Preparation of *p*-Phenylene-3,3'-bis(1-allyltetrahydrothiophenium) Dibromide and Its Reactions in Basic Solution

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p-Phenylene-3,3'-bis(1-allyltetrahydrothiophenium) dibromide **1**, prepared from *p*-phenylene-3,3'-diacrylaldehyde **3**, when treated with aqueous sodium hydroxide gave a sulfonium salt polymer. Pyrolysis of this in an attempt to form the highly conjugated polymer, poly(*p*-phenylenehexa-1,3,5-trienylene) gave, however, only carbonyl-containing compounds. Although no polymerization occurred in basic methanol, a reaction intermediate was shown by UV–VIS and ^{1}H NMR spectroscopy to have been formed.

Recently, interest has increased in conjugated polymers because of their potential as both electroconducting materials, and third-order non-linear optical (NLO) materials.[1-4] Poly(*p*-phenylenehexa-1,3,5-trienylene) (PPHT), a new polymer (Fig. 1), is expected to show high electroconductivity and NLO activity as a result of its extended π-conjugated system. Furthermore, it should be more stable than polyacetylene as a consequence of having phenylene groups in the polymer main chain. Although, we have previously synthesized PPHT by the Wittig reaction,[5,6] it was obtained as a powder which was only sparingly soluble in organic solvents, a result perhaps of its rigid structure. This problem made it impossible to prepare high quality PPHT films.

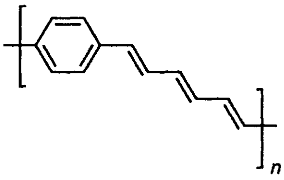


Fig. 1

Films of poly(arylenevinylene) polymers can be readily obtained from sulfonium salt pre-polymers, which are soluble in polar solvents, by pyrolysis. Since poly(*p*-phenylenevinylene) (PPV)[7] and its 2,5-disubstituted derivative[8] were so prepared ($\bar{M}_n$ values $> 3 \times 10^4$) and also poly(2,5-thienylenevinylene) (PTV),[9] poly(2,5-furylenevinylene),[10] poly(1,4-naphthalenevinylene)[11] and poly(2,5-selenophenediylvinylene),[12] we hoped to apply the same method to the synthesis of PPHT.

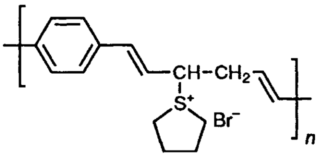
This paper reports the preparation of the sulfonium salt **1**, and its reaction upon treatment with aqueous and methanolic sodium hydroxide.

Results and Discussion

Preparation of the Sulfonium Salt **1**.—The synthetic route to the salt **1** is shown in Scheme 1. Although the diester **2** failed to react with lithium aluminium hydride (LAH) in benzene, in diethyl ether it was converted into the dialcohol **4** (40%).

However, since a side reaction resulted in the reduction of double bonds and production of by-products containing 3-hydroxypropyl groups, we attempted the reduction of the aldehyde **3** under the same conditions. While the reduction of cinnamaldehyde, a model compound, in benzene gave cinnamyl alcohol in high yield, no reaction occurred between the dialdehyde **3** and LAH under similar conditions. The reduction of the dialdehyde **3** to give the diol **4** (73%) was eventually achieved with sodium borohydride ($NaBH_4$) in water; methanol as solvent gave a lower yield of product. In addition to compound **4** the reaction mixture contained much material with only one reduced carbonyl group. Attempts to obtain higher yields at elevated temperatures (70 °C), or using a greater concentration of the dialdehyde were unsuccessful. The dibromide **5** was prepared from the diol **4** by a similar procedure to that given for cinnamyl bromide.[13] Reaction of this dibromide with tetrahydrothiophene (THT) in methanol–chloroform afforded the desired sulfonium salt **1** in high yield. The salt was somewhat unstable in air and gradually decomposed to an unidentified brown material over several months, even when stored at low temperature (5 °C).

Reaction of the Sulfonium salt **1** *in Aqueous Base*.—An aqueous solution of the salt **1** (0.050 mol dm^{-3}; 10 cm^3) at 0 °C and under a nitrogen atmosphere was treated dropwise with aqueous sodium hydroxide (0.10 mol dm^{-3}; 5 cm^3). The colour of the reaction mixture changed from colourless to deep yellow after a few minutes and a yellow precipitate was formed when the mixture was stirred for 1 h. The precipitate was filtered off and dried under reduced pressure at room temperature. Although a small amount of a sticky red material remained insoluble, most of the precipitate slowly dissolved in methanol, suggesting that it was a polymer. It was considered to be poly[*p*-phenylene{3-(tetrahydrothiophen-1-10)hexa-1,5-dien-1,6-ylene}bromide] **6** (Fig. 2).



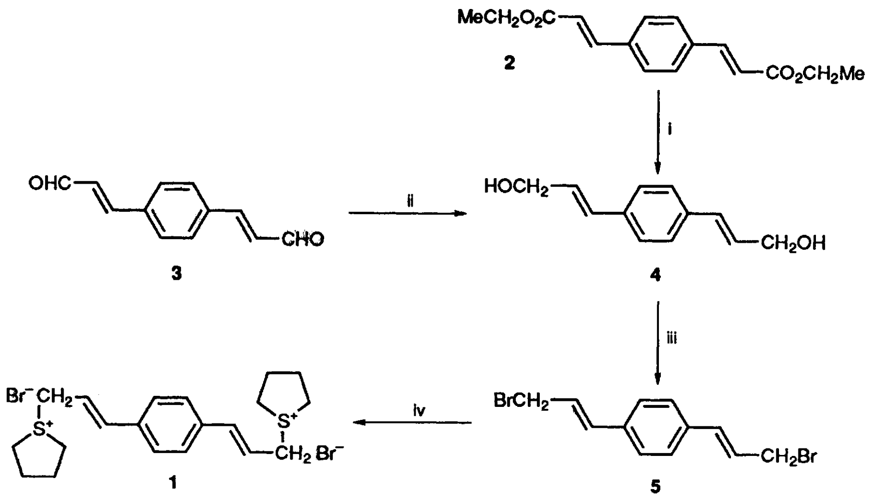
6

Fig. 2

The UV-VIS spectrum of the polymer **6** [Fig. 3(a)] has an absorption maximum at 292 nm, essentially the same as that of the salt **1** (299 nm).

This finding agreed with the expectation that the salt and polymer would differ little in the length of their chromophores. Weak absorption at 408 nm in the spectrum of the polymer but absent in that of the salt was attributed to the presence of an intermediate formed during polymerization. This is similar to the strong absorption at 412 nm which was observed when the reaction was conducted in basic methanol, and is discussed later in this paper.

The polymer **6** showed the following ^{1}H NMR signals: $\delta_H(CD_3OD)$ 7.5 (s br, ArH), 6.6, 6.3 and 6.0 (all br, olefinic H), 3.4–3.6 and 2.2–2.5 (all m, THT CH_2's) and 2.5–3.0 (polymer chain CH_2's). A CH signal was expected in the ^{1}H NMR



Scheme 1 *Reagents and conditions:* i, LAH in diethyl ether; ii NaBH$_4$ in H$_2$O; iii, PPh$_3$Br$_2$ in MeCN; iv, THT in MeOH–CHCl$_3$

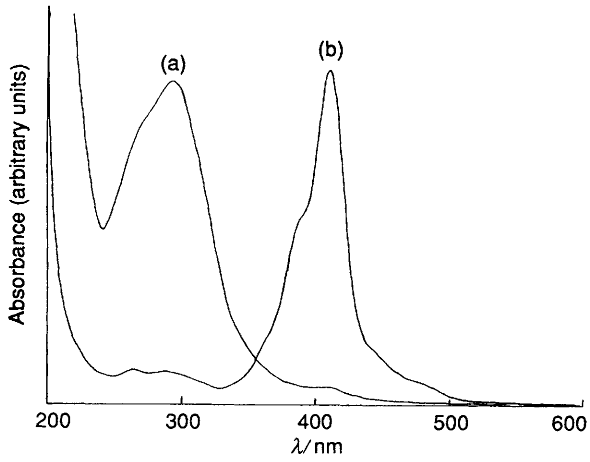


Fig. 3 UV–VIS spectra of (a) polymer **6** and (b) compound **X** in methanol

spectrum (observed in the pre-polymer PPV at δ 5.05)[14] but was not observed. Consideration of the effect of double bonds on the chemical shift of CH, led us to expect the signal to be at δ *ca.* 4.7 but the two strong resonances due to the solvent at δ 4.7 and 4.9 prevented this.

The polymer **6** showed IR absorption at 810 and 971 cm^{-1} (C–H deformations of *p*-disubstituted benzene rings and *trans* double bonds, respectively), 2923 and 2856 cm^{-1} (C–H stretching vibrations of the CH$_2$ and CH in the THT rings and the polymer main chain) and 1601 and 1168 cm^{-1} (new absorption observed after polymerization but unassigned). There was no carbonyl absorption at 1670–1730 cm^{-1}, indicating the absence of CHO or CO$_2$H groups.

Pyrolysis of the Polymer **6**.—In the expectation that pyrolysis of the polymer **6** would produce a film of PPHT, as in the case of PPV, a methanol solution of it was cast on a glass plate which was then heated at 250 °C for 2–4 h at 10^{-3} Torr. A yellow solid was obtained as a thermal product. Its IR spectrum showed absorption at 996 cm^{-1} (C–H out-of-plane vibration of the trienes), although the intensity was low. The peak at 1675 cm^{-1}, together with that due to the *trans*-vinylene groups at 962 cm^{-1}, indicated the presence of –CH=CH–CHO groups. Since the polymer **6** was free of carbonyl groups before pyrolysis (IR analysis), these were assumed to be formed either by decomposition of the polymer **6** during pyrolysis, or by oxidation of PPHT in air after pyrolysis. If the former is the case then the source of oxygen must be residual water and/or the hydroxide ion used in the polymerization and not oxygen from the air, since the pyrolysis was conducted *in vacuo*. Since these carbonyl groups must be formed by cleavage of the main chain of the polymer **6** or PPHT, it might be expected that there would be some soluble components formed in the process. However, no thermal products were found to be soluble in dichloromethane or methanol.

Similar findings have been reported in the preparation of PTV. Carbonyl compounds were found after pyrolysis even at 10^{-6} Torr.[15] In order to prevent the formation of these compounds, PTV was prepared by pyrolysis of the 'methoxy precursor polymer' with catalytic amounts of hydrochloric acid.[15] Unfortunately, in this case, the sulfonium groups of the polymer **6** could not be substituted with methoxy groups. For example, no change was detected in the NMR spectrum even after a methanol solution of the polymer had been stirred at room temperature. The polymer when stirred in methanol at reflux gave a product which was insoluble in methanol but soluble in chloroform. Its molecular weight was found to be 2–3,000 by gel-permeation liquid chromatography (polystyrene standard). However, the IR spectrum of the product was virtually the same as that obtained after pyrolysis at 250 °C.

Reaction of the Sulfonium Salt **1** *in Basic Methanol*.—The polymer **6** was obtained after the reaction of the salt **1** with aqueous sodium hydroxide. However, the polymer proved to be water-insoluble and no further polymerization appeared to occur. It was considered that the reaction of the salt **1** in basic methanol would give a polymer with higher molecular weight than that obtained in water, since both compounds **1** and **6** were soluble in methanol.

On adding a solution of sodium hydroxide (0.10 mol dm^{-3}, 1 cm^3) at 0 °C to a solution of the salt **1** (0.01 mol dm^{-3}, 10 cm^3) in methanol, the reaction mixture soon turned from colourless to intense yellow, a process followed by UV–VIS spectroscopy. The absorption of the salt at 299 nm disappeared and a new absorption emerged at 412 nm as the amount of added sodium hydroxide increased (Fig. 4).

When the solution was stirred at 0 °C for 2 h after the complete disappearance of the absorption at 299 nm it gave no further spectral change; however, slow discolouration was noted over a longer period (4–5 h) with the absorption maximum changing from 412 to 265 nm. The absorption maximum of this

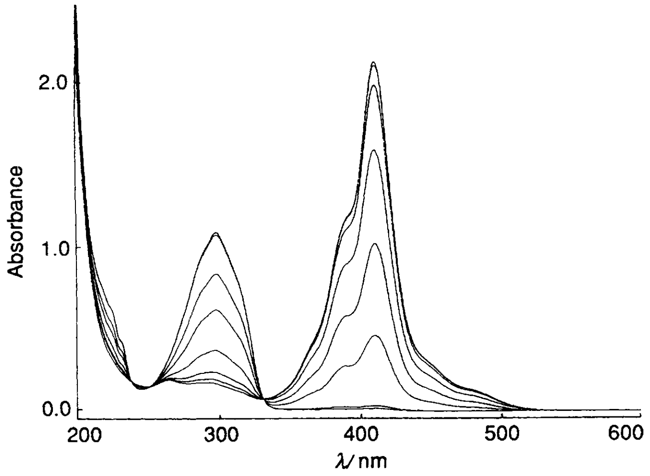
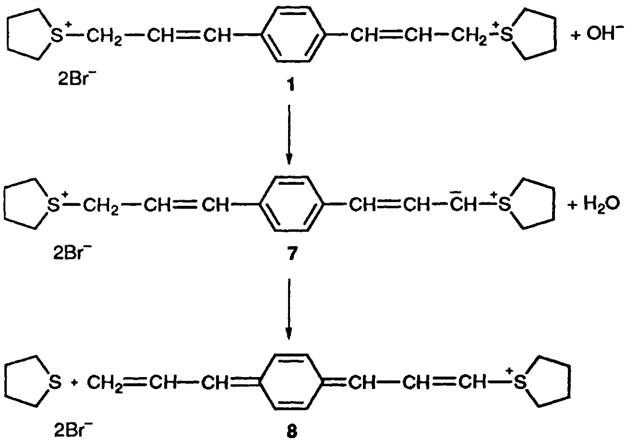


Fig. 4 Changes in UV–VIS spectra during the reaction of the salt **1** with sodium hydroxide in methanol at 0 °C

yellow material **X** was observed at a different wavelength to that of the polymer **6** (Fig. 3). If compound **X** is an unknown polymer, the absorption maximum should shift gradually to longer wavelength as polymerization proceeds. Actually, isosbestic points were observed at 332, 252 and 239 nm. Compound **X** was thus not a polymer but a low molecular weight material.

For the polymerization of the sulfonium salt monomer of PPV the 'Wessling mechanism' has been proposed, which includes a mono-ylide and a *p*-xylylene derivative as the reaction intermediates.[16–18] Therefore, compound **X** may possibly have the structure of either a mono-ylide **7** or *p*-xylylene derivative **8** (Scheme 2).



Scheme 2

For further clarification of the structure of compound **X**, the reaction was also followed by ^{1}H NMR spectroscopy. Measurements were carried out in deuteriomethanol at room temperature. When a solution of sodium hydroxide (1.6 mol dm^{-3}, *ca.* 0.05 cm^3) was added to one of the salt **1** (0.01 mol dm^{-3}, 0.7 cm^3), the spectrum showed the disappearance of the salt coincident with growth of new signals at δ 6–8 and those due to eliminated THT (δ 1.85–1.95 m and 2.70–2.80 m) (Fig. 5).

Two sets of multiplets at δ 2.2–2.5 and 3.4–3.7 were tentatively assigned to THT CH$_2$'s in compound **X**. Peak integrals of these signals showed that equimolecular amounts of compound **X** and free THT were formed from the salt. Although further experiments are required to confirm the peak assignments, these observations suggest that compound **X** is not the mono-ylide **7** formed by mere deprotonation of the salt, but actually the *p*-xylylene derivative **8** which should be formed from the ylide with elimination of THT. Compound **X** was quite stable so that the UV–VIS and NMR spectra could be obtained even in air at room temperature. This agreed with the expectation that the compound **8** is predicted to be stabilized by its long conjugated system.

While the salt **1** produced the polymer **6** in aqueous base, it gave no polymer in methanol. The failure of the polymerization in methanol is attributed to either the low solubility of the salt, or to the higher stability of the reaction intermediate resulting in a stopped reaction. Further investigations into the reactions of the salt **1** in basic methanol are now in progress, and the results will be reported elsewhere.

Experimental

M.p.s were determined on a Laboratory Device Mel-Temp melting point apparatus and are reported uncorrected. High resolution mass spectra were obtained using a Hitachi M-80B instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 270 spectrometer with tetramethylsilane as internal reference; *J* values are given in Hz. IR and UV–VIS spectra were recorded on a Perkin-Elmer 1720 and a Hitachi U-3210 spectrometer, respectively.

p-Phenylene-3,3'-bis(ethyl acrylate) **2** was prepared from *p*-phenylene-3,3'-diacrylic acid (Aldrich) according to the literature.[19] *p*-Phenylene-3,3'-diacrylaldehyde **3** was synthesized by aldol condensation between acetaldehyde and terephthaldehyde.[20]

p-*Phenylene*-3,3'-*bis*(*allyl alcohol*) **4**.—*Reduction of the diester* **2**. To a solution of the diester **2** (0.50 g, 1.8 mmol) in freshly distilled diethyl ether (100 cm^3) was added a suspension of LAH (0.35 g, 9.1 mmol) in diethyl ether (35 cm^3). After the mixture had been stirred at −20 °C for 3–4 h, it was diluted with water (300 cm^3) and then poured into saturated aqueous ammonium tetrachloride. The products were extracted with diethyl ether (500 cm^3) and the extract was washed with water (500 cm^3), dried (MgSO$_4$), and evaporated under reduced pressure to give a yellow oil. This crystallized from chloroform to afford of the *dialcohol* **4** (0.14 g, 40%); m.p. 135–136 °C (Found: M$^+$, 190.0994. Calc. for $C_{12}H_{14}O_2$: *M*, 190.0993); δ_H(270 MHz; CDCl$_3$) 7.35 (4 H, s), 6.60 (2 H, dt, *J* 15.83 and 1.32), 6.37 (2 H, dt, *J* 15.83 and 5.61) and 4.33 (4 H, dd, *J* 5.60 and 1.32). The OH protons were not detected; ν_{max}(KBr)/cm^{-1} 3367s, 2920w, 2856w, 1654m, 1511m, 1085s, 1007s, 972sh, 967s, 855m and 776m.

Reduction of the dialdehyde **3**. A mixture of the dialdehyde **3** (0.50 g, 2.7 mmol) and NaBH$_4$ (0.13 g, 3.4 mmol) was stirred in water (25 cm^3) for 20 h at 40 °C. This suspension was diluted with water (250 cm^3) and then quenched with saturated aqueous sodium carbonate (250 cm^3). The products were extracted with diethyl ether (500 cm^3) and the extract was dried (MgSO$_4$) and evaporated under reduced pressure. Recrystallization of the residue from benzene gave the dialcohol **4** (0.37 g, 73%), the NMR spectrum of which was identical with that of the alcohol obtained from the diester **2**.

p-*Phenylene*-3,3'-*bis*(*allyl bromide*) **5**.—A solution of bromine (8% w/w) in acetonitrile was added dropwise to a solution of triphenylphosphine (0.83 g, 3.2 mmol) in acetonitrile (30 cm^3) at 0 °C until the resultant solution was slightly yellow. Addition of a little triphenylphosphine turned the solution colourless. After the mixture had been stirred for 1 h, a solution of the diol **4** (0.30 g, 1.6 mmol) in acetonitrile (150 cm^3) was added to it and the mixture was stirred for a further 1 h at room temperature. The solvent was evaporated under reduced pressure. Ethanol in water (60%, 150 cm^3) was added to the residue and the resulting precipitate was filtered and dried at room temperature to give

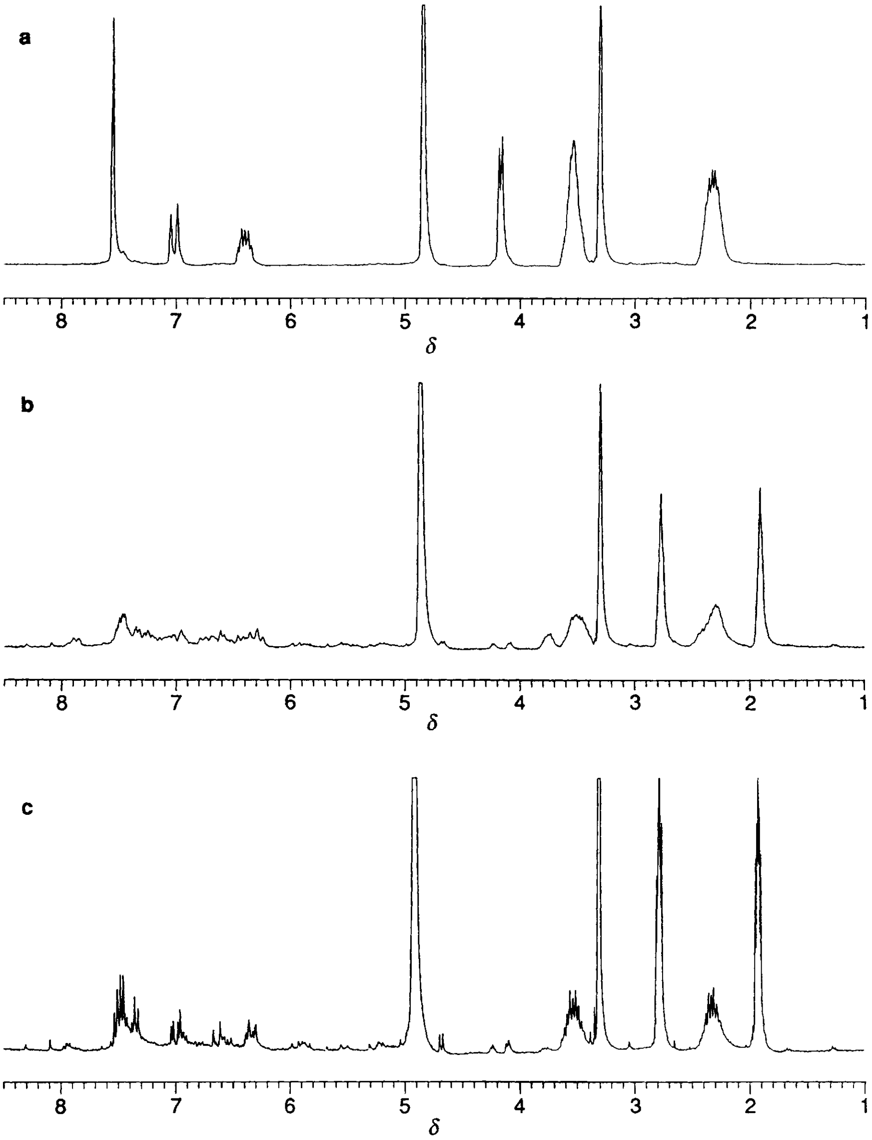


Fig. 5 Changes in NMR spectra during the reaction of the salt **1** with sodium hydroxide in deuteriomethanol at room temperature; **a** before reaction, **b** reaction time 10 min, and **c** 40 min

the pure *dibromide* **5** as pale yellow crystals (0.35 g, 69%); m.p. 160–162 °C (Found: M^+, 313.9338. Calc. for $C_{12}H_{12}Br_2$: *M*, 313.9306); δ_H(270 MHz; $CDCl_3$) 7.35 (4 H, s), 6.63 (2 H, d, *J* 15.50), 6.41 (2 H, dt, *J* 15.50 and 7.75) and 4.17 (4 H, dd, *J* 7.75 and 0.81); ν_{max}(KBr)/cm^{-1} 1642w, 1436w, 1412w, 1213sh, 1200s, 1139w, 972s, 966s, 810s, 585m and 514m.

p-*Phenylene*-3′,3′-*bis*(1-*allyltetrahydrothiophenium*) *Dibromide* **1**.—THT (0.61 g, 6.9 mmol) was added dropwise to a solution of the bromide **5** (0.10 g, 0.32 mmol) in chloroform (15 cm^3) and methanol (35 cm^3). The mixture was stirred at 0 °C for 30 min and then at room temperature for 7 h. After concentration of the mixture under reduced pressure acetone (50 cm^3) was added to it. The resulting precipitate was filtered off and dried at room temperature to give the *sulfonium salt* **1** as a pale yellow solid (0.12 g, 76%); m.p. 164 °C (decomp.); δ_H(270 MHz; CD_3OD) 7.55 (4 H, s), 7.01 (2 H, d, *J* 16.07), 6.40 (2 H, dt, *J* 15.44 and 7.72), 4.16 (4 H, d, *J* 7.43), 3.41–3.66 (8 H, m) and 2.19–2.47 (8 H, m); δ_C(67.8 MHz; CD_3OD) 142.50, 138.19, 129.48, 118.12, 46.83, 44.16 and 30.67; ν_{max}(KBr)/cm^{-1} 3025w, 2969m, 2950m, 1644m, 1510w, 1413s, 1313m, 1261w, 1072m, 988s, 910w, 863w, 814w, 625w and 520m.

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