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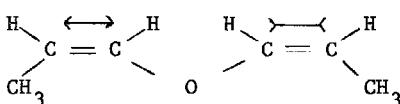
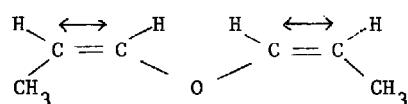
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COUPLING OF THE DOUBLE BOND STRETCHING VIBRATION IN DIVINYL ETHERS

Key Words: Divinyl ethers, Infrared spectra, Raman spectra.

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Examination of the infrared and Raman spectra of cis, cis-dipropenyl ether (which was produced by isomerization of diallyl ether)^{2,3} has produced evidence for strong vibrational coupling between the two double-bonds. This ether has strong bands at 1656 cm^{-1} in the infrared and at 1691 cm^{-1} in the Raman. The 1658 cm^{-1} band in the Raman is about 10 fold less intense than the strong polarised band. Thus it appears reasonable to associate the strong IR and Raman bands with the asymmetric and symmetric vibrations shown.

(a) 1656 cm^{-1} (s) 1691 cm^{-1}

These structures would correspond to C_{2v} symmetry if all the C atoms, the O atom and the double-bond H atoms are coplanar. An additional requirement is that the conformations of the methyl groups be such that the molecule has a plane of symmetry (C_s) perpendicular to the plane passing through the principal axis. The arithmetic average of the above frequencies is very close to the uncoupled frequencies observed for cis-propenyl n-butyl and n-hexyl

ethers shown in the Table.^{3,4} It should also be noted that the resultant dipole moment in the double-bond direction should be very small or nil. Thus the 1691 cm^{-1} band should be extremely weak in the I.R.

Table

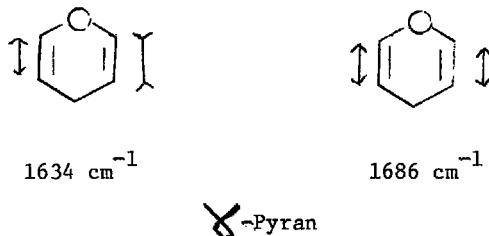
The Double-Bond Stretching Frequencies of Some Vinyl Ethers

Ethers	I.R. ^a	(C=C) cm^{-1}	Raman ^b
vinyl methyl ⁶	1616s, 1639m, 1652m		
vinyl 2-methoxyethyl	1618s, 1637m		1620s, 1637s
divinyl ⁷	1619vs, 1623sh 1641s, 1672vw		1627sP, 1643vsP 1670sP
<u>cis</u> -propenyl n-butyl ⁴	1672s		
<u>trans</u> -propenyl n-butyl ⁴	1661s, 1681m		
<u>cis</u> -propenyl n-hexyl ³	1672s		1671s
<u>cis</u> , <u>cis</u> -dipropenyl ³	1656s		1658vw, 1691vsP
<u>cis</u> , <u>trans</u> -dipropenyl ³	1661s		
<u>trans</u> , <u>trans</u> -dipropenyl ³	1662s		
Δ -2,3-dihydro- γ -pyran	1645s		
γ -pyran ⁵	1634s, 1686s		

a. Nonpolar solvent, CCl_4 or CS_2

b. Pure liquid

The doublet observed in γ -pyran⁵ could also be due to coupled vibrations except now both the asymmetric and symmetric vibrations should be strongly I.R. active since there is large resultant C-O dipole in the double bond direction. Only a strong singlet is noted at 1645 cm^{-1} for Δ -2,3-dihydro- γ -pyran in the I.R.



The reported vibrational frequencies between 1600 and 1700 cm^{-1} of di-vinyl ether could be interpreted similarly except now there are four bands in the IR and three bands in the Raman⁷. We propose that the 1619 cm^{-1} band in the IR and the 1670 cm^{-1} band in the Raman correspond to the coupled asymmetric and symmetric vibrations, respectively, of the C_{2v} rotational isomer (see representation I Fig. 1 in reference 7 and the discussion on dipropenyl ether above). It should be noted that Clague and Danti have assigned the 1628 and 1649 cm^{-1} bands in the vapor spectrum to the asymmetric and symmetric modes of the two double bonds in the other rotational isomers⁷ respectively. We have observed weak Raman scattering for the pure liquid at 1618 cm^{-1} . We feel that the large intensity differences noted for the 1619 and 1670 cm^{-1} absorptions in the IR and Raman favor our assignment for the reasons discussed above under dipropenyl ether.

REFERENCES AND FOOTNOTES

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