Journal of Molecular Structure, 129 (1985) 57—67
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

STRUCTURE AND VIBRATIONAL ASSIGNMENT OF *gauche*-1,3-BUTADIENE

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(Received 17 January 1985)

ABSTRACT

The completely optimized structures and harmonic force fields of the *s-trans*(*anti*)- and *gauche*-isomers of 1,3-butadiene have been computed at the ab initio Hartree—Fock level using the 6-31G basis set. The *gauche* dihedral angle was found to be 34 8° from the planar *s-cis*(*syn*)-configuration of the 1,3-butadiene molecule. Seven scale factors for correcting the theoretical force constants of the *trans*-isomer were calculated from the experimental frequencies of light and heavy *trans*-1,3-butadienes. The correction of the *gauche*-butadiene force field was then carried out using these scale factors, and the vibrational problems were solved for *gauche* forms of C_4H_6, $CD_2CHCHCD_2$, C_4D_6, $^{13}CH_2CHCH^{13}CH_2$, and $^{13}CH_2CHCHCH_2$. The total assignment of the experimental vibrational frequencies of these isotopomers is given The conclusion drawn is that the quantum mechanical geometry and the scaled quantum mechanical force field correctly simulate the structure and the experimental frequencies of the butadiene *gauche*-conformer

INTRODUCTION

During the last few years a series of studies has been completed in which many of the experimental vibrational frequencies of the second rotational isomeric form of 1,3-butadiene have been observed [1—4]. However, the suggested interpretations of the experimental spectrum were different in some cases [1—8]. The analysis of the "hot" band progression of the Raman active torsional overtone $2\nu_{13}$ of 1,3-butadiene allowed the construction of a potential energy curve of internal rotation around the central C—C bond [9]. This curve turned out to be applicable to the series of its isotopomers [10]. According to this experimental curve the second form of the C_4H_6 molecule is rotated about 23° from the planar *s-cis*-form(*syn*-form) [9, 10]. The most recent quantum mechanical calculations give an angle of internal rotation of about 38° from the planar *s-cis*-form [11—14]. The direct electron diffraction measurement does not allow the determination of the exact structure of the second form [15].

0022-2860/85/$03.30

Calculations of the vibrational frequencies have been carried out for a planar *s-cis*-form of 1,3-butadiene [3—8], the force constants being transferred in some cases from the *s-trans*-form force field [3, 4, 8]. A calculation for the *gauche*-form (40° from the planar *cis*-configuration) has also been published; however, the same force field was used as for the *s-cis*-configuration [4] which is probably the reason why its results practically coincided with those on the *cis*-configuration calculation [4].

In this connection it is of interest to perform the quantum mechanical computation of the structure and the harmonic force field of the second rotational isomeric form of 1,3-butadiene and to predict the vibrational frequencies of this conformer. This in turn can be used to facilitate the assignment of the observed frequencies for this conformer.

METHOD OF COMPUTATION

The geometrical parameters and force constants of the *trans*- and *gauche*-isomers of 1,3-butadiene were computed by the ab initio Hartree—Fock method using the 6-31G basis set and gradient optimization [16] The completely optimized structural parameters of these two forms of 1,3-butadiene are given in Table 1.

At present, the combination of the theoretical and the experimental information was accepted as usual practice in the force field calculations of homologous series of molecules (see, for example, ref 17). According to this technique the force fields are calculated for a standard (calculated ab initio and then experimentally corrected) geometry. Further the force constants are corrected by empirical scale factors. However, the main purpose of this work is to predict the vibrational frequencies of *gauche*-C_4H_6 and to assign those that have been observed experimentally. Hence the transition to a

TABLE 1

Completely optimized geometry of *trans*- and *gauche*-1,3-butadiene

Parameter	*trans*-C_4H_6	*gauche*-C_4H_6
$C{=}C^a$	1.3276	1.3266
$C{-}C^a$	1.4645	1.4739
$C{-}H_{trans\text{-}terminal}{}^a$	1.0726	1.0730
$C{-}H_{cis\text{-}terminal}{}^a$	1.0748	1.0741
$C{-}H^a$	1.0767	1.0769
$\angle C{=}C{-}C^b$	124.29	125.76
$\angle C{=}C{-}H_{trans\text{-}terminal}{}^b$	121.79	121.51
$\angle C{=}C{-}H_{cis\text{-}terminal}{}^b$	121.80	122.04
$\angle C{=}C{-}H^b$	119.55	118.89
Dihedral angle^b	0.0	34.78
Energy^c	—154.864576	—154.859731

[a] Angstrom units [b] Degrees [c] Atomic units.

standard geometry was not made and force fields were computed for the theoretical structures of the *trans*- and *gauche*-isomers. The force constants as obtained in cartesian coordinates were transformed into the internal vibrational coordinates in order to correct them using empirical scale factors. As internal coordinates, the local valence coordinates were chosen [18]. The coupling force constants are small in these coordinates, and it is easier to assign the calculated frequencies by their vibrational forms (normal-mode vectors, or eigenvectors). The definition of these coordinates for *trans*-1,3-butadiene is given in ref. 17.

The scaling procedure has been previously described [5, 19]. It is a congruent transformation of the force constant matrix. The values of the scale factors were obtained by minimizing the weighted mean-square deviation between the calculated and the experimental fundamental frequencies for the *trans*-form of light and heavy 1,3-butadiene using a program written by Dr. G. Pongor The experimental vibrational frequencies and their assignment for the *trans*-conformers of the C_4H_6 and C_4D_6 molecules are well known since 14 isotopomers of this molecule have been investigated [3, 20, 21] The values of the scale factors obtained are given in Table 2. As a starting approximation, the scale factors used were those calculated for the *trans*-form of 1,3-butadiene in ref 17 (see the last column in Table 2).

Correction of the theoretical force constant matrix of *gauche*-1,3-butadiene was performed using the seven scale factors calculated for the *trans*-conformer. The empirically corrected force constants obtained for the *trans*- and *gauche*-forms of butadiene are given in Tables 3 and 4. The vibrational problems were solved with these force fields for the *trans*-isomers of C_4H_6 and C_4D_6 (Table 5) and the *gauche*-isomers of C_4H_6, $C_4H_2D_4$, C_4D_6, 1,4-$^{13}C_2$-C_4H_6, and 1-^{13}C-C_4H_6 (Table 6). The assignment of the experimental frequencies of the *gauche*-conformer was carried out using data on the potential energy distribution taking into account the isotopic shifts

TABLE 2

Optimized scale factors

Scale factor	Basis set		
	6-31G (this work)	4 31G [22]	4-21G [17]
C—C stretch	0.8514	0.887—0.909	0.9215
C=C stretch	0.7573	0.869—0.872	0.8657
C—H stretch	0.8301	0.881—0.890	0.8677
C=C—C, C=C—H in-plane	0.7944	0.793—0.816	0.8025
C—C torsion	0.9979	--	1.095
C—H, =CH_2 wag	0.6706	0.718—0.746	0.7217
C=C twist	0.7980	0.793—0.816	0.7337

TABLE 3

Scaled force constant matrix of *trans*-1,3-butadiene[a]

	1	2	3	4	5	6	7	8
1	5.087							
2	0.299	8.521						
3	0.299	−0.069	8.521					
4	−0.004	0.046	0.007	5.209				
5	−0.004	0.007	0.046	0.002	5.209			
6	0.004	0.064	−0.002	0.026	0.001	5.138		
7	0.004	−0.002	0.064	0.001	0.026	0.0	5.138	
8	0.054	0.068	0.019	0.015	−0.001	0.0	0.011	5.048
9	0.054	0.019	0.068	−0.001	0.015	0.011	0.0	0.0
10	0.211	0.168	0.065	0.047	0.013	−0.059	−0.002	−0.150
11	0.211	0.065	0.168	0.013	0.047	−0.002	−0.059	−0.048
12	0.180	−0.184	−0.011	0.009	−0.003	−0.027	0.011	−0.002
13	0.180	−0.011	−0.184	−0.003	0.009	0.011	−0.027	0.022
14	−0.005	−0.197	−0.001	0.058	0.0	0.056	0.001	−0.007
15	−0.005	−0.001	−0.197	0.0	0.058	0.001	0.056	−0.006
16	0.041	0.008	0.009	0.097	0.002	−0.105	0.003	−0.035
17	0.041	0.009	0.008	0.002	0.097	0.003	−0.105	−0.003

	9	10	11	12	13	14	15	16
9	5.048							
10	−0.046	1.055						
11	−0.150	0.153	1.055					
12	0.022	0.005	−0.046	0.525				
13	−0.002	−0.046	0.005	0.037	0.525			
14	−0.006	−0.012	−0.009	0.015	−0.001	0.447		
15	−0.007	−0.009	−0.012	−0.001	0.015	0.0	0.447	
16	−0.003	0.083	0.011	0.039	0.0	0.002	−0.001	0.527
17	−0.035	0.011	0.083	0.0	0.039	−0.001	0.002	0.003

	17	18	19	20	21	22	23	24
17	0.527							
18		0.029						
19		0.003	0.246					
20		0.003	−0.009	0.246				
21		0.0	0.024	−0.003	0.232			
22		0.0	−0.003	0.024	0.0	0.232		
23		0.005	0.0	−0.013	0.0	−0.004	0.126	
24		0.005	−0.013	0.0	−0.004	0.0	−0.004	0.126

[a] For definition and order of internal coordinates see ref. 17

DISCUSSION

The calculated geometrical parameters of the two molecular forms corroborate the changes which are expected when passing from a *trans* to a *gauche*-conformer. An accentuation in the alternation of the carbon—carbon bonds

TABLE 4

Scaled force constant matrix of *gauche*-1,3-butadiene[a]

	1	2	3	4	5	6	7	8
1	4.968							
2	0.277	8.543						
3	0.277	−0.061	8.543					
4	−0.003	0.048	−0.002	5.190				
5	−0.003	−0.002	0.048	0.001	5.190			
6	−0.008	0.061	0.013	0.026	0.0	5.166		
7	−0.008	0.013	0.061	0.0	0.026	0.009	5.166	
8	0.068	0.077	0.003	0.015	0.005	−0.001	0.0	5.034
9	0.068	0.003	0.077	0.005	0.015	0.0	−0.001	0.015
10	0.266	0.151	−0.022	0.050	−0.008	−0.077	−0.011	−0.150
11	0.266	−0.022	0.151	−0.008	0.050	−0.011	−0.077	0.041
12	0.186	−0.191	0.024	0.009	0.007	−0.027	0.002	−0.003
13	0.186	0.024	−0.191	0.007	0.009	0.002	−0.027	0.0
14	−0.006	−0.199	−0.007	0.059	0.001	0.058	−0.001	−0.007
15	−0.006	−0.007	−0.199	0.001	0.059	−0.001	0.058	−0.001
16	0.029	0.010	−0.003	0.095	0.002	−0.098	0.003	−0.037
17	0.029	−0.003	0.010	0.002	0.095	0.003	−0.098	0.008
18	0.009	0.018	0.018	−0.001	−0.001	0.001	0.001	−0.012
19	−0.014	0.0	0.004	0.003	0.0	0.001	0.001	−0.008
20	−0.014	0.004	0.0	0.0	0.003	0.001	0.001	0.0
21	−0.013	0.003	0.003	0.002	0.001	−0.007	0.0	0.0
22	−0.013	0.003	0.003	0.001	0.002	0.0	−0.007	0.0
23	0.028	−0.001	0.003	0.002	0.0	0.004	0.001	−0.001
24	0.028	0.003	−0.001	0.0	0.002	0.001	0.004	−0.004

	9	10	11	12	13	14	15	16
9	5.034							
10	0.041	1.091						
11	−0.150	0.016	1.091					
12	0.0	0.008	0.062	0.531				
13	−0.003	0.062	0.008	−0.009	0.531			
14	−0.001	−0.012	−0.004	0.015	−0.003	0.446		
15	−0.007	−0.004	−0.012	−0.003	0.015	0.003	0.446	
16	0.008	0.067	−0.021	0.040	0.009	0.0	0.002	0.529
17	−0.037	−0.021	0.067	0.009	0.040	0.002	0.0	0.005
18	−0.012	0.035	0.035	0.001	0.001	−0.004	−0.004	−0.007
19	0.0	−0.016	0.006	0.004	−0.011	0.003	0.0	0.004
20	−0.008	0.006	−0.016	−0.011	0.004	0.0	0.003	0.005
21	0.0	−0.009	0.001	0.001	−0.004	0.001	0.002	0.004
22	0.0	0.001	−0.009	−0.004	0.001	0.002	0.001	0.002
23	−0.004	0.014	0.039	0.001	−0.008	0.0	−0.003	−0.002
24	−0.001	0.039	0.014	−0.008	0.001	−0.003	0.0	−0.001

TABLE 4 (continued)

	17	18	19	20	21	22	23	24
17	0.529							
18	−0.007	0.017						
19	0.005	−0.001	0.243					
20	0.004	−0.001	0.008	0.243				
21	0.002	0.0	0.026	0.004	0.235			
22	0.004	0.0	0.004	0.026	0.0	0.235		
23	−0.001	0.003	−0.002	0.008	0.0	0.003	0.128	
24	−0.002	0.003	0.008	−0.002	0.003	0.0	0.004	0.128

[a]For definition and order of internal coordinates see ref 17.

is observed with decreasing length of the C=C bond and increasing length of the C—C bond (see Table 1). Furthermore, the value of the C=C—C angle increases noticeably, resulting in some decrease of the C=C—H angle. These changes are possibly connected with disturbances of the conjugation in the skew configuration.

Our use of the optimized geometry, rather than a standard or experimental geometry, gave a set of force constant scaling factors somewhat different from those of other authors (Table 2) for the *trans*-form. This is most noticeable for the scale factors of the stretching force constants, since they depend strongly on the adopted geometry. This effect was greatest in the case of the scale factor for stretching the C=C bond since the deviation of the calculated value of this bond length from the standard geometry was the largest. Deviation from the scale factors given in ref. 17 is caused by the use of a different basis set in the present work; in addition a reversal of the assignment for the ν_{10} and ν_{23} frequencies of *trans*-C_4D_6 was accepted (see below). The procedure of scaling was also slightly different from that used in Ref. 22. Nevertheless, the set of scale factors obtained as a whole is quite close to that obtained in ref. 17, and thus the structures of the force constant matrices for the *trans*-form are similar in the present work and in ref. 17 (Table 3).

Comparing the force fields of the *trans*- and *gauche*-conformers, it is interesting to note the appearance of large non-diagonal elements in the force constant matrix of the *gauche*-form which are situated at the "intersection" of in-plane and out-of-plane coordinates. This clearly demonstrates that using the force constants of the *trans*-form to calculate the vibrational frequencies of the *gauche*-form is not in general justified.

Frequencies of the *trans*-form, calculated with the empirically corrected force field, are in good agreement with the experimental results (Table 5). It should be noted that there is some disagreement as to the assignment of the ν_{10} and ν_{23} bands of *trans*-C_4D_6. In refs. 3, 4, and 17 it was suggested that the assignment of bands at 768.8 cm^{-1} and 735.6 cm^{-1} be interchanged in comparison with the earlier suggested assignment [20]. However, experimental study of the IR spectra of the *trans*-C_4D_6 molecule in the crystalline phase

TABLE 5

Experimental and calculated fundamental vibrational frequencies of *trans* forms of 1,3 butadiene and d_6-1,3-butadiene

Assignment	*trans* CH_2=CH–CH=CH_2								*trans*-CD_2=CD–CD=CD_2							
	Sym.	ν	Exp [20]	Calc	Sym.	ν	Exp. [20]	Calc.	Sym.	ν	Exp. [8, 20]	Calc.	Sym.	ν	Exp [3, 20]	Calc.
$\nu(CH_2)$str.	a_g	1	3101	3110	b_u	17	3102	3110	a_g	1	2341	2316	b_u	17	2336	2316
ν(C–H)str.		2	3014	3035		18	3056	3036		2	2262	2251		18	2255	2251
$\nu(CH_2)$str		3	3014	3021		19	3010[a]	3027		3	2205	2205		19	2215	2206
ν(C=C)str.		4	1643	1668		20	1599	1591		4	1583	1604		20	1523	1497
$\delta(CH_2)$sc.		5	1442	1456		21	1385	1388		5	1048	1050		21	1042	1053
ρ(C–H)r.		6	1291[a]	1290		22	1296.2	1304		6	919	926		22	1009	1005
ν(C–C)str.		7	1205	1214		—	—	—		7	1186	1178		—	—	—
$\rho(CH_2)$r		8	890	878		23	990.6	909		8	739	730		23	768.8	749
δ(C=C–C)b.		9	513	507		24	301	292		9	440	439		24	253.5	246
χ(C–H)w.	a_u	10	1013.2	1021	b_g	14	967	975	a_u	10	735.6	768	b_g	14	795	796
$\chi(CH_2)$w.		11	907.8	912		15	911	911		11	718.5	715		15	702	687
$\tau(CH_2)$tw.		12	524.5	512		16	753	739		12	381	374		16	603	598
τ(C–C)tor.		13	163	163		—	—	—		13	140	141		—	—	—

[a] Corrected on Fermi resonance. Values expressed in cm^{-1}

TABLE 6

Experimental and calculated fundamental vibrational frequencies of *gauche*-forms of 1,3-butadiene, 1,1,4,4, d_4-1,3 butadiene, d_6-1,3-butadiene, 1,4-$^{13}C_2$-1,3 butadiene, and 1-^{13}C-1,3 butadiene

Assignment	Sym	$CH_2CHCHCH_2$		$CD_2CHCHCD_2$		$CD_2CDCDCD_2$		$^{13}CH_2CHCH^{13}CH_2$		$^{13}CH_2CHCHCH_2$ [a]	
		Exp. [3, 4]	Calc.	Exp. [4]	Calc.	Exp [3, 4]	Calc.	Exp. [3]	Calc	Exp. [3]	Calc.
1 $\nu(CH_2)$str.	*a*	3103	3112	2337	2317	2335	2317	3068	3099	3100	3110
2 ν(C–H)str		3030	3041	3013	3036	2256	2253	–	3038	–	3040
3 $\nu(CH_2)$str		3014	3026	2228	2219	2222	2207	3008	3027	3010	3030
4 ν(C=C)str		1633	1635	1592	1590	1552	1582	1612	1614	1626	1632
5 $\delta(CH_2)$sc.		1425	1448	1084	1090	–	1009	1424	1423	1424	1447
6 ρ(C–H)r		–	1318	1305	1311	–	838	–	1312	–	1315
7 $\rho(CH_2)$r.		–	1057	–	723	708	723	–	1053	–	1055
8 χ(C–H)w		983	987	927	921	–	776	–	986	982	986
9 $\chi(CH_2)$w.		915[b]	918	726	744	712	701	907[b]	909	913	918
10 ν(C–C)str.		–	865	944	969	1165	1159	–	857	–	861
11 γ(C=C)tw.		727	729	694	592	587	588	731	728	731	729
12 δ(C=C–C)b.		–	271	–	234	–	232	–	265	–	268
13 τ(C–C)tor.		–	155	–	136	–	122	–	154	–	155
14 $\nu(CH_2)$str	*b*	3103	3109	2337	2314	2335	2315	–	3096	–	3098
15 ν(C–H)str		3039	3033	3025	3019	2256	2246	–	3023	–	3024
16 $\nu(CH_2)$str		3014	3016	2228	2219	2222	2203	–	3016	–	3016
17 ν(C=C)str		1612	1629	–	1577	1528	1531	–	1608	–	1611
18 $\delta(CH_2)$sc		1403	1423	1031	1040	1056	1068	1401	1422	1401	1422
19 ρ(C–H)r.		–	1286	1285	1292	877	875	–	1278	–	1281
20 $\rho(CH_2)$r		1087	1094	–	945	–	1009	1077	1084	1083	1089
21 χ(C–H)w		996	1002	914	913	753	761	996	1002	996	1002
22 $\chi(CH_2)$w		914	918	727	731	715	709	907	909	905	909
23 δ(C=C–C)b.		596	604	498	505	492	497	596	603	597	604
24 τ(C–C)tw		468	451	373	358	360	345	467	450	467	451

Values expressed in cm^{-1}. [a]All the vibrations belong to the *a* symmetry type [b]Values as estimated from $\nu_9 + \nu_{12}$ (1829 cm^{-1} and 1814 cm^{-1}, respectively) [3] allows, by analogy with C_4H_6, assignment of the band at 735.6 cm^{-1} to the out-of-plane vibration ν_{19} of the C—D bond. Provided that the structure of the C_4H_6 and the C_4D_6 crystals are the same, this assignment is corroborated by the value and the direction of shift, the value of splitting, and the polarization of components of the split band in the IR spectrum when passing from the gas phase to the crystal for the frequency pairs of 907.8—718.5 cm^{-1} and 1013.2—735.6 cm^{-1} (Table 5). The spectral region under consideration and a detailed discussion are given in ref. 23.

The calculation of the vibrational frequencies of *trans*-C_4H_6 showed that the ν_{19} frequency should be reassigned. Indeed, in the IR spectrum of C_4H_6 in condensed phase there are five bands instead of three, i e 2972, 2998, 3023, 3044, and 3084 cm^{-1} [24]. Those at 2998 cm^{-1} and 3023 cm^{-1} are weak and are possibly combination bands On going from the vapour to the solid state, shifts of 10—20 cm^{-1} to the low frequency are observed. Such a low frequency of the strong band at 2972 cm^{-1} (2985 cm^{-1} in vapour) could be explained by a shift due to a Fermi resonance with a combination band ($1643 + 1385 = 3028$, $a_g \times b_u$) and by a phase shift Obviously, the value of the vibrational frequency ν_{19} in the condensed phase should be equal to $(2972 + 3023)/2 = 2997$ cm^{-1}. Then in the gas phase it should be situated approximately at 3010 cm^{-1} (Table 5) and indeed, this vibrational frequency in the molecules $CH_2CHCDCD_2$ and *trans*-$CHDCHCHCH_2$ is observed at 2997 cm^{-1} and 3003 cm^{-1}, respectively [20]. The vibrational frequency ν_6 in the C_4H_6 molecule is also corrected by Fermi resonance [20] (Table 5).

The assignment of the vibrational frequencies of *gauche*-C_4H_6 (Table 6) coincides in general with the results given in Refs. 3 and 4 and differs in the interpretation of frequencies from Ref. 8 for vibrations ν_{12}, ν_{23}, and ν_{24} In Ref. 8 the experimental bands at 472 cm^{-1} and 475 cm^{-1} [2] are assigned to the ν_{12} and ν_{23} vibrations Later, only one band ascribed to ν_{24} (Table 6) was observed in this region of the C_4H_6 spectrum [3, 4]. The 596 cm^{-1} band interpreted as ν_{24} in Ref. 8 was reassigned to ν_{23} [3, 4].

Table 6 also contains the experimental and the calculated vibrational frequencies for the *gauche*-forms of the $C_4H_2D_4$ and the C_4D_6 molecules. In the case of the $C_4H_2D_4$ molecule the present calculation allows the reassignment of the vibrational frequencies ν_5 and ν_{18} in comparison with the assignment in Ref. 4 The frequency of the $=CD_2$ group scissoring is very characteristic and should not depend on the rotation angle around the C—C bond. For the *trans*-conformers of the $C_4H_2D_4$ and the C_4D_6 molecules this frequency is about 1050 cm^{-1} [20] which corroborates the assignment of the 1084 cm^{-1} band to ν_5. The experimental band at 927 cm^{-1} corresponds very well to the 60 cm^{-1} shift of the calculated vibrational frequency ν_8 when passing from C_4H_6 to $C_4H_2D_4$.

For the C_4D_6 molecule the present calculations confirmed the assignment of the experimental band at 877 cm^{-1} to ν_{19} [3] in contradiction to its interpretation as ν_6 [4].

The most interesting fact in the assignment of the vibrational frequencies of the *gauche*-conformers of $C_4H_2D_4$ and C_4D_6 is the inverse isotopic shift [25] of the C—C bond stretching frequency ν_{10} (Table 6). A similar inverse isotopic shift was observed for the stretching frequencies ν_{10} and ν_{33} of the C—C bond in the *trans-cis-trans*-1,3,5-hexatriene molecule on going to its 2,3,4,5-tetradeuteroanalogues [26]. It should be noticed that in the *trans*-form substitution of the H atoms by D atoms shifted the stretching frequency of the C—C bond very little (ν_7 in Table 5), while in the *gauche*-form it resulted in an increase of this frequency to 300 cm^{-1} (ν_{10} in Table 6).

The calculated values of the vibrational forms (normal-mode vectors or eigenvectors), distribution of potential energy [27, 28] and the isotopic shifts of the experimental vibrational frequencies confirmed the adopted assignments for all molecules studied

Table 6 gives the results of the vibrational frequency calculation of the *gauche*-forms of 1-^{13}C-1,3-butadiene and 1,4-$^{13}C_2$-1,3-butadiene. The isotopic shifts for these molecules are small and do not give any essential information in addition to the data already existing for C_4D_6 and $C_4H_2D_4$. However, the spectra of these molecules give further confirmation for the experimental detection of the bands belonging to the second rotational isomeric form of 1,3-butadiene.

CONCLUSIONS

The calculation of the vibrational frequencies of the second rotational isomeric form of 1,3-butadiene showed that all its observed frequencies may be assigned to vibrations of the *gauche*-form with a rotation angle of about 34.8° from the planar *s-cis*-configuration. An additional experimental argument for the realization of the *gauche*-form is the manifestation in the IR spectrum of the bands of the ν_8, ν_9, and ν_{11} vibrations. In the case of an *s-cis*-configuration these must belong to the a_2 symmetry type and be forbidden in the IR spectrum

Good agreement between the calculated and experimental vibrational frequencies of the *gauche*-form and the difference of its force field from that of the *trans*-form demonstrates the possibility of using the same set of scale factors for several structural isomers and shows in general the inaccuracy of transferring force constants from one rotational isomer to another.

The calculation performed is an additional example of the solution of the structural problem by means of the gradient technique the application of which was discussed in detail in Ref. 29.

ACKNOWLEDGEMENT

The authors are deeply grateful to Dr. Yu. Furukawa for providing the experimental data on vibrational frequencies of *gauche*-1,1,4,4-d_4-1,3-butadiene.

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