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

A Theoretical Study of the Stereochemical Effects of *tert*-Butyl Substituents in 1,3-Butadiene

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For 1,3-butadiene and for all mono- and di-*tert*-butyl derivatives potential energy curves, as function of the C=C–C=C dihedral angle, have been calculated by molecular mechanics methods (MM3). The stereochemical implication of these results are discussed for each of the compounds. The minimum-energy conformer of each derivative has been optimized by ab initio HF calculations, using GAUSSIAN 90 and a 3-21G basis set.

1. Introduction

It is well known that many highly substituted 1,3-dienes prefer conformations with non-planar diene systems[2]. It has furthermore been shown[3] that photochemical reactions of 1,3-butadienes bearing *tert*-butyl groups follow reaction paths different from that of the unsubstituted hydrocarbon, with the actual outcome of these photoisomerizations depending on the substitution pattern. The reason for this behavior has been attributed to variations in the orientation of the C=C–C=C system of the different dienes.

Figure 1 shows formulas for the 35 possible homogeneously substituted 1,3-butadienes bearing, in the present case, *tert*-butyl substituents. They are arranged in columns according to the number of substituent groups. Only a few of them are known so far, and some of them, for example the extremely strained **36**, will perhaps never be synthesized.

The present work is aimed at a systematic study of the stereochemical consequences of the introduction of *tert*-butyl substituents into a 1,3-butadiene skeleton. The potential-energy curves for rotation around the central C^2–C^3 bond will be calculated for all mono- and disubstituted compounds by using the MM3 method. In addition, the structure of the minimum-energy conformers will be optimized by using ab initio calculations.

2. Nomenclature

The various 1,3-butadiene derivatives may be referred to by their individual numbers given in Figure 1. We find that the paper will be easier to read if we use symbolic names that indicate the structure of the molecules. We have therefore introduced a system of names for the molecules under discussion, where the first character, M or D, indicates whether the derivative is mono- or disubstituted. The numbers that follow indicate the positions of the substituents. For substituents in the 1- or 4-position it will furthermore be necessary to show the correct stereochemical orientation, and the symbols C or T following one of these numbers indicate whether the substituent is *cis* or *trans* relative to the C=C–C=C chain. The symbol D1T4C is for example a synonym for 1-*trans*-4-*cis*-di-*tert*-butyl-1,3-butadiene, or – more correctly – (3*E*,5*Z*)-2,2,7,7-tetramethyl-3,5-octadiene.

The conjugated carbon atoms are numbered from 1 to 4. In the monosubstituted derivatives the tertiary carbon atom is referred to as C^5, while the two present in disubstituted molecules are referred to as C^5 and C^9.

3. Calculation Procedures

Molecular-mechanics calculations, using Allinger's MM3 program[4], have been carried out for the three mono-*tert*-butyl- and the nine di-*tert*-butyl-1,3-butadiene molecules. Calculations for unsubstituted 1,3-butadiene have been carried out for reference purposes. For all species the potential energy curve has been calculated as function of the C=C–C=C dihedral angle, using 30° increments. The MM3 potential-energy curves for the monosubstituted derivatives are shown in Figure 2 and those for the disubstituted ones in Figures 3–6. The calculated potential-energy curve for 1,3-butadiene is included as reference in all of these figures. The calculated energies, from which the potential-energy curves are constructed, are listed in Table 1. Each of the potential energy curves is commented on below.

Ab initio calculations, using 3-21G basis sets, have been carried out for the minimum-energy conformers of all the mono- and disubstituted derivatives, utilizing the program GAUSSIAN 90[5]. The calculations have been performed on a CRAY X-MP/28 at SINTEF/NTH in Trondheim. The

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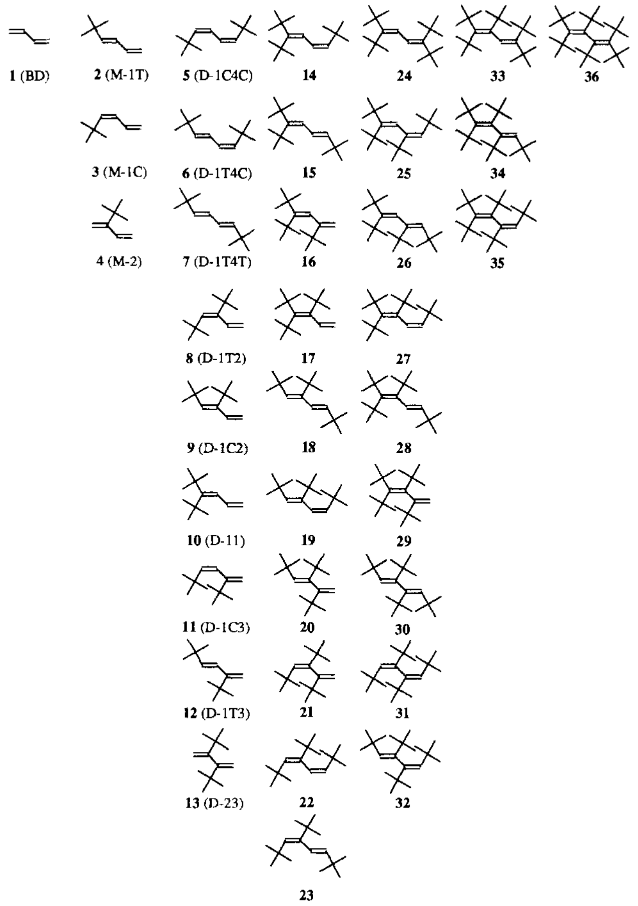

Figure 1. Schematic representations of the carbon skeleton of 1,3-butadiene and its *tert*-butyl derivatives, arranged in rows with increasing number of substituents

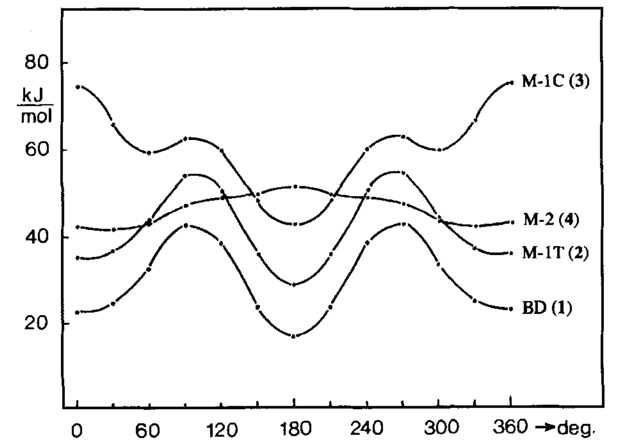

Figure 2. The MM3 potential energies for monosubstituted *tert*-butyl-1,3-butadienes as a function of the C=C−C=C dihedral angle

results are presented in Tables 2−6. For some of the derivatives a number of the geometrical parameters are shown in parentheses, indicating that they have not been optimized. This has been done in order to reduce the computational time, and the restrictions have been applied only to parameters that are assumed to be of minor importance for the

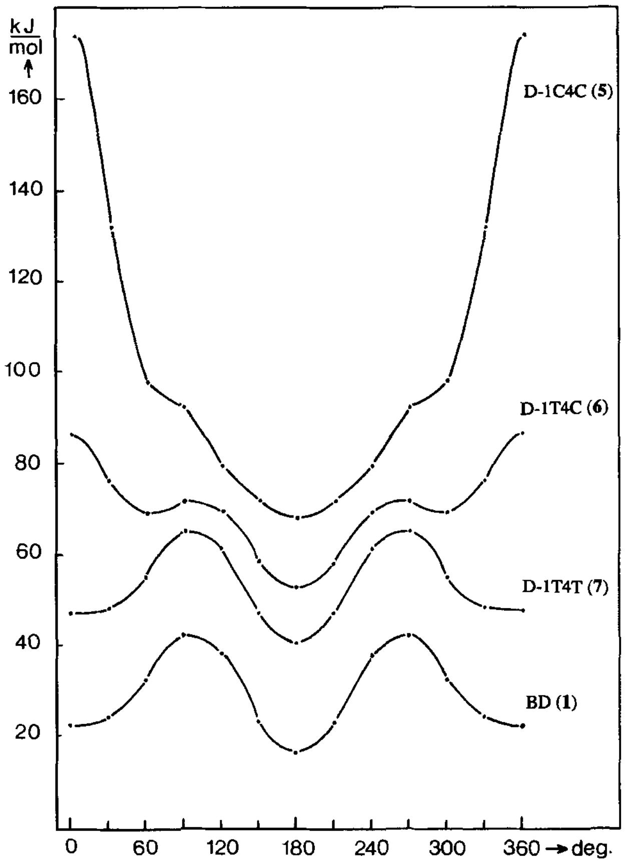

Figure 3. The MM3 potential energies for 1,4-di-*tert*-butyl-1,3-butadienes as a function of the C=C−C=C dihedral angle

general stereochemistry of the compound in question. The values for the non-varied valence- and dihedral-angle parameters have been transferred from the optimized MM3 geometries. This is also the case with the hydrogen valence and dihedral angles that are not shown in tables, while the C−H bond lengths have been optimized as $C_{sp^2}-H$ and $C_{sp^3}-H$.

Analogous ab initio calculations have been carried out for 1,3-butadiene, although more sophisticated calculations are available for this molecule[6]. It is, however, essential that comparisons are being made on the basis of data originating from the same sources. Table 7 shows some important valence and dihedral angles for these molecules in their minimum-energy conformations while Table 8 compiles the calculated C−C bond lengths.

4. Monosubstituted tert-Butyl-1,3-butadienes

The potential-energy curves calculated for the three monosubstituted *tert*-butyl-1,3-butadienes are shown in Figure 2. The sterical energies of these molecules are dominated by two factors: a) The steric strain within the *tert*-butyl group itself and b) the interaction between this group and the conjugated 1,3-butadiene backbone.

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

When the *tert*-butyl group is introduced into the 1-*trans* position, the increased steric-strain energy, compared to

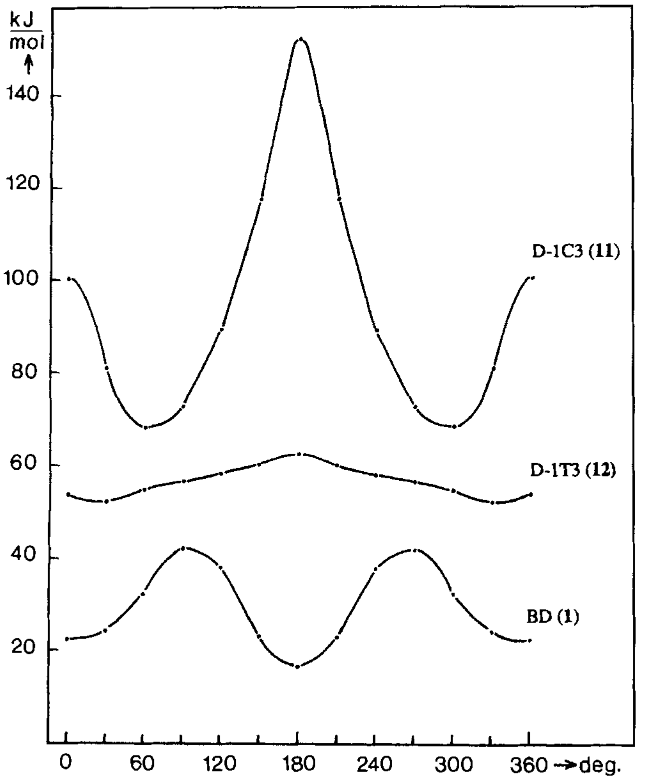

Figure 4. The MM3 potential energies for 1,3-di-*tert*-butyl-1,3-butadienes as a function of the C=C–C=C dihedral angle

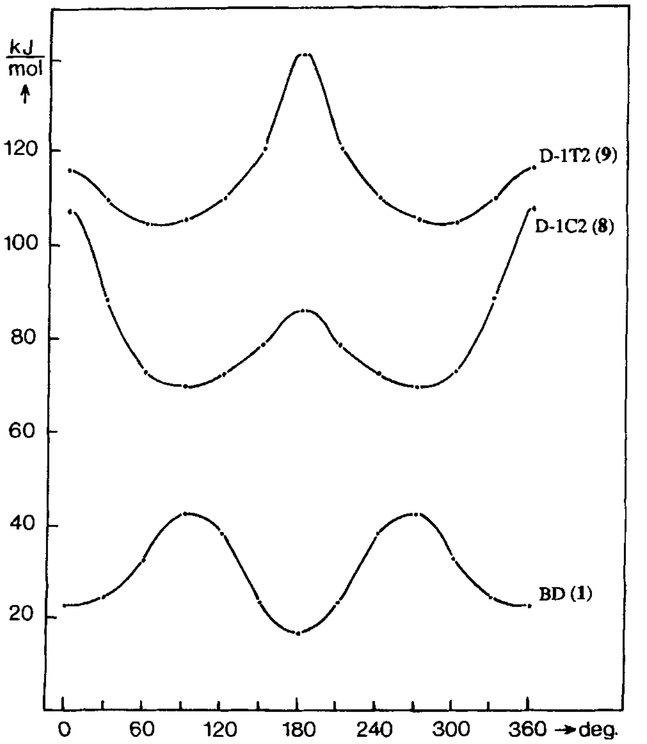

Figure 5. The MM3 potential energies for 1,2-di-*tert*-butyl-1,3-butadienes as a function of the C=C–C=C dihedral angle

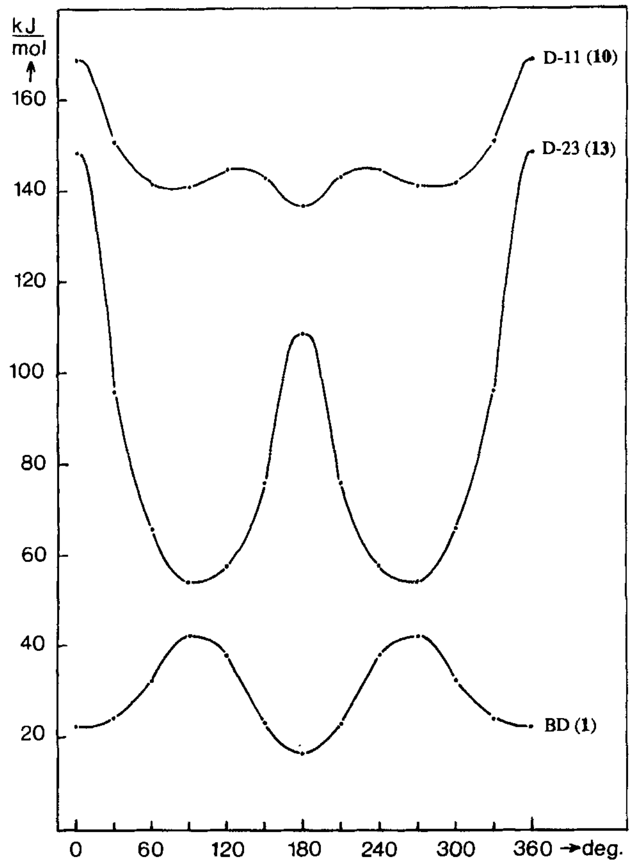

Figure 6. The MM3 potential energies for 1,1- and 2,3-di-*tert*-butyl-1,3-butadienes as a function of the C=C–C=C dihedral angle

that present in the parent 1,3-butadiene molecule, is primarily due to the strain energy inherent in the *tert*-butyl substituent. This is apparent from the shape of the M-1T potential-energy curve (see Figure 2), which parallels that of unsubstituted 1,3-butadiene. The energy difference between the M-1T and BD molecules is accordingly approximately independent of the C=C–C=C dihedral angle.

The bulkiness of the *tert*-butyl substituent does, however, result in an unusually large $C^2{=}C^1{-}C_{tBu}$ valence angle (127.4°) (see Table 7).

4.2 1-*cis-tert*-Butyl-1,3-butadiene (3, M-1C)

The steric-strain energy within the M-1C *tert*-butyl group is comparable to that of M-1T. The increased sterical energy of M-1C comparent to that of M-1T (see Figure 1) is due to a substantial energy contribution from interaction between the substituent and the 1,3-butadiene backbone. The latter contribution is strongly conformation-dependent and is at its maximum in a *syn* conformation [θ(C=C–C=C) 0°]. The total effect on the potential-energy curve therefore involves a shift of the second high-energy minimum from a broad region close to *syn*, as in BD and M-1T, to a *gauche* minimum, corresponding to a C=C–C=C dihedral angle of ca. 60°. According to the data presented in Figure 2 the energy difference between the two M-1C potential energy minima (ca. 17.2 kJ/mol) is about three times larger than in the case of BD and M-1T (ca. 5.9–6.6 kJ/mol).

Table 1. Steric energies [kJ/mol] as a function of the C=C−C=C dihedral angle (θ) calculated for 1,3-butadiene and its mono- and di-*tert*-butyl derivatives; results from the MM3 calculations

		θ: 0°	30°	60°	90°	120°	150°	180°
BD	(**1**)	22.2	24.0	32.2	42.0	37.8	23.2	16.3
M-1T	(**2**)	34.8	36.0	43.3	53.5	49.9	35.1	28.2
M-1C	(**3**)	74.3	65.6	59.1	62.1	59.5	47.6	41.9
M-2	(**4**)	41.9	41.1	42.9	46.9	48.3	49.0	50.5
D-11	(**10**)	168.8	150.5	140.4	140.8	144.7	142.9	132.2
D-1T2	(**9**)	115.8	109.1	104.3	105.0	109.3	120.3	140.5
D-1C2	(**8**)	107.0	88.0	72.2	69.3	72.0	77.9	85.6
D-1T3	(**12**)	53.9	52.2	54.8	56.7	58.3	59.9	62.6
D-1C3	(**11**)	100.5	81.1	68.2	72.8	89.1	117.4	151.7
D-1T4T	(**7**)	47.2	47.9	54.7	64.8	61.3	46.7	39.9
D-1C4C	(**5**)	174.1	131.8	97.4	91.7	79.1	71.4	67.9
D-1T4C	(**6**)	86.1	76.1	69.0	71.6	69.3	58.2	52.8
D-23	(**13**)	148.4	95.9	65.6	53.8	57.5	79.8	108.3

Table 2. 1,3-Butadiene (BD, **1**); geometry parameters obtained from ab initio calculations (HF/3-21G); distances [Å], angles [°]

C=C	1.3205
C^2-C^3	1.4947
C^1-H^1	1.0725
C^1-$H^{1'}$	1.0744
C^2-H	1.0756
$\angle C^1=C^2-C^3$	123.96
$\angle C^1=C^2-H$	119.91
$\angle C^2=C^1-H^1$	121.80
$\angle C^2=C^1-H^{1'}$	121.80
θ(C=C-C=C)	180.0
HF(a.u.)	**-154.0594565**

Table 3. Monosubstituted *tert*-butyl-1,3-butadienes; geometry parameters [Å or °] and energies, as obtained from ab initio calculations (HF/3-21G)

	M-1T (2)	**M-1C (3)**	**M-2 (4)**
$C^1=C^2$	1.3215	1.3227	1.3225
$C^3=C^4$	1.3224	1.3212	1.3184
C^2-C^3	1.4662	1.4757	1.4902
C-C^5	1.5167	1.5358	1.5345
C-CH_3	1.5433	1.5467	1.5443
$\angle C^1=C^2-C^3$	123.6	128.0	119.6
$\angle C^2-C^3=C^4$	124.4	121.9	124.2
$\angle C=C-C^5$	127.4	129.5	124.3
$\angle C-C^5-C^6$	112.3	111.5	112.0
$\angle C-C^5-C^7$	108.5	107.9	109.7
$\angle C-C^5-C^8$	108.5	111.5	108.8
θ(C=C-C=C)	180.0	180.0	49.2
θ(C=C-C^5-C^6)	0.0	62.1	-4.5
θ(C=C-C^5-C^7)	~ 120	180.0	115.6
θ(C=C-C^5-C^8)	~ -120	-62.1	-124.6
HF(a.u.) (-309.xx)	**.3425514**	**.3326385**	**.3344904**
Δ E (kJ/mol)	**0.0**	**26.0**	**21.2**

Table 4. 1,1- and 1,2-Di-*tert*-butyl-1,3-butadienes; geometry parameters [Å or °] and energies, as obtained from ab initio calculations (HF/3-21G)

	D-11 (10)	**D-1T2 (8)**	**D-1C2 (9)**
$C^1=C^2$	1.3344	1.3350	1.3227
$C^3=C^4$	1.3247	1.3189	1.3180
C^2-C^3	1.4735	1.5019	1.4916
C^1-C^5	1.5687	1.5339	1.5232
$C^{2(1)}$-C^9	1.5635	1.5479	1.5561
C-CH_3	1.5481	1.5422	1.5412
$\angle C^1=C^2-C^3$	134.1	114.1	124.6
$\angle C^2-C^3=C^4$	121.4	124.6	124.2
$\angle C^2=C^1-C^5$	115.7	140.0	133.3
$\angle C^{1(2)}=C^{2(1)}-C^9$	124.0	131.9	119.2
$\angle C^1-C^5-C^6$	(113.4)	(107.3)	(108.1)
$\angle C^1-C^5-C^8$	(112.9)	(110.0)	(109.0)
$\angle C^{2(1)}-C^9-C^{10}$	(112.1)	(113.2)	(110.4)
$\angle C^{2(1)}-C^9-C^{11}$	(115.7)	(110.2)	(1110.4)
$\angle C^{2(1)}-C^9-C^{12}$	(110.2)	(111.7)	(111.8)
θ(C=C-C=C)	180.0	60.4	81.0
θ(C=C^1-C^5-C^6)	(5.4)	(38.7)	(24.8)
θ(C=C^1-C^5-C^7)	(122.4)	(156.5)	(144.3)
θ(C=C^1-C^5-C^8)	(-113.2)	(-87.5)	(-98.3)
θ(C=$C^{2(1)}$-C^9-C^{10})	(35.7)	(53.7)	(60.5)
θ(C=$C^{2(1)}$-C^9-C^{11})	(152.6)	(-67.5)	(-60.6)
θ(C=$C^{2(1)}$-C^9-C^{12})	(-85.3)	(173.2)	(179.9)
HF(a.u.) (-464.xx)	**.5769953**	**.5846842**	**.5993223**
Δ E (kJ/mol)	**128.9**	**107.9**	**69.5**

For the M-1C isomer the bulkiness of the *tert*-butyl substituent brings about enlarged $C^2=C^1-C_{tBu}$ (129.5°) and $C^1=C^2-C^3$ (128.0) valence angles.

4.3 2-*tert*-Butyl-1,3-butadiene (4, M-2)

Figure 2 shows that the M-2 potential-energy curve differs dramatically from those of M-1T and M-1C. While the

Table 5. 1,3- and 2,3-Di-*tert*-butyl-1,3-butadienes; geometry parameters [Å or °] and energies, as obtained from ab initio calculations (HF/3-21G)

	D-1T3 (12)	D-1C3 (11)	D-23 (13)
$C^1{=}C^2$	1.3190	1.3216	1.3208
$C^3{=}C^4$	1.3224	1.3215	1.3208
$C^2\text{-}C^3$	1.4947	1.4926	1.5099
$C^{1(2)}\text{-}C^5$	1.5158	1.5204	1.5499
$C^3\text{-}C^9$	1.5371	1.5451	1.5499
$C\text{-}CH_3$	1.5438	1.5421	1.5455
$\angle C^1{=}C^2\text{-}C^3$	122.6	131.1	118.4
$\angle C^2\text{-}C^3{=}C^4$	119.7	120.3	118.4
$\angle C^{2(1)}{=}C^{1(2)}\text{-}C^5$	127.4	134.3	121.6
$\angle C^4{=}C^3\text{-}C^9$	123.9	121.7	121.6
$\angle C^{1(2)}\text{-}C^5\text{-}C^6$	112.4	(114.5)	110.7
$\angle C^{1(2)}\text{-}C^5\text{-}C^7$	108.8	(108.1)	112.6
$\angle C^{1(2)}\text{-}C^5\text{-}C^8$	(108.8)	(109.6)	108.3
$\angle C^3\text{-}C^9\text{-}C^{10}$	(112.4)	(111.4)	110.7
$\angle C^3\text{-}C^9\text{-}C^{11}$	(108.8)	(109.5)	112.6
$\angle C^3\text{-}C^9\text{-}C^{12}$	(108.8)	(111.6)	108.3
$\theta(C{=}C\text{-}C{=}C)$	53.9	67.3	99.1
$\theta(C{=}C^{1(2)}\text{-}C^5\text{-}C^6)$	(0.0)	(24.2)	47.6
$\theta(C{=}C^{1(2)}\text{-}C^5\text{-}C^7)$	120.5	(143.2)	169.0
$\theta(C{=}C^{1(2)}\text{-}C^5\text{-}C^8)$	(-120.5)	(-99.0)	-71.7
$\theta(C{=}C^3\text{-}C^9\text{-}C^{10})$	(0.0)	(-53.4)	47.6
$\theta(C{=}C^3\text{-}C^9\text{-}C^{11})$	(120.5)	67.2)	169.0
$\theta(C{=}C^3\text{-}C^9\text{-}C^{12})$	(-120.5)	(-173.3)	-71.7
HF(a.u.) (-464.xx)	**.6171347**	**.6017453**	**.6007043**
Δ E (kJ/mol)	**22.7**	**63.1**	**65.9**

Table 6. 1,4-Di-*tert*-butyl-1,3-butadienes; geometry parameters [Å or °] and energies, as obtained from ab initio calculations (HF/3-21G)

	D-1T4T (7)	D-1C4C (5)	D-1T4C(6)
$C^1{=}C^2$	1.3215	1.3236	1.3217
$C^3{=}C^4$	1.3215	1.3236	1.3223
$C^2\text{-}C^3$	1.4677	1.4762	1.4766
$C^1\text{-}C^5$	1.5170	1.5379	1.5165
$C^4\text{-}C^9$	1.5170	1.5379	1.5349
$C\text{-}CH_3$	1.5434	1.5474	1.5441
$\angle C^1{=}C^2\text{-}C^3$	123.7	126.8	121.2
$\angle C^2\text{-}C^3{=}C^4$	123.7	126.8	127.8
$\angle C^2{=}C^1\text{-}C^5$	127.4	129.5	127.3
$\angle C^3{=}C^4\text{-}C^9$	127.4	129.5	129.1
$\angle C^1\text{-}C^5\text{-}C^6$	112.7	111.6	112.2
$\angle C^1\text{-}C^5\text{-}C^7$	108.3	107.7	108.5
$\angle C^1\text{-}C^5\text{-}C^8$	108.3	111.6	108.5
$\angle C^4\text{-}C^9\text{-}C^{10}$	112.7	111.6	111.5
$\angle C^4\text{-}C^9\text{-}C^{11}$	108.3	107.7	107.7
$\angle C^4\text{-}C^9\text{-}C^{12}$	108.3	111.6	111.5
$\theta(C{=}C\text{-}C{=}C)$	180.0	180.0	180.0
$\theta(C{=}C^1\text{-}C^5\text{-}C^6)$	0.0	62.1	(0.0)
$\theta(C{=}C^1\text{-}C^5\text{-}C^7)$	120.8	180.0	(120)
$\theta(C{=}C^1\text{-}C^5\text{-}C^8)$	-120.8	-62.1	(-120)
$\theta(C{=}C^4\text{-}C^9\text{-}C^{10})$	0.0	62.1	(60)
$\theta(C{=}C^4\text{-}C^9\text{-}C^{11})$	120.8	180.0	(180)
$\theta(C{=}C^4\text{-}C^9\text{-}C^{12})$	-120.8	-62.1	(-60)
HF(a.u.) (-464.xx)	**.6257853**	**.6046061**	**.6158636**
Δ E (kJ/mol)	**0.0**	**55.6**	**26.1**

1-substituted isomers exhibit energy minima for the *anti* conformation, this orientation corresponds to an energy maximum in the case of M-2. The shape of its potential curve shows no resemblance to those of the two M-1 curves, and the calculated potential energy varies over a much smaller range (ca. 9 kJ/mol) than that of M-1T (ca. 25 kJ/mol) and M-1C (ca. 32 kJ/mol). The M-2 potential-energy curve has only one rather shallow minimum, corresponding to a *gauche* conformation [$\theta(C{=}C{-}C{=}C)$: 30–50°].

The reason behind the differences in the potential curves for the three monosubstituted 1,3-butadiene isomers is due to the nature of the interaction between the *tert*-butyl group and the 1,3-butadiene backbone in the three cases. In M-1T this interaction is only reflected in the somewhat enlarged $C{=}C{-}C_{tBu}$ valence angle. In the more heavily strained M-1C molecule the $C{=}C{-}C_{tBu}$ as well as the $C^1{=}C^2{-}C^3$ angles are opened up to 129.5 and 128.0°, respectively. In addition, the repulsive interaction between the *tert*-butyl substituent and the C^4H_2 methylene group destabilizes the *syn* conformation of M-1C further, and adds to the destabilization already present in the *syn*-1,3-butadiene backbone. In M-2 the steric repulsion between the *tert*-butyl and the C^4H_2 groups counteracts that involving the two C^1H_2 and C^4H_2 methylene groups, resulting in a potential-energy curve that is relatively flat compared to the two M-1 potential-energy curves. The former type of repulsive interaction is obviously the dominating one. The MM3 results presented in Figure 2 indicate that the maximum repulsion between the *tert*-butyl and the C^4H_2 groups (*anti* conformation) is 2–3 times larger than that involving the two C^1H_2 and C^4H_2 methylene groups (*syn* conformation). This estimate is based on the following reasoning: The sterical interactions between the terminal methylene groups in the BD and M-2 molecules are probably of nearly the same magnitude, i.e. ca. 5.9 kJ/mol more favorable for the *anti* than for the *syn* conformation. The other type of sterical interaction in M-2 involving the *tert*-butyl and the C^4H_2 groups has its minimum for the *syn* orientation and reaches a maximum for the *anti* conformation. The estimate of the order of magnitude of the latter effect is therefore arrived at by adding the calculated energy difference between the M-2 *anti* and *syn* conformers (ca. 8.6 kJ/mol) to the energy difference between *syn* and *anti* BD conformers (ca. 5.9 kJ/mol), giving a total of 14.5 kJ/mol.

Table 7 shows that the calculated C–C–C valence angles of M-2 are fairly normal, except perhaps for the relative small $C^1{=}C^2{-}C^3$ value (119.6°). Because of the interrelation between the $C{=}C{-}C_{tBu}$ and $C^1{=}C^2{-}C^3$ angles in M-2, the sterical requirements of the *tert*-butyl group cannot be met by substantial deviation from "normal" C–C–C valence angles. The relatively small $C^1{=}C^2{-}C^3$ angle supports, however, the statement above about the

Table 7. Angles and relative energies [kJ/mol] for minimum-energy conformers of 1,3-butadiene and its mono- and di-*tert*-butyl derivatives; results from ab initio HF/3-21G calculations

		ΔE	$\theta(C{=}C\text{-}C{=}C)$	$\angle C^1{=}C^2\text{-}C^3$	$\angle C^2\text{-}C^3{=}C^4$	$\angle C{=}C\text{-}C^5$	$\angle C{=}C\text{-}C^9$
BD	(1)	-	180.0	124.0	124.0	-	-
M-1T	(2)	0.0	180.0	123.6	124.4	127.4	-
M-1C	(3)	26.0	180.0	128.0	121.9	129.5	-
M-2	(4)	21.2	49.2	119.6	124.2	124.3	-
D-1,1	(10)	128.9	180.0	134.1	121.4	115.7	124.0
D-1T2	(9)	107.9	60.4	114.1	124.6	140.0	131.9
D-1C2	(8)	69.5	81.0	124.6	124.2	133.3	119.2
D-1T3	(12)	22.7	53.9	122.2	119.7	127.4	123.9
D-1C3	(11)	63.1	67.3	131.1	120.3	134.3	121.7
D-1T4T	(7)	0.0	180.0	123.7	123.7	127.4	127.4
D-1C4C	(5)	55.6	180.0	126.8	126.8	129.5	129.5
D-1T4C	(6)	26.1	180.0	121.2	127.8	127.3	129.1
D-23	(13)	65.9	99.1	118.4	118.4	121.6	121.6

Table 8. Bond distances and relative energies [kJ/mol] for minimum-energy conformers of 1,3-butadiene and its mono- and di-*tert*-butyl derivatives; results from ab initio HF/3-21G calculations

		ΔE	$C^1{=}C^2$	$C^3{=}C^4$	$C^2\text{-}C^3$	$C\text{-}C^5$	$C\text{-}C^9$	$C\text{-}CH_3$
BD	(1)	-	1.321	1.321	1.495	-	-	-
M-1T	(2)	0.0	1.322	1.322	1.466	1.517	-	1.543
M-1C	(3)	26.0	1.323	1.321	1.476	1.536	-	1.547
M-2	(4)	21.2	1.323	1.318	1.490	1.535	-	1.544
D-1,1	(10)	128.9	1.334	1.325	1.474	1.569	1.564	1.548
D-1T2	(9)	107.9	1.335	1.319	1.502	1.534	1.548	1.542
D-1C2	(8)	69.5	1.323	1.318	1.492	1.523	1.556	1.541
D-1T3	(12)	22.7	1.319	1.322	1.495	1.516	1.537	1.544
D-1C3	(11)	63.1	1.322	1.322	1.493	1.520	1.545	1.542
D-1T4T	(7)	0.0	1.322	1.322	1.468	1.517	1.517	1.543
D-1C4C	(5)	55.6	1.324	1.324	1.476	1.538	1.538	1.547
D-1T4C	(6)	26.1	1.322	1.322	1.477	1.517	1.535	1.544
D-23	(13)	65.9	1.321	1.321	1.510	1.550	1.550	1.546

relative magnitude of the two types of repulsive sterical interaction being present in M-2.

5. Disubstituted *tert*-Butyl-1,3-butadienes

The potential-energy curves calculated for the nine di-*tert*-butyl-1,3-butadienes are shown in Figures 3–6. The steric-strain energy present in a disubstituted 1,3-butadiene molecule is influenced by each of the substituents in the same manner as described for the monosubstituted compounds above. Additionally, the mutual interaction between the two substituents will effect the total strain energy. The contribution from the latter type of interaction varies dramatically with the relative position of the two substituents, from being nearly negligible in 1-*trans*,4-*trans*-di-*tert*-butyl-1,3-butadiene to being the dominating effect for the 1,1- and 2,3-disubstituted isomers.

5.1 1-*trans*,4-*trans*-Di-*tert*-butyl-1,3-butadiene (7, D-1T4T)

The potential-energy curves calculated for the three 1,4-disubstituted 1,3-butadiene derivatives are presented in Figure 3. According to these data the difference in strain energy between D-1T4T and BD is, within 0.4 kJ/mol, equal to twice the energy difference between M-1T and BD. This is true over the entire potential-energy range and indicates that there is no interaction between the two *tert*-butyl substituents in this isomer.

This view is supported by the HF/3-21G calculations (see Tables 7 and 8) which have resulted in equal bond lengths, valence and dihedral angles for the D-1T4T and M-1T molecules.

5.2 1-*cis*,4-*cis*-Di-*tert*-butyl-1,3-butadiene (5, D-1C4C)

There is not the same degree of parallelism in the stereochemical behavior between D-1C4C and M-1C, as discussed above for D-1T4T and M-1T. This is mainly due to two factors.

One of these concerns the interaction between the two *tert*-butyl groups, which for D-1C4C is substantial over most of the potential-energy range. Figure 3 shows that the potential-energy curve of D-1C4C (**5**) does not have two minima, as do the potential curves for BD and D-1T4T, but instead has one minimum for the *anti* orientation and one inflection point in the 60−90° region. The very high strain energy over the entire range of the D-1C4C potential curve, escept in the region close to the energy minimum at *anti*, indicates that it will hardly be possible by any physical method to identify conformers other than *anti* for this molecule. The other factor is linked to the more restricted freedom of the D-1C4C molecule, compared to M-1C, with respect to the adjustment of its geometry parameters in order to reduce the total steric strain. This may be illustrated by the calculated (HF/3-21G) $C^1{=}C^2{-}C^3$ and $C^2{-}C^3{=}C^4$ angles for the two molecules, presented in Table 7. In the more flexible monosubstituted compound these angles are 128.0 and 121.9°, while both angles for reasons of symmetry are equal (126.8°) in D-1C4C. The somewhat larger $C^1{=}C^2{-}C^3$ angle, combined with a relatively small $C^2{-}C^3{=}C^4$ angle, appears to be the optimum local arrangement for the 1-*cis*-*tert*-butyl group, but this angle distribution is not feasible in the doubly substituted molecule. The $C{=}C{-}C_{tBu}$ angles are, however, calculated to be the same, 129.5°, in both molecules.

Another illustration of the significance of the restricted freedom in D-1C4C relative to that in M-1C, is the calculated energy difference (HF/3-21G) between D-1C4C and D-1T4T (55.6 kJ/mol), which is more than twice the energy difference between M-1C and M-1T (2 × 26 = 52 kJ/mol).

5.3 1-*trans*,4-*cis*-Di-*tert*-butyl-1,3-butadiene (6, D-1T4C)

The excess steric energy of D-1T4C over that of BD [ΔE(D1T4C − BD)] is very similar to the sum of the excess energies of M-1T and M-1C [ΔE(M-1T − BD) + ΔE(M-1C − BD)] over the entire dihedral angle range. It might therefore be concluded that the effects of 1-*trans*- and of 4-*cis*-*tert*-butyl groups in 1,3-butadiene are additive, and that the sterical interaction between the two *tert*-butyl groups in D-1T4C is negligible.

The valence angle distribution in D-1T4C (see Table 7) is in agreement with this conclusion, as $\sphericalangle C^1{=}C^2{-}C^3$ and $\sphericalangle C^2{=}C^1{-}C_{tBu}$ (121.2 and 127.3°) are similar to those in M-1T (123.6 and 127.4°), while $\sphericalangle C^2{-}C^3{-}C^4$ and $\sphericalangle C^3{=}C^4{-}C_{tBu}$ (127.8 and 129.1°) are nearly equal to the corresponding angles in M-1C (128.0 and 129.5°).

5.4 1-*trans*,3-Di-*tert*-butyl-1,3-butadiene (12, D-1T3)

The potential-energy curves calculated for the two 1,3-disubstituted 1,3-butadiene derivatives are presented in Figure 4. Also for the D-1T3 molecule do the effects originating from each of the two *tert*-butyl substituents appear to be additive, with minimal interaction between the two substituents and the shape of the D-1T3 potential-energy curve (see Figure 3) is strikingly similar to that of M-2 (see Figure 2). Both molecules have *gauche* energy minima, with similar MM3 dihedral angles (D-1T3: 53.9°; M-2: 49.2°). The stereochemical properties are therefore primarily determined by the effects originating from the substituent in 3-position.

The most important valence angles in the *trans*-substituted part ($\sphericalangle C^1{=}C^2{-}C^3$: 122.2° and $\sphericalangle C^2{=}C^1{-}C_{tBu}$: 127.4°) may be compared to analogous angles in M-1T (**2**) ($\sphericalangle C^1{=}C^2{-}C^3$: 123.6° and $\sphericalangle C^2{=}C^1{-}C_{tBu}$: 127.4°), while the ones most heavily influenced by the 3-*tert*-butyl group ($\sphericalangle C^2{-}C^3{=}C^4$: 119.7°; $\sphericalangle C^4{=}C^3{-}C_{tBu}$: 123.9°) may be compared to the structurally similar angles in M-2 ($\sphericalangle C^1{=}C^2{-}C^3$: 119.6° and $\sphericalangle C^1{=}C^2{-}C_{tBu}$: 124.3°).

5.5 1-*cis*,3-Di-*tert*-butyl-1,3-butadiene (11, D-1C3)

The D-1C3 potential-energy function (see Figure 4) shows no resemblance to those calculated for the structurally related monosubstituted M-1C and M2- molecules. The D-1C3 molecule has one (two) distinct energy minimum, corresponding to a (±)-*gauche* conformation, and the calculated (MM3) barriers in directions *syn* and *anti* are ca. 33 and 84 kJ/mol, respectively. This is in agreement with the potential energy of D-1C3 being to a very large degree dominated by strong repulsions between the two *tert*-butyl groups. These repulsions are at their maximum in the *anti* conformation, but appear to influence the energy and stereochemistry to varying degrees in all conformations. An indication of this is the valence angle distribution in the minimum-energy conformation, as calculated by HF/3-21G (see Table 7), where the $C^1{=}C^2{-}C^3$ (131.1°) and $C^2{=}C^1{-}C_{tBu}$ (134.3°) angles are found to be ca. 3 and 5° degrees larger than the already very large corresponding angles in M-1C ($C^1{=}C^2{-}C^3$: 128.0°; $C^2{=}C^1{-}C_{tBu}$: 129.5°).

5.6 1-*trans*,2-Di-*tert*-butyl-1,3-butadiene (8, D-1T2)

The potential-energy curves calculated for the two 1,2-disubstituted 1,3-butadiene derivatives are presented in Figure 5. The major contribution to the steric-strain energy of D-1T2 stems from the mutual repulsion between the two *tert*-butyl groups and is accordingly independent of the conformation of this isomer.

The potential-energy curve (Figure 5) may be compared to that of M-2 because the variation in potential energy in both molecules is determined by the interaction between the unsubstituted vinyl group and the other part of the molecule, where the substituent in 2-position is the dominating factor. Figures 5 and 2 show that the D-1T2 and M-2 potential-energy curves do both have only one (two) energy minimum [(±)-*gauche*], while the *anti* orientation corresponds to an energy maximum. The potential barriers are, however, much larger in D-1T2 than in M-2. This is easily explained on the basis of the secondary effect of the two (*Z*) substituents in 1,2-position. The primary effect is to open up the $C^2{=}C^1{-}C_{tBu}$ and $C^1{=}C^2{-}C_{tBu}$ valence angles to 140.0 and 131.9°, compared to the $C^1{=}C^2{-}C_{tBu}$ angle of 124.3° in M-2. The secondary effect of these enlarged valence angles is to increase the van der Waals repulsions between the D-1T3 vinyl group and its surroundings, especially in the *anti*, but also in the *syn* conformation.

5.7 1-*cis*,2-Di-*tert*-butyl-1,3-butadiene (9, D-1C2)

Because of the mutual 1-*cis*,2-*cis* orientations of the two D-1C2 substituents it is unlikely that direct sterical interactions between the two *tert*-butyl groups will have a significant influence on the potential-energy curve, which may be compared to those of the monosubstituted M-1C and M-2 molecules. If the calculated (MM3) excess-strain energy values of D-1C2 in Table 1, ΔE(D-1C2 − BD), are compared to the sums of the excess-strain energies of M-1C and M-2, ΔE(M-1C − BD) + ΔE(M-2 − BD) over the region of the variable C=C−C=C dihedral angle, the former energy exceeds the latter by merely 2.1−6.3 kJ/mol in the range from 30 to 150° for the dihedral angle. This is in accordance with the view that the steric strain introduced by the two substituents is approximately additive in this region. For the *anti* and *syn* conformers the calculated excess steric energy is 9.6 and 36.8 kJ/mol, respectively. This indicates that the secondary effect of the presence of two 1-*cis*,2-*cis* substituents implies some contribution to the total strain energy in D-1C2, due to limitations in the possibilities of adjusting the stereochemical environments around each of the *tert*-butyl groups. The effect is, however, moderate, except in the *syn* conformation. In the region close to the potential-energy minimum (θ: 81°, cf. Table 7) the calculated relative strain energy of D-1C2 compared to that of M-1C + M-2 is modest (2.5 kJ/mol) and may be associated with the valence-angle distributions in the three molecules (Table 9).

Table 9. Selection of valence angles [°] for 1-*cis*,2-di-*tert*-butyl- (**9**), 1-*cis*-*tert*-butyl- (**3**) and 2-*tert*-butyl-1,3-butadiene (**4**)

	$\angle C^1{=}C^2{-}C^3$	$\angle C^2{-}C^3{=}C^4$	$\angle C^2{=}C^1{-}C_{t\text{-}But}$	$\angle C^1{=}C^2{-}C_{t\text{-}But}$
D-1C2, 9	124.6°	124.2°	133.3°	119.2°
M-1C, 3	128.0°	121.9°	129.5°	-
M-2, 4	119.6°	124.2°	-	124.3°

5.8 1,1-Di-*tert*-butyl-1,3-butadiene (10, D-11)

The calculated MM3 potential energy of the D-11 molecule varies from 130 to 167 kJ/mol, and this molecule is therefore clearly the most strained of the disubstituted isomers. The strain energy is primarily due to steric repulsions between the two bulky *tert*-butyl groups bound to the same carbon atom. The potential-energy curve (see Figure 6) has a minimum for the *anti* conformation and a second broad minimum for the *gauche* orientation. The calculated energy difference between the two minima is ca. 8 kJ/mol, and in accordance with this the compound is expected to be approximately conformationally homogeneous (*anti*) under normal conditions.

The data in Tables 7 and 8 reveal that the steric strain in D-11 is primarily manifested in the very large $C^1{=}C^2{-}C^3$ angle (132.2°) and in the unusually long $C_{sp^2}{-}C_{sp^3}$ bonds (1.563 Å) that connect the *tert*-butyl groups to the C^1 atom.

5.9 2,3-Di-*tert*-butyl-1,3-butadiene (13, D-23)

The potential-energy curve calculated for D-23 (see Figure 6) has one well-defined minimum, corresponding to an approximately perpendicular conformation. The shape of the potential-energy curve shows that the interaction between the two substituents is strongly dependent on the conformation. This may be illustrated by the differences in excess D-23 strain energies, relative to that in BD [ΔE(D-23 − BD)], over twice the excess strain energies of M-2 [2 × ΔE(M-2 − BD)]. According to these rough calculations the excess strain energies of D-23 being twice as large as those of M-2 are: *syn*: 87.0 kJ/mol; θ = 90−120°: <2.1 kJ/mol; *anti*: 23.4 kJ/mol. The potential-energy minimum (99.1°; see Table 5) must obviously be a result of minimizing the steric repulsions between the two *tert*-butyl substituents.

6. General Discussion

6.1 Conformation

Among the twelve mono- and disubstituted *tert*-butyl-1,3-butadiene derivatives that have been studied, the following six have minimum potential energy for the *anti* conformation: M-1T, M-1C, D-11, D-1T4T, D-1C4C, D-1T4C. These molecules have one property in common: they are not substituted in 2- or 3-position. It therefore seems reasonable to conclude that unless a 1,3-diene is substituted in 2- or 3-position, an *anti* arrangement of the conjugated double bonds is to be expected.

For the other six derivatives the minimum-energy conformers have non-planar diene systems, with C=C−C=C dihedral angles between 49 and 99°. D-23 is the only one, among the derivatives studied, with a dihedral angle (99.1°) larger than 90°. The structure and conformation of D-23 have recently been studied by X-ray (XR)[7] and by gas electron diffraction (GED)[1]. The observed C=C−C=C dihedral angle (XR: 96.6°; GED: 101.5 ± 3.8°) is in perfect agreement with the theoretical result. The minimum-energy conformer is in this case determined by the sterical interactions between the two *tert*-butyl substituents. The thermochemistry of D-23 has been studied by Roth et al.[8], and their data are discussed in terms of an approximately perpendicular conformation, in agreement with the experimental GED[1] and XR[7] results, as well as with the calculations reported here.

The preferred conformation for each of the molecules M-2 (θ: 49.2°), D-1T3 (θ: 53.9°) and D-1T2 (θ: 60.4°) is probably determined by the same forces that are responsible for the conformation of the metastable form of 1,3-butadiene: a) sterical interactions between the C^1H_2 and C^4H_2 groups, and b) the π-electron interaction. The data calculated for M-2, D-1T3 and D-1T2 are in accordance with the first of these effects being the most dominant. This may be illustrated by the data taken or calculated from Tables 7 and 8 (Table 10).

Table 10. Selection of valence angles [°] for 2-*tert*-butyl- (**4**), 1-*trans*,3-di-*tert*-butyl- (**12**) and 1-*trans*,2-di-*tert*-butyl-1,3-butadiene (**8**)

	θ(°)	$\angle C^1{=}C^2\text{-}C^3$	$+ \angle C^2\text{-}C^3$	$=C^4$ (°)	$r(C^1\cdots C^4)$ (Å)
M-2, 4	49.2	119.6	+ 124.2	= 243.8	3.032
D-1T3, 12	53.9	122.2	+ 119.7	= 241.9	3.032
D-1T2, 8	60.4	114.1	+ 124.6	= 238.7	3.029

The calculated $C^1\cdots C^4$ distances are approximately identical in the three derivatives. The C=C−C valence angles are, however, widely different, and the molecules seem to adjust their C=C−C=C dihedral angles in order to obtain the energetically most favorable distance between the two terminal methylene groups. A recent gas electron diffraction study of M-2[1] has provided a somewhat smaller C=C−C=C dihedral angle (32.1 ± 9.0°), but as this molecule has a very shallow potential energy minimum (see Figure 2), the differences in methodology may in fact lead to different theoretical and experimental results. In the derivatives D-1C2 (θ: 81.0°) and D-1C3 (θ: 67.3°) the minimum-energy conformation must be primarily determined by the sterical interactions between the 1-*tert*-butyl substituent and the C^4H_2 group. These types of interaction are more complicated than those discussed above, as they involve also the valence and dihedral angles of the three methyl groups in the substituent.

There are not many studies of similar molecules available for comparison with our results. Brouwer et al.[9] have, however, recently studied the steric perturbation of the conjugated triene chromophor, and among the molecules included in their study is (3*Z*)-3-*tert*-butyl-1,3,5-hexatriene (Z-3). NMR Nuclear Overhauser Enhancement difference experiments have revealed that the dominating conformer is cZt, where c and t denote a non-planar *s-cis* and a planar *s-anti* C−C bond. Ab initio HF calculations, using the same basis set that has been applied in the present study, 3-21G, give a torsion angle for the c C−C bond of 60°. Among the derivatives that have been studied in the present work, D-1C2 has a structure that is most closely related to that of Z-3. The structural similarity between D-1C2 and Z-3 involves the conjugated backbone and the 2-*tert*-butyl substituent in D-1C2 and the $C^{1(4)}{=}C^{2(3)}$(*tert*-butyl)$-C^{3(2)}{=}C^{4(1)}$ part of Z-3. (For clarity we have therefore changed the numbering of the atoms in Z-3. The correct numbers are given in parentheses.) The difference is due to the nature of the 1-*cis* substituent, which in D-1C2 is a *tert*-butyl group and in Z-3 a vinyl group with *s-anti* orientation. The steric repulsion between the terminal CH_2 group and the 1-*cis* substituent is larger when the substituent is a *tert*-butyl than when it is a vinyl group with *s-anti* orientation. The relative magnitude of the dihedral angles calculated for Z-3 (60°)[9] and D-1C2 (81°) is therefore very reasonable.

6.2 Bond Lengths

The calculated C=C bond lengths (see Table 8) vary from 1.318 Å (M-2 and D-1C2) to 1.335 Å (D-1T2), and the maximum difference of 0.017 Å shows that the C=C bond lengths are only modestly influenced by the steric strain present in these molecules.

This is different for the calculated C^2-C^3 bond lengths, where the maximum difference is 0.044 Å. The derivatives with *anti* minimum-energy conformation have C^2-C^3 bond lengths in the range of 1.466−1.477 Å, while those for non-planar diene systems are between 1.490 Å and 1.510 Å. The calculated results are therefore in accordance with the theory of π-electron delocalization − which is at its maximum for a coplanar π system − and its effect on bond lengths. In some of the conformers, particularly in D-23, steric strain is also expected to contribute to stretching the C^2-C^3 bond. Small hybridization differences in the carbon atoms, due to different angle distributions, might also be of some importance. The main effect, however, is believed to be the differences in π-bond order of the C^2-C^3 bonds.

The variations in the $C-C_{subst.}$ bond lengths may be illustrated by the difference between the $C-C^5$ bond of 1.517 Å in M-1T and D-1T4T and 1.569 Å and 1.564 Å in D-11. In the latter case the bonds have obviously been stretched in order to reduce the van der Waals repulsions between the two geminal *tert*-butyl substituents. A similar, but smaller effect might be seen by comparing the $C-C^5$ bonds in M-1T or D-1T4T (1.517 Å) and in M-1C or D-1C4C (1.536 Å; 1.538 Å).

6.3 Valence Angles

Table 7 shows the most important valence angles resulting from the ab initio calculations. They vary over large intervals, in accordance with the generally accepted principle that it is easier to deform an angle than to stretch a bond in order to reduce steric strain. $C^1{=}C^2-C^3$ angles smaller than 120° are calculated for M-2, D-1T2 and D-23. These derivatives are all substituted in 2-position, and the small $C^1{=}C^2-C^3$ angles reflect the steric requirements of the bulky C^2 substituents. The inclination toward small C=C−C valence angles for such derivatives is, however, often counteracted by other forces, which is demonstrated by the $C^1{=}C^2-C^3$ angles calculated for D-1C2 (124.6°), D-1T3 (122.2°) and D-1C3 (131.1°).

A *cis-tert*-butyl substituent in 1- or 4-position generally results in a $C{=}C-C_{subst.}$ angle of ca. 130° (M-1C: 129.1°; D-1C2: 133.3°; D-1C3: 134.3°; D-1C4C: 129.5°). The only exception to this behavior is found for D-11 (124.0°), where the repulsions between the two substituent groups prevent a further opening of this angle.

6.4 Orientation of the *tert*-Butyl Groups

The *tert*-butyl groups in M-1T, M-2 and D-1T4T have been found to have normal orientations, with approximately local C_3 symmetry around the $C-C^5$ bond and one $C-CH_3$ bond eclipsing the nearest C=C bond. Derivatives with *cis*-

substituted C^1 or C^4 atoms do, however, tend to have substituents that are rotated nearly 60°, relative to eclipsing of one $C-CH_3$ bond. Such orientations, corresponding to maximum torsional strain at the $C-C_{\text{subst.}}$ bond, are calculated for the *tert*-butyl substituents in M-1C and D-1C4C. The explanation behind such energetically unfavorable orientations is expected to be found in simultaneous reduction in sterical repulsions, which more than compensate for the increased torsional energy.

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[1] Part IV: H. Hopf, M. Trætteberg, H. Lipka, R. Hänel, *Chem. Ber.* **1994**, *127*, 1459–1467, preceding paper.

[2] [2a] K. W. F. Kohlrausch, H. Wittek, *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 227–232. – [2b] G. Köbrich, A. Mannschreck, R. A. Misra, G. Rissmann, M. Rösner, W. Zündorf, *Chem. Ber.* **1972**, *105*, 3794–3806.

[3] H. Hopf, H. Lipka, M. Trætteberg, *Angew. Chem.* **1994**, *106*, 232–233; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 204–205.

[4] N. Allinger, Y. H. Yuh, J.-H. Lii, *J. Am. Chem. Soc.* **1989**, *111*, 8551–8566.

[5] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachira, M. A. Robbs, J. C. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, *GAUSSIAN90*, Gaussian Inc., Pittsburgh PA, **1990**.

[6] H. O. Villar, M. Dupuis, *Theor. Chim. Acta* **1992**, *83*, 155–163.

[7] W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz, R. Boese, *Chem. Ber.* **1991**, *124*, 2499–2521.

[8] W. R. Roth, H.-W. Lennartz, W. von E. Doering, W. R. Dolbier, Jr., J. C. Schmidhauser, *J. Am. Chem. Soc.* **1988**, *110*, 1883–1889.

[9] A. M. Brouwer, L. Bezemer, H. J. C. Jacobs, *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 138–143.

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