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Spectra and Structure of Organogermanes. XIII.[1] Microwave Spectrum of Trimethylbromogermane

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The rotational spectra of five Ge and two Br isotopic species of trimethylbromogermane have been investigated in the region 26.5–40.0 GHz. The ground-state rotational constants, $\bar{B}$, were found to be 1226.48, 1230.39, 1232.37, 1234.40, 1238.51, 1240.49, 1244.33, 1248.27, and 1252.33 for the $(CH_3)_3{}^{76}Ge^{81}Br$, $(CH_3)_3{}^{74}Ge^{81}Br$, $(CH_3)_3{}^{73}Ge^{81}Br$, $(CH_3)_3{}^{72}Ge^{81}Br$, $(CH_3)_3{}^{70}Ge^{81}Br$, $(CH_3)_3{}^{76}Ge^{79}Br$, $(CH_3)_3{}^{74}Ge^{79}Br$, $(CH_3)_3{}^{72}Ge^{79}Br$, and $(CH_3)_3{}^{70}Ge^{79}Br$ molecules, respectively. The utilization of Kraitchman's equations leads to an r_s value of the GeBr distance of 2.323 ± 0.001 Å. By assuming reasonable carbon–hydrogen distances and angles, the following additional structural parameters were obtained: $r(GeC) = 1.936 \pm 0.006$ Å and $\angle CGeBr = 106.3 \pm 0.1°$. The determined structural parameters are compared to the corresponding ones for similar molecules.

Introduction

It was first noted by Lide and Mann[2] from their microwave work that the CF bond distance in *tert*-butyl fluoride, $(CH_3)_3CF$, was significantly longer than that in methyl fluoride, CH_3F. Since then, several similar examples have been found to have longer CX bond distances in $(CH_3)_3CX$ molecules compared to the corresponding hydrides. These examples have included the molecules in which X = H,[3a] Cl,[3b] $C\equiv CH$,[4] and $C\equiv N$.[4] Such a systematic elongation of the CX bond in $(CH_3)_3CX$ compounds in contrast to those found in CH_3X may therefore be considered as a characteristic property of the *tert*-butyl group; however, no completely satisfactory explanation has yet appeared.

From early microwave work[5] on trimethylbromosilane, $(CH_3)_3SiBr$, the SiBr bond distance (2.24 ± 0.02 Å) has been determined and it appears to be longer than that in silyl bromide[6] (2.209 ± 0.001 Å) even considering the experimental errors. The structures of trimethylchlorosilane,[7] $(CH_3)_3SiCl$, and trimethylchlorogermane,[8] $(CH_3)_3GeCl$, have been studied recently. Unfortunately, the SiCl bond length elucidated in this study was not accurate enough to make a comparison with the SiCl bond distance in silyl chloride, SiH_3Cl. Interestingly enough, the GeCl bond distance (2.170 ± 0.001 Å) in $(CH_3)_3GeCl$ was determined to be 0.022 Å longer than the corresponding distance in germyl chloride (2.148 ± 0.003 Å).[9] In order to determine if this is a general characteristic property of the trimethylgermyl compounds, we have undertaken a study of the microwave spectrum of trimethylbromogermane. The presence of naturally abundant isotopes of both the bromine and the germanium atoms makes it possible to determine the r_s(GeBr) bond distance and the skeletal parameters of the trimethylgermyl group. The results are discussed and compared with those obtained for other trimethylgermyl compounds.

Experimental Section

The sample of trimethylbromogermane was obtained from a commercial source and used without further purification. The microwave spectrum of trimethylbromogermane was observed in the R-band frequency range (26.5–40.0 GHz) by using a Hewlett-Packard Model 8460A MRR spectrometer with 33.33-kHz square-wave Stark modulation. All measurements were made while the cell was packed with Dry Ice. The sample pressure was varied in the 20–60 μ range.

Results

The microwave spectrum of trimethylbromogermane is composed of several bands which are equally spaced. The bandwidths slightly increase with frequency. This information indicates that each band is composed of the same rotational transitions arising from different naturally abundant isotopic species in the ground vibrational state as well as in excited vibrational states of the low-frequency modes. Thus, the rotational transition of each band can be readily assigned. Since the bromine atom is much further away from the center of mass than the germanium atom, the separation due to the different isotopic species of bromine (^{79}Br and ^{81}Br) in the same band is expected to be larger than those of germanium (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge). The presumed structure gave a fairly good prediction of the frequency spacings, and the temperature study clearly indicated ground-state lines of the major isotopic species. Our preliminary assignment was made to the ground state of the major isotopic species, ^{70}Ge, ^{72}Ge, and ^{74}Ge with ^{79}Br and ^{81}Br. Further confirmation on this assignment, was made by observing the relative intensities of the spectral lines of the major species for the $15 \leftarrow 14$ transition at several different Stark voltages. Assignment to the minor isotopic species, $(CH_3)_3{}^{76}Ge^{81}Br$, $(CH_3)_3{}^{73}Ge^{81}Br$, and $(CH_3)_3{}^{76}Ge^{79}Br$, was consequently made from the predicted spacing. Subsequent to the final assignment, the substitution method[10] was used to calculate from all the possible combinations the coordinates of the germanium and the bromine atoms along the molecular symmetric axis. For a specific isotopic species, the constant coordinates indicated our assignment was correct.

In Figure 1 is shown the $14 \leftarrow 13$ transition at a Stark field of 200 V/cm with the major assignments to the isotopic species. Because of the interference caused by the closely spaced excited-state lines and the Stark components of other lines, the peak heights do not represent the correct intensities. Frequencies were measured with an accuracy of about 0.1 MHz for the transitions of the major isotopic species. The accuracy is poorer for the other isotopic species (about ±0.5 MHz). No measurement was made on

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Table I. Rotational Frequencies (MHz) and Rotational Constants (MHz) of Trimethylbromogermane at the Ground Vibrational State

	14 ← 13		15 ← 14		16 ← 15		
	ν	B^a	ν	B^a	ν	B^a	$\bar{B}^b$
$(CH_3)_3{}^{76}Ge^{81}Br$	34,340.8	1226.46	36,795.0	1226.50	39,246.9	1226.47	1226.48
$(CH_3)_3{}^{74}Ge^{81}Br$	34,451.01[c]	1230.393	36,911.72	1230.391	39,372.20	1230.381	1230.388
$(CH_3)_3{}^{73}Ge^{81}Br$			36,971.0	1232.37	39,435.8	1232.37	1232.37
$(CH_3)_3{}^{72}Ge^{81}Br$	34,563.26	1234.402	37,031.79	1234.393	39,500.55	1234.392	1234.396
$(CH_3)_3{}^{70}Ge^{81}Br$	34,678.77	1238.528	37,155.49	1238.516	39,631.98	1238.499	1238.514
$(CH_3)_3{}^{76}Ge^{79}Br$			37,214.7	1240.49	39,695.4	1240.48	1240.49
$(CH_3)_3{}^{74}Ge^{79}Br$	34,841.51	1244.340	37,329.97	1244.332	39,818.50	1244.328	1244.333
$(CH_3)_3{}^{72}Ge^{79}Br$			37,448.02	1248.267	39,944.58	1248.268	1248.268
$(CH_3)_3{}^{70}Ge^{79}Br$	35,065.31	1252.333	37,569.97	1252.332			1252.333

[a] The rotational constant is calculated from the corresponding transitional frequency. [b] $\bar{B}$ is the arithmetic mean rotational constant. [c] The uncertainty in the measured frequency is ±0.1 MHz for the major isotopic species and ±0.5 MHz for the minor species.

Table II. Rotational Frequencies (MHz) and Rotational Constants (MHz) of Trimethylbromogermane in the First Excited Vibrational State

	14 ← 13		15 ← 14		16 ← 15	
	ν	B^a	ν_{14}	B^a	ν_{15}	B^a
$(CH_3)_3{}^{76}Ge^{81}Br$	34,290.6	1224.66	36,739.5	1224.65	39,189.9	1224.68
$(CH_3)_3{}^{74}Ge^{81}Br$	34,402.7	1228.67	36,861.1	1228.70	39,317.3	1228.67
$(CH_3)_3{}^{72}Ge^{81}Br$	34,514.8	1232.67	36,979.7	1232.66	39,445.2	1232.66
$(CH_3)_3{}^{70}Ge^{81}Br$	34,629.9	1236.78	37,103.1	1236.77	39,575.9	1236.75
$(CH_3)_3{}^{74}Ge^{79}Br$	34,793.0	1242.61	37,277.8	1242.59	39,762.9	1242.59
$(CH_3)_3{}^{72}Ge^{79}Br$	34,902.5	1246.52	37,395.5	1246.52		
$(CH_3)_3{}^{70}Ge^{79}Br$	35,015.7	1250.56	37,516.5	1250.55		

[a] The rotational constant B is calculated from the corresponding transitional frequency.

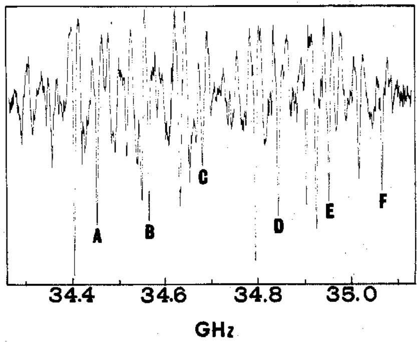

Figure 1. The microwave spectrum of the 14 ← 13 transition of trimethylbromogermane at a Stark field of 200 V/cm. The ground-state transitions are indicated as follows: A, $(CH_3)_3{}^{74}Ge^{81}Br$; B, $(CH_3)_3{}^{72}Ge^{81}Br$; C, $(CH_3)_3{}^{70}Ge^{81}Br$; D, $(CH_3)_3{}^{74}Ge^{79}Br$; E, $(CH_3)_3{}^{72}Ge^{79}Br$; F, $(CH_3)_3{}^{70}Ge^{79}Br$

$(CH_3)_3{}^{73}Ge^{79}Br$ since the rotational frequencies are overlapped or interfered with by the intense excited-state line due to $(CH_3)_3{}^{72}Ge^{79}Br$. In Table I are listed the rotational frequencies and rotational constants of nine isotopic species of trimethylbromogermane in the ground vibrational state. Neither the quadrupole splittings due to Br ($I = {}^3/_2$) or ${}^{73}Ge$ ($I = {}^9/_2$) nuclei nor fine structures due to the centrifugal distortion have been observed with our present experimental conditions. We did not measure any of the 13 ← 12, 12 ← 11, or 11 ← 10 transitions, since the intensity was weak and the measurement of these additional transitions would not give any further information unless the quadrupole components could be observed.

A strong excited-state line was found on the low-frequency side of each ground-state transition. These lines were identified as resulting from excited states by the temperature study even though they were approximately 50 MHz lower than the ground state. These results are consistent with the similar observations for the corresponding chloride. Frequency measurements and species assignments for these excited states are listed in Table II.

Structure

In our present study, the amount of information available is insufficient for the complete determination of the molecular structure. Since it will be shown that the location of the hydrogen atoms in the methyl groups is insensitive to the observed moments of inertia, the skeletal structure may be determined with good accuracy. The coordinates of the Ge and Br atoms were calculated by using Kraitchman's substitution method[10] and the results are summarized in Table III. Since both atoms did not lie close to the center of mass, the r_s structure obtained should be very reliable. Thus, it is shown in the last row of Table III that the r_s(GeB) parameters obtained by using different isotopic molecules as the parent molecules agree very well. The results indicate not only the correctness of our assignment but also the reliability of the r_s(GeBr) structure.

After obtaining the GeBr bond parameter, the GeC bond distance and the GeCBr angle have been determined by the least-squares fitting to the observed rotational constants under the assumptions of six different methyl group structures. With an initial guess of the GeC bond distance (r_0) and GeCBr angle (θ_0), corrections to these parameters were obtained by solving simultaneously the truncated Taylor's series as

$$B^i = B_0{}^i + \frac{\partial B^i}{\partial r}\Delta r + \frac{\partial B^i}{\partial \theta}\Delta\theta$$

where B^i is the experimental rotational constant and $B_0{}^i$ is the calculated rotational constant from an initial given set of parameters for the ith isotopic molecule. $\partial B^i/\partial r$ and $\partial B^i/\partial\theta$ are the partial differentials of the rotational constant of the ith molecule with respect to the GeC bond distance and GeCBr angle, respectively. Δr and $\Delta\theta$ are the differences between the corresponding better values and the initial values. Further iteration can be carried out by using a new given set of parameters obtained from the previous calculation. In the present calculation, both parameters converge very fast so that no more than two iterations were needed.

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Table III. Calculation of the r_s(GeBr) Distance from Different Isotopic Species[a]

	Original molecule			
Substituted molecule	$(CH_3)_3{}^{76}Ge^{81}Br$	$(CH_3)_3{}^{74}Ge^{81}Br$	$(CH_3)_3{}^{72}Ge^{81}Br$	$(CH_3)_3{}^{70}Ge^{81}Br$
	(A) Calculation of $\lvert Z\rvert$(Ge)			
$(CH_3)_3{}^{76}Ge^{81}Br$		0.8130	0.8211	0.8295
$(CH_3)_3{}^{74}Ge^{81}Br$	0.8050		0.8209	0.8295
$(CH_3)_3{}^{72}Ge^{81}Br$	0.8048	0.8127		0.8297
$(CH_3)_3{}^{70}Ge^{81}Br$	0.8049	0.8129	0.8213	
$\lvert Z\rvert(Ge)_{av}$	0.8049	0.8129	0.8211	0.8295
	(B) Calculation of $\lvert Z\rvert$(Br)			
$(CH_3)_3{}^{76}Ge^{79}Br$	1.5183			
$(CH_3)_3{}^{74}Ge^{79}Br$		1.5103		
$(CH_3)_3{}^{72}Ge^{79}Br$			1.5014	
$(CH_3)_3{}^{70}Ge^{79}Br$				1.4935
r_s(GeBr)[b]	2.3232	2.3231	2.3225	2.3230

[a] All numbers are in units of Angstrom. [b] $r_s(GeBr) = \lvert Z\rvert(Ge)_{av} + \lvert Z\rvert(Br)$.

Table IV. Structural Parameters of Trimethylbromogermane[a]

	1	2	3	4	5	6
r(GeBr)[b]	2.323	2.323	2.323	2.323	2.323	2.323
r(CH)[c]	1.095	1.095	1.095	1.095	1.105	1.085
∠GeCH[c]	109.7	110.7	111.7	112.7	109.7	109.7
r(GeC)	1.940	1.936	1.933	1.930	1.937	1.942
∠BrGeC	106.3	106.3	106.3	106.3	106.3	106.3

[a] Bond distance is in units of Angstroms and bond angle is in units of degrees. [b] r(GeBr) is the substituted structure as calculated in Table III. [c] Assumed parameter.

The calculation is summarized in Table IV. In each case, the calculated rotational constants for all species are in agreement with the observed values within 0.02 MHz. It can be seen that r(GeC) and the ∠BrGeC are not sensitive to the assumed structure for the methyl groups. Any variation in the methyl group parameters should be within the chosen range as given in Table IV; consequently, the determined values are $r(GeC) = 1.936 \pm 0.006$ Å and $\angle CGeBr = 106.3 \pm 0.1°$.

Discussion

The GeBr bond distance (2.323 ± 0.001 Å) obtained in the present study is explicitly longer than that in GeH_3Br (2.2970 ± 0.0002 Å).[11] Consideration has been given to the possibility of a centrifugal distortion effect since our effective rotational constants were obtained from high J transitions. From our present experimental data, we could not obtain any significant information on the centrifugal distortion constant. If trimethylbromogermane has the same magnitude for D_J as found for trimethylchlorogermane, the rotational constants calculated from different rotational transitions should have a difference of at least 0.05 MHz. In looking at the constancy of the rotational constants as calculated from the different transitions it appears safe to give an upper limit of 2.8×10^{-4} MHz for D_J. By using this value and assuming that all the isotopic molecules have the same centrifugal distortion effect, the correction to the rotational constants (listed in the last column of Table I) should be smaller than 0.126 MHz. After performing this correction, the rotational constants were found to yield identical r_s(GeBr) distances to those obtained without the correction within our experimental error. Consequently, we can conclude in the case of trimethylbromogermane that the r_s(GeBr) distance is independent of the centrifugal effect and the GeBr distance in trimethylbromogermane is definitely longer than in germyl bromide.

In consideration of the effect of centrifugal distortion on the skeletal structure, one must check to see how the rotational constants vary with r(GeC) and ∠CGeBr. From our least-squares calculation, it was found in the most sensitive case that $\Delta B/\Delta r = -360$ and $\Delta B/\Delta\theta = -10.2$. Thus, our maximum correction to the rotational constants (0.126 MHz) would give a correction to r and θ less than 0.00035 Å and 0.013°, respectively, which is certainly within our quoted errors. Another consideration must be given to the centrifugal distortion effect which, if D_{JK} is large enough, will cause resolvable K components or broadening of the line for a given rotational transition. Since the center of mass of trimethylbromogermane is outside the trimethylgermyl moiety, D_{JK} is expected to have a positive value. Thus, the rotational transition will consist of some high K components extended to the lower frequency side of the low K components. As far as D_{JK} is concerned, it is generally true that the higher J transitions will have a larger frequency separation in the K components. Experimentally, we have observed neither hyperfine structure due to the first-order centrifugal distortion constant, D_{JK}, nor any asymmetry in the line shape as expected for the case of unresolved K structure. In addition, the half-width for the lower J transition is slightly larger than that for the higher J transition. These observations suggest that the centrifugal distortion effect is unimportant compared to the nuclear quadrupole effect.

In order to predict how the nuclear quadrupoles might affect the rotational transition lines, we have calculated the quadrupole splitting by assuming the same quadrupole coupling constant as found for germyl bromide.[11] In this calculation, the second-order effect is found to be negligibly small in comparison with the first-order quadrupole effect. Our calculation indicated that all the intense quadrupole components for $K \leqslant 4$ form the main band of the observed transition, since the $14 \leftarrow 13$ transition is observed to have a half-width of 2.5 MHz. Other intense quadrupole components are expected to be at a sufficient distance from this main line to give rise to resolvable fine structure. However, any other single intense component has an intensity only 5% of the main band which would make it experimentally difficult to observe. These low K quadrupole components are more or less symmetric with respect to the unperturbed line and, consequently, the measured frequency should not be far from the unperturbed transitional frequency. Any deviation of the measured effective frequencies from the hypothetical "true" frequencies would still give structural parameters falling within the quoted experimental errors.

A comparison of the skeletal structures of trimethylgermyl compounds is quite interesting and their parameters are listed in Table V. Precise GeX distances are available

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Table V. Structural Parameters in GeH_3X and $(CH_3)_3GeX$

	GeH_3X				$(CH_3)_3GeX$			
X	∠HGeH, deg	r(GeH), Å	r(GeX), Å	Ref	∠CGeC, deg	r(GeC), Å	r(GeX), Å	Ref
H	109.7	1.527 ± 0.003	1.527 ± 0.003	*a*	109.6 ± 0.1	1.947 ± 0.005	1.532 ± 0.001	*b*
Cl	110.9 ± 1.5	1.52 ± 0.03	2.148 ± 0.003	*c*	112.8 ± 0.08	1.9400 ± 0.0001	2.170 ± 0.001	*d*
Br	109.4 ± 4	1.44 ± 0.1	2.2970 ± 0.0002	*e*	112.4 ± 0.1	1.936 ± 0.006	2.323 ± 0.001	*f*

[a] Obtained by infrared contour analysis: L. P. Lindman and M. K. Wilson, *J. Chem. Phys.*, **22**, 1723 (1954). [b] J. R. Durig, M. M. Chen, and Y. S. Li, to be submitted for publication. [c] See ref 9. [d] See ref 8. [e] See ref 11 and A. H. Sharlaugh, B. S. Pritchard, V. G. Thomas, J. M. Mays, and B. P. Dailey, *Phys. Rev.*, **79**, 189 (1950). [f] Present work.

for all the molecules. There may appear to be some question about the longer GeX distance in trimethylgermane compared to germanium hydride, since the GeH distance in trimethylgermane is the r_s distance whereas in germane it is an r_0 value. The r_0 value is usually larger than the corresponding r_s value for the same molecule. For this reason, it is logical to conclude that the GeX distance is longer in trimethylgermane than in germane, which would be similar to the other cases listed in the same table. This longer GeX distance in trimethylgermyl compounds compared to the hydrides may arise from the increase in the amount of ionic bonding due to the methyl substitution. The absence of observable quadrupole splitting information has prevented us from calculating the percentage of the ionic bond.[9] However, from the GeBr bond distance, it is estimated that the GeBr bond has a double-bond character of only 7% which is small in comparison with the 15% for germyl bromide.

An examination of the structural parameters listed in Table V shows that the CGeC angle opens appreciably and the GeC distance decreases by the substitution of a chlorine or bromine atom for the hydrogen in trimethylgermane. Thus, it appears that the trimethylgermyl parameters are somewhat dependent on the substituents. However, the structures of the trimethylgermyl moiety in the chloride and bromide are quite similar to each other. Microwave work on $(CH_3)_3GeCN$ and $(CH_3)_3GeNC$ is currently in progress in this laboratory and the results will be reported later.

Registry No. $(CH_3)_3{}^{76}Ge^{81}Br$, 36965-95-4; $(CH_3)_3{}^{74}Ge^{81}Br$, 36926-72-4; $(CH_3)_3{}^{73}Ge^{81}Br$, 36926-73-5; $(CH_3)_3{}^{72}Ge^{81}Br$, 36926-74-6; $(CH_3)_3{}^{70}Ge^{81}Br$, 36926-75-7; $(CH_3)_3{}^{76}Ge^{79}Br$, 36926-76-8; $(CH_3)_3{}^{74}Ge^{79}Br$, 36926-77-9; $(CH_3)_3{}^{72}Ge^{79}Br$, 36926-78-0; $(CH_3)_3{}^{70}Ge^{79}Br$, 36926-79-1.

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Deprotonation of Pentaborane(9) Derivatives. Evidence for Tautomerism and Isomerization of Resulting Anions

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Deprotonation of $1\text{-}CH_3B_5H_8$, $2\text{-}CH_3B_5H_8$, $1\text{-}ClB_5H_8$, and $1\text{-}BrB_5H_8$ by potassium hydride yielded $1\text{-}CH_3B_5H_7^-$, $2\text{-}CH_3B_5H_7^-$, $1\text{-}ClB_5H_7^-$, and $1\text{-}BrB_5H_7^-$. Low-temperature pmr studies (−90 to −130°) gave evidence of partial quenching of tautomerism of the bridging protons in $2\text{-}CH_3B_5H_7^-$ but not in the case of the apically substituted anions. Boron-11 nmr studies showed evidence of isomerization of $1\text{-}CH_3B_5H_7^-$ to $2\text{-}CH_3B_5H_7^-$. The relative acidities of these boron hydrides was found to be in the order $1\text{-}ClB_5H_8 > B_5H_9 > 1\text{-}CH_3B_5H_8 \cong 2\text{-}CH_3B_5H_8$.

Introduction

The reported deprotonation of pentaborane(9),[1-3] hexaborane(10),[3-5] and tetraborane(10)[6,7] by alkali metal hydrides, methyllithium, or ammonia has demonstrated the ability of the intermediate boron hydrides to act as Bronsted acids. The relative acidities of these boron hydrides has been shown to increase with increasing size of polyhedral frameworks[3] of composition B_nH_{n+4}: $B_{10}H_{14} > B_6H_{10} > B_5H_9$. In the cases of B_5H_9[1] and B_6H_{10}[4] the proton is removed from a bridging site in the base of the pyramidal framework. Rapid tautomerism of the remaining bridge protons in $B_5H_8^-$ and $B_6H_9^-$ has been invoked[2,3] to explain the apparent magnetic equivalence of the boron atoms observed in the boron-11 nmr spectra. To date accompanying pmr spectral studies to support such evidence has not been cited.

We report in this paper a study of the effects of methyl, chloro, and bromo substituents on the B_5H_9 framework with regard to relative Bronsted acidities and properties of the resulting anions as studied by proton and boron-11 nmr spectra. Pmr evidence for tautomerism of the bridging protons is presented as well as partial quenching of tautomerism in $2\text{-}CH_3B_5H_7^-$ at low temperatures.

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