Tetrahedron. Vol. 32, pp 1179 to 1181. Pergamon Press 1976 Printed in Great Britain

CONTRIBUTIONS OF RESONANCE, HYBRIDIZATION, AND NONBONDED INTERACTIONS TO THE STRUCTURE OF BUTADIENE

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(*Received in USA* 22 *October* 1975; *Received in UK for publication* 18 *December* 1975)

Abstract—The fully optimized geometries of four rotational conformers of butadiene have been calculated *ab initio* in order to investigate the relative importance of resonance, hydridization and nonbonded interactions. The results indicate that the short central C–C bond is primarily due to hydridization, although resonance makes a minor contribution. The resonance stabilization of the planar conformers is responsible for the relatively large barrier to internal rotation, whereas the nonbonded interactions are only important in destabilizing the sterically crowded *cis* conformer.

Since the earliest quantum mechanical descriptions of molecules, butadiene has been regarded as a typical example of resonance in a conjugated system.[1] The facts that the C–C single bond is considerably shorter than that of ethane and that the molecule has a planar equilibrium conformation have been attributed to π-electron delocalization which gives the single bond some amount of double bond character, and which is most effective in a planar molecule. When more sophisticated methods were applied, it became apparent that the delocalization was less than predicted by the simple Hückel method.[2] It was even argued that the effects of resonance were so small as to be negligible, the C–C bond shortening instead being attributed to different hydridization[3,4] or lesser nonbonded repulsion.[5] This work is an attempt at evaluating the relative importance of the proposed effects on the structure and rotational isomerism of butadiene.

METHOD

In a comparison of this type, it is advantageous not to introduce any possible bias by using empirically adjusted parameters such as the "standard" length of an sp^2–sp^2 C–C bond or the constants in empirically assumed nonbonded potentials, both of which assumptions can differ considerably between authors.[6,7] This criterion suggests the use of an *ab initio* method. Since the interpretation of the results rests on rather small geometry differences, the calculations should preferably use the optimized theoretical structures of the different conformers rather than using the experimentally derived structural parameters of the *trans* structure. (The discussion of conjugation was confused for many years by erroneous experimental results indicating that the C–C bonds in nonplanar cyclooctatetraene were shorter then in butadiene.[8]) Furthermore, previous investigations have shown that geometry optimization is of primary importance in determining whether the second stable isomer is a planar *cis* or nonplanar *gauche* form.[9,10]

For the present study, the force method of Pulay[11] has been used since it makes possible the simultaneous optimization of the many geometrical parameters in a molecule such as butadiene and because the method has been shown to reproduce small structural differences between conformers with high accuracy.[12] The only constraint imposed on the structures of the conformers was that the two ethylene parts of the molecule remain planar while rotating around the central C–C bond. A (7, 3) basis set[13] of Gaussian lobe functions contracted to ⟨5, 3⟩ as ⟨3, 1, 1, 1, 1; 3⟩ was used for the C atom (see Ref. 14 for the nomenclature). For the H atoms, three uncontracted s functions were used with orbital exponents 4.90, 0.82 and 0.18. In order to save computer time, calculations were done only for four rotamers with dihedral angles 0° (*trans*), 90°, 140° (since other studies[10] have yielded a minimum energy conformer at this angle), and 180° (*cis*).

RESULTS AND DISCUSSION

(1) *Equilibrium structure.* The energies of the conformers are shown in Table 1 and the structures in Table 2. The values of the rotational barrier and the energy difference between the *trans* and the second stable conformer are in good agreement with experiment. The

Table 1. Calculated energies of butadiene conformers

	Energy with Fixed Structure[a]		Energy with Optimized Structure	
τ	atomic units +154.	kcal relative to trans	atomic units +154.	kcal relative to trans
0°	−.7428526	(0.0)	−.7460882	(0.0)
90°	−.7329759	6.20	−.7370408	5.68[b]
140°	−.7378561	3.14	−.7415334	2.86[b]
180°	−.7352242	4.79	−.7405824	3.45

[a] Geometry constrained to that observed experimentally for the trans conformer except for torsional angle, τ. [b] Experimental barrier: 5.0 kcal. Experimental difference between trans and other stable conformer: 2.3 kcal. (J. C. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, J. Chem. Phys. 14, 67 (1946).

Table 2. Structures[a] of butadiene conformers

	Experimental		Calculated			
	NMR[b]	ED[b]	0° (trans)	90°	140°	180°
C-C	(1.463)	1.463±0.003	1.463	1.484	1.474	1.473
C=C	(1.341)	1.342±0.002	1.320	1.316	1.319	1.320
C-H	1.080[c]	1.093 ±0.009	1.074	1.075	1.074	1.074
C-H'	1.080	1.093	1.071	1.072	1.071	1.071
C-H''	1.080	1.093	1.073	1.072	1.072	1.072
C-C=C	121.7°	123.6°±0.3°	124.7°	124.4°	125.2°	127.0°
C=C-H'	119.7°	120.9° ±1.2°	121.8°	121.6°	121.5°	121.1°
C=C-H''	126.8°	120.9°	121.8°	121.8°	121.8°	122.7°
C=C-H	116.2°	120.9°	119.6°	119.4°	119.3°	118.2°

[a] Bond lengths in Å, angles in degrees. Angles defined in Fig. 1. The calculated values are those predicted by relaxation of forces on the atoms. Estimated internal accuracy is better than 0.001 Å and 0.1°.

[b] NMR from Ref. 16, electron diffraction r_α^0 structure from Ref. 15.

[c] Values in brackets assumed equal.

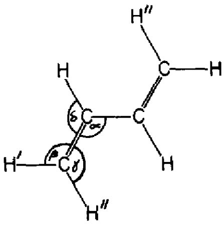

Fig. 1. Labelling of the atoms in butadiene.

calculated *trans* equilibrium structure is seen to be in better agreement with the electron diffraction[15] than with the NMR results,[16] the main discrepancy being the C=C double bonds, which this basis set seems to consistently underestimate by about 0.02 Å.[17] The experimental r_α^0 C–H distances are expected to be longer than the theoretical estimates of r_e because of vibrational averaging. The calculated average of the three C=C–H angles is 121.1°, in very good agreement with the electron diffraction value.

(2) *Structure changes during rotation.* The C–C bond length has its maximum at 90° where the C=C bonds have their minimum value. This correlation shows that resonance delocalization is important in stabilizing the planar *trans* and *cis* forms and in making the rotational barrier larger than that in ethane. The resonance shortening of the single bond is, however, much less (0.02 Å) than that found[12] in HNO_2 (0.07 Å). Mulliken[2] estimated that about 40% of the C–C bond shortening in butadiene relative to ethane (1.532 Å)[18] is due to resonance. The present results indicate that the resonance effect is even smaller.

The calculated C–C bond length of the $\tau = 140°$ conformer (1.474 Å), is very close to the experimental value of the single bonds in cyclooctatetraene where the corresponding angle is about 120°.[8] The C–H bonds vary very little during the rotation.

The C–C=C angles show considerable change—they open up about 3° in the *cis* form, a change which has been noted previously.[9,10] The methylene groups are also tilted outwards by about 1° in the *cis* form and the C–C bond is 0.01 Å longer than in the *trans* form. These changes increase the nonbonded H''... H'' distance from 2.01 to 2.34 Å. The magnitudes and directions of the changes clearly show the importance of nonbonded replusions in destabilizing the crowded *cis* conformer. The facts that the C–C bond is shorter in the *cis* than in the 90° form and that it is not much longer than in the *trans* form indicate, however, that nonbonded interactions are not responsible for sp^2–sp^2 bonds being shorter than sp^3–sp^3 bonds. This is also confirmed by the small differences in bond angles between the *trans* and the 90° forms, although it would be energetically favorable to deform angles rather than bonded distances. The calculations thus support the view that the short C–C bond is due mainly to the intrinsic character of the sp^2 hydridized carbon, although there is no direct way of calculating the hybridization effect.

(3) *Nature of the second stable conformer.* The calculations correctly predict that the most stable form is the *trans* form which is favored both by resonance and nonbonded interactions, whereas the two effects work against each other in the *cis* conformation. The nature of the second stable form, which experiments indicate is present in about 5% abundance[19,20] is difficult to determine. The calculated dipole moment of both the *cis* and the *gauche* conformers is about 0.08 D, explaining why attempts to observe the second stable form by microwave[21] and molecular beam[22] methods have failed. NMR experiments suggest a *gauche* form,[23,24] while vibrational spectroscopic data have been interpreted as indicating either the *gauche*[25] or the *cis*[20] form. Table 1 shows that the *gauche* is clearly more stable than the *cis* if rigid rotation is assumed. With geometry optimization, the difference is reduced to 0.6 kcal, which is not conclusive.

Most semiempirical methods predict the gauche form to be the second stable species, although some have the *cis* lower, and some have the *gauche* more stable then the experimentally observed *trans*.[26,27] Previous *ab initio* calculations all show a very small *cis–gauche* energy difference.[9,10,28,29] Configuration interaction, which has not been included in the present treatment, led to a stabilization of the *cis* conformer relative to the gauche in one report[28] and to just the opposite result in another.[29]

CONCLUSION

The calculations indicate that the main reason for the short C–C bond in butadiene is an intrinsic property of sp^2–sp^2 bonds, but that resonance delocalization is responsible for a minor part of the shortening and for the large rotational barrier. Nonbonded interactions only play a major role in destabilizing the sterically crowded *cis* conformer. The question of whether the second conformer is *cis* or *gauche* is still not resolved, and will probably be settled only by an experimental method that yields direct structural information.

Acknowledgements—This research has been supported by a grant from the Robert A. Welch Foundation. We would also like to express our sincere appreciation to Dr. Peter Pulay for providing us with a copy of program MOLPRO written by Dr. Pulay and Dr. W. Meyers.

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