Supporting Information Part 1

Conformations and CH/π Interactions in Aliphatic Alkynes and Alkenes

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Carbon 1s photoelectron spectra of a series of alkenes with the possibility of displaying conformational equilibria have been recorded with high resolution. Here, the spectra of trans-2-pentene, 1-hexene, trans-2-hexene, trans-3-hexene, 1,5-hexadiene are presented in Figure 1 and analyzed in the following. The experimental carbon 1s ionization energies found for the present alkenes are tabulated in the main text. The presentation builds on and presupposes knowledge of the discussion of 1-butene and 1-pentene in the main text.

Trans-2-pentene

Trans-2-pentene may be obtained from 1-butene by replacing a hydrogen by methyl in the *trans* position, and similar to 1-butene, trans-2-pentene may exist as *AC* and *SP* conformers. The con-

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Table 1: The chemical shifts of the trans-2-pentene conformers computed at the MP4SDQ/tzp level of theory. All shifts in eV relative to ethyne.

Carbon	*SP*	*AC*	*SP-AC*
C1	-0.686	-0.659	-0.027
C2	-1.129	-1.065	-0.064
C3	-1.147	-1.141	-0.006
C4	-0.686	-0.727	0.041
C5	-0.783	-0.844	0.061

formers are related through rotation about the C3–C4 bond as can be seen in Figure 2.

To explore potential spectral differences between the *AC* and *SP* conformers, vibrational lineshapes were calculated at the B3LYP/tzp level of theory and shifts in carbon 1s ionization energies were computed with MP4SDQ/tzp, for each carbon atom in both conformers. None of the five sites of ionization gave rise to significant differences in lineshapes between the two conformers. The computed energy shifts, however, are summarized in Table 1 and show noticeable differences between *SP* and *AC* for C2 and C5. The C2 and C5 shifts are possibly caused by the 4-center CH/π interaction indicated with dashed lines in Figure 2. Similar to what we experienced in the 1-butene analysis, a model that allow for contributions from both the *SP* and *AC* conformer does not provide a better least-squares fit than either of the two single-conformer models. In particular, the recorded spectrum is described well by the *AC* conformer alone, as shown in Figure 1(a).

Table 2: The chemical shifts (in eV, relative to ethyne) of conformer *I* (group A conformers) and *II* (group B conformers) of 1-hexene computed at the MP4SDQ/tzp level of theory.

Carbon	*I*	*II*	*I-II*
C1	-1.130	-1.136	0.006
C2	-0.733	-0.734	0.001
C3	-0.776	-0.761	-0.015
C4	-0.933	-0.923	-0.010
C5	-0.837	-0.972	0.135
C6	-0.805	-0.854	0.049

1-Hexene

By rotating about the C2–C3, C3–C4, and C4–C5 bonds of 1-hexene, it is possible to define 14 candidate conformer structures. In a microwave spectroscopy study,[1] only seven of these were identified and assigned in the spectra. However, both theoretical calculations at the MP2/6-31G* level of theory and observations of the rotational spectra suggest that two of the conformers are substantially more stable than the other five. These conformers are denoted conformer *I* and *II* in Figure 3.

Conformers *I* and *II* of 1-hexene correspond to the two most stable conformers of the structurally related 1-pentene. Following the analysis of the 1-pentene spectrum, theoretical lineshape models based on these two conformers were used in a fit to the observed C1s spectrum. In a loose sense, conformer *I* profiles are thought to represent the contribution from any conformer that does not display a 5-center CH/π interaction, making up group A, while conformer *II* represents those that do; group B. By including only model peaks derived from conformers *I* and *II*, the number of vibrational profiles is reduced from 42 (6 carbons x 7 conformers) to 12 (6 carbons x 2 conformers), and further down to 8 by exploiting the fact that both C1s shifts and vibrational lineshape for C1-C4 are very similar between these conformers as documented in Table 2.

The carbon 1s photoelectron spectrum of 1-hexene is shown in Figure 1(b) along with the fitting model. The least-squares analysis gives as result that 84% of the C5+C6 intensity is described by group A, leaving 16% for group B, with an estimated uncertainty of 10%. However, it is quite conceivable that there are conformers that differ in their spectral response from both conformer *I* and *II* and thus contribute to both groups A and B. One possible candidate in this respect is included as conformer *III* in Figure 3. For this reason, we do not proceed to deduce conformational populations from the A/B intensity ratio.

Table 3: The chemical shifts of the four trans-2-hexene conformers computed at the MP4SDQ/tzp level of theory. All shifts in eV relative to ethyne.

Carbon	*I*	*III*	*IV*	*II*	Max. shift diff.
C1	-0.680	-0.677	-0.704	-0.675	0.029
C2	-1.105	-1.102	-1.167	-1.108	0.065
C3	-1.181	-1.197	-1.186	-1.181	0.016
C4	-0.882	-0.876	-0.843	-0.868	0.039
C5	-0.909	-0.905	-0.865	-0.891	0.044
		Group A		Group B	
C6	-0.847	-0.919	-0.811	-0.990	0.179

Trans-2-Hexene

Trans-2-hexene may be obtained from 1-pentene by replacing the hydrogen in *trans* position by methyl. This alkene has five potential conformers like 1-pentene, and these are illustrated in Figure 4. G3 calculations from this work indicate that conformer *V* is very little populated compared to the other conformers, only 2%. This is comparable with what we obtained for the same conformer of 1-pentene, 3%. This result is in agreement with Fraser *et al.*,[2] and based on this conformer *V* is disregarded in the following analysis.

Shifts in C1s ionization energies and vibrational profiles were calculated for conformers *I-IV* and the energy shifts are summarized in Table 3. C1-C5 have similar shifts and also very similar vibrational profiles for the four conformers. For C6, however, there are significant differences in both shifts and profiles between conformer *II* on the one hand, and the other conformers, on the other. Hence, conformer *I* and *II* were chosen to represent the group A and B conformers respectively in a least-squares fitting model to the observed spectrum. Group A represents conformers that do not have a 5-center CH/π interaction, while group B contains the one conformer that does possess it; conformer *II*.

From this analysis, it is evident that the fitting strategy used for 1-pentene (described in the main text) may also be applied for trans-2-hexene. C1-C5 were described by conformer *I* profiles and considered common to all conformers, while C6 is described in terms of two vibrational structures, computed for conformers *I* and *II* as representative for groups A and B, respectively. The resulting

fit is shown in Figure 1(c), and the optimal weight factors are found to be 60% of group A (*I*, *III* and *IV*) and 40% of group B (*II*) (±5%).

Table 4: The chemical shifts (in eV) of the four trans-3-hexene conformers computed at the MP4SDQ/tzp level of theory and relative to ethyne.

Carbon	*+AC+AC*	*-AC+AC*	*ACSP*	Max. shift diff.
C1	-0.860	-0.861	-0.802	0.059
C2	-0.752	-0.749	-0.710	0.042
C3	-1.199	-1.196	-1.204	0.008
C4	-1.199	-1.196	-1.263	0.067
C5	-0.752	-0.749	-0.775	0.026
C6	-0.860	-0.861	-0.879	0.019

Trans-3-hexene

Trans-3-hexene is related to trans-2-pentene through replacement of the methyl group in *trans* position by an ethyl group. All four conformers are shown in Figure 5, and can be obtained by rotation about the C2–C3 and C4–C5 bonds. A gas electron diffraction study reported three of the four proposed conformers of trans-3-hexene[3] and identified these as *+AC+AC*, *-AC+AC* and *ACSP*, cf Figure 5. Furthermore, an IR/Raman vibrational study was conducted to identify *-AC+AC* as the most stable conformer.[4] With these results in mind, supported by G3 and B3LYP/tzp calculations performed in this work predicting only 1 and 0% of the *SPSP* conformer respectively, the *SPSP* conformer was neglected in our analysis.

For 1-butene and trans-2-pentene, one conformer was found sufficient to describe the carbon 1s photoelectron spectrum satisfactory. As shown in Figure 5, the trans-3-hexene conformers have the same structural character as the two conformers of 1-butene and trans-2-pentene, focusing at the C1-C4 and C1-C5 moieties of the trans-3-hexene molecule respectively. Hence, it is likely that one conformer will be sufficient to describe the trans-3-hexene spectrum satisfactory as well.

To explore the possibility for resolving the trans-3-hexene conformers in the C1s spectrum, MP4SDQ/tzp shifts[5] were calculated for all conformers except *SPSP*, cf Table 4. For the *+AC+AC*

and *-AC+AC* conformers, there are very small differences in shift for all three unique carbons. However, the *ACSP* conformer provides appreciable shift differences in comparisons with the other conformers, up to 0.067 eV. Vibrational lineshapes were computed using B3LYP/tzp and no significant differences were found between the conformers.

Since both energy shifts and profiles are very similar for the *+AC+AC* and *-AC+AC* conformers, *+AC+AC* was chosen to represent this group of conformers. Hence, the trans-3-hexene spectrum was fitted using *+AC+AC* and *ACSP* profiles separately and in combination. Both a combination of the two conformers as well as *ACSP* alone provide least-squares fits with large discrepancies between our model and the experiment. However, the agreement between the *+AC+AC* model and the experiment is satisfactory, as shown in Figure 1(d).

For unsaturated symmetric molecules like ethyne, the effect of vibronic coupling should preferably be taken into account when describe the detailed structure of the C1s photoelectron spectrum.[6] This applies to trans-3-hexene, and in our analysis of the trans-3-hexene spectrum, all diabatic lines for C3 are split into two identical vibrational profiles that are displaced by 74 meV as determined in the least-squares fit. This splitting is surprisingly large compared to related molecules, and in a similar fit for C2 in trans-2-butene, a more realistic value of 36 meV was obtained. The relatively large vibronic coupling split of 74 meV may partly be caused by limitations in the single-conformer model.

Table 5: The chemical shifts (in eV) of *anti* (group A conformers) and *skew* (group B conformers) of 1,5-hexadiene computed at the MP4SDQ/tzp level of theory, relative to ethyne.

Carbon	*Anti*	*Skew*	*Anti-Skew*
C1	-1.048	-1.113	0.065
C2	-0.662	-0.783	0.121
C3	-0.680	-0.669	-0.011
C4	-0.680	-0.668	-0.012
C5	-0.662	-0.667	0.005
C6	-1.048	-1.073	0.025

1,5-Hexadiene

Based on structural considerations, 1,5-hexadiene may possess ten unique conformers, and *ab initio* calculations suggest that two of these stand out as the most stable ones.[7,8] These two conformers, *anti* and *skew*, are illustrated in Figure 6. While the *skew* conformer has the possibility for a 5-center CH/π interaction, *anti* has not. On the basis of the results from Refs.[7] and,[8] the other eight conformers are excluded in the following analysis. *Anti* represents all conformers without the 5-center CH/π interaction (group A), and *skew* represents all conformers possessing it (group B). Shifts in C1s energies[5] and vibrational profiles were calculated for both conformers to compare the two conformational spectra, and the energy data are summarized in Table 5.

Due to symmetry, the *anti* and *skew* conformers have three and six unique carbon atoms, respectively. Hence, C1-C3 and C4-C6 provide the same shifts for *anti* while they are all different for the *skew* conformer. C2 stands out with prominent differences in both shifts and vibrational profiles between the two groups, while C1 shows an energy shift of 0.066 eV. These results indicate that it is necessary to include both conformers in the analysis.

A fit based solely on lineshapes from the *anti* conformer does not provide a satisfactory representation of the experimental spectrum. However, the fit based on *skew* alone was satisfactory, describing all the important features of the spectrum. In the case where both conformers were included, the overall fit between the model and experimental spectrum did not improve noticeably compared to the *skew* fit. Therefore, *skew* profiles alone are sufficient to describe the carbon 1s photoelectron spectrum of 1,5-hexadiene, as shown in Figure 1(e). Even though we are not able to quantify the amount of the two groups of conformers, these results suggest that the group B conformers are more populated than are the group A conformers. A closer inspection of the fit reveals too much intensity of the main peak. This disagreement indicates an underestimation of bending modes when core-ionizing at C3 and C4.

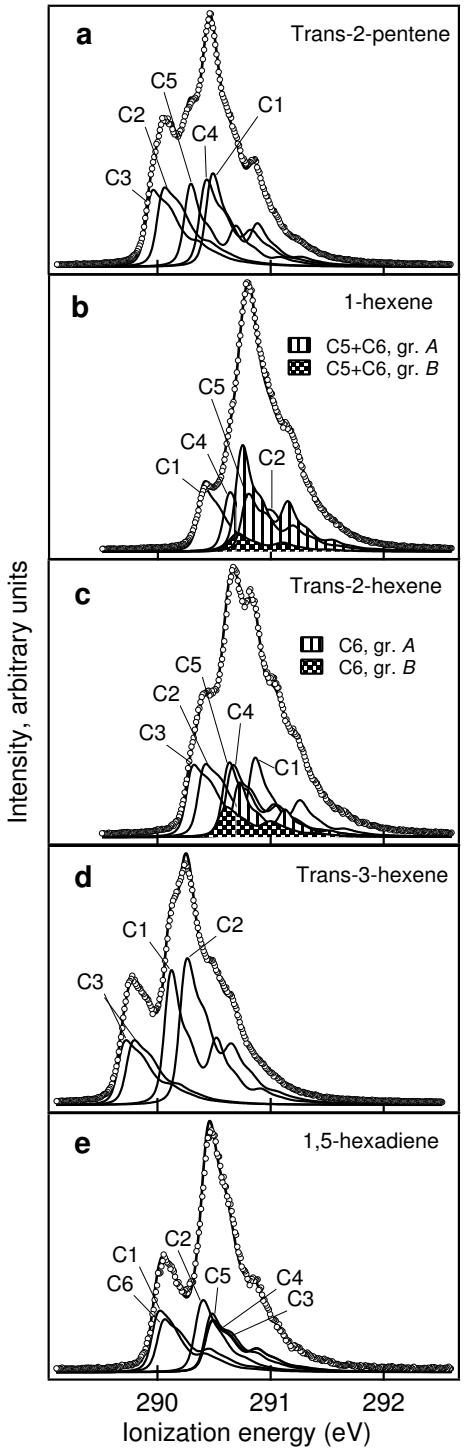

Figure 1: The carbon 1s photoelectron spectra of (a) trans-2-pentene, (b) 1-hexene, (c) trans-2-hexene, (d) trans-3-hexene and (e)1,5-hexadiene. The circles represent the experimental spectrum, the thick solid line the overall theoretical spectrum, and the thin solid lines the theoretical atom-specific lineshape models. In figures (b) and (c) the shaded areas represent carbons where the shifts and profiles are significantly different between two groups of conformers (see text for details).

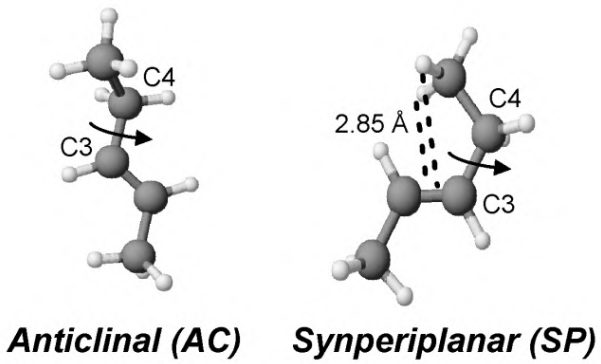

Figure 2: The structure of the two conformers of trans-2-pentene.

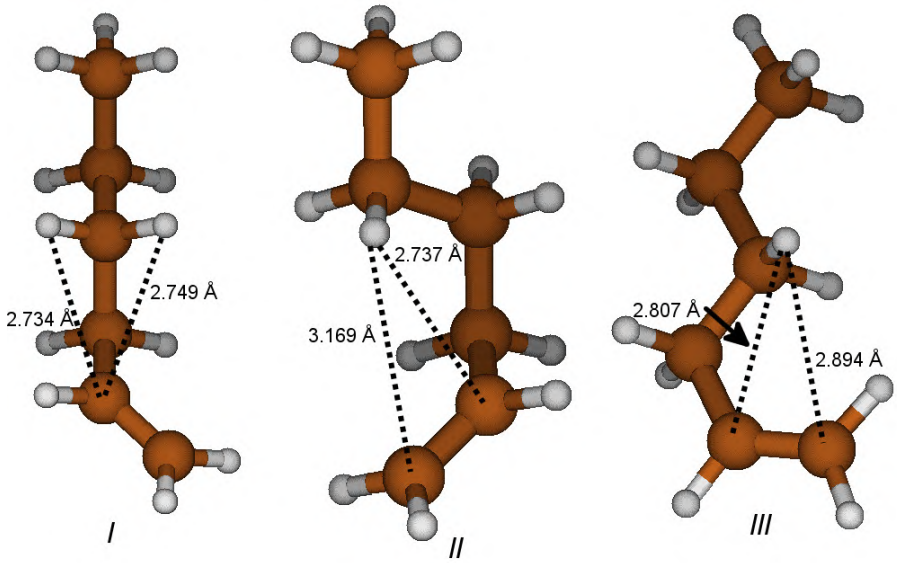

Figure 3: The structure of conformer *I*, *II* and *III* of 1-hexene.

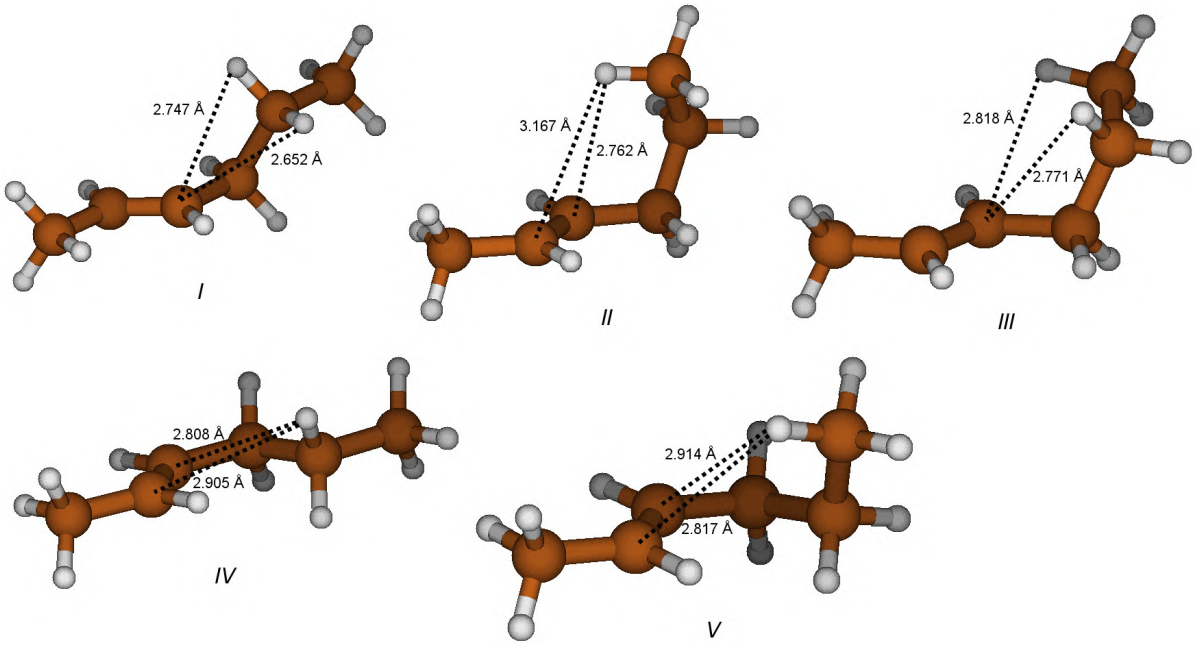

Figure 4: The structure of conformers *I*– *V* of trans-2-hexene.

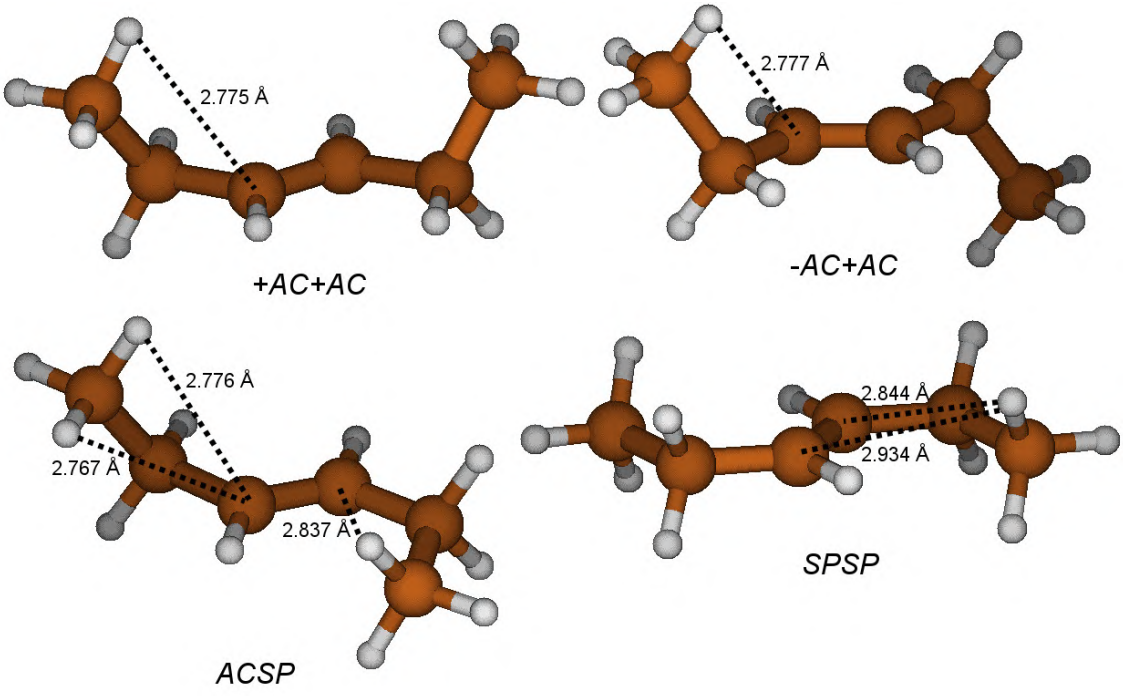

Figure 5: The structure of the four possible conformers of trans-3-hexene.

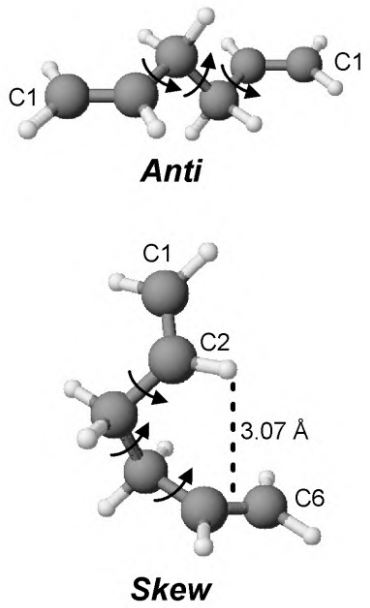

Figure 6: The structure of the *anti* and *skew* conformers of 1,5-hexadiene.

References

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