Highly Substituted Dienes and Polyenes, IX[◇]

The Molecular Structure of 4-*tert*-Butyl-5,5-dimethyl-1,3-hexadiene (1,1-Di-*tert*-butyl-1,3-butadiene)☆

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Received August 8, 1997

Keywords: Dienes, conjugated / Dienes, highly substituted / Conformation analysis / Steric hindrance / Ab initio calculations

The highly strained hydrocarbon 4-*tert*-butyl-5,5-dimethyl-1,3-hexadiene (**3**) has been prepared and its molecular structure and conformation have been studied experimentally by the gas-electron diffraction method and by theoretical ab initio (HF/6-31G*) calculations. The 1,3-diene skeleton assumes an *anti* conformation, and the sterical strain primarily manifests itself in the following structural details: The butadiene C=C−C angle on the substituted side is larger than normal (GED: 128.2°; HF/6-31G*: 132.7°); the Z-oriented *tert*-butyl group is rotated to a nearly staggered position relative to the C1=C2 double bond, forming a cogwheel system together with the other *tert*-butyl group, which has the normal eclipsed conformation relative to C1=C2; the $C1-C_{tBu}$ and $C-CH_3$ bonds are both elongated compared to those in unstrained compounds, and the formally $C(sp^2)-C(sp^3)$ $C1-C_{tBu}$ bonds are longer than the formally $C(sp^3)-C(sp^3)$ ones in the methyl groups.

Among the nine possible di-*tert*-butyl-substituted 1,3-butadienes semiempirical calculations show that the 1,1-substituted isomer, 4-*tert*-butyl-5,5-dimethyl-1,3-hexadiene (**3**), to be abbreviated D11BD here, is clearly the sterically most strained one[2]. The calculated energy difference between the minimum energy conformer of D11BD and that of the isomer with the second highest potential energy, (3*Z*)-3-*tert*-butyl-5,5-dimethyl-1,3-hexadiene (*Z*-D12BD), is ca. 35 kcal mol^{-1}. The energy differences to the other di-*tert*-butyl-substituted 1,3-butadienes are estimated to be in the 68−88 kcal mol^{-1} region. Even though the calculated strain energies for the conformers of each molecule are not very accurate, there is no doubt that they give a qualitatively correct description of the sterical strain in these molecules, and that **3** is sterically considerably more strained than any of the other di-*tert*-butyl-1,3-butadiene isomers.

When two *tert*-butyl groups are bonded to the same carbon atom in a molecule nonbonded repulsions between the two substituent groups will be very large, if normal geometry parameters are to be preserved. This is the case whether the substituted carbon atom is saturated ("sp^3-hybridised") or unsaturated ("sp^2-hybridised"), although the strain is expected to be largest in the case of a saturated carbon atom, because of the smaller reference $C_{tBu}-C-C_{tBu}$ angle, which forces the substituents closer together. It is, however, well known that it is generally energetically favourable for a sterically strained molecule to distribute the strain in small portions over the entire molecule, rather than concentrating it in one particular type of sterical strain, such as nonbonded repulsions. The structures of *gem*-di-*tert*-butyl organic compounds are therefore expected to show unusual structural parameters as a result of distributing the total sterical strain as effectively as possible.

The molecular structure of gaseous di-*tert*-butylmethane has been studied by Bartell and Bradford[3]. In this molecule the most dramatic effect of the sterical strain is manifested in an unusually large $C_{tBu}-C-C_{tBu}$ angle of 128.0(6.0)°. In addition there are other smaller geometrical effects that may be attributed to the two *gem*-di-*tert*-butyl substituents, such as a slightly elongated average C−C bond length [1.545(5) Å], as for example that in neopentane[4] (1.537 Å), and torsional displacements [15.1(6.0)°] of the two *tert*-butyl groups relative to staggered orientation.

The molecular structure of tri-*tert*-butylmethane has also been studied[5]. In this hydrocarbon the sterical strain cannot be relieved primarily by increasing the $C_{tBu}-C-C_{tBu}$ angle, as in the case for di-*tert*-butylmethane, because of the additional steric repulsion from a third *tert*-butyl group.

[◇] Part VIII: Ref.[1].

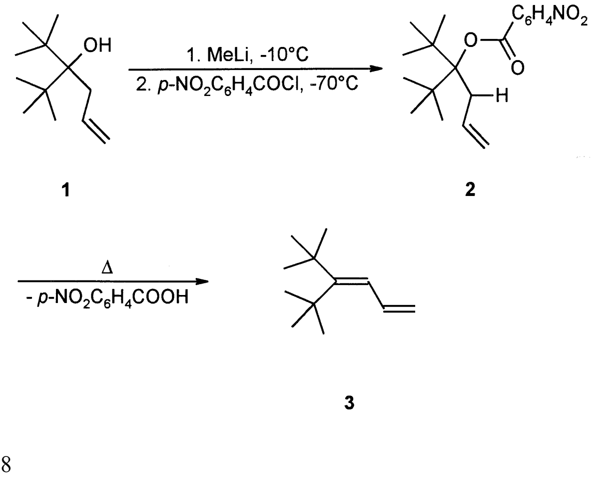
The $C_{tBu}-C-C_{tBu}$ angle is found to be somewhat enlarged (116.0°), but the most noticeable effect of the sterical strain is manifested in $C-C_{tBu}$ bond lengths of 1.611(5) Å, which are the longest reported by electron diffraction for an acyclic hydrocarbon. The extreme congestion is also reflected in the average $C_{Me}-C-C_{Me}$ and $C-C_{Me}-H$ angles of the *tert*-butyl groups [105.7(0.2) and 114.2(1.0)°, respectively].

The purpose of the present investigation is to study on the one hand the distribution of steric strain caused by two *tert*-butyl substitutents bonded geminally to an unsaturated carbon atom, and on the other hand its effect on the structure and conformation of the 1,3-diene skeleton. It is of interest to note that in spite of numerous efforts, nobody has so far succeeded in synthesising the doubly *gem*-di-*tert*-butyl-substituted unsaturated molecule, tetra-*tert*-butylethene[6][7][8][9][10][11]. This molecule is structurally related to **3**, but is of course additionally strained due to steric interference between the two pairs of *cis*-1,2-di-*tert*-butyl substituents across the double bond. Another molecule, that may be considered as derived from tetra-*tert*-butylethene, by pairwise connecting a methyl group from each of the two *gem* substituents, is bi(2,2,5,5-tetramethylcyclopentylidene). The formation of the two five-membered rings reduce the sterical strain, and this molecule has been synthesised[12].

Synthesis and Gas-Electron Diffraction

Synthesis: The hydrocarbon **3** was prepared by dehydration of the known homoallyl alcohol **1**[13]. After numerous unsuccessful attempts – application of the classical dehydration reagents (inter alia *p*-toluenesulfonic acid, thionyl chloride in pyridine, heating in hexamethylphosphoric acid triamide) resulted in the formation of isomers of **3** – the following indirect route finally yielded the desired D11BD. Treatment of the alcohol **1** with methyllithium in diethyl ether and quenching of the formed alkoxide with *p*-nitrobenzoyl chloride at −70°C provided the ester **2** in 77% yield. When this was subjected to ester pyrolysis at 160°C the diene **3** was produced in 80% yield. Structure proof of both **2** and **3** rests on the usual analytical and spectroscopic data which are given in the Experimental Section.

Scheme 1. Preparation of 4-*tert*-butyl-5,5-dimethyl-1,3-hexadiene (D11BD, **3**)



Gas-Electron Diffraction Recordings: Electron-diffraction diagrammes were recorded with a Balzer's Eldigraph KD-G2 unit[14][15] using an r^3 sector and Kodak Electron Image plates. The nozzle tip temperature was 42.0°C during the experiments. The electron-diffraction wavelength was 0.058720 Å, as calibrated against the diffraction pattern of benzene. Electron-diffraction photographs were recorded at nozzle-to-plate distances of 498.46 mm (5 plates) and 248.64 mm (6 plates). The 25-cm plates were of relatively inferior quality, and one of the plates had to be discarded. The outer part of the 25-cm data were especially noisy, and the outer s limit was therefore set to 21.75 cm^{-1}. The experimental data were treated in the usual way[16], and the modification function used was $s \cdot f_C{}^{-2}$. The complex scattering factors by Ross et al.[17] were used, and the inelastic factors were those of Tavard et al.[18] The experimental molecular intensity curve is presented in Figure 1.

Structure Study; Results and Discussion

Theoretical Calculations: Ab initio optimisation calculations were carried out on D11BD, using the GAUSSIAN94 programme package[19], at the HF/6-31G* level. Less advanced calculations of the molecular structure and torsional potential of D11BD have earlier been carried out[2], using Allinger's MM3 programme[20]. As these calculations indicate that the D11BD potential energy curve has a well-defined minimum at *anti* orientation, a fully optimised HF/6-31G* calculation was carried for the *anti* conformer. Because of the relatively large size of the D11BD molecule these types of calculations are very demanding on the computational resources. The D11BD torsional potential was therefore studied by optimising only selected molecular parameters [$\angle C1=C2-C3$, $r(C1-C5)$, $r(C1-C)$], fixing the other parameters at the values obtained for the *anti* conformer, while the C=C−C=C dihedral angle was kept fixed in the region 0−180°, at intervals of 30°. The calculated relative potential energies [kcal mol^{-1}] along the torsional potential were: 180°: 0.0; 150°: +2.5; 120°: +4.1; 90°: +5.1; 60°: +13.0; 30°: +22.9; 0°: +22.4. The energy differences are probably somewhat too large because the reference structure (180°) has been fully optimised, while the structure of the other conformers were only partly optimised.

Selected structural parameters for the D11BD *anti* conformer, as obtained from the HF/6-31G* optimisation, are presented in Table 1, while the short nonbonded distances, as well as some structural parameters of relevance to these interactions, are given in Table 2. The numbering of the atoms is shown in Scheme 2. In order to facilitate the readability of the molecular model only the hydrogen atoms at C2 and C3 are included, in addition to the carbon atoms.

The vibrational amplitudes and shrinkage corrections, necessary for an electron-diffraction study, were for all interatomic distances in D11BD calculated using the programme ASYM40[21]. The cartesian force constants calculated by the GAUSSIAN94 programme at the HF/3-21G level were used as an initial force field. The scaling constants introduced in order to compensate for the well-

Figure 1. Experimental and theoretical molecular intensities of **3** and the differences between the two curves

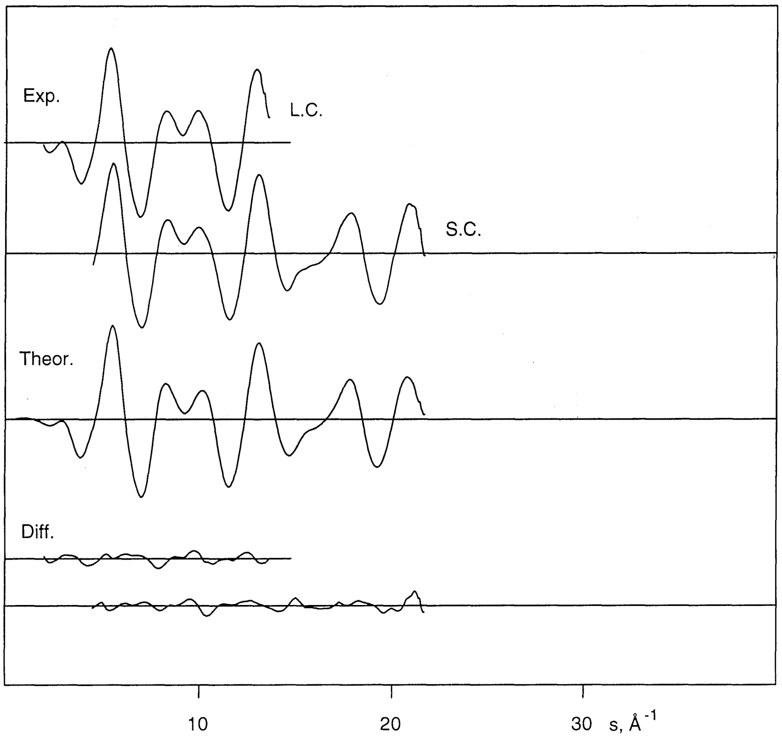


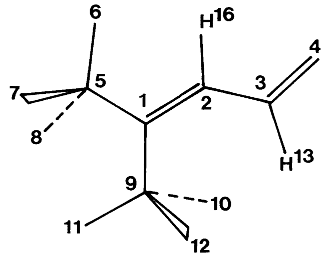
Table 1. Selected molecular structure parameters obtained for D11BD (**3**) by ab initio optimisation calculations (HF/6-31G*); distances in Å, angles in °

$C1=C2$	1.3381	$C1-C5-C6$	112.8
$C3=C4$	1.3246	$C1-C5-C7$	110.0
$C2-C3$	1.4750	$C1-C5-C8$	113.1
$C1-C5$	1.5621	$C1-C9-C10$	110.1
$C1-C9$	1.5680	$C1-C9-C11$	117.5
$C-CH_3$	1.5451−1.5481	$C1-C9-C12$	109.2
		$C2=C1-C5-C6$	−7.1
		$C2=C1-C5-C7$	110.2
$C1=C2-C3$	132.7	$C2=C1-C5-C8$	−126.0
$C2-C3=C4$	121.9	$C2=C1-C9-C10$	54.5
$C2=C1-C5$	117.0	$C2=C1-C9-C11$	172.3
$C2=C1-C9$	120.4	$C2=C1-C9-C12$	−67.6
$C1=C2-16H$	117.6	$C5-C1-C9$	122.5
$C3-C2-16H$	109.7		
$C2-C3-13H$	120.5		
$C4=C3-13H$	117.6		

Table 2. Short nonbonded distances in D11BD (**3**) and some relevant geometrical parameters from the optimised ab initio model

	Interacting groups	
tert-butyl ··· *tert*-butyl	*tert*-butyl ··· vinyl (*Z*)	*tert*-butyl ··· 16H (*Z*)
(C7)21H···30H(C11): 1.96 Å	C3···C10: 3.16 Å	16H···C6: 2.25 Å
(C8)25H···31H(C11): 2.06 Å	C3···C12: 3.33 Å	16H···18H: 2.01 Å
∠C5−C7−21H: 113.6°	13H···C10: 2.77 Å	16H···19H: 2.15 Å
∠C5−C8−25H: 113.6°	13H···C12: 2.83 Å	
∠C9−C11−30H: 114.3°		
∠C9−C11−31H: 112.3°		

Scheme 2. Simplified molecular model of **3**, showing the numbering of the carbon atoms and the hydrogen atoms at C2 and C3



known overestimation of the calculated frequencies, due to neglect of electron correlation, were set equal to 0.893[22].

The GED Study: D11BD is a large and complicated molecule for a GED study, especially since there is no symmetry in the molecule. It is therefore not possible to determine all structure parameters independently, and some assumptions about the structure are required. The theoretical calculations are of great help in this respect. In the present study the following assumptions have been made, based on the theoretical HF/6-31G* optimisation results: a) The differences between the three $C1-C5-CH_3$ angles are set equal to those calculated, using the smallest angle ($C1-C5-C7$) as a parameter. The $C1-C9-CH_3$ angles are treated similarly, and here also the smallest angle ($C1-C9-C12$) is used as a parameter. b) All $C-C-H_{Me}$ and $C=C-C-H$ angles were fixed at the calculated values. c) The differences within each of the two sets of $C2=C1-C-CH_3$ dihedral angles are fixed at the calculated values; the differences were close to ± 120°. d) All $C-CH_3$, $C(sp^3)-H$ and $C(sp^2)-H$ bonds, respectively, were set equal.

When these approximations were introduced in the D11BD molecular model, 18 parameters are necessary to describe the geometry of the model, namely: *8 bond lengths:*

C2−C3, C1=C2, Δ[(C1=C2) − (C3=C4)], C1−C5, Δ[(C1−C9) − (C1−C5)], C−CH_3, C(sp^3)−H and C(sp^2)−H; *7 valence angles:* C1=C2−C3, C2−C3=C4, C2=C1−C5, Δ[(C2=C1−C5) − (C2=C1−C9)], C1−C5−C7, C1=C2−H and H−C4−H; *3 dihedral angles:* C1=C2−C3=C4, C2=C1−C5−C6 and C2=C1−C9−C10.

The molecular structure of **3** has been determined by GED from least-squares refinements of the molecular intensity data, in combination with information obtained from the RD curve. Vibrational amplitudes (u_{ij}) and perpendicular correction coefficients (K_{ij}) for all 306 interatomic distances (ignoring all H−H distances except the 1,3 distances) were calculated by ASYM40, as described above. The geometry of the molecule was based on an r_α molecular model, which includes corrections for shrinkage effects[23]. The two bond-length differences Δ[(C1=C2) − (C3=C4)] and Δ[(C1−C9) − (C1−C5)] were, however, introduced in the r_a model, as the ab initio r_e and the GED r_a differences are expected to be comparable, while the r_α differences might be substantially influenced by the perpendicular amplitude vibrations. This may be illustrated by the shrinkage corrections for r(C1=C2) and r(C3=C4) which amount to 0.0036 Å and 0.0575 Å, respectively.

Because of the combined effects of the relatively poor quality of the short camera GED experimental data and the complexity of the molecular structure, it was not straightforward to arrive at unambiguous GED structural results for this molecule. As described above, information from the ab initio calculations, especially those describing the positions of the hydrogen atoms, have been incorporated in the GED model. The majority of the parameters describing the carbon skeleton have, however, been determined from the GED data, as shown in Table 3.

Table 3. Structure parameters from the GED study of D11BD (**3**); distances (r_a) in Å, angles in °[a]

C1=C2	1.380(6)	C1−C5−C6	112.3
C3=C4	1.366	C1−C5−C7	109.5(1.0)
C2−C3	1.533(22)	C1−C5−C8	112.6
C1−C5	1.557(12)	C1−C9−C10	(110.2)
C1−C9	1.563	C1−C9−C11	(117.0)
C−CH_3	1.551(6)	C1−C9−C12	(109.2)
C(sp^3)−H	1.122(14)	C2=C1−C5−C6	−1.1(3.2)
C(sp^2)−H	(1.095)	C2=C1−C5−C7	116.2
C1=C2−C3	128.2(1.6)	C2=C1−C5−C8	−120.0
C2−C3=C4	121.2(2.1)	C2=C1−C9−C10	44.2(2.1)
C2=C1−C5	116.1(6)	C2=C1−C9−C11	162.0
C2=C1−C9	119.5	C2=C1−C9−C12	−77.9
		C1=C2−C3=C4	−192.5(15.1)
C1=C2−H16	(117.6)		
C3−C2−H16	(109.7)		
C2−C3−H13	(120.5)		
C4=C3−13H	(117.6)		

[a] Parameters in parentheses are kept constant; parameters without standard deviations in parentheses are tied to a similar parameter, as described in the text.

There is generally good agreement between the experimental structure parameters and those from the HF/6-31G* optimisation. The experimental and final theoretical molecular intensity functions are shown in Figure 1, while the corresponding radial distribution curves are presented in Figure 2. The two theoretical curves were calculated from the parameters listed in Table 3. Because of the large number of C−C bonds in **3** it is difficult to illustrate these in the RD curve. They may, however, be identified from Table 4, which lists the nonbonded C−C distances in order of increasing length; the table also includes the calculated vibrational amplitudes.

Discussion: The calculated ab initio HF/6-31G* torsional potential function for D11BD shows one well-defined minimum at *anti* orientation of the C=C−C=C fragment, and the energy rises rather steeply at both sides of this energy minimum. These data do therefore present strong evidence for the assumption that gaseous D11BD is conformationally homogeneous (*anti*). The experimental GED data are also in agreement with the presence of only the *anti*-D11BD conformer.

The details of the stereochemistry of D11BD will in the following be discussed with respect to the theoretical HF/6-31G* results, as these are more detailed than those from the GED study. Such an approach is considered to be justified since there are no serious discrepancies between the theoretical and experimental model.

The sterical strain involving *gem*-substituted *tert*-butyl groups in the saturated molecules di-*tert*-butylmethane and in tri-*tert*-butylmethane, is for the former molecule primarily reduced by opening up the C_{tBu}−C−C_{tBu} angle to 128.0°, while this angle was found to be ca. 116° in the latter molecule (vide supra). Enlarged average C−C bond lengths were observed for both molecules, and especially for the most heavily congested one, tri-*tert*-butylmethane, where an extremely long C−C_{tBu} bond (1.611 Å) was observed.

The C_{tBu}−C−C_{tBu} angle of 122.5° (see Table 1) is also considerably larger than for example the CH_3−C−CH_3 angle observed for isobutene (115.6°)[24]. This angle enlargement is, however, not the most remarkable structural feature of D11BD.

Let us start by analysing the sterical strain in this molecule. Apart from the mutual repulsion of the two *tert*-butyl groups, each of these groups will also experience some repulsion from the *Z*-oriented group at the other end of the C1=C2 bond, namely 16-H or the vinyl group, −HC3=C4H_2. As the vinyl group occupies considerably more space than a hydrogen atom, it is obvious that the sterical strain will be most severe for the *tert*-butyl group that is *Z*-oriented relative to this group. This is manifested in several of the parameters, for example in the difference between the two C2=C1−C_{tBu} angles, where the one that is *Z*-oriented to the vinyl group is 3.6° larger than the other one. Another remarkable detail concerns the orientations of the *tert*-butyl groups, where one of the groups assumes the normal orientation, with one C−CH_3 bond eclipsing the C1=C2 bond, while the other group assumes the torsionally unfavourable staggered orientation relative to the double bond. This is accompanied by two energetically favourable events that must outweigh the increase in torsional energy due to the distortion: 1) If both *tert*-butyl groups were to assume the normal eclipsed orientation relative to the C1=C2 bond, two pairs of methyl groups with unfavourable 1,3-diaxial (*gauche* +/*gauche* −) orientation would give rise to severe

Figure 2. Experimental and theoretical RD curves for **3** and the differences between the two curves

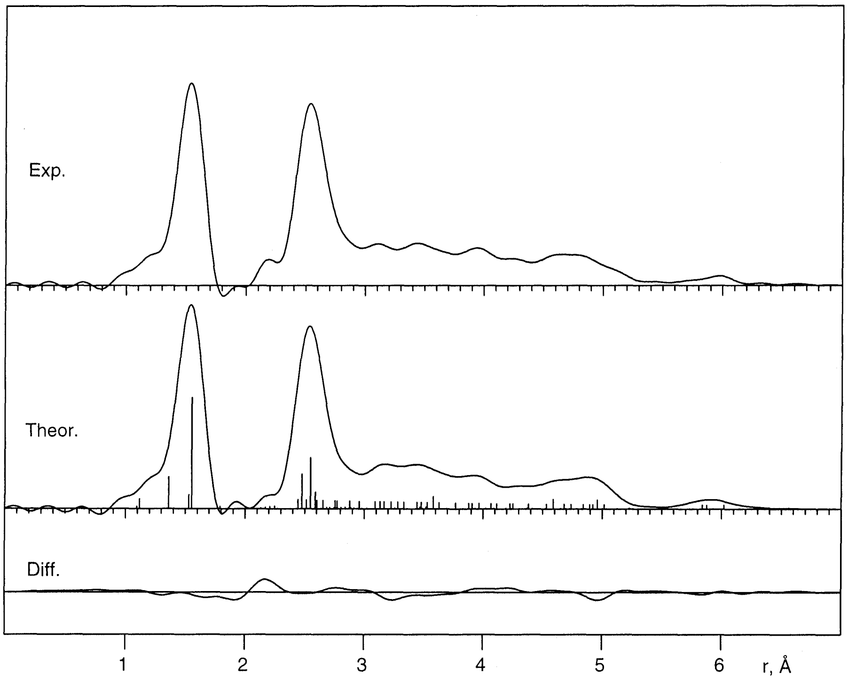


Table 4. Nonbonded C−C distances (r_a) in D11BD (**3**) from the GED study and calculated vibrational amplitudes (u_{ij}); both quantities are given in Å; the number of dots between the atoms is equal to the number of valence angles separating them

distance	r_a	u_{ij}	distance	r_a	u_{ij}
C10•C11	2.444	0.0696	C2••C7	3.525	0.1164
C6•C8	2.468	0.0715	C2••C8	3.595	0.1067
C6•C7	2.473	0.0722	C7•••C12	3.604	0.2254
C11•C12	2.480	0.0731	C5••C12	3.640	0.1222
C2•C5	2.491	0.0602	C1••C4	3.782	0.0636
C2•C4	2.510	0.0618	C2••C11	3.887	0.0742
C1•C12	2.537	0.0745	C5••C10	3.908	0.1080
C2•C9	2.541	0.0619	C3••C5	3.973	0.0676
C1•C7	2.541	0.0768	C6••C9	4.068	0.0752
C7•C8	2.553	0.0773	C4••••C10	4.139	0.2795
C1•C10	2.555	0.0748	C8•••C10	4.219	0.2032
C10•C12	2.561	0.0780	C3•••C6	4.250	0.0897
C1•C6	2.582	0.0678	C4•••C9	4.402	0.1030
C1•C8	2.588	0.0769	C8•••C12	4.534	0.1156
C1•C3	2.616	0.0604	C3•••C11	4.599	0.0948
C1•C11	2.652	0.0741	C4••••C12	4.611	0.2030
C5•C9	2.756	0.0697	C6•••C11	4.686	0.1015
C2••C6	2.767	0.0796	C7•••C10	4.752	0.1019
C3•••C10	2.888	0.1470	C6•••C12	4.854	0.1369
C2••C10	2.962	0.1022	C3•••C7	4.895	0.1336
C3••C9	3.098	0.0904	C4••••C6	4.903	0.1329
C8•••C11	3.132	0.1482	C4•••C5	4.960	0.0853
C3••C11	3.174	0.0962	C3•••C8	4.973	0.1154
C2••C12	3.223	0.1150	C6•••C10	5.007	0.1357
C7••C9	3.299	0.1157	C4••••C7	5.836	0.1982
C8••C9	3.331	0.1084	C4••••C11	5.898	0.1207
C7•••C11	3.470	0.1287	C4••••C8	6.025	0.1694
C3•••C12	3.472	0.1585			

steric repulsion. This repulsion is reduced when one of the *tert*-butyl groups is distorted. 2) The repulsion involving the distorted *tert*-butyl group and the *Z*-oriented substituent at C2 will also be reduced.

The reduction of the nonbonded repulsion involving both *tert*-butyl groups, is insensitive to which of the *tert*-butyl groups is distorted, but as the sterical strain for the *tert*-butyl group that is *Z*-oriented to the vinyl group is considerably larger than that for the other one, it is not surprising that torsional distortion is taking place at this group. This orientation of the *tert*-butyl groups in D11BD is similar to that observed for tetra-*tert*-butyl-1,3-butadiene in the solid state[25], and is in agreement with the concept of allylic 1,3-strain[26].

Another remarkable feature of the D11BD structure is the very large C1=C2−C3 angle of 132.7°. The opening up of this angle contributes significantly toward reducing the repulsion involving the *Z*-oriented *tert*-butyl and vinyl groups.

The hydrogen atoms at C2 and C3 are bent away from the *tert*-butyl groups (see Table 1), and do therefore contribute toward reducing the overall sterical strain in the molecule. This is not obvious from the values of the C1=C2−H and C4=C3−H angles, as they are of equal magnitude. The two C−C−H angles related to the C2−C3 bond differ, however, by nearly 11°, and the distortions are explained by the tendency to increase the distance from each of these hydrogen atoms to their *Z*-oriented *tert*-butyl group.

The ab initio calculations indicate that the C1=C2 bond is somewhat larger than the other C=C bond in the molecule (1.3381 vs. 1.3246 Å). Calculated C=C bonds based on HF ab initio calculations are generally found to be too small, and this is also true in the present case. The calculated C=C bond difference of 0.0137 Å is, however, probably of the correct order of magnitude. The elongation of the C1=C2 bond might be explained by the combined effect of hybridisation changes due to unusual valence angles and to sterical strain. According to the experimental GED results the C1=C2 bond is clearly elongated relative to the C−C double bond in 1,3-butadiene[27]. It should also be noted that the two $C1-C_{tBu}$ bonds in D11BD, which are formally C(sp^2)−C(sp^3) bonds, are longer than the formally C(sp^3)−C(sp^3) bonds involving the methyl groups. As pointed out above, comparable $C-C_{tBu}$ bond elongations are observed for the sterically strained molecules di-*tert*-butylmethane[3] and tri-*tert*-butylmethane[5].

If the valence and dihedral angles in **3** had assumed the "normal" magnitudes, the nonbonded van-der-Waals repulsion would have been tremendous. As a consequence of the sterical adjustments in the molecule the number of high-energy nonbonded distances have been greatly reduced, and the remaining nine interactions are shown in Table 2. The interactions between the *gem*-di-*tert*-butyl groups involve four hydrogen atoms, and the C−C−H angles involving these hydrogen atoms are several degrees larger than the average of the other C−C−H angle (110.4°), thereby increasing the strained nonbonded H···H distances.

H. H. and M. T. acknowledge the support from the *Alexander-von-Humboldt-Stiftung/Max Planck Foundation* through the award of a 1994 Max Planck Forschungspreis. We are grateful to *Hans-Vidar Volden* for the recording of the experimental electron diffraction data. This work has received support from *The Research Council of Norway* (program for Supercomputing) through a grant of computing time.

Experimental Section

Spectrometers and other equipment used have already been described in the previous publications of this series[1][2][28].

p-Nitrobenzoate **2** *of 4-tert-Butyl-5,5-dimethyl-1-hexen-4-ol* (**1**): To a solution of 5.66 g (31.0 mmol) of **1**[13] in 50 ml of anhydrous diethyl ether 21 ml of a 1.5 M solution of methyllithium in diethyl ether is added at an internal temp. of −10°C. After stirring the reaction mixture for 30 min at 0°C, it is cooled to −70°C and 5.75 g (31.0 mmol) of *p*-nitrobenzoyl chloride in 50 ml of diethyl ether is added. The cooling bath is removed and when the solution has reached room temp. (after 2 h), it is hydrolysed and extracted several times with diethyl ether. After drying ($MgSO_4$), the solvent is removed in vacuo, and the resulting solid residue is recrystallised from ethanol: 8.18 g (77%) of the ester **2**, yellow needles, m.p 96°C. − ^{1}H NMR (400.1 MHz, $CDCl_3$, int. TMS): δ = 1.27 (s, 18 H, *t*Bu), 3.40 (dt, ^3J = 6.8, ^4J = 1.7, ^4J = 1.7 Hz, 2 H, 3-H), 5.00 (dq, ^2J = 1.6, $^3J_{trans}$ = 17.0, ^4J = 1.7 Hz, 1 H, 1-H$_a$), 5.09 (dq, ^2J = 1.6, $^3J_{cis}$ = 10.2, ^4J = 1.7 Hz, 1 H, 1-H$_b$), 6.06 (ddt, ^3J = 6.9, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.0 Hz, 1 H, 2-H), 8.18−8.33 (m, 4 H, Ar-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.6 (s), 150.2 (s), 138.2 (d), 137.9 (s), 130.6 (d), 123.6 (d), 115.1 (t), 99.45 (s), 43.9 (s), 37.4 (t), 30.1 (q). − IR (KBr): $\tilde{\nu}$ = 1709 cm^{-1}, 1395, 1298. − UV (acetonitrile): λ_{max} (log ε) = 192 nm (4.55), 262 (4.13). − MS (70 eV); *m/z* (%): 276 (5) [M$^+$ − *t*Bu], 150 (100), 57 (18). − $C_{19}H_{27}NO_4$ (333.41): calcd. C 68.44, H 8.16; found C 68.48, H 8.20.

4-tert-Butyl-5,5-dimethyl-1,3-hexadiene (**3**, D11BD): In a sealed tube 3.5 g (10.5 mmol) of **2** is slowly heated up to its m.p. (96°C) and subsequently to 160°C until it has resolidified. After cooling to room temp., the crude pyrolysis mixture is dissolved in diethyl ether, and the solution is dried with $MgSO_4$. The solvent is removed in a rotary evaporator and the residue is fractionated by kugelrohr distillation. At 85°C/15 Torr 1.40 g (80%) of **3** distills as a colourless liquid. Purification by preparative gas chromatography (SE-54 column at 110°C) yields an analytically pure sample. − ^{1}H NMR (400.1 MHz, $CDCl_3$, int. TMS): δ = 1.23 (s, 9 H, *t*Bu), 1.36 (s, 9 H, *t*Bu), 5.03−5.09 (m, 2 H, 4-H), 6.02 (d, ^3J = 11.2 Hz, 1 H, 2-H), 6.93−7.03 (m, ^3J = 11.2 Hz, 1 H, 3-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 156.8 (s), 136.4 (d), 124.4 (d), 115.9 (t), 38.7 (s), 37.7 (s), 33.7 (q), 31.8 (q). − IR (film): $\tilde{\nu}$ = 3087 cm^{-1}, 1620, 1391, 1367, 901. − UV (acetonitrile): λ_{max} (log ε): 242 nm (3.94). − MS (70 eV); *m/z* (%): 166 (12) [M$^+$], 109 (100), 57 (92). − $C_{12}H_{22}$ (166.31): calcd. C 86.67, H 13.33; found C 86.58, H 13.31.

☆ This paper is dedicated to Professor *Klaus Hafner* on the occasion of his 70th birthday.

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