# Theoretical Evidence of Hyperconjugation for Polyacetylene Methyl Rotation

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We theoretically investigated the rotational barrier of the methyl rotation in a series of polyacetylenes (see Fig. 1). The rotational barriers have been calculated to be 907-928 cm^{-1} (2.60-2.65 kcal mol^{-1}) at the MP2/6-31G++(d,p) level and 1007-1031 cm^{-1} (2.88-2.95 kcal mol^{-1}) at the HF/6-31G++(d,p) level, indicating that the electron correlation effect is marginal. Those values are somewhat large as for free rotors, suggesting that a special hyperconjugative interaction might affect the *cis* (or *trans*) conformer. Moreover, the nearly unique value for the rotational barrier in the series of polyacetylenes studied clearly shows this type of interaction is local.
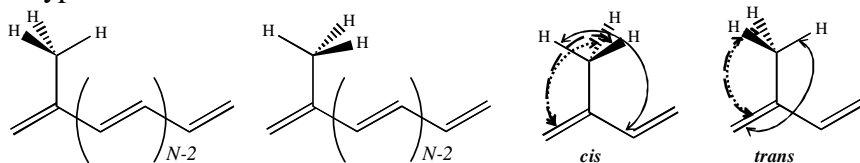
Fig. 1. Structure of the two conformations of polyacetylene.   **Fig. 2.** Hyperconjugative mechanism in the two conformations of 2-methyl-1,3-butadiene.

Based on the donor acceptor scheme given by the NBO analysis calculated for the MP2 optimized structures, the hyperconjugative interactions for the cis conformations take place between the π-bond of C=C and each of the two CH σ-bonds of the methyl group staggered to C=C (π(C=C)–2σ*(CH)), 2σ(CH)–σ*(CC) and 2σ(CH)–π*(C=C) in one hand, and between the CH σ-bond of the methyl group that belongs to the plane of the molecule with the C–C single bond in α-position to C=C, on the other hand ((σ(CC)–σ*(CH) and σ(CH)–σ*(CC), see Fig. 2).

To quantitatively evaluate the hyperconjugative energy, we employed the Orbital Deletion Procedure (ODP) technique in which certain specific atomic orbitals are forced to be vacant [1-3]. Supported by the ODP calculation performed at the HF/6-31++G(d,p) level, both NBO and ODP analysis show that the largest interaction is 2σ(CH)–π*(CC) one in all the polyacetylenes studied, with an energy difference of 1.16

kcal mol^{-1} more important for the *cis* conformation of 2-methyl-1,3-butadiene (see Table 1). Furthermore, the calculations show that not only the π(C=C)–2σ*(CH) hyperconjugation is responsible for the stability of the *cis* conformation, but also might be the origin of the rotational barrier, since the energy difference was evaluated to be 2.74 kcal mol^{-1} (see Table 1). Other types of interaction were also found important, as can be seen in Table 1, such as 2σ(CH)–σ*(CC) and σ(CH)–σ*(CC). However, their *cis-trans* energy differences are negligible compared with those of the first two interactions.

By deleting the selected antibonds orbitals responsible for the hyperconjugation in the methyl group one could recognize that, effectively, the rotational barrier is mainly originating from the interaction of π(C=C) with the 2σ*(CH) of the methyl group. This can be easily understood from a well matched overlap between the two 2σ*(CH) with π(C=C).

Table 1. Donor-acceptor scheme analysis in the two conformations of 2-methyl-1,3-butadiene obtained from ODP technique

Deleted interaction	*cis* [a]	*trans* [a]	ΔE [b]
π(CC)–2σ*(CH)	6.73	3.99	–2.74
2σ(CH)–σ*(CC)	4.54	4.90	0.36
2σ(CH)–π*(CC)	7.97	6.81	–1.16
σ(CC)–σ*(CH)	0.95	0.76	–0.19
σ(CH)–σ*(CC)	5.30	4.47	–0.83
Deleted orbital			
2σ*(CH)	8.28	5.49	–2.79
σ*(CH)	2.23	2.42	0.19

MP2 optimized structures were used. ODP calculations were performed at HF/6-31++G(d,p). [a] The values are the energy contribution (in kcal mol^{-1}) by deleting selected bond-antibonds interactions or antibond orbitals. [b] ΔE = E$_{cis}$-E$_{trans}$ is the difference of energy contributions in *cis* and *trans* conformations given by ODP.

References

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