

AB INITIO STRUCTURES AND VIBRATIONAL ANALYSIS OF THE ISOPRENE CONFORMERS

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(Received 27 November 1986; in final form 18 February 1987)

SUMMARY

Complete gradient optimizations of the structures and the calculation of the harmonic force fields of the *s-trans(anti)* and *gauche* conformers of isoprene (2-methylbuta-1,3-diene) are reported at the RHF/6-31G level. The dihedral angle of the *gauche* conformer is found to be 41.0° from the planar *s-cis(syn)* form. The force fields obtained are refined using scale factors transferred from analogous calculations for *trans*-butadiene-1,3 and ethane. The direct vibrational problems are solved for both conformers of isoprene. A complete assignment of the experimental vibrational frequencies is given.

INTRODUCTION

The experimental vibrational frequencies of the high-energy form of isoprene (2-methylbuta-1,3-diene, $\text{CH}_2=\text{CCH}_3-\text{CH}=\text{CH}_2$) were measured a few years ago [1, 2]. Compton et al. [1] studied the temperature dependence of the Raman and IR spectra of liquid isoprene. Some experimental frequencies which disappeared on freezing in the $150\text{--}700\text{ cm}^{-1}$ region were assigned to a high energy rotational isomer, the structure of which was assumed to be *s-cis(syn)*.

Sheridan [2] studied the IR spectra of crystalline samples in the $400\text{--}2000\text{ cm}^{-1}$ region. These samples were obtained by freezing gaseous isoprene at room temperature and at 600°C , respectively. Consequently narrower bands were observed than in the spectra of the liquid sample. Some frequencies of a minor form were detected and again assigned to an *s-cis* conformer [2].

From gas electron diffraction measurements [3] the abundance of the *trans(anti)* form was determined to be about 95.3%, while the rest (4.7%)

was interpreted as a *gauche* conformer with a dihedral angle of 73.5° . For this value of dihedral angle of a *gauche* form and for a planar *s-trans* form the gradient CNDO/2 harmonic force fields were calculated [3]. A complete analysis of the experimental spectra of these two conformers was performed using the results of the computed force fields.

A study of the vapor phase Raman spectrum of isoprene resulted in the observation of a polarized band at 223.7 cm^{-1} [4]. This band was assigned to the 2—0 transition of the torsional vibration of the *s-cis* form. The corresponding potential energy curve of internal rotation was constructed. However, the ab initio gradient calculation of the potential curve (at the Hartree—Fock level with the Roos and Siegbahn (7, 3) basis set contracted to (4, 2)) showed conclusively that a *gauche* conformer with the dihedral angle of about 43.6° [5] was more stable than an *s-cis*-form. The following refinement of this curve by frequencies of the torsional "hot" bands of *s-trans*-isoprene and by the torsional overtone of its high energy rotational isomer displaced the position of the *gauche* well to 39.2° [6].

Very recent conformational analyses of butadiene-1,3 also showed the existence of a *gauche* form (see, for example, refs. 7—10 and references therein).

Recently two papers devoted to the detection and analysis of the structure of the second rotational isomeric forms of 2-methylbutadiene-1,3 [11] and 2,3-dimethylbutadiene-1,3 [12] were published. They involved a study of the UV spectra (in the argon matrix) of "frozen" equilibria of the two forms of these compounds at 600 K and 1100 K, respectively. The appearance of a band attributed to the minor conformer in the UV spectrum of solid 2-methylbutadiene-1,3 the maximum of which was red shifted relative to the corresponding maximum of the abundant *s-trans*-form, was interpreted as a manifestation of the planar structure of the metastable high energy *s-cis*-form [11]. Observation of a band of the second form in the UV spectrum of 2,3-dimethylbutadiene-1,3, the maximum of which was blue shifted relative to that of the major *s-trans*-form, was explained by a non-planar structure of the metastable high energy *gauche* conformer [12].

In this connection it seems essential to reinvestigate the structures and the vibrational spectra of these two forms of isoprene using more sophisticated theoretical techniques.

METHOD

The structural parameters and the force fields of the *s-trans* and *gauche* conformers of isoprene were computed by the ab initio SCF method using the 6-31G basis set [13] and gradient optimization [14]. Table 1 contains the completely optimized geometrical parameters of these two conformers. The numbering of atoms is as indicated in Fig. 2. of ref. 3.

Force fields were calculated for the theoretical structures of *s-trans* and *gauche* forms. The force constants as calculated in cartesian coordinates were

TABLE 1

Completely optimized geometries of *trans*- and *gauche*-isoprene

Parameter ^a	Experimental ^b	Calculated	
		<i>trans</i>	<i>gauche</i>
C ₁ =C ₂ (CH ₃)	1.340(0 ₆)	1.3310	1.3288
C ₃ =C ₄	1.340(0 ₆)	1.3277	1.3261
C ₂ -C ₃	1.463(1 ₅)	1.4750	1.4816
C ₂ -C ₅	1.512(1 ₇)	1.5083	1.5105
C ₁ -H ₇ (<i>cis</i> -terminal)	1.076(3)	1.0741	1.0730
C ₁ -H ₆ (<i>trans</i> -terminal)	1.076(3)	1.0730	1.0737
C ₄ -H ₁₃ (<i>cis</i> -terminal)	1.076(3)	1.0730	1.0738
C ₄ -H ₁₂ (<i>trans</i> -terminal)	1.076(3)	1.0728	1.0733
C ₃ -H ₁₁	1.076(3)	1.0764	1.0779
C ₅ -H ₈ (in-plane)	1.110(6)	1.0818	1.0820
C ₅ -H ₉	1.110(6)	1.0852	1.0855
C ₅ -H ₁₀	1.110(6)	1.0852	1.0864
∠C ₁ =C ₂ (CH ₃)-C ₃	121.4(0.3)	119.89	122.35
∠C ₂ (CH ₃)-C ₃ =C ₄	127.3(0.3)	126.22	125.63
∠C ₁ =C ₂ -C ₅	121.0(0.2)	121.72	122.29
∠C ₂ =C ₁ -H ₇ (<i>cis</i> -terminal)	124.3(1.0)	121.70	121.81
∠C ₂ =C ₁ -H ₆ (<i>trans</i> -terminal)	124.3(1.0)	121.95	121.63
∠C ₃ =C ₄ -H ₁₂ (<i>trans</i> -terminal)	124.3(1.0)	121.15	121.50
∠C ₃ =C ₄ -H ₁₃ (<i>cis</i> -terminal)	124.3(1.0)	122.81	121.94
∠C ₄ =C ₃ -H ₁₁	123.4	118.77	118.94
∠C ₂ -C ₅ -H ₈ (in-plane)	109.1(1.4)	110.95	111.49
∠C ₂ -C ₅ -H ₉	109.1(1.4)	111.08	110.86
∠C ₂ -C ₅ -H ₁₀	109.1(1.4)	111.08	110.79
∠C ₁ =C ₂ -C ₃ =C ₄ (dihedral)	0.0	0.00	41.00
∠H ₇ -C ₁ =C ₂ -C ₃	0.0	0.00	1.77
∠H ₆ -C ₁ =C ₂ -C ₃	0.0	0.00	180.88
∠H ₈ -C ₅ -C ₂ =C ₁	0.0	0.00	0.08
∠H ₁₀ -C ₅ -C ₂ =C ₁	0.0	0.00	120.46
∠H ₉ -C ₅ -C ₂ =C ₁	0.0	0.00	-120.67
∠H ₁₃ -C ₄ =C ₃ -C ₂	0.0	0.00	1.06
∠H ₁₂ -C ₄ =C ₃ -C ₂	0.0	0.00	180.36
∠H ₁₁ -C ₃ =C ₄ -H ₁₂	0.0	0.00	2.02
Energy		-193.88617	-193.88251

^aSee Fig. 2 of ref. 3; bond lengths in Ångstroms, angles in degrees and energies in atomic units. ^bValue from ref. 3.

transformed into the local symmetry (valence) coordinates [15] and refined using empirical scale factors [16]. The scaling procedure (a congruent transformation of the force constant matrix) was described earlier [17, 18]. The majority of scale factors were taken from the scale factor set of butadiene-1,3 [7] found using the same basis set. The other scale factors were obtained by the least squares method upon refining the *ab initio* (HF/6-31G) force field

of ethane. The values of these scale factors were calculated by minimizing the weighted mean-square deviations [19] between the calculated (at the optimized geometry) and the experimental frequencies of light and heavy ethane [20]. Definition of the local valence coordinates, values of the empirical scale factors and the empirically refined force constants for the two conformers have been deposited with the British Library Lending Division at Boston Spa as Sup. Pub. No. 26334 (9 pages). It should be stressed that the vibrational frequencies of the rotational isomers were not used in the refinement of force fields. In this sense they may be considered as a priori force fields.

The vibrational problems for *s-trans* and *gauche* conformers of isoprene were then solved with these force fields (Table 2). The assignment of the experimental frequencies was carried out using information about the intensity of the bands, peculiarities of spectra in the liquid and the crystalline phases and data on the vibrational forms (eigenvectors) and the potential energy distribution.

DISCUSSION

The calculated structure of *s-trans*-isoprene reproduces the most important features of the experimental r_α geometry quite well (Table 1). First of all this concerns the difference between the angles $\angle C_1=C_2(CH_3)-C_3$ and $\angle C_2(CH_3)-C_3=C_4$ which is equal to 5.9° from the gas electron diffraction data [3] and 6.3° from the present ab initio calculation. The shortening of the central single C_2-C_3 bond in comparison with the C_2-C_5 bond of the methyl group is reproduced correctly (theoretical and experimental values are 0.033 and 0.049 Å, respectively). Comparison of the calculated *s-trans* and *gauche* structures clearly shows the disturbance of conjugation in the skew conformer. Indeed, the length of the $C=C$ bond decreases and the length of the central C_2-C_3 bond increases when passing from the *s-trans* to the *gauche* conformer. The value of the angle $\angle C_1=C_2(CH_3)-C_3$ increases by analogy with butadiene-1,3 [7]. However, the high value of the angle $\angle C_2(CH_3)-C_3=C_4$ decreases somewhat.

In general, the present calculations of the structures of these two conformers coincide with the results of ref. 5. However, for the most accurately measured parameters of the *s-trans* form, it can be seen that the current expansion of the basis set improves the agreement between theory and experiment. Besides, the dihedral angle, $\angle C_1=C_2-C_3=C_4$, of the *gauche* form obtained in the present calculation (41.0°) is closer to the value of 39.2° calculated from the experimentally refined potential energy curve of internal rotation [6] than the value 43.6° obtained in ref. 5.

It should be stressed that the height of the *gauche-cis* barrier of isoprene is equal to 254.6 cm^{-1} [6, 10] and the frequency of the 0-2 torsional transition of the *gauche* form is 233.7 cm^{-1} [4]. This means that there are three vibrational torsional levels in the *gauche* well and the vibrational analysis of

TABLE 2

Experimental and calculated vibrational frequencies (cm^{-1}) of the *trans* and *gauche* conformers of isoprene

ν	Approximate description	Species (C_s)	<i>Trans(anti)</i>		<i>Gauche</i>			Calc.
			Expt.	Calc.	Experiment			
			[1, 22]		Liquid [1]	Crystal [2]	From <i>trans</i>	
1	$\nu(\text{CH}_2)$ asym. str.	a'	3097 ^a	3115			3097	3111
2	$\nu(\text{CH}_2)$ asym. str.		3092	3107			3092	3108
3	$\nu(\text{C-H})$ str.		3020 ^a	3027			3020	3014
4	$\nu(\text{CH}_2)$ sym. str.		2988	3044			2988	3035
5	$\nu(\text{CH}_2)$ sym. str.		2978	3032			2978	3032
6	$\nu(\text{CH}_3)$ asym. str.		2956	3006			2956	3004
7	$\nu(\text{CH}_3)$ sym. str.		2916 ^a	2922			2916	2915
8	$\nu(\text{C=C})$ sym. str.		1638 ^a	1660			1638	1638
9	$\nu(\text{C=C})$ asym. str.		1603	1599			1638	1631
10	$\delta(\text{CH}_3)$ asym. def.		1466	1472		1465		1464
11	$\delta(\text{CH}_2)$ sym. sci.	1426 ^a	1442			1426	1440	
12	$\delta(\text{CH}_2)$ asym. sci.	1414	1410		1430		1421	
13	$\delta(\text{CH}_3)$ sym. def.	1388	1396			1388	1398	
14	$\nu(\text{C-C})$ str.	1303	1323		1255		1259	
15	$\delta(\text{C-H})$ bend	1291 ^a	1303			1291	1301	
16	$\rho(\text{CH}_3)$ rock	1069	1080			1012	1010	
17	$\rho(\text{CH}_2)$ asym. rock	1012	1002			1069	1093	
18	$\rho(\text{CH}_2)$ sym. rock	953 ^a	957			953	959	
19	$\nu(\text{C-CH}_3)$ str.	780 ^a	773			780	785	
20	$\delta(\text{C=C-C})$ sym. bend	523 ^a	525			288	263	
21	$\delta(\text{C=C-CH}_3)$ bend	412 ^a	419	311			355	
22	$\delta(\text{C=C-C})$ asym. bend	288	273	419			405	
23	$\nu(\text{CH}_3)$ asym. str.	a''	2928	2974			2928	2965
24	$\delta(\text{CH}_3)$ asym. def.		1442	1452		1460		1451
25	$\rho(\text{CH}_3)$ rock		1034	1063			1034	1054
26	$\chi(\text{C-H})$ wag		990	999		1010		994
27	$\chi(\text{CH}_2)$ wag		903	912		920		919
28	$\chi(\text{CH}_2)$ wag		891	902			891	902
29	$\tau(\text{CH}_2)$ tw.		755	763		750		756
30	$\tau(\text{CH}_2)$ tw.		622	628	635	655		640
31	$\chi(\text{C-CH}_3)$ wag		401	398	555	550		545
32	$\tau(\text{CH}_3)$ tor.		199.3	204				173
33	$\tau(\text{C-C})$ tor.		152.7	152			127 ^b	120

^a Vapour phase Raman spectrum [22]. ^b Value calculated from the experimentally refined potential curve of isoprene [6].

the *gauche* rotational isomer may be carried out without drawing upon the theory of the molecular vibrations with large amplitudes [21].

The vibrational frequencies of the *s-trans* conformer, calculated with the empirically refined force fields, are in good agreement with the experimental

frequencies and corroborate, as a rule, the assignments given in ref. 3. (Table 2). Comparison of the experimental spectrum of isoprene with the corresponding data on ethane [20] makes it possible to interchange the interpretation of two pairs of bands at 2956 cm^{-1} and 2928 cm^{-1} and at 1414 cm^{-1} and 1388 cm^{-1} [3]. The values of these pairs of vibrational frequencies are quite close and it is rather difficult to assign them without taking into account additional experimental information. As for the third pair of close frequencies, 412 cm^{-1} and 401 cm^{-1} , the band at 412 cm^{-1} was observed in the vapour phase Raman spectrum [22] as a rather intense band. This means that this band cannot belong to an out-of-plane mode (a'') and must be assigned to the in-plane vibration of the skeleton. The band at 401 cm^{-1} is too weak in order to be detected in the gas Raman spectrum [22] which is characteristic for the out-of-plane modes. Therefore, the assignment of the bands at 412 cm^{-1} and 401 cm^{-1} should also be interchanged.

The values of the vibrational frequencies of the *gauche* conformer were calculated in ref. 3 for a dihedral angle of 73.5° from the planar *cis* form. The present calculation was performed for the molecular model with the dihedral angle 41.0° . Nevertheless, for the majority of experimental frequencies of the *gauche* form the assignment does not change (Table 2). First of all this is true for the six "out-of-plane" modes ν_{24} , ν_{26} , ν_{27} , ν_{29} , ν_{30} and ν_{31} . Among them the ν_{30} and ν_{31} modes are the most reliable, since they were observed in two independent experiments [1, 2]. The assignment of the IR bands at 1010 , 920 , 750 , 655 and 550 cm^{-1} [2] to the "out-of-plane" modes is supported by the argument that such vibrations must manifest the most intensive bands in the IR spectrum.

The change of the dihedral angle of the molecular model (73.5° to 41.0°) resulted in the calculated frequencies of the ν_{21} and ν_{22} modes changing from 382 cm^{-1} and 299 cm^{-1} [3] to 355 cm^{-1} and 405 cm^{-1} , respectively.

The calculated value 405 cm^{-1} corresponds to the experimental band at 419 cm^{-1} quite well. The agreement between the calculated value 355 cm^{-1} and the experimental band at 311 cm^{-1} is somewhat worse. It should be mentioned here that the band at 311 cm^{-1} was measured in the IR spectrum of liquid isoprene as a weak shoulder on the 280 cm^{-1} band [1] and, therefore, may undergo a shift in the direction of lower frequencies.

A reassignment is suggested for the central carbon-carbon single bond stretching in comparison with ref. 3. The vibrational forms and potential energy distribution of the calculated values 1259 cm^{-1} and 1301 cm^{-1} indicated that these frequencies should be assigned as $\nu(\text{C-C})_{\text{str.}}$ and $\delta(\text{C-H})_{\text{bend.}}$, respectively. By analogy with the *s-trans* conformer the assignment of the ν_{12} and ν_{13} vibrations was also interchanged. The ν_{16} and ν_{17} modes mutually changed the values of their vibrational frequencies.

It was impossible to assign the *gauche* conformer only one weak band at 665 cm^{-1} from the work of Sheridan [2] and one weak band at 435 cm^{-1} from the paper by Compton et al. [1]. The explanation of the appearance of these two bands was given in ref. 3. Although the band at 435 cm^{-1} is situated in the region available to Sheridan [2], this band was not detected in his work.

An analysis of the refined force fields showed that the values of the force constants, situated at the "intersection" of the "in-plane" and "out-of-plane" coordinates of the *gauche* conformer are rather large. The same situation was observed for the *gauche* form of butadiene-1,3 [7]. This indicated again that using the force constants of the *s-trans* form to calculate the vibrational frequencies of a *gauche* conformer can result in significant mistakes in analyzing the experimental spectrum of a molecule.

The use of correlation between the position of the UV band maximum and the angle of mutual rotation of double bonds in a conjugated system to evaluate the structure of different derivatives of butadiene-1,3 was discussed many years ago [23]. "A fundamental ambiguity in interpreting electronic spectra in terms of steric conformation of conjugated systems about single bond" [23] was illustrated for the cyclopentadiene-1,3 molecule with coplanar *s-cis* double conjugated bonds [24] and for the non-planar cyclohexadiene-1,3 [25] and cycloheptadiene-1,3 [26] molecules with non-planar *gauche* configuration of double bonds as examples. This is connected with the fact that both *s-cis-trans* isomerism and non-planarity of a molecule can bring about very similar consequences in UV spectra. Indeed, maxima of the UV bands of these three molecules, even taking into account the shifts according to Woodward's rule [27], are red shifted with respect to the maximum of planar butadiene-1,3 (see Table 3 of ref. 23 and Table 2 of ref. 28). Methyl derivatives of butadiene-1,3 and hexatriene-1,3,5 may serve as another example. They are, for instance, the non-planar molecules $(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ [29] and Z-2,5-dimethylhexatriene-1,3,5 [30]. In the first case the maximum of the UV band is red shifted from that of the *s-trans*-butadiene-1,3 [23]. In the spectrum of the second molecule the maximum of the UV band is blue shifted with respect to the corresponding maximum of Z-hexatriene-1,3,5 [30] even taking Woodward's rule [27] into account.

As for the theoretical prediction of shifts of the UV bands for different forms of butadiene-1,3 [28], the corresponding calculations were performed in the π -electron approximation including the non-planar configurations in which, "its validity is much less certain than for the planar systems" [28]. Besides, these semi-empirical calculations were carried out under the assumption of a rigid rotation model, i.e. without taking into account the changes of the central single C—C bond length and the C=C—C angles. However, it is now well known [8] that these molecular parameters of butadiene-1,3 undergo noticeable changes during rotation around the single C—C bond. Perhaps these and other changes of geometry would have an effect on the calculated UV spectrum.

For these reasons the appearance of a band of the minor high energy form of a conjugated molecule on the red or blue side from the maximum of the major *s-trans*-form in the UV spectrum may not serve as an unambiguous indication that the high energy form realizes the planar or non-planar configuration.

It should also be noticed that the UV spectra of butadiene-1,3, 2-methylbutadiene-1,3 and 2,3-dimethylbutadiene-1,3 [31] consist of three main bands corresponding to electronic transitions the structures of which are determined by the proper vibrational manifolds. Separations of these bands are equal to 6–7 nm, i.e. they are quite close to the shifts (5–14 nm) which were observed in refs. 11, 12 and 32 for maxima of the high energy rotational isomeric forms with respect to major planar *s-trans* conformations of these molecules. The matrix effects (~ 3 nm) should also be taken into account (see butadiene in refs. 30–32). Obviously, the picture of the UV spectra of the high energy conformers would be more complex and would consist of more bands. That is why, when only one band of high energy form is observed it most probably means that the other, larger, portion of the spectrum is overlapped by stronger bands of the major *s-trans* conformer. The appearance of such a band on the blue side from the bands of the major *s-trans*-conformer shows that it is not, in all probability, the "origin" band; however, the band shift should be measured for the "origin" bands. This means that the real band shifts may differ from the values as measured in refs. 11, 12 and 32.

If we assume, as do Mui and Grunwald [11] and Squillacote et al. [12, 32], that the non-planar high energy conformers give rise to the blue shift and the planar high energy conformers cause the red shift, it suggests that the planar *s-cis* forms possess higher conjugation and are more stable than the planar *s-trans* forms. This follows from the assumption that the maxima of the UV bands of the *s-trans* forms are situated between the maxima of non-planar *gauche* forms and planar high conjugated *s-cis* forms [11, 12] (see, e.g., isoprene in Table 2 of ref. 12). However, this conclusion contradicts the experimental data obtained by Mui and Grunwald [11] and Squillacote et al. [12, 32].

Thus, the investigation of UV spectra of butadiene-1,3 [32], 2-methylbutadiene-1,3 [11] and 2,3-dimethylbutadiene-1,3 [12] is very important from the point of view of the experimental detection of the high energy conformers of these molecules. However, it is impossible, unfortunately, to determine the structure of these metastable high energy forms from the poorly resolved UV absorption spectra.

CONCLUSIONS

The analysis performed on the *ab initio* molecular models shows that isoprene undergoes the greatest changes in the vibrational spectrum for the stretch mode of the central carbon–carbon bond, ν_{14} , and for the deformation skeletal modes ν_{20} , ν_{21} , ν_{22} and ν_{31} when passing from the *s-trans* to the *gauche* form. As for the stretching vibrations of the double bonds, the transition to the *gauche* conformer decreases the resonance splitting of their frequencies. Such a splitting is characteristic of such planar conjugated structures. A detailed consideration of the direction and values of such shifts is given in Table 2. As a result of this analysis eleven experimental bands at 311, 419,

550 (555), 655 (635), 750, 920, 1010, 1255, 1430, 1460 and 1465 cm^{-1} are assigned as fundamentals of the *gauche* conformer with the dihedral angle 41.0° . This result is in agreement with the experimental and theoretical data on the *gauche* isomer of butadiene-1,3 with the dihedral angle 34.8° (see, for example, ref. 7). It is of interest to note that the existence of *gauche*-butadiene-1,3 was discussed on the basis of electron diffraction data in pioneering work by Bastiansen [33] in 1948.

ACKNOWLEDGEMENT

Authors are deeply indebted to Professor N. A. Allinger for helpful discussion of the problem.

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