MP2/cc-pVDZ level of theory to propose that the *trans*-isomer is non-planar, with the phenyl ring more distant from the protonation site twisted out of plane by 18°.[1] With the larger cc-pVTZ basis set, both the C_1 twisted and C_s planar geometries are found to be local minima, whereas only the planar structure is a minimum at the DFT ωB97X-D/6-311+G(2df,p) level. Single-point energies at the DLPNO-CCSD(T)/cc-pVTZ level indicate that the twisted geometry lies slightly lower in energy than the planar geometry (by 0.6 kJ/mol).

A relaxed scan around the N−N−C−C coordinate at the RI-MP2/cc-pVTZ level suggests that the planar geometry is a minimum lying slightly higher in energy (0.7 kJ/mol) than the twisted minimum. Relaxation from the planar geometry to the twisted geometry at the RI-MP2/cc-pVTZ level has a tiny barrier. Beyond 18°, the energy rises steeply and is above 30 kJ/mol by 80°. Due to the low, flat potential energy curve in the torsional coordinate, at 300 K the molecule will execute large amplitude vibrational motion, and should have a quasi-planar structure. A scan over the analogous coordinate in *trans* NH_2ABH^+ displays a single minimum at the planar geometry.

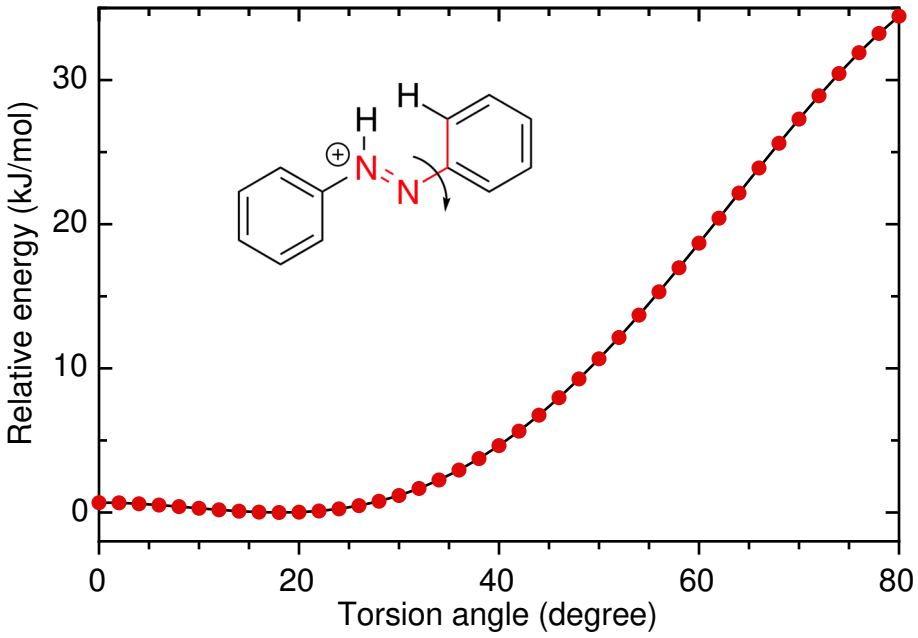

Figure S2: Potential energy curve for torsion around the indicated dihedral angle for ABH^+. The curve was calculated at the RI-MP2/cc-pVTZ level, with all coordinates except for the indicated dihedral angle relaxed at each point. The RI-MP2/cc-pVTZ calculations were performed using the ORCA 3.0.3 program.[2]

Collision cross sections

The approach to measuring collision cross sections has been explained in ref. 3. Briefly, the drift mobility (K) of a drift ion is given by the Mason-Schamp equation:

$$K = \frac{3ze}{16N}\sqrt{\frac{2\pi}{\mu k_{\mathrm{B}} T}}\left(\frac{1}{\Omega}\right) = \frac{l^2}{t_{\mathrm{d}} V} \tag{S1}$$

where ze is the molecular charge, N the buffer gas number density, μ the reduced mass of the ion and buffer gas, k_{B} the Boltzmann constant, T the temperature, and Ω the orientationally-averaged collision cross section.

Equation S1 can be rearranged to give a linear relationship between the collision cross section Ω and the arrival time at the detector t_{d}:

$$\Omega = A t_{\mathrm{d}} \mu^{-1/2} \tag{S2}$$

where A is a constant which describes the temperature and pressure dependence, and is determined by linear regression of literature collision cross sections against measured arrival times for a series of tetraalkylammonium cations.[4,5] Once A is known, the collision cross sections for ABH^+ and NH_2ABH^+ can be determined. These values are shown in Table S1.

Table S1: Measured (Ω_m) and calculated (Ω_c) collision cross sections for isomers of ABH^+ and NH_2ABH^+.

Molecule	Ω_m (Å^2)	Ω_c (Å^2)
ABH^+		
trans	138.8	142
cis	136.7	142
NH_2ABH^+		
trans isomer a	145.6	149
trans isomer b		148
trans isomer c		160
cis isomer a	141.2	148
cis isomer b		149
cis isomer c		159

Calculated geometries of ABH^+

Planar *trans*-ABH^+ (DFT, ωB97X-D/6-311+G(2df,p))

```
C -3.89331 -0.71555 -2.06611
C -2.54422 -0.61889 -1.82548
C -2.06466 -0.84638 -0.52320
C -2.94923 -1.16704 0.51352
C -4.30317 -1.26074 0.25733
C -4.77152 -1.03560 -1.02770
H -4.27745 -0.54342 -3.06296
H -1.88999 -0.36895 -2.65352
H -2.54595 -1.33588 1.50383
H -4.99105 -1.50807 1.05483
H -5.83232 -1.10789 -1.23393
N -0.74545 -0.78619 -0.12751
N 0.15654 -0.51042 -0.93936
C 1.52487 -0.43280 -0.60030
C 2.40684 -0.11220 -1.62548
C 1.95549 -0.66832 0.70056
C 3.75698 -0.02499 -1.34027
H 2.04748 0.06742 -2.63354
C 3.30658 -0.57668 0.96589
H 1.24488 -0.91596 1.47713
C 4.20467 -0.25673 -0.04798
H 4.45794 0.22348 -2.12602
H 3.66621 -0.75560 1.97073
H 5.26200 -0.18826 0.17426
H -0.06214 -0.32134 -1.92172
```

Planar *trans*-ABH$^+$ (RI-MP2/cc-pVTZ)

```
C -3.86375239707663 -0.71268158293154 -2.07880182538195
C -2.50844731496143 -0.62233722126573 -1.81053438706186
C -2.06051471321711 -0.85288873620490 -0.49572927921864
C -2.97100720569819 -1.17003852926064 0.52728649644614
C -4.32544465592822 -1.25594537840748 0.24009314112522
C -4.77251356988500 -1.02781701047538 -1.06029535862708
H -4.22118088951549 -0.53851105985191 -3.08369703867081
H -1.83839331086398 -0.37765559569232 -2.62593608238237
H -2.58455901161350 -1.33985556685440 1.52246016957290
H -5.02927609269543 -1.49904724598454 1.02277919469048
H -5.82719358545049 -1.09406776843607 -1.28848298664516
N -0.74821181331685 -0.80288999269777 -0.05687297482172
N 0.15697051279348 -0.51927156103571 -0.89426411642760
C 1.51356860733297 -0.43824902117414 -0.57970191044530
C 2.37816006397709 -0.11097398947702 -1.63075209936928
C 1.96811027243000 -0.67485738000928 0.72340213489696
C 3.73775531019238 -0.01765431102539 -1.36977623981187
H 1.99226648754245 0.06574303711827 -2.62759322501635
C 3.32832974085207 -0.57627833685489 0.96090061313875
H 1.26721903775025 -0.92487939871806 1.50541396814270
C 4.20974055717733 -0.24980142569289 -0.07775193801347
H 4.42329003574354 0.23357810593217 -2.16552500251771
H 3.70972058458408 -0.75316174066834 1.95602582028782
H 5.26895903914866 -0.17699161725054 0.12493217544904
H -0.08357568930199 -0.33046667308148 -1.87457924933887
```

Twisted *trans*-ABH$^+$ (RI-MP2/cc-pVTZ)

```
C -3.86592299919885 -0.36520290279639 -1.94747863354252
C -2.52642492858077 -0.24584859749932 -1.61382053437280
C -2.05635738141130 -0.89371560734003 -0.45548910551254
C -2.93189438725280 -1.61114938185926 0.37697563773136
C -4.26547002306607 -1.73454850774481 0.01600973731966
C -4.73177755107038 -1.11792715211970 -1.14548400987120
H -4.24696751324761 0.14511987840622 -2.82061803951821
H -1.89152278744816 0.40047570524185 -2.20864811767006
H -2.53460239237155 -2.07193581564329 1.27054403694780
H -4.94280889775466 -2.29927767792174 0.64016321503550
H -5.77481501161857 -1.20015376013235 -1.41767411140226
N -0.74252025906566 -0.88468433881928 -0.01888513423004
N 0.14561834362572 -0.56632682020463 -0.86396558618505
C 1.50289485705450 -0.45193176267409 -0.56967343756553
C 2.35329476642644 -0.17226465057486 -1.64625228034090
C 1.97266422821399 -0.61494534065276 0.73963104670646
C 3.71512970511952 -0.06008870852850 -1.40598751322253
H 1.95420743832034 -0.04942543251603 -2.64597982953245
C 3.33512879695957 -0.50027473689639 0.95566620303517
H 1.28062156451876 -0.82132128531606 1.54225261764258
C 4.20285611999695 -0.22483537143047 -0.10917535031223
H 4.39064989665000 0.15424825073474 -2.22089752761648
H 3.72880572319068 -0.62054870414069 1.95447112087911
H 5.26381259233250 -0.13550011056892 0.07748250607691
H -0.12235990032259 -0.39153716900325 -1.84143691047976
```

cis-ABH$^+$ (DFT, ωB97X-D/6-311+G(2df,p))

```
C -2.52275 2.46377 1.24807
C -1.52758 1.78810 0.58545
C -1.23523 0.45811 0.96981
C -1.96691 -0.15010 2.01022
C -2.94852 0.55104 2.67478
C -3.22439 1.85581 2.29138
H -2.76396 3.47813 0.95849
H -1.00284 2.27644 -0.21985
H -1.73066 -1.17466 2.26766
H -3.50272 0.08583 3.47886
H -4.00023 2.41238 2.80344
N -0.32012 -0.40975 0.43826
N 0.52955 -0.15365 -0.44212
C 0.86237 1.08898 -1.09935
C 0.40825 1.30171 -2.38940
C 1.65369 2.00447 -0.42484
C 0.73998 2.49423 -3.01383
H -0.20027 0.55904 -2.89109
C 1.97798 3.18866 -1.06537
H 2.00391 1.79703 0.57903
C 1.51763 3.43367 -2.35227
H 0.39203 2.68563 -4.02065
H 2.59675 3.91856 -0.55955
H 1.77563 4.36138 -2.84704
H 1.08485 -0.96743 -0.69824
```

NH_2ABH^+

All NH_2ABH^+ geometries were calculated at the DFT ωB97X-D/6-311+G(2df,p) level of theory.

trans-(a)

```
C -3.28869 -0.26547 1.70642
C -1.90637 -0.19205 1.70178
C -1.27712 0.98648 1.31266
C -2.02724 2.09931 0.92544
C -3.40404 2.01674 0.93313
C -4.03498 0.83782 1.32247
H -3.78306 -1.17989 2.00832
H -1.29644 -1.03718 1.99637
H -1.52311 3.00802 0.62557
H -3.99716 2.87227 0.63514
H -5.11684 0.78401 1.32477
C 2.12762 1.90099 1.05414
C 2.81776 3.04984 0.68884
C 2.82450 0.75368 1.43703
C 4.20251 3.06858 0.70212
H 2.25437 3.92587 0.39453
C 4.20404 0.75999 1.45359
H 2.26997 -0.13170 1.71682
C 4.86210 1.92040 1.08476
H 4.73890 3.96720 0.41681
H 4.75099 -0.12890 1.74994
N 0.12929 0.95301 1.34440
N 0.71145 1.99489 1.00284
N 6.34532 1.92513 1.11108
H 6.71101 2.80310 0.73772
H 6.70591 1.82074 2.06285
H 6.73222 1.16596 0.54532
```

trans-(b)

```
C -3.39067 -0.12851 1.90259
C -2.00933 -0.14765 1.87132
C -1.31583 0.91152 1.28248
C -2.01174 1.96785 0.67844
C -3.38946 1.96806 0.70584
C -4.07878 0.92821 1.32531
H -3.93140 -0.94091 2.37005
```

H -1.44490 -0.96107 2.30897
H -1.50322 2.76116 0.14057
H -3.93654 2.77059 0.22838
H -5.16143 0.93869 1.33888
C 2.15545 1.82908 1.10744
C 2.79145 3.05935 0.91751
C 2.90340 0.65817 1.27761
C 4.15781 3.12871 0.90180
H 2.20895 3.96531 0.78350
C 4.26690 0.72652 1.26337
H 2.39963 -0.28887 1.41787
C 4.93013 1.96209 1.07649
H 4.64976 4.08196 0.75503
H 4.85156 -0.17591 1.39349
N 0.06769 0.80092 1.34175
N 0.76704 1.81239 1.12500
N 6.27287 2.01804 1.06293
H 6.75818 2.88758 0.93007
H 6.83054 1.19155 1.18623
H 0.31592 2.71772 0.95644

trans-(c)

C -3.39776 -0.22773 1.68233
C -2.01407 -0.22551 1.70106
C -1.33616 0.92769 1.32992
C -2.01005 2.07760 0.94094
C -3.39183 2.05789 0.92805
C -4.08656 0.91189 1.29651
H -3.93642 -1.12123 1.96960
H -1.47108 -1.11546 2.00233
H -1.45961 2.96355 0.65635
H -3.93320 2.94569 0.62756
H -5.16889 0.90933 1.28217
C 2.148350 1.80204 1.08862
C 2.80594 2.99442 0.70090
C 2.93657 0.68412 1.47226
C 4.16372 3.08253 0.69085
H 2.19224 3.83815 0.41117
C 4.29103 0.76463 1.46478
H 2.48776 -0.25402 1.77862
C 4.94447 1.96782 1.07329
H 4.65279 4.00119 0.39182
H 4.88975 -0.08922 1.75785
N 0.07732 0.88329 1.36448

```
  N 0.80562 1.86279 1.04928
  N 6.27712 2.03231 1.07081
  H 6.75827 2.87260 0.79796
  H 6.84164 1.24503 1.34116
  H 0.48403 -0.00242 1.66433
```

cis-(a)

```
C -1.80301 -1.80700 -0.30710
C -1.03693 -1.07774 0.58609
C -0.71507 0.24086 0.29069
C -1.21942 0.85768 -0.84904
C -2.01909 0.13074 -1.71502
C -2.29575 -1.20431 -1.45648
H -2.03926 -2.84150 -0.09186
H -0.68076 -1.51649 1.51023
H -1.02221 1.90599 -1.03586
H -2.43938 0.61215 -2.58950
H -2.91971 -1.76890 -2.13799
C 1.59529 1.67512 -0.33483
C 1.80822 2.92532 -0.90661
C 2.10950 0.52806 -0.93574
C 2.49345 3.03191 -2.10181
H 1.43408 3.80994 -0.40708
C 2.81510 0.62792 -2.11915
H 1.95508 -0.43947 -0.47662
C 2.98338 1.87815 -2.68209
H 2.64801 4.00569 -2.55402
H 3.21821 -0.26408 -2.58658
N 0.04972 0.94460 1.27016
N 1.02734 1.63085 0.97181
N 3.76434 1.99062 -3.93737
H 3.47549 2.80936 -4.47662
H 4.76788 2.07762 -3.75510
H 3.62652 1.17032 -4.53148
```

cis-(b)

```
C 3.67677 -1.88213 2.15317
C 2.75039 -1.65602 1.15336
C 1.77482 -0.66833 1.32095
C 1.78380 0.15280 2.45828
C 2.74984 -0.04750 3.41905
C 3.67911 -1.07669 3.28201
H 4.41443 -2.66545 2.03884
```

H 2.75581 -2.23532 0.23877
H 1.07348 0.96047 2.57034
H 2.78505 0.60059 4.28526
H 4.42102 -1.23409 4.05500
C -1.13620 0.25288 1.26647
C -2.11517 1.20762 0.97739
C -1.19879 -0.47580 2.45856
C -3.10667 1.47935 1.88180
H -2.08616 1.75242 0.03939
C -2.20096 -0.22258 3.35356
H -0.48019 -1.25441 2.67368
C -3.17144 0.77215 3.09815
H -3.85088 2.23292 1.65663
H -2.25922 -0.80134 4.26725
N 0.95835 -0.48776 0.21193
N -0.19932 -0.01381 0.24857
N -4.14154 1.02668 3.99418
H -4.84671 1.71978 3.81659
H -4.21080 0.50618 4.85050
H -0.56045 0.15569 -0.68933

cis-(**c**)

C -2.52518 -2.42802 2.30550
C -1.86494 -1.74328 1.29750
C -2.02081 -0.36911 1.21395
C -2.83203 0.33222 2.09127
C -3.48654 -0.36481 3.09455
C -3.32877 -1.73941 3.20344
H -2.41570 -3.50202 2.38520
H -1.23252 -2.26509 0.58942
H -2.94273 1.40540 1.99321
H -4.12519 0.16683 3.78832
H -3.84438 -2.27950 3.98748
C 0.69475 0.91131 1.18941
C 1.89205 1.60530 0.84503
C 0.59548 0.35947 2.50600
C 2.91649 1.74965 1.72233
H 1.95587 2.01841 -0.15379
C 1.61848 0.50275 3.38350
H -0.28502 -0.17610 2.82406
C 2.80670 1.19920 3.02229
H 3.81631 2.28103 1.43842
H 1.53857 0.08292 4.37909
N -1.33184 0.34967 0.17447

```
N -0.18141 0.88662 0.18064
N 3.79810 1.32724 3.90113
H 4.64576 1.81547 3.66486
H 3.73142 0.94007 4.82739
H -1.81100 0.46343 -0.71122
```

References

(1) Féraud, G.; Dedonder-Lardeux, C.; Jouvet, C.; Marceca, E. *J. Phys. Chem. A* **2016**, *120*, 3897–3905.

(2) Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.

(3) Bull, J. N.; Scholz, M. S.; Coughlan, N. J. A.; Bieske, E. J. *Phys. Chem. Chem. Phys.* **2017**, *19*, 12776–12783.

(4) Campuzano, I.; Bush, M. F.; Robinson, C. V.; Beaumont, C.; Richardson, K.; Kim, H.; Kim, H. I. *Anal. Chem.* **2012**, *84*, 1026–1033.

(5) May, J. C.; Goodwin, C. R.; Lareau, N. M.; Leaptrot, K. L.; Morris, C. B.; Kurulugama, R. T.; Mordehai, A.; Klein, C.; Barry, W.; Darland, E.; Overney, G.; Imatani, K.; Stafford, G. C.; Fjeldsted, J. C.; McLean, J. A. *Anal. Chem.* **2014**, *86*, 2107–2116.