106. *The Polarities of Enols.*

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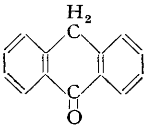
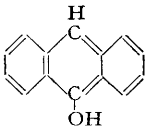
The following dipole moments are recorded (refractivity method; solvent, benzene): anthrone, 3·5 D., ethyl salicylate, 2·7 D., ethyl *p*-hydroxybenzoate, 2·8 D. The moment of anthranol has been estimated as 1·9—2·0 D., *i.e.*, greater than is usual for phenols and naphthols.

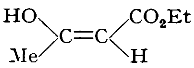
The experiments now recorded were part of an attempt to examine the polarities of enols. The literature reveals that compounds possessing the ·C(OH):CH·CO· unit in a manner such that internal chelation is unlikely for stereo-structural reasons (*e.g.*, dimedone; Hukins and Le Fèvre, *J.*, 1949, 898) are unusually acidic (Taylor and Ewbank, *J.*, 1926, 2818; Bennett, *Chem. and Ind.*, 1926, 960). Phenols, naphthols, etc., also have this quality and can of course be regarded as enols containing the simpler fragment ·C(OH):CH·, yet in no such case has the dipole moment of the corresponding keto-isomeride been recorded. Anthrone (I) and anthranol (II) initially seemed to be a pair of molecules with the desired relationship, since, in solution, they form ultimately an equilibrium with (I) predominating (Beilstein, " Handbuch, etc.," VII, 473; VII*, 257; Meyer, *Annalen*, 1911, **379**, 37; 1913, **396**, 133; 1920, **420**, 113). It later transpired that 100% pure anthranol has never been isolated (Bäckstrom and Beatty, *J. Physical Chem.*, 1931, **35**, 2531). We therefore proceeded first to study anthrone itself in benzene, to obtain its specific polarisations at given concentrations (cf. Table I), and then to prepare a succession of separate



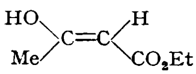
(I.)



(II.)



(III.)



(IV.)

quantities of "anthranol," each being analysed by the iodine procedure of Băckstrom and Beatty (*loc. cit.*) and, simultaneously, submitted to dielectric-polarisation measurements as though it were a single substance. Anthranol contents ranging from 18 to 45% were obtained. On the assumption that only (I) and (II) are concerned, and that a simple mixture rule applies to the observed specific polarisations, moments up to 2 D. were indicated for (II). Reproducibility was, however, poor and continued to be so despite all efforts at improvement.

An estimate of similar order follows from the moment now found for anthranol methyl ether (1·5 D.). Noting that between a phenol and its methyl ether there is commonly a polarity difference of 0·4—0·5 D., it would seem that anthranol has a moment of 1·9—2·0 D., *i.e.*, some 1·5 D. lower than that of anthrone, but notably higher than those of phenol (1·6—1·7) or the two naphthols (1·0—1·5). Attempts to prepare equilibrium mixtures from the ketonic isomeride in benzene or hexane have also been made, but unsuccessfully—a not unexpected result since Meyer's experiments (*Annalen*, 1913, **396**, 133) suggest that strong electrolytes are required. Further, it is relevant that infra-red spectroscopic methods have not shown the presence of any enol form of anthrone in carbon tetrachloride solutions (Flett, *J.*, 1948, 1441).

We have also prepared 9-phenanthrol, but found it to be too sparingly soluble in benzene for measurement.

Dipole Moments of Ethyl Salicylate and p-*Hydroxybenzoate.*—Results for these two compounds are given below. Le Fèvre and Welsh (*J.*, 1949, 1909) estimated the moment of the enolic form of ethyl acetoacetate as 1·7 D. Since this enol might exist as a *cis*- or a *trans*-form, (III) or (IV), it seemed of interest to examine ethyl salicylate and ethyl *p*-hydroxybenzoate—molecules in which the hydroxyl groups and carbethoxy-groups are in the same relative configurations as in (III) and (IV). However, the moments observed (2·7 and 2·8 D., respectively) are too nearly equal to be relevantly useful. It is notable that the parent *o*- and *p*-acids also have similar moments (2·63 and 2·73 D.; Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1265).

EXPERIMENTAL.

Materials.—Anthrone was prepared from anthraquinone (*Org. Synth.*, Coll. Vol. I, p. 60) and recrystallised from a benzene–light petroleum (3 : 1); m. p. 152°. Anthranol-containing specimens were obtained and analysed as described by Băckstrom and Beatty (*loc. cit.*).

Anthranol methyl ether was isolated directly from anthrone by the method of Meyer and Schlösser (*Annalen*, 1920, **420**, 126) and crystallised from a little light petroleum; m. p. 93·5—94·5°.

The ethyl salicylate was a fractionated commercial specimen, b. p. 230—232°. Its *p*-isomer was from a similar source, and was recrystallised from water to m. p. 116°.

Measurements.—These were made by routine methods (cf. *J.*, 1948, 1949) and are tabulated below under the usual headings. The solvent used was benzene throughout.

Anthrone.

$10^5 w_1$	238	373	604	878	972	1177	1489	1657
ε^{25}	2·289	2·299	2·317	$2{\cdot}338_8$	2·346	2·366	2·389	2·401
d_4^{25}	0·87434	0·87474	0·87528	0·87556	0·87620	0·87676	0·87710	0·87690
P_1 (c.c.) ...	298	302	312	321	317	329	326	326

Whence $\alpha\varepsilon_2 = 7{\cdot}02 + 56w_1$; $\beta d_2 = 0{\cdot}259_5 - 2{\cdot}9w_1$.

Anthranol methyl ether.

$10^5 w_1$	1277	1836	2451	2928	3660	4064
ε^{25}	2·2907	2·2960	2·3074	2·3111	2·3226	2·3283
d_4^{25}	0·87650	0·87808	0·87940	0·88056	0·88336	0·88419

Whence $\alpha\varepsilon_2 = 1{\cdot}36_5$ (mean); $\beta d_2 = 0{\cdot}238$ (mean).

Ethyl salicylate.

$10^6 w_1$	9215	12,060	17,932
ε^{25}	2·3164	2·3301	2·3605
d_4^{25}	0·87620	0·87536	0·87676

Whence $\alpha\varepsilon_2 = 4{\cdot}82$ (mean); $\beta d_2 = 0{\cdot}187$ (mean).

Ethyl p-*hydroxybenzoate.*

$10^6 w_1$	2908	3977	4483	5589	5656	6414
ε^{25}	2·2872	2·2942	2·2975	2·3020	2·3028	2·3053
d_4^{25}	0·87468	—	0·87486	—	0·87520	—

Whence $\alpha\varepsilon_2 = 5{\cdot}31$ (mean); $\beta d_2 = 0{\cdot}267$ (mean).

Results.—These have been calculated *via* the equations $_\infty P_T = M_1[p_2(1 - \beta) + C\alpha\varepsilon_2]$, and $\mu = 0{\cdot}221(_\infty P_T - R_L)^{\frac{1}{2}}$ (at 25°; cf. Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1). For benzene, $p_2 = 0{\cdot}3409$ c.c. and $C = 0{\cdot}1881$.

Substance.	M_1.	$(\alpha\varepsilon_2)_{w_1=0}$.	$(\beta)_{w_1=0}$.	$_\infty P_T$.	$[R_L]_D$.	μ, D.
Anthrone	194·1	7·02	0·297	302·8	57·5 *	3·46
Anthranol methyl ether	208·1	$1{\cdot}36_5$	0·272	105·1	61·5 *	1·46
Ethyl salicylate	166·1	4·82	0·214	195·1	44·8 †	2·71
Ethyl *p*-hydroxybenzoate ...	166·1	5·31	0·306	205·2	43·3 *	2·81
					44·1 ‡	2·80

* Calc. from atomic and bond refractions. † Cf. I.C.T., vol. I, 227.

‡ Calc. from ethyl benzoate (42·6 c.c.) and hydroxylic oxygen (1·5 c c.).

Previous Determinations.—These are as follows: Anthrone: $(_\infty P_T)_{20°} = 341$ c.c. in benzene, and $\mu = 3{\cdot}66$ D. using $[R_L]_D = 58$ c.c. (Coomber and Partington, *J.*, 1938, 1444). Ethyl salicylate: $\mu = 2{\cdot}88$ D. in benzene at 40·2° (Hrynakowsky and Kalinowsky, *Compt. rend.*, 1933, **197**, 483; actual polarisations not recorded).

Our results for anthrone differ from those of Coomber and Partington in that their P_1 values, calculated by the usual mixture relation, *increased* with dilution, while ours *decrease*. Consequently, our final μ (3·46) is lower than theirs (3·66). We therefore mention that the above eight anthrone solutions have been examined singly or in pairs on occasions widely spaced over nine months, and have involved different batches of benzene. The contrast cannot easily be ascribed to instrumental "drifts," evaporation, etc.

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