Supplementary Information for: "Photoisomerization of β-Ionone Protonated Schiff Base in the Gas Phase"

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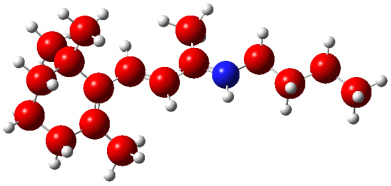
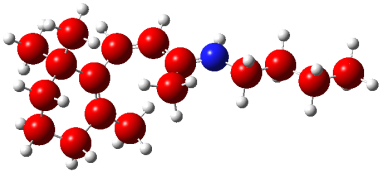
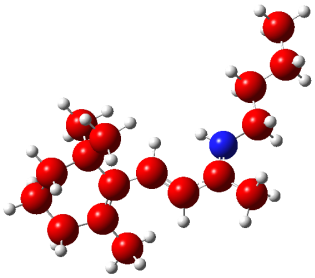
1 Calculated structures and collision cross sections



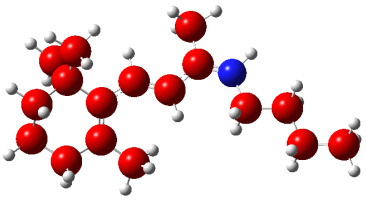
(a) 6*s*-*cis*(-)



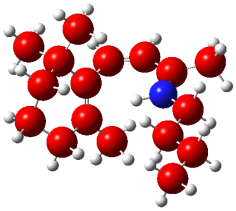
(b) 7-*cis*-6*s*-*cis*(-)



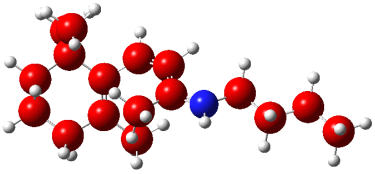
(c) 8-*cis*-6*s*-*cis*(-)



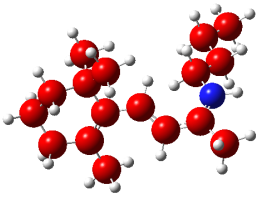
(d) 9-*cis*-6*s*-*cis*(-)



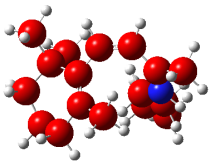
(e) 7,8-*cis*-6*s*-*cis*(-)



(f) 7,9-*cis*-6*s*-*cis*(-)

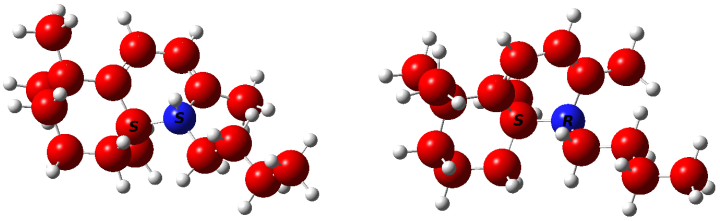


(g) 8,9-*cis*-6*s*-*cis*(-)



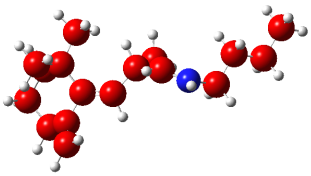
(h) 7,8,9-*cis*-6*s*-*cis*(+)

Figure S.1: Representative geometric isomers of β-ionone protonated Schiff base (BIPSB).

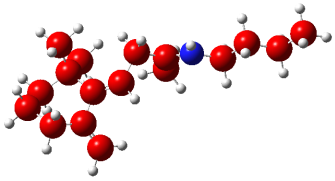


(a) bicyclic BIPSB — C(*S*), N(*S*) (b) bicyclic BIPSB — C(*S*), N(*R*)

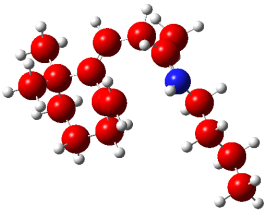
Figure S.2: Diastereomers of the bicyclic BIPSB structure. The stereochemistry at each chiral centre is indicated.



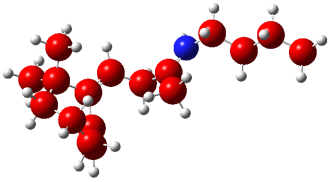
(a) all-*trans* (chair)



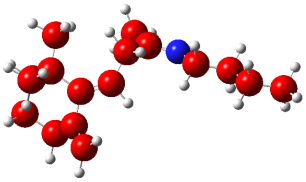
(b) all-*trans* (boat)



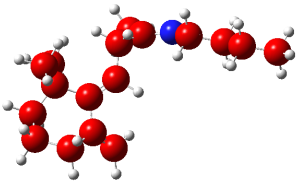
(c) 6*s*-*cis* (chair)



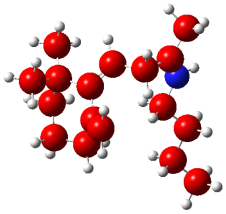
(d) 6*s*-*cis* (boat)



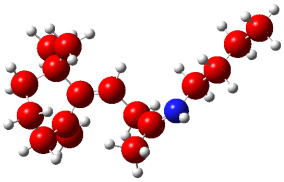
(e) 9-*cis* (chair)



(f) 9-*cis* (boat)



(g) 6,9-*cis* (chair)



(h) 6,9-*cis* (boat)

Figure S.3: Representative geometric isomers of γ-ionone protonated Schiff base (GIPSB). Note that the ionone ring can adopt either a boat or chair conformation.

Table S.1: Relative energies (ΔE) and collision cross sections with N_2 at 295 K for isomers of β-ionone. Energies and geometries were determined at the DFT M06-2X/cc-PVDZ level. Note that we could not locate a 7,8s,9-*tricis*-6s-*cis*(-) minimum. Collision cross sections were determined using the trajectory method in Mobcal[1,2] with collision parameters taken from ref. 3.

species	ΔE (kJ/mol)	$\overline{\Omega}_{calc}$ (Å^2)
β-ionone protonated Schiff base		
all-*trans*-6s-*cis*(-)	9.4	173.6
all-*trans*-6s-*cis*(+)	7.4	173.9
all-*trans*-6s-*trans*	6.7	172.5
7-*cis*-6s-*cis*(-)	17.8	167.6
7-*cis*-6s-*cis*(+)	20.9	165.6
7-*cis*-6s-*trans*	19.1	166.2
8s-*cis*-6s-*cis*(-)	17	172.7
8s-*cis*-6s-*cis*(+)	14.0	172.7
8s-*cis*-6s-*trans*	14.0	171.4
9-*cis*-6s-*cis*(-)	6.3	172.6
9-*cis*-6s-*cis*(+)	5.6	171.7
9-*cis*-6s-*trans*	0.0	171.1
7,8s-*cis*-6s-*cis*(-)	10.3	165.4
7,8s-*cis*-6s-*cis*(+)	9.7	163.7
7,8s-*cis*-6s-*trans*	61.3	164.5
7,9-*cis*-6s-*cis*(-)	20.7	166.2
7,9-*cis*-6s-*cis*(+)	20.4	165.7
7,9-*cis*-6s-*trans*	19.6	165.7
8s,9-*cis*-6s-*cis*(-)	19.2	172.3
8s,9-*cis*-6s-*cis*(+)	19.9	172.3
8s,9-*cis*-6s-*trans*	19.0	171.4
7,8s,9-*cis*-6s-*cis*(-)	*	*
7,8s,9-*cis*-6s-*cis*(+)	19.8	160.2
7,8s,9-*cis*-6s-*trans*	22.0	167.6
bicyclic isomer		
S,S (chair)	14.7	162.5
S,R (chair)	22.7	160.6
retro-γ-ionone protonated Schiff base		
all-*trans* (chair)	66.6	172.6
all-*trans* (boat)	72.6	169.6
6-*cis* (chair)	31.0	166.2
6-*cis* (boat)	59.2	170.4
9-*cis* (chair)	68.0	172.5
9-*cis* (boat)	73.9	171.2
6,9-*cis* (chair)	38.5	166.9
6,9-*cis* (boat)	57.4	171.4

2 Effective collision cross sections for *trans*, 7-*cis*, 9-*cis*, and 7,9-*cis* isomers of BIPSB

Effective collision cross sections for a BIPSB isomer in a particular configuration of the C_7=C_8 and C_9=N double bonds are estimated by averaging over their respective 6s and 8s conformations. That is:

$$\overline{\Omega}_{calc} = \sum_{i=1}^{5} \Omega_i e^{\frac{-\Delta E_i}{RT}} \Big/ \sum_{i=1}^{5} e^{\frac{-\Delta E_i}{RT}} \tag{1}$$

where the sum is over the 6s-*cis*(-), 6s-*cis*(+) and 6s-*trans* , 8s-*trans*, and 8s-*cis* isomers with the input data given in Table S1. In each case, ΔE_i is the relative energy corrected for vibrational zero point energy and T=300 K (approximately the effective temperature in the drift region). The averaged cross sections are given in Table S2.

Table S.2: Average collision cross sections with N_2 at 300 K for *trans*, 7-*cis*, 9-*cis*, and 7,9-*cis* isomers of BIPSB obtained through a Boltzmann average over contributing 6s and 8s isomers listed in Table S1.

BIPSB isomer	$\overline{\Omega}_{calc}$ (Å^2)
trans	173.1
7-*cis*	164.5
9-*cis*	171.3
7,9-*dicis*	164.6

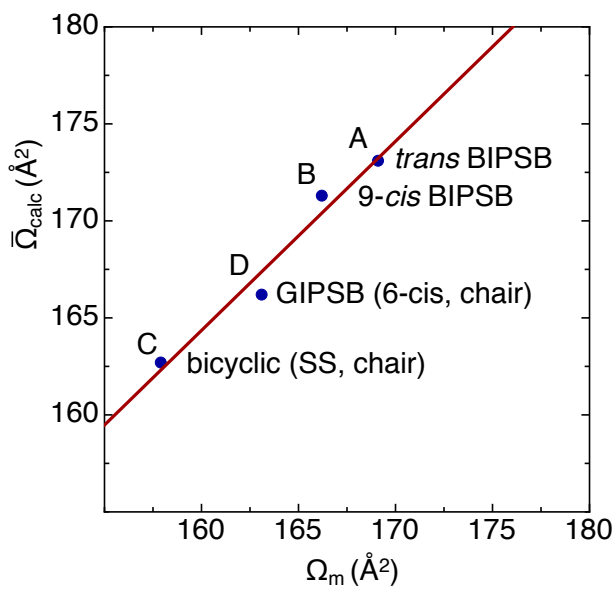


Figure S.4: Calculated collision cross sections for BIPSB isomers in N_2 buffer gas, plotted against measured collision cross sections for isomers corresponding to peaks A–D. A linear fit is shown in red. Data are provided in Table 1 of the paper.

3 Transition states for cyclization and [1-5] sigmatropic H shift

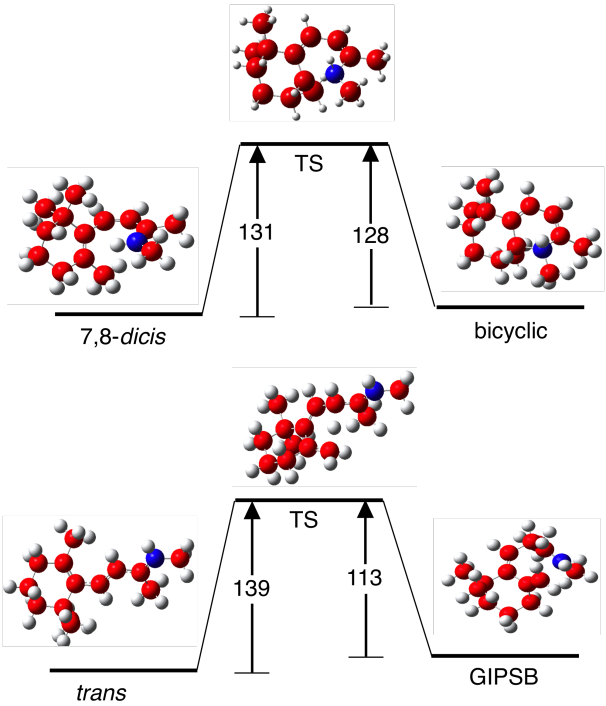


Figure S.5: Top - transition state between the 7,9-*dicis* isomer and bicyclic isomer. Bottom - transition state between the *trans* isomer and γ-ionone protonated Schiff base. Calculations are at the DFT M06-2X/cc-PVDZ level with energies (in kJ/mol) corrected for zero point vibrational energy. For computational expediency the butyl chain attached to the N atom was replaced by a methyl group.

4 Fitted BIPSB arrival time distribution

Figure S.6 shows the ATD for BIPSB which can be fitted to a sum of 4 Gaussian peaks corresponding to isomers A, B, C and D. The electrosprayed solution had been exposed to UV light to enhance the concentrations of isomers C and D.

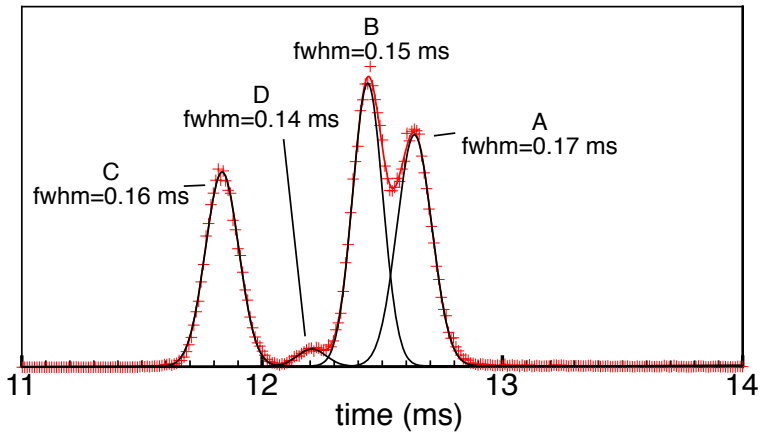


Figure S.6: ATD for electrosprayed β-ionone protonated Schiff base (N_2 buffer gas, P=6.4 Torr), fitted with four Gaussian peaks (A, B, C and D). The peak widths correspond to a resolution of $\approx$80 for the ion mobility spectrometer.

References

[1] Mesleh, M.; Hunter, J.; Shvartsburg, A.; Schatz, G.; Jarrold, M. *J. Phys. Chem.* **1996**, *100*, 16082–16086.

[2] Shvartsburg, A. A.; Jarrold, M. F. *Chem. Phys. Lett.* **1996**, *261*, 86–91.

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