297. *Alleged Geometrical Isomerism in Certain Anils, and the Dipole Moment of Phenanthridine.*

By V. de Gaouck and R. J. W. Le Fèvre.

The red and the yellow forms of *p*-homosalicylideneaniline and ethyl salicylidene-*p*-aminobenzoate have identical polarities in benzene solutions; their differences are therefore probably due to dimorphism and not geometrical isomerism in the Hantzsch–Werner sense. The dipole moments of phenanthridine and benzophenoneanil are recorded and discussed in relation to the suggestion previously made that benzylideneaniline has a *trans*-structure.

VERY few claims have been made for the isolation of anils, R·CH:NR′, in two geometrically isomeric pairs. We have already reported (J., 1938, 741) that the two crystallographically distinct varieties of salicylideneaniline (Anselmino, *Ber.*, 1907, **40**, 3465) become identical when dissolved in benzene, and now we record data relating to two further instances in which the physical differences between the solid forms are greater than with salicylideneaniline. The first is *p*-homosalicylideneaniline, which exists in an orange-red and a yellow form, rapid crystallisation *with cooling* producing the latter, and slow crystallisation *above* 32°, the former; the yellow may be irreversibly transformed into the red modification by application of heat, and Anselmino (*loc. cit.*) found slight differences between their absorption spectra. The second instance is ethyl salicylidene-*p*-aminobenzoate, which likewise exists in a yellow and a red form (Manchot and Furlong, *Ber.*, 1909, **42**, 3030); the former is obtained by mixing concentrated alcoholic solutions of the components and quickly crystallising the product, the latter by slow crystallisation from a diluted solution of the anil. The yellow crystals are 6-sided tables, m. p. 87·5°, and the red are long prisms with rectangular ends, m. p. 83° (followed by immediate solidification and reversion to the yellow variety, m. p. 87·5°). Ebullioscopically and cryoscopically both forms are unimolecular in benzene.

If the underlying cause of such differences were isomerism of the Hantzsch–Werner type, the forms would be unlikely to have the same dipole moments. The measurements tabulated below were therefore made. They indicate that, in benzene solution, the polarities of the red and yellow pairs are—in both cases—identical.

EXPERIMENTAL.

Measurements.—These relate to solutions in benzene. The apparatus and methods used are described in "Dipole Moments" (Methuen, 1938, pp. 29—35). In the following tables the symbols used are: w_1 the weight fraction of the solute in a solution, ε the dielectric constant of the solution at a frequency *ca.* 1200 kc., d the density of the solution compared with $d_{4°}^{25°}$ for benzene = 0·87378, p the specific polarisation of the solution, and ${}_TP_\infty$ the total polarisation of the solute at infinite dilution. The last two quantities have been calculated, since the densities and dielectric constants of the solutions show rectilinear dependence upon the concentration, *i.e.* (subscripts 1 and 2 being used to denote solute and solvent respectively), $d = d_2(1 + \beta w_1)$ and $\varepsilon = \varepsilon_2(1 + \alpha w_1)$. The specific polarisation at infinite dilution is then obtained from the equation $p_\infty = p_2(1 - \beta) + C\alpha\varepsilon_2$, where $p_2 = (\varepsilon_2 - 1)/(\varepsilon_2 + 2)d_2$ and $C = 3/d_2(\varepsilon_2 + 2)^2$. Where M is the molecular weight of the solute, the total molecular polarisation at infinite dilution is given by ${}_TP_\infty = Mp$ c.c. The refractive indices and specific and molecular refractions respectively are given under $n_D^{25°}$, r_{12}, and $[R_L]_D$, the last constant being obtained from the expression $[R_L]_D = M[r_2 + (r_{12} - r_2)/w_1]$.

From these data we infer that in these cases, like that of salicylideneaniline, only *one* molecular species is present in each solution, and the alleged "isomerism" is really due to dimorphism, such as that which must be responsible for the two forms of benzophenoneanil (Knoevenagel, *J. pr. Chem.*, 1914, **89**, 38) for which no geometrical isomerism is possible, or a phenomenon similar to that studied by Hertel and Schneider (*Z. Elektrochem.*, 1931, **37**, 536), who report that the molecular compound 4-bromo-1-naphthylamine–2 : 4-dinitrophenol has many points of behaviour in common with the above anils; *e.g.*, it occurs as two forms, red, m. p. 85°, and yellow, m. p. 91°, distinguished from one another by their crystal habits and

X-ray diffraction patterns; the lattice changes completely when the red (unstable) modification passes into the yellow (stable) form.

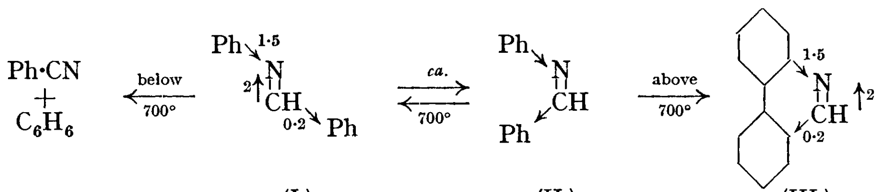
The trans-*Structure of Benzylideneaniline.*—Our opinion (J., 1938, *loc. cit.*) that the single known benzylideneaniline is the *trans*-form depended only upon the *identity* of moment found for it and its *pp'*-dichloro-derivative. The numerical value of this property is of little help in this case since it is clear from simple vectorial additions that no great differences between resultant polarities are to be anticipated for structures (I) and (II). If the following be assumed : $\mu_{Ph \rightarrow N} = 1{\cdot}5$, $\mu_{C \rightarrow Ph} =$ *ca.* 0·2 (*cf.* $\mu_{phenanthrene}$, Briegleb, *Z. physikal. Chem.*, 1932, *B*, **16**, 276), $\mu_{C=N} = 2$ (cf. our determination of $\mu_{benzophenoneanil}$, p. 1394), all angles = 120°, it is evident that the moment of the *cis*-form might even be slightly less than that of the *trans*.

$1000w_1$.	$\epsilon_{25°}$.	$\alpha\epsilon_2$.	$d_{4°}^{25°}$.	βd_2.	$n_D^{25°}$.	r_{12}.	$[R_L]_D$.
			Benzene.				
0	2·2725	—	0·87378	—	1·49724	0·33503	—
			p-*Homosalicylideneaniline* (*yellow form*).				
4·5848	2·2953	4·60	0·87460	0·180	1·49791	0·33509	71·90
6·3250	2·3043	5·00	0·87496	0·186	1·49800	0·33501	71·90
7·0484	2·3051	5·03	0·87517	0·197	1·49829	0·33509	71·90
7·4560	2·3104	5·08	0·87520	0·190	1·49832	0·33507	71·89
			p-*Homosalicylideneaniline* (*red form*).				
4·9068	2·2941	4·40	0·87467	0·184	1·49790	0·33506	71·90
5·8636	2·3020	5·05	0·87480	0·174	1·49806	0·33510	71·90
6·8637	2·3024	4·36	0·87502	0·181	1·49825	0·33513	71·90
7·1450	2·3100	5·25	0·87511	0·186	1·49836	0·33516	71·90
			Ethyl salicylidene-p-*aminobenzoate* (*yellow form*).				
5·1566	2·2891	3·22	0·87494	0·255	1·49784	0·33492	91·66
6·7308	2·2940	3·20	0·87521	0·213	1·49800	0·33491	91·66
8·5887	2·3055	3·84	0·87576	0·230	1·49820	0·33488	91·67
8·6694	2·3089	(4·20)	0·87564	0·215	1·49828	0·33491	91·67
			Ethyl salicylidene-p-*aminobenzoate* (*red form*).				
4·3611	2·2870	3·22	0·87490	0·261	1·49786	0·33495	91·66
5·5595	2·2914	3·40	0·87492	0·201	1·49820	0·33500	91·66
7·3501	2·2971	3·35	0·87541	0·222	1·49820	0·33495	91·67
8·5018	2·3040	3·70	0·87563	0·218	1·49836	0·33496	91·67

Mean values and results.

	M.	$\alpha\epsilon_2$.	βd_2.	$_TP_\infty$ (c.c.).	$[R_L]_D$ (c.c.).	μ, D.
p-Homosalicylideneaniline (yellow form)	211	4·93	0·188	252·1	71·90	2·95
,, (red form)	211	4·77	0·181	246·5	71·90	2·91
Ethyl salicylidene-*p*-aminobenzoate (yellow form)	269	3·42	0·228	241·68	91·66	2·69
,, ,, (red form) ...	269	3·44	0·225	241·68	91·66	2·69

In connexion with this point we have now examined the dipole moment of phenanthridine (III), since this should clearly be of the order to be expected for the lacking *cis*-modification (II) of (I). The values actually found for (I) and (III) are compared beneath their formulæ with those estimated from the data quoted above, and are seen to differ in the sense forecast.



(I.) (II.) (III.)

	(I.)	(II.)	(III.)
Found	$1{\cdot}5_7$	?	$1{\cdot}5_0$
Calc.	1·9	1·6	1·6

Finally, regarding the relative stabilities of types (I) and (II), if these are in fact so widely different that at ordinary temperatures all anils occur in one form only, then the development of an equilibrium between the geometrical isomers in a given case will require a high temperature. Now, the pyrogenetic formation of phenanthridine from benzylideneaniline is obviously less likely to occur by the loss of 2 atoms of hydrogen from (I) than from (II); of interest therefore is Pyl's observation (*Ber.*, 1927, **60**, 287) that below 700° the thermal decomposition of benzylideneaniline gives mainly benzonitrile and benzene and only at higher temperatures (? when the *trans-cis*-inversion becomes notable) does the production of phenanthridine become appreciable.

Dielectric Polarisation Data for Phenanthridine and Benzophenoneanil.—The measurements recorded below were obtained with specimens of phenanthridine and benzophenoneanil prepared as described respectively by Pictet and Ankersmit (*Annalen*, 1891, **266**, 142), m. p. 104°, after crystallisation from aqueous alcohol, and Reddelien (*Ber.*, 1909, **42**, 4760), m. p. 112° after crystallisation from absolute alcohol.

$100w_1$.	$\epsilon_{25°}$.	$\alpha\epsilon_2$.	$d_{4°}^{25°}$	βd_2.	$n_D^{25°}$	r_{12}.	$[R_L]_D$.
0	2·2725	—	0·87378	—	1·49724	0·33503	—
			Phenanthridine.				
0·1930	2·2760	1·80	0·87421	0·223	—	—	—
0·2657	2·2776	1·92	0·87439	0·229	—	—	—
0·2659	2·2774	1·84	0·87438	0·226	—	—	—
0·2741	—	—	0·87440	0·225	1·49759	0·33499	61·1

whence ${}_TP_\infty$ = 107·6 c.c., $[R_L]_D = 61$, and $\mu = 1{\cdot}5_0$ (for comparison the corresponding data for benzylideneaniline are 112·6, 61·6, $1{\cdot}5_7$ respectively).

Benzophenoneanil.

2·861	2·3343	2·16	0·87934	0·194
4·690	2·3719	2·12	0·88293	0·195
5·503	2·3875	2·09	0·88451	0·195

$[R_L]_D$, calc. from H = 1·1, C_6H_6 = 26, and benzylideneaniline = 62, 86 c.c.

whence ${}_TP_\infty$ = 170·7 c.c. and $\mu = 2{\cdot}0_3$.

Previous Measurements on Benzophenoneanil.—Bergmann (*Ber.*, 1932, **65**, 446) reports $({}_TP_\infty)_{12\cdot7°}$ = 186 c.c., and μ = 1·97; Hampson (Table of Dipole Moments, *Trans. Faraday Soc.*, 1934, **30**, Appendix) gives $({}_TP_\infty)_{25°}$ = 167 c.c., which is in good agreement with that now found by us.

The authors are grateful to Dr. G. S. Whitby, Director of the Chemical Research Laboratory, Teddington, for the loan of a specimen of phenthridine nitrate, and also to the Chemical Society for grants.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C. 1.

[*Received, May 3rd,* 1939.]