138. *A Contribution to the Stereochemistry of Anils.*

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

The dipole moments now recorded for certain simple Schiff's bases, R·CH:NR′, show that these are compounds in which the groups R and R′ stand in the *trans*-relation about the C═N linking.

The possibility that phototropic changes in this group of compounds involve configurational changes of the *cis* $\rightleftharpoons$ *trans* type is diminished by the present work.

The possibility that phototropy (*i.e.*, the reversible change of colour occurring when certain compounds are exposed to light; *Z. physikal. Chem.*, 1899, **30**, 140) involves configurational changes has led us to consider the stereochemistry of anils, because among these are found the best common examples of this phenomenon (*e.g.*, salicylidene-*m*-toluidine; Senier and Shepheard, J., 1909, **95**, 441, and later papers).

The space formulæ of these compounds are not well established. In certain cases, the isolation of two forms has been claimed (cf. Hantzsch and Schwab, *Ber.*, 1901, **34**, 822), but these are of doubtful authenticity and may possibly be due to dimorphism rather than geometrical isomerism (Freudenberg, " Stereochemie," 1933, p. 1097).

In the course of the present work we have examined two of these examples. Anselmino (*Ber.*, 1907, **40**, 3465) has stated that two crystallograph cally different forms of salicylideneaniline, *d* 1·087 and 1·184 (Jaeger, *ibid.*, p. 3474), are produced by cooling either a hot alcoholic or a ligroin solution. We have therefore prepared two such specimens and made dielectric-constant and density measurements for various solutions of them in benzene. These results are tabulated below, together with the coefficients of increase of dielectric constant and density with concentration ($\alpha\varepsilon_2$ and βd_2 respectively). The identity of these values for both materials shows that in solution only *one* molecular species is present. Therefore, it may be assumed that this alleged case of isomerism is also due to polymorphism.

Salicylideneaniline (*M*, 197).

w_1.	$\epsilon_{25^\circ}^{1200}$.	$d_{4^\circ}^{25^\circ}$.	$\alpha\epsilon_2$.	βd_2.	$n_D^{25^\circ}$.	r_{12}.	$[R_L]_D$.
0·0061235	2·2954	0·87503	3·74	0·204	1·49813	0·33035	66·6
0·0076107	2·3012	0·87535	3·77	0·206	1·49826	0·33501	65·5
0·0085037	2·3092	0·87557	4·27	0·208	1·49839	0·33499	65·1
0·0103572	2·3117	0·87601	3·78	0·208	1·49877	0·33504	67·9

(The above data refer to a specimen obtained from ligroin, and those below to one obtained by recrystallisation from alcohol.)

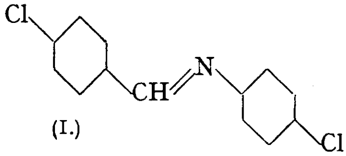
0·0049824	2·2910	0·87484	3·71	0·213	1·49807	0·33507	67·1
0·0073309	2·2996	0·87529	3·70	0·206	1·49827	0·33503	66·0
0·0081481	2·3031	0·87548	3·75	0·209	1·49834	0·33500	65·0
0·0113446	2·3156	0·87613	3·80	0·207	1·49897	0·33511	67·4

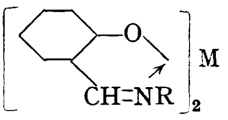
Another apparently clear claim for the discovery of two different forms was made by Brewster and Millam (*J. Amer. Chem. Soc.*, 1933, **55**, 763) for 5-bromosalicylidene-*o*-toluidine; according to them, varieties of m. p. 165° * or 86·5° were obtained by heating together the aldehyde and the amine respectively with or without addition of alcohol. In several attempts to follow the brief directions, we have always obtained the form of lower m. p.

As the common Schiff's bases, therefore, presumably occur in one form only, it became of interest to determine the natures of these forms and whether they are derived from a general configuration. To this end we have prepared, and made dipole-moment measurements on, the compounds named in the following table :

	M.	$\alpha\epsilon_2$.	βd_2.	${}_\infty P_1$.	$[R_L]_D$.	μ, D.
Benzylideneaniline	181	1·85	0·170	112·6	61·6	1·57
p-Chlorobenzylideneaniline	215·5	1·96	0·215	134·8	69·9	1·77
p-Chlorobenzylidene-*p*-toluidine	229·5	2·41	0·232	161·5	73·5	2·06
p-Chlorobenzylidene-*p*-chloroaniline	250	1·37	0·291	121·3	71·0	1·56
Salicylideneaniline	197	3·75	0·208	190·1	66·4	2·45
Salicylidene-*m*-toluidine	211	3·84	0·192	208·5	70·2	2·59
o-Methoxybenzylideneaniline	212	5·10	0·192	259·8	71·7	3·02
5-Bromosalicylideneaniline	263	1·52	0·331	130·9	101·5	1·19

From the essential identity—within the limits of experimental error—of the moments of benzylideneaniline and *p*-chlorobenzylidene-*p*-chloroaniline (I), it is evident that the latter compound must have a *trans*-structure and that, in it, the two C–Cl links must be approximately parallel. Such a conclusion is completely reconcilable, if normal valency angles and atomic dimensions are assumed, with the values found for *p*-chlorobenzylideneaniline and its 4′-methyl derivative. It is therefore not improbable that throughout the whole series the *trans*-configuration is so much the more stable that it alone occurs.


(I.)


(II.)

The analysis of the data for the *o*-hydroxy-compounds is rendered exceedingly difficult by the possibilities of intramolecular rotation. Thus, both the hydroxyl and the CH=NR groups can, by rotation about the links holding them to the benzene nucleus, present various mutual orientations, for which resultant dipole moments varying by as much as 3 D. will be

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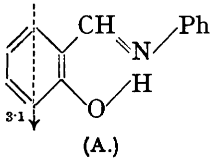
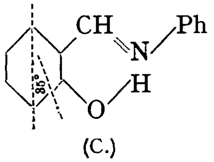
* This m. p. is very close to that of 5-bromosalicylic acid.

appropriate. In this connexion, however, we may mention that whilst this work was in progress Hunter and Marriott (J., **1937**, 2000) described a number of bimolecular metallic derivatives of the salicylidene-anils and formulated them as co-ordination compounds of the type (II). They recognise this as evidence for the *trans*-configuration of those particular anils and further cite the infra-red spectroscopic investigations of Wulf, Hendricks, Hilbert, and Liddel (*J. Amer. Chem. Soc.*, **1936, 58,** 1991) together with supporting solubility and m. p. relationships.

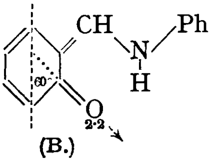
The present measurements are not in discord with this suggestion, for, although admittedly the magnitude of the moment determined experimentally for such a system cannot be estimated with any certainty, yet we note that the observed figure stands *within* the limits which may reasonably be expected for the two chief extreme unreal structures (A) and (B). These we have estimated by assuming that the oxygen, hydrogen, and nitrogen



(A.)



(C.)



(B.)

atoms and the methin and phenyl groups all subtend angles of 120° with their immediate neighbours and that the following link moment values apply: CH=N, 2·5; Ph—N, 1·5; C—O, 0·7; C=O, 2·3; H—O, 1·5; H—N, 1·6 D. On these premises, (A) has a resultant of approximately 3·1 D. acting nearly vertically, and (B) one of 2·2 D. acting roughly parallel to the C=O axis. The apparent direction of the resultant in the real structure (C) may, however, be inferred from the observed moment of 5-bromosalicylideneaniline (1·19 D.), by regarding this value as arising from the interaction of the C–Br vector along the oxygen ⟶ carbon directions in (A) and (B) with the resultant, 2·45, found for salicylideneaniline. The direction of action of the latter is thence found as 35° to the vertical (C), *i.e.*, *between* the values for (A) and (B).

Finally, attention may be directed to the differences in moment between salicylideneaniline and its methyl ether. Since resonance of the type discussed is impossible with the latter, it might be expected to have the larger moment, corresponding to (A), but against this must be offset the effect of the replacement of the greater $\mathrm{H \rightarrow O}$ link moment by the smaller $\mathrm{CH_3 \rightarrow O}$ value (cf. phenol, $\mu = 1{\cdot}7$; anisole, $\mu = 1{\cdot}2$ D.) The actual experimental value is 3·02 D.

Since it seemed possible that light might cause an inversion of configuration, as it does in the similar cases of certain oximes, azo-compounds, etc., we have several times throughout the present work made the solutions in brown glass bottles and rigorously excluded white light until after the dielectric-constant measurements had been completed. Such solutions were then exposed in quartz cells to the direct light of a mercury arc for periods up to 12 hours, transferred as rapidly as possible to the dielectric-constant apparatus, and re-measured. In no case was any significant change observed, a negative result kindly confirmed—for solutions of far lower concentrations than those employed by us—by Dr. G. S. Hartley, of this department, using an electric photometric method.

We conclude, therefore, that the present work diminishes the possibility that phototropic changes among the anils involve configurational inversions of the *cis* ⇌ *trans*-type.

EXPERIMENTAL.

*Preparation of Materials.—Salicylidene-*m*-toluidine.* The crude solid from a direct condensation, dissolved in ethyl alcohol at room temperature and cooled to − 20°, gave yellow needles, m. p. 39° (cf. Gallagher, *Bull. Soc. chim.*, 1921, **29**, 683).

p-*Chlorobenzylidene-aniline and -*p*-chloroaniline.* The crude materials, washed first with very dilute acetic acid, then with water, and finally crystallised from alcohol, afforded pale yellow plates, m. p. 62°, and yellowish-white needles, m. p. 112°, respectively (Walther and Raetze, *J. pr. Chem.*, 1902, **65**, 265).

p-*Chlorobenzylidene-*p*-toluidine and 5-bromosalicylideneaniline.* These were prepared as in the previous cases. Both were crystallised from alcohol, and formed needles, m. p. 125°, and golden needles, m. p. 119°, respectively. 5-Bromosalicylaldehyde was conveniently prepared according to Brewster and Millam (*loc. cit.*).

Benzylidene- and salicylidene-aniline. After recrystallisation from alcohol, benzylideneaniline had m. p. 49·5°. Salicylideneaniline was recrystallised from alcohol and from ligroin; this procedure was claimed by Anselmino (*loc. cit.*) to produce two crystallographically different forms, m. p. 50·5°, one appearing as needles from alcohol, the other as rhombs from ligroin.

o-*Methoxybenzylideneaniline.* The product of direct condensation at 100° was cooled to − 70° with ether–solid carbon dioxide. After recrystallisation from alcohol, the substance formed needles, m. p. 44° (cf. Noelting, *Ann. Chim. Phys.*, 1910, **19**, 540).

Dipole-moment Measurements.—These were carried out in benzene at 25° and 1200 kc. The apparatus and other details are described elsewhere. The necessary observations are tabulated below and on p. 742 under the following headings: w_1, the weight-fraction of the solute in the solutions; $\varepsilon_{25°}^{1200}$ and $d_{4°}^{25°}$, the dielectric constants and densities of the solutions at the above

w_1.	$\epsilon_{25°}^{1200}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	βd_2.	$n_D^{25°}$.	r_{12}.	$[R_L]_D$.
0	2·2725	0·87378	—	—	1·49724	0·33503	—
Benzylideneaniline (*M*, 181).							
0·0052333	2·2822	0·87468	1·85	0·172	1·49786	0·33504	61·0
0·0069171	2·2859	0·87497	1·94	0·172	1·49811	0·33507	61·6
0·0071341	2·2853	0·87499	1·79	0·170	1·49813	0·33506	61·4
0·0101883	2·2912	0·87548	1·83	0·170	1·49857	0·33513	62·4
p-*Chlorobenzylideneaniline* (*M*, 215·5).							
0·0042378	2·2808	0·87472	1·96	0·222	1·49779	0·33497	69·1
0·0062911	2·2845	0·87517	1·91	0·210	1·49802	0·33497	70·1
0·0079835	2·2844	0·87548	1·99	0·217	1·49828	0·33493	69·7
0·0087396	2·2895	0·87563	1·99	0·213	1·49833	0·33497	70·6
p-*Chlorobenzylidene*-p-*toluidine* (*M*, 229·5).							
0·0031769	2·2803	0·87449	2·45	0·223	1·49770	0·33501	75·4
0·0042419	2·2805	0·87477	2·39	0·234	1·49780	0·33497	73·6
0·0045232	2·2843	0·87484	2·61	0·234	1·49783	0·33495	72·8
0·0048470	2·2845	0·87499	2·47	0·249	1·49786	0·33491	71·7
0·0079771	2·2901	0·87676	2·21	0·248	1·49845	0·33458	73·9
0·0107257	2·2975	0·87694	2·33	0·207	1·49853	0·33455	—
p-*Chlorobenzylidene*-p-*chloroaniline* (*M*, 250).							
0·0046280	2·2788	0·87513	1·36	0·292	—	—	—
0·0052943	2·2789	0·87532	1·38	0·290	1·49781	0·33476	71·0
0·0057531	—	0·87545	—	—	1·49791	0·33477	72·5
0·0098592	2·2846	0·87666	1·36	0·292	1·49823	0·33449	70·1
0·0101210	2·2863	0·87599	1·36	0·291	—	—	—
0·0111398	—	0·87700	—	—	1·49861	0·33447	71·2
0·0155380	2·2942	0·87818	1·40	0·291	1·49871	0·33418	70·4
Salicylidene-m-*toluidine* (*M*, 211).							
0·0058417	2·2943	0·87490	3·71	0·192	1·49797	0·33501	69·98
0·0071484	2·3004	0·87515	3·90	0·192	1·49821	0·33505	71·30
0·0093173	2·3078	0·87556	3·79	0·191	1·49837	0·33499	69·79
0·0100746	2·3121	0·87572	3·93	0·192	1·49865	0·33508	71·73
0·0145614	2·3291	0·87682	3·89	(0·209)	1·49914	0·33495	69·53
0·0152670	2·3305	0·87713	3·80	(0·194)	1·49929	0·33491	69·03
o-*Methoxybenzylideneaniline* (*M*, 212).							
0·005893	2·2988	0·87489	4·53	—	1·49805	0·33506	72·1
0·0070782	—	0·87518	—	0·192	—	—	—
0·0095929	2·3297	0·87562	5·21	—	1·49855	0·33507	71·0
0·0103988	2·3298	0·87575	5·50	—	1·49859	0·33503	72·0
0·0105390	—	0·87578	—	0·187	—	—	—
0·0107650	—	0·87589	—	0·196	—	—	—
0·0120743	—	0·87610	—	0·192	—	—	—
5-*Bromosalicylideneaniline* (*M*, 263).							
0·0018171	2·2739	0·87433	(0·77)	(0·303)	1·49753	0·33499	(93·92)
0·0034715	2·2776	0·87498	1·55	0·304	1·49773	0·33485	101·7
0·0046364	2·2797	0·87536	1·50	0·345	1·49787	0·33477	102·9
0·0071798	2·2833	0·87626	1·50	0·345	1·49823	0·33464	100·0

frequency and temperature; $\alpha\varepsilon_2$ and βd_2, the rates of change of dielectric constants and density with weight-fraction, expressed by $\varepsilon_{12} = \varepsilon_2(1 + \alpha w_1)$ and $d_{12} = d_2(1 + \beta w_1)$; $n_D^{25°}$, the refractive index of the solutions for the Na line; r_{12}, their specific refractions; and $[R_L]_D$, the corresponding values for the molecular refractions of the solute.

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

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