162. *Dipole Moments of Polyene–Acid Adducts.*

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The dipole moments of polyene–acid adducts in benzene are relatively large, comparable with, or greater than, the moments of authentic ion-pairs in the same solvent. This confirms the previous suggestion that the adducts are also ion-pairs formed by proton transfer to the conjugated double bonds of the polyenes.

It has been reported [1] that, in aprotic solvents, acids HA and conjugated polyenes P undergo a reversible reaction:

$$\mathrm{HA} + \mathrm{P} \rightleftharpoons \mathrm{Adduct} \qquad \text{(A)}$$

These adducts have been characterised by their equilibrium coefficients, K', electronic spectra, and electrical conductances. The dipole moments of some of these adducts have now been deduced from measurements of benzene solutions and are compared with those of the free polyenes, the acids, and the corresponding tri-n-butyl- and triethyl-ammonium salts.

Experimental and Results

Purification of the polyenes and of the acids has been described.[1] Benzene was fractionally crystallised, and kept over sodium wire. Dielectric constants were determined at 10^6 c.p.s.

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[1] Wassermann, *J.*, 1954, 4329; *J.*, 1959, 983, 986; *Mol. Phys.*, 1959, 2, 226; French, Roubinek, and Wassermann, *J.*, 1961, 1953.

and 25° by a heterodyne-beat method by means of an apparatus similar to that of Few, Smith, and Witten [2] modified so as to increase the accuracy of measurements for solutions of very low concentration.

The orientation polarisation, ${}_{\mu}P_2$, of a solute is given approximately by: [3]

$$ {}_{\mu}P_2 = 3M_2v_1(\alpha - \gamma)/(\varepsilon_1 + 2)^2, \tag{1}$$

where M_2 is the molecular weight of the solute, v_1 and ε_1 are the specific volume and dielectric constant, respectively, of the solvent, and α and γ are the limiting values of $d\varepsilon/dw$ and dn^2/dw, respectively, at zero concentration, w being the weight fraction of solute. For the trialkylammonium salts $\alpha \gg \gamma$, and it has been assumed that this holds also for the polyene–acid adducts, the solutions of which were too highly coloured to permit study of their refractive indices. Hence, since the solute concentration c (in mole/l.) is given by $100w/M_2v$ it follows that

$$ {}_{\mu}P_2 = 3M_2v_1\alpha/(\varepsilon_1 + 2)^2 = 3000\alpha'/(\varepsilon_1 + 2)^2, \tag{2}$$

where α' is the limiting value of $d\varepsilon/dc$ at zero concentration. This is a modified form of the Guggenheim relation,[4] from which the dipole moment can be derived in the usual way as $\mu = 0{\cdot}01281\sqrt{({}_{\mu}P_2T)}$.

In determinations of ${}_{\mu}P_2$ for the polyene–acid adducts the solid polyene was dissolved in measured volumes of a stock solution of the acid in benzene. The polyene concentration was in all cases so small that reaction (A) did not significantly alter the acid concentration. In calculating α' of eqn. (2), it had to be taken into account that in these experiments $\Delta\varepsilon$ and c are not overall values but relate to the polyene–acid adducts. These $\Delta\varepsilon$ values, which varied with time owing to consecutive reactions,[1] were extrapolated back to the time of mixing the polyene with the acid, thereby affording a dielectric-constant increment $\Delta\varepsilon_0$ over the value for the solvent. The extrapolated increment was taken to be the sum of two terms, namely, $\Delta\varepsilon_0 = \Delta\varepsilon_a + \Delta\varepsilon_p$, $\Delta\varepsilon_a$ relating to the adduct and $\Delta\varepsilon_p$ to the " free " polyene. Upper limits of the latter term were estimated by measuring the dielectric constants of the polyenes in benzene without acid, the upper limits of the dipole moments (25°) being β-carotene 2·8, methylbixin 5·4, lycopene 2·8, and polymer A 4·4 D. Polymer A (French, *et al.*[1]) was prepared from cyclopentadiene under conditions conducive to formation of conjugated double bonds. For estimation of $\Delta\varepsilon_\mu$ a knowledge of the concentration of the " free " polyene is also required; this was calculated from the stoicheiometric concentrations and the equilibrium coefficients, K'.

The range of stoicheiometric polyene concentration is shown in the fifth column of Table 1, the last column giving the dipole moments of the polyene–acid adducts, the error of which is about ±10%. This is greater than that of conventional dipole-moment measurements, because extrapolation was necessary to obtain $\Delta\varepsilon_0$ and because the concentration of the polyene–acid adduct, computed from the stoicheiometric concentrations and K', was in some experiments the difference of terms of similar magnitude. In most measurements with trichloroacetic or

TABLE 1.

Dipole moments of polene–acid adducts in benzene at 25°.

Polyene	Acid (co-solvent)	Molarity acid	K' (mole/l.)	[Polyene] (10^{-3} mole/l.)	No. of solns.	Dipole moment (D)
β-Carotene	$CCl_3{\cdot}CO_2H$	0·990	6·0	0·336—5·32	6	8·2
β-Carotene	,,	0·493	0·96	1·37—5·70	3	20
β-Carotene	,,	0·248	0·63	2·10—5·79	3	18
Methylbixin	,,	1·00	4·0	1·15—9·16	3	8
Lycopene	,,	1·00	4·0	0·569—3·98	4	12
Polymer A	,,	1·00	6·1	0·409—8·17	4	19
β-Carotene	$CH_2Cl{\cdot}CO_2H$	0·859	<0·02	1·19—5·97	3	>30
Polymer A	,,		0·060	2·10—8·83	3	>16
β-Carotene	Picric acid	0·342	3·0	0·663—2·61	3	7·3
β-Carotene	,,	0·229	3·0	0·754—2·96	3	7·3
Polymer A	,,	0·229	10	3·22—11·4	3	3·7

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[2] Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.

[3] Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

[4] Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

TABLE 2.

Dipole moments of trialkylammonium salts in benzene at 25°.

Solute		Concn. (10^{-3} mole/l.)	No. of solns.	Dipole moment (D)	
				Bauge and Smith [5]	Previous work
$NHBu^n_3$	trichloroacetate *	10·0—40·0	3	9·0	—
$NHBu^n_3$	trichloroacetate	1·30—43·0	16	9·25	—
$NHEt_3$	trichloroacetate	0·870—23·5	6	8·80	—
$NHBu^n_3$	monochloroacetate	1·30—56·0	12	6·25	—
$NHEt_3$	monochloroacetate	1·43—37·2	6	6·73	—
$NHBu^n_3$	picrate	0·400—14·0	19	11·84	13·1,[a] 11·9,[b] 11·4 [c]
$NHEt_3$	picrate	0·660—19·4	6	11·66	11·7 [b]

[a] Geddes and Kraus.[9] [b] Maryott.[10] [c] Davies and Williams.[11]

* With M-$CCl_3{\cdot}CO_2H$ as co-solvent.

picric acid $\Delta\varepsilon_a$ was larger than $\Delta\varepsilon_p$, the estimated error of about ±10% also taking care of the fact that only upper limits of $\Delta\varepsilon_p$ could be determined. The equilibrium coefficients, K', of trichloroacetic or picric acid are larger than those of monochloroacetic acid. With the latter acid $\Delta\varepsilon_a$ was not larger than $\Delta\varepsilon_p$, because the position of equilibrium (A) is shifted towards the left-hand side; thus the dipole moments in lines 7 and 8 of Table 1 are merely lower limits, the numerical values of which depend very markedly on those of K'. Moreover, a sufficiently accurate K' value for the β-carotene–monochloroacetic acid adduct could not be determined (see ref. 1) and the value of 0·02 l./mole is an upper limit.

The dipole moments of some alkylammonium salts are in Table 2; these results, included for comparison, are taken from a more precise investigation [5] at present in progress. The following dipole moments in benzene are also of interest here: trichloroacetic acid [6] 2·0, monochloroacetic acid [7] 2·29, picric acid [8] 1·51, tri-n-butylamine [5] 0·877, and triethylamine [5] 0·855 D. It will be seen, therefore, that most of the dipole moments in Tables 1 and 2 are large compared with the sum of the moments of the constituent acid and polyene or amine.

DISCUSSION

The solutes listed in the first column of Table 2 and other ammonium salts are known to form ion-pairs in benzene solution, the relatively large dipole moments [9-11] being essentially the result of charge separation. The moments of most of the polyene–acid adducts in Table 1 are also relatively large, which supports the proton transfer previously [1] postulated from the acid to the polyene. Thus the adducts of reaction (A) can be regarded as ion-pairs and can be formulated as $PH^+ \ldots A^-$, the proton being taken up by the conjugated double bonds of the polyenes.[1] Polymer A appears to contain an ester group, the carbon–oxygen double bond not being conjugated with the carbon–carbon double bonds (French, *et al.*[1]). In this case protons may be transferred, not only to the conjugated carbon–carbon double bonds, but also to the ester group. Unpublished experiments show, however, that proton transfer to an ester group alone does not give rise to dipole moments as large as those in lines 6 or 8 of Table 1. The fact that the high moments of the adducts do not arise from the presence of excess of the free acid, HA, as co-solvent is shown by the results in lines 1, 2, and 3 of Table 1, and lines 1 and 2 of Table 2, which indicate that a decrease of the co-solvent produces either an increase of the dipole moment or has no significant effect. It has been found [5,9,10] that the dipole moments and the concentration-dependence of the orientation polarisation of ammonium salts depend on the natures of the cations and the anions. Structural influences also play a rôle in the case of the

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[5] Bauge and Smith, unpublished work.

[6] From the data of Le Fèvre and Vine, *J.*, 1938, 1795.

[7] Pohl, Hobbs, and Gross, *J. Chem. Phys.*, 1941, **9**, 408.

[8] Richards and Walker, *Trans. Faraday Soc.*, 1961, **57**, 406.

[9] Geddes and Kraus, *Trans. Faraday Soc.*, 1936, **32**, 585.

[10] Maryott, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 1.

[11] Hooper and Kraus, *J. Amer. Chem. Soc.*, 1943, **56**, 2265; Davies and Williams, *Trans. Faraday Soc.*, 1960, **56**, 1619; Richardson and Stern, *J. Amer. Chem. Soc.*, 1960, **82**, 1296; Gilkerson and Srivastara, *J. Phys. Chem.*, 1961, **65**, 272.

polyene–acid adducts. These may arise through variation of the mutual attractions (partly due to dispersion forces) between strongly polarisable cations PH^+ and anions A^-, and through variations of charge delocalisation in the former species. It is not surprising, therefore, that the dipole moments of these adducts vary within a fairly large range, from 3·7 to more than 30 D, and that, on passing from one acid adduct to another (*e.g.*, from a trichloroacetate to a picrate) the dipole moments of polyene and ammonium salts change in a different manner.

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