October, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (10), 2875—2879 (1979) 2875

Vibrational Spectra and Normal Coordinate Calculations for Methyl-1-propynylmercury(II) and Its Deuterated Analogues†

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(Received March 31, 1979)

Infrared spectra (4000—80 cm^{-1}) of $CH_3HgC{\equiv}CCH_3$, $CD_3HgC{\equiv}CCH_3$, $CH_3HgC{\equiv}CCD_3$, and $CD_3HgC{\equiv}CCD_3$ have been obtained in carbon tetrachloride, carbon disulfide and benzene solutions, as well as in the solid state at liquid nitrogen temperature. Raman spectra (4000—0 cm^{-1}) have also been recorded on benzene solutions and on solids at room temperature. Assignments for all the fundamentals have been made assuming C_{3v} molecular symmetry. Normal coordinate calculations have been carried out in order to confirm the proposed assignments.

In a previous paper[1] a report was given on the vibrational spectra and normal coordinate calculations for methylethynylmercury(II). The study has now been extended to methyl-1-propynylmercury(II). Although many acetylides of the type $RHgC{\equiv}CR'$ have been prepared,[2] no vibrational study on these compounds except methylethynylmercury(II) seems to have been reported. In the present study, infrared and Raman spectra have been obtained for methyl-1-propynylmercury(II) and its deuterated analogues. Assignments for all the fundamentals are made assuming C_{3v} symmetry. Normal coordinate calculations have been carried out in order to confirm the proposed assignments.

Experimental

Methyl-1-propynylmercury(II) was prepared in the following way.

Methylmercury(II) iodide was dissolved in an aqueous solution of potassium hydroxide. Methylacetylene, generated by the action of 1,2-dibromopropane with potassium hydroxide in ethanol,[3] was passed through the solution. White precipitates were filtered and washed with water and then dried in a desiccator over potassium hydroxide pellets. The crude product was purified by sublimation in a vacuum.

Deuterated compounds were prepared in a similar way using methyl-d_3-mercury(II) bromide and/or methylacetylene-d_4, prepared from methyl-d_3-magnesium bromide and mercury(II) bromide, and by the action of D_2O with magnesium carbide,[4] respectively.

Methyl-1-propynylmercury(II) melts at 80—81 °C (no value was found in literature). The mercury content was determined for the undeuterated compound by the method of Spahr *et al.*[5] Found, 78.0%. Calcd for C_4H_6Hg, 78.8%. The molecular weight was also cryoscopically determined in benzene. Calcd for C_4H_6Hg, 255. Measured, 260.

The infrared spectra in the range 4000—400 cm^{-1} were recorded on a Perkin-Elmer 337 spectrophotometer in annealed solid films at liquid nitrogen temperature. Cooling was necessary to prevent sublimation during the course of the measurements. The spectra were also obtained in carbon tetrachloride and carbon disulfide solutions. The instrument was calibrated in the usual way.[6]

Far-infrared spectra in the range 400—80 cm^{-1} were recorded on a Hitachi FIS-III Far-infrared spectrophotometer which had been evacuated in order to remove atmospheric water vapor. The spectra were measured in annealed solid films at liquid nitrogen temperature in order to prevent sublimation. The spectra in benzene solutions were also obtained using polyethylene bags. The instrument was calibrated with water vapor frequencies.

Raman spectra were recorded in the solid state in capillary tubes on a JEOL JRS-S1 Raman spectrophotometer equipped with a 50 mW NEC GLG 108 He-Ne laser. The instrument was calibrated with the emission lines of Ne. The spectra were also measured in benzene solutions in order to obtain qualitative polarizations.

Results and Vibrational Assignments

The infrared and Raman spectra of the four isotopic methyl-1-propynylmercury(II) are shown in Figs. 1 and 2. The symmetry coordinates are summarized in Table 1 and observed frequencies are given in Tables 2—4.

The CHgC skeleton is linear in many organomercurials.[7] It is thus reasonable to assume the same skeleton for the present compounds. Since the two methyl groups in each compound are separated from each other to a greater extent than those in dimethylmercury(II),[8] where the free rotation of methyl groups is believed to be present, it is likely that the free rotation

TABLE 1. DESCRIPTION OF THE SYMMETRY COORDINATES FOR METHYL-1-PROPYNYLMERCURY(II)

Vibrational mode	Coordinate	
	A_1	E
$CH_3(CD_3)$ st. (Me–CC)	S_1	S_{10}
$CH_3(CD_3)$ st. (Me–Hg)	S_2	S_9
C≡C st.	S_3	
$CH_3(CD_3)$ def. (Me–CC)	S_4	S_{11}
$CH_3(CD_3)$ def. (Me–Hg)	S_5	S_{12}
C–C st.	S_6	
$CH_3(CD_3)$ rock. (Me–CC)		S_{13}
$CH_3(CD_3)$ rock. (Me–Hg)		S_{14}
CH_3–$Hg(CD_3$–) st.	S_7	
Hg–CC st.	S_8	
CCC def.		S_{15}
CCHg def.		S_{16}
CHgC def.		S_{17}

Abbreviations: st., stretching; def., deformation; rock., rocking.

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† A preliminary report of this work was presented at the 37th National Meeting of the Chemical Society of Japan, Yokohama, April 1978.

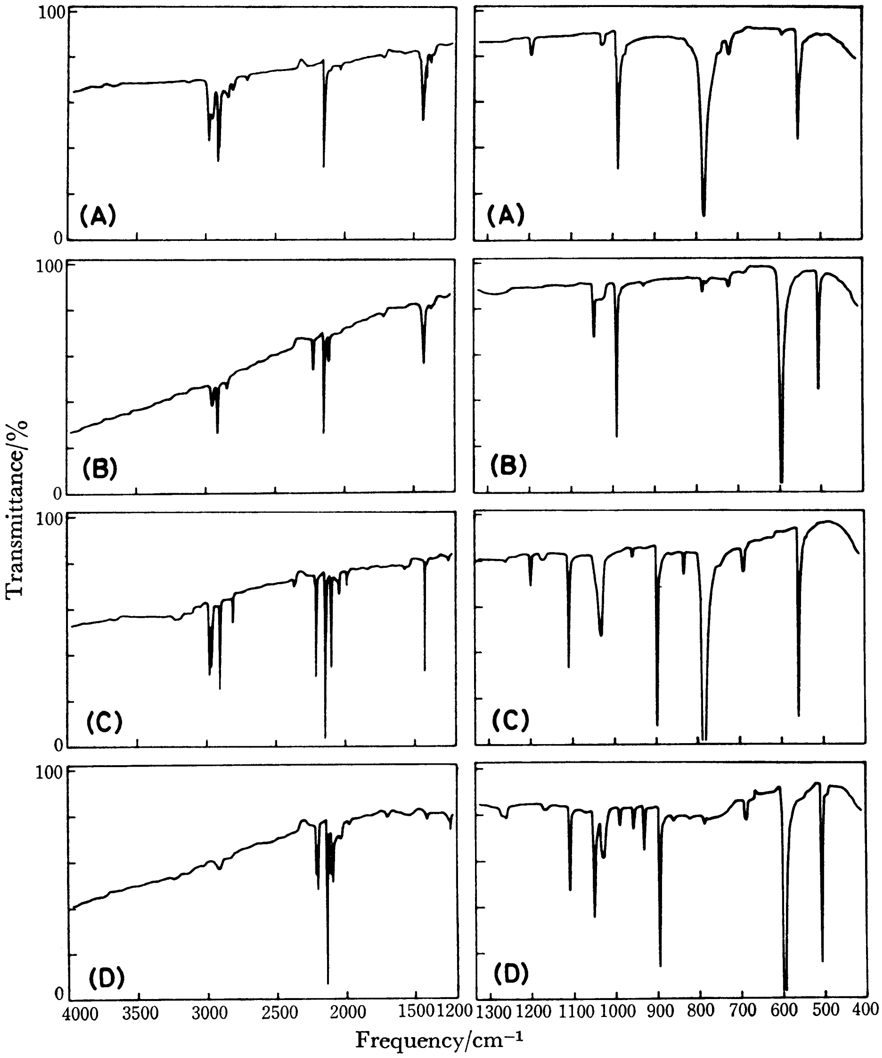

Fig. 1. Infrared spectra of $CH_3HgC{\equiv}CCH_3$ (A), $CD_3HgC{\equiv}CCH_3$ (B), $CH_3HgC{\equiv}CCD_3$ (C), and $CD_3HgC{\equiv}CCD_3$ (D), in the solid state at −196 °C.

Table 2. Observed and calculated frequencies (cm^{-1}) for $CH_3HgC{\equiv}CCH_3$

No.	Infrared		Raman		Calcd	PED	
	solid	soln	solid	soln			
1	2911	2914	2910	2915 p	2920	$100S_1$	
2	2901	2906	2900	2905 p	2904	$98S_2$	
3	2150	2157	2147	2158 p	2152	$85S_3$	$11S_6$
4	1380	1367	1370	1371	1371	$93S_4$	
5	1197	1200	1196	1202 p	1201	$78S_5$	$17S_2$
6	990	997			997	$77S_6$	$17S_8$
7	556	553	555	556 p	558	$91S_7$	
8	336	340	330	340 p	341	$74S_8$	$12S_7$
9	2980	2977	2980	2980	2981	$100S_9$	
10	2950	2945	2948		2956	$100S_{10}$	
11	1435	1437	1430		1440	$91S_{11}$	
12	1421	1412			1416	$97S_{12}$	
13	1028	1021	1025		1030	$88S_{13}$	
14	782	772	785		780	$97S_{14}$	
15			366	363	365	$74S_{15}$	$25S_{16}$
16	220	203	219	205	200	$79S_{16}$	$21S_{17}$
17			73		76	$69S_{17}$	$29S_{16}$

Abbreviation: p, polarized.

Table 3. Observed and calculated frequencies (cm^{-1}) for $CD_3HgC{\equiv}CCH_3$

No.	Infrared		Raman		Calcd	PED		
	solid	soln	solid	soln				
1	2914	2913	2910	2910 p	2920	$100S_1$		
2	2119	2120	2113	2107 p	2119	$94S_2$		
3	2151	2159	2145	2160 p	2152	$84S_3$	$11S_6$	
4	1375	1370	1368	1372	1372	$93S_4$		
5	929	930	929	932 p	927	$69S_5$	$19S_2$	$10S_7$
6	991	997			999	$73S_6$	$15S_8$	
7	507	504	505	508 p	503	$78S_7$	$12S_5$	
8	337	339	338	340 p	337	$71S_8$	$15S_7$	
9	2230	2228	2220	2220	2222	$99S_9$		
10	2950	2950	2951		2956	$100S_{10}$		
11	1429	1437	1430		1440	$91S_{11}$		
12	1046	1026	1030		1025	$98S_{12}$		
13	1029	1026	1030		1030	$88S_{13}$		
14	596	589			579	$99S_{14}$		
15			364	360	365	$74S_{15}$	$25S_{16}$	
16	212	195	210	196	199	$80S_{16}$	$20S_{17}$	
17			70		69	$70S_{17}$	$28S_{16}$	

Abbreviation: p, polarized.

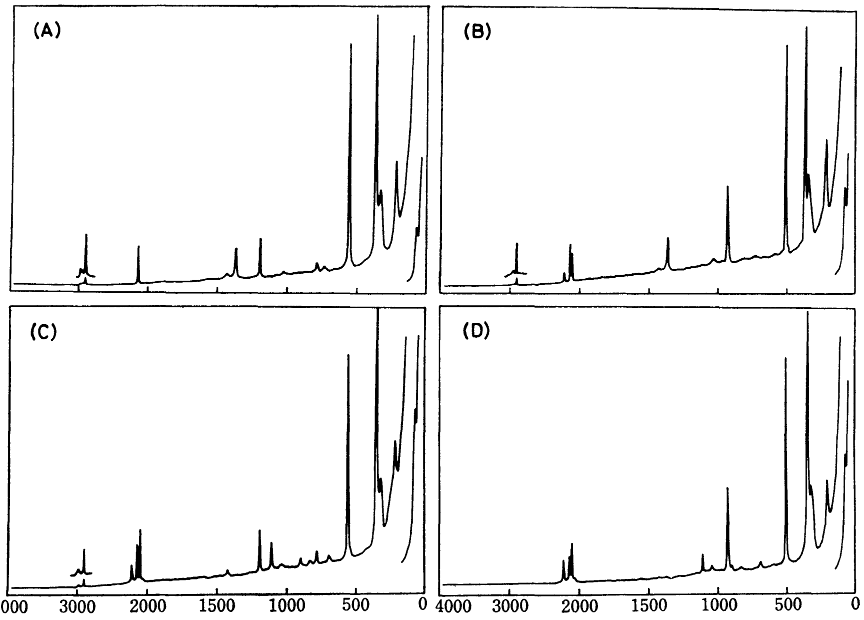

Fig. 2. Raman spectra of $CH_3HgC{\equiv}CCH_3$ (A), $CD_3HgC{\equiv}CCH_3$ (B), $CH_3HgC{\equiv}CCD_3$ (C), and $CD_3HgC{\equiv}CCD_3$ (D), in the solid state at room temperature.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $CH_3HgC{\equiv}CCD_3$

No.	Infrared		Raman		Calcd	PED		
	solid	soln	solid	soln				
1	2102	2107	2105	2110 p	2092	$78S_1$	$20S_3$	
2	2902	2903	2905	2908 p	2905	$97S_2$		
3	2149	2156	2152	2150 p	2167	$65S_3$	$20S_1$	$12S_6$
4	1110	1113	1108	1111	1109	$54S_4$	$38S_6$	
5	1200	1200	1190	1201 p	1201	$79S_5$	$17S_2$	
6	899	903	896		902	$39S_6$	$40S_4$	$18S_8$
7	559	556	555	560 p	555	$93S_7$		
8	321	325	313	325 p	326	$72S_8$	$10S_7$	
9	2979	2977	2981		2981	$100S_9$		
10	2217	2209	2221	2220	2204	$98S_{10}$		
11	1032	1038	1039		1033	$94S_{11}$		
12	1425	1412	1425		1416	$97S_{12}$		
13	835	829	830		817	$84S_{13}$	$11S_{15}$	
14	783	774	780		780	$97S_{14}$		
15	345		347	348	343	$68S_{15}$	$28S_{16}$	
16	209	196	209	195	192	$75S_{16}$	$24S_{17}$	
17			72		74	$67S_{17}$	$30S_{16}$	

Abbreviation: p, polarized.

takes place also in methyl-1-propynylmercury(II). However, the observed spectra can satisfactorily be explained on the assumption of C_{3v} symmetry (a staggered form) for these molecules. With this symmetry, the molecule is expected to have $8A_1$, A_2, and 9E vibrational modes, in which the A_2 mode is inactive in both the infrared and Raman spectra, while the A_1 and the E modes are active in both.

Since the vibrational coupling of the two methyl groups in a molecule is expected to be very small, vibrations of one methyl group are hardly influenced by deuteration of the other. Taking their isotopic shifts and polarizations of Raman bands into consideration, together with the data for related compounds,[9,10] assignments for the methyl groups are easily made.

A strong infrared absorption at *ca.* 2150 cm^{-1} in each isotopic species is hardly affected by deuteration and the corresponding Raman band in solution is polarized. This is undoubtedly assigned to the C≡C stretching.

C–C stretching vibrations for $CH_3C{\equiv}N$ and $CH_3C{\equiv}CH$[10] have been observed at *ca.* 900 cm^{-1}. We have assigned the strong infrared bands at *ca.* 990 cm^{-1} for $CH_3HgC{\equiv}CCH_3$ and $CD_3HgC{\equiv}CCH_3$ to this mode. Upon deuteration of the 1-propynyl group, these bands shift to *ca.* 900 cm^{-1} for $CH_3HgC{\equiv}CCD_3$ and $CD_3HgC{\equiv}CCD_3$, suggesting a vibrational coupling between the C–C stretching and the vibrations of the neighbouring methyl group.

The remaining skeletal vibrations are expected to appear below 600 cm^{-1}. In the solution Raman spectrum for $CH_3HgC{\equiv}CCH_3$, the four bands appear at 556, 363, 340, and 205 cm^{-1}, the bands at 556 and 340 cm^{-1} being polarized. Upon deuteration of the methyl group ($CD_3HgC{\equiv}CCH_3$), the 556 cm^{-1} band shifts to 508 cm^{-1}, while the 340 cm^{-1} band remains at the same position. In contrast, the 340 cm^{-1} band shifts to 325 cm^{-1} upon deuteration of the 1-propynyl group ($CH_3HgC{\equiv}CCD_3$). Thus, the 556 cm^{-1} band can be assigned to the CH_3–Hg stretching and the 340 cm^{-1} to the Hg–CC stretching vibrations. The remaining two bands at 363 and 205 cm^{-1} seem to be due to the skeletal deformations. The former band slightly shifts to lower frequency upon deuteration of the 1-propynyl group, while the latter band exhibits a very small isotopic shift upon deuteration of either methyl or 1-propynyl group. The HgCC deformation in $CH_3HgC{\equiv}CH$[1] has been assigned at 272 cm^{-1}, lower than the CCC deformation in $CH_3C{\equiv}CH$[10] at 336 cm^{-1}. From the results, the 205 cm^{-1} band is assigned to HgCC deformation and the 306 cm^{-1} to CCC deformation.

The assignment of CHgC deformation is fairly difficult, since the mode is expected to appear below 150 cm^{-1} in weak intensity. In this study, the Raman bands at *ca.* 70 cm^{-1} in the solid state were tentatively assigned to this mode. No solution Raman spectra in this range could be observed owing to obscurity in the background.

Normal Coordinate Calculations and Discussion

Normal coordinate calculations were carried out by Wilson's GF-matrix method on an ACOS 77/700 computer at the Computer Center, Tohoku University, using the iterative least-squares procedure in the usual way. For lack of structural data, the molecular parameters were transferred from those of CH_3HgCl,[11] $CH_3HgC{\equiv}N$[12] and $CH_3C{\equiv}CH$;[13] r(C–H) of CH_3CC, 1.11 Å; r(C–H) of CH_3, 1.10 Å; r(C–C), 1.46 Å; r(C≡C), 1.21 Å; r(CH_3–Hg), 2.08 Å; r(Hg–CC), 2.05 Å; ∠HCH of CH_3CC, 108.5°; ∠HCH of CH_3, 110.7°. The least-squares refinement was carried out in terms of the symmetry force constants, which were fitted to the infrared frequencies in solutions, except for the HgCC and CHgC deformations which were taken from the Raman spectra for solutions and solids, respectively, for the four isotopic species simultaneously.

The symmetry force constants, together with uncertainties from the last cycle of the least-squares refinements, are given in Table 6. The average errors are 0.35% and 0.97% for the A_1 and E vibrations, respectively, the sum of the weighted squares of errors $\sum(\lambda_{obsd}-\lambda_{calcd})^2/\lambda_{obsd}$ being 2.39×10^{-3} and 2.54×10^{-3} for the A_1 and E vibrations, respectively. The agreements between the calculated and the observed frequencies are satisfactory for the four isotopic species (Tables 2—5). The potential energy distributions are also given in these tables. A strong vibrational coupling exists between the C–C stretching and the CD_3 symmetric deformations (Tables 4 and 5, mode Nos. 4 and 6).

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $CD_3HgC{\equiv}CCD_3$

No.	Infrared		Raman		Calcd	PED
	solid	soln	solid	soln		
1	2102	2106	2101	2110 p	2092	$78S_1$ $20S_3$
2	2117	2120	2119	2121 p	2120	$94S_2$
3	2149	2156	2154	2158 p	2168	$66S_3$ $19S_1$ $12S_6$
4	1110	1113	1109	1113	1110	$54S_4$ $38S_6$
5	932	935	929	929 p	935	$64S_5$ $18S_2$ $10S_7$
6	896	905			896	$32S_6$ $30S_4$ $17S_5$ $14S_8$
7	507	504	505	509 p	500	$79S_7$ $12S_5$
8	320	325	322	325 p	323	$70S_8$ $14S_7$
9	2225	2227	2225	2232	2222	$99S_9$
10	2213	2211	2210	2210	2204	$98S_{10}$
11	1051	1035	1040		1033	$94S_{11}$
12	1030	1035	1040		1025	$98S_{12}$
13	822	820	829		817	$84S_{13}$ $11S_{15}$
14	587	589	592		579	$99S_{14}$
15			349	347	343	$68S_{15}$ $28S_{16}$
16	202	190	201	190	191	$77S_{16}$ $22S_{17}$
17			70		68	$69S_{17}$ $29S_{16}$

Abbreviation: p, polarized.

TABLE 6. SYMMETRY FORCE CONSTANTS AND THEIR UNCERTAINTIES FOR METHYL-1-PROPYNYLMERCURY(II)[a]

		σ			σ
F_1	4.890	0.015	F_9	4.721	0.012
F_2	4.630	0.075	F_{10}	4.648	0.012
F_3	14.098	0.070	F_{11}	0.546	0.003
F_4	0.571	0.005	F_{12}	0.513	0.003
F_5	0.534	0.025	F_{13}	0.680	0.007
F_6	5.168	0.122	F_{14}	0.428	0.004
F_7	2.478	0.079	F_{15}	0.533	0.096
F_8	2.992	0.242	F_{16}	0.316	0.019
			F_{17}	0.228	0.030
$F_{2,5}$	−0.548	0.077			
$F_{4,6}$	−0.364	0.020	$F_{15,16}$	0.259	0.060
$F_{5,7}$	−0.096	0.040			
$F_{7,8}$	−0.471	0.225			

a) The stretching force constants are given in mdyn/Å, the deformation force constants in mdyn·Å, the stretching-deformation interaction constants in mdyn.

TABLE 7. COMPARISON OF FORCE CONSTANTS (mdyn/Å)

	f(M–CC)	f(M–CH_3)
$CH_3HgC{\equiv}CCH_3$	2.99[a]	2.48[a]
$CH_3HgC{\equiv}CH$	2.83[1]	2.54[1]
CH_3HgCl		2.55[9]
CH_3HgBr		2.48[9]
CH_3HgI		2.38[9]
$SiH_3C{\equiv}CH$	3.30[14]	
$SiH_3C{\equiv}CSiH_3$	3.35[14]	
$SiH_3C{\equiv}CCH_3$	3.30[14]	
SiH_3CH_3		2.97[14]
$Si(CH_3)_4$		2.88[15]
$GeH_3C{\equiv}CH$	3.46[16]	
GeH_3CH_3		2.87[17]
$Ge(CH_3)_4$		2.65[15]

a) This work.

In these calculations, the symmetry force constants F_7 and F_8 turn out the CH_3–Hg and Hg–CC valence stretching force constants. A comparison of force constants is given in Table 7. We see that the force constants for the M–CC bond are always larger than those for the M–CH_3 bond. This is in line with the expectation on the basis of the hybridization of the carbon atom adjacent to the metal atom; the sp hybrid in M–CC and the sp^3 hybrid in M–CH_3, make the former bond stronger than the latter.

One of authors (Y.I.) wishes to express his thanks to Assist. Prof. Fumio Watari for helpful suggestions throughout this work and for the computer programs used in calculations.

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