

203. *Properties of Ion Pairs formed by Proton Transfer to Methoxyphenylpolyenealdehydes.*

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The light-absorption spectra of  $\omega$ -*p*-methoxyphenylpolyenealdehydes with 1—7 conjugated double bonds have been measured with and without trichloroacetic acid in benzene and in benzene-dioxan. The observed effects, together with the results of electrical conductivity measurements, show that proton transfer from the acid to the polyenes takes place. Equilibrium coefficients of these reactions have been determined.

THE basicity of carotene and azulene is sufficient for proton-transfer reactions to be studied in aprotic solvents. It is of interest to extend earlier experiments<sup>1,2</sup> by varying the nature of the conjugated polyene, in a systematic manner, while using one and the same acid. The present investigation deals with the proton-acceptor properties of  $\omega$ -*p*-methoxyphenylpolyenealdehydes,<sup>3</sup>  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}:\text{CH}]_n\cdot\text{CHO}$  ( $n = 1-7$ ), the proton donor being trichloroacetic acid.

EXPERIMENTAL

The seven polyenealdehydes were kept in evacuated containers at 0° in the dark until shortly before use. The m. p.s agreed with the published values.<sup>3</sup> Commercial dioxan was dried and redistilled. The purification of trichloroacetic acid, ethyl trichloroacetate, and benzene, and the techniques used for carrying out spectrophotometric and conductivity measurements have

<sup>1</sup> Wassermann, *J.*, 1954, 4239.

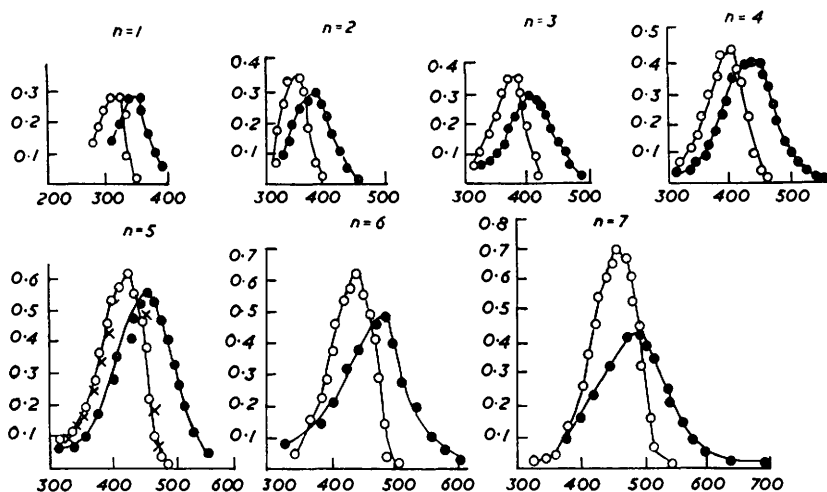
<sup>2</sup> Wassermann, *ibid.*, 1955, 585.

<sup>3</sup> Marshall and Whiting, *ibid.*, 1956, 4082.

been described.<sup>1</sup> In the optical tests, the solutions contained the antioxidant  $\alpha$ -tocopherol in concentration about 20 times smaller than that of the polyene. Control experiments showed that  $\alpha$ -tocopherol had no effect, except to prevent a small drift of the optical densities of solutions containing acid. Concentrations of trichloroacetic acid were calculated from the stoichiometric molecular weight, as in previous papers; <sup>1, 2, 4</sup> it is realised that this acid forms a dimer under the conditions of these experiments.

*Results.*—The light absorption of these polyenealdehydes with and without trichloroacetic acid in benzene solution is shown in Fig. 1. On addition of acid there is a shift of the spectra

FIG. 1. Light absorption of  $\omega$ -p-methoxyphenylpolyenealdehydes.



$n$  = no. of conjugated double bonds. Temp.  $\sim 20^\circ$ . Ordinate,  $10^{-5}\epsilon$ ; abscissa, wavelength ( $\mu$ ). Solvents:  $\circ$ , benzene (no acid);  $\times$ , benzene, 1.0M with respect to ethyl trichloroacetate;  $\bullet$ , benzene, 1.84M with respect to trichloroacetic acid.

towards longer wavelength, which is responsible, in most cases, for a visual change of colour (Table 1). The spectra of these polyenes were also measured in a benzene solution which was

TABLE 1. Colour of benzene solutions of  $\omega$ -p-methoxyphenylpolyenealdehydes. (In these tests the solution was  $\sim 10^{-5}M$  in polyene and  $\sim 0.5M$  in trichloroacetic acid; temp.  $\sim 20^\circ$ .)

No. of conjugated double bonds, $n$ ...	1	2	3	4	5, 6, 7
Without acid .....	Colourless	Colourless	Pale yellow	Pale yellow	Yellow
With acid .....	Colourless	Pale yellow	Yellow	Deep yellow	Red

1M with respect to ethyl trichloroacetate, in benzene-dioxan, and in chloroform. The absorption spectra are not significantly altered by addition of dioxan and ethyl trichloroacetate, or by using chloroform instead of benzene. This is shown in Figs. 1 and 5 and in Table 2, where  $\lambda_{\max}$  and  $\epsilon_{\max}$  in the range 290—1000  $\mu$  are listed. (For definition of  $\epsilon$  see ref. 1; the values for chloroform solution were taken from ref. 3.)

The relatively large alteration of the spectra on addition of acid (A) is interpreted as being due to a proton transfer from (A) to the polyene (B):



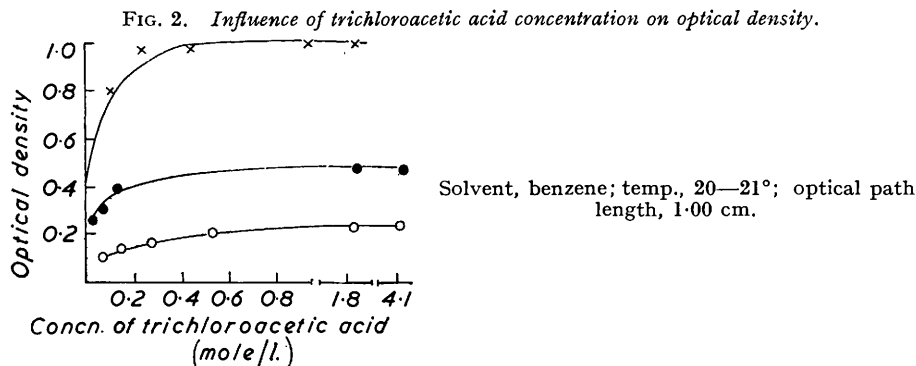
where  $C^+ \dots D^-$  is an ion pair. The proportion of B converted into  $C^+ \dots D^-$  can be determined by measuring optical density as a function of acid concentration, as shown in Fig. 2 for the polyenes with  $n = 1, 4$ , and 7. Similar results were obtained with light of other wavelengths, with solutions of the other polyenes, and with different concentrations of these proton

<sup>1</sup> Rubin, Steiner, and Wassermann, *J.*, 1949, 3046.

acceptors. It is assumed, as before,<sup>1,2</sup> that  $\alpha$  in eqn. (1) is unity and that the equilibrium coefficient of this proton transfer is given by

$$K = ([C^+ \dots D^-]/[A][B]) \times f_{O^+ \dots D^-} / f_A \times f_B$$

where the factor in the round brackets, designated by  $K'$ , is estimated from optical densities,  $K$  being deduced from  $K'$  by an extrapolation method.<sup>1,2</sup> The assumption that  $\alpha$  is unity is



Symbol .....	×	●	○
$n$ .....	1	4	7
Polyene concn. (mole/l. $\times 10^5$ ) .....	5.52	1.52	1.14
Wavelength of light ( $m\mu$ ) .....	360	460	560

The part of the abscissa covering the range 0.9–4.1 is not drawn to scale.

FIG. 3. Equilibrium measurements with polyene,  $n = 3$ . Influence of the trichloroacetic acid concentration on  $\log_{10} K'$ .

Solvent, benzene; temp., 21°; wavelength, 440  $m\mu$ ;  $10^5[\text{polyene}]$ : ○ = 1.64, ● = 4.92. Value of  $(\log_{10} K')_{[A] \rightarrow 0} = 1.47 \pm 0.02$ ;  $K = 30 \pm 3$  l./mole.

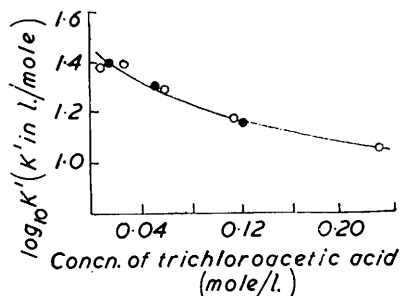


TABLE 2. Light absorption ( $\lambda$  in  $m\mu$ ) of  $\omega$ -*p*-methoxyphenylpolyenealdehydes.

(Solvents: b = benzene; b + d = benzene, 4.54M in dioxan; c = chloroform. Temp.  $\sim 20^\circ$ .)

$n$	Solvent	Without acid				$n$	Solvent	Without acid			
		$\lambda_{\text{max.}}$	$10^{-5}\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$10^{-5}\epsilon_{\text{max.}}$			$\lambda_{\text{max.}}$	$10^{-5}\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$10^{-5}\epsilon_{\text{max.}}$
1	b	320	0.28	345	0.28	5	b	420	0.62	450	0.57
	b + d	320	0.27				b + d	420	0.65		
	c	321	0.31				c	426	0.68		
2	b	350	0.35	380	0.30	6	b	440	0.63	475	0.48
	b + d	350	0.33				b + d	440	0.62		
	c	352	0.42				c	443	0.77		
3	b	375	0.34	410	0.29	7	b	455	0.68	485	0.43
	b + d	378	0.38				b + d	460	0.53		
	c	380	0.52				c	459	0.90		
4	b	400	0.42	435	0.38						
	b + d	400	0.42								
	c	403	0.61								

consistent with the observation that  $(K')_{[A] \rightarrow 0}$  is independent of the initial concentration of the polyene,  $[B]$ , within the limits of the specified experimental error. If it is assumed that  $\alpha > 1$  or  $\frac{1}{2}$  the extrapolated  $K'$  values depend on  $[B]$ . For the polyene with  $n = 3$ , for example, measurements at different acid concentrations with  $[B] = 1.65 \times 10^{-5}$  and

$4.92 \times 10^{-5}$  mole/l. were carried out. In both sets  $K'_{[A] \rightarrow 0}$  was  $30 \pm 3$  l./mole, if  $\alpha$  was taken as unity. If, however, an  $\alpha$  value of 2 was employed, extrapolated  $K'$  values of respectively  $4 \times 10^3$  and  $8 \times 10^3$  (l./mole)<sup>2</sup> were computed; and similar discrepancies occur if it is assumed that  $\alpha = \frac{1}{2}$ . An alternative expression of a "concentration" equilibrium coefficient, in which activity corrections are omitted, is <sup>5</sup>  $K'' = S/i$ , where  $S$  is the slope and  $i$  the intercept of the plot of  $[A][B]/d_A$  against  $[A]$  ( $d_A =$  optical density).  $K''$  can be determined, with sufficient

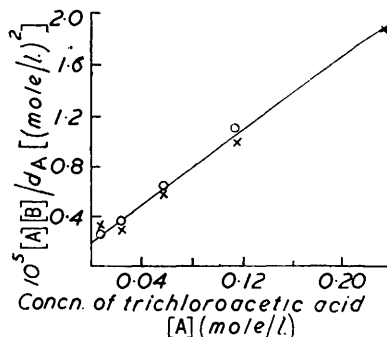


FIG. 4. *Equilibrium measurements with polyene, n = 4. Influence of trichloroacetic acid concentration on [A][B]/d<sub>A</sub> (for significance of symbols, see text).*

Solvent, benzene; temp., 20°; wavelength 480 mμ; optical path length, 1.00 cm.; 10<sup>5</sup>[Polyene]: × = 1.52; ○ = 4.56;  $K'' =$  slope/intercept =  $33 \pm 3$  l./mole.

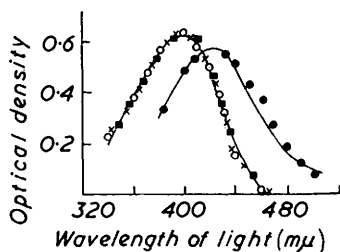
accuracy, by varying  $[A]$  between 0.02 and 0.2 mole/l., whereas an estimation of  $K'$  involves measurements with  $[A] > 0.5$  mole/l. Results of typical experiments showing the dependence of  $\log K'$  and of  $[A][B]/d_A$  on  $[A]$  are in Figs. 3 and 4. Table 3 shows the values of  $K$  and  $K''$ , the wavelengths of the light used, and the polyene concentrations.

TABLE 3. *Equilibrium coefficients of proton-transfer reactions in benzene at ~20°.*

No. of conjugated double bonds, $n$	$K$	$K''$	$\lambda$ (mμ)	10 <sup>5</sup> [polyene]
		(l./mole)		
1	25 ± 3	28 ± 3	350, 360	1.84, 5.52
2	30 ± 4	25 ± 3	400	3.12
3	30 ± 3	30 ± 4	420, 440, 460	1.64, 4.92
4	32 ± 3	33 ± 4	460	1.52, 4.56
5	32 ± 3	31 ± 3	480, 500	1.33, 3.99
6	36 ± 4	34 ± 4	520	1.12, 3.36
7	32 ± 3	31 ± 3	560	0.114, 1.14

If benzene solutions of these polyenes, B, are made 4–5M with respect to dioxan no significant change occurs in the spectra. If, on the other hand, the same amount of dioxan is added to a benzene solution of the polyene-trichloroacetic acid adduct, C<sup>+</sup> . . . D<sup>-</sup>, there is a change of the spectra as shown by the typical results in Fig. 5. Similar observations were made with all the other polyenes.

FIG. 5. *Influence of dioxan on the light absorption by an adduct C<sup>+</sup> . . . D<sup>-</sup>; experiments with polyene, n = 4.*



Solvent, benzene; temp., 21°; optical path length, 1.00 cm. A solution was made,  $3 \times 10^{-5}$ M in polyene and 0.2M in trichloroacetic acid; immediately after mixing, solvent and dioxan were added, the final solution being 4.54M in dioxan,  $1.52 \times 10^{-5}$ M in polyene, and 0.115M in acid. Results with this solution are denoted by ×; those with other solutions were:

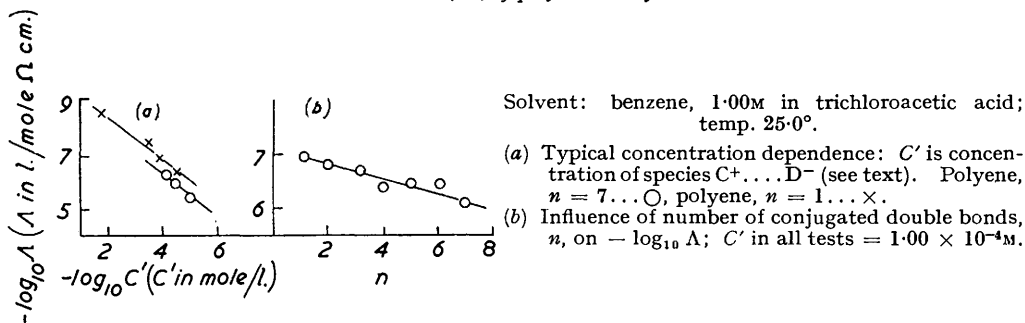
- 1.52 × 10<sup>-5</sup>M in polyene and 0.115M in acid; no dioxan . . . . . ●
- 1.52 × 10<sup>-5</sup>M in polyene, 4.54M in dioxan; no acid . . . . . ○
- 1.52 × 10<sup>-5</sup>M in polyene; no dioxan, no acid . . . . . ■

The specific electrical conductance,  $\kappa$ , of the adducts C<sup>+</sup> . . . D<sup>-</sup> in benzene solution, 1.00M in trichloroacetic acid, is larger than that of the acid or the polyenes alone, as shown by the following typical figures, relating to 25.0° and to the polyene,  $n = 1$ :  $\kappa \times 10^{11}$  ( $\Omega^{-1}$  cm.<sup>-1</sup>) was  $2.48 \pm 0.03$ ,  $1.00 \pm 0.10$ , and  $0.03 \pm 0.01$ , respectively, for solutions (i)  $2.76 \times 10^{-5}$ M in

<sup>5</sup> Page, *Trans. Faraday Soc.*, 1953, **49**, 637.

polyene and 1.00M in acid, (ii) 1.00M in acid (no polyene), and (iii)  $1.84 \times 10^{-2}$ M in polyene (no acid). Molar electrical conductivities,  $\Lambda$ , were computed from  $\Lambda = (\kappa - \kappa')/c'$ , where  $\kappa$  and  $\kappa'$  are the specific conductances of  $C^+ \dots D^-$  in the presence of acid and of the acid alone and  $C'$  is the concentration of  $C^+ \dots D^-$ , which is practically identical with the stoichiometric concentration of B. The concentration dependence of  $\Lambda$  as observed in two typical experiments, and the various  $\Lambda$  values for a specified concentration  $C'$ , are in Fig. 6. The range of  $C'$  values for the two polyenes with  $n = 1$  and 7 is shown in Fig. 6(a). These

FIG. 6. Molar electrical conductivities,  $\Lambda$ , of polyene aldehyde-trichloroacetic acid adducts.



polyenes are the most and the least soluble member of the series respectively;<sup>3</sup> the concentration range in the experiments with the other polyenes was intermediate between those specified in the Figure.

#### DISCUSSION

The equilibrium coefficients are represented by  $RT \ln K = T\Delta S - \Delta H = T\Delta S_g + T\Delta S_1 - \Delta H_g - \Delta H_1$ , where the overall entropy and heat changes,  $\Delta S$  and  $\Delta H$ , are split into  $\Delta S_g$  and  $\Delta H_g$  relating to reaction (1) in the gas phase, and into  $\Delta S_1$  and  $\Delta H_1$ , the entropies and heats of solution. Addition of protons to these methoxypolyenealdehydes leads to mesomeric carbonium-ion derivatives, which are stabilised by resonance energy. If it is assumed that the proton adds to the carbonyl or methoxy-groups, the resonance energy must increase with increasing number,  $n$ , of repeating  $\text{CH}:\text{CH}$  units; and it is probable, therefore, that the numerical value of  $\Delta H_g$  will also increase on passing from the ion pair  $(C^+ \dots D^-)_{n-1}$  to  $(C^+ \dots D^-)_{n-7}$ . The figures in Table 3 show, however, that the  $K$  values relating to these proton additions in benzene solution remain practically constant. This is probably due to the fact that the trends of  $\Delta H_g$  and  $\Delta H_1$  oppose each other, the ion pair with the smallest number of conjugated double bonds being most extensively solvated, because of reduced delocalisation of the positive charge. Furthermore, the possibility must be considered of a second compensating mechanism, in which the influence of  $\Delta H_g$  and  $\Delta H_1$  is counteracted by that of  $\Delta S_g$  and  $\Delta S_1$ .

The postulated proton transfer in reaction (1) is in accordance with the observed influence of the basic solvent dioxan, which decomposes the ion pair  $C^+ \dots D^-$ , with quantitative re-formation of the polyenes. Thus, under appropriate experimental conditions, reaction (1) is not necessarily disturbed by side and consecutive reactions. These effects are shown by the typical results in Fig. 5, from which it follows that the basic solvent competes successfully with the polyene for the proton derived from the acid.

The charge separation in these proton-transfer reactions to polyenes is proved by the electrical conductance of the adducts  $C^+ \dots D^-$ . The molar electrical conductivities,  $\Lambda$  (Fig. 6), are either larger than those of authentic salts in benzene solution, at comparable concentration, or of the same order. Conductance maxima or minima were not observed in the limited range of concentration tested, there being a linear functional relation between  $\log \Lambda$  and the logarithm of the concentration, as in the previously investigated systems.<sup>1,2</sup> This indicates<sup>6</sup> that triple ions or higher aggregates play no significant rôle

<sup>6</sup> Fuoss and Krauss, *J. Amer. Chem. Soc.*, 1933, **55**, 2387; Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206.

and that the carriers of electric current are formed by  $C^+ \dots D^- \rightleftharpoons C^+ + D^-$ . This equilibrium must be far to the left-hand side, because the dielectric constant of solvent and co-solvent <sup>7</sup> is small.

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<sup>7</sup> Le Fèvre and Vine, *J.*, 1938, 1795.

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