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# DECISIVE ROLE OF $\pi$ CONJUGATION IN THE CENTRAL BOND LENGTH SHORTENING OF BUTADIENE

J. P. DAUDEY, G. TRINQUIER,* J. C. BARTHELAT and J. P. MALRIEU

Laboratoire de Physique Quantique, Equipe de Recherche Associée au C.N.R.S. No. 821, Université Paul Sabatier, 118, route de Narbonne, 31077 Toulouse Cedex, France

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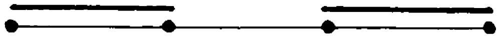
**Abstract**—The influence of $\pi$ conjugation and hyperconjugation in the shortening of the central C–C bond in butadiene with respect to a $C_{sp^3}$–$C_{sp^3}$ bond in alkanes is theoretically investigated by a *direct* analysis. As expected from simple $\pi$ models it is demonstrated that the origin of this shortening is mainly due to $\pi$ conjugation in the planar s-trans conformation while hyperconjugation largely compensates the lack of $\pi$ conjugation in the perpendicular form and leads to a similar shortening of the central bond, These results contradict one of the conclusions of a recent *ab initio* study.

Butadiene is strongly localized (i.e. poorly conjugated) and even simple $\pi$-Hückel Hamiltonian with equal C–C resonance integrals leads to alternating $\pi$ bond orders. When bond alternation is introduced through different resonance integrals, the contrast between the terminal (double) bonds and the central (single) bond is increased. The classical chemical notation



seems therefore more correct than the delocalized description

The experimental geometry and all ($\sigma + \pi$) nonempirical calculations confirm the strong bond alternation. The central bond (1.463 Å)[1,2] is longer than ethylene or butadiene double bonds (1.34 Å) but *significantly* shorter than the non-conjugated $C_{sp^3}$–$C_{sp^3}$ bonds in alkanes (1.532 Å).[3] This shortening of 0.07 Å was classically attributed to the weak $\pi$ conjugation between the double bonds.

In a recent theoretical study, Skaarup, Boggs and Skancke[4] performed full geometry optimizations for planar and perpendicular conformations of butadiene at the *ab initio* SCF level with a fairly large basis set. In their calculation, the central C–C bond varies only by 0.02 Å between the planar *s-trans* and the perpendicular conformations. Since $\pi$ conjugation is negligible in the perpendicular geometry they concluded that the shortening of 0.07 Å observed for the central C–C bond must be mainly attributed (for 0.05 Å) to other factors as sp$^2$ hybridization. Bartell[5] immediately questioned this attribution but from a purely logical point of view, invoking changes in the nonbonded interactions. A more radical criticism can be raised against the conclusions of Skaarup, Boggs and Skancke.[4] If $\pi$ conjugation disappears in the perpendicular conformation, then the nuclear energy varies, the $\sigma$ distribution is modified, and the $\sigma - \pi$ interactions are strongly perturbed.

In the planar conformation the distinction between $\sigma$ and $\pi$ electrons is evident. For the perpendicular case, it is always possible to define one localized $\pi$ MO on each C=C fragment. The SCF localized MO $\pi_1$ (see Fig. 1) which is mainly located on the 2p$_z$ atomic orbitals of atoms $C_1$ and $C_2$ has $\sigma$ tails on the system 2 and the $\sigma$ MO's of system 1 have components on the 2p$_y$ atomic orbitals of atoms $C_3$ and $C_4$. This effect which is known as hyperconjugation stabilizes the perpendicular form and tends to compensate the loss of direct $\pi$ conjugation. The purpose of the present work is to give a *direct* estimate of both $\pi$ conjugation in the planar form and hyperconjugation in the perpendicular conformation.

## METHOD

The best way to evaluate $\pi$ conjugation (or hyperconjugation effects) in a given conformation is to suppress it artificially by an appropriate modification of the wavefunction corresponding to the conformation studied, all others factors being kept fixed. This procedure follows the analysis of the rotational barrier of ethane performed by Sovers *et al.*[6] ten years ago. In order to solve the controversy about the origin of the barrier, they introduced a very crude wavefunction

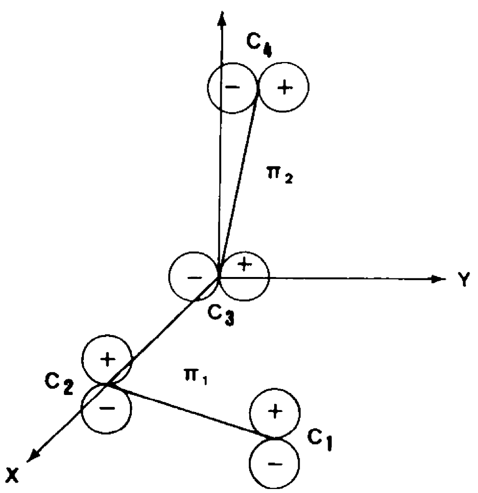


Fig. 1. Axis for perpendicular butadiene.

with fully localized non polar C–H bonds and they already obtained the right order of magnitude for the rotational barrier. Therefore they proved that the barrier was essentially due to the *repulsions* between the CH bonds of the methyl groups.

Our procedure is as follows:

(i) for a given geometry, a full SCF calculation is performed leading to the SCF wavefunction $\phi = |\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2\sigma_1\bar{\sigma}_1\ldots\sigma_n\bar{\sigma}_n|$ and energy $E_{SCF} = \langle\phi|H|\phi\rangle$ (labelled $E_{SCF\perp}$ for perpendicular geometries).

(ii) the two SCF $\pi$ MO's are replaced by two ethylenic $\pi$ MO's $\pi_1'$ and $\pi_2'$ obtained by an SCF calculation of ethylene in the same basis set and properly orthonormalized.

(iii) the energy of the new $\sigma$ SCF, $\pi$-localized determinant

$$\phi' = |\pi_1'\bar{\pi}_1'\pi_2'\bar{\pi}_2'\sigma_1\bar{\sigma}_1\ldots\sigma_n\bar{\sigma}_n|$$

is calculated as the mean value of H

$$E' = \langle\phi'|H|\phi'\rangle$$

and the $\pi$ delocalization energy is defined as

$$\Delta E_\pi = E' - E_{SCF}. \qquad (1)$$

As far as hyperconjugation in the perpendicular forms is concerned, the procedure is complicated by the non-orthogonality between the $\pi$ MO of a $CH_2{=}CH{-}$ fragment and the $\sigma$ MO's of the other fragment. The $\sigma$–$\pi$ mixing is removed by projecting the SCF $\sigma$ MO's onto the subspace orthogonal to the $\pi[\pi_1', \pi_2']$ subspace; the resulting $\sigma'$ MO's only differ from the SCF $\sigma$ MO's by a cut off of their tails on the $\pi$ MO's. The new set $(\pi', \sigma')$ is orthonormalized and defines an hyperconjugationless determinant

$$\phi_\perp' = |\pi_1'\bar{\pi}_1'\pi_2'\bar{\pi}_2'\sigma_1'\bar{\sigma}_1'\ldots\sigma_n'\bar{\sigma}_n'|$$

the energy of which

$$E_\perp' = \langle\phi_1'|H|\phi_\perp'\rangle$$

leads to hyperconjugation energy

$$\Delta E_{hyper} = E_\perp' - E_{SCF\perp}. \qquad (2)$$

(iv) The final step of our demonstration is the variation of the central C–C bond distance. The shift of the equilibrium distance obtained from the curves corresponding to $E_{SCF}$ and $E'$ provides a non-ambiguous evaluation of the influence of $\pi$ conjugation on this bond length. The influence of hyperconjugation in the perpendicular form is obtained by comparing the curves relative to $E_{SCF\perp}$ and $E_\perp'$.

All calculations were made in a [31/31] Gaussian-type basis set for carbon and [31] basis set for hydrogen. Pseudopotentials were used for carbon following the methodology of Barthelat and Durand.$^7$ We used a version of the HONDO program of Dupuy *et al.*$^8$ which was modified by one of us (J.P.D.) to include pseudopotentials.

Since the differences of geometrical structure between ethylene and $CH_2{=}CH{-}$ fragments of butadiene are small, we took the optimized geometry of ethylene (determined with the same basis set)$^9$ for $CH_2{=}CH{-}$ fragments in butadiene and optimized only the central bond length for the planar *s-trans* and perpendicular conformations.

## RESULTS AND DISCUSSION

*Planar* s-trans *conformation.* Under these conditions the SCF optimized central bond length is 1.476 Å,$^{10}$ and the conjugation energy defined by eqn (1) is 10.4 kcal/mol. The $E_{SCF}$ ($\pi$ delocalized) and E′ ($\pi$ localized) potential curves are shown in Fig. 2(a). The minimum of E′ is located at 1.521 Å. This is somewhat shorter than the value obtained for ethane with the same basis set (1.546 Å) but much longer than the SCF value (1.476 Å). In the light of these first results, about 64% (0.045 Å) of the central bond length shortening would be specifically due to $\pi$ conjugation, the remainder (0.025 Å) being due to other factors like $sp^3 \rightarrow sp^2$ hybridization change.

*Perpendicular conformation.* In the rigid rotator approximation, the internal rotational barrier is calculated as 6.5 kcal/mol in good agreement with the corresponding value obtained by Skaarup, Boggs and Skancke.$^4$ When the central bond relaxation occurs this value decreases to 6.2 kcal/mol for a distance of 1.499 Å (Fig 2(b)). The experimental barrier is 5.0 kcal/mol$^{11}$ (for a review of the complete torsional potential curve, see Ref. 12) while the literature value$^4$ taking into account full geometry relaxation is 5.7 kcal/mol. The lengthening of the C–C bond in our calculation is indeed very small (0.023 Å) and similar to the literature value$^4$ (0.021 Å). However if we performed a calculation without hyperconjugation effects as described before we obtained a large shift of the potential curve $E_\perp'$ (see Fig 2(b)) leading to an equilibrium distance of 1.541 Å which is very close to the ethane value. A striking observation which can be made on Table 1 is the equivalent lengthening when

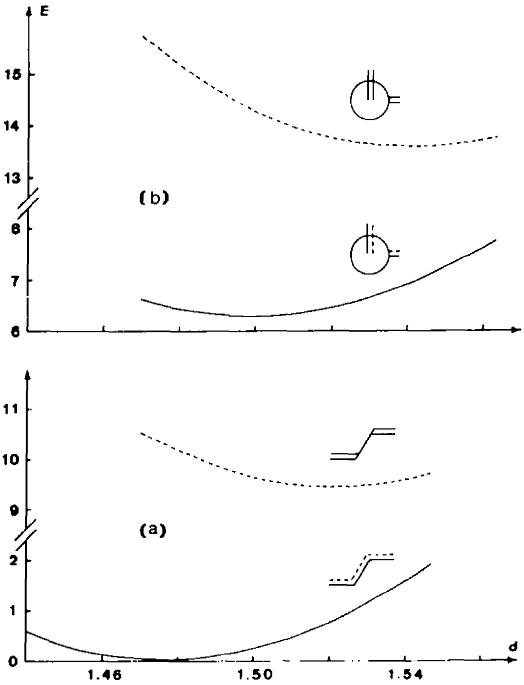


Fig. 2. Potential curves of planar (a) and perpendicular (b) butadiene. Full lines: Standard SCF calculations; dashed lines: $\pi$ localized calculation. The energy origin refers to the planar equilibrium geometry in the standard SCF calculation. Energy values are in kcal/mol and distances in Å.

Table 1. Optimized central C–C bond length in planar and perpendicular butadienes and in ethane

| | Planar s-*trans* butadiene | | Perpendicular butadiene | | |
|---|---|---|---|---|---|
| | Standard SCF | $\pi$ localized | Standard SCF | $\pi$ localized | ethane |
| d(Å) | 1.476 | 1.521 | 1.499 | 1.541 | 1.546 |

preventing either $\pi$ conjugation in the planar conformation (0.045 Å) or hyperconjugation in the perpendicular conformation (0.042 Å). So it is not surprising that the estimated hyperconjugation energy as defined by eqn (2) is 8.9 kcal/mol, almost as large as $\pi$ conjugation energy in the planar form (10.4 kcal/mol).

## CONCLUSION

We have shown that it is possible to give, in the frame of *ab-initio* calculations, a clear content to the $\pi$ conjugation concept (which was well defined in simpler models as Hückel method) and to extend it to hyperconjugation in perpendicular forms. In our formulation we compare the standard SCF wave function and a modified wave function in which $\pi$ localization is imposed. We then escape to the problem of mixing of several effects which occurs in the comparison of different conformations.

The application of these ideas to the problem of the central bond length in butadiene leads to two results. First, the $\pi$ conjugation is actually responsible for most part of the central bond shortening as it was classically explained by $\pi$ electrons models. Secondly, if the bond length remains almost as short in the perpendicular form this is due to the hyperconjugation effects which appear of the same order of magnitude as $\pi$ conjugation.

*Note added in proof.* During the publication of this work a similar analysis was proposed by H. Kollmar (*J. Am. Chem. Soc.* **101**, 4832 (1979)) for the conjugation in the planar form of butadiene.

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