THE DIPROPENYL ETHERS: VIBRATIONAL AND ¹³C NMR SPECTRA

HELEN C. HOLLEIN and WILLIAM H. SNYDER*

Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, NJ 07102 (U.S.A.)

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ABSTRACT

The infrared vapor phase and solution spectra and the Raman liquid phase spectra as well as the ¹³C NMR absorption have been examined for the dipropenyl ether isomers, i.e. cis, cis (I), cis, trans (II) and trans, trans (III). Evidence based on double bond vibrational coupling, the simple nature of the spectra and the assignment of most of the fundamentals shows only one planar s-trans, s-trans conformation for each isomer. The strong double bond coupling probably indicates that substantial "through space" electron delocalization between the double bonds must be involved, and that this reduces or takes precedence over oxygen electron delocalization in the order I > II > III. The "cis effect" is explained by a dipolar interaction of β -methyl hydrogen with ether oxygen, which is absent in the trans-propenyl structures.

INTRODUCTION

In an earlier paper we reported evidence for vibrational coupling of the double bonds in *cis*, *cis*-dipropenyl ether (I) based on some preliminary IR and Raman spectral data which we obtained for this isomer [1, 2]. We felt that it was essential to make a more detailed examination of the vibrational spectra of I and also of the *cis*, *trans* (II) and *trans*, *trans* (III) isomers. In particular, we were interested in examining evidence for or against the existence of rotational conformers and vibrationally coupled double bonds. Also germane is the origin of the "*cis* effect" which is shown by these isomers. Thus, in this paper we report IR, Raman and ¹³C NMR spectra.

EXPERIMENTAL

Compound I was prepared by the potassium t-butoxide catalysed rearrangement of diallyl ether. Compounds II and III were obtained by isomerizing I with 3 to 4 mol% of mercuric acetate for 24 h at 60°C; the equilibrium mixture contained approximately 42, 46 and 12% of I, II and III respectively. Another isomerization was carried out at 80°C for 39 h using about 6 mol%

^{*}Author to whom correspondence should be addressed.

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catalyst. In the latter run significant quantities of *cis*- and *trans*-propenyl acetate were also produced. Unfortunately, the acetates have boiling points very close to II and III and they could not be separated by distillation on a 200 plate spinning band column. However, the esters could be readily removed from II and III by treating the liquids with solid potassium hydroxide on a high vacuum system and the vapors which were free of carbonyl absorption could be readily transferred to a gas cell. Sufficient samples to obtain solution spectra were obtained from the 60° C isomerization by separating the isomers via gas chromatography (25% THEED on 60/80 Chromosorb W) at a column temperature of 90° C and collecting the vapors directly in solvent CS_2 .

Vapor phase spectra were obtained in a conventional 10 cm cell fitted with CsI windows on a Perkin-Elmer 457 infrared spectrometer (4000– 250 cm⁻¹). Solution spectra (CS₂) were run in a 1 mm cell with NaCl windows on a Perkin-Elmer 21 spectrometer (4000–650 cm⁻¹). Raman spectra on pure I and impure II and III (the major impurities were 12 and 19% *cis*- and *trans*-propenyl acetates in II and III respectively) were obtained in the liquid phase (92.5 to 3123.1 cm⁻¹) on a Jarrel Ash 400 spectrometer with an Ar– Ne laser. Another sample of II containing about 3% I and 13% III was run in the liquid state on a Perkin-Elmer LR-1 Laser Raman spectrometer.

Decoupled ¹³C NMR spectra were obtained using a JEOL JNM-PS-100 spectrometer with an internal deuterium lock. Acetone- d_6 was used as solvent and TMS as the internal standard.

CONFORMATIONS

Before we proceed to discussion of the spectra, it is useful to identify the important conformers of I, II and III. Courtauld models of the three isomers are useful for this purpose.

There is only one stable planar form for I, but two each for II and III as shown in the abbreviated representations in Fig. 1. It is important to note that in IIb and IIIb (s-cis, s-trans) the double bonds are approximately orthogonal and this would preclude the occurrence of vibrational coupling in these conformers. Thus only Ia, IIa and IIIa (s-trans, s-trans) could give rise to



Fig. 1. Planar conformations of the dipropenyl ethers.

coupling of this type. In addition, the models show that there are significantly larger non-bonded repulsions between the α - and β -vinyl hydrogens in IIb and IIIb than are present between the two α hydrogens in Ia—IIIa.

For the non-planar forms we can derive six to eight different conformers each from Ia, IIa and IIIa by an extreme 90° rotation of the C-O bonds so that the double bond is placed above or below the plane of the reference planar form. The 90° rotation is done for convenience only and does not mean that the non-planar forms have to be formed by this much rotation. In fact, evidence from the literature suggests that stable non-planar forms may have approximately $10-50^{\circ}$ rotation from the planar conformations in Fig. 1 to give an energy minimum [3, 4]. In any event, by using our notation in Figs. 1-3 one can readily perceive the approximate shapes of the principal planar and non-planar forms. We use the notation A or B in these figures for indicating whether the double bond is respectively above or below the plane of the original reference structure. Thus we note from Fig. 2 that, (a) Ic and Id; Ig and Ih; IIc and IId; IIe and IIf; IIg and IIh; IIi and IIj; IIIc and IIId; and IIIg and IIIh all have mirror image relationships and therefore each pair is of equal energy if identical amounts of C—O rotation are used to produce them; (b) the pairs Ie, f and IIIe, f are identical.



Fig. 2. Non-planar conformers from Ia-IIIa.



Fig. 3, Non-planar conformers from IIb and IIIb.

Further, we must still consider the non-planar forms available from IIb and IIIb by rotation around the right hand C—O bonds as indicated in Fig. 3. The pairs IIk, m and IIIk, m have individually mirror image relationships and, therefore, each pair has the same energy.

We should be able to represent the different planar and non-planar forms of I, II and III in terms of the usual conformational energy diagrams typical of ethane, propane, butane, etc., by utilizing eclipsed, staggered and gauche arrangements of the attached groups (e.g. Newman projections). The β methyl groups can be readily handled in this way. Since the atoms directly attached to the double bond are all coplanar, the hydrogens on the methyl group can either be staggered or eclipsed with respect to the β -vinyl hydrogen. If they are staggered, then the remaining methyl hydrogen is eclipsed with respect to the ether oxygen only in the *cis* propenyl groups in I and II, regardless of whether the overall structure (neglecting the methyl hydrogens) is planar or non-planar. It seems eminently reasonable to assume that these cis structures with the methyl hydrogen eclipsed to the oxygen (Fig. 4) are of lower energy and represent minima because of dipolar attractive forces developed between the positive methyl hydrogen and the negative ether oxygen. No such structures are possible with the *trans* propenyl groups in II and III; but in these isomers when the methyl hydrogens are staggered with respect to the β -vinyl hydrogen, the remaining methyl hydrogen is eclipsed with respect to the α -vinyl hydrogen and the alternate structure produced by a 60° rotation involves eclipsing of the β -vinyl hydrogen.

Rotation around the two C—O bonds in Ia—IIIa can lower the repulsive interactions between the two α -vinyl hydrogens, but only at the expense of uncoupling the double bond vibration. Such rotation in IIb and IIIb similarly can relieve the α , β vinyl hydrogen repulsions.

In conclusion then, I can have one planar plus three non-planar, II can have two planar plus five non-planar, and III can have two planar plus four non-planar conformers of different energy, each of which in principle could lead to a different IR and Raman spectrum.

VIBRATIONAL SPECTRA

The observed IR and Raman frequencies for I, II and III are collected in Tables 1—3, respectively. It should be noted that the intensities reported in CS_2 solution were rather high so that the assigned intensities are not as reliable as those for the vapor phase. Further, the resolution and accuracy of



Fig. 4. Diagram showing H...O dipolar interaction in the cis-propenyl ether group.

TABLE 1

IR (cm ⁻¹)		Raman (cm ⁻¹)	Assignment	
Vapor (CsI)	CS ₂ Sol.	Liquid		
3049 w		3057 s 2982 vw	v cis C—H vinyl	
2933 w		2921 vs) 2890 sh (ν C—H methyl, asym	
2883 w		2866 m 2772 vw 2728 vw	u cis C—H methyl, sym	
1726 vw		2120 VW		
1690 vw		1691 vvs	ν C=C sym	
1663 / s 1658 /	1656 s	1654 vw	ν C=C asym	
1000 5.		1449 w	Methyl asym deformation	
1403 sh 1395 m {	1399 m—s	1406 w) 1386 vw (<i>Cis</i> C—H i.p. rock	
1356 m	1357 s	1362 w	Methyl sym deformation	
1253 s	1252 s	1256 s	Cis C-H i.p. rock	
1138 vs	1129 vs	1133 vw	ν C-O-C asym + Me i.p. rock	
1082 w	1078 m—s		ν C—C asym	
1035 sh		1028 vw	Methyl o.o.p. rock	
	973w	967 vw	ν C—OC sym	
928 vw	928 w	946 m	Cis HC=CH twist	
		897 w	ν C—C sym	
794 vw	800 w			
718 m	722 s	728 vw	Cis C—H o.o.p. wag	
ز 697 sh	693 w—m	694 vw)	—	
}		596w }	Skeletal vibrations	
444 w)		441 w)		
		338 w	CO-Cip bend	
		234 vw	Methyl torsion	
		160 vw	Vinyl—oxygen torsion	

Vibrational frequencies and assignments for cis, cis-dipropenyl ether, I

TABLE 2

Vibrational frequencies and assignments for cis, trans-dipropenyl ether, II

IR (cm ⁻ ')		Raman (cm ⁻¹)	Assignment
Vapor (CsI)	CS ₂ Solution	Liquid	
3053 w		3055 m	ν cis C—H vinyl
20.20		3041 w	v trans C—H vinyl
2969 sh			
2939 w } 2904 w }		2926 vs } 2896 m }	ν C—H methyl, asym
2877 w		$2871 \ m$	ν trans C—H methyl, sym
		2005) 2749 vw	v cis C—H metnyl, sym
1777 vw			
1685 vw		1694 s	ν C=C sym
1661 (s	1661 s	1666 w	ν C=C asym
1633 sh			
1450 vw		1459 vw	Methyl asym deformation
1399 m		1397 vw)	
		1382 vw∫	CIS C-H I.p. rock
1364 w	1357 w	1360 vw	Methyl sym deformation
1323 w	1328 w)	1318 vw)	
1281 w	1280 m—s }	}	Trans C—H i.p. rock
1273)	_	1270 vw)	
1248 m	1252 m—s	1249 w	Cis C-H i.p. rock
1176 vs	1168 vs	1161 vw	ν C-O-C asym
1137 w	$\frac{1137}{1131}$ m—s	1131 vw	Methyl i.p. rock
1095 w	1101) 1114 m	1098 vw	v C - C asym
	1029 w	1031 vw	Methyl o o p. rock
993 w	999 w—m		
	981 w—m	985 vw	ν C—O—C sym
923 w	928 m	937 vw	Cis HC=CH twist
910 sh	916s		Trans C-H 0.0.p. wag
		904 vw	ν CC sym
795 vw	787 w	788 vw	Trans HC=CH twist
710 vw	723 m		Cis C-H o.o.p. wag
	693 vw	682 vw)	
		637 vw (Skeletal vibrations
367 VW 460 vvv (467 101	
100 •••)		353 vw	C-O-Cip bend
		230 vw	Methyl torsion
		195 vw	Vinyl—oxygen torsion

TABLE 3

IR (cm ⁻¹)		Raman (cm ⁻¹)	Assignment	
Vapor (CsI)	CS ₂ Solution	Liquid		
3050 w		3043 m	v trans C—H vinyl	
2940 w } 2902 w }		2933 vs) 2902 m)	u C—H methyl, asym	
2873 w		2871 m 2760 w	ν trans C—H methyl, sym	
1763 vw 1742 vw 1717 vw				
1690 w		1698 m—s 1676 m—s	v C=C sym Propenyl acetate [5]	
1669 \ m_c				
1662 { ^m s	1662 s	1657 w—m	ν C=C asym	
1460 vw		1452 w—m 1383 w—m	Methyl asym deformation	
1367 vw	1357 w		Methyl sym deformation	
1339 w	1346 w 1289 sh	1338 w—m	Trans C-H i.p. rock	
$1278 \} m$	1279 sh }	1277 } w-m	Trans C-H i.p. rock	
1271)	1272 m)	1264)		
1198 vs	1183 vs	1100	ν C—O—C asym	
1135 vw	1131 m	1139 vw	Methyl i.p. rock	
1103 w	1109 m	1104 vw	v C—C asym	
1039 w	1040 m	1033 vw	Methylo.o.p. rock	
000	0.00	996 vw	ν C-O-C sym	
923 m	920 s	924 vw	Trans C-H o.o.p. wag	
700	500	908 vw	v C-C sym	
793 w	786 w—m 721 w—m	790 w	Trans HC=CH twist	
	691 vw	J		
	668 mm			
	000 VW 3	626.00	Skeletal vibrations	
475 w		474 vw		
		383 w	C–O–C i.p. bend	
		286 vw	Methyl torsion	
		207 vw	Vinyl—oxygen torsion	

Vibrational frequencies and assignments for trans, trans-dipropenyl ether, III

the band positions were not as good as for the vapor phase spectra since the Perkin-Elmer 21 spectrometer uses a NaCl prism. For this reason, the C—H stretching frequencies in solution are not reported.

Perusal of the vapor phase IR spectra for the three isomers in Figs. 5-7 shows in all cases surprisingly few intense bands and remarkably few bands overall for these seventeen atom molecules which can theoretically have 45 fundamentals without considering degeneracy. Further, if appreciable



Fig. 5. Vapor phase IR spectrum of cis, cis-dipropenyl ether, I.



Fig. 6. Vapor phase IR spectrum of cis, trans-dipropenyl ether, II.



Fig. 7. Vapor phase IR spectrum of trans, trans-dipropenyl ether, III.

amounts of different rotational isomers were present, we might expect very complicated spectra indeed. One is almost led to the conclusion without even analyzing the data in detail that if various conformers are present then there must be a great predominance of only one form in each case.

The strongest case we can make for the absence of any appreciable amounts of other conformers comes from examination of the double bond region in the IR and Raman. The vapor phase spectra show either two or three bands in this region of approximately equal intensity, but in solution only one band is observed. This multiplet structure in the vapor very likely is due to the presence of rotational fine structure which shows up in separation of the P and R branches. In solution this rotational fine structure would not be observed. In the Raman liquid phase absorption, this rotational fine structure is of course also absent. Thus for each isomer we observe one strong IR and Raman band with the latter absorption occurring at a considerably higher frequency. As reported before for I, this is due to the presence of strong vibrational coupling [1, 2]. Our results for II and III also show this coupling and the absence of any other significant double bond absorption.

On the basis of our previous identification of the $C_{2\nu}$ conformer (Ia) for I and from thermodynamic studies, Taskinen and Virtanen have proposed IIa and IIIa as the major conformers for II and III [4]. Comparison of the enthalpies for isomerization of I to II (2.0 ± 0.1 kJ mol⁻¹) and II to III (1.7 ± 0.3 kJ mol⁻¹) indicates that there is no major change of conformation in the isomerization reaction. Our present study of the vibrational spectra, i.e. the coupling of the double bonds and the absence of other bands in this region, strongly supports the assignment of Ia, IIa and IIIa as the only stable conformations for I, II and III.

Additional evidence for the existence of a single conformer for each isomer is found in the asymmetric C—O—C stretching region with one dominant IR band for I, II and III. Other bands in the C—O—C region are readily attributed to fundamentals which must be present in these molecules. This evidence for a single conformer is in stark contrast with the existence of multiple conformations commonly reported for enol ethers and dihaloethylenes. Divinyl ether [6], *cis*- and *trans*-dimethoxyethylene [7], methyl vinyl ether [8, 9], ethyl vinyl ether [10, 11], *trans*-methyl propenyl ether [12], *trans*-ethyl propenyl ether [12, 13], and *trans*- β -chlorovinyl methyl ether [14] all display multiple bands in the C=C region due to multiple conformations. Note, however, that *cis*-methyl propenyl ether [12], *cis*-ethyl propenyl ether [12, 13] and *cis*- β -chlorovinyl methyl ether [14] are reported to exist as single rotamers (non-planar) with relatively simple spectra.

As mentioned before, the dipropenyl ethers are non-linear molecules composed of seventeen atoms each yielding a maximum of 45 fundamental modes of vibration. All of the fundamentals should be Raman active, but the C_{2v} conformer of I and III (Ia and IIIa) has a maximum of eight IR inactive frequencies of the A_2 symmetry series [15a]. The planar conformer of II (IIa) is of C_s symmetry, so all of the observed frequencies should be both IR and Raman active.

For symmetrical diethers, the C—O—C symmetric stretch should be IR inactive [16] as observed at 996 cm⁻¹ in III, but a weak band appears for this vibration in the solution IR spectrum at 973 cm⁻¹ in I. In *cis*-dimethoxyethylene, the skeletal bands at 545 cm⁻¹ and 380 cm⁻¹ are identified as A_2 bands of the C_{2v} conformer [7]. Corresponding IR inactive bands occur at 596 cm⁻¹ and 338 cm⁻¹ in I and at 636 cm⁻¹ and 383 cm⁻¹ in III, although the presence or absence of the 383 cm⁻¹ band in III may be questionable from closer study of Fig. 7. The methyl torsion is reported to be IR inactive in dimethyl ether [15b], and only appears in the Raman spectrum at 286 cm⁻¹ in III. The methyl torsion at 234 cm⁻¹ in the Raman spectrum of I is below the range of our IR measurements. The symmetric C—C stretches at 897 cm⁻¹ in I and 908 cm⁻¹ in III are also absent from the IR spectra. Some breakdown of symmetry rules occurs in complex molecules. When allowed and forbidden vibrations have similar frequencies, Coriolis interactions can excite the normally IR inactive vibrations [17]. Also, weak bands may appear at forbidden frequencies due to combinations or overtones from other vibrations, so the presence of weak bands at 973 cm⁻¹ in I or at 383 cm⁻¹ in III does not necessarily conflict with the assignment of a planar conformation. On the other hand, Raman bands which appear to be IR inactive may simply be too weak to be observed or vice versa. Although all of the vibrational modes in I, II and III should be Raman active, it is interesting to note that the very strong asymmetric C—O—C stretch at 1198 cm⁻¹ in the IR spectra of III is absent from the Raman spectrum. The tentative identification of four or five IR inactive bands for I and III is submitted as supplementary evidence for the assignment of conformers Ia and IIIa. The primary evidence must still be the double-bond coupling.

Examination of the vapor phase IR spectra of I and II in Figs. 5 and 6 shows narrow, well-defined band envelopes for the asymmetric C=C and C-O-C stretching vibrations, as expected for the planar conformers, Ia and IIa. In III (Fig. 7), however, these vibrations produce broader, triangularshaped bands which indicate that III may be non-planar. On the other hand, the asymmetric C-O-C stretching frequencies for both II and III are in the 1225-1172 cm⁻¹ region where planar conformers are assigned for other enol ethers [6-8, 11, 12, 14]. Although positive identification of a planar structure is sometimes ambiguous, we submit that the vibrational coupling of the double bonds in I, II and III strongly favors assignment of the planar rotamers, Ia, IIa and IIIa. Even if III is slightly non-planar, its conformation must still be quite close to IIIa.

Concerning this double bond coupling, the behavior of the dipropenyl ethers is very similar to s-trans-1,3-butadiene which has a ν -sym and asym at 1630 cm⁻¹ (Raman) and 1596 cm⁻¹ (IR), respectively [18, 19]. The frequency separations observed for these vibrations in I, II and III are also remarkably similar to butadiene (approximately 34 cm⁻¹). Our results suggest that with I—III, this "through space" coupling takes precedence over electron delocalization or resonance of the electron pair on the ether oxygen with the vinyl carbon π -electrons. The "through space" coupling presumably also involves electron delocalization with the largest effect being observed in I. Thus the average C=C stretch is noticeably lower for I and increases from I to III, suggesting that the double bond coupling is strongest in I as observed from the relative intensities of the Raman/IR double bond symmetric/asymmetric stretches. In addition, the absolute Raman intensities of the symmetric C=C vibration show a quite noticeable decrease in going from I to III.

That there is competition between double bond and oxygen resonance is shown by comparison of the asymmetric C-O-C stretching frequencies which increase significantly from I to III. Thus the oxygen double bond character due to resonance is lowest in I. Although III must have considerable delocalization involving the oxygen electrons as witnessed in a relatively high C-O-C frequency, this effect is not so strong that it prevents double bond coupling in this isomer.

In divinyl ether, two major conformations are observed: a planar s-trans, s-trans form with double bond coupling and a non-planar form with $10-50^{\circ}$ rotation from the s-cis, s-trans structure [2-4]. Electron delocalization with oxygen apparently takes precedence over "through space" coupling in this case, leading to two stable rotamers both of which have relatively high asymmetric C-O-C stretching frequencies [6]. In the dipropenyl ethers, the electron donor character of the β -methyl groups with respect to the more electronegative double bonds evidently enhances the electron density in these bonds and favors the "through space" coupling phenomena, so that the planar s-trans, s-trans conformations predominate in I, II and III at ordinary temperatures.

The origin of the "cis effect" shown by the dipropenyl ethers [4], we believe, can be readily explained by noting that only in the cis isomers is a dipolar interaction between the eclipsed methyl hydrogen and the ether oxygen possible (Fig. 4). In the trans structures, this dipole must be separated to a larger distance at the cost of higher potential energy. This explanation also correlates with known stabilities of the alkyl propenyl ethers where the cis stability increases as the electron donor ability of the attached alkyl group increases (Me < Et < i-Pr < t-Bu) and modifies the charge on the oxygen atom [20-22]. Thus while methyl cis-propenyl ether is very slightly less stable than its trans counterpart, the cis isomer predominates increasingly in going from Et to t-Bu alkyl substituents at 25°C.

The known ¹H NMR [4] and ¹³C NMR shifts (Table 4) for I—III also agree with this explanation. Thus δ for the methyl protons is larger (lower field) and δ for the methyl carbon is smaller (higher field) in the *cis* structure, while both the vinyl protons and carbons occur at slightly higher field. The latter observation is consistent with the slightly increased donor character of the two β -methyl groups in the *cis* isomers.

The closer proximity of the opposed dipoles in the *cis* structures as an explanation for the "*cis* effect" was originally proposed by Crump for the 1-halopropenes [23]. We have previously explained the *cis* stability in the dimethoxyethylenes and the dihaloethylenes in terms of the interaction

TABLE 4

 $^{13}\mathrm{C}$ NMR shifts (& TMS) for the dipropenyl ethers

Atom	(I) cis,cis	(II) cis,trans	(III) trans,trans
α -Vinyl carbon	144.5	143.4(c) and $145.8(t)$	144.8
β-Vinyl carbon	102,9	103.0(c) and $103.6(t)$	104.0
Methyl carbon	9.4	8.9(c) and $12.2(t)$	12.2

between like dipoles [24], and Taskinen and Sainio have extended that explanation to halogen-containing vinyl ethers [25].

FREQUENCY ASSIGNMENTS

Since the spectra of the dipropenyl ethers are relatively uncomplicated, it is possible to assign most of the observed frequencies as seen in Tables 1–3. Due to the symmetry of the molecule in I and III, the number of fundamentals actually observed is far fewer than the maximum possible. Vibrations from identical bonds in the two halves of the molecule may couple to give a symmetric plus an asymmetric vibrational frequency as observed for the C–O, the C=C and the C–C stretches. If the identical bonds in the two propenyl groups do not couple, a single degenerate vibration may result as observed for the four vinyl C–H stretches in I and III, and for the various vibrational frequencies of the two methyl groups in all three isomers.

All of the fundamentals are expected to occur in II with *cis* and *trans* vibrations for each of the bonds. In both the ¹³C and ¹H NMR spectra, a complete set of *cis* and *trans* shifts are observed for II (Table 4 and refs. 4, 26). In the Raman and IR spectra, however, only one band is generally observed for a particular mode of vibration in II, with a frequency intermediate between that observed for I and III. Exceptions are for vinyl C—H where both *cis* and *trans* frequencies are observed in II for the stretching vibration and for the in-plane and out-of-plane deformations.

The strongest Raman bands in II and III are the methyl C—H asymmetric stretches at 2926 cm⁻¹ and 2933 cm⁻¹, followed by the symmetric C=C stretching vibrations at 1694 cm⁻¹ and 1698 cm⁻¹. Standard assignment of band intensities for the vapor phase IR and Raman data is reflected in Tables 1—3 [27], with the exception of the 1691 cm⁻¹ band in I. The Raman band at 1691 cm⁻¹ (the symmetric C=C stretch) in I is three times more intense than the methyl C—H asymmetric stretching vibration at 2921 cm⁻¹, and this intense band has been given a special assignment of vvs or very very strong! The methyl C—H asymmetric stretch is the second strongest Raman band in I and is of comparable intensity to the same bands in II and III. The 2921 cm⁻¹ band has been assigned the very strong or 100% value for I, which makes the Raman intensity assignments consistent with II and III. Note that the 1691 cm⁻¹ band is a uniquely intense vibration, and is much stronger than the symmetric C=C stretches for II and III or than any other band in the three Raman spectra.

The C-H stretching modes for enol ethers are similar to those for alkenes. These vibrations are weak in the IR spectra but fairly strong in the Raman spectra. The methyl C-H symmetric and asymmetric stretches and deformations are well documented in the literature and require no detailed explanations [19, 28, 29]. Band splitting is common for these vibrations. The asymmetric methyl C-H stretch often appears as two peaks due to the existence of two separate asymmetric modes. The lower frequency peak in this case is generally weaker [19] as observed in I-III.

The vinyl C–H stretching vibrations occur in the 3050-3000 cm⁻¹ frequency range [29]. In the dipropenyl ethers, the environments of the vinyl C-H's are different; i.e. the two vinyl hydrogens next to the oxygen atom may be expected to have a different frequency than the two vinyl hydrogens next to the methyl groups. A separate band due to the vinyl C–H stretch next to the oxygen is reported at 3042 cm^{-1} for divinyl ether [6], but only one band is observed in this region for I and III. In the dimethoxyethylenes. the symmetry of the molecule is such that the two vinyl C-H stretches should be identical. Two vinyl C-H stretching vibrations at 3065 cm⁻¹ and 3015 cm^{-1} in *cis*-dimethoxyethylene and at 3050 cm⁻¹ and 3015 cm⁻¹ in trans-dimethoxyethylene [7] evidently derive from the existence of multiple conformations in these compounds. The presence of only one vinyl C-H stretching frequency at 3057 cm⁻¹ for I and at 3043 cm⁻¹ for III may be taken as additional evidence for the presence of only one conformer in these isomers. The vinyl C-H stretch is a strong Raman band in I and a medium intensity Raman band in III. Two vinyl C-H stretching vibrations are observed in II. By comparison of the frequencies and intensities with I and III, the medium intensity Raman band at 3055 cm^{-1} in II is assigned to the cis vinyl C—H stretch and the weaker band at 3041 cm⁻¹ is assigned to the trans vinyl C-H stretch, suggesting only one conformer for II as well.

The C=C stretch in vinyl ethers is greatly intensified by the proximity to the oxygen atom [29]. The asymmetric C=C stretching vibrations are the second strongest bands in the IR spectra of I, II and III. The symmetric C=C stretches are the second strongest bands in the Raman spectra of II and III, and the 1691 cm⁻¹ symmetric C=C stretch in I is the strongest band in any of the Raman spectra. We previously reported the coupling of the double bonds in I with the symmetric C=C stretch at a higher frequency and stronger in the Raman, and the asymmetric C=C stretch at a lower frequency and stronger in the IR [1, 2]. The same vibrational coupling is observed for II and III as seen in Table 5 and is only expected for the planar conformations: Ia, IIa and IIIa.

The C=C stretching frequency is predicted at $1662-1631 \text{ cm}^{-1}$ for a *cis* alkene and at $1678-1668 \text{ cm}^{-1}$ for a *trans* alkene [29]. In the vinyl ethers and haloalkenes, however, the *cis* C=C stretch is generally at a higher frequency than the *trans* C=C stretch [12, 14, 24]. The averages of the symmetric

TABLE 5

Double bond stretching frequencies and intensities

	Raman			IR (av.)	Average
	sym C=C	asym C=C	Ratio	asym C=C	(cm ⁻¹)
I	1691 vvs	1654 vw	60:1	1660 s	1676
II	1694 s	1666 w	3:1	1662 s	1678
III	1698 ms	1657 w—m	2:1	1664 ms	1681

and asymmetric C=C stretches are 1676 cm^{-1} in I and 1681 cm^{-1} in III. Since the frequencies of the *cis* bonds in I and the *trans* bonds in III are similar, only one set of coupled frequencies is observed in II with an average of 1678 cm^{-1} . The averages are approximately as predicted for alkenes with the *trans* vibrations slightly higher than the *cis* vibrations.

The double bond coupling is by far the strongest in I as indicated by the relative intensities of the Raman/IR pairs and by the relative intensities of the two Raman bands for each isomer in Table 5. The stronger coupling in I may be related to the increased donor character of the β -methyl groups which would tend to place higher electron density in both double bonds simultaneously. This vibrational coupling also indicates that there is probably appreciable electron delocalization between the double bonds and reduced electron delocalization of the individual double bonds with the oxygen electrons. This latter contention is supported by a substantially lower asymmetric C—O—C stretching frequency in I than in II or III (see below).

Compound II should present an intermediate case between I and III, but exhibits only slightly greater double bond coupling than III. Also note that the asymmetric C—O—C vibration in II is much closer to III than I. Thus the reduced double bond coupling in both II and III is accompanied by substantially more delocalization involving the oxygen electrons as reflected in the higher frequency C—O—C stretches.

Two vinyl C---H out-of-plane deformations are produced by in-phase and out-of-phase coupling of the two vinyl hydrogens in a *cis* or *trans* alkene group. The in-phase, out-of-plane deformation gives a medium to strong intensity IR vibration commonly labelled the vinyl C---H "wag" which is well documented in the literature [19, 29]. The out-of-phase, out-of-plane vinyl C--H deformation gives a weak Raman band around 960 cm⁻¹ for a *cis* alkene bond or 740 cm⁻¹ for a *trans* alkene bond [29] and results in a twisting vibrational mode for the vinyl group.

The two vinyl C—H out-of-plane deformations are reported at 935 cm⁻¹ and 781 cm⁻¹ in *trans*-methyl propenyl ether and at 933 cm⁻¹ and 777 cm⁻¹ in *trans*-ethyl propenyl ether [12]. The *trans* vinyl C—H wag is assigned to the IR bands at 916 cm⁻¹ in II and 920 cm⁻¹ in III. The only Raman band in the 781—740 cm⁻¹ region in III is the 790 cm⁻¹ band which is the most intense vibration below 1200 cm⁻¹ in III. The *trans* vinyl C—H twist is assigned to the 790 cm⁻¹ band in III and to the 788 cm⁻¹ band in II.

The two vinyl C—H out-of-plane deformations are reported at 725 cm⁻¹ and 951 cm⁻¹ in *cis*-methyl propenyl ether and at 724 cm⁻¹ and 934 cm⁻¹ cis-ethyl propenyl ether [12]. The *cis* vinyl C—H wag is assigned to the IR bands at 722 cm⁻¹ in I and 723 cm⁻¹ in II. The most intense vibration below 1200 cm⁻¹ in I is the medium intensity Raman band at 946 cm⁻¹. This band falls in the 960—934 cm⁻¹ region and is assigned as the *cis* vinyl C—H twist. In II, the *cis* vinyl C—H twist is assigned to the 937 cm⁻¹ Raman band.

Since two out-of-plane vinyl C—H deformations have been identified, we also expect to find two in-plane vinyl C—H deformation modes or in-plane

"rocks" due to the in-phase and out-of-phase coupling of the vinyl hydrogens. The *cis* vinyl in-plane rock normally occurs at $1429-1397 \text{ cm}^{-1}$ [29], and the *trans* vinyl in-plane rock at $1310-1290 \text{ cm}^{-1}$ [19] in the IR spectra. A second *cis* vinyl in-plane rock which appears around 1260 cm^{-1} in the Raman is allowed in the IR by symmetry considerations, but may be weak [19]. Colthrup et al. assign the in-phase, in-plane rock in 1,2-dialkyl ethylenes to an IR band near 1405 cm^{-1} for *cis* compounds and to a Raman band near 1305 cm^{-1} for *trans* compounds [29]. The out-of-phase, in-plane rock is assigned to a Raman band near 1265 cm^{-1} in *cis* compounds and to an IR band near 1295 cm^{-1} in *trans* compounds [29].

In divinyl ether a CH₂ rock near 1075 cm⁻¹ and a CH rock near 1300 cm⁻¹ are expected [29]. The CH₂ rock is reported at 1116 cm⁻¹, but the CH rock splits into two bands at 1323 cm⁻¹ and 1299 cm⁻¹. The appearance of two CH rocking vibrations in divinyl ether is attributed to either multiple conformations or to coupling of the hydrogens across the central C—O—C bond [6]. In I and III, three vinyl in-plane rocks appear instead of two, and six vinyl in-plane rocks (*cis* and *trans*) instead of four appear in II. Since we find no evidence for multiple conformations in any other region of the spectra of I, II or III, we attribute the band splitting in the dipropenyl ethers to coupling of the in-phase and out-of-phase rocking modes in the Courtauld models for the planar conformers Ia, IIa and IIIa shows that it would be rather difficult for the a hydrogens not to interact. Also, since the four vinyl carbons display coupled symmetric and asymmetric vibrations, similar coupling can be expected for the four vinyl hydrogens.

The *cis* vinyl in-plane rock at 1256 cm⁻¹ in I is of particular interest because it is strong in both the Raman and the IR (the third strongest band in each case). The vinyl in-plane rock at 1261 cm⁻¹ in *cis*- β -chlorovinyl methyl ether [14] is also strong in both the Raman and the IR, and strong IR bands are reported at 1265 cm⁻¹ in *cis*-methyl propenyl ether and at 1255 cm⁻¹ in *cis*-ethyl propenyl ether [12]. The remaining *cis* and *trans* vinyl in-plane rocks in Tables 1–3 are assigned in accordance with the literature discussed above.

The asymmetric C-O-C stretches are assigned to the strongest IR bands at 1198 cm⁻¹ in III, 1176 cm⁻¹ in II and 1138 cm⁻¹ in I. The other bands in this region are assigned to the methyl in-plane and out-of-plane rocks and the asymmetric C-C stretch as discussed below. The methyl in-plane rock is usually found at 1150-1120 cm⁻¹ [29] and is assigned to bands at 1137 cm⁻¹ in II and 1135 cm⁻¹ in III. The asymmetric C-O-C stretching vibration at 1138 cm⁻¹ in I coincides with the methyl in-plane rock. The methyl in-plane and out-of-plane rocks occur at 1159 cm⁻¹ and 1012 cm⁻¹ in methyl vinyl ether [8] and at 1169 cm⁻¹ and 980 cm⁻¹ in methyl acetate [30]. The methyl out-of-plane rock is assigned to the bands at 1028 cm⁻¹ in I, 1031 cm⁻¹ in II and 1033 cm⁻¹ in III, which makes the averages for the inplane and out-of-plane rocks in the dipropenyl ethers similar to these other compounds. The other set of bands in the asymmetric C—O—C region at 1082 cm⁻¹ in I, 1095 cm⁻¹ in II and 1103 cm⁻¹ in III is assigned to the asymmetric C—C stretch. The asymmetric C—C stretch is expected to be less intense in the IR than the asymmetric C—O—C stretch, as observed. Since the double bonds and the vinyl hydrogens are evidently coupled in I, II and III, coupling of the carbon—carbon single bonds to give a symmetric plus an asymmetric stretch is anticipated. When the two methyl groups are attached to the same carbon as in $(CH_3)_2CHX$, the asymmetric stretch is reported at 1140-1120 cm⁻¹ and the symmetric stretch at 890-870 cm⁻¹ [31]. The symmetric C—C stretch mixes with the methyl in-plane rock in normal alkanes to give bands at 900—880 cm⁻¹ and 1150-1120 cm⁻¹ [29]. In I, II and III, the symmetric C—C stretch is assigned to the Raman bands at 897 cm⁻¹, 904 cm⁻¹ and 908 cm⁻¹, respectively, which is close to the 900-870 cm⁻¹ range expected.

The symmetric C—O—C stretch occurs at 930—830 cm⁻¹ [32] in the Raman for aliphatic ethers, but the bands in this region for I, II and III are already assigned. The asymmetric C—O—C stretch is higher for vinyl ethers than aliphatic ethers [29], so the symmetric C—O—C stretch may also be somewhat higher and is assigned to the Raman bands at 967 cm⁻¹ in I, 985 cm⁻¹ in II and 996 cm⁻¹ in III. The assignments of the symmetric C—O— C and C—C stretches appear reasonable, because the latter is slightly more intense in the Raman.

The low frequency vibrations in the Raman spectra of methyl vinyl ether have been assigned as follows: 205 ± 15 cm⁻¹, torsion around the vinyloxygen bond; $240 \pm 10 \text{ cm}^{-1}$, methyl torsion; and $327 \pm 2 \text{ cm}^{-1}$, in-plane mode involving bending of the C-O-C angle [9, 33]. The three lowest frequency bands in I, II and III are in the same range and are assigned to the same vibrational modes that were specified in methyl vinyl ether (see Tables 1-3). The C-O-C in-plane bend for the C_{2v} conformers, Ia and IIIa, is a totally symmetric vibration and is IR inactive in I at 338 cm^{-1} and in III at 383 cm^{-1} . The remaining vibrational frequencies in the 700–400 cm⁻¹ region may be assigned to the *cis* and/or *trans* C-C=C skeletal modes [34], but similar bands in divinyl ether at 585-455 cm⁻¹ [6], in methyl vinyl ether at 585 cm⁻¹ [8], and in the monopropenal ethers at 653-615 cm⁻¹ [12] are assigned to the C=C–O skeletal deformations. Based on these publications, a clear choice for assignment of either C-C=C or C=C-O deformation modes cannot be made for the skeletal vibrations in the 700–400 cm^{-1} frequency range in I, II or III. The skeletal bending modes in normal hydrocarbons [29] and alkyl ethers [32] show considerable mixing of the C–C–C, C–C– O and C—O—C frequencies rather than isolated vibrations, and similar mixing of the C=C=O and C=C=C modes probably occurs in the propential ethers.

In divinyl ether, three skeletal bending modes are expected; but six skeletal frequencies plus the vinyl—oxygen torsion are observed in the region below 700 cm⁻¹ due to the presence of multiple conformations. For the seven atom nonlinear skeleton in the dipropenyl ethers, five skeletal bending modes are expected [29] but only four are observed in I at 694 cm⁻¹, 596 cm⁻¹,

441 cm⁻¹ and 338 cm⁻¹. Similar frequencies appear in II and III, again pointing to the presence of only one conformer for each isomer.

CONCLUSIONS

Only one conformer is present in each of the dipropenyl ethers. The evidence presented here includes the overall simplicity of the spectra, and the presence of only one asymmetric C—O—C stretch, one *cis* and/or *trans* vinyl C—H stretch, and two coupled C=C stretches for each isomer. All of the intense bands in I, II and III are accounted for; and the only vibrational mode with multiple frequencies is the vinyl C—H in-plane rock, where multiplicity is attributed to vibrational coupling of the vinyl hydrogens across the central C—O—C bond.

The exceptionally strong double bond coupling, tentative identification of several A_2 bands, and the shapes of the IR bands all indicate that I is a planar molecule with C_{2v} symmetry. The double bond coupling in II and III and the thermodynamic studies by Taskinen indicate that these molecules are quite similar to I. The narrow, well-defined band envelopes in the vapor phase IR spectrum of II support assignment of a planar s-trans, s-trans conformer for II, and the tentative identification of several IR inactive bands supports assignment of a planar C_{2v} conformer for III. In reference to the double bond coupling, it seems likely that substantial electron delocalization must be involved and that this type of stabilization must be sufficient to make the planar s-trans, s-trans forms predominate even at ordinary temperatures.

The "*cis* effect" is most easily explained by considering the dipole—dipole attraction of the eclipsed methyl hydrogen with the ether oxygen. This non-bonded interaction must substantially lower the energy of the *cis* propenyl group relative to the *trans* structure.

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