136. *Spectroscopic Studies. Part II.*[1] *The Infrared Spectra and Structure of Methoxyacetonitrile and Chloromethyl Methyl Ether.*

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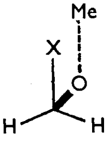
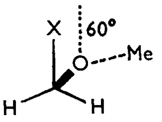
The infrared spectra of methoxyacetonitrile and chloromethyl methyl ether have been studied for solutions and the vapour and the liquid state. The band contours prove that the molecules in the vapour state are most stable when they have a slightly twisted *trans*-conformation.

METHOXYACETONITRILE, $MeO{\cdot}CH_2{\cdot}CN$, and chloromethyl methyl ether, $MeO{\cdot}CH_2Cl$, differ only in that the nitrile group of one is replaced by a chlorine atom in the other. Since the nitrile group and the chlorine atom have approximately the same electronegativity and mass it is reasonable to expect that the vibrational frequencies of the $MeO{\cdot}CH_2$ group will change little from one to the other compound.



(I)



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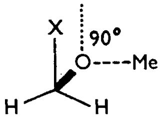

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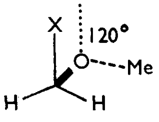

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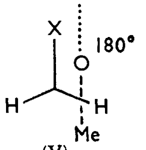

(V)

In both molecules rotation about the $MeO-CH_2X$ bond is possible (see I—V). In their most stable states the molecules will have particular conformations corresponding to definite values for the moments of inertia. A study of the band contours, obtained from vapour-phase spectra, then, should give a reliable indication as to the most stable conformation.

Chloromethyl methyl ether and the corresponding sulphide have been studied by Hayashi.[2] The Raman spectra of both our compounds have been recorded.[2,3]

Experimental.—Methoxyacetonitrile was prepared by addition of an excess of dimethyl sulphate to the product of reaction between potassium cyanide and aqueous formaldehyde

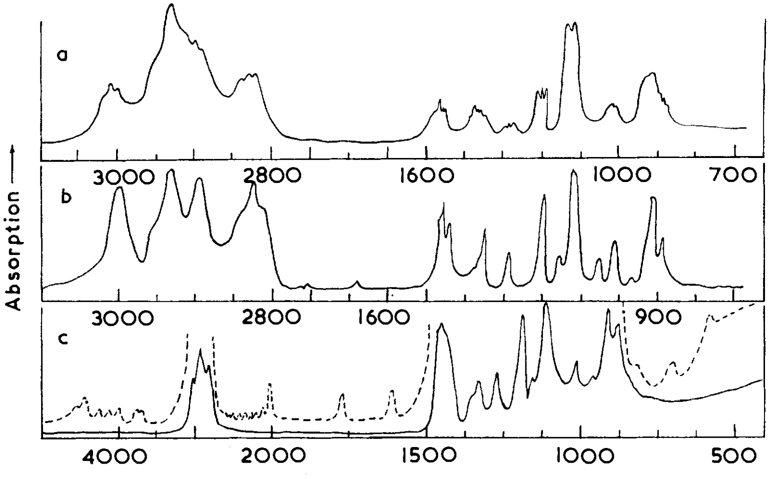

FIG. 1. Infrared spectra of $MeO{\cdot}CH_2{\cdot}CN$: (a) vapour (~100 mm.; 120°); (b) ~0·1M-solution; (c) liquid.

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[1] Part I, Yarwood and Orville-Thomas, *J.*, 1963, 5991.

[2] Hayashi, *Nippon Kagaku Zasshi*, 1959, **80**, 1079.

[3] Kohlrausch and Ypsilanti, *Z. phys. Chem.*, 1935, *B*, **29**, 290.

at <10°. The product was extracted with ether, dried, recovered, and distilled at 1 atm. (b. p. 121°; lit.,[4] 119°/736 mm.).

Chloromethyl methyl ether, prepared by reaction between methanol, aqueous formaldehyde, and hydrogen chloride,[5] had b. p. 58·5° (lit., 55—60°).

The spectra were recorded on a Grubb-Parsons G.S. 2A double-beam infrared spectrometer calibrated with ammonia.

A Pyrex-glass vapour cell which allowed a temperature variation over the range 20—200° was used for the vapour spectra. Matched metal cells (4·72 and 9·78 mm. in length) were used for solution spectra (chloroform, carbon tetrachloride, and carbon disulphide). The spectra of capillary and 0·1 mm. liquid films were also obtained.

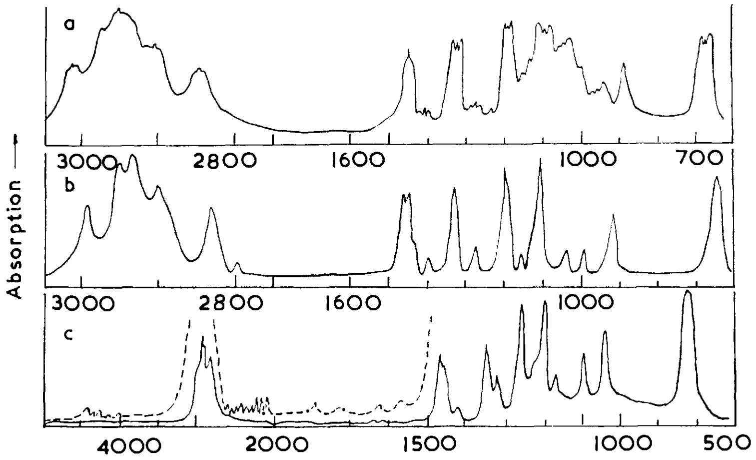

FIG. 2. Infrared spectra of $MeO\cdot CH_2Cl$: (a) vapour (~100 mm.; 60°); (b) ~0·1M-solution; (c) liquid.

The spectra are reproduced in Figs. 1 and 2 and the frequencies given in Tables 1 and 2.

TABLE 1.

Infrared spectrum of methoxyacetonitrile.

Liquid			Solutions			
Raman	Capillary	0·75 mm.	CCl_4 (0·5 cm.)	CS_2 (0·5 cm.)	Vapour	Assignment
		4447				3008 + 1450 = 4458
		4404				2946 + 1460 = 4406
		4356				3008 + 1370 = 4378
		4269				3008 + 1287 = 4295
		4201				3008 + 1196 = 4204
		4064				2916 + 1158 = 4074
		3949				2837 + 1115 = 3952
		3640				2256 + 1380 = 3636
		3568				2257 + 1289 = 3546
		3132				2257 + 886 = 3143
					3018	CH_2 Antisym. stretch
3009	3008		3007	3002	3010	
					3000	
2980				2963		CH_2 Sym. stretch
	2946		2940		2950	
2933			2936	2932	2931	CH_3 Antisym. stretch
					2908	CH_3 Antisym. stretch
2914	2916		2902	2893	2897	
					2889	
2872						
			2849	2843	2831	CH_3 Sym. stretch
2832	2837		2832	2824	2822	

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[4] Polstorff and Meyer, *Ber.*, 1912, **45**, 1905.
[5] Marvel and Porter, *Org. Synth.*, 1941, **1**, 377.

TABLE 1. (*Continued.*)

Liquid			Solutions			
Raman	Capillary	0·75 mm.	CCl_4 (0·5 cm.)	CS_2 (0·5 cm.)	Vapour	Assignment
		2656				1289 + 1370 = 2659
	2627	2629				1460 + 1158 = 2618
		2603		2595		1460 + 1158 = 2618
	2463	2464				1289 + 1196 = 2485
	2442	2444				1289 + 1158 = 2447
	2389	2390				2 × 1196 = 2392
	2302	2301				2 × 1158 = 2316
2243	2256				2251	CN Stretch
	2207	2206				2 × 1115 = 2230
	2105	2105			2136	1115 + 1014 = 2129
	2064	2061		2078	2060	886 + 1196 = 2082
	2023	2021		2025		886 + 1158 = 2044
	1757	1758	1758	1760		2 × 886 = 1772
	1631	1631				1290 + 360 = 1650
					1474	CH_2 Bend
	1466				1467	CH_3 Antisym. bend
	1458		1461		1460	
1455			1455		1456	
1435	1439		1437		1441	CH_3 Antisym. bend
	1380		1378		1376	
	1374				1370	CH_3 Sym. bend
1363			1367		1364	
	1359		1354		1359	CH_2 Wag
				1351	1349	
					1294	
1285	1289		1284	1282	1288	CH_2 Twist
					1279	
	1242					1014 + (240) = 1254
					1207	
1185	1196		1188	1192	1200	CH_3 Rock
					1193	
	1158		1158	1156	1161	CH_3 Rock
1112	1115		1117	1117	1136	COC Asym. stretch
					1128	
					1023	
	1014			1012	1017	CH_2 Rock
					1009	
	990					1360 − 360 = 1000
	961			965		2256 − 1289 = 967
955						
					937	
914	915		919	917	922	COC Sym. stretch
					924	
					899	
882	886		885		890	C–C Stretch
					882	
	844	838				2 × 420 = 840
	704	709		694		2 × 350 = 700
	586	586				350 + 240 = 590
404	(425)					COC Bend
352	(360)					CCO Bend
242	(230)					CCN Bend

TABLE 2.

Infrared spectrum of chloromethyl methyl ether.

Liquid			Solution			
Raman	Capillary	0·1 mm.	CCl_4	CS_2	Vapour	Assignment
		4459				2295 + 1470 = 4465
		4413				2958 + 1470 = 4428
		4284				2903 + 1397 = 4300
		4207				2903 + 1320 = 4223
		4091				2837 + 1278 = 4115
		4028				2837 + 1193 = 4030
		3961				2837 + 1120 = 3957
3027	2995		2994	3030	3013	CH_2 Antisym. stretch
2980	2958		2948	2940	2980	CH_2 Sym. stretch

TABLE 2. (*Continued.*)

Liquid			Solution			
Raman	Capillary	0·1 mm.	CCl_4	CS_2	Vapour	Assignment
2950	2943		2932	2926	2946	CH_3 Antisym. stretch
2912	2903		2897	2862	2901	CH_3 Antisym. stretch
2837	2837		2830	2824	2844	CH_3 Antisym. stretch
	2778		2770	2805		1460 + 1320 = 2780
		2632				2 × 1320 = 2640
		2606				1460 + 1156 = 2616
2464		2464				1470 + 996 = 2466
		2438				1320 + 1120 = 2440
		2389				2 × 1193 = 2386
		2311				1397 + 920 = 2317
		2238				1320 + 920 = 2240
		2193				1278 + 920 = 2198
	2108	2113				1193 + 920 = 2113
	2032	2036				920 + 1120 = 2040
		1845				2 × 920 = 1840
		1776				2903 − 1120 = 1783
		1650				1320 + 350 = 1650
		1576				2995 − 1397 = 1598
1470	1470				1476	CH_2 Bend
	1467				1470	
1460			1461		1458	CH_3 Antisym. bend
	1453				1451	CH_3 Antisym. bend
1435	1440		1446		1440	
1398	1397		1396		1408	
					1400	CH_3 Sym. bend
					1392	
					1331	
1321	1320		1317	1315	1324	CH_2 Wag
					1317	
					1286	
1279	1278			1273	1278	CH_2 Twist
					1270	
1231					1236	1397 − 160 = 1237
					1206	
					1198	CH_3 Rock
					1190	
	1156		1156	1153	1156	
1147					1148	CH_3 Rock
				1138	1138	
					1138	
1128			1131	1129	1128	COC Asym. stretch
	1120				1121	
					1092	1450 − 350 = 1100
					1064	1397 − 350 = 1047
	1042		1043	1043	1054	
					1008	
998	996			990	1000	CH_2 Rock
					993	
					943	
920	920		925	917	937	COC Sym. stretch
					932	
		805				350 + 466 = 816
					686	
					679	
651	646			640	677	C–Cl Stretch
					670	
455	466					COC Bend
357	(350)					OCCl Bend
177	(160)					Me–O Torsion
107						MeO–CH_2Cl Torsion

The Stable Conformations.—The type of contour obtained for vibrational bands (*i.e.*, the *PQR* structure) and the *P–R* sub-band separation depend critically on the moments of inertia of the molecule. These, in turn, depend on the conformation (see I—V). As one part of the molecule rotates with respect to the other the absolute and the relative magnitudes of the three principal moments of inertia change; consequently the band contours and separations change.

Molecular dimensions have not been determined for methoxyacetonitrile or for chloromethyl methyl ether. Hence, from a study of similar molecules the parameters given in Table 3 were chosen. With these values moments of inertia were calculated for each of the conformations illustrated (see Table 4).

TABLE 3.

Dimensions of $MeO\cdot CH_2X$.

	C–O	∠COC	∠OCX	C–C(I)	C–N(I)	C–Cl(II)
$MeO\cdot CH_2\cdot CN$	1·42	110°	111°	1·47	1·16	—
$MeO\cdot CH_2Cl$	1·42	110	112°	—	—	1·74

TABLE 4.

Calculated moments of inertia, rotational constants, and *P–R* separations.

	I_A	A	I_B	B	I_C	C	$\Delta\nu$(P–R) (cm.$^{-1}$)
$MeO\cdot CH_2\cdot CN$							
I	53	0·53	166	0·17	219	0·13	21·1
II	41	0·68	224	0·13	270	0·10	17·9
III	28	0·99	157	0·18	175	0·16	21·5
IV	38	0·75	266	0·11	343	0·08	16·1
V	17	1·65	321	0·09	338	0·08	13·9
$MeO\cdot CH_2Cl$							
I	63	0·45	161	0·17	224	0·13	20·4
II	51	0·55	205	0·14	244	0·12	18·0
III	23	1·20	147	0·19	161	0·18	20·9
IV	59	0·47	242	0·12	329	0·09	15·5
V	14	2·02	304	0·09	318	0·09	13·5

The moments of inertia indicate that the molecules approximate to symmetric rotors, especially for conformations near to (V). By means of the theory developed by Gerhard and Dennison[6] the P–R separations have been calculated, for parallel-type bands, from the expression,

$$\Delta\nu(P,R) = \frac{S}{\pi}\left(\frac{kT}{I}\right)^{\frac{1}{2}}$$

where $S = 0{\cdot}721/(\beta + 4)^{1.13}$, $\beta = (I - I_A)/I_A$,

and $I = (I_B + I_C)/2$.

The values obtained are given in Table 4, and expressed diagrammatically in Fig. 3. The *P–R* separations found experimentally for parallel-type bands (or type *A* bands, as described by Badger and Zumwalt[7]) are given in Table 5.

TABLE 5.

Observed *P–R* separations of parallel-type bands.

$MeO\cdot CH_2\cdot CN$				$MeO\cdot CH_2Cl$			
1349 1359 1364	15 ± 1	1123 1128 1136	13 ± 1	1408 1400 1392	16 ± 1	1156 1148 1138	18 ± 1
1279 1288 1294	15 ± 1	1009 1017 1023	14 ± 1	1331 1324 1317	14 ± 1	1121 1128 1138	17 ± 1
1193 1200 1207	14 ± 1	924 932 937	13 ± 1	1286 1278 1270	16 ± 1	686 679 677 670	16 ± 1

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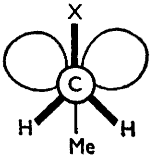
[6] Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

[7] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

From a comparison of the observed and calculated *P–R* separations it is evident that, in both cases, the stable conformations are very close to model (V). That is, the " heavy "-atom skeleton is almost planar-*trans* in form. This conclusion differs from that of Hayashi[2] who favours a *gauche* conformation (II) for chloromethyl methyl ether in the vapour state.

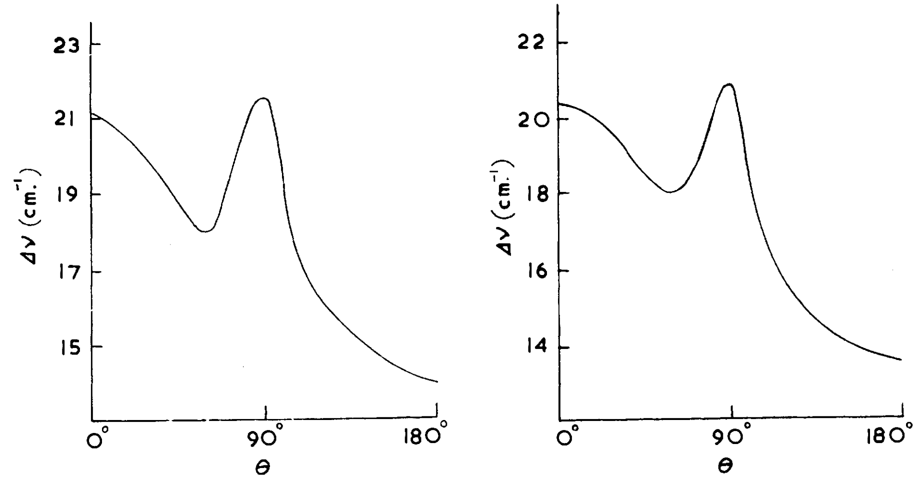


If the oxygen lone-pairs forming atomic dipoles are taken into account the terminal groups are seen to be staggered about the C–O bond. In terms of bond–bond and bond–lone-pair repulsions this represents a most reasonable model.

Vibrational Assignment.—All the fundamental modes of vibration are infrared-active. The vibrations can be conveniently divided for discussion into (i) the methyl and methylene vibrations and (ii) those associated with the COCX skeleton.

(i) CH *Vibrations.* Tables 1 and 2 contain the assignments for these molecules made on the basis of vapour-phase band contours and comparisons with related molecules. The ranges within which the various types of methyl vibrations occur are well-known and there is little uncertainty in the assignments made.

Assignment of frequencies to the methylene bond-stretching modes is straightforward, but this is not so with the various deformation modes since they tend to vary over large spectral regions. For example the CH_2 rocking band occurring at 1176 cm.$^{-1}$ in methylene difluoride is at 714 cm.$^{-1}$ for methylene di-iodide, a decrease of some 39%. In a recent study[8] relations have been found between the methylene deformation frequencies in CH_2XY molecules and the electronegativity product $\chi(X)\chi(Y)$. These correlations have been used to predict group electronegativities of 3·76 (MeO) and 3·20 (CN) corresponding to values centred near 1470, 1340, 1250, and 1000 cm.$^{-1}$, respectively, for the bending, wagging, twisting, and rocking CH_2 vibrations. The observed values are in good accord with these predictions.



(A) (B)

FIG. 3. *P–R* Separations: (A) $MeO{\cdot}CH_2{\cdot}CN$; (B) $MeO{\cdot}CH_2Cl$.

(ii) *Skeletal vibrations.* Three bands are expected to arise from the skeletal stretching vibrations in chloromethyl methyl ether. Two of these are best regarded as an asymmetric and a symmetric stretching mode of the COC grouping, ν_a(COC) and ν_s(COC) whilst the third, ν(CCl), is primarily localised within the CCl band. In methoxyacetonitrile there are four stretching modes, ν_a(COC), ν_s(COC), and two others which can be approximately described as ν(CC) and ν(CN).

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[8] Jones and Orville-Thomas, *Spectrochim. Acta*, **1963**, in the press.

The ν(CN) fundamental occurs near 2250 cm.$^{-1}$, in all phases, with the very low intensity characteristic of β-oxygenated nitriles.

Assignment of the vibrations of the COCX chain in these molecules was facilitated by direct comparison of the vapour spectra. Three absorption bands, of strong to medium intensity, were found in the region 1150—800 cm.$^{-1}$ of the spectrum of methoxyacetonitrile. The strong absorption with an almost pure *B*-type contour, at 1132 cm.$^{-1}$, is assigned to the ν_a(COC) stretching vibration. The frequency of the carbon–oxygen stretching vibration for gaseous methanol is 1030 cm.$^{-1}$. If it is assumed that coupling between the stretching modes of vibration of the COC chain results in splitting of degenerate energy levels to give energy-level pairs equally spaced on either side of the unperturbed ν(CO) vibrational level, it can be predicted that the frequency of the symmetric stretching vibration of the COC chain will be near $1030 - (1130 - 1030) = 930$ cm.$^{-1}$. Two absorption bands, with hybrid contours, at 932 and 890 cm.$^{-1}$, were observed in the vapour spectrum of methoxyacetonitrile. The higher-frequency band is therefore assigned to ν_s(COC) and the other to ν(CC). This assignment is supported by the fact that replacement of the nitrile group by chlorine results in the disappearance of the 890 cm.$^{-1}$ band, but does not significantly perturb the spectrum above 900 cm.$^{-1}$. This is to be expected because the chlorine atom does not differ much in mass or electronegativity from the nitrile group.

It has been shown that for molecules exhibiting rotational isomerism certain group frequencies are characteristic of particular isomeric conformations. For example, for *trans*-monochlorinated hydrocarbons ν(CCl) varies from 726 (n-propyl) to 616 cm.$^{-1}$ (t-pentyl), and the *gauche*-frequencies range between 645 and 560 cm.$^{-1}$ for the same series.[9] In the spectra of chloromethyl methyl ether only one ν(CCl) band, centred at 646 cm.$^{-1}$, was detected. The band contours indicate clearly that this band should be assigned to ν(CCl) in the *trans*-conformation. The absence of a second ν(CCl) band indicates that the *gauche*-isomer is present to a very small extent, if at all.

The bond-bending fundamentals of the skeleton lie below the range studied. The vibrations can be approximately described for MeO·CH$_2$Cl as COC bending [*b*(COC), *b*(OCCl), both in the plane of the skeleton framework], and an out-of-plane vibration which could be described as *b*(OC) or *b*(CCl): for MeO·CH$_2$·CN one has *b*(COC), *b*(OCC), *b*(CCN) (all in-plane) and either *b*(OC) or *b*(CN) (out-of-plane).

The corresponding frequencies are expected to be below 500 cm.$^{-1}$.

Three weak bands, at 838, 709, and 586 cm.$^{-1}$, were observed in the spectrum of liquid methoxyacetonitrile. These can be assigned as overtone or combination bands in a number of ways. The interpretation of other combination bands observed in the higher-frequency region is made more plausible if these frequencies are assigned as follows:

$$b(\text{COC}) \approx b(\text{OCC}) = 425\ \text{cm.}^{-1};\quad b(\text{CNN}),\ \text{in-plane} = 360\ \text{cm.}^{-1};$$
$$b(\text{CCN}),\ \text{out-of-plane} = 230\ \text{cm.}^{-1}.$$

The torsional modes of methyl groups about a C–O bond have been assigned tentatively[10] to bands at 160 and 230 cm.$^{-1}$. The torsional mode around a MeO–CH$_2$X bond would be expected to have an even lower frequency.

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[9] Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 1164.

[10] Herzberg, " Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1945.