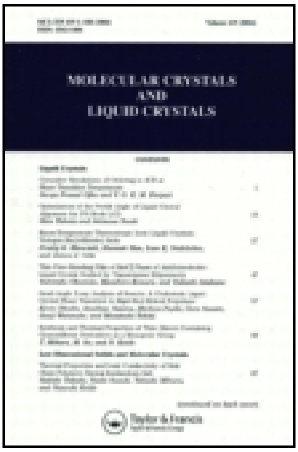

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FTIR Studies of Trimethylene Linked Bis-Diacetylene Derivatives

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FTIR Studies of Trimethylene Linked Bis-diacetylene Derivatives

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FTIR spectra of a series of bis-diacetylenes were studied. An absorption at about 2255 cm^{-1} due to stretching vibrations of the diacetylene system (observed in all cases as a relatively intensive peak) has been found to be very characteristic for these diacetylene derivatives, as well as a strong coupling of the CH_2 wagging vibration modes resulting in splitting of the absorption peaks at 1300–1360 cm^{-1}.

Keywords: FTIR, diacetylene, bis-diacetylene

INTRODUCTION

Diacetylenes and so called bis-diacetylenes are recently extensively studied because of their potential application in molecular electronics.[1–4] This work is to discuss properties of some bis-diacetylene derivatives of trimethylene series in the light of FTIR data.

EXPERIMENTAL

All compounds examined were obtained in our laboratory. The synthetic procedures are well known[5,6] and some modifications have been published separately.[3,4,7] FTIR spectra were measured in KBr discs or as thin films with the aid of Perkin-Elmer Model 1600 FT-IR Spectrophotometer.

RESULTS AND DISCUSSION

We have studied FTIR spectra (Figure 1) of compounds called bis-diacetylenes of a general formula:

$$R—C{\equiv}C—C{\equiv}C—(CH_2)_3—C{\equiv}C—C{\equiv}C—R'$$

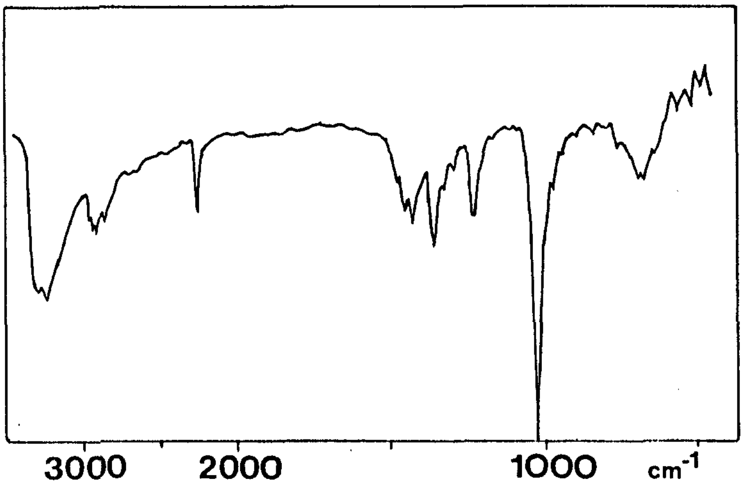

FIGURE 1 FTIR spectrum of (**8**).

where R = C_3H_7 (**9,10,11**), CH_2OH (**8**), CH_2OBz (**12,13**) and R′ = CH_2OH (**8,9,12**), CH_2OBz (**13**), $CH_2OPO(OCH_3)OH$ (**10**), CH_2OSO_3H (**11**) as well as some intermediates and starting materials useful in comparative studies: $HC{\equiv}C{-}(CH_2)_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_2OH$ (**6**), $IC{\equiv}C{-}(CH_2)_3{-}C{\equiv}CI$ (**2**), $C_3H_7{-}C{\equiv}CI$ (**1**), $HC{\equiv}C{-}(CH_2)_3{-}C{\equiv}CH$ (**5**) and $HC{\equiv}C{-}CH_2OH$ (**4**).

This is a new class of diacetylene derivatives which polymerize in a solid state topologically controlled process forming unsaturated and conjugated, thus electrically conducting chains of a controlled spacing.[3,4] It is understood that properties of the diacetylene system in a crystal lattice of different derivatives are of great interest. Substituents not only can modify general features of molecules but also change the crystal structure and ability of diacetylene units to polymerize in mild conditions.

All the spectra examined consist of typical absorption peaks at about 3300 cm^{-1} (OH stretching), 3295 cm^{-1} ($C{\equiv}C{-}H$ stretching), 2950 cm^{-1} (C—H stretching), 2255 cm^{-1} ($C{\equiv}C{-}C{\equiv}C$ stretching), 2120 cm^{-1} ($C{\equiv}C$ stretching), 1360–1300 cm^{-1} (CH_2 wagging), 1020 cm^{-1} (C—O stretching), 970 cm^{-1} ($C{\equiv}C{-}CH_2$ rocking) and 640 cm^{-1} ($C{\equiv}C{-}H$ bending), but obviously, appearance and position of these peaks is dependent on the structure of particular molecules. A strong absorption at about 970 cm^{-1} is assigned to a rocking mode of the $C{\equiv}C{-}CH_2$ system and it has been observed for all compounds examined. The spectra were measured in a condense phase (solids as a suspension in KBr and liquids as a thin film), thus intermolecular interactions give some contribution to the frequency of vibrations and the intensity of absorption. Generally, because of symmetry of molecules, we have observed a weak ir absorption except for $C{\equiv}CH$ and C—O stretching modes, as well as $C{\equiv}CH$ and $C{\equiv}CCH_2$ bending and rocking modes, and vibrations of strongly polarized substituents as OH, OSO_3H and $OPO(OCH_3)OH$. Conversion of the isolated triple bond ($C{\equiv}C$) into a diacetylene system ($C{\equiv}C{-}C{\equiv}C$) results in an increase in intensity and frequency of the stretching vibrations. The position of the absorption peak changes from 2118 cm^{-1} and 2120 cm^{-1} for hepta-

1,6-diyne (**5**) and propargyl alcohol (**4**), respectively, to 2254 cm^{-1} for trimethylene linked bis-diacetylenediol (**8**) related to these substrates. This is probably caused by an increase in the electron density due to a positive induction effect of substituents R and R′, together with a well known electron repulsion of the triple bond and some unability of the diacetylene system to spread electrons along the diacetylene unit due to resonance. The central single bond in the diacetylene grouping is weak (each of the triple bonds is able to react as an isolated triple bond[5]) and this fact is responsible for small coupling between stretching vibrations of conjugated triple bonds. In consequence, the stretching modes of diacetylene system appear in a very narrow frequency range (Table I). In contrast, the stretching vibrations of single bonds separated by much stronger triple bond are usually strongly coupled. However, no splitting of the bending vibrations at about 640 cm^{-1} was observed for (**6**) and (**7**) because of the small difference in electronegativity between X and C in the substituent of type CH_2X (where $X = CH_2$), the splitting is clearly observed in the case of propargyl alcohol (**4**), now $X = OH$, see Table I. Also wagging modes of CH_2 groups, attached directly to a triple bond, are strongly coupled in all examined compounds giving a series of 2–3 more or less intensive peaks in the range of 1300–1360 cm^{-1} (Table I). This absorption is very characteristic for CH_2 groups attached on at least one side of the triple bond.[5]

A considerable increase in the force constant of the triple bond is also observed in the series of iodine derivatives (**1–3**), now the frequency of the stretching mode changes from 2118 cm^{-1} to 2185 cm^{-1}. Thus, some substituents and structural features can be responsible for a substantial rise of the force constant of triple bonds leading to an increase in their frequency of stretching vibrations. Higher intensity of absorption in bis-diacetylenes is caused by unsymmetrical substitution of diacetylene units, but also partially due to an increase in the number of triple bonds. The molecules of bis-diacetylenediol and its derivatives, even symmetrically substituted, are non-centrosymmetric because of their conformation and most of vibration modes are active in both ir and Raman spectroscopy. In particular, the high frequency symmetric stretching mode of a diacetylene system (about 2250 cm^{-1}), usually not observed in the ir spectra of symmetrically substituted diacetylenes,[5] is active in the ir spectra of bis-diacetylenediols and their derivatives giving a relatively intensive sharp absorption peak at about 2255 cm^{-1}. This is a very characteristic feature of a diacetylene system. We found this absorption to be extremely strong in the case of mono- and dibenzyl derivatives of bis-diacetylenediol because of unsymmetrical substitution of diacetylene units. Even molecules of dibenzyl derivative (**13**) are non-centrosymmetric, despite "symmetrical substitution," due to their conformation.

One of the most important conclusions derived from our FTIR studies of bis-diacetylenediol (**8**) is its well ordered crystal structure with all diacetylene units located in the same or nearly equivalent environment (single and sharp absorption peaks are observed, e.g. about 2555 cm^{-1} due to stretching of diacetylene system). That means that both diacetylene groups in a bis-diacetylenediol molecule (if any) are able to polymerize in a topologically controlled process. This feature has been confirmed independently during our studies on kinetics of UV light induced solid state polymerization of bis-diacetylenediols and related diacetylenes.[8]

TABLE I

Comparison of ir absorpiton due to main vibration modes for: 1-iodopentyne (**1**), 1,7-diiodohepta-1,6-diyne (**2**), 1,8-diiodoocta-1,7-diyne (**3**), propargyl alcohol (**4**), hepta-1,6-diyne (**5**), deca-2,4,9-triyn-1-ol (**6**), undeca-2,4,10-triyn-1-ol (**7**), trideca-2,4,9,11-tetrayne-1,13-diol (**8**), pentadeca-2,4,9,11-tetrayn-1-ol (**9**), sodium methyl pentadeca-2,4,9,11-tetraynyl phosphate (**10**), sodium pentadeca-2,4,9,11-tetraynyl sulfate (**11**), 1-benzyloxytrideca-2,4,9,11-tetrayn-13-ol (**12**), 1,13-dibenzyloxytrideca-2,4,9,11-tetrayne (**13**).

	Vibration modes (v-stretching, w-wagging, δ-rocking, τ-bending)											
Compound	vO—H broad	vC≡C—H	vC≡C—C≡C	vC≡C	wC≡C—CH$_2$			vP=O or vS=O	v≡C—C≡	vC—O—P	vC—O	δCH$_2$	τC≡CH
(**1**)				2184.8	1338.1	1324.8						969.5	
(**2**)				2184.5	1342.2	1324.9	1310.6					954.0	
(**3**)				2177.3	1344.5							954.0	
(**4**)	3337.9	3288.8		2119.8	1361.5		1299.8		1228.9[a]		1028.4	978.9 915.3	646.6 666.3
(**5**)		3298.2		2117.7	1346.5	1327.2	1312.1						637.7
(**6**)	3354.8	3295.3	2255.0	2114.7	1346.1	1327.3	1310.4		1231.6		1022.7	969.7	637.4
(**7**)	3355.0	3295.3	2254.9	2114.0	1356.1	1327.3			1232.3		1023.5	968.4	635.3
(**8**)	3236.2		2254.4		1352.2	1325.7			1231.8		1024.7 1014.1	965.3	
(**9**)	3350.5		2255.9 2239.0		1344.9	1326.0	1309.9		1231.5		1023.3	966.1	
(**10**)	3328.0		2257.6		1349.0	1328.8		1237.5		1100.1	1037.6 1062.1	961.2	
(**11**)	3385.9		2255.7		1343.9	1328.0	1310.2	1254.8	1231.9		1024.0 1059.5	972.8 919.4	
(**12**)	3417.0		2255.3		1352.9		1311.7		1231.9		1025.2 1071.9		
(**13**)			2255.3		1351.9		1312.2		1231.3		1027.3 1072.6		

[a] ≡C—C—OH.

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