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The Infrared Spectrum of 2-Methoxyethylmercuric Iodide and its Tetradeuterio Analog¹

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The fundamental vibrational frequencies for 2-methoxyethylmercuric iodide and 1,1,2,2-tetradeuterio-2-methoxyethylmercuric iodide have been obtained from the infrared spectra of two solids. The frequencies obtained are consistent with the assumption that the all-*trans* isomer is preferred in the solid state. On melting, a few new peaks appear, but it is concluded that the all-*trans* isomer is still the most stable in the melt.

Mizushima and his co-workers² have demonstrated the utility of vibrational spectroscopy in the investigation of internal rotation in molecules. In the present paper the infrared spectra of solid and liquid 2-methoxyethylmercuric iodide (I) and its 1,1,2,2-tetradeuterio analog II are discussed.

Results

Both I and II have melting points of 42°. The parts of a demountable cell were heated on a hot-plate, and a small quantity of I or II was allowed to melt on one of the salt plates. The cell was then removed from the hot-plate and assembled. The resulting film remained liquid for about one-half hour during which its infrared spectrum was recorded. After solidification the infrared spectrum of the thin layer of solid was recorded. A Perkin-Elmer model 21 spectrophotometer with a sodium chloride prism was used throughout. It is thought to give an accuracy of ± 2 cm^{-1} at frequencies less than 2000 cm^{-1} and ± 10 cm^{-1} at frequencies above 2000 cm^{-1} . The spectra were scanned from 4000 to 650 cm^{-1} . Table I shows the peaks observed and their relative intensities. To remove the possibility that decomposition takes place on melting, spectra of I and II were also obtained in carbon tetrachloride and carbon disulfide solution. These are essentially identical with the spectra of the pure liquids.

Discussion

There are at least two single bonds in I and II about which rotation will give rise to isomers. A total of five stable rotational isomers can be pictured. They are shown in Newman projection in Fig. 1.

Even in its most symmetrical form, I has only a symmetry plane, so all 33 of its fundamental vibrational frequencies should be infrared active. If only one isomer is present, a total of 15 fundamentals should occur in range 650 to 1500 cm^{-1} , eight methylene deformation frequencies, four methyl deformations, two carbon-oxygen stretching frequencies and one carbon-carbon stretching frequency. The spectrum of solid I shows just 15 peaks in this region. The spectrum of II shows one less peak, presumably because the deuterio equivalent of the 724 cm^{-1} peak in I falls off scale. The two solids were, therefore,

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(2) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, Chap. 2.

TABLE I
INFRARED SPECTRA OF I AND II

I		II	
Solid	Liquid	Solid	Liquid
3000 med.	2980 str.	3000 wk.	2980 med.
2930 v. str.	2930 v. str.	2935 med.	2920 v. str.
2895 v. str.	2880 v. str.	2900 med.	2890 str.
2850 sh.			
2820 v. str.	2820 v. str.	2920 med.	2800 v. str.
2725 wk.	2720 wk.		2220 v. wk.
		2195 sh.	
		2170 med.	2160 ined.
2110 v. wk.		2070 med.	2050 med.
2030 v. wk.			
1993 v. wk.			1575 wk.
1475 v. str.	1475 sh.		
1458 v. str.	1460 med.	1457 str.	1460 med.
1434 wk.	1452 med.	1434 wk.	1450 med.
1410 str.	1409 wk.		
1376 v. str.	1376 v. str.		
	1289 wk.		
1259 str.	1260 str.		
		1220 med.	1220 med.
1214 v. str.	1213 med.		
	1200 sh.		1200 wk.
1170 med.	1175 med.	1170 v. str.	1168 v. str.
		1137 v. wk.	1142 med.
1135 v. str.	1130 str.		
1110 sh.	1105 v. str.		
		1106 v. str.	1110 v. str.
1090 str.	1080 v. str.		
		1071 v. str.	1076 str.
		1050 med.	1050 med.
1022 v. str.	1025 med.		
		975 v. str.	974 med.
962 wk.	964 wk.		
		960 v. str.	963 v. str.
	930 str.		935 wk.
		920 str.	917 med.
900 v. str.	905 v. str.	902 med.	905 sh.
			888 med.
			857 str.
			845 med.
		735 med.	735 sh.
724 med.	725 med.		
		710 med.	715 med.
	695 wk.		
			680 wk.

^a There is a strong, continuous absorption between the bracketed frequencies.

assumed to be conformationally homogeneous materials. It has been shown that the *trans* isomer of 1,2-disubstituted ethanes is usually the more stable in the solid^{3,4} so it was assumed that the spectra of the solids are the spectra of the *trans-trans* isomers.

The Carbon-Hydrogen Stretching Region.—The two fairly intense peaks at 2170 and 2070 cm^{-1} in II are presumably the asymmetric and symmetric stretching frequencies of the methylene groups. The corresponding frequencies in I are assigned to the strong bands at 2930 and 2820 cm^{-1} . The asymmetric and symmetric stretching frequencies of the methyl group are assigned to the 3000 and 2895 cm^{-1} peaks in I, both of which appear in II, also. (The shift to 2900 cm^{-1} is well within the experimental uncertainty.) These assignments are rather arbitrary, but they are in fairly good agreement with the frequencies usually associated with methylene groups and methyl groups.⁵ The other peaks observed between 2000 and 3000 cm^{-1} in the spectra of solid I and II can all be reasonably explained as overtones or combination tones, for which this region is notorious. The methylene frequencies, along with their isotopic ratios, are shown in Table II.

The Methylene Deformations.—The methylene deformations were assigned by analogy with the corresponding frequencies in 1-chloro-2-bromoethane⁶ and by use of the isotopic shifts. The frequencies are listed in Table II along with the isotopic ratios, $\nu_{\text{H}}/\nu_{\text{D}}$, and the corresponding isotopic ratios in 1,2-dibromoethane.⁷ The numbering system is according to Neu and Gwinn.⁷

In general both the assigned frequencies and the ratios $\nu_{\text{H}}/\nu_{\text{D}}$, are very similar to those in the dihalo compounds. The value of ν_{15} is higher than that usually observed and $\nu_{\text{H}}/\nu_{\text{D}}$ for this frequency is much lower than in dibromoethane. The difference is thought to be due to coupling with the carbon-oxygen stretching frequency, particularly in the case of II. Such coupling would be much less effective in the dibromoethane because of the greater disparity in the frequencies. The large number of frequencies involved and the fact that several frequencies are not available make it unattractive to attempt a product rule check, but the correspondence of the isotopic ratios with those in dibromoethane make it *very* likely that such a check would be satisfactory.

The Methyl Deformations.—Four frequencies between 1500 and 650 cm^{-1} are identical, within experimental uncertainty, in the spectra of solid I and solid II. These are assigned to the deformation frequencies of the methyl group as shown in Table III. The specific assignments were made by analogy.⁸ Table III also shows the stretching frequencies of the methyl group.

- (3) W. Edgell and G. J. Glockler, *J. Chem. Phys.*, **9**, 375 (1941).
 (4) S. Mizushima, Y. Morino and M. Takeda, *ibid.*, **9**, 826 (1941).
 (5) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 14.
 (6) J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **48**, 128 (1952).
 (7) J. T. Neu and W. D. Gwinn, *J. Chem. Phys.*, **18**, 1642 (1950).
 (8) R. N. Jones and C. Sandorfy, in "Chemical Applications of Spectroscopy," A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 342, 350.

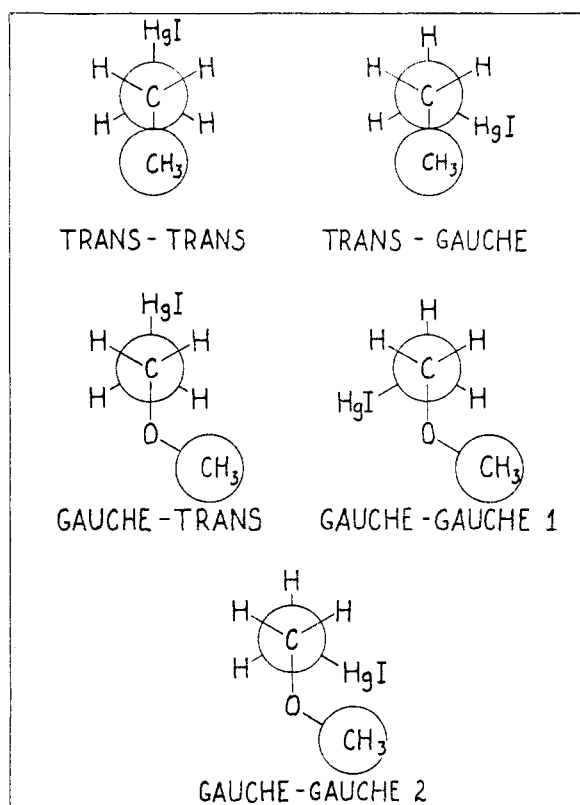


Fig. 1.—The rotational isomers of 2-methoxyethylmercuric iodide.

Other Fundamentals.—Of the 33 fundamentals 20 have now been accounted for. Of the remaining 13, ten are expected to be out of the range of the present spectra. These are the three torsional oscillations, the carbon-mercury stretching frequency, the iodine-mercury stretching frequency, four heavy-atom deformations, and a tenth frequency which is either a deformation or a torsional oscillation, depending on whether or not the carbon-mercury iodine angle is 180° .⁹ The three remaining fundamentals which should be observed are the carbon-carbon stretching frequency and two carbon-oxygen stretching frequencies. These should all be strongly coupled to the methylene deformation frequencies and to each other, and should all occur between 1000 and 1200 cm^{-1} in I.^{7,10} The carbon-oxygen frequencies are usually intense and the carbon-carbon frequency should be more than usually intense in this case because of the two very dissimilar atoms (oxygen and mercury) attached to the two carbon atoms. In the spectrum of solid I there are still three strong, unassigned bands at 1135, 1110 and 1090 cm^{-1} . The corresponding bands in solid II seem to be at 1106, 1050 and 975 cm^{-1} . It does not seem profitable to try to specify the modes corresponding to these frequencies more closely.

Structure of Solid I and II.—With this, all the observed peaks in the spectra of solid I and II have been assigned. Although there may be one or two inversions, the over-all pattern seems quite

- (9) H. Sawatzky and G. F. Wright, *Can. J. Chem.*, **36**, 1555 (1958).
 (10) Reference 5, pp. 108, 116.

TABLE II
 ASSIGNMENT OF METHYLENE FREQUENCIES

Assign- ment	Frequency		ClCH ₂ CH ₂ Br	$\nu_{\text{H}}/\nu_{\text{D}}$	
	I	II		I-II	BrCH ₂ - CH ₂ Br
ν_1 } sym.	2820	2070	2972 ^a	1.36	1.36
	2820	2070	2974 ^a	1.36	1.35
ν_{11} } asym.	2930	2170	3037 ^a	1.35	1.33
	2930	2170	3018 ^a	1.35	1.39
ν_2 } bend	1410	1137	1439	1.24	1.25
	1475	1220	1446	1.21	1.37
ν_8 } wag	1376	1071	1284	1.28	1.26
	1214	960 ^b	1203	1.27	1.32
ν_9 } twist	1022	735	1111	1.39	1.39
	1259	920 ^b	1258 ^c	1.36	1.36 ^c
ν_9 } rock	724	(542) ^d	763	..	1.34
	962	710	961	1.35	1.36

^a These are the corresponding frequencies in dibromoethane—those for the chlorobromo compound do not seem to be available. ^b The assignment of the 960 cm.⁻¹ peak and the 920 cm.⁻¹ peak can be interchanged freely. The present assignment was chosen because of a better correspondence of the intensities. ^c This frequency and the corresponding isotopic ratio are those of Brown and Sheppard,⁶ rather than those of Neu and Gwinn.⁷ ^d This frequency is off scale on our instrument. It was assigned so as to make $\nu_{\text{H}}/\nu_{\text{D}}$ correspond to the same ratio in the dibromo compound.

 TABLE III
 THE METHYL DEFORMATION FREQUENCIES

Assignment	Frequency, cm. ⁻¹		Assignment	Frequency, cm. ⁻¹	
	I	II		I	II
Asym. stretch (2)	3000	3000	Sym. bend	1434	1434
Sym. stretch	2895	2900	Rock	1070	1070
Asym. bend (2)	1458	1457	Rock	900	902

reasonable. This provides very strong support for the hypothesis that solid I and II are conformationally homogeneous. The similarity between the present assignments and those for the *trans*-dihaloethanes supports the hypothesis that the geometry about the carbon-carbon bond, at least, is *trans*.

Liquid I and II.—All the fundamentals observed in solid I and II can also be identified in the spectra of the liquids. The frequency shifts accompanying the change in state are small; most of them less than 5 cm.⁻¹. Although there is some redistribution of intensities, there is no noticeable general reduction. These observations suggest that the bulk of the material retains its solid-state geometry in the liquid. (The film thicknesses are necessarily

identical since the solid films were obtained from the liquid films by allowing them to solidify.)

In addition to those peaks that are also present in the solids, a number of new peaks appear in the liquids. In general they are of rather low intensity. They are shown, along with their relative intensities, in Table IV. Considering the number and intensity of the new peaks, it seems unlikely that more than one new isomer is present. Evidence has been presented that the oxygen atom and the mercury atom on adjacent carbon atoms prefer a *trans* orientation.¹¹ Accordingly the new peaks are probably those of the *gauche-trans* isomer, in which a *trans* relationship is maintained for oxygen and mercury atoms. The present work seems wholly in accord with and therefore strengthens the conclusion that the oxygen atom and the mercury atom prefer a *trans* orientation.¹¹

TABLE IV

PEAKS OF THE *trans-gauche* ISOMER (CM.⁻¹)

I	1289 wk.	1200 sb	930 str.	695 wk.		
II	1200 wk.	935 wk.	888 med.	857 str.	845 med.	680 wk.

Experimental

The preparation and properties of I have been previously described.¹² The deuterio analog was prepared in essentially the same way from tetradeuterioethylene. The latter was generated by heating 2 g. (0.01 mole) of perdeuterio-1,2-dibromoethane (New England Nuclear Corp., 99% isotopic purity) in 1-butanol with an excess of zinc dust at 50–75°.¹³ The resulting gas passed into an evacuated gas reservoir. From there it was passed into an evacuated 100-ml. flask containing 3.0 g. (0.0094 mole) of mercuric acetate and 90 ml. of methanol. The reaction flask was cooled first with Dry Ice-acetone and then with liquid nitrogen as the gas was passed in, and stirred magnetically as long as it was liquid. The progress of the gas absorption was followed manometrically. After the gas was absorbed, the reaction flask was cut off from the rest of the system by a stopcock and allowed to warm up to room temperature, stirring being resumed as soon as the reaction mixture melted. The reaction was assumed to be complete when room temperature was reached. The product was worked up as before.¹² Yields of 1.5 g. of product were obtained; m.p. 42–43°.

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(11) M. M. Kreevoy, N. Takashina and L. L. Schlaeger, Abstracts of the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 5–14, 1960, p. 79-O.

(12) M. M. Kreevoy and L. T. Ditsch, *J. Org. Chem.*, **25**, 134 (1960).

(13) Gladstone and Tribe, *Ber.*, **7**, 364 (1874).