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Registry No. $CF_3CH(OH)CH(NH_2)CH_2Ph$, 124044-49-1; BOC-Ala-Val-OH, 60209-59-8; BOC-Ala-Val-NHCH(Bzl)CH(OH)CF_3, 124044-50-4; BOC-Ala-Val-Phe-CF_3, 124044-51-5; $H_2C{=}C(Me)OAc$, 108-22-5; Bz-Arg-OEt, 971-21-1; Z-Arg-pNA, 29542-03-8; Ala-Ala-Phe-pNA, 61043-41-2; Z-Tyr-OMe, 13512-31-7; Z-Leu-OMe, 51021-87-5; BOC-Leu-OMe, 63096-02-6; Z-Val-OMe, 24210-19-3; BOC-Met-Leu-OMe, 66880-59-9; Fm-Met-Leu-OMe, 124044-52-6; Z-Tyr-Gly-Gly-Phe-OMe, 98254-08-1; BOC-Tyr(Bzl)-Gly-Gly-OEt, 87423-40-3; BOC-Tyr(Bzl)-Gly-Gly-Hpy, 124044-53-7; BOC-Tyr-D-Ala-Phe-Gly-OEt, 78330-92-4; BOC-Tyr-D-Ala-Phe-Gly-Hpy, 124044-54-8; BOC-Tyr-D-Ala-Phe-OMe, 124044-55-9; Met-OMe·HCl, 2491-18-1; D-Arg-OMe, 65160-70-5; Ala-NH_2, 7324-05-2; Phe-NH_2, 5241-58-7; Leu-NH_2, 687-51-4; D-Leu-OMe, 23032-21-5; Phe-$NHCH_2Ph$, 6455-20-5; Phe-Leu-NH_2, 38678-59-0; Tyr-Pro-Ser(Bzl)-NH_2, 124044-56-0; Gly-Tyr-Pro-Ser(Bzl)-NH_2, 124044-57-1; Z-Tyr-D-Arg-OMe, 102683-28-3; Z-Leu-Ala-NH_2, 62074-75-3; BOC-Leu-Phe-NH_2, 33900-15-1; BOC-Leu-Leu-NH_2, 124044-58-2; Z-Val-D-Leu-OMe, 53941-41-6; BOC-Met-Leu-Leu-NH_2, 124044-59-3; BOC-Met-Leu-Phe-$NHCH_2Ph$, 124044-60-6; Fm-Met-Leu-Phe-$NHCH_2Ph$, 124044-61-7; Z-Tyr-Gly-Gly-Phe-Leu-NH_2, 71591-21-4; BOC-Tyr(BzD)-Gly-Gly-Phe-Leu-NH_2, 81638-88-2; BOC-Tyr-D-Ala-Phe-Gly-Tyr-Pro-Ser(Bzl)-NH_2, 124044-62-8; (±)-$AcNHCH(CH_2CH_2Ph)COOMe$, 36061-01-5; (±)-AcNHCH(Ph)COOMe, 36061-00-4; (±)-AcNHCH(C_6H_4-*p*-OH)COOMe, 72651-18-4; DL-Leu-OBzl, 80089-22-1; DL-Tyr-OMe, 18869-47-1; DL-Phe-OMe, 15028-44-1; (±)-$H_2NCH(CH_2CH_2Ph)COOEt$, 46460-24-6; (±)-PhCH(OH)COOMe, 4358-87-6; (±)-$PhCH_2SCH_2CH(Me)COOMe$, 124044-63-9; (±)-PhCH(OMe)COOMe, 56143-21-6; (±)-$CH_3CH(OH)COOMe$, 2155-30-8; (±)-$CH_3CH(C_6H_4$-*p*-Bu-*i*)COOMe, 114376-60-2; (±)-$Cl(CH_2)_3CH(OAc)CH_3$, 124044-65-1; $ZNHCH(CH_2OH)_2$, 71811-26-2; (±)-$Cl(CH_2)_3CH(OH)CH_3$, 69459-96-7; $AcOCH{=}CH_2$, 108-05-4; (*R*)-$AcNHCH(CH_2CH_2Ph)COOMe$, 36060-87-4; (*R*)-AcNHCH(Ph)COOMe, 36060-85-2; (*R*)-AcNHCH(C_6H_4-*p*-OH)COOMe, 72691-40-8; D-Leu-OBzl, 46741-65-5; D-Tyr-OMe, 3410-66-0; D-Phe-OMe, 21685-51-8; (*R*)-$H_2NCH(CH_2CH_2Ph)COOEt$, 124044-66-2; (*S*)-PhCH(OH)COOMe, 21210-43-5; (*R*)-$PhCH_2SCH_2CH(Me)COOMe$, 56751-44-1; (*S*)-PhCH(OMe)COOMe, 26164-27-2; (*R*)-$CH_3CH(OH)COOMe$, 17392-83-5; (*S*)-$AcNHCH(CH_2CH_2Ph)COOH$, 96613-91-1; (*S*)-AcNHCH(Ph)COOH, 42429-20-9; (*S*)-AcNHCH(C_6H_4-*p*-OH)COOH, 37784-24-0; Leu-OH, 61-90-5; Tyr-OH, 60-18-4; Phe-OH, 63-91-2; (*R*)-PhCH(OH)COOH, 611-71-2; (*S*)-$PhCH_2SCH_2CH(Me)COOH$, 73672-15-8; (*R*)-PhCH(OMe)COOH, 3966-32-3; (*S*)-$CH_3CH(OH)COOH$, 79-33-4; (*R*)-$ZNHCH(CH_2OH)CH_2OAc$, 124044-68-4; (*S*)-$H_2NCH(C_6H_4$-*p*-OH)COOH, 32462-30-9; (*R*)-$H_2NCH(CH_2CH_2Ph)COOH$, 82795-51-5; (*R*)-$PhCOSCH_2CH(Me)COOH$, 74407-70-8; (*S*)-$PhCOSCH_2CH(Me)COOH$, 72679-02-8; subtilisin, 9014-01-1; thymidine, 50-89-5; uridine, 58-96-8; 2'-deoxycytidine, 951-77-9; cytidine, 65-46-3; 2'-deoxyadenosine, 958-09-8; adenosine, 58-61-7; methyl 2-deoxy-*β*-D-ribofuranoside, 51255-18-6; 5'-*O*-acetylthymidine, 35898-31-8; 5'-*O*-acetyluridine, 6773-44-0; 5'-*O*-acetyl-2'-deoxycytidine, 72560-70-4; 5'-*O*-acetylcytidine, 18531-23-2; 5'-*O*-acetyl-2'-deoxyadenosine, 72560-67-9; 5'-*O*-acetyladenosine, 2140-25-2; methyl 5'-*O*-acetyl-2-deoxy-*β*-D-ribofuranoside, 116466-99-0; polymethionine (homopolymer), 26062-47-5; polymethionine (SRU), 26854-80-8; (±)-*N*-(ethoxycarbonyl)-2-(2-furyl)glycine methyl ester, 113531-30-9; (±)-methyl 2-(6-methoxynaphth-2-yl)propanoate, 42589-75-3; DL-*N*-acetyl-*α*-methyltryptophan methyl ester, 124044-64-0; *cis*-cyclopenten-3,5-diol, 29783-26-4; (±)-methyl 7-(3-hydroxy-5-oxocyclopent-1-en-1-yl)heptanoate, 40098-26-8; (*R*)-*N*-(ethoxycarbonyl)-2-(2-furyl)glycine methyl ester, 113452-70-3; (*S*)-*N*-(ethoxycarbonyl)-2-(2-furyl)glycine, 124044-67-3; poly(L-homophenylalanine), homopolymer, 124044-69-5; poly(L-homophenylalanine), SRU, 124044-70-8; (3*R*)-*cis*-5-acetoxycyclopenten-3-ol, 60176-77-4.

Microwave Spectra of Isotopic Species and Substitution Structure of Cyclohexane

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Abstract: The rotational spectra of cyclohexane-*1,1*-d_2, cyclohexane-^{13}C-*1,1*-d_2, cyclohexane-d_1 (equatorial and axial), and cyclohexane-*1,1,2,2,3,3*-d_6 have been measured between 8 and 26 GHz with a pulsed microwave Fourier transform spectrometer. From their analysis the rotational constants and the quartic centrifugal distortion constants have been determined. The complete substitution structure has been deduced from these rotational constants. Measurements of the Stark effect have provided information on the dipole moment induced by deuterium substitution.

Carbocyclic compounds have challenged chemists for a long time to derive their structures and conformations. Early electron diffraction studies established that the chair form is the most stable conformer for saturated six-memered rings in general and for cyclohexane in particular.[1,2] Several later investigations by gas electron diffraction have improved the structure of cyclohexane.[3-7] The best values for the structural parameters are ∠CCC = 111.4 (2)°, r_g(C–C) = 1.536 (2) Å, and r_g(C–H) = 1.121 (4) Å with the assumption of equal bond lengths for axial and equatorial hydrogens.[6] Complementary information on the structure of cyclohexane was obtained from ab initio calculations.[8,9]

Due to its D_{3d} symmetry, the chair conformation of cyclohexane does not possess a permanent electric dipole moment, and so the powerful method of microwave spectroscopy could not be used to determine the substitution structure. However, some structural parameters followed from rotational constants which were obtained from the analysis of the pure rotational Raman spectrum of C_6H_{12} and C_6D_{12}.[10]

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It is now appropriate to make a new attempt to determine the complete structure of cyclohexane from spectroscopic data. Pulsed microwave Fourier transform (MWFT) spectroscopy has demonstrated a striking capability to detect the weak rotational spectra of molecules with extremely small electric dipole moments. In particular, it was possible to measure rotational transitions of benzene-d_1,[11] benzene-*1,2*-d_2 and benzene-*1,3*-d_2,[12] and *s-trans*-1,3-butadiene-*1,1*-d_2[13] as well as cyclobutane-d_1[14] and cyclobutane-*1,1*-d_2.[15] The unsymmetrical substitution of hydrogen by deuterium gave rise to a vibrationally induced dipole moment of the order of 0.01 D.[15,16]

We report here the observation of the pure rotational spectra of five isotopomers of cyclohexane between 8 and 26 GHz. The analysis of these spectra provided the rotational constants which allowed the complete determination of the substitution structure. No assumptions were made besides the molecular symmetry. Accurately measured Stark splittings of selected transitions for three isotopomers were used to estimate the vibrationally induced dipole moment.

Experimental Section

Chemicals. The isotopically substituted cyclohexanes were prepared according to the following known procedures. Cyclohexane-*1,1*-d_2 (CH-d_2): Cyclohexanone was reduced with $LiAlD_4$ to cyclohexanol-*1*-d_1. The latter was converted to the tosylate by reaction with *p*-toluenesulfonyl chloride.[17] The tosylate was reduced with a mixture of LiD and $LiAlD_4$ or with a better yield with $LiB(C_2H_5)_3D$ to CH-d_2.[18] Cyclohexane-d_1 (CH-d_1-eq, CH-d_1-ax): The Grignard reagent prepared from bromocyclohexane was reacted with D_2O to form a 1:1 mixture of CH-d_1-eq and CH-d_1-ax.[19] Cyclohexane-*1,1,2,2,3,3*-d_6 (CH-d_6): Base-catalyzed exchange of the α hydrogens in cyclohexanone with D_2O produced cyclohexanone-*2,2,6,6*-d_4.[20] The latter was reduced with Zn in DCl/D_2O to CH-d_6.[21] Cyclohexane-^{13}C-*1,1*-d_2 (CH-^{13}C-d_2): 1,5-Dibromopentane was reacted with $K^{13}CN$, and the product was hydrolyzed with HCl forming pimelic-*1,7*-$^{13}C_2$ acid.[22] The Ba salt of the acid was heated to 450 °C, and cyclohexanone-*1*-^{13}C distilling off was collected. Further reaction steps to CH-^{13}C-d_2 followed then exactly the procedure for CH-d_2 above. The raw product of every isotopomer synthesized was purified by preparative gas chromatography to higher than 99.5% purity.

MWFT Spectrometer. For all measurements an Ekkers–Flygare-type MWFT spectrometer[23] with waveguide cells operating in the 8–26 GHz range was used. Our design is similar to that described by Bestmann et al.[24] Its operation for the measurements of rotational spectra of molecules with small electric dipole moments has previously been described[11-15] and will be summarized only briefly. Microwave pulses of 400–1000 ns duration with a peak power of 10–40 W were used to polarize the sample gas. The transient molecular emission signal was amplified and downconverted with a superheterodyne detection system to the range 0–50 MHz. The signals were then digitized at a rate of 100 MHz for 512 channels. The pulses were repeated at a rate of 50 kHz. For higher resolution spectra, the emission signal was downconverted to 0–10 MHz and digitized at a rate of 20 MHz, while the pulse repetition rate was reduced to 20 kHz. Up to 500 million pulse responses were accumulated digitally for signal-to-noise ratio enhancement. The power spectrum was recovered with 256 points over the frequency domain of 0–50 MHz or 0–10 MHz after a Fourier transformation. Accurate transition frequencies of weak lines were determined from power spectra by using a Lorentzian line shape analysis. The spectra were recorded at sample pressures between 0.7 and 4.0 Pa (5–30 mTorr) and a cell temperature of −70 °C.

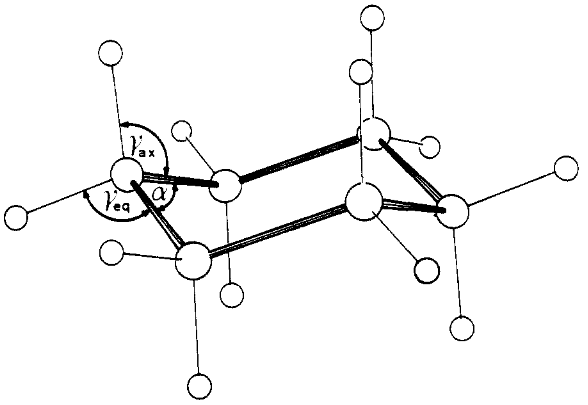

Figure 1. Molecular model of the chair form of cyclohexane.

For the Stark effect measurements in the 12–18 GHz range the simple waveguide cell of the MWFT spectrometer was replaced by a 2.5 m long P-band Stark cell. The latter had an inside cross section of 15.8 × 7.9 mm and carried a 0.5 mm thick septum in grooves insulated with Teflon tape from the waveguide.[25] Static electric fields of up to 8200 V cm^{-1} were generated in the cell from dc voltages of up to 3000 V. The electric field was calibrated with the Stark effect of OCS assuming a value of 0.71519 D for its dipole moment.[26]

Results

Assignment and Analysis of Rotational Spectra. Preliminary rotational constants of the isotopomers CH-d_2, CH-^{13}C-d_2, CH-d_1-eq, CH-d_1-ax, and CH-d_6 were calculated from structural parameters reported in the literature.[8,10] The first four isotopomers have a plane of symmetry perpendicular to the intermediate inertial axis. Their rotational spectra are expected to exhibit μ_a-type as well as μ_c-type transitions. For the CH-d_6 isotopomer the deuterium substitution switches a and b inertial axes leading to μ_b- and μ_c-type transitions. The dipole components are assumed to result from a net bond moment along each C–D bond. From the available structural data, calcuations indicate that the predicted rotational spectra of CH-d_2, CH-^{13}C-d_2, and CH-d_1-eq consist of stronger μ_a-type transitions than μ_c-type transitions. The ratio is reversed for CH-d_1-ax.

The measurements started with CH-d_2. Here the μ_a-type R-branch transitions 3(0,3)–2(0,2) and 3(1,3)–2(1,2) were searched first since the *K* splitting of roughly 30 MHz of this pair was characteristic and well predicted for an oblate asymmetric rotor. Then the band head of the μ_a-type Q-branch series $J(K_a,4)$–$J(K_a,5)$ was located. Improved rotational constants were adjusted by using these initial measurements. With these constants, further transitions including even μ_c-type R-branch lines were assigned readily. Finally, the frequencies of 10 R-branch transitions were measured between $J = 1$ and 5 and of 31 Q-branch transitions between $J = 5$ and 27.

After the first isotopomer had been measured, the molecular model was revised. Better predictions resulted for the remaining isotopomers which reduced the time required in searching for new rotational transitions. For CH-d_1-eq and CH-^{13}C-d_2, a number of transitions were located and assigned without difficulties. Measurements on the former species included frequencies of nine R-branch transitions between $J = 1$ and 5 and of 30 Q-branch transitions between $J = 7$ and 27 and on the latter species frequencies of six R-branch transitions between $J = 1$ and 3 and of 18 Q-branch transitions between $J = 5$ and 20. For CH-d_1-ax, only seven μ_c-type R-branch transitions were observed between $J = 0$ and 3. Although a broad frequency range was searched,

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Table I. Rotational Constants (MHz), Quartic Centrifugal Distortion Constants (kHz), and Planar Moments of Inertia[a] (uÅ^2) for Isotopically Substituted Species of Cyclohexane

	CH-d_2	CH-^{13}C-d_2	CH-d_1-eq	CH-d_1-ax	CH-d_6
A	4242.6090 (10)	4241.5056 (14)	4305.3039 (14)	4243.8744 (87)	3748.5614 (20)
B	3963.8913 (10)	3901.9628 (14)	4090.1954 (14)	4163.2279 (87)	3728.7780 (19)
C	2366.8203 (10)	2345.0474 (18)	2391.3781 (10)	2436.0265 (8.0)	2197.3567 (15)
Δ_J	0.542 (25)	0.501 (113)	0.508 (28)	0.0[b]	0.425 (43)
Δ_{JK}	−0.189 (40)	−0.226 (35)	−0.218 (46)	0.0[b]	−0.148 (20)
Δ_K	0.589 (29)	0.626 (25)	0.641 (31)	0.0[b]	0.388 (22)
δ_J	0.1603 (62)	0.1533 (54)	0.1570 (75)	0.0[b]	0.1231 (16)
δ_K	0.259 (15)	0.268 (13)	0.306 (17)	0.0[b]	0.1877 (66)
M_{aa}	110.9512	112.9387	108.7536	104.8836	115.3547
M_{bb}	102.5754	102.5704	102.5802	102.5768	114.6394
M_{cc}	16.5445	16.5805	14.8050	16.5076	20.1801
N^c	41	24	39	7	131
J_{max}	27	20	27	3	26
σ^d	0.008	0.006	0.008	0.039	0.015

[a] Conversion factor of 505 379.08 MHz uÅ^2. [b] Constrained to zero. [c] Number of transitions in the fit. [d] Mean standard deviation of a measured transition frequency (MHz).

Table II. Substitution Coordinates (Å) in the Principal Axis System of Cyclohexane-*1,1-d*$_2$ from the Equations of Kraitchman and from the Equations of Rudolph

nucleus	coordinate	Kraitchman[a]	Rudolph[b]
^{13}C	a	1.4158 (1)	1.4153 (17)
	c	0.1925 (3)	0.1925 (13)
H$_{ax}$	a	1.4822 (1)	1.4826 (16)
	c	1.2918 (1)	1.2918 (18)
H$_{eq}$	a	2.4414[c]	2.4415 (3)
	c	0.1843[c]	0.1842 (38)

[a] Uncertainties are estimated from the propagated standard deviations of the rotational constants. They are given in parentheses in units of the last digit. [b] Uncertainties are calculated from the formulas of Rudolph.[29] [c] The propagated uncertainties are too pessimistic due to the large standard deviation of the rotational constant C of CH-d_1-ax.

Table III. Structural Parameters of Cyclohexane from the Equations of Kraitchman, from the Equations of Rudolph, and from the Least-Squares Fit

parameter	Kraitchman	Rudolph	fit[a]
	bond length (Å)		
C–H$_{ax}$	1.101	1.101	1.1013 (39)
C–H$_{eq}$	1.093	1.093	1.0933 (15)
C–C			1.5300 (32)
	bond angle (deg)		
HCH	106.71	106.65	106.65 (27)
CCC			111.28 (30)
CCH$_{ax}$			108.83 (32)
CCH$_{eq}$			110.55 (29)
CCCC			55.26 (82)

[a] Estimated uncertainties, see text.

Table IV. Electric Dipole Moment Components (D) of Isotopically Substituted Species of Cyclohexane

isotopomer	transition	$\|M\|$	μ_a	μ_b	μ_c
CH-d_2	3(0,3)–2(0,2) 3(1,3)–2(1,2)	1, 2	≤0.01		0.0055 (1)
CH-d_1-eq	3(0,3)–2(0,2) 3(1,3)–2(1,2)	0, 1, 2	≤0.01		0.0021 (1)
CH-d_6	3(1,3)–2(0,2) 3(0,3)–2(1,2)	0, 1, 2		0.023 (2)	0.0055 (2)

no μ_c-type Q-branch transitions were located, a result which must be attributed to their low intensity. From the low J R-branch transitions alone the rotational constant C could not be determined as accurately as A and B. The assignment of the μ_b-type spectrum of CH-d_6 was rather difficult. The appearance of many weak lines in the relevant regions prevented the location of the Q-branch band heads. Stark splittings were used to identify finally 15 R-branch transitions between $J = 1$ and 5. The Q-branch series could then be assigned. Most of the K doublets were not resolved resulting in 71 frequencies for transitions between $J = 6$ and 26. Tables with listings of all measured transition frequencies are available as Supplementary Material.

Rotational constants and quartic centrifugal distortion constants were adjusted in iterative least-squares fits for all isotopomers except for CH-d_1-ax. For the latter, the small number of observed transitions required the constraint of the distortion constants to zero. The results are collected in Table I. The centrifugal distortion constants are defined according to Watson's asymmetric reduction in the prolate I^r representation.[27]

Molecular Structure. The molecular geometry of the chair conformation of cyclohexane assuming D_{3d} symmetry is completely defined by six parameters, i.e., the C–C bond length, the CCC angle α, two C–H bond lengths, and two HCC angles γ_{ax}, γ_{eq} for the axial and equatorial hydrogens, respectively (cf. Figure 1). The dihedral CCCC angle φ of the puckered ring is related to α by $\cos \varphi = -\cos \alpha/(1 + \cos \alpha)$. In all isotopomers studied, a single symmetry plane of the original symmetry of cyclohexane is retained. CH-d_2 was selected as the parent molecule. The substitution coordinates of carbon and both axial and equatorial hydrogens were calculated in the inertial axis system of CH-d_2 from the differences of moments of inertia of the additionally singly substituted isotopomers CH-^{13}C-d_2, CH-d_1-ax, and CH-d_1-eq. The general three-dimensional equations of Kraitchman[28] were used, but the small or imaginary b coordinates were disregarded because all substitutions occurred in the symmetry plane. The results are listed in Table II. Almost identical results were obtained with the formulas of Rudolph[29] which are specialized for substitutions in a symmetry plane. They are included in Table II.

The complete set of six structural parameters of cyclohexane-d_0 (CH-d_0) cannot be determined directly from the substitution coordinates in Table II, because the inertial axis system of CH-d_2 is shifted and rotated by an unknown amount with respect to that of CH-d_0. Due to the D_{3d} symmetry, the substitution coordinates of a single carbon in the inertial axis system of CH-d_0 would be directly related to the C–C bond length and the CCC angle. However, the six parameters were calculated from the differences of the planar moments of inertia [$M_{aa} = (-I_a + I_b + I_c)/2$, and cyclic permutations of a, b, and c] between the parent molecule CH-d_2 and the isotopomers CH-^{13}C-d_2, CH-d_1-eq, and CH-d_1-ax with a least-squares procedure. The computer program employed is exactly analogous to the program GEOM described previously,[30] which fits the differences of the moments of inertia instead of the planar moments of inertia. Center-of-mass and product-of-inertia conditions were automatically fulfilled in the least-squares fit. The

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Table V. A Comparison of Structural Parameters of Cyclohexane

parameter	ab initio r_e[a]	ab initio r_e[b]	microwave r_s[c]	electron diffraction r_g[d]	electron diffraction r_g[e]	electron diffraction r_a[f]	Raman r_0[g]
			bond length (Å)				
$C-H_{ax}$	1.0857	1.088	1.1013	1.119	1.121	1.119	1.102
$C-H_{eq}$	1.0840	1.086	1.0933	1.119	1.121	1.119	1.102
C–C	1.5425	1.534	1.5300	1.535	1.536	1.528	1.535
			bond angle (deg)				
HCH	107.3	106.94	106.65	105.3	107.5	110.0	110.0
CCC	110.9	111.37	111.28	111.3	111.4	111.1	111.4
CCH_{ax}	109.2	109.13	108.83			108.8	
CCH_{eq}	110.1	110.08	110.55			108.8	
CCCC	56.2	55.03	55.26	55.1	54.9	55.9	54.9

[a] Reference 8. [b] Reference 9. [c] This work. [d] Reference 7. [e] Reference 6. [f] Reference 5. [g] Reference 10.

results are given in Table III and compared to values calculated from the substitution coordinates of Table II. All substitutions of the isotopomers considered occurred in the inertial plane *ab*. Therefore, only six independent differences of planar moments of inertia were available for the determination of six structural parameters. The remaining three differences of M_{bb} (cf. Table I) were small and resulted exclusively from the zero-point vibrational contributions. Uncertainties of the structural parameters were estimated from the differences between the fitted parameters using the planar moments of inertia and those using the program GEOM with the moments of inertia. When CH-d_6 was included in the fit procedure, the structural parameters changed slightly within the uncertainties given. The rotational constants *B* of CH-d_0 and CH-d_{12} determined from the rotational Raman spectrum[10] could not be used for improving the structure with the least-squares fit. They were not compatible with the data from the microwave spectra, and the fits diverged.

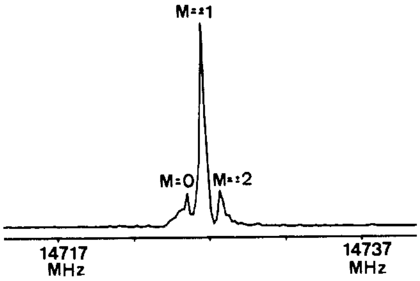

Figure 2. Stark splitting of the rotational transition 3(1,3)–2(0,2) of cyclohexane-*1,1,2,2,3,3*-d_6. A section of 20 MHz out of the 50 MHz wide power spectrum is shown, recorded with a sample pressure of 20 mTorr, temperature of 205 K, microwave carrier frequency of 14726.9 MHz, pulse power of 30 W, pulse width of 500 ns, electric field of 4660 V cm^{-1}, and an integration time of 30 min (9 × 10^7 pulses). The relative intensities of the individual M components depend strongly on the narrow excitation bandwidth.

Electric Dipole Moments. All measured isotopomers of cyclohexane were oblate asymmetric tops with asymmetry parameters $\kappa = (2B - A - C)/(A - C)$ between 0.642 and 0.974. The energy levels with large K_c values exhibit only small asymmetry splittings. The corresponding Stark splittings of the levels 2(0,2), 2(1,2), 3(0,3), and 3(1,3) followed a fast mixed order shift due to the near degeneracies. This fact allowed us to resolve completely all Stark components even for these "nonpolar" molecules. Shifts of up to 4 MHz were observed for electric fields of 8000 V cm^{-1}. A typical Stark pattern is depicted in Figure 2 for CH-d_6, where all three Stark components are clearly resolved.

The Stark shifts depended linearly on the electric field within the experimental accuracy. The Stark coefficients were calculated with second-order perturbation theory for the pairs of nearly degenerate levels for each electric field value measured.[31] For CH-d_2 and CH-d_1-eq, the purely second-order contribution of the μ_a component was too small to be noticeable. Therefore, the μ_a component must be smaller than 0.01 D. For CH-d_6 the small μ_b component was determined from its second-order contribution. The influence of the polarizability on the Stark splittings was checked with the formula given in Gordy and Cook.[32] We used the polarizability components $\alpha_\perp = 12.4 \times 10^{-40}$ C m^2 V^{-1} and $\alpha_\parallel = 11.0 \times 10^{-40}$ C m^2 V^{-1} determined by Craven et al.[33] from the depolarization ratio and refractive index measurements of cyclohexane extrapolated to infinite wavelength. The contribution reached at most 13 kHz for an electric field of 8000 V cm^{-1} which can safely be neglected. The results for the determination of the electric dipole components are given in Table IV.

Discussion

The results from the least-squares structure in Table III show that this structure is indistinguishable from the substitution structure by using the formulas of Kraitchman[28] and Rudolph[29] provided that only differences of the planar moments of inertia are considered with respect to the parent molecule. Because a member of each set of equivalent nuclei of cyclohexane was substituted by an isotope, the complete substitution structure was obtained without any assumption besides that of the molecular symmetry D_{3d}.

A comparison of structural parameters obtained from different experimental methods which are based on different operational definitions must be viewed with caution. In the previous gas electron diffraction studies,[1-7] either r_g or r_a values were reported, while the Raman investigation[10] only yielded an incomplete r_0 structure. A detailed comparison of the bond lengths in r_s, r_g, or r_a structures of organic molecules by Kuchitsu and Cyvin[34] showed that the r_s length for C–C single bonds is consistently smaller than the r_g length by 0.009 (6) Å, whereas the r_a length is smaller than the r_g length by 0.003 (1) Å. Similar systematic deviations exist between the substitution structure and the one from ab initio calculations which is assumed to be near the equilibrium structure r_e. Schäfer et al.[35] compared ab initio structures from fully geometry optimized calculations with the 4-21G basis set with substitution structures. They found that C–C single bond lengths were 0.014 (3) Å longer in the ab initio structures, and the C–H bond lengths were 0.013 (5) Å shorter than in the substitution structure. The bond angles agree quite well in all structures.

The substitution structure is compared in Table V to the structures which were previously determined by gas electron diffraction, Raman spectroscopy, and ab initio calculations. When the systematic differences of structural parameters from different experimental determinations are considered as explained above, the agreement between the reported values is surprisingly good. Deviations of the bond lengths from expected values are smaller

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Table VI. Differences between the C–D and C–H Bond Moments (D) from Isotopically Substituted Species of Cyclohexane

isotopomer	dipole component	bond moment
CH-d_2	μ_c	0.0081
CH-d_1-eq	μ_c	0.0069
CH-d_6	μ_b	0.0115
	μ_c	0.0079

than 0.005 Å except for the C–H bond lengths determined by electron diffraction which are substantially longer. The angles are consistent within 2°. Much better agreement is observed between the angles of the substitution structure and those from the ab initio calculation with the 4-31G basis set.[9] From our results, we found that the axial C–H bonds are not exactly parallel to the molecular symmetry axis but are tilted away from it by an angle of 1.5°.

The axial and equatorial C–H bond lengths and CCH angles of the substitution structure are different in the same sense as predicted from the ab initio calculation. However, the difference of the r_s bond lengths of 0.008 Å is much larger than the expected r_e difference of 0.002 Å. An independent estimate of this difference was obtained from the correlation between C–H stretching frequencies and corresponding bond lengths given by McKean.[36] Caillod et al.[37] determined the stretching frequencies of cyclohexane $\nu(\text{C–H}_{eq})$ to be larger than $\nu(\text{C–H}_{ax})$ by 31 cm^{-1}. This leads to a difference in the bond lengths of 0.003 Å, which is closer to the values from the ab initio calculations. A similar exaggeration of the difference between in-plane and out-of-plane C–H bond lengths in the methyl group of acetaldehyde was observed previously for the substitution structure.[30]

It will be assumed that the small vibrationally induced electric dipole moment of the isotopomers of cyclohexane studied here originates from equal contributions along each C–D bond. By using the substitution structure, the measured μ_b and μ_c dipole components are converted to an effective difference between the C–H and C–D bond moment. The results listed in Table VI show a considerable scatter with a mean value of 0.0086 D. Fliege and Dreizler[16] collected a list of such differences which range from 0.0031 to 0.0141 D for eight molecules studied so far. Our mean value fits nicely in this range.

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Registry No. CH-d_0, 110-82-7; CH-d_1, 26168-37-6; CH-d_2, 33744-45-5; CH-^{13}C-d_2, 124382-54-3; CH-d_6, 2652-64-4.

Supplementary Material Available: Listings of measured rotational frequencies of CH-d_2, CH-^{13}C-d_2, CH-d_1-eq, CH-d_1-ax, and CH-d_6 (Tables VII–XI) (6 pages). Ordering information is given on any current masthead page.

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Electron Tunneling in a Cofacial Zinc Porphyrin–Quinone Cage Molecule: Novel Temperature and Solvent Dependence

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Abstract: The zinc porphyrin–quinone cage molecule ZnPQ(Ac)$_4$ exists as two slowly equilibrating conformers differing in the interplanar porphyrin–quinone distance and thus in the size of the cavity. The close conformer, PQ$_a$, shows only a 4-fold change in rate of quenching of fluorescence in 21 solvents of widely varying properties. Rate constants have been measured in four solvents over wide ranges of temperature: 300–80 K. The activation energies in five solvents are small, varying between −1 and +2 kJ/mol. The quenching rates of the singlet state of the more distant conformer PQ$_b$ vary over a somewhat greater range (10-fold) in these solvents with activation energies of +4 kJ/mol. The activation energies of the foward and reverse electron transfer from the triplet state average +7 kJ/mol. The rates are little affected by viscosity including transition to the glassy state. The weak temperature and solvent dependence of electron transfer in ZnPQ(Ac)$_4$ can best be explained by nonadiabatic electron tunneling. The triplet reaction stores >90% of the energy of the excited state in the free energy of the products. The interesting observation was made that increasing the molar volume of the solvent decreased the conformer equilibrium constant.

The determination of the structure of the bacterial photosynthetic reaction centers by X-ray crystallography[1,2] has focused efforts to explain and duplicate their remarkable efficiency. A striking characteristic of the reaction center is the spacing of the molecules (except for the primary donor, a dimer of bacteriochlorophyll) at about 5 Å beyond the van der Waal's radii. This is close to the optimum distance predicted for electron tunneling reactions.[3] A characteristic of this transfer mechanism is its temperature independence.[4,5] Several porphyrin quinone molecules with varying degrees of structural rigidity and porphyrin–quinone separation have been prepared and their photophysical properties determined.[6] However, little work has been done on

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