392 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **56**, *392—399 (1983)* [Vol. 56, No. 2

Molecular Force Fields of *s-trans*-1,3-Butadiene and the Second Stable Conformer

Yukio Furukawa,† Hideo Takeuchi,† Issei Harada,† and Mitsuo Tasumi*
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received July 23, 1982)

Normal-coordinate analyses of *s-trans*-1,3-butadiene and its various deuterated and ^{13}C-substituted analogs were performed using the group-coordinate force field, and a set of force constants was determined. The infrared spectra of the second stable conformer of 1,3-butadiene-d_0, -1,1,4,4-d_4, and -d_6 were analyzed on the basis of normal-coordinate calculations of the planar *s-cis* form and a nonplanar *gauche* form. Such an analysis suggests that the second stable conformer takes a *gauche* form rather than the *s-cis*. To increase the number of reliable data to be used in this study, the infrared and Raman spectra of the d_0, 1,1,4,4-d_4, and d_6 species were observed in low-temperature Ar matrices. The infrared spectra of the second stable conformer were also observed using a combination of the high-temperature nozzle and low-temperature matrix techniques.

1,3-Butadiene has been a target molecule of numerous structural, spectroscopic, and theoretical studies. Part of these studies has treated the structure of the most stable *s-trans* form of this molecule$^{1-5)}$ and the assignments of the vibrational spectra arising from this form.$^{6-15)}$ On the other hand, various efforts have been made toward the elucidation of the internal-rotation potential and the second stable conformer around the central C–C bond.$^{16-23)}$ This subject has been studied also by various methods of quantum-chemical calculations.$^{24-33)}$ Interest in this direction of study has been renewed by the recent observation of the infrared bands associated with the second stable conformer trapped in low-temperature Ar matrices.$^{34-36)}$ The in-plane vibrational frequencies as well as the in-plane force constants of the *s-trans* and *s-cis* forms were calculated by an *ab initio* method$^{37)}$ and the normal-coordinate analyses based on the observed data for deuterated and ^{13}C-substituted species were also performed.$^{36)}$

The purpose of the present study is twofold. (1) One is to obtain reliable force constants which can be conveniently used (at least as initial values) in the normal-coordinate analyses of longer molecules with conjugated double bonds, for example, isomers of 1,3,5-hexatriene, poly(acetylene), various isomers of retinal and β-carotene, *etc.* Although many authors have already reported various sets of force constants of *s-trans*- and *s-cis*-1,3-butadiene,$^{13-15,36,37)}$ those force constants do not seem satisfactory for such a purpose. (2) The other is to examine if it is possible to obtain information on the internal-rotation angle of the second stable conformer through the normal-coordinate analyses. Whether the second stable conformer is in the planar *s-cis* form or in the nonplanar (*gauche*) form is a long-standing problem which still remains to be solved.

Reliable experimental data are absolutely necessary for this kind of study. Therefore, we have observed the infrared and Raman spectra of 1,3-butadiene and its 1,1,4,4-d_4 and d_6 analogs in low-temperature Ar matrices. Also, we have observed the infrared spectra of these compounds using a combination of the high-temperature nozzle and the low-temperature Ar matrix techniques, in order to obtain the bands due to the second stable conformer. In this way we have confirmed the results of other authors for the d_0 and d_6-samples$^{34-36)}$ and have obtained the data for the 1,1,4,4-d_4 analog for the first time.

Method

Infrared and Raman Measurements. Infrared and Raman spectra were observed for 1,3-butadiene-d_0 and two deuterated analogs (1,1,4,4-d_4 and d_6) in low-temperature Ar matrices. The d_0 sample was obtained from Takachiho Kagaku Kogyo Co., Ltd. (purity 99%) and the d_4 and d_6 samples from Merck Sharp and Dohme Canada Ltd. (98 atom% D). No further purification was undertaken.

Infrared spectra were recorded on a Hitachi 260-50 infrared spectrophotometer. Raman spectra were observed on a Raman spectrometer consisting of a Spex 1401 double monochromator, an NEC GLG 3300 Ar-ion laser, an HTV 649 photomultiplier and a home-made photon counter.

The low-temperature apparatus for the low-temperature matrix infrared measurements consisted of a CTI Model 21 Cryocooler and a sample chamber equipped with a CsI plate, KBr windows, and a fine Pyrex nozzle through which the Ar/sample mixture was passed. The temperature of the nozzle could be raised to about 770 K with a surrounding tungsten heater. The temperature of the Ar/sample mixture was monitored with an alumel-chromel thermocouple placed inside the nozzle. For low-temperature Raman measurements an Osaka Oxygen Co. Cryo Mini D equipped with a cold head of silver-coated copper and a sample chamber with quartz windows was used.

TABLE 1. INTERNAL COORDINATES

Symbol	Description
Δr_{ij}	Stretching of the bond linking the atoms i and j
$\Delta\phi_{ijk}$	Bending of the angle between the two bonds r_{ij} and r_{jk}
$\Delta\theta_{i-jkl}$	Out-of-plane bending of the plane formed by the atoms i(apex), j, k, and l.
Δt_{ij}	Torsion around the bond r_{ij}

---

† Present address: Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980.

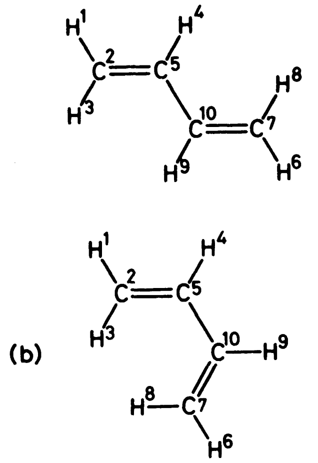

Fig. 1. Numbering of the atoms of (a) *s-trans-* and (b) *s-cis-*1,3-butadiene.

Normal Coordinate Analysis. The normal coordinate analyses of 1,3-butadiene-d_0 and its deuterated and ^{13}C-substituted analogs were performed using the program NCTB[38] on a FACOM M190 computer system at the Laboratory of International Collaboration on Elementary Particle Physics, Faculty of Science, the University of Tokyo.

The structure and numbering of atoms of *s-trans-* and *s-cis-*1,3-butadiene are shown in Fig. 1. The notations for the internal coordinates are given in Table 1. The out-of-plane bending coordinate ($\Delta\theta_{i-jkl}$) and the torsional coordinate (Δt_{ij}) are defined according to the IUPAC recommendations.[39] Therefore, $\Delta\theta_{i-jkl}$ is defined as

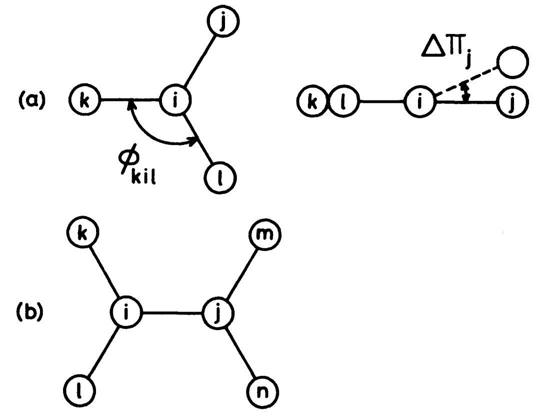

Fig. 2. Numbering of the atoms and the angles relating to the definitions of (a) out-of-plane bending and (b) torsion.

$$\Delta\theta_{i-jkl} = \Delta\pi_j \sin\phi_{kil}$$

where $\Delta\pi_j$ and ϕ_{kil} are given in Fig. 2(a). The sign of $\Delta\theta_{i-jkl}$ is defined in such a way that $\Delta\pi_j$ is plus when the atom j moves above the plane defined by the atoms k, i, and l. The torsional coordinate Δt_{ij} is defined as

$$\Delta t_{ij} = (\Delta\tau_{kijm} + \Delta\tau_{kijn} + \Delta\tau_{lijm} + \Delta\tau_{lijn})/4,$$

where $\Delta\tau_{xijy}$ denotes the change in the individual torsional angle between the bonds xi and yj [see Fig. 2(b)].

Group coordinates were defined on the basis of the internal coordinates as given in Table 2. (Previously the group coordinates were called the local-symmetry coordinates.[40])

In the first step of the normal coordinate analysis the

TABLE 2. GROUP COORDINATES[a)]

Group coordinate	Mode [Abbreviation]
$S_a^1=(\Delta r_{12}+\Delta r_{23})/\sqrt{2}$	CH$_2^1$ symmetric stretching [ν_s(CH$_2^1$)]
$S_a^2=(\Delta r_{67}+\Delta r_{78})/\sqrt{2}$	CH$_2^2$ symmetric stretching [ν_s(CH$_2^2$)]
$S_b^1=(\Delta r_{12}-\Delta r_{23})/\sqrt{2}$	CH$_2^1$ antisymmetric stretching [ν_a(CH$_2^1$)]
$S_b^2=(\Delta r_{67}-\Delta r_{78})/\sqrt{2}$	CH$_2^2$ antisymmetric stretching [ν_a(CH$_2^2$)]
$S_c^1=\Delta r_{45}$	CH^1 stretching [ν(CH^1)]
$S_c^2=\Delta r_{90}$	CH^2 stretching [ν(CH^2)]
$S_d^1=\Delta r_{25}$	C=C^1 stretching [ν(C–C^1)]
$S_d^2=\Delta r_{70}$	C=C^2 stretching [ν(C=C^2)]
$S_e^1=(2\Delta\phi_{123}-\Delta\phi_{325}-\Delta\phi_{521})/\sqrt{6}$	CH$_2^1$ scissors [δ(CH$_2^1$)]
$S_e^2=(2\Delta\phi_{678}-\Delta\phi_{870}-\Delta\phi_{076})/\sqrt{6}$	CH$_2^2$ scissors [δ(CH$_2^2$)]
$S_f^1=(\Delta\phi_{325}-\Delta\phi_{521})/\sqrt{2}$	CH$_2^1$ rocking [γ_r(CH$_2^1$)]
$S_f^2=(\Delta\phi_{870}-\Delta\phi_{076})/\sqrt{2}$	CH$_2^2$ rocking [γ_r(CH$_2^2$)]
$S_g^1=(2\Delta\phi_{250}-\Delta\phi_{054}-\Delta\phi_{452})/\sqrt{6}$	C=C–C^1 deformation [δ(CCC^1)]
$S_g^2=(2\Delta\phi_{705}-\Delta\phi_{509}-\Delta\phi_{907})/\sqrt{6}$	C=C–C^2 deformation [δ(CCC^2)]
$S_h^1=(\Delta\phi_{452}-\Delta\phi_{054})/\sqrt{2}$	CH^1 in-plane bending [δ(CH^1)]
$S_h^2=(\Delta\phi_{907}-\Delta\phi_{509})/\sqrt{2}$	CH^2 in-plane bending [δ(CH^2)]
$S_i=\Delta r_{50}$	C–C stretching [ν(C–C)]
$S_j^1=\Delta\theta_{2-135}$	CH$_2^1$ wagging [γ_w(CH$_2^1$)]
$S_j^2=\Delta\theta_{7-680}$	CH$_2^2$ wagging [γ_w(CH$_2^2$)]
$S_k^1=\Delta\theta_{5-420}$	CH^1 out-of-plane bending [γ_w(CH^1)]
$S_k^2=\Delta\theta_{0-975}$	CH^2 out-of-plane bending [γ_w(CH^2)]
$S_l^1=\Delta t_{25}$	CH$_2^1$ twisting [γ_t(CH$_2^1$)]
$S_l^2=\Delta t_{70}$	CH$_2^2$ twisting [γ_t(CH$_2^2$)]
$S_m=\Delta t_{50}$	C–C torsion [τ(C–C)]

a) The index zero in the subscripts corresponds to the atom 10.

TABLE 3. DEFINITION OF GROUP-COORDINATE FORCE CONSTANTS

Symbol	Description
(1) In-plane force constants	
(i) Diagonal force constants	
F_a	CH_2 symmetric stretching
F'_a	CD_2 symmetric stretching
F''_a	CHD symmetric stretching
F_b	CH_2 antisymmetric stretching
F'_b	CD_2 antisymmetric stretching
F''_b	CHD antisymmetric stretching
F_c	CH stretching
F'_c	CD stretching
F_d	C=C stretching
F_e	CH_2 scissors
F_f	CH_2 rocking
F_g	C=C–C deformation
F_h	CH in-plane bending
F_i	C–C stretching
(ii) Off-diagonal force constants	
F_{dd}	C=C stretching/C=C stretching
F_{de}	C=C stretching/CH_2 scissors
F_{dg}	C=C stretching/C=C–C deformation
F_{dh}	C=C stretching/CH in-plane bending
F_{di}	C=C stretching/C–C stretching
F_{eh}	CH_2 scissors/CH in-plane bending
F_{fh}	CH_2 rocking/CH in-plane bending
F_{gi}	C=C–C deformation/C–C stretching
F_{hi}	CH in-plane bending/C–C stretching
F_{gg}	C=C–C deformation/C=C–C deformation
F_{hh}	CH in-plane bending/CH in-plane bending
(2) Out-of-plane force constants	
(i) Diagonal force constants	
F_j	CH_2 wagging
F_k	CH out-of-plane bending
F_l	CH_2 twisting
F_m	C–C torsion
(ii) Off-diagonal force constants	
F_{jk}	CH_2 wagging/CH out-of-plane bending
F_{kl}	CH out-of-plane bending/CH_2 twisting ($\underline{CH_2}$=$\underline{CH}$–)
F_{kk}	CH out-of-plane bending/CH out-of-plane bending
F'_{kl}	CH out-of-plane bending/CH_2 twisting ($\underline{CH_2}$=CH–$\underline{CH}$=CH_2)
F_{ll}	CH_2 twisting/CH_2 twisting

modified Urey-Bradley-Shimanouchi force field[40] based on the work of Abe[13] was assumed. However, it became clear that some force constants were strongly correlated and accordingly had large uncertainties. Then, we employed the group-coordinate force field (GCFF),[41] which was previously called the local-symmetry force field (LSFF).[40] The definition of the GC force constants used are given in Table 3.

s-trans-*1,3-Butadiene*: The planar C_{2h} structure[4] with $r_{C=C}=1.342$ Å, $r_{C-C}=1.463$ Å, $r_{C-H}=1.093$ Å, $\phi_{C=C-C}=123.6°$, and $\phi_{C=C-H}$ (three kinds) $=120.9°$ was used in the present calculation. The least-squares adjustments of the in-plane GC force constants were made against 96 observed frequencies in total (11 for d_0, 11 for 1,1,4,4-d_4, 11 for d_6, 9 for 1,1,2-d_3, 9 for *trans,trans*-1,4-d_2, 8 for *cis,cis*-1,4-d_2, 7 for 2,3-d_2, 10 for *trans*-1-d_1, 4 for *cis*-1-d_1, 7 for 1,4-$^{13}C_2$, and 9 for 1-$^{13}C_1$). The observed frequencies of the d_0, 1,1,4,4-d_4, and d_6 samples were obtained from the present low-temperature matrix infrared and Raman measurements. The observed frequencies of the other deuterated and ^{13}C-substituted analogs were selected from Refs. 13—15 and 36. The following assumptions were made to obtain a good fit between the calculated and observed frequencies using a relatively small number of force constants (9 diagonal and 11 off-diagonal). (a) The CH_2 and CH stretching frequencies (CD_2, CD, and CHD stretching as well) were not included in the least-squares adjustments because of their uncertainties due to possible Fermi resonances. The diagonal force constants (F_a and F_b for CH_2 and F_c for CH) were fixed to the values given in Table 4 and no off-diagonal constants were taken into account. Slightly different values were used for the diagonal force constants of CD_2 (F'_a and F'_b), CD (F'_c), and CHD (F''_a and F''_b). (b) The off-diagonal force constants F_{di}(C=C/C–C) and F_{dd}(C=C/C=C) had large uncertainties when they were included in the least-squares adjustments. Therefore, these force constants were fixed to the values which were obtained from an *ab initio* calculation.[37]

For the out-of-plane vibrations nine force constants listed in Tables 3 and 4 were determined by the least-squares method against 74 observed frequencies in total (7 for d_0, 7 for 1,1,4,4-d_4, 7 for d_6, 6 for 1,1,2-d_3, 5 for *trans,trans*- 1,4-d_2, 5 for *cis,cis*-1,4-d_2, 5 for *cis,trans*-1,4-d_2, 4 for 2,3-d_2, 6 for *trans*-1-d_1, 5 for *cis*-1-d_1, 6 for 2-d_1, 6 for 1,4-$^{13}C_2$, and 5 for 1-$^{13}C_1$). Here again, the observed data of the d_0, 1,1,4,4-d_4, and d_6 samples were from the present measurements, while those of the other deuterated and ^{13}C-substituted analogs were taken from Refs. 13—15 and 36. Choice of the kinds of force constants used was somewhat arbitrary, but the agreement between the calculated and observed frequencies was quite satisfactory.

Second Stable Conformer of 1,3-Butadiene: Since the structure of the second stable conformer of 1,3-butadiene has not been experimentally determined, two model structures, *s-cis* and *gauche*, were chosen for normal coordinate analysis. For the *s-cis* form all the bond lengths and bond angles were set equal to those of the *s-trans* form and the internal-rotation angle around the central C_5–C_{10} bond was rotated by 180° from *s-trans* as shown in Fig. 1(b). The same kinds of force constants as used for *s-trans* were taken into account. Normal-coordinate calculations were carried out in two steps. At first the force constants of *s-trans* were transferred to *s-cis* and the observed infrared bands of the latter were assigned with reference to the results of this calculation. The force constants of *s-cis* were then adjusted in order to obtain the best fit between the calculated and observed frequencies. In this procedure the force constants associated with the in-plane vibrations of the terminal CH_2 group were fixed to the values of *s-trans*. The off-diagonal force constants, F_{dd} and F_{di}, were again fixed to the values obtained from an *ab initio* calculation.[37] The other six force constants, F_d, F_g, F_h, F_i, F_{gg}, and

TABLE 4. GROUP-COORDINATE FORCE CONSTANTS OF *s-trans, s-cis,* AND *gauche* 1,3-BUTADIENE AND THEIR UNCERTAINTIES (IN PARENTHESES). UNITS ARE mdyn Å^{-1} (=10^2 N m^{-1}) FOR STRETCHING AND STRETCH-STRETCH INTERACTION FORCE CONSTANTS, mdyn (=10^{-8} N) FOR STRETCH-BEND INTERACTION FORCE CONSTANTS, AND mdyn Å (=10^{-18} N m) FOR BENDING, BEND-BEND INTERACTION, AND TORSIONAL FORCE CONSTANTS.

Force constant	*s-trans*	*s-cis*	*gauche*
In-plane			
F_a	5.068	5.068	5.068
F'_a	5.214	5.214	5.214
F''_a	5.570	—	—
F_b	5.057	5.057	5.057
F'_b	5.123	5.123	5.123
F''_b	4.724	—	—
F_c	4.995	4.995	4.995
F'_c	4.981	4.981	4.981
F_d	8.886(0.105)	8.976(0.122)	9.003(0.075)
F_e	0.455(0.003)	0.455	0.455
F_f	0.577(0.007)	0.577	0.577
F_g	0.691(0.011)	0.699(0.193)	0.546(0.070)
F_h	0.519(0.006)	0.532(0.011)	0.531(0.007)
F_i	5.428(0.164)	4.964(0.286)	4.914(0.155)
F_{dd}	−0.1	−0.1	−0.1
F_{de}	−0.197(0.012)	−0.197	−0.197
F_{dg}	0.257(0.095)	0.257	0.257
F_{dh}	0.232(0.030)	0.232	0.232
F_{di}	0.4	0.4	0.4
F_{eh}	−0.013(0.004)	−0.013	−0.013
F_{fh}	0.056(0.005)	0.056	0.056
F_{gi}	0.082(0.049)	0.082	0.082
F_{hi}	−0.225(0.023)	−0.225	−0.225
F_{gg}	0.073(0.010)	0.008(0.193)	−0.026(0.071)
F_{hh}	0.037(0.004)	0.024(0.011)	0.021(0.007)
Out-of-plane			
F_j	0.297(0.001)	0.297	0.297
F_k	0.409(0.005)	0.352(0.006)	0.387(0.015)
F_l	0.511(0.005)	0.533(0.009)	0.550(0.018)
F_m	0.109(0.005)	0.046(0.003)	0.055(0.009)
F_{jk}	0.055(0.002)	0.045(0.003)	0.038(0.008)
F_{kl}	−0.027(0.002)	−0.010(0.003)	−0.028(0.009)
F_{kk}	−0.005(0.004)	0.024(0.005)	0.013(0.015)
F'_{kl}	0.023(0.002)	−0.026(0.003)	−0.014(0.009)
F_{ll}	−0.017(0.005)	0.011(0.008)	−0.003(0.017)

F_{hh}, were adjusted freely by the least-squares method using 30 observed frequencies in total (6 for d_0, 7 for 1,1,4,4-d_4, 7 for d_6, 5 for 1,4-$^{13}C_2$, 5 for 1-$^{13}C_1$). The observed data for the 1,4-$^{13}C_2$ and 1-$^{13}C_1$ analogs were taken from Ref. 36. As for the out-of-plane vibrations, the eight force constants, F_k, F_l, F_m, F_{jk}, F_{kl}, F_{kk}, F'_{kl}, and F_{ll} were adjusted freely by the least-squares method using 28 observed frequencies (7 for d_0, 6 for 1,1,4,4-d_4, 4 for d_6, 5 for 1,4-$^{13}C_2$, 6 for 1-$^{13}C_1$). Only the CH_2 wagging force constant, F_j, was fixed to the value of *s-trans*.

As the structural parameters of the *gauche* form the values calculated by Skaarup *et al.*[30] were slightly modified with reference to the deviations between the *ab initio* and experimental results for the *s-trans* form. The parameters used were as follows: $r_{C=C}=1.341$ Å, $r_{C-C}=1.474$ Å, $r_{C-H}=1.092$ Å, $\phi_{C=C-C}=119.3°$, $\phi_{C=C-H}(2\text{-}5\text{-}4)=119.3°$, $\phi_{C=C-H}(5\text{-}2\text{-}3)=121.5°$, $\phi_{C=C-H}(5\text{-}2\text{-}1)=121.8°$, and t(internal-rotation angle around C_5–C_{10})$=40°$ from *s-cis*. In the normal-coordinate analysis of the *gauche* form no interaction force constants between the "in-plane" and "out-of-plane" coordinates were taken into account. Under the same assumptions as made for the *s-cis* case the 14 force constants were determined from 58 observed frequencies by the least-squares method.

Results

The infrared and Raman spectra of 1,3-butadiene and its 1,1,4,4-d_4 and d_6 analogs observed in low-temperature Ar matrices are shown in Figs. 3 and 4. Since the Ar/sample ratio was not high, the sample molecules might not be completely isolated in the Ar matrix. However, the sharpness of individual bands inherent to the low-temperature matrix measurements made it possible to detect many weak bands. The Raman spectra of these compounds in low-temperature

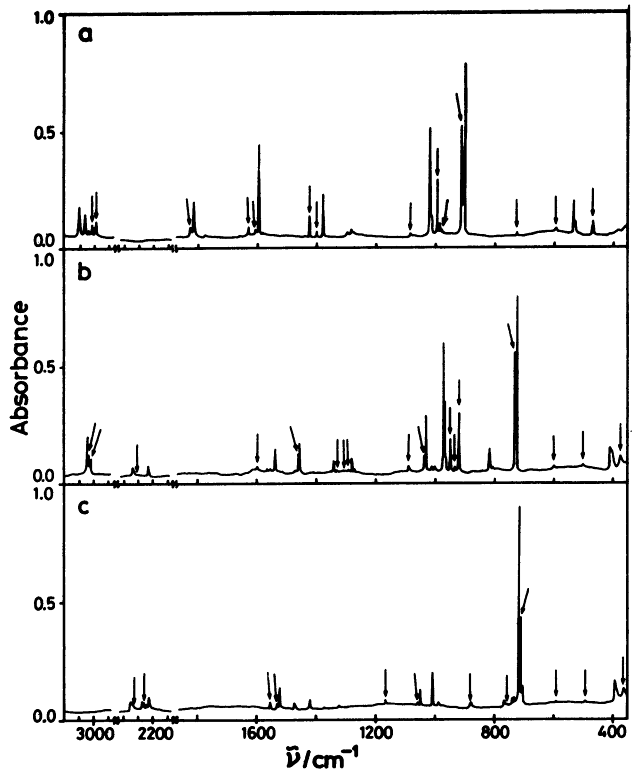

Fig. 3. Infrared spectra of (a) 1,3-butadiene-d_0, (b) -1,1,4,4-d_4, and (c) -d_6 observed in Ar matrices at 20 K. Mixtures of Ar and the samples (Ar/sample ratio 250) were heated to about 770 K in the nozzle and then deposited onto the cold CsI plate. The arrows indicate the bands due to the second stable conformer.

Ar matrices were observed in this study for the first time. The infrared spectra in Fig. 3 were observed from the low-temperature Ar matrices obtained by depositing a mixture of Ar and the sample which had been heated to about 770 K. Therefore, the intensities of the bands due to the second stable conformer are enhanced in Fig. 3 and they are indicated with arrows. The bands without arrows are associated with the most stable *s-trans* form. The bands with arrows were found to decrease in intensity on irradiation of light from a Xe-lamp, indicating that these bands were due to the second stable conformer.[35] Our present results for the d_0 and d_6 samples (Figs. 3a and 3c) agreed with the findings of previous authors,[34-36] except for some minor features. Huber-Wälchli and Günthard[36] observed more bands than we did; for example, we could not observe the medium-intensity band at 1740 cm^{-1} of the d_0 species which they assigned to a combination tone of the second stable conformer. The infrared spectrum of the second stable conformer of the 1,1,4,4-d_4 species (Fig. 3b) was obtained for the first time.

The results of normal-coordinate analyses will be described below.

Discussion

Band Assignments and Force Constants of the s-trans *Form.* As described earlier, we started the normal-coordinate analyses of 1,3-butadiene and its deuterated and ^{13}C-

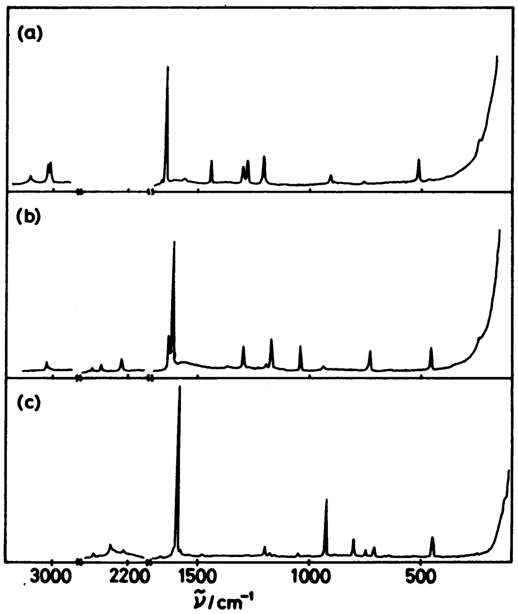

Fig. 4. Raman spectra of (a) 1,3-butadiene-d_0, (b) -1,1,4,4-d_4, and (c) -d_6 observed in Ar matrices (Ar/sample ratio 50) at 15 K. Excitation wavelength, 514.5 nm.

TABLE 5. OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES OF *s-trans*-1,3-BUTADIENE-d_0 AND MODE ASSIGNMENTS

Species	No.	Obsd $\tilde{\nu}$/cm^{-1}	Calcd $\tilde{\nu}$/cm^{-1}	Mode and PED[a)]
a_g	ν_1	3105	3102	$\nu_a(\mathrm{CH_2^*})$ 49
	ν_2	3025	3039	$\nu(\mathrm{CH^*})$ 47
	ν_3	3014	2997	$\nu_s(\mathrm{CH_2^*})$ 46
	ν_4	1644	1645	$\nu(\mathrm{C{=}C^*})$ 36, $\nu(\mathrm{C{-}C})$ 21
	ν_5	1441	1446	$\delta(\mathrm{CH_2^*})$ 38, $\nu(\mathrm{C{-}C})$ 11
	ν_6	1279	1296	$\delta(\mathrm{CH^*})$ 18, $\nu(\mathrm{C{=}C^*})$ 10
	ν_7	1206	1203	$\nu(\mathrm{C{-}C})$ 27, $\delta(\mathrm{CH^*})$ 14, $\gamma_r(\mathrm{CH_2^*})$ 11
	ν_8	887	901	$\nu(\mathrm{C{-}C})$ 37, $\gamma_r(\mathrm{CH_2^*})$ 29
	ν_9	513	510	$\delta(\mathrm{CCC^*})$ 33
a_u	ν_{10}	1022	1019	$\gamma_t(\mathrm{CH_2^*})$ 31, $\gamma_w(\mathrm{CH^*})$ 18
	ν_{11}	905	908	$\gamma_w(\mathrm{CH_2^*})$ 51
	ν_{12}	535	527	$\gamma_w(\mathrm{CH^*})$ 28, $\gamma_t(\mathrm{CH_2^*})$ 21
	ν_{13}	163[b)]	162	$\tau(\mathrm{C{-}C})$ 89
b_g	ν_{14}	974	969	$\gamma_w(\mathrm{CH^*})$ 30, $\gamma_t(\mathrm{CH_2^*})$ 25
	ν_{15}	908	910	$\gamma_w(\mathrm{CH_2^*})$ 50
	ν_{16}	754	751	$\gamma_t(\mathrm{CH_2^*})$ 24, $\gamma_w(\mathrm{CH^*})$ 18
b_u	ν_{17}	3103	3101	$\nu_a(\mathrm{CH_2^*})$ 50
	ν_{18}	3062	3029	$\nu(\mathrm{CH^*})$ 46
	ν_{19}	2986	2997	$\nu_s(\mathrm{C{=}H_2^*})$ 48
	ν_{20}	1597	1601	$\nu(\mathrm{C{=}C^*})$ 37, $\delta(\mathrm{CH_2^*})$ 17
	ν_{21}	1381	1387	$\delta(\mathrm{CH_2^*})$ 33, $\nu(\mathrm{C{=}C^*})$ 10
	ν_{22}	1297	1293	$\delta(\mathrm{CH^*})$ 33
	ν_{23}	988	995	$\gamma_r(\mathrm{CH_2^*})$ 40, $\delta(\mathrm{CH^*})$ 16
	ν_{24}	301[b)]	300	$\delta(\mathrm{CCC^*})$ 55

a) The asterisk in the mode notation indicates that the two group coordinates of the same mode (having superscript 1 and 2) have equal PED's; for example, $\nu_a(\mathrm{CH_2^*})$ 49 represents $\nu_a(\mathrm{CH_2^1})$ 49 and $\nu_a(\mathrm{CH_2^2})$ 49. In this Table PED's are not normalized to a total of 100. b) Ref. 18.

Table 6. Observed and calculated vibrational frequencies of *s-trans*-1,3-butadiene-1,1,4,4-d_4 and mode assignments

Species	No.	Obsd $\tilde{\nu}/\mathrm{cm}^{-1}$	Calcd $\tilde{\nu}/\mathrm{cm}^{-1}$	Mode and PED[a)]
$\mathrm{a_g}$	ν_1	3026	3038	$\nu(\mathrm{CH}^*)$ 49
	ν_2	2316	2340	$\nu_a(\mathrm{CD}_2^*)$ 49
	ν_3	2225	2233	$\nu_s(\mathrm{CD}_2^*)$ 46
	ν_4	1612	1602	$\nu(\mathrm{C{=}C}^*)$ 34, $\nu(\mathrm{C{-}C})$ 26
	ν_5	1298	1296	$\delta(\mathrm{CH}^*)$ 30
	ν_6	1170	1183	$\nu(\mathrm{C{-}C})$ 46
	ν_7	1040	1036	$\delta(\mathrm{CD}_2^*)$ 40
	ν_8	740	726	$\gamma_r(\mathrm{CD}_2^*)$ 34
	ν_9	454	462	$\delta(\mathrm{CCC}^*)$ 31
$\mathrm{a_u}$	ν_{10}	968	957	$\gamma_w(\mathrm{CH}^*)$ 25, (CD_2^*) 23
	ν_{11}	722	724	$\gamma_w(\mathrm{CD}_2^*)$ 51
	ν_{12}	404	399	$\gamma_t(\mathrm{CD}_2^*)$ 29, $\gamma_w(\mathrm{CH}^*)$ 21
	ν_{13}	149[b)]	148	$\tau(\mathrm{C{-}C})$ 89
$\mathrm{b_g}$	ν_{14}	940	934	$\gamma_w(\mathrm{CH}^*)$ 43
	ν_{15}	728	732	$\gamma_w(\mathrm{CD}_2^*)$ 44
	ν_{16}	610[c)]	602	$\gamma_t(\mathrm{CD}_2^*)$ 31
$\mathrm{b_u}$	ν_{17}	3037	3027	$\nu(\mathrm{CH}^*)$ 50
	ν_{18}	2337	2339	$\nu_a(\mathrm{CD}_2^*)$ 49
	ν_{19}	2228	2236	$\nu_s(\mathrm{CD}_2^*)$ 46
	ν_{20}	1533	1525	$\nu(\mathrm{C{=}C}^*)$ 44
	ν_{21}	1274	1263	$\delta(\mathrm{CH}^*)$ 45
	ν_{22}	1028	1022	$\delta(\mathrm{CD}_2^*)$ 46
	ν_{23}	811	811	$\gamma_r(\mathrm{CD}_2^*)$ 44
	ν_{24}	258[c)]	262	$\delta(\mathrm{CCC}^*)$ 52

a) See the footnote a) of Table 5. b) Ref. 18. c) Ref. 13.

Table 7. Observed and calculated vibrational frequencies of *s-trans*-1,3-butadiene-d_6 and mode assignments

Species	No.	Obsd $\tilde{\nu}/\mathrm{cm}^{-1}$	Calcd $\tilde{\nu}/\mathrm{cm}^{-1}$	Mode and PED[a)]
$\mathrm{a_g}$	ν_1	2349	2342	$\nu_a(\mathrm{CD}_2^*)$ 47
	ν_2	2275	2275	$\nu(\mathrm{CD}^*)$ 34, $\nu_s(\mathrm{CD}_2^*)$ 10
	ν_3	2218	2220	$\nu_s(\mathrm{CD}_2^*)$ 37, $\nu(\mathrm{CD}^*)$ 11
	ν_4	1592	1586	$\nu(\mathrm{C{=}C}^*)$ 36, $\nu(\mathrm{C{-}C})$ 29
	ν_5	1199	1190	$\nu(\mathrm{C{-}C})$ 37, $\delta(\mathrm{CD}_2^*)$ 11
	ν_6	1050	1030	$\delta(\mathrm{CD}_2^*)$ 33
	ν_7	925	918	$\delta(\mathrm{CD}^*)$ 35
	ν_8	743	723	$\gamma_r(\mathrm{CD}_2^*)$ 32, $\nu(\mathrm{C{-}C})$ 24
	ν_9	445	451	$\delta(\mathrm{CCC}^*)$ 31
$\mathrm{a_u}$	ν_{10}	766	759	$\gamma_w(\mathrm{CD}^*)$ 23, $\gamma_t(\mathrm{CD}_2^*)$ 22
	ν_{11}	715	717	$\gamma_w(\mathrm{CD}_2^*)$ 41
	ν_{12}	391	389	$\gamma_w(\mathrm{CD}^*)$ 25, $\gamma_t(\mathrm{CD}_2^*)$ 24
	ν_{13}	142[b)]	139	$\tau(\mathrm{C{-}C})$ 92
$\mathrm{b_g}$	ν_{14}	800	796	$\gamma_w(\mathrm{CD}^*)$ 43, $\gamma_w(\mathrm{CD}_2^*)$ 14
	ν_{15}	705	702	$\gamma_w(\mathrm{CD}_2^*)$ 33
	ν_{16}	603[c)]	592	$\gamma_t(\mathrm{CD}_2^*)$ 39
$\mathrm{b_u}$	ν_{17}	2350	2339	$\nu_a(\mathrm{CD}_2^*)$ 49
	ν_{18}	2269	2263	$\nu(\mathrm{CD})$ 23, $\nu_s(\mathrm{CD}_2^*)$ 22
	ν_{19}	2222	2209	$\nu(\mathrm{CD})$ 25, $\nu_s(\mathrm{CD}_2^*)$ 25
	ν_{20}	1521	1511	$\nu(\mathrm{C{=}C}^*)$ 43
	ν_{21}	1046	1043	$\delta(\mathrm{CD}_2^*)$ 30, $\delta(\mathrm{CD}^*)$ 14
	ν_{22}	1006	989	$\delta(\mathrm{CD}_2^*)$ 16, $\delta(\mathrm{CD}^*)$ 15, $\gamma_r(\mathrm{CD}_2^*)$ 10
	ν_{23}	738	738	$\gamma_r(\mathrm{CD}_2^*)$ 32, $\delta(\mathrm{CD}^*)$ 24
	ν_{24}	250	255	$\delta(\mathrm{CCC}^*)$ 53

a) See the footnote a) of Table 5. b) Ref. 18. c) Ref. 13.

Table 8. Observed and calculated vibrational frequencies of *s-cis*-1,3-butadiene-d_0 and mode assignments

Species	No.	Obsd $\tilde{\nu}/\mathrm{cm}^{-1}$	Calcd $\tilde{\nu}/\mathrm{cm}^{-1}$	Mode and PED[a)]
$\mathrm{a_1}$	ν_1	3103	3101	$\nu_a(\mathrm{CH}_2^*)$ 49
	ν_2	3014	3033	$\nu(\mathrm{CH}^*)$ 47
	ν_3	2986	2997	$\nu_s(\mathrm{CH}_2^*)$ 47
	ν_4	1633	1627	$\nu(\mathrm{C{=}C}^*)$ 38, $\nu(\mathrm{C{-}C})$ 17
	ν_5	1425	1432	$\delta(\mathrm{CH}_2^*)$ 34, $\nu(\mathrm{C{-}C})$ 15
	ν_6		1338	$\delta(\mathrm{CH}^*)$ 27
	ν_7	1087	1075	$\gamma_r(\mathrm{CH}_2^*)$ 22, $\nu(\mathrm{C{-}C})$ 16, $\delta(\mathrm{CH}^*)$ 13
	ν_8		878	$\nu(\mathrm{C{-}C})$ 54, $\gamma_r(\mathrm{CH}_2^*)$ 20
	ν_9		256	$\delta(\mathrm{CCC}^*)$ 47
$\mathrm{a_2}$	ν_{10}	983[b)]	980	$\gamma_t(\mathrm{CH}_2^*)$ 29, $\gamma_w(\mathrm{CH}^*)$ 22
	ν_{11}	915[c)]	914	$\nu_w(\mathrm{CH}_2^*)$ 50
	ν_{12}	727[b)]	729	$\gamma_w(\mathrm{CH}^*)$ 23, $\gamma_t(\mathrm{CH}_2^*)$ 19
	ν_{13}	136[d)]	135	$\tau(\mathrm{C{-}C})$ 97
$\mathrm{b_1}$	ν_{14}	3103	3101	$\nu_a(\mathrm{CH}_2^*)$ 49
	ν_{15}	3014	3034	$\nu(\mathrm{CH}^*)$ 47
	ν_{16}	2986	2998	$\nu_s(\mathrm{CH}_2^*)$ 47
	ν_{17}	1612	1623	$\nu(\mathrm{C{=}C}^*)$ 37, $\delta(\mathrm{CH}_2^*)$ 12
	ν_{18}	1403	1415	$\delta(\mathrm{CH}_2^*)$ 35, $\delta(\mathrm{CH}^*)$ 11
	ν_{19}		1278	$\delta(\mathrm{CH}^*)$ 23
	ν_{20}		1043	$\gamma_r(\mathrm{CH}_2^*)$ 35, $\delta(\mathrm{CH}^*)$ 13
	ν_{21}	596	591	$\delta(\mathrm{CCC}^*)$ 42
$\mathrm{b_2}$	ν_{22}	996	997	$\gamma_t(\mathrm{CH}_2^*)$ 36, $\gamma_w(\mathrm{CH}^*)$ 14
	ν_{23}	914	909	$\gamma_w(\mathrm{CH}_2^*)$ 51
	ν_{24}	470	470	$\gamma_w(\mathrm{CH}^*)$ 40, $\gamma_t(\mathrm{CH}_2^*)$ 15

a) See the footnote a) of Table 5. b) See the text as for the assignment of these bands. c) Estimated from $\nu_{11}+\nu_{23}=1829\ \mathrm{cm}^{-1}$. d) Ref. 21.

substituted analogs using the modified Urey-Bradley-Shimanouchi force constants obtained by Abe.[13)] Since the band assignments by Abe and other authors[36)] mostly seemed reasonable, we refined the GC' force constants on the basis of their assignments. By fixing the force constants relating to the carbon-hydrogen stretching (F_a, F_b, and F_c) and the interaction force constants between the skeletal stretchings (F_{dd} and F_{di}) to reasonable values (see the section of Method), a convergent set of force constants was obtained with satisfactorily small uncertainties as given in Table 4. The results of calculation for the d_0, 1,1,4,4-d_4, and d_6 species in the *s-trans* form are shown in Tables 5—7, together with the observed frequencies. The results of calculation for the other deuterated and ^{13}C-substituted analogs are available on request.

Internal-rotation Angle of the Second Stable Conformer. The normal frequencies of the planar *s-cis* and nonplanar *gauche* forms were calculated in the same manner as is described in the section on Method. The results of calculations for the d_0 species are given in Tables 8 and 9. Similar tables for the 1,1,4,4-d_4 and d_6 species are available from the authors on request. The force constants obtained for the *s-cis* and *gauche* forms are also listed in Table 4. Although most of the observed frequencies can be interpreted on the basis of either the *s-cis* or *gauche* form, the presence of a very weak band at

TABLE 9. OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES OF *gauche*-1,3-BUTADIENE-d_0 AND MODE ASSIGNMENTS

Species	No.	Obsd $\tilde{\nu}$/cm^{-1}	Calcd $\tilde{\nu}$/cm^{-1}	Mode and PED[a)]
a	ν_1	3103	3098	$\nu_a(\mathrm{CH}_2^*)$ 50
	ν_2	3014	3032	$\nu(\mathrm{CH}^*)$ 46
	ν_3	2986	3000	$\nu_s(\mathrm{CH}_2^*)$ 47
	ν_4	1633	1629	$\nu(\mathrm{C{=}C}^*)$ 38, (C–C) 18
	ν_5	1425	1432	$\delta(\mathrm{CH}_2^*)$ 36, $\nu(\mathrm{C{-}C})$ 13
	ν_6		1328	$\delta(\mathrm{CH}^*)$ 29
	ν_7	1087	1081	$\gamma_r(\mathrm{CH}_2^*)$ 24, $\nu(\mathrm{C{-}C})$ 16, $\delta(\mathrm{CH}^*)$ 12
	ν_8	983	982	$\gamma_t(\mathrm{CH}_2^*)$ 29, $\gamma_w(\mathrm{CH}^*)$ 23
	ν_9	915[b)]	915	$\gamma_w(\mathrm{CH}_2^*)$ 47
	ν_{10}		872	$\nu(\mathrm{C{-}C})$ 55, $\gamma_r(\mathrm{CH}_2^*)$ 18
	ν_{11}	727	731	$\gamma_w(\mathrm{CH}^*)$ 21, $\gamma_t(\mathrm{CH}_2^*)$ 18
	ν_{12}		256	$\delta(\mathrm{CCC}^*)$ 46
	ν_{13}	136[c)]	137	$\tau(\mathrm{C{-}C})$ 89
b	ν_{14}	3103	3098	$\nu_a(\mathrm{CH}_2^*)$ 50
	ν_{15}	3014	3032	$\nu(\mathrm{CH}^*)$ 46
	ν_{16}	2986	3001	$\nu_s(\mathrm{CH}_2^*)$ 47
	ν_{17}	1612	1619	$\nu(\mathrm{C{=}C}^*)$ 37, $\delta(\mathrm{CH}_2^*)$ 13
	ν_{18}	1403	1413	$\delta(\mathrm{CH}_2^*)$ 34, $\delta(\mathrm{CH}^*)$ 11
	ν_{19}		1278	$\delta(\mathrm{CH}^*)$ 24
	ν_{20}		1040	$\gamma_r(\mathrm{CH}_2^*)$ 36, $\delta(\mathrm{CH}^*)$ 11
	ν_{21}	996	996	$\gamma_t(\mathrm{CH}_2^*)$ 35, $\gamma_w(\mathrm{CH}^*)$ 15
	ν_{22}	914	907	$\gamma_w(\mathrm{CH}_2^*)$ 50
	ν_{23}	596	597	$\delta(\mathrm{CCC}^*)$ 20, $\gamma_w(\mathrm{CH}^*)$ 17
	ν_{24}	470	465	$\delta(\mathrm{CCC}^*)$ 23, $\gamma_w(\mathrm{CH}^*)$ 19

a) See the footnote a) of Table 5. b) Estimated from $\nu_9+\nu_{22}=1829$ cm^{-1}. c) Ref. 21.

983 cm^{-1} and a weak band at 727 cm^{-1} is better acounted for by assuming the *gauche* form. When the *s-cis* form is assumed, both of these bands must be assigned to the infrared-inactive a_2 modes, ν_{10} and ν_{12}, in which the CH_2 twisting and CH out-of-plane bending are almost equally coupled. The corresponding bands are found at 927 cm^{-1} (ν_{10}) and 594 cm^{-1} (ν_{12}) for the 1,1,4,4-d_4 species and at 587 cm^{-1} (ν_{12}) for the d_6 species. It is likely that the a_2 modes of the *s-cis* form (C_{2v}) are made infrared-active due to the lowering of molecular symmetry from C_{2v} (*s-cis*) to C_2 (*gauche*).

As described above, the second stable conformer probably exists in the *gauche* form rather than in the *s-cis* form. However, it is interesting to note that most of the infrared bands due to the second stable conformer can be reasonably assigned on assuming the planar *s-cis* form. Therefore, as far as the vibrational assignment for a less stable conformer of a compound with conjugated double bonds is concerned, it seems justifiable to use the *s-cis* form as a practical model instead of paying too much attention to the problem of internal-rotation angle which is inherently difficult to determine.

Assignments of Infrared and Raman Bands. Most of the infrared and Raman bands shown in Figs. 3 and 4 could be assigned. The tables which list the observed infrared and Raman frequencies together with their assignments are available from the authors on request.

References

1) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

2) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, **17**, 163 (1962).

3) A. R. H. Cole, G. M. Mohay, and G. A. Osborne, *Spectrochim. Acta, Part A*, **23**, 909 (1967).

4) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967—1968).

5) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **4**, 41 (1969).

6) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

7) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Am.*, **40**, 438 (1950).

8) L. M. Sverdlov and N. V. Tarasova, *Opt. Spectrosc.*, **9**, 159 (1960).

9) R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).

10) E. M. Popov and G. A. Kogan, *Opt. Spectrosc.*, **17**, 362 (1964).

11) Yu. N. Panchenko, Yu. A. Pentin, V. I. Tyulin, and V. M. Tatevskii, *Opt. Spectrosc.*, **16**, 536 (1964).

12) I. S. Borshagovskaya, Yu. N. Panchenko, and Yu. A. Pentin, *Opt. Spectrosc.*, **22**, 194 (1967).

13) K. Abe, Ph. D. Thesis, The University of Tokyo, Tokyo, Japan, 1970.

14) Yu. N. Panchenko, *Spectrochim. Acta, Part A*, **31**, 1201 (1975).

15) E. Benedetti, M. Aglietto, S. Pucci, Yu. N. Panchenko, Yu. A. Pentin, and O. T. Nikitin, *J. Mol. Struct.*, **49**, 293 (1978).

16) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

17) W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

18) A. R. H. Cole, A. A. Green, and G. A. Osborne, *J. Mol. Spectrosc.*, **48**, 212 (1973).

19) R. L. Lipnick and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **95**, 6370 (1973).

20) J. R. Durig, W. E. Bucy, and A. R. H. Cole, *Can. J. Phys.*, **53**, 1832 (1975).

21) L. A. Carreira, *J. Chem. Phys.*, **62**, 3851 (1975).

22) D. A. C. Compton, W. O. George, and W. F. Maddams, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1666.

23) K. Kveseth, R. Seip, and D. A. Kohl, *Acta Chem. Scand., Ser. A*, **34**, 31 (1980).

24) R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968).

25) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).

26) B. Dumbacher, *Theor. Chim. Acta*, **23**, 346 (1972).

27) U. Pincelli, B. Cadioli, and B. Lévy, *Chem. Phys. Lett.*, **13**, 249 (1972).

28) P. N. Skancke and J. E. Boggs, *J. Mol. Struct.*, **16**, 179 (1973).

29) Yu. N. Panchenko, P. Pulay, and F. Török, *J. Mol. Struct.*, **34**, 283 (1976).

30) S. Skaarup, J. E. Boggs, and P. N. Skancke, *Tetrahedron*, **32**, 1179 (1976).

31) J. A. Altman and W. F. Reynolds, *J. Mol. Struct.*, **36**, 149 (1977).

32) C. W. Bock, P. George, M. Trachtman, and M. Zanger, *J. Chem. Soc., Perkin Trans. 2*, **1979**, 26.

33) P. George, C. W. Bock, and M. Trachtman, *J. Mol. Struct.*, **69**, 183 (1980).

34) P. Huber-Wälchli, *Ber. Bunsenges. Phys. Chem.*, **82**, 10 (1978).

35) M. E. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *J. Am. Chem. Soc.*, **101**, 3657 (1979).

36) P. Huber-Wälchli and Hs. H. Günthard, *Spectrochim. Acta, Part A*, **37**, 285 (1981).

37) C. W. Bock, M. Trachtman, and P. George, *J. Mol. Spectrosc.*, **84**, 243 (1980).

38) T. Shimanouchi, "Computer Program for Normal Coordinate Treatment of Molecules," The University of Tokyo, Tokyo (1968).

39) IUPAC Commission on Molecular Structure and Spectroscopy, *Pure Appl. Chem.*, **50**, 1707 (1978).

40) T. Shimanouchi, "The Molecular Force Field," in "Physical Chemistry. An Advanced Treatise," ed by H. Eyring, D. Henderson, and W. Jost, Academic Press, New York (1970), Vol. IV, Chap. 6, pp. 233—306.

41) H. Matsuura and M. Tasumi, "Force Fields for Large Molecules," in "Vibrational Spectra and Structure," ed by J. R. Durig, Elsevier, Amsterdam, Vol. 12, in press.