ARTICLE

Electronic Supplementary Information

Conformational Diversity and Environmental Implications of *Trans*-2-Pentenal

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Table S1 The equilibrium geometries of the main *trans*-2-pentenal conformers in the ground electronic states calculated at the CAM-B3LYP/aug-cc-pVDZ level.

	S_0		D_0	
	tt-cis	***tt-gauche***	***tt-cis***	***tt-gauche***
Bond length (Å)				
1C-2O	1.212	1.212	1.238 (0.026)[a]	1.237 (0.025)
1C-3H	1.116	1.116	1.115 (-0.001)	1.115 (-0.001)
1C-4C	1.468	1.468	1.413 (-0.055)	1.415 (-0.053)
4C-5C	1.338	1.338	1.366 (0.028)	1.365 (0.027)
5C-6C	1.496	1.495	1.472 (-0.024)	1.472 (-0.023)
6C-7C	1.523	1.531	1.521 (-0.002)	1.540 (0.009)
4C-8H	1.090	1.092	1.088 (-0.002)	1.089 (-0.003)
5C-9H	1.095	1.096	1.095 (0.000)	1.096 (0.000)
6C-10H	1.102	1.098	1.106 (0.004)	1.096 (-0.002)
7C-12H	1.098	1.097	1.097 (-0.001)	1.096 (-0.001)
Bond angle (°)				
2O-1C-3H	120.4	120.4	112.2 (-8.2)	112.3 (-8.1)
2O-1C-4C	124.4	1244	126.5 (2.1)	126.4 (2.0)
1C-4C-5C	120.6	121.0	117.8 (-2.8)	118.0 (-3.0)
4C-5C-6C	126.9	125.8	125.4 (-1.5)	124.8 (-1.0)
5C-6C-7C	115.8	112.3	117.4 (1.6)	111.9 (-0.4)
Dihedral angle (°)				
2O-1C-4C-5C	180.0	-179.9	180.0 (0.0)	-179.7 (0.2)
1C-4C-5C-6C	180.0	-179.7	180.0 (0.0)	-179.9 (-0.2)
4C-5C-6C-7C	180.0	-122.3	180.0 (0.0)	-127.1 (-4.8)

[a] The values in parentheses denote the geometrical changes upon ionisation with respect to the neutral conformer.

Table S2 Energetics data of *trans*-2-pentenal calculated at various levels.

Level	conformer	ΔE (S_0)[a]	IE	ΔIE[b]	Level	ΔE (S_0)[a]	IE	ΔIE[b]
B3LYP/ cc-pVTZ	*tt*-cis	0	75,020	0	M06-2x/ aug-cc-pVTZ	0	77,239	0
	tt-gauche	-68	75,156	136		160	77,394	155
	tc-cis	680	75,041	21		706	77,285	46
	tc-gauche	611	75,149	129		858	77,455	216
B3LYP/ aug-cc-pVTZ	*tt*-cis	0	75,248	0	ωB97XD/ cc-pVTZ	0	75,240	0
	tt-gauche	-29	75,393	145		73	75,458	218
	tc-cis	762	75,191	-57		581	75,379	139
	tc-gauche	735	75,303	56		670	75,576	336
B3LYP/ aug-cc-pVTZ	*tt*-cis	0	75,391	0	ωB97XD/ aug-cc-pVDZ	0	75,609	0
	tt-gauche	-70	75,532	141		102	75,845	236
	tc-cis	772	75,347	-44		658	75,680	72
	tc-gauche	926	75,237	-153		780	75,898	289
CAM-B3LYP/ cc-pVTZ	*tt*-cis	0	75,758	0	ωB97XD/ aug-cc-pVTZ	0	75,504	0
	tt-gauche	-8	75,987	229		71	75,729	225
	tc-cis	605	75,886	128		674	75,582	78
	tc-gauche	601	76,107	349		764	75,786	282
CAM-B3LYP/ aug-cc-pVDZ	*tt*-cis	0	75,964	0	MP2/ cc-pVDZ	0	80,055	0
	tt-gauche	27	76,206	242		14	80,250	194
	tc-cis	700	76,016	52		705	80,354	298
	tc-gauche	732	76,247	283		709	80,555	499
CAM-B3LYP/ aug-cc-pVTZ	*tt*-cis	0	76,123	0	MP2/ aug-cc-pVDZ	0	79,783	0
	tt-gauche	-11	76,360	236		-5	79,997	213
	tc-cis	714	76,177	53		799	80,022	238
	tc-gauche	712	76,401	277		788	80,240	457
M06-2x/ cc-pVTZ	*tt*-cis	0	77,000	0	MP2/ aug-cc-pVTZ	0	80,910	0
	tt-gauche	158	77,150	150		23	81,109	199
	tc-cis	605	77,113	113		806	81,135	225
	tc-gauche	755	77,279	279		826	81,336	426
M06-2x/ aug-cc-pVDZ	*tt*-cis	0	76,370	0				
	tt-gauche	196	76,908	178				
	tc-cis	705	76,770	40				
	tc-gauche	886	76,953	223				

[a] Relative energies with zero-point energy correction for the other conformers with respect to the *tt-cis* conformer in both the neutral (S_0) and cationic (D_0) states. [b] Relative ionisation energies of the other conformers with respect to the *tt-cis* conformer.