Highly Substituted 1,3-Dienes, IV[1]

An Experimental and Theoretical Study of the Stereochemical Properties of 2-*tert*-Butyl-1,3-butadiene and 2,3-Di-*tert*-butyl-1,3-butadiene

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The molecular structure and conformation of 2-*tert*-butyl-1,3-butadiene (**1**) and of 2,3-di-*tert*-butyl-1,3-butadiene (**2**) have been studied by the gas electron diffraction method. The monosubstituted compound is observed to have a *gauche* orientation ($\varphi = 32°$) of the conjugated C=C bonds. The forces determining the preferred conformation of this molecule (*syn* or *gauche*) appear to be similar to those operative in the case of the high-energy conformer of unsubstituted 1,3-butadiene. The disubstituted compound has an approximately perpendicular orientation of the C=C−C=C system ($\varphi = 101.5°$), and in this case the preferred orientation is described as a result of minimalization of the nonbonded interactions. − Theoretical calculations of the structure and conformation of the two molecules have been carried out by molecular mechanics (MM3) and by ab initio (HF/3-21G) methods. The results from both sets of calculations are in good agreement with the observed structures of the two compounds.

1. Introduction

1,3-Butadiene is the simplest hydrocarbon where π electron conjugation is present and may be observed, and this compound may therefore be considered as a prototype acyclic conjugated hydrocarbon molecule.

Already in the early days of quantum chemistry the conjugation in 1,3-butadiene was described as a substantial delocalization of its π electrons. This should affect the C−C bond lengths in a characteristic way, as described by Schomaker and Pauling in 1939[2] and by Pauling in his famous book "The Nature of the Chemical Bond"[3]. Pauling and Schomaker's description of the phenomenon of conjugation was based on their gas electron diffraction study of 1,3-butadiene[2], which showed that the central C−C bond length (1.46 Å) was substantially shorter than a normal C−C single bond (1.54 Å), corresponding to a double bond character of 18% of the C^2-C^3 bond. This picture was in general agreement with results from HMO calculations carried out by Coulson for 1,3-butadiene, resulting in a π bond order of 0.447 for the central C−C bond[4].

For a period of 20 years Pauling's description of the relationship between π electron delocalization and the length of the $C_{sp^2}-C_{sp^2}$ bond was generally accepted. In 1959 Dewar and Schmeising challenged this theory and contended that the length of any C−C single bond is determined by the state of hybridization of the carbon atoms involved in the bonding[5]. Since the covalent radius of a sp^2-hybridized carbon atom is smaller than that of a sp^3-hybridized one, they described the short central C−C bond in 1,3-butadiene as being due to the state of hybridization, discarding any influence from π electron delocalization. On the contrary, they assumed that the π electrons in all polyenes were localized to one of the double bonds.

The question of whether the central C−C bond in 1,3-butadiene is determined solely by the covalent radius of the sp^2 carbon atoms, as claimed by Dewar and Schmeising, or if a certain amount of π electron delocalization also has an influence, may be studied experimentally as well as theoretically. Theoretical quantum-chemical calculations may give information about the π electron density distribution, and experimental structure determinations may give information about structure parameters, including bond lengths.

In the following decades numerous experimental[6−9] and theoretical [10−14] structure studies, with increasing degree of accuracy, were carried out for butadienes as well as for linear and for branched polyenes. Two different approaches may be applied in the experimental studies.

a) One may study a molecule with a bond between two sp^2-hybridized carbon atoms that do not have donating π electrons. Bicyclopropyl is a molecule that should approximately fit this description, as the cyclopropyl group is generally considered to be a poor π electron donor, while the magnitude of the NMR CH-coupling constants $^1J_{CH}$ = 160.45 Hz[15] of cyclopropane indicates clearly that the carbon orbitals participating in its C−H-Bonds are sp^2-hybridized[15]. The same result emerges from the observed

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C–H bond length (r_e = 1.083 Å) and the H–C–H bond angle (θ_e = 114.5°)[16]. The central bond in bicyclopropyl is therefore expected to be a "pure" sp^2-sp^2 bond with no or a negligible amount of π electron contribution. The length of such a bond may then be compared to the C^2-C^3 bond in 1,3-butadiene, which is expected to be the shorter one if extensive π electron delocalization is taking place.

b) Another approach is to study the length of the central C–C bond in 1,3-butadiene as a function of the dihedral angle associated with this bond. A conjugative π electron delocalization will be at its optimum in a planar conformation, while it will be absent in a conformation where the two halves of the molecule are orthogonal to one another. The hybridization of the carbon atoms remains the same in these two extreme conformations, while π electron delocalization is possible only in the former one. If π electron delocalization is absent or minimal in planar 1,3-butadiene, torsion around the central C–C bond should not influence the length of this bond.

Studies based on approach a) have been carried out for bicyclopropyl[12,16–19]. The central C–C bond was determined to be 1.499 Å by gas electron diffraction (GED)[16], 1.492 Å from X-ray diffraction[19], and 1.487 by ab initio calculations[12,20]. These results should be compared to similar data obtained for 1,3-butadiene, where the length of the central C–C bond is observed by GED to be 1.467 Å[9] and calculated by the ab initio method to be 1.468 Å[11] or 1.463 Å[14]. The difference in bond length between the two types of $C_{sp^2}-C_{sp^2}$ bonds, ca. 0.02–0.03 Å, may be attributed to π electron delocalization being present in 1,3-butadiene and negligible in bicyclopropyl.

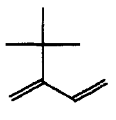
Another stereochemical effect that may be ascribed to the difference in π electron distribution between bicyclopropyl and 1,3-butadiene, as discussed above, is manifested in the conformational behavior of the two molecules. 1,3-Butadiene assumes almost exclusively a planar *anti* conformation[9,11,12], while bicyclopropyl exists in a conformational equilibrium, consisting of about equal parts of *anti* and *gauche* conformers[12,16,21].

The present study represents an attempt to apply approach b) in order to elucidate these problems. Because of the strong tendency of conjugated hydrocarbons to assume a planar *anti* conformation of the conjugated C=C bonds, it is necessary to force the C=C bonds away from their preferred orientation, for example by introducing large substituents such as *tert*-butyl groups. This does of course complicate the structural problem, because sterical strain will simultaneously be introduced into the molecule, and it might prove difficult to separate the effects originating from π electron delocalization and nonbonded repulsion.

In the present work 1,3-butadienes bearing *tert*-butyl groups in 2- and in 2,3-positions have been studied. These derivatives have been chosen because the nonbonded repulsions introduced by *tert*-butyl substituents are in these positions expected to exert a maximum effect on the destabilization of the *anti* conformer of a monosubstituted *resp.* disubstituted 1,3-butadiene molecule.

2. Theoretical Calculations

The two molecules that are being studied here, 2-*tert*-butyl-1,3-butadiene (**1**) and 2,3-di-*tert*-butyl-1,3-butadiene (**2**), are too large for accurate GED determinations, unless some geometric constraints are introduced in order to decrease the number of geometric parameters. Until recently this problem was usually dealt with by assuming parameters – expected to be of similar size – to be equal. A much better alternative is to calculate the structures of such molecules by ab initio methods and subsequently use the obtained structural results as a guide for freezing small geometric differences between similar parameters.



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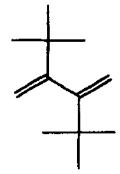

2

dihedral angle (φ) : 32.1° 101.5°

In the present case ab initio calculations were carried out for molecules **1** and **2**, using the program GAUSSIAN 90[22]. The calculations were performed with a CRAY X-MP/28 supercomputer at SINTEF/NTH in Trondheim. The results based on a 3-21G basis set are presented in Table 1.

The two substituted butadienes are also very large molecules for an ab initio study. In order to reduce the computing time all C–C–H angles in the methyl groups were defined by the same valence angle parameter. As some of the methyl groups are heavily involved in the sterical strain present in these molecules, this assumption is certainly not a very accurate one. On the other hand, this assumption is not expected to influence the calculated geometries dramatically.

Molecular mechanics calculations were carried out for both molecules[23]. The MM3 structure parameters calculated for the minimum-energy conformers of **1** and **2** are included in Table 1. In addition to these data MM3 potential energy curves, as a function of the C=C–C=C dihedral angle, were calculated for dihedral angle increments of 15°. The results from these calculations are discussed below.

3. Gas Electron Diffraction (GED) Study: Structure Refinements and Results

The molecular structures of the two sterically hindered butadiene molecules were studied by least-squares refinements on the molecular intensity data. Normal coordinate calculations were carried out for both molecules, based on the valence force field presented in Table 2. The force field is based on data published for other similar molecules[24]. These calculations yielded vibrational amplitudes (u_{ij}) for all interatomic distances as well as the perpendicular correction coefficients (K_{ij}), necessary for carrying out a GED study based on a r_α molecular model which includes corrections for shrinkage effects[25].

Table 1. Structure parameters calculated for 2-*tert*-butyl-1,3-butadiene (**1**) and 2,3-di-*tert*-butyl-1,3-butadiene (**2**) by the ab initio method (AI), using the 3-21G basis set, and by the molecular mechanics (MM3) methods

Dist.(Å)	**AI** **1**	**MM3** **1**	**AI** **2**	**MM3** **2**	**Val.ang.(°)**	**AI** **1**	**MM3** **1**	**AI** **2**	**MM3** **2**
C^1=C^2	1.323	1.350	1.321	1.344	C^1=C^2-C^3	119.6	119.9	118.4	118.1
C^3=C^4	1.318	1.345	1.321	1.344	C^2-C^3=C^4	124.2	124.6	118.4	118.1
C^2-C^3	1.490	1.484	1.510	1.518	C^1=C^2-C^5	124.3	121.9	121.6	120.7
C^2-C^5	1.535	1.527	1.550	1.525	C^2-C^5-C^6	112.0	113.6	110.7	110.9
C-CH_3	1.544	1.546	1.546	1.545	C^2-C^5-C^7	109.7	109.4	112.6	112.1
$C_{sp}2$-H	1.073	1.100	1.073	1.100	C^2-C^5-C^8	108.8	110.1	108.3	109.7
$C_{sp}3$-H	1.084	1.112	1.083	1.112	C^2=C^1-H^1	123.0	122.4	122.8	122.0
Dihedral angles									
C=C-C=C	49.2	27.2	99.1	100.9	C^2=C^1-$H^{1'}$	120.9	121.4	121.4	120.6
C^1=C^2-C^5-C^6	- 4.5	-13.0	47.6	53.3	<C-C-H>	110.6	111.9	110.6	111.9
C^1=C^2-C^5-C^7	115.6	107.3	169.0	173.1	C^3=C^4-$H^{4'}$	121.8	122.1	121.4	120.6
C^1=C^2-C^5-C^8	-124.6	-132.8	-71.7	-67.0	C^3=C^4-H^4	121.6	120.5	122.8	122.0
					C^4=C^3-H	119.2	117.2	-	-

Table 2. Valence force constants [in mdyn $Å^{-1}$ and mdyn Å rad^{-1}] used in the normal coordinate calculations on 2-*tert*-butyl-1,3-butadiene (**1**) and 2,3-di-*tert*-butyl-1,3-butadiene (**2**)

Type	**Valence coord.**	**Value**	**Type**	**Valence coord.**	**Value**
Stretch	C=C	8.733	**Torsion**	C=C	0.249
	C^2-C^3	5.092		C^2-C^3	0.618
	C^2-C^5	4.720		C^2-C^5	0.060
	C-CH_3	4.485		C^5-CH_3	0.100
	$C_{sp}2$-H	5.185	**O.o.pl.**	C=C	0.2532
Bend	C=C-C	1.037	**Str./Str.**	C=C,C-C	0.348
	C^3-C^2-C^5	1.037		C^2-C^5,C-CH_3	0.250
	C^2-C^5-CH_3	0.650	**Str./Bend**	C=C,C=C-H	0.336
	C=C-H	0.582		C=C,C=C-C	0.276
	C-C-H(Me)	0.617			
	H-$C_{sp}2$-H	0.411			
	H-$C_{sp}3$-H	0.550			

For both molecules the vibrational amplitudes for the nonbonded distances were kept fixed at the values calculated from the normal coordinate analyses (see Table 4), while those for the CC and CH bond distances were refined in groups.

Because of the large number of similar internuclear distances in each of the two molecules the GED studies were by no means trivial, and a large number of different sets of approximations and of molecular models were tested for both molecules.

3.1. 2-*tert*-Butyl-1,3-butadiene (1)

Compound **1** is a much smaller molecule than **2**. The number of internuclear distances contributing to the GED scattering pattern is therefore considerably smaller for **1** than in the case of **2**. But because **1** lacks any symmetry, while **2** has a 2-fold axis of symmetry, the number of different geometric parameters necessary for the descripton of the geometry is larger for **1**, and the complexity of a GED study of **1** is accordingly somewhat greater than for **2**. For both molecules the number of independent geometric parameters needed for a complete description of the molecular structure is so large that it is necessary to introduce some assumptions or restrictions among the parameters. Because of the nature of **1** the number of assumptions/restrictions that have to be introduced are expected to be larger for this molecule.

Many different sets of parameters with inherent parameter restrictions were tested in the GED study of **1**. The final GED results are based on a model calculated from the following 11 independent geometric parameters: *Bond lengths*: $C^1{=}C^2$, $C^2{-}C^3$, $C^2{-}C^5$, $C_{sp^3}{-}H$, *valence angles*: $C^1{=}C^2{-}C^3$, $C^1{=}C^2{-}C^5$, $C^2{-}C^5{-}C^8$, C−C−H (Me), $C^2{=}C^1{-}H^1$, *dihedral angles*: C=C−C=C, $C^1{=}C^2{-}C^5{-}C^6$. The numbering of the atoms used in this study is shown in Fig. 2.

Inherent in this model are the following assumptions, which almost exclusively are based on the calculated ab initio results presented in Table 2:

1) $r_a(C^3{=}C^4) = r_a(C^1{=}C^2) - 0.004$ Å, 2) $r_a(C{-}CH_3) = r_a(C^2{-}C^5) + 0.001$ Å, 3) $r_a(C_{sp^2}{-}H) = r_a(C_{sp^3}{-}H) - 0.011$ Å, 4) $\angle C^2{-}C^3{=}C^4 = \angle C^1{-}C^2{-}C^3 + 4.55°$, 5) the $C^2{-}C^5{-}C^6$ and $C^2{-}C^5{-}C^7$ angles are 3.2 resp. 0.88° larger than $\angle C^2{-}C^5{-}C^8$, 6) the $C^3{=}C^4{-}H^4$, $C^3{=}C^4{-}H^{4'}$, and $C^2{=}C^1{-}H^1$ valence angles were assumed to be 0.71, 0.89, and 2.18° larger than $\angle C^2{=}C^1{-}H^{1'}$, 7) the $C^1{=}C^2{-}C^5{-}C^7$ and $C^1{=}C^2{-}C^5{-}C^8$ dihedrals angles were rotated +120 resp. −120° relative to $\theta(C^1{=}C^2{-}C^5{-}C^6)$, 8) local C_{3v} symmetry in the methyl groups, 9) coplanarity of the bonds connected to each of the C=C groups.

This might seem like an unacceptably long list of assumptions, but many of these (1, 2, 3, 6) will not influence significantly the structure parameters that give information about the manner the molecule copes with the unavoidable sterical strain problems. Assumptions 4 and 5 are directly associated with the question of how the sterical strain is distributed within the molecule, but as these assumptions are based on ab initio calculations, and are also in accordance with general knowledge in the field of structural chemistry, the introduction of these assumptions is not expected to seriously reduce the reliability of the experimentally obtained structure results. Assumption 9 is supported by the theoretical calculations, which showed insignificant deviations from coplanarity. Similar theoretical results were obtained for **2**.

The final results obtained from the GED study of **1** are presented in Table 3, while the theoretical molecular intensity curve and the corresponding radial distribution curve calculated for this model are shown in Figures 1 and 2, together with their experimental counterparts.

3.2. 2,3-Di-*tert*-butyl-1,3-butadiene (2)

Also in this case a number of different approaches were tried in order to determine the structural and conformational parameters as accurately as possible. The final results are based on the following 12 independent geometric parameters: *Bond lengths*: C=C, $C^2{-}C^3$, $C^2{-}C^5$, $C{-}CH_3$, C_{sp^3}-H, *valence angles*: $C^1{=}C^2{-}C^3$, $C^1{=}C^2{-}C^5$, $C^2{-}C^5{-}C^8$, C−C−H (Me), $C^2{=}C^1{-}H^{1'}$, *dihedral angles*: C=C−C=C, $C^1{=}C^2{-}C^5{-}C^6$ (see Figure 4 for numbering of the atoms).

The assumptions on which the experimental model is based are similar to those use for **1**, i.e.: 1) Equal $C{-}CH_3$ bond length (this assumption is implicit in assumption no. 2 for molecule **1**), 2) $r_a(C_{sp^2}{-}H) = r_a(C_{sp^3}{-}H) - 0.010$ Å, 3) the $C^2{-}C^5{-}C^6$ and $C^2{-}C^5{-}C^7$ angles are 2.4 resp. 4.4° larger than $\angle C^2{-}C^5{-}C^8$, 4) the $C^2{=}C^1{-}H^1$ valence angle is assumed to be 1.5° larger than $\angle C^2{=}C^1{-}H^{1'}$, 5) the $C^1{=}C^2{-}C^5{-}C^7$ and $C^1{=}C^2{-}C^5{-}C^8$ dihedral angles were rotated +121.5 resp. −119.2° relative to $\theta(C^1{=}C^2{-}C^5{-}C^6)$, 6) local C_{3v} symmetry in the methyl groups, 7) coplanarity of the bonds connected to each of the C=C groups.

The reduced complexity of the GED study of **2** compared to that of **1** is illustrated by the fact that is was possible to determine all four structurally different C−C bonds lengths independently for this molecule, while the number of restrictions connected to the C−C bonds, as well as the number of structurally different bond lengths, is larger for molecule **1**, which has two structurally different C=C bonds.

Table 3. Structure parameters for 2-*tert*-butyl-1,3-butadiene (**1**) and 2,3-di-*tert*-butyl-1,3-butadiene (**2**), as determined by GED least-squares intensity refinements. Distances in Å, angles in degrees, 2 σ in parentheses

	1			**2**		
Bond lengths	$\mathbf{r_a}$	**u**		$\mathbf{r_a}$	**u**	
$C^1{=}C^2$	1.347(3)[a]	0.0485	(27)	1.346(2)	0.0462	(9)
$C^3{=}C^4$	1.343[a]	0.0488		(1.346)	(0.0462)	
$C^2{-}C^3$	1.485(10)	0.0538		1.543(19)	0.0510	
$C^2{-}C^5$	1.535(3)[b]	0.0549		1.519(7)	0.0523	
$C{-}CH_3$	1.545[b]	0.0558		1.545(3)	0.0532	
$C_{sp}2{-}H$	1.098[c]	0.0799	(30)	1.094[d]	0.0773	(14)
$C_{sp}3{-}H$	1.109(3)[c]	0.0817		1.104(2)[d]	0.0791	
Valence angles						
$C^1{=}C^2{-}C^3$	121.7(1.2)[e]			118.3(1.0)		
$C^2{-}C^3{=}C^4$	126.2[e]			(118.3)		
$C^1{=}C^2{-}C^5$	123.0(1.7)			122.8(5)		
$C^2{-}C^5{-}C^6$	113.0[f]			111.0[i]		
$C^2{-}C^5{-}C^7$	110.7[f]			113.0[i]		
$C^2{-}C^5{-}C^8$	109.8(9)[f]			108.6(6)[i]		
C-C-H (Me)	110.8(2.1)[g]			111.5(7)[g]		
$C^2{=}C^1{-}H^{1'}$	122.0(4.3)[h]			121.5(2.7)[j]		
$C^2{=}C^1{-}H^1$	124.2[h]			123.0[j]		
$C^3{=}C^4{-}H^{4'}$	122.9[h]			(121.5)		
$C^3{=}C^4{-}H^4$	122.7[h]			(123.0)		
$C^4{=}C^3{-}H^3$	120.3[h]			-		
Dihedral angles						
C=C-C=C	32.1(9.0)			101.5(3.8)		
$C^1{=}C^2{-}C^5{-}C^6$	-5.8(6.0)[k]			46.1(2.0)[l]		
$C^1{=}C^2{-}C^5{-}C$	114.2[k]			167.6[l]		
$C^1{=}C^2{-}C^5{-}C^8$	-125.8[k]			-73.1[l]		
$\mathbf{R_1}$ (%)	6.09			3.70		
$\mathbf{R_2}$ (%)	10.68			6.16		

[a,b,c,d,e,f,h,i,j,k,l] Parameters combined by the calculated ab initio parameter difference(s). See Table 2. – [g] All C−C−H angles in CH_3 groups assumed to be equal.

Table 3 contains the structure parameters determined for **2**. The theoretical molecular intensity curve and the corresponding RD curve calculated from these parameters are presented in Figures 3 and 4, together with the experimental curves.

4. Discussion

The structure and conformation of each of the two sterically hindered butadienes will first be discussed separately. Thereafter, the structural differences between the two molecules will be commented on.

4.1 2-*tert*-Butyl-1,3-butadiene (1)

The results obtained from the experimental GED study and the ab initio calculations are generally in good agree-

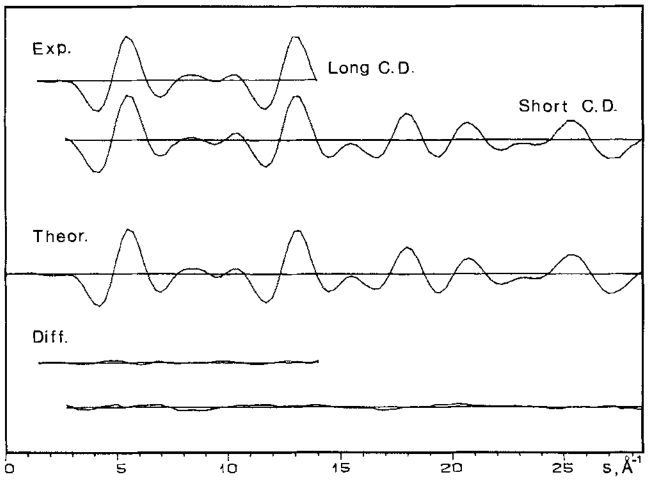

Figure 1. Experimental and theoretical molecular intensities for **1** and the difference curves; the theoretical curve is calculated from the parameters listed in Table 3

ment. The experimental and theoretical studies do both show that the π system in **1** has a nonplanar conformation which is relatively close to *syn*, but which may be more appropriately referred to as *gauche*.

The ab initio calculation gives a $C^2-C^3=C^4$ valence angle that is 4.5° larger than $\angle C^1=C^2-C^3$. This result, which is incorporated as a restriction in the experimental model, is reasonable because an enlarged $C^2-C^3=C^4$ angle will reduce the nonbonded repulsion between the C^1 and C^4 methylene groups for the observed conformation. A similar increase in $\angle C^1=C^2-C^3$ will of course have the same effect, but as an enlargement of this angle would be accompanied by increased nonbonded repulsions between the carbons in positions 1 and 3 and the methyl groups of the *tert*-butyl substituent, the net effect would be increased steric energy.

Table 4, which lists the nonbonded C–C distances for both molecules, shows that there are several nonbonded distances that are shorter than the sum of the van der Waals radii of two carbons, ca. 3.4 Å[3], and these distances will accordingly contribute to an increased van der Waals steric energy. Most of this energy is, however, caused by the repulsions involving the *tert*-butyl groups and the C^1 or C^3 atoms ($C^1\cdots C^6$, $C^3\cdots C^7$, $C^3\cdots C^8$), and is therefore independent of the conformation of the π system of the molecule. The one additional nonbonded C–C distance that contributes significantly to the nonbonded van der Waals repulsion, $C^1\cdots C^4$, is obviously conformation-dependent.

As pointed out in the introduction, a conjugated hydrocarbon will generally prefer an *anti* orientation of the C–C double bonds, unless such a conformation gives rise to increased steric energy, for example due to severe sterical interaction. For molecule **1** an *anti* conformation of the C=C–C=C system will be accompanied by strong repulsions between the C^4 methylene group and the methyl groups centered at C^7 and C^8 in the *tert*-butyl substituents

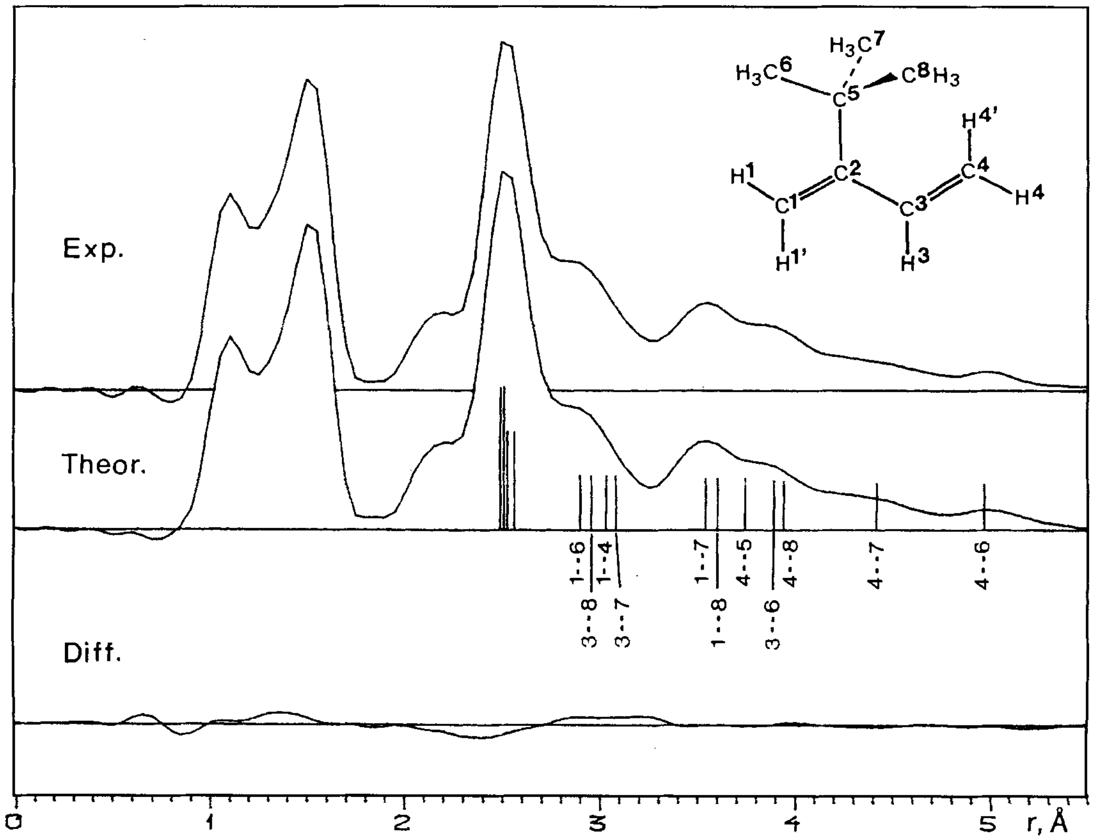

Figure 2. Experimental and theoretical radial distribution curves for **1**; the theoretical curve is calculated from the parameters listed in Table 3. The numbering of the atoms that has been applied is illustrated. The vertical bars indicate the position of the various nonbonded CC distances

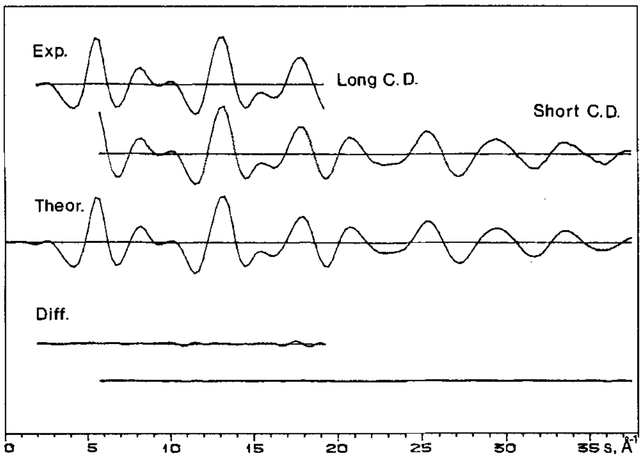

Figure 3. Experimental and theoretical molecular intensities for **2** and the difference curves; the theoretical curve is calculated from the parameters listed in Table 3

and is therefore energetically unfavorable. Similar and probably more severe nonbonded repulsions (see Figure 5) will destabilize a perpendicular relative orientation of the C=C bonds.

For a *syn* orientation of the C–C double bonds the steric repulsions involving C^4 and the *tert*-butyl group will vanish. This is true for all conformers of **1** with a C=C–C=C dihedral angle within the region of ca. ±60°, as the inherent nonbonded repulsions involving the vinyl group and the *tert*-butyl substituent in such cases will be negligible. The preferred conformation of the π system of **1** must therefore be governed by the same factors that are primarily responsible for the preferred conformation of the high-energy conformer of 1,3-butadiene, namely the torsional potential at the $C^2–C^3$ bond and the nonbonded repulsions between the C^1 and C^4 methylene groups. The influence of the size of the C=C–C angles is implicit in the latter factor.

In 1,3-butadiene the concentration of the high-energy form is very small, and it is accordingly difficult to study the structure of this conformer experimentally. Many studies, experimental[26–31] as well as theoretical[13,32–37] have, however, been aimed at trying to establish the nature of this conformer, and there have been many discussions about whether the metastable form of 1,3-butadiene has a planar *syn* or a nonplanar *gauche* conformation. The Raman spectrum of 1,3-butadiene, especially the part that belongs to the single-bond torsional mode, has been analyzed to obtain structural information about the high-energy second conformer. Unfortunately, the portion of the spectrum recorded appears to be compatible with both structures[26,27]. Polarized IR spectra of the matrix-isolated metastable conformer provides strong evidence in favor of a planar *syn*

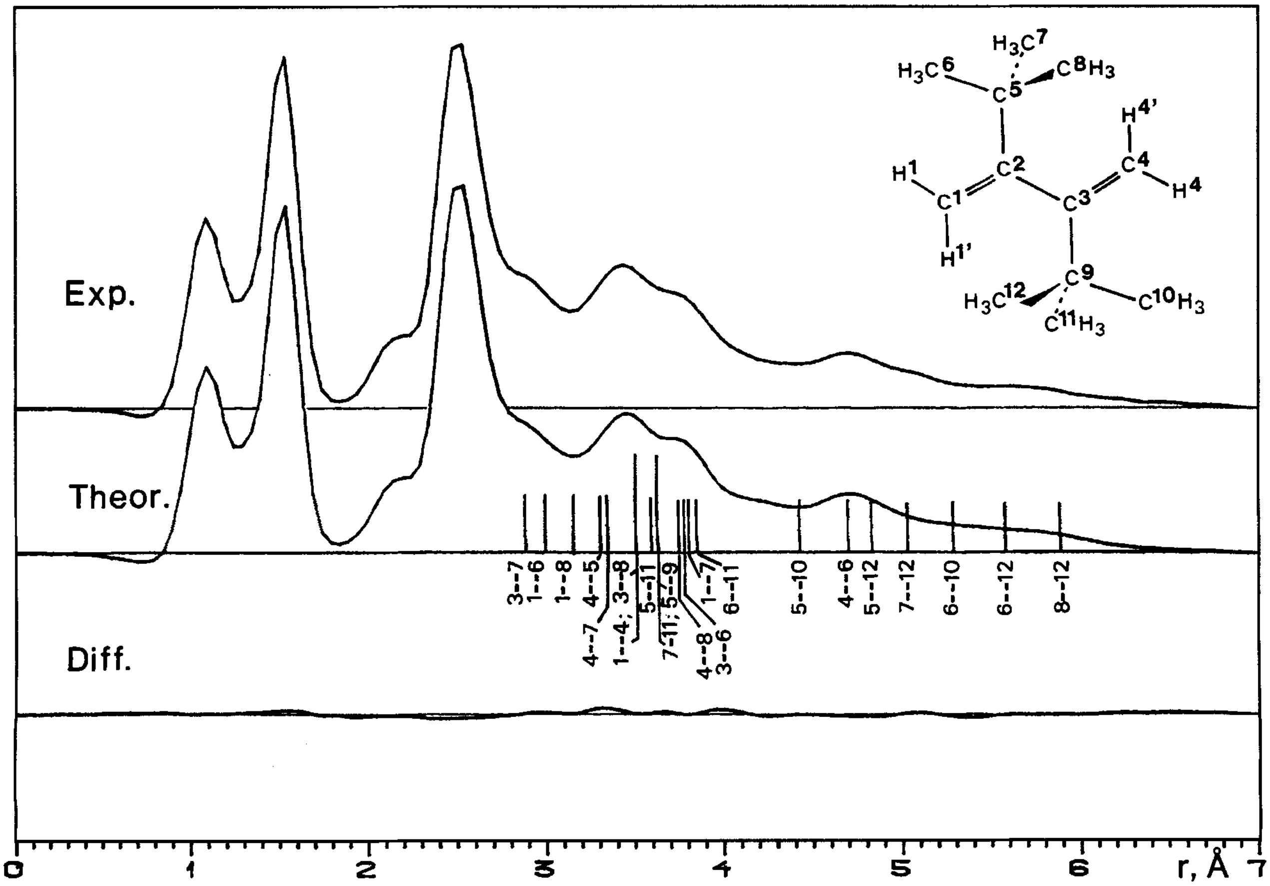

Figure 4. Experimental and theoretical radial distribution curves for **2**; the theoretical curve is calculated from the parameters listed in Table 3. The numbering of the atoms that has been applied is illustrated. The vertical bars indicate the position of the various nonbonded CC distances

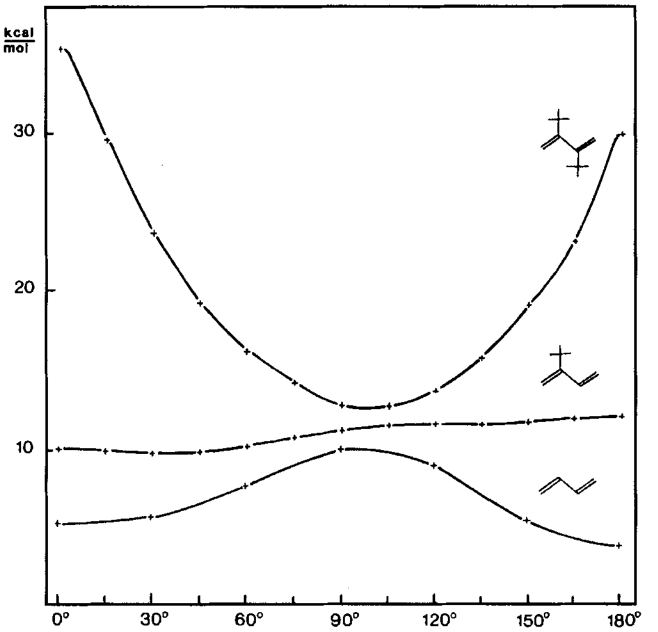

Figure 5. Potential energies of **1** and **2** and 1,3-butadiene as function of the C=C−C=C dihedral angle. The data are based on MM3 calculations[24]

structure[30,31]. Theoretical quantum-chemical calculations using a large basis set do, however, all indicate that a *gauche* structure, characterized by a torsional angle between 30 and 41° is energetically favored over a planar *syn* structure by about 4 kJ/mol[32−37].

The observed conformation of **1**, which is determined by the same factors as those operative in the high-energy form of 1,3-butadiene, is of special interest because in this case it represents a minimum-energy conformer, which can be determined with a high degree of accuracy. The observed conformation for **1** supports the view that *gauche* is the preferred conformation also for the metastable conformer of 1,3-butadiene.

4.2. 2,3-Di-*tert*-butyl-1,3-butadiene (2)

Also for this molecule there is a fairly good agreement between the structural results obtained from the experimental GED and theoretical ab initio calculation studies. Both investigations show that the π system adopts an approximately perpendicular conformation with no conjugation between the two C−C double bonds. This is not a surprising result, as the same effects that destabilize an *anti* conformation in **1** will be even more dominating in the case of **2**, as this molecule bears a *tert*-butyl group in the 3- as well as in the 2- position. For this molecule a *gauche* conformation, similar to that observed for **1**, is unattainable because a *gauche* conformer of **2** would be even more destabilized than an *anti* one due to very strong nonbonded repulsions between the two *tert*-butyl substituents, which would practically overlap. The conformation of the π system must therefore be determined by the nonbonded repulsions, and the preferred C=C−C=C dihedral angle will almost exclusively be a result of minimization of the van der Waals steric energy. The agreement between the calculated (ab initio: 99.1°; MM3: 100.9°) and observed (101.5 ± 3.8°) C=C−C=C dihedral angle is excellent. Compound **2** was studied in the solid phase by Roth et al.[38]. Their results are generally in good agreement with our gas-phase data, and their observed C=C−C=C dihedral angle is 96.6°[38].

Table 4. Nonbonded CC distances (r_a, Å) obtained from the GED studies and their calculated vibrational amplitudes (in Å)

2-*tert*-Butyl-1,3-butadiene (1)							
1,3	$C^1.C^5$	2.531	0.0638	**1,4**	$C^1..C^6$	2.894	0.1310
	$C^1.C^3$	2.475	0.0624		$C^1..C^7$	3.538	0.1265
	$C^6.C^8$	2.486	0.0865		$C^1..C^8$	3.603	0.1200
	$C^6.C^7$	2.478	0.0865		$C^3..C^6$	3.896	0.0807
	$C^7.C^8$	2.506	0.0865		$C^3..C^7$	3.097	0.1661
	$C^2.C^7$	2.529	0.0833		$C^3..C^8$	2.967	0.1653
	$C^2.C^8$	2.514	0.0834		$C^1..C^4$	3.033	0.1203
	$C^2.C^4$	2.504	0.0621		$C^4..C^5$	3.741	0.1001
	$C^2.C^6$	2.566	0.0830				
	$C^3.C^5$	2.545	0.0722	**1,5**	$C^4..C^8$	3.950	0.2373
					$C^4..C^7$	4.408	0.1687
					$C^4..C^6$	4.978	0.1143
2,3-Di-*tert*-butyl-1,3-butadiene (2)							
1,3	$C^1.C^5$	2.517	0.0631	**1,4**	$C^1..C^6$	2.985	0.1434
	$C^1.C^3$	2.479	0.0611		$C^1..C^7$	3.809	0.0857
	$C^6.C^8$	2.519	0.0867		$C^1..C^8$	3.156	0.1497
	$C^6.C^7$	2.501	0.0867		$C^3..C^6$	3.790	0.1063
	$C^7.C^8$	2.506	0.0867		$C^3..C^7$	2.885	0.1414
	$C^2.C^6$	2.515	0.0824		$C^3..C^8$	3.553	0.1503
	$C^2.C^7$	2.556	0.0823		$C^1..C^4$	3.351	0.1225
	$C^2.C^8$	2.490	0.0823		$C^4..C^5$	3.306	0.1518
	$C^2.C^9$	2.630	0.0677		$C^5..C^9$	3.624	0.1595
1,5	$C^4...C^6$	4.702	0.1382	**1,6**	$C^6....C^{10}$	5.289	0.3070
	$C^4...C^7$	3.336	0.3121		$C^6....C^{11}$	3.855	0.3791
	$C^4...C^8$	3.758	0.2567		$C^6....C^{12}$	5.581	0.2890
	$C^5...C^{10}$	4.422	0.2284		$C^7....C^{11}$	3.618	0.5665
	$C^5...C^{11}$	3.596	0.3075		$C^7....C^{12}$	5.030	0.2810
	$C^5...C^{12}$	4.830	0.1713		$C^8....C^{12}$	5.892	0.1531

There is another anomaly worth commenting upon in the structure of **2**. While the *tert*-butyl substituent in **1** was observed to have a normal orientation relative to the substituted C−C double bond with one of the methyl groups approximately eclipsing this bond, the experimental as well as the theoretical study of **2** show that its *tert*-butyl groups are rotated by 40−50° relatively to the orientation observed for the *tert*-butyl group in **1**. This orientation of the substituent groups in **2** is expected to correspond to nearly maximum torsional energy at the $C_{sp^2}-C_{sp^3}$ bonds. Inspection of a perpendicular molecular model of **2** shows that if one

Table 5. Experimental conditions for recording the GED data of 2-*tert*-butyl-1,3-butadiene (**1**) and 2,3-di-*tert*-butyl-1,3-butadiene (**2**)

	1		**2**	
Apparatus	Balzer`s [44,45]		Oslo [46]	
Nozzle-to-plate dist. (mm)	496.73	246.81	48	23
Nozzle temperature (K)	297	297	346 - 358	
Elect. wavelength (W.l) (Å)	0.058720	0.058720	0.063820	0.063820
W.l. calibrated against	Benzene		Benzene	
No. of plates	5	5	6	7
Sector number	x	x	x	x
Type of plates[a]	KEI	KEI	KEI	KEI
Data range				
s_{min} (Å^{-1})	1.50	2.75	1.25	5.75
s_{max} (Å^{-1})	14.00	28.50	19.75	39.00
νs (Å^{-1})	0.25	0.25	0.25	0.25

[a] KEI: Kodak Electron Image.

methyl group is eclipsing each of the C−C double bonds, two of methyl groups − one from each *tert*-butyl substituent − will be very close to one another giving rise to strong nonbonded repulsions. The observed orientation of the *tert*-butyl groups reduces the nonbonded repulsions between the two methyl groups. It is of interest to note that the same orientation of the *tert*-butyl substituents was observed also in the solid state[38]. The distortion of the substituents of **2** in the crystal is therefore hardly a result of crystal packing forces.

From the list of nonbonded C−C distances in Table 4 it will be seen that three types of nonbonded C−C distances ($C^1\cdot\cdot C^6$, $C^1\cdot\cdot C^8$, $C^3\cdot\cdot C^7$) are substantially smaller than the sum of the van der Waals radii of two carbon atoms. These are, however, due to interactions between the *tert*-butyl substituents and their vicinal carbon atoms, and are accordingly independent of the conformation of the π system. Among the conformation-dependent CC distances there are three ($C^4\cdot\cdot C^7$, $C^1\cdot\cdot C^4$, $C^4\cdot\cdot C^5$) that are slightly smaller than the optimum van der Waals distance. In the observed conformation the nonbonded repulsion between the two *tert*-butyl substituents is therefore negligible, and the conformation appears to be the result of a very delicate balance between forces involving the various structural parameters in order to avoid such repulsions.

4.3. Comparison and General Discussion

The accuracy of the experimental structure parameters for **2** is higher than that observed for **1**. This is primarily due to three factors: a) The scattering range is larger for **2** than for **1** (see Table 5), b) the lower symmetry of **1** requires more structure parameters for the definition of its geometry, and c) the potential energy well for C^2-C^3 rotation is much steeper for **2** than for **1**.

The difference in accuracy is manifested in the standard deviations of the observed molecular parameters, in the *R* factors (see Table 3) and is also apparent from the difference curves between experimental and theoretical intensity curves (see Figures 1 and 3) and radial distribution curves (Figures 2 and 4). These circumstances do, however, not imply that the structural results observed for **1** are unreliable.

Figure 5 shows the calculated (MM3[23]) potential energy curves for **1** and **2** as a function of the C=C−C=C dihedral angle. The corresponding curve for 1,3-butadiene is shown for comparison. The curves clearly illustrate that the sterical problems in the case of **2** are much more severe than those in the case of **1**, and that the nearly perpendicular conformation is the only possible one for **2**.

For **1** the MM3 calculations give a minimum potential energy for a C=C−C=C dihedral angle of 27.2°, in qualitative agreement with the experimental GED result (32.1°) and with the ab initio calculations (49.2°). The calculated energy difference between the *syn*/*gauche* and the *anti* conformation for this molecule is of similar absolute magnitude as the calculated energy difference between the same conformers of 1,3-butadiene, but in the case of **1** the low-energy conformer is *gauche*, while the stable conformer of 1,3-butadiene is *anti*.

One of the aims of the present study was to elucidate the influence of π electron delocalization on the C^2-C^3 bond length. Neither **1** nor **2** have an optimal conformation for maximum π electron overlap and maximum π electron delocalization. The conformation of **1** does, however, allow for a certain degree of π electron delocalization. As a crude estimate one might assume that the π electron density of the C^2-C^3 bond is proportional to cos²(C=C−C=C). Accordingly the π electron density of **1** should be about 70% of that in planar 1,3-butadiene, while it should be negligible in **2**. From the calculated and observed differences between the $C_{sp^2}-C_{sp^2}$ bond lengths in 1,3-butadiene (1.468 Å) and bicyclopropyl (1.499 Å) the effect originating from π electron delocalization in 1,3-butadiene is estimated to be about 0.02 Å. The effect resulting from π electron delocalization on the C^2-C^3 bonds in **1** and **2** is expected to be somewhat smaller. The observed C^2-C^3 bond lengths in **1** and **2** differ by 0.058 Å, and the sum of the estimated error limits of the two bonds is 0.029 Å. The magnitude of the observed difference of the two C^2-C^3 bonds therefore indicates that the central C−C bond in **2** is elongated also because a long C^2-C^3 bond will contribute to a reduction of the nonbonded repulsions between the two halves of the molecule. We estimate that the two types of influence, reduced π electron delocalization and nonbonded repulsions, have about equal effects on the elongation of the C^2-C^3 bond in **2**, relative to that in **1**.

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Experimental

2,3-Di-tert-butyl-1,3-butadiene (**2**) was synthesized according to the method of Brandsma[39].

2-tert-Butyl-1,3-butadiene (**1**) was synthesized earlier[40,41], but in the present study a different procedure, analogous to the one used by Djahanbini for the synthesis of other monosubstituted 1,3-dienes from 2,3-butadien-1-ol, was chosen[42]. – Preparation: 8.2 ml of *tert*-butyl chloride was dissolved in 40 ml of THF and allowed to react with 1.82 g (75 mmol) of magnesium turnings to give the Grignard compound. 1.08 g (7.5 mmol) of CuBr was added, and the mixture was stirred for 5 min. Then 10.31 g (50 mmol) of the phosphate formed by the reaction of 2,3-butadien-1-ol with diethyl chlorophosphate was dissolved in 40 ml of THF, and the obtained solution was added dropwise. The mixture was stirred first for 2 h at 0°C, then for 12 h at room temp. Subsequently 100 ml of a NH_4Cl solution was added, and the organic phase was extracted with a 1 N NH_4Cl solution. In order to improve separation in the distillation process, 50 ml of pentane was added, and THF was removed by repeated (10 times) washing with water. Subsequent distillation gave 3.8 g of a fraction with b.p. 100°C (b.p. of 2-*tert*-butyl-1,3-butadiene was reported to be 100°C[41]). In accordance with the synthesis of other monosubstituted 1,3-butadienes by this method, the distillate contained ca. 10% of the Grignard coupling product 2,2,3,3-tetramethylbutane (bi-*tert*-butyl), which could not be removed by distillation. The pure compound was isolated by preparative gas chromatography (SE-30). Since the NMR data for **1** have not been reported in the literature, they are included here: ^1H NMR (400 MHz): $\delta = 6.42$ (dd, $^3J_{cis} = 10.8$, $^3J_{trans} = 17.1$ Hz, 1H, 3-H), 5.39 (dd, $^3J_{trans} = 17.1$, $^2J = 2.2$ Hz, 1H, 4-H_a), 5.06, 4.79 (both m, each 1H, 1-H), 5.01 (dd, $^3J_{cis} = 10.8$, $^2J = 2.2$ Hz, 1H, 4-H_b), 1.09 (s, 9H, 6-H). – ^{13}C NMR (100.6 MHz): $\delta =$ 156.75 (s, C-2), 137.03 (d, C-3), 114.6, 107.16 (tt, C-1/4), 34.99 (s, C-5), 29.30 (q, C-6).

GHD Data Reduction: The experimental conditions used for recording the GED data are summarized in Table 5. The calculations of the scattering amplitudes and phases, the data reduction and the corrections to the $s/|f_c'|^2$-modified molecular intensities were carried out as described in ref.[43]. A diagonal weighting scheme was applied, and the standard deviations should be augmented by a factor of two to account for data correlation. The experimental molecular intensity curves and the corresponding radial distribution (RD) curves are shown in Figures 1–4.

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