

The Vibrational Spectra and Structure of Dimethyl Carbonate and its Conformational Behavior¹

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The infrared spectra of dimethyl carbonate in the liquid and solid phases and the Raman spectrum of the liquid phase are reported. The evidence suggests that dimethyl carbonate exists as an equilibrium mixture of at least two conformers in the liquid state. An experimental value for the enthalpy difference of the two conformers of 2.6 ± 0.5 kcal/mol is obtained from the temperature dependency of the infrared spectrum.

Dimethyl carbonate crystallizes as an oriented polycrystalline film and polarized infrared spectra of the solid have been obtained. These have been utilized, along with the liquid phase data to obtain an improved vibrational assignment. There appears to be a solid-solid phase change in dimethyl carbonate in the vicinity of 140 K, but the details of this change are not known.

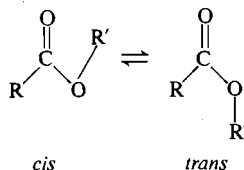
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On rapporte le spectre infrarouge du carbonate de diméthyle dans les phases liquide et solide et le spectre Raman de la phase liquide. Les données suggèrent que le carbonate de diméthyle existe sous forme d'un mélange à l'équilibre d'au moins deux conformères dans l'état liquide. On obtient une valeur expérimentale pour la différence d'enthalpie entre les deux conformères de 2.6 ± 0.5 kcal/mol à partir de la dépendance sur la température des spectres infrarouges.

Le carbonate de diméthyle cristallise sous forme de film polycristallin orienté et on a pu obtenir les spectres infrarouges polarisés du solide. On a utilisé ceux-ci de même que les données en phase liquide pour obtenir des attributions vibrationnelles améliorées. Il semble qu'il y a un changement de phase solide-solide dans le carbonate de diméthyle à proximité de 140 K, mais on ne connaît pas les détails de ce changement. [Traduit par le journal]

Introduction

Ever since the concept of hindered internal rotation about single bonds was established, it has been expected that esters of simple carboxylic acids might exist in a conformational equilibrium in their fluid states. Such an equilibrium is expected, on theoretical grounds, to involve the two planar conformations shown below.



The nomenclature used here is probably the most common, although many other investigators use the reverse notation of *cis* and *trans*.

Very many investigators have sought experimental evidence for the existence of such an equilibrium, but conclusive results have been

very difficult to obtain. Jones and Owen (1) have recently written a very comprehensive review of this previous work. The conclusion which must be drawn from this previous work is that there has not appeared in the literature any report of the experimental confirmation of the existence of *trans* conformers of esters except "when ring-formation dominates the molecular structure (lactones) and possibly when the alkyl group R' becomes too large to be accommodated in the space allowed by the *cis* structure" (1). The latter case has been discussed in more detail by Oki and Nakanishi (2, 3) and George *et al.* (4). Both of these groups have observed the presence of a conformational equilibrium in *t*-butyl formate (but not in *t*-butyl acetate). Their results indicate that the *cis* structure is the more stable, but whereas Oki and Nakanishi reported the enthalpy difference between conformers to be 2.2 ± 0.7 kcal/mol by n.m.r. methods, George *et al.* found the value to be 150 ± 20 cal/mol by infrared methods. In addition, Oki and Nakanishi (3) have reported that methyl *t*-butyl carbonate exists as a conformational

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equilibrium in which the most stable conformer is the one in which the methyl group has the *cis* conformation while the *t*-butyl group possesses the *trans* conformation. Their data are not very conclusive, however.

It would appear that the ideal simple compound for investigation of such a conformational equilibrium is dimethyl carbonate. In the case of dimethyl carbonate the only possible conformers are those which differ by internal rotation about the C—O bonds. In addition, there is a statistical weight factor of two in dimethyl carbonate which is not possessed by other simple esters such as methyl formate or methyl acetate. This leads to higher populations of the *cis-trans* conformer, thereby making it easier to detect experimentally (the nomenclature used here arises from the possibility of two ester groups orienting in either the *cis* or *trans* conformation). As Jones and Owen (1) point out, the barrier to rotation in dimethyl carbonate should be lower than that in other esters due to greater electron delocalization. This has no direct bearing on the equilibrium, but does have implications with regard to the experimental approach.

The temperature dependence of the dipole moment of dimethyl carbonate has been reported by Mizushima and Kubo (5) and the results interpreted in terms of one conformer only, the *cis-cis*. Collingwood *et al.* (6) have studied the vibrational spectra of the compound and report that they found no evidence for the existence of a second conformer. They conclude that the structure is the *cis-cis* conformer on the basis of the contours of the vapor phase infrared spectrum and the small number of polarized Raman bands in the liquid phase. The latter is evidence for a C_{2v} structure and the *trans-trans* form is too sterically hindered to be considered seriously.

We have previously given a preliminary report (7, 8) of the results of a thorough study of the vibrational spectra of dimethyl carbonate and the evidence that it exists in a conformational equilibrium mixture in the liquid phase. We report the details and complete results herewith.

Experimental

Dimethyl carbonate was purchased from Aldrich Chemical Company, Incorporated, and fractionally distilled. The constant boiling fraction (90 °C/760 mm Hg) was used for spectral studies. Although the infrared spec-

trum of the redistilled material was identical to the original, it was found that the solid-solid phase change discussed later could only be readily observed with the redistilled material.

Infrared spectra in the 4000–250 cm^{-1} region were recorded on a Perkin-Elmer Model 180 infrared spectrophotometer and those in the 300–50 cm^{-1} region on a Digilab, Inc., Model FTS-14, Fourier Transform spectrometer. Raman spectra were recorded on a Cary Model 81 Raman spectrometer using an argon ion laser source.

Low temperature infrared spectra were obtained utilizing a conventionally designed low temperature infrared cell mounted in an evacuable chamber fitted with windows for the passage of the infrared beam. The cell was cooled by a stream of nitrogen gas which had been previously cooled by passing through a copper coil immersed in liquid nitrogen and whose flow rate could be controlled by a needle valve. The temperature was monitored by a thermocouple in contact with one of the cell windows. Nominal temperatures as low as 120 K could be reached by controlling the flow of nitrogen gas.

Polarized infrared spectra were obtained utilizing the standard Model 180 polarizer accessory consisting of a gold wire grid mounted on a silver bromide substrate. Oriented polycrystals were obtained by simply cooling the sample below the freezing point, usually fairly rapidly (about 10°/min). No annealing was necessary.

The liquid phase infrared and Raman spectra of dimethyl carbonate are reproduced in Figs. 1 and 2. Typical polarized infrared spectra of crystalline dimethyl carbonate at nominal temperatures of 253 K have been previously published (8) and those at 120 K are reproduced in Figs. 3 and 4. The observed infrared and Raman bands of the liquid and high temperature solid phase are given in Table 1. The frequency accuracy is expected to be $\pm 4 \text{ cm}^{-1}$ in the Raman spectrum and $\pm 2 \text{ cm}^{-1}$ in the infrared spectra, at the worst.

Results

Conformational Behavior

If one studies the liquid phase Raman spectrum of dimethyl carbonate carefully, one is led to the conclusion that it is a rather unusual spectrum for a single compound in a single conformation. Overtones and combination bands are nearly always absent in the Raman spectrum unless they are intensified by Fermi resonance. As a result, one usually sees a few less Raman lines than the number of fundamental modes of vibration predicted for the molecule in question. This is generally true due to the fact that a few fundamental modes are usually weak or so closely spaced that they are unresolvable. Whatever the structure of dimethyl carbonate, it should have 30 fundamental modes of vibration active in the Raman spectrum. Although there are 28 distinct Raman bands, it is clear that not all of the fundamental modes are being resolved. In the CH stretching region there are six ob-

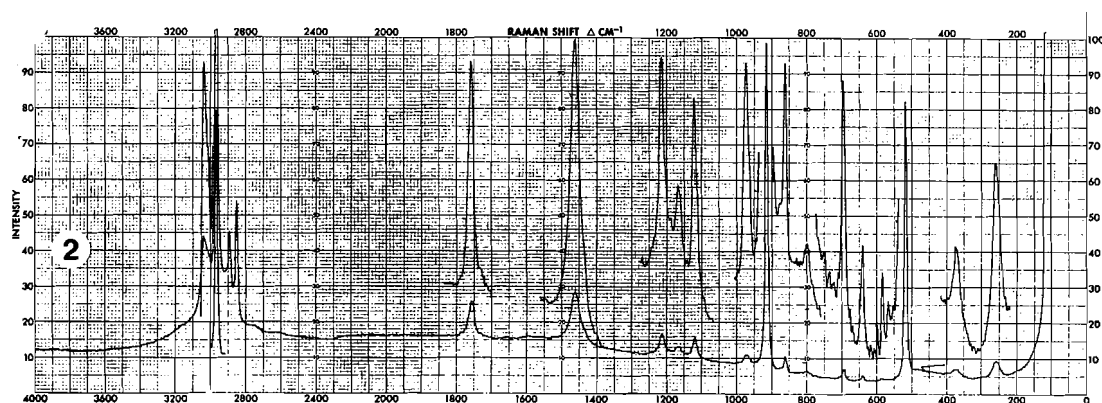
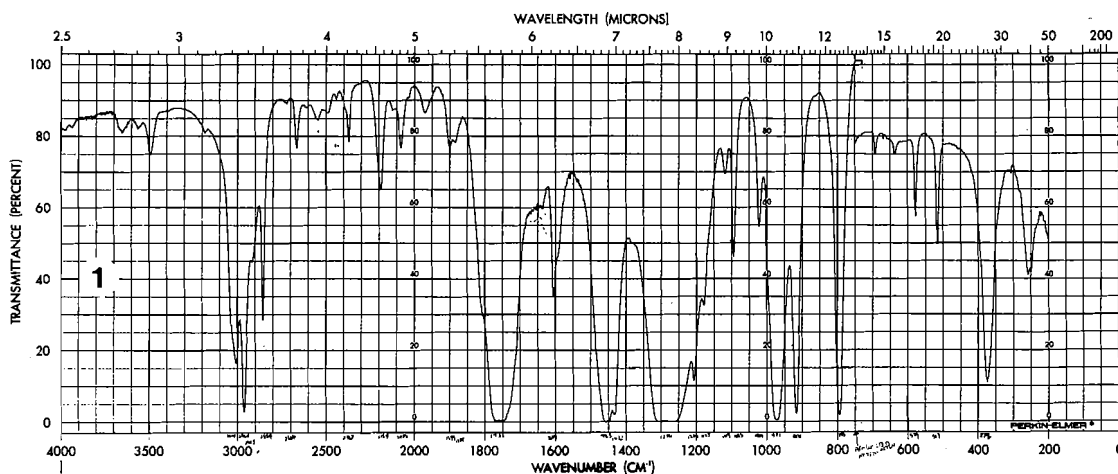


FIG. 1. The infrared spectrum of dimethyl carbonate (liquid, nominal path length 0.05 mm).

FIG. 2. The Raman spectrum of liquid dimethyl carbonate.

served bands, but three are obviously too low in frequency for fundamental modes of methyl esters. Two can be readily assigned as overtones of two CH_3 bending modes in Fermi resonance with the fundamentals. These are very typical features in the spectra of many compounds containing methyl groups. The third is a weak shoulder which can be assigned as a combination band. We are therefore failing to resolve three fundamentals in this region. A similar behavior occurs in the $1400\text{--}1500\text{ cm}^{-1}$ region where one expects six CH_3 bending modes. Only two Raman bands can be observed here, however, and they are not well-resolved. It is then clear that the Raman spectrum has more bands than are expected for a single compound in a single conformation. This immediately leads one to suspect a conformational equilibrium. Com-

parison with the liquid phase infrared spectrum indicates that nearly all of the Raman bands have infrared counterparts (although this is formally not expected for a C_{2v} molecule, it is quite reasonable in view of the nature of the A_2 modes and is discussed later). Several of the observed bands disappear, however, when the sample is cooled and the infrared spectrum of the crystal recorded. This is still further evidence for the existence of a conformational equilibrium in the liquid phase. All of these bands that disappear on cooling are quite weak in either the infrared or Raman spectrum, however, and this is probably the reason that Collingwood *et al.* failed to recognize the existence of a second conformer. This behavior is illustrated by the bands at 1095 , 863 , 640 , and 583 cm^{-1} . The first and last are very weak in the Raman but relatively

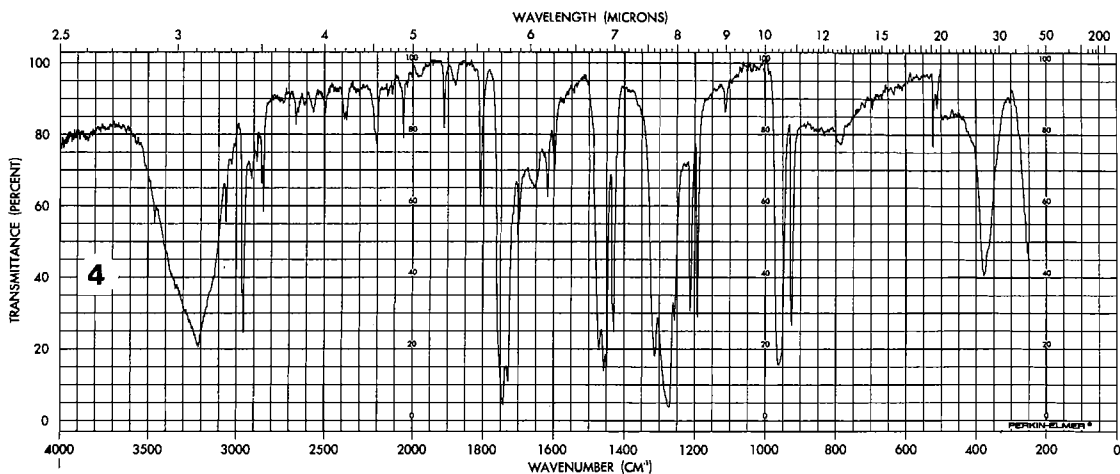
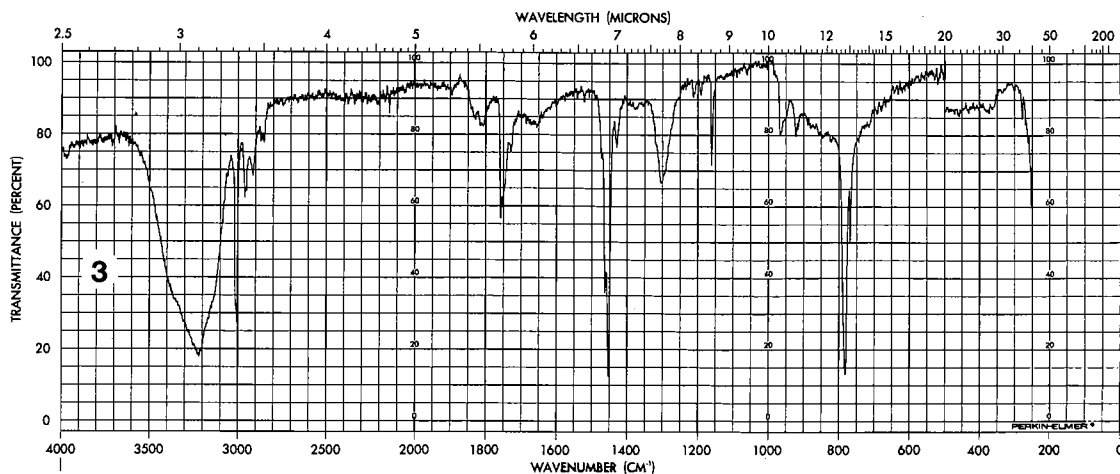


FIG. 3. The polarized infrared spectrum of dimethyl carbonate at 120 K (reference polarizer setting at 0°). The broad band centered at about 3200 cm^{-1} is due to a small amount of ice on the windows.

FIG. 4. The polarized infrared spectrum of dimethyl carbonate at 120 K (reference polarizer setting at 90°). The broad band centered at about 3200 cm^{-1} is due to a small amount of ice on the windows.

strong in the infrared while the second and third show the reverse behavior. A fifth band at 2189 cm^{-1} in the infrared spectrum of the liquid disappears on crystallization. This band can be readily assigned as the overtone of the 1095 cm^{-1} band, of course. There are other minor features in the spectra that behave similarly.

As a final test of a conformational equilibrium, the temperature dependence of the relative infrared absorbances of two bands, one of which disappears in the crystal spectrum, were measured. Since relatively long path lengths were required for these measurements, the 1095 cm^{-1} band overlapped the 1120 cm^{-1} band rather

strongly. Therefore the $580/518\text{ cm}^{-1}$ pair were chosen for the measurements since they were relatively well isolated. Their weakness leads to relatively large absorbance errors, however. The relative absorbances of the $580/518\text{ cm}^{-1}$ bands as a function of temperature over the range $13\text{--}47^\circ\text{C}$ were measured. The graph of the logarithm of these ratios versus the reciprocal of the absolute temperature has a good deal of scatter due to inherent lack of accuracy, but it generally shows the trend expected for bands due to different conformers (8). The line was obtained by least squares analysis and treatment of the data in the standard way (9) yields

TABLE 1. The observed vibrational bands of dimethyl carbonate (in cm^{-1})^a

Raman (liquid)	Infrared (liquid)	Polarized infrared ^b		Assignment
		θ	$\theta + 90^\circ$	
	3978 vw			$\nu_{22} + \nu_{11} = 3980$
	3938 vw			$\nu_8 + \nu_1 = 3944$
	3661 w			$\nu_3 + \nu_6 + \nu_{23} = 3661$
	3565 vw			$\nu_3 + \nu_4 + \nu_{24} = 3568$
	3505 mw			$2\nu_3 = 3520$
			3478 vw	$\nu_9 + \nu_{17} = 3479$
3036 mP	3193 vw			$\nu_3 + \nu_4 = 3196$
	3028 sh		3038 sh	ν_1, ν_{16}
3016 sh	3007 ms	3016* m		ν_{25}
		3009* m	3005 w	ν_{11}
		2973 w		$\nu_6 + \nu_3 = 2969$
2964 vsP	2961 s	2961 w	2964* m	ν_2
2915 sh	2914 vw	2908 vvw	2960* m	ν_{17}
2891 sP			2908 vw	$\nu_4 + \nu_{18} = 2916$
2850 sP	2857 m	2861 vw	2855 w	$2\nu_5$ F.R. ν_2
	2665 mw		2662 vw	$2\nu_4$ F.R. ν_2
	2614 vw		2624 vw	$\nu_5 + \nu_6 = 2667$
				$\nu_5 + \nu_{27} = 2621$
				$\nu_4 + \nu_{13} = 2617$
	2549 w		2550 vvw	$2\nu_{20} = 2558$
	2491 vw			$\nu_{20} + \nu_6 = 2488$
	2441 vw			$\nu_5 + \nu_{22} = 2431$
	2398 sh			$\nu_7 + \nu_{20} = 2399$
	2369 mw	2362 w	2365 w	$\nu_6 + \nu_{27} = 2372$
		2335 w	2340 w	$\nu_6 + \nu_7 = 2329$
			2223 sh	$\nu_4 + \nu_{28} = 2233$
			2205 w	$\nu_8 + \nu_{20} = 2195$
	2189 m			Conformer ($2 \times 1095 = 2190$)
	2121 vw			$\nu_4 + \nu_{29} = 2122$
	2077 mw			$\nu_8 + \nu_{27} = 2079$
	2037 vw	2037 vvw	2037 vw	$\nu_8 + \nu_7 = 2036$
	1971 w		1970 vvw	$\nu_5 + \nu_9 = 1976$
	1904 mw		1906 w	$\nu_6 + \nu_{23} = 1901$
	1885 mw	1895 vw		$\nu_8 + \nu_{22} = 1889$
	1847 sh	1835 w	1843 vvw	$2\nu_{28} + \nu_{10} = 1851$
	1810 sh	1812 w	1808 w	$\nu_4 + \nu_{24} = 1808$
		1780 m	1781 m	ν_3 (crystal components)
		1769 m	1766 sh	
1758 mP	1760 vs	1755 sh	1751 s	
		1731 vw	1729 mw	
	1706 sh	1705 vw	1705 w	$\nu_{10} + \nu_{26} = 1710$
		1653 vvw	1653 w	$\nu_{22} + \nu_{23} = 1659$
	1637 vw		1635 w	$\nu_7 + \nu_9 = 1638$
	1606 m	1604 vw	1609 w	$\nu_8 + \nu_{23} = 1608$
1595 vvw	1596 sh			Conformer?
		1558 vw	1558 w	$\nu_{13} + \nu_{24} = 1564$
		1540 vvw	1540 w	$\nu_{10} + \nu_{20} = 1549$
	1508 sh	1504 vvw	1506 vw	$\nu_7 + \nu_{24} = 1492$
				F.R. ν_5, ν_{19}
1461 mP	1458 vs	1460* sh	1460* m	ν_5, ν_{19}
1453 sh			1452.7* ms	ν_{12}
		1451.0* m		ν_{26}
	1436 m	1429 w	1434* m	ν_{18}
			1430* m	ν_4
1270 vvw	1279 vs	1294 ms	1294 vw	ν_{20}
			1268 mw	$\nu_7 + \nu_{30} = 1256?$
1215 mP	1209 w	1208 vw	1208 m	ν_6, ν_{21}

TABLE 1. (Concluded)

Raman (liquid)	Infrared (liquid)	Polarized infrared ^b		Assignment
		θ	$\theta + 90^\circ$	
1190 vvw		1190 vvw	1190 mw	ν_{13} Conformer?
1165 m	1181 w	1158 w	1158 vw	ν_{27}
1122 mP	1120 w	1117 vvw	1117 w	ν_7
1094 vw	1095 m			Conformer
	1021 mw			Conformer
		989 vvw	982 vw	$\nu_{28} + \nu_{29} = 984$
974 w	973 s	969 mw	969 ms	ν_{22}
916 sP	916 s	920 w	920 m	ν_8
863 wP	862 vvw			Conformer
799 vw	797 s	786 ms	786 w	ν_{28}
695 w	692 w		690 vvw	ν_{23}
640 w	637 w			Conformer
599 vvw				Conformer
583 vw	580 m			Conformer
518 sP	518 m	519 vvw	519 w	ν_9
372 w	372 ms	375 w	373 m	ν_{24}
260 mP	257 m	257 m	252 m	ν_{10}
200 vvw	198 vw			ν_{14}, ν_{29}
	136 m			ν_{15}, ν_{30}

^a v = very, w = weak, m = medium, s = strong, sh = shoulder, F.R. = Fermi Resonance, P = polarized.
^b High temperature solid phase except where designated *, low temperature solid phase.

a value of ΔH of 2.6 ± 0.5 kcal/mol. These results, taken together, suggest that the liquid phase of dimethyl carbonate exists as a conformational equilibrium of at least two conformers.

Vibrational Assignment

Collingwood *et al.* (C.L.W.) have published an assignment based on vapor phase infrared contours and Raman polarization data. The assignment assumes, however, that only the *cis-cis*, C_{2v} , structure is present. Their lack of infrared spectra of the crystal has therefore led to certain misassignments. In addition, we find ourselves in disagreement with C.L.W. in regard to the experimental observation of a number of weak bands. Finally, we have assigned two of the A_2 modes from our low temperature solid phase infrared spectrum under the assumption that the site symmetry of dimethyl carbonate in this phase is lower than C_{2v} . This assumption is discussed further in the next section. The assignments of the fundamental modes are compared in Table 2.

In the CH stretching region our assignment of the liquid phase spectrum is essentially identical with that of C.L.W. There are three accidental

degeneracies (ν_1 with ν_{16} , ν_2 with ν_{17} , and ν_{11} with ν_{25}). In the 120 K spectrum, however, the latter two degeneracies are split.

The first assignment disagreement between C.L.W. and ourselves occurs in the CH_3 bending region. This is a very difficult region because six fundamental modes occur here and there is a great deal of accidental degeneracy. Although our liquid infrared data agrees with that of C.L.W., our Raman data does not. C.L.W. observe Raman bands at 1456 and 1414 cm^{-1} . We have searched for the 1414 cm^{-1} band, but are unable to find it. We do observe a shoulder at 1453 cm^{-1} , however, on a major band at 1461 cm^{-1} . Since our infrared spectrum has bands at 1458 and 1436 cm^{-1} , it seems clear that the 1453 cm^{-1} shoulder must be the A_2 CH_3 antisymmetric bending mode, ν_{12} . Since symmetric methyl bending modes are almost invariably lower in frequency than the corresponding antisymmetric modes, we prefer to assign 1436 cm^{-1} as ν_4 and ν_{18} and the 1458 cm^{-1} band as ν_5 , ν_{19} , and ν_{26} . At 120 K, the degeneracy between ν_4 and ν_{18} is split, but that between ν_5 and ν_{19} is not. In addition, we observe two bands at 1452.7 and 1451.0 cm^{-1} of opposite polarization in the oriented crystal at

TABLE 2. Assignment of fundamental modes of vibration of dimethyl carbonate

C_{2v} symmetry species	Frequency number	Approximate mode	Frequency		Collingwood <i>et al.</i> (6) ^c
			Liquid ^a	Solid ^b	
A_1	ν_1	νCH_3 (asym)	3028	3038	3032
	ν_2	νCH_3 (sym)	2961	2964 ^e	2964 ^d
	ν_3	$\nu\text{C}=\text{O}$	1760	1751	1774
	ν_4	δCH_3 (sym)	1436	1430 ^e	1458
	ν_5	δCH_3 (asym)	1458	1460 ^e	1414 ^d
	ν_6	δCH_3 (rock)	1209	1208	1195 ^d
	ν_7	νOCO (sym)	1120	1117	1116 ^d
	ν_8	$\nu\text{CH}_3-\text{O}$	916	920	922
	ν_9	δOCO	518	519	857 ^d
	ν_{10}	δCOC	257	255	518
A_2	ν_{11}	νCH_3 (asym)	3007	3009 ^e	3004
	ν_{12}	δCH_3 (asym)	1453 ^d	1452.7 ^e	1432
	ν_{13}	δCH_3 (rock)	1190 ^d	1190	1234 ^d
	ν_{14}	CH_3O torsion	198	—	—
	ν_{15}	CH_3 torsion	136	—	—
B_1	ν_{16}	νCH_3 (asym)	3028	3038	3032
	ν_{17}	νCH_3 (sym)	2961	2960 ^e	2965
	ν_{18}	δCH_3 (sym)	1436	1434 ^e	1458
	ν_{19}	δCH_3 (asym)	1458	1460 ^e	1414 ^d
	ν_{20}	νOCO (asym)	1279	1294	1299
	ν_{21}	δCH_3 (rock)	1209	1208	1160 ^d
	ν_{22}	$\nu\text{CH}_3-\text{O}$	973	969	989
	ν_{23}	δOCO_2 (rock)	692	690	634
	ν_{24}	δCOC	372	374	579 ^d
B_2	ν_{25}	νCH_3 (asym)	3007	3016 ^e	3004
	ν_{26}	δCH_3 (asym)	1458	1451.0 ^e	1432
	ν_{27}	δCH_3 (rock)	1165 ^d	1158	1210 ^d
	ν_{28}	δOCO_2 (rock)	797	786	801
	ν_{29}	CH_3O torsion	198	—	—
	ν_{30}	CH_3 torsion	136	—	—

^aInfrared value unless otherwise indicated.^bHigh temperature solid phase infrared value unless otherwise indicated.^cVapor phase infrared value unless otherwise indicated.^dRaman liquid value.^eLow temperature solid phase value.

120 K. These bands, which can only be resolved by utilizing the polarizer, are assigned to ν_{12} and ν_{26} .

The CH_3 rocking modes are all assigned in the 1150–1250 cm^{-1} region, but our data are quite different from that reported by C.L.W. They observed no infrared vapor bands in this region, but did observe liquid phase bands at 1162, 1176, and 1210 cm^{-1} . They assigned the four methyl rocking modes from their Raman spectra with the four bands and their relative intensities being 1160 (2), 1195 (4), 1210 (1), and 1234 (1). The 1195 cm^{-1} band was reported to be polarized. We do not observe the 1234 cm^{-1} band, the 1215 cm^{-1} band is the strongest Raman band in this region and we find it to be polarized, the 1190 cm^{-1} band is very weak, and the 1165 cm^{-1} is the second strongest in the

region. A liquid phase infrared band is found corresponding to the 1215 band, but not to the 1165 and 1190 cm^{-1} bands. The crystal infrared spectrum has bands at 1190 and 1158 cm^{-1} , however. This assignment requires that two of the methyl rocks remain accidentally degenerate and ν_6 and ν_{21} have been chosen as corresponding to the strongest Raman and infrared band observed. The choice for ν_{13} and ν_{27} is then arbitrary and we have chosen the highest frequency as ν_{13} .

The four skeletal stretching modes involving the ether-like bonds present no difficulty and we agree with C.L.W. as to their assignment.

The only fundamentals remaining to be assigned are the skeletal bending modes. These are expected below 900 cm^{-1} , where the remaining nonassigned bands are found. Because

of a lack of crystal spectra, C.L.W. assigned as fundamentals bands at 857, 634, and 579 cm^{-1} . These correspond to a second conformer, however, as we have previously discussed. They then assigned five Raman bands between 500–198 cm^{-1} as difference bands, the lowest of the ground states being 792 cm^{-1} . This must certainly be incorrect since at room temperature such a high level could not be significantly populated.

The two OCO_2 rocking modes are expected to be the highest in frequency of the skeletal bending modes and C.L.W. have assigned ν_{28} by infrared vapor phase contours. We therefore agree in our assignment of ν_{28} , but assign ν_{23} , the in-plane rocking mode to the next highest frequency found in the solid, 692 cm^{-1} .

There are three more nontorsional skeletal bending modes and three major bands remaining in both the infrared and Raman spectra. Two of these Raman bands are polarized and therefore correspond to the two remaining A_1 modes, ν_9 and ν_{10} . The higher frequency one is chosen as δOCO and the lower as δCOC since the former could be expected at a higher frequency. The remaining depolarized Raman band is then assigned as the B_1 , δCOC bending mode.

In a number of studies of compounds containing methoxy groups (10–12), it has been reported that methoxy torsions occur in the range 170–215 cm^{-1} and the corresponding methyl torsions at 130–150 cm^{-1} . We therefore assign the two methoxy torsions, ν_{14} and ν_{29} , as being accidentally degenerate at 198 cm^{-1} and the two methyl torsions as being accidentally degenerate at 136 cm^{-1} .

Crystal Spectra

We have earlier reported (7, 8) that dimethyl carbonate can be crystallized between alkali halide windows as a highly oriented film. We have earlier reported that this phenomenon is rather general with other compounds (13). It is therefore feasible to study the polarized infrared spectra of dimethyl carbonate at low temperatures. Unfortunately, the crystal structure of dimethyl carbonate has not been reported and the results of a polarized infrared spectral study are therefore not unambiguously interpretable. Nevertheless, some information can be drawn from such low temperature studies.

If the sample used is one that has been purified, there appears to be a solid–solid phase

change at a nominal temperature of about 140 K. The orientation of the crystals is not destroyed by this phase change since strong polarization effects are noted in the spectra of both phases. Comparison of the spectra in Figs. 3 and 4 with those published earlier (8) leads to the conclusion that the low temperature phase spectra are much more complicated than those of the higher temperature phase, with a great deal of band splitting and sharpening. The change in the spectra is a sudden one, however, and therefore indicates an actual change in crystal or molecular structure. The high temperature solid phase spectra have no significant temperature dependency, but the low temperature solid phase spectra do. In general, the splittings observed in the spectra of the low temperature phase increase as the temperature is lowered. This behavior is typical of crystal splittings in organic crystals, due probably to lattice contraction effects.

The three A_2 modes which are above the low frequency transmission limit of the windows are all methyl modes which might be expected to be accidentally degenerate with other methyl modes of the same type but of different symmetry. This appears to be true with ν_{11} , but ν_{12} and ν_{13} do appear to be resolved in the Raman spectrum of the liquid. In the high temperature solid phase infrared spectrum ν_{12} and ν_{13} also appear, but ν_{11} does not. If the assignment is correct, this indicates that the site symmetry of the high temperature crystal is less than C_{2v} . In the low temperature solid phase infrared spectra a new band appears which can be assigned to ν_{11} . It must be noted, however, that this assignment is quite arbitrary. The band may simply be due to crystal splitting, *i.e.* the same molecular mode split by intermolecular interactions. Nevertheless, ν_{11} , ν_{12} , and ν_{13} must occur very near their present assignment frequencies.

Conclusions

The spectral data for dimethyl carbonate are all consistent with the existence of a conformational equilibrium in the liquid state. In view of previous structural studies, the major conformer must be the *cis-cis*, C_{2v} structure. The second structure would be expected, on theoretical grounds, to be the *cis-trans* C_s structure. There is no experimental evidence confirming this structure as a second conformer, however.

The ΔH value obtained experimentally is quite high, but is in the range predicted for ester conformations (1). It corresponds to a relative concentration of the second conformer of about 1% at ambient temperatures in the absence of a statistical weight factor. If the second conformer is the *cis-trans* structure it would possess a statistical weight factor of two, doubling its relative concentration. If the second conformer is one in which one methyl group is not coplanar with the remainder of the molecule, however, the statistical weight factor would be four.

The recording of the solid state infrared spectra of dimethyl carbonate has, in addition to providing evidence for the conformational equilibrium, allowed improvements in the assignment of the fundamental modes of vibration. Collingwood *et al.* have assigned second conformer bands as fundamentals of the *cis-cis* conformer and these assignments have been corrected.

Dimethyl carbonate crystallizes as an oriented polycrystalline film and polarized infrared spectra may be obtained. In the absence of a known crystal structure, these cannot be fully interpreted. Nevertheless, they indicate that the site symmetry is lower than C_{2v} . It appears that dimethyl carbonate undergoes a solid-solid phase transition in the neighborhood of 140 K,

but the exact nature of this transition is not known.

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