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# Fourier transform infrared studies on charge-transfer interactions of plastoquinones and $\alpha$ -tocopherol quinone with their hydroquinone forms and monogalactosyldiacylglycerol

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## Abstract

Fourier transform infrared (FTIR) spectra of plastoquinone-9 (PQ-9), plastoquinone-3 (PQ-3),  $\alpha$ -tocopherol quinone ( $\alpha$ -TQ), their reduced forms, monogalactosyldiacylglycerol (MGDG), quinone-hydroquinone (Q-QH<sub>2</sub>) and Q-QH<sub>2</sub>-MGDG mixtures in thin films have been measured. The spectra were recorded directly on samples evaporated from hexane and after precooling at liquid nitrogen temperature. It was found that pure QH<sub>2</sub> molecules are hydrogen bonded and occur mainly in polymeric forms, but in mixtures with corresponding quinones, they show only the presence of dimers. The quinones in Q-QH<sub>2</sub> mixtures in a liquid state do not form hydrogen bonds, but after solidification most of their carbonyl groups are hydrogen bound to hydroquinones, which facilitates the formation of charge-transfer (CT) complexes. Hydrogen bonds in CT complexes between PQ-9 and PQH<sub>2</sub>-9 were found to occur also in MGDG matrix. There were also some indications found on Q-QH<sub>2</sub> interactions in a liquid state. The peak responsible for C-O stretching vibrations of hydroxyl groups in liquid Q-QH<sub>2</sub> mixtures is strongly reduced, and after solidification there appeared two new peaks due to stretching vibrations as a result of hydrogen bonding. Only for PQ-9 and PQH<sub>2</sub>-9 in solid state did crystallization bands appear below 900 cm<sup>-1</sup>, which originate from skeletal vibrations of the isoprenoid side chain of both compounds. The possibility of the existence of CT complexes of different stoichiometry in apolar solutions is also considered.

**Keywords:** Plastoquinone;  $\alpha$ -Tocopherol quinone; Hydroquinone; Monogalactosyldiacylglycerol; Charge-transfer complex; FTIR spectroscopy

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## 1. Introduction

Plastoquinone-9 (PQ-9),  $\alpha$ -tocopherol quinone ( $\alpha$ -TQ) and their reduced forms (PQH<sub>2</sub>-9 and

$\alpha$ -TQH<sub>2</sub>, respectively) are constituents of thylakoid membranes of chloroplasts [1]. PQ-9 and its hydroquinone form, which occur in the lipid part of the membrane, are hydrogen carriers in the photosynthetic electron transport system [2]. The hydrophobic core of the thylakoid membrane in which PQ-9 and PQH<sub>2</sub>-9 move is highly fluid because of the high degree of unsaturation of acyl chains of monogalactosyldiacylglycerol (MGDG), which is the most abundant lipid of the thylakoid membrane [3].

Experiments on model systems showed that PQ-9 and  $\alpha$ -TQ in organic solvents [4] and unsaturated fatty acids [5] form charge-transfer (CT) complexes with their reduced forms. As was found based on infrared measurements, carbonyl groups of PQ-9 and  $\alpha$ -TQ in apolar solvents in CT complexes do not form hydrogen bonds with hydroxyl groups of hydroquinone rings [4]. CT spectra of the investigated prenylquinones consist of two bands, one short-wavelength band (350–380 nm) which dominates in solution [4,5] and a long-wavelength band (500–600 nm) which dominates in solid state [5]. There is also some evidence on CT interactions between PQ-9 and its hydroquinone in MGDG monolayers [6], which may indicate the possibility of the formation of CT complexes also in native biological membranes. So far, only a few prenylquinones were examined by infrared spectroscopy and mainly in KBr discs [7,8]. This technique was already applied to the analysis of CT complexes formed between simple quinones and hydroquinone in solid state [9]. In all such complexes a new hydrogen bound carbonyl band at about 1633 cm<sup>-1</sup> was observed. The principal bonding force in Q-QH<sub>2</sub> systems is  $\pi$ - $\pi$  interaction, however, hydrogen bridges between the carbonyl group of Q and hydroxyl group of the QH<sub>2</sub> molecule provide an additional stabilizing force in such complexes.

Important information about interactions between different molecules can be obtained from FTIR spectra. Change in a particular interaction manifests itself as a shift in frequency for a specific vibrational mode or as a lineshape change, and the discrete frequency ranges can be attributed to different groups of atoms in the

molecules investigated. The method is very sensitive and even detects small changes in bond energies against high background absorption.

In recent years the FTIR technique has been successfully applied for studies of such problems as orientation of lipids [10,11], properties of different lipid phases and their transitions [12–14], lipid-protein interactions [15], and others. By using this method, light-induced changes in properties of quinones associated with photochemical reactions in bacterial reaction centers [16] and plant photosynthesis [17] have been recently investigated.

In the present studies, we applied FTIR spectroscopy to examine in more detail the specific molecular interactions between PQ-9, PQ-3,  $\alpha$ -TQ and their reduced forms in solid, liquid state and in mixture with MGDG, with special emphasis on modes of interaction occurring in CT complexes.

## 2. Materials and methods

PQ-9 and PQ-3 were obtained as a gift from Hoffman-La Roche (Basle, Switzerland) and  $\alpha$ -TQ was purchased from Eastman Kodak Co. All three quinones were purified by TLC as described in ref. [18]. Natural MGDG was from Lipid Products (Nutfield, Surrey) and was used without further purification. The solutions of all compounds investigated were prepared in hexane. Samples for measurements were prepared by evaporating small amounts of appropriate compounds or their mixtures on silica plates under nitrogen in the form of a thin layer and then removing traces of the solvent under a vacuum in the sample chamber of the spectrometer. Since hydroquinones easily oxidize to quinones upon contact with oxygen, the sample chamber was filled with nitrogen before placing the samples there. The spectra were taken in the range of 4000–400 cm<sup>-1</sup> on a BOMEM FTIR spectrometer and were an average of 100 scans. Since it is difficult to remove traces of organic solvents from the investigated hydroquinones and MGDG, spectra of the same sample were recorded several times to check if there were any changes in their shape during the course of measurement.

After recording of spectra at room temperature, samples were cooled in liquid nitrogen for a while and then warmed back to room temperature in a stream of nitrogen and the spectra were recorded again. FTIR spectra were taken for all pure compounds, Q-QH<sub>2</sub> mixtures (1:1 molar ratio), Q(H<sub>2</sub>)-MGDG (1:5 and 1:10 molar ratios) and Q-QH<sub>2</sub>-MGDG mixtures (1:1:5 and 1:1:10 molar ratios).

### 3. Results

In Table 1 are shown peaks of all pure components investigated in the range of 4000–1600 cm<sup>-1</sup> and in Figs. 1 and 2 spectra of PQH<sub>2</sub>-9 and MGDG, respectively, in the range of 3500–600 cm<sup>-1</sup>. PQ-9 evaporated from apolar solvents remains as an oily liquid, and after low temperature treatment it solidifies showing a supercooling effect (m.p. 46°C). Its solidification occurs even above 0°C but requires a longer time. Crystallization of PQ-9 causes refinement of its spectrum in the C-H stretching region and long-wavelength shifts of bands responsible for  $\nu(\text{C=O})$  and  $\nu(\text{C=C})$  of the ring. In spectra of hydroquinones, marked changes are observed in the OH stretching region. Both PQH<sub>2</sub>-9 (Figs. 1 and 3) and  $\alpha$ -TQH<sub>2</sub> show in this region the presence of a shoulder and a broad band. The long-wavelength shoulder originates from dimers of QH<sub>2</sub> molecules bound by hydrogen bonds, and the main band represents these molecules bound in polymeric chains by the same type of bonds [19]. Only this kind of hydrogen bonding is observed for crystal structures of PQH<sub>2</sub>-3. Cooling of PQH<sub>2</sub>-9 (contraction of crystals) causes permanent association of dimers into polymers. On the other hand, the position of the band corresponding to hydroxyl groups of galactose moiety of MGDG suggests that these groups occur in dimeric state [19]. Presence of very weak C=O peaks in PQH<sub>2</sub>-3 and  $\alpha$ -TQH<sub>2</sub> spectra indicates trace amounts of their oxidized forms.

Mixtures of all three investigated quinones with their reduced forms show a colour change (presence of new electronic absorption bands) in comparison with that of individual components in the liquid, and especially in the solid state, which is

Table 1

Absorption bands in the range 4000–1600 cm<sup>-1</sup> of PQ-9, PQ-3,  $\alpha$ -TQ, corresponding hydroquinones and MGDG before and after low temperature pretreatment. Intensity: w (weak), m (medium), s (strong); vibrations:  $\nu$  (stretch), as (asymmetric), sym (symmetric); other abbreviations: dim (dimeric), polym (polymeric), sh (shoulder), v (very).

Position (cm <sup>-1</sup> )	Assignment	Change after precooling
<b>PQ-9</b>		
(yellow liquid)		(yellow solid)
2967 s	$\nu_{\text{as}}(\text{CH}_3)$	2964
2918–2921 s	$\nu_{\text{as}}(\text{CH}_2)$	2942, 2913.5, 2906
2852.5 s	$\nu_{\text{sym}}(\text{CH}_2)$	2855–2846
1652 s	$\nu(\text{C=O})$	1645
1617 m	$\nu(\text{C=C})$ ring	1614
<b>PQ-3</b>		
(yellow liquid)		
2969 s	$\nu_{\text{as}}(\text{CH}_3)$	
2923 s	$\nu_{\text{as}}(\text{CH}_2)$	
2856 s	$\nu_{\text{sym}}(\text{CH}_2)$	2852
1652 s	$\nu(\text{C=O})$	1651
1617 m	$\nu(\text{C=C})$ ring	
<b><math>\alpha</math>-TQ</b>		
(yellow liquid)		
~ 3550 w	$\nu(\text{O-H})$ dim	
2953 s	$\nu_{\text{as}}(\text{CH}_3)$	2950
2927 s	$\nu_{\text{as}}(\text{CH}_2)$	2927.5
2867–2870 s	$\nu_{\text{sym}}(\text{CH}_3)$	2870
~ 2853.5 s	$\nu_{\text{sym}}(\text{CH}_2)$	
1645 s	$\nu(\text{C=O})$	
1623.5 w, sh	$\nu(\text{C=C})$ ring	
<b>PQH<sub>2</sub>-9</b>		
(white solid)		
~ 3477 m, sh	$\nu(\text{O-H})$ dim	disappears
~ 3299–3306 m, broad	$\nu(\text{O-H})$ polym	~ 3250
2965 s	$\nu_{\text{as}}(\text{CH}_3)$	
2919 s	$\nu_{\text{as}}(\text{CH}_2)$	2914
2854 s	$\nu_{\text{sym}}(\text{CH}_2)$	
1666 w	$\nu(\text{C=C})$ chain	1664.5
<b>PQH<sub>2</sub>-3</b>		
(white solid)		
~ 3275 s, broad	$\nu(\text{O-H})$ polym	
2964 s	$\nu_{\text{as}}(\text{CH}_3)$	
2924 s	$\nu_{\text{as}}(\text{CH}_2)$	
2854 s	$\nu_{\text{sym}}(\text{CH}_2)$	
1664.5 w	$\nu(\text{C=C})$ chain	
1651 w	$\nu(\text{C=O})$ of PQ-3 traces	

Table 1 (continued).

Position (cm <sup>-1</sup> )	Assignment	Change after precooling
<b><math>\alpha</math>-TQH<sub>2</sub></b>		
(white solid)		
~ 3380 m, sh	$\nu(\text{O-H})$ dim	2951
3257–3270 m, broad	$\nu(\text{O-H})$ polym	
2953 s	$\nu_{\text{as}}(\text{CH}_3)$	
2925 s	$\nu_{\text{as}}(\text{CH}_2)$	
2869 s	$\nu_{\text{sym}}(\text{CH}_3)$	
~ 2855 s, sh	$\nu_{\text{sym}}(\text{CH}_2)$	
1643 w	$\nu(\text{C=O})$ of $\alpha$ -TQ traces	
<b>MGDG</b>		
(white solid)		
3430–3440 s	$\nu(\text{O-H})$ dim	1656
3011 s	$\nu(\text{=C-H})$ <i>cis</i>	
2961.5 s	$\nu_{\text{as}}(\text{CH}_3)$	
2930 s	$\nu_{\text{as}}(\text{CH}_2)$	
~ 2873 s, sh	$\nu_{\text{sym}}(\text{CH}_3)$	
2855 s	$\nu_{\text{sym}}(\text{CH}_2)$	
1740.5 s	$\nu(\text{C=O})$ ester	
1653–1657 w	$\nu(\text{C=C})$	

caused by the formation of CT complexes (for their electronic CT spectra see [4,5]). Their infrared spectra show some changes as compared with the spectra of their components (Table 2). In the liquid state, most of the polymeric hydrogen bonds are broken and dimers of hydroquinones mainly occur. The absence of a carbonyl group shift suggests that it does not take part in hydro-

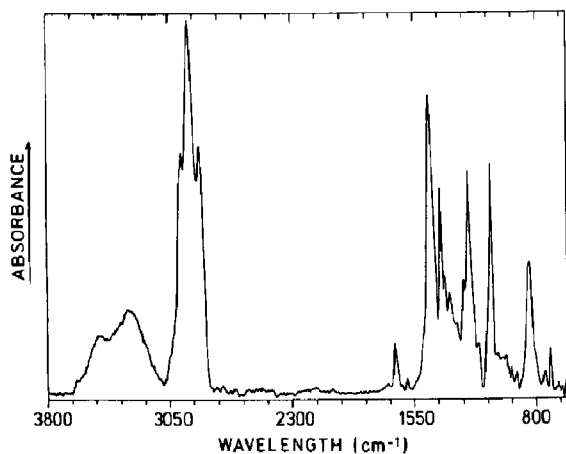


Fig. 1. FTIR absorption spectrum of PQH<sub>2</sub>-9 in the range 3800–600 cm<sup>-1</sup>.

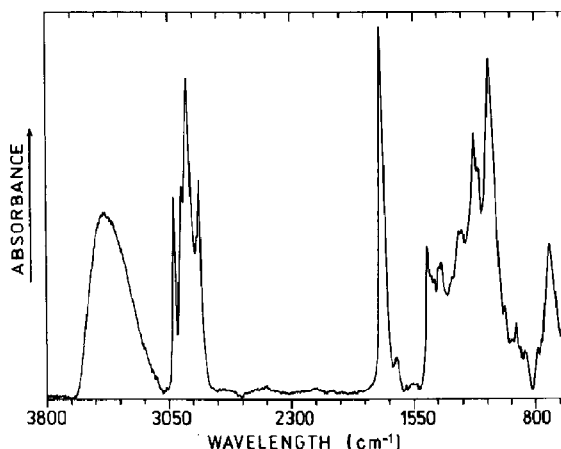


Fig. 2. FTIR absorption spectrum of MGDG in the range 3800–600 cm<sup>-1</sup>.

gen bond formation in the liquid state. After solidification, further changes in PQ-3–PQH<sub>2</sub>-3 and PQ-9–PQH<sub>2</sub>-9 spectra occur. The OH dimeric peak becomes sharper and more intense and the OH polymeric band disappears, despite the fact that the mixture (and also hydroquinones) solidifies. But now hydrogen bound dimers are formed by hydroquinone OH groups and C=O groups of quinones, which is evident by the appearance of a new peak at 1627 cm<sup>-1</sup> and

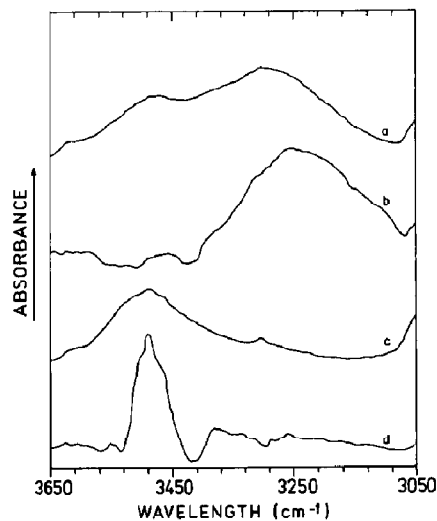


Fig. 3. FTIR absorption spectra of: PQH<sub>2</sub>-9 before (a) and after (b) precooling, PQ-9–PQH<sub>2</sub>-9 mixture before (c) and after (d) precooling in the range 3650–3050 cm<sup>-1</sup>.

decrease of the free C=O peak intensity (Fig. 4). The new peak corresponds to a hydrogen bonded carbonyl group in the CT complex [9]. A band corresponding to PQ-9 carbonyl groups which are not hydrogen bound (C=O free band) in solid mixture with PQH<sub>2</sub>-9 does not show spectral shifts as in the pure solid state, indicating that even not hydrogen-bound PQ-9 molecules interact with PQH<sub>2</sub>-9. On the other hand, PQ-9 mixed with

Table 2

Absorption bands in the range 4000–1600 cm<sup>-1</sup> of Q-QH<sub>2</sub>, Q-MGDG and Q-QH<sub>2</sub>-MGDG mixtures before and after precooling. Numbers in brackets are the molar ratios of the mixture components; hb — hydrogen bound. Other abbreviations as in Table 1

Position (cm <sup>-1</sup> )	Assignment	Change after precooling
<b>PQ-9–PQH<sub>2</sub>-9 (1:1)</b>		
(orange liquid)		
3492 m, broad	$\nu(\text{O-H})$ dim	~ 3488 sharp
~ 3305 w, sh	$\nu(\text{O-H})$ polym	disappears
2967 s	$\nu_{\text{as}}(\text{CH}_3)$	2961
2919 s	$\nu_{\text{as}}(\text{CH}_2)$	2914
2854 s	$\nu_{\text{sym}}(\text{CH}_2)$	2851
1650.5 s	$\nu(\text{C=O})$	s → w
1617 m	$\nu(\text{C=C})$ of Q ring	1618
	$\nu(\text{C=O})$ hb	new 1627 m
<b>PQ-3–PQH<sub>2</sub>-3 (1:1)</b>		
(orange liquid)		
3487 m, broad	$\nu(\text{O-H})$ dim	3473–3493 sharp
~ 3300 w, sh	$\nu(\text{O-H})$ polym	disappears
2966 s	$\nu_{\text{as}}(\text{CH}_3)$	
2923.5 s	$\nu_{\text{as}}(\text{CH}_2)$	
2855 s	$\nu_{\text{sym}}(\text{CH}_2)$	2852.5
1650 s	$\nu(\text{C=O})$	s → w
1617 m	$\nu(\text{C=C})$ of Q ring	1618.5
	$\nu(\text{C=O})$ hb	new 1627 m
<b><math>\alpha</math>-TQ–<math>\alpha</math>-TQH<sub>2</sub> (1:1)</b>		
(brown liquid)		
3410 m, broad	$\nu(\text{O-H})$ dim	peak → sh
3270 w, sh	$\nu(\text{O-H})$ polym	sh → peak 3265
2953.5 s	$\nu_{\text{as}}(\text{CH}_3)$	2955
2927 s	$\nu_{\text{as}}(\text{CH}_2)$	
2869 s	$\nu_{\text{sym}}(\text{CH}_3)$	
1644 s	$\nu(\text{C=O})$	
<b>PQ-9 bands in mixture with PQH<sub>2</sub>-9 and MGDG (1:1:5)</b>		
(pale yellow solid)		
as PQ-9	$\nu(\text{C=O})$	1652
	$\nu(\text{C=O})$ hb	new 1627
	$\nu(\text{C=C})$ ring	1617

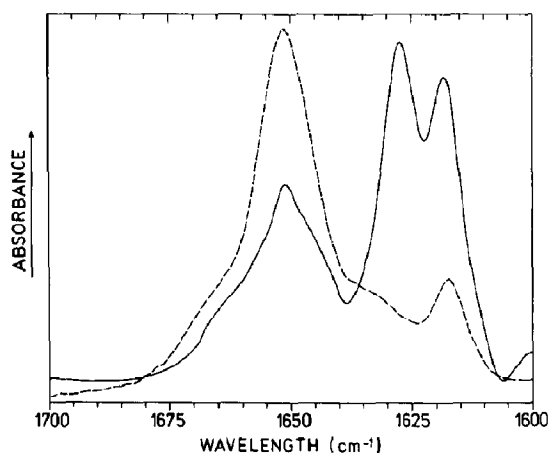


Fig. 4. FTIR absorption spectra of PQ-9–PQH<sub>2</sub>-9 mixture before (— — —) and after (—) precooling in the range 1700–1600 cm<sup>-1</sup>.

MGDG (1:5 molar ratio) shows the same band positions before and shifts after precooling as in the case of pure PQ-9. This indicates that PQ-9 in mixture with MGDG crystallizes as in a pure form. PQ-3 and  $\alpha$ -TQ in Q-MGDG and Q-QH<sub>2</sub>-MGDG systems show the same band positions as in the pure state. As in the PQ-9–PQH<sub>2</sub>-9 mixture so in the mixture of these compounds with MGDG (1:1:5 molar ratio), after precooling, does a band of hydrogen bonded carbonyl group of PQ-9 appear and the intensity of free carbonyl band decreases. This mixture, after precooling, shows a characteristic colour change (Table 2) connected with the appearance of an electronic CT band. When the molar proportion of MGDG in such a mixture is raised to 10, then the hydrogen bonded C=O groups are no longer detectable, probably because of their low intensity as compared to MGDG background. Hydrogen bound carbonyl groups are also not observed in precooled mixtures of PQ-3–PQH<sub>2</sub>-3–MGDG (1:1:5 molar ratio). Most probably this results from the localization of the former two compounds in the more polar regions of MGDG matrix, i.e., in conditions unfavorable for CT complex formation [6].

In the 1600–400 cm<sup>-1</sup> spectral region of solid PQ-9, three new bands appear (Table 3) which are absent in its liquid state spectrum and are assigned as crystallization bands [8]. Similar to

Table 3

Absorption bands in the range 1600–400  $\text{cm}^{-1}$  of PQ-9, PQ-39  $\alpha$ -TQ and MGDG before and after precooling. Vibrations:  $\delta$  (bend),  $\beta$  (in-plane bend),  $\gamma$  (out-of-plane bend),  $\rho$  (rock); cryst. (crystallization bands). Other abbreviations as in Table 1

Position ( $\text{cm}^{-1}$ )	Assignment	Change after precooling
<b>PQ-9</b>		
1445.5 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	
1380.5 s	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	1382.5
1316 m		1318
1263 vw		1265 vw $\rightarrow$ m
1238.5 w		disappears
		new 1212 w
		new 1184 w
		disappears
1163.5 w		
1101 m	$\beta(\text{C-H})$ ring	1104 m
983.5 w		
		new 962 w
881.5–884 w	$\gamma(\text{C-H})$ ring cryst.	new 874 s
840.5 m	$\gamma(\text{C-H})$ chain cryst. cryst.	new 795 s new 752 m
<b>PQ-3</b>		
1446 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	1443 s
1378.5–1380 s	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	
1316 s		
1266 w		1263–1265 w $\rightarrow$ vw
1238.5 m		
1165.5 m		
1100 m	$\beta(\text{C-H})$ ring	
983.5 m		
883.5–885.5 m	$\gamma(\text{C-H})$ ring	
830–854 w	$\gamma(\text{C-H})$ chain	
<b><math>\alpha</math>-TQ</b>		
1463.5 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	1461.5
1375.5 s	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	
1306 m		
1067 w		1069
932 w		926–952
714 m		711
<b>MGDG</b>		
1463 m	$\delta(\text{CH}_2)$ , $\delta_{\text{as}}$ ( $\text{CH}_3$ )	
1393 w, 1378 w	$\beta(\text{O-H})$ , $\beta(\text{C-H})$ ring, $\delta_{\text{sym}}$ ( $\text{CH}_3$ )	
1247–1267 w		
1167 m	$\nu(\text{C-O})$ ester	
1143 sh	$\nu(\text{C-O})$ ether	
1072 s	$\nu(\text{C-O})$ OH	
708 m	$\rho(\text{CH}_2)$ chain, $\gamma(\text{C-H})$ cis $\gamma(\text{O-H})$	705

Table 4

Absorption bands in the range 1600–400  $\text{cm}^{-1}$  of PQH<sub>2</sub>-9, PQH<sub>2</sub>-3 and  $\alpha$ -TQH<sub>2</sub> before and after precooling. Abbreviations as in Tables 1 and 3

Position ( $\text{cm}^{-1}$ )	Assignment	Change after precooling
<b>PQH<sub>2</sub>-9</b>		
1594 w	$\nu(\text{C=C})$ ring	
1449 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	
1383 m	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	1384 m
1214 s	$\nu(\text{C-O})$	1215
1076 s	$\beta(\text{C-H})$ ring ? cryst.	875 m
837 m	$\gamma(\text{C-H})$ chain cryst. cryst.	835, 851 m 796 m 752 w
708 w		706 m
<b>PQH<sub>2</sub>-3</b>		
1594 w	$\nu(\text{C=C})$ ring	
1452.5 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	
1382 m	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	
1356 w		
1214 s	$\nu(\text{C=O})$	
1077 s	$\beta(\text{C-H})$ ring ?	
851 w, 834 w	$\gamma(\text{C-H})$ chain	
802 m		
706 w		
<b><math>\alpha</math>-TQH<sub>2</sub></b>		
1463 s	$\delta_{\text{as}}$ ( $\text{CH}_3$ ), $\delta(\text{CH}_2)$	1462
1377 m	$\delta_{\text{sym}}$ ( $\text{CH}_3$ )	
1320 m		1317
1247 s	$\nu(\text{C-O})$ ring	
1082 m		1080
912 m		
840 w		

PQ-9, in the PQH<sub>2</sub>-9 spectrum, after precooling, crystallization bands appear (Table 4), although of a lower intensity, which are not present in PQH<sub>2</sub>-9 spectrum directly after evaporation from hexane solution. The most apparent changes in the 1600–400  $\text{cm}^{-1}$  spectral range of Q-QH<sub>2</sub> mixtures occur in the C-O stretching region (Table 5). The strong  $\nu(\text{C-O})$  bands of PQH<sub>2</sub>-9 and PQH<sub>2</sub>-3 (Fig. 5) in liquid Q-QH<sub>2</sub> mixtures undergo strong reduction in intensity as compared to the spectra of individual hydroquinones. After solidification, new strong peaks appear at 1195  $\text{cm}^{-1}$  and at 1161–1162  $\text{cm}^{-1}$ , which correspond to  $\nu_{\text{as}}$  (C-O) and  $\nu_{\text{sym}}$  (C-O) vibrations of hydro-

Table 5

Absorption bands in the range 1600–400  $\text{cm}^{-1}$  of Q-QH<sub>2</sub> mixtures, Q-MGDG and Q-QH<sub>2</sub>-MGDG mixtures before and after precooling. Abbreviations as before

Position ( $\text{cm}^{-1}$ )	Assignment	Change after precooling
<i>PQ-9-PQH<sub>2</sub>-9</i>		
1448 s	$\delta_{\text{as}}(\text{CH}_3)$ , $\delta(\text{CH}_2)$	1447 s
1383 s	$\delta_{\text{sym}}(\text{CH}_3)$	1382
		new 1327 m
1319.5 m	Q (1316 m)	disappears
		new 1287 m
1245 m	O (1238.5 w)	sh
1215 w	$\nu(\text{C-O})$ , QH <sub>2</sub> (1214 s)	1212.5 sh
	$\nu_{\text{as}}(\text{C-O})$ CT	new 1195 m
	$\nu_{\text{sym}}(\text{C-O})$ CT	new 1161 m
1096 sh	Q (1101 m)	
1080 m	QH <sub>2</sub> (1076 s)	1077 m
984 w	Q	
		new 942.5 w
	cryst.	new 872 w
842 m	$\gamma(\text{C-H})$ chain	843
	cryst.	new 797 m, 755 w
710 w	QH <sub>2</sub>	700 s
<i>PQ-3-PQH<sub>2</sub>-3</i>		
1451 s	$\delta_{\text{as}}(\text{CH}_3)$ , $\delta(\text{CH}_2)$	1445
1380 s	$\delta_{\text{sym}}(\text{CH}_3)$	1377
		new 1327 m
1319.5 m	Q (1316 m)	disappears
		new 1288 m
1244 m	Q (1239 m)	1241 w
1214 w	$\nu(\text{C-O})$ , QH <sub>2</sub> (1214 s)	sh
	$\nu_{\text{as}}(\text{C-O})$ CT	new 1195 m
	$\nu_{\text{sym}}(\text{C-O})$ CT	new 1162 s
1080 s	QH <sub>2</sub> (1077 s)	1079
837 vw	$\gamma(\text{C-H})$ chain	840 s
801 m	QH <sub>2</sub>	799 s
709 w	QH <sub>2</sub>	700 m
<i><math>\alpha</math>-TQ-<math>\alpha</math>-TQH<sub>2</sub></i>		
1463 s	$\delta_{\text{as}}(\text{CH}_3)$ , $\delta(\text{CH}_2)$	
1377 s	$\delta_{\text{sym}}(\text{CH}_3)$	
1309 w	Q (1306 w)	1308
1254 m	$\nu(\text{C-O})$ , QH <sub>2</sub> (1247 m)	1253 m
1211 w		1214 w
1083 m	QH <sub>2</sub>	1081 w
1050 w	QH <sub>2</sub> (sh)	
917–932 m	Q (932 w)	
843 vw	QH <sub>2</sub> (840 w)	843 w
715 m	Q	713.5 m
<i>PQ-9-PQH<sub>2</sub>-9 bands in mixture with MGDG (1:1:5)</i>		
1319 w	Q	1324
		new ~1287 sh
	$\nu_{\text{as}}(\text{C-O})$ CT	new ~1200 sh
	cryst.	new 873 w, 796 w

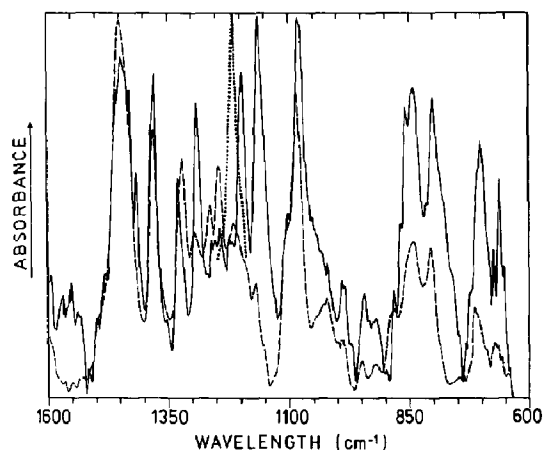


Fig. 5. FTIR absorption spectra of PQ-3-PQH<sub>2</sub>-3 mixture before (—) and after (---) precooling in the range 1600–600  $\text{cm}^{-1}$  and a fragment of PQH<sub>2</sub>-3 spectrum (.....) in the  $\nu(\text{C-O})$  region.

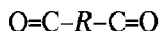
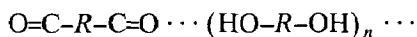
quinone OH groups hydrogen bonded to C=O groups of quinone in CT complex. Simultaneously,  $\nu(\text{C-O})$  peak of OH groups bound with each other nearly completely disappears.

A spectrum of PQ-9-PQH<sub>2</sub>-9 with MGDG mixture (1:1:5 molar ratio) shows characteristic peaks or shoulders (Table 5) indicating on CT interaction between PQ-9 and PQH<sub>2</sub>-9 also in the presence of MGDG.

#### 4. Discussion

The above-presented results give evidence that in the solid mixtures of PQ-9-PQH<sub>2</sub>-9 and PQ-3-PQH<sub>2</sub>-3 mixtures CT complexes stabilized by hydrogen bonds between components of the complex are formed. Such complexes can also occur in MGDG matrix as shown for the PQ-9-PQH<sub>2</sub>-9 system. Since in all cases where hydrogen bound quinone groups are formed, a small peak for free carbonyl group is also observed, the question arises as to what the proportion of the unbound carbonyl groups and the hydrogen bonded is. As calculated from Fig. 4, taking into account that the intensity of the  $\nu(\text{C=C})$  peak does not change after solidification, we can calculate that about 20% of all Q carbonyl groups remain in a free state. It is also evident that an increase in the

intensity of the hydrogen bound carbonyl group is much less than the decrease in intensity of the free carbonyl group. This is probably caused by a lower extinction coefficient of the hydrogen bound C=O group. Analogical calculations for PQ-3-PQH<sub>2</sub>-3 and PQ-9-PQH<sub>2</sub>-9-MGDG mixtures give values about 25% and 30%, respectively. In solid Q-QH<sub>2</sub> mixtures, where OH groups of hydroquinones are nearly exclusively hydrogen bound in dimers with both carbonyl groups of a Q molecule or with OH groups of other QH<sub>2</sub> molecules, some free Q molecules, or more probably complexes in which one C=O group is hydrogen bound and the other is free, may also be present. Since there is no peak for free OH groups observed (at  $\sim 3610\text{ cm}^{-1}$ ) in any of the mixtures, there cannot be complexes formed of the above type of 1:1 stoichiometry; however, complexes of Q/QH<sub>2</sub> ratio of 2:1 or 2:2 could explain the observed results as presented below:



where *R* is the Q or QH<sub>2</sub> ring, *n* is 1 or 2 and dotted lines represent hydrogen bonds. Here the molecules are shown in linear array but CT interactions would be most effective in a parallel arrangement of ring planes of all three components.

In the liquid state of Q-QH<sub>2</sub> mixtures, there are neither hydrogen bound C=O groups formed nor do free OH groups exist. Apart from free Q molecules, some of them are bound to QH<sub>2</sub> dimers (or small amounts of polymers) by  $\pi$ - $\pi$  CT interactions. This view is supported by some changes in the  $1600\text{--}400\text{ cm}^{-1}$  region of Q-QH<sub>2</sub> mixtures as compared to the superposition of the individual component spectra and also by the colour change of these mixtures.

In apolar solvents where the investigated prenylquinones form CT complexes with their reduced forms, it was also found that carbonyl groups do not form hydrogen bonds [4]. It is also known that phenols in concentrated solutions occur as dimers, whereas during diluting of such solutions, phenol dimers gradually dissociate into monomeric forms [20,21]. It means that Q-QH<sub>2</sub>

CT complexes at high concentrations in apolar solvents occur in Q:QH<sub>2</sub>  $\cdots$  QH<sub>2</sub> or Q:QH<sub>2</sub>  $\cdots$  QH<sub>2</sub>:Q forms, where ‘:’ stands for  $\pi$ - $\pi$  CT interaction and ‘ $\cdots$ ’ for hydrogen bonds. On diluting they would dissociate into Q:QH<sub>2</sub> and free monomeric QH<sub>2</sub>. It was found that in apolar solvents, a  $\nu(\text{C}=\text{O})$  band of PQ-9 occurs in a doublet form, whereas upon addition of PQH<sub>2</sub>-9 this splitting disappears [4], which is explained in terms of CT interaction. Splitting of the C=O band has been already reported for asymmetrically substituted quinones [22] and it may arise from the non-equivalent influence of other ring substituents on the two carbonyl groups, which can be further enhanced by the anisotropy of the immediate surroundings of the Q molecule. Absence of splitting of the C=O band was observed for all three pure quinones investigated in the present study and also for their solutions in nujol and n-octanol (data not shown). However, the increased temperature of PQ-9 solution in n-octanol induced reversible splitting of the carbonyl peak (data not shown). These facts suggest that the splitting occurs in media of low viscosity (hexane, CCl<sub>4</sub>, warmed n-octanol) and disappears at high viscosity (nujol, pure Q). This indicates that the mobility of PQ-9 molecules in apolar solvents on contact with PQH<sub>2</sub>-9 in the form of a CT complex undergo high deceleration, which can be easily explained if the PQ-9 molecule would be bound to PQH<sub>2</sub>-9 dimers.

The presence of crystallization bands in pre-cooled PQ-9 and PQH<sub>2</sub>-9 is probably due to skeletal vibrations of the side chain of these molecules in solid state and they are not influenced by PQ-9-PQH<sub>2</sub>-9 interaction or MGDG matrix. On the other hand, long-wavelength shift of PQ-9  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{C})$  ring vibrations which also occur after solidification of pure PQ-9, are not found in PQ-9-PQH<sub>2</sub>-9 alone, or in a mixture of these compounds with MGDG, because of the interaction of the PQ-9 ring with the PQH<sub>2</sub>-9 ring.

The results presented here show that FTIR spectroscopy can be applied to the investigation of CT complexes, especially for those that are associated with hydrogen bond formation.



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