310. *The Phototropy of Anils, and a Note on the Phototropy of Solutions of the Leuco-cyanides of Malachite- and Brilliant-greens.*

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

(A) Phototropy among anils appears to occur only in the solid state; in solution, no such changes of colour or other properties can be produced by illumination. The nature and position of substituent groups strongly influence the phototropic process. Previous explanations for this phenomenon are mentioned, and a new one advanced depending upon intermolecular resonance in the crystal lattice.

(B) The phototropic changes described in the literature for the leuco-cyanides named above have been confirmed when alcohol is the solvent. In benzene solution, however, no phototropy has been found.

The dipole moments of the two leuco-cyanides and the leuco-base of malachite-green have been determined. The values obtained illustrate the facilitation of mesomerism by the R_2N group.

Of more than 300 known anils, only 25 have been reported to show phototropy (*i.e.*, a colour change caused and maintained by light of certain wave-lengths, decaying in darkness, and being reversed by exposure to light of other wave-lengths), and of these, 18 are derivatives of salicylaldehyde, and 3 of *p*-hydroxybenzaldehyde. Regarding phototropy in general, no satisfactory explanation of wide applicability has yet been given. Polymorphism (Stobbe, *Annalen*, 1899, **305**, 171), the formation of stereo- or other isomerides (Senier and Shepheard, J., 1909, **95**, 441), the existence of molecular aggregates which, in the solid state, are affected by isomeric changes (Senier, Shepheard, and Clark, J., 1912, **101**, 1950), polymerisation in the chemical sense (Padoa and Zazzaroni, *Atti R. Accad. Lincei*, 1915, **24**, 828), and intramolecular changes involving hydrogen atoms (Chattaway, J., 1906, **89**, 462) have all been held to be responsible for different classes of phototroptic substances.

By restricting the present work to anils, it was hoped to limit these possibilities. Our first experiments were designed to ascertain whether the changes are intra- or inter-molecular. To this end, a careful search has been made for any trace of phototropy in solution, because the separating action of the solvent molecules on those of the solute should not greatly affect an intramolecular mechanism (provided the solvent does not absorb light of the phototropically active wave-length; see later) but would presumably extinguish any effects depending upon inter-molecular relationships.

Various anils—such as salicylidene-*m*-toluidine, which is one of the most phototropic of this class—have been studied in benzene, carbon tetrachloride, and chloroform solutions, spectrophotometrically and dielectrically. The following types of experiment have been performed.

(1) A solid sample was illuminated in the light from a mercury arc, and when its colour was fully developed, it was immediately dissolved in a solvent and examined for any change in absorption with time (certain of these observations were kindly made by Dr. G. S. Hartley with his audio-photometer; others were made by us with a Hilger " Spekker photoelectric absorptiometer "). In no case was any change noted, a conclusion that was not unexpected since we had previously found that absorption spectra (in absolute-alcoholic solution) of a number of yellow and red solid modifications of anils had become identical within the minimum time necessary for making up the solutions and exposing them in the spectrometer (*i.e.*, less than 1 minute). Curves in which $\log_{10} \varepsilon$ is plotted against wave-length are given on p. 1461. A point of interest is that, by Goodeve and Kitchener's technique (*Trans. Faraday Soc.*, 1937, **34**, 190), the light reflected at 45° from a surface of salicylidene-*m*-toluidine has been examined spectroscopically. No notable differences between the limits 2000—4000 A were seen whether the yellow solid modification, the alcoholic solution prepared from it, or the exposed material was used. The reflection spectra of both solid varieties have strong bands at about 4050 and 5000 A, the latter being slightly widened with the darkened form.

(2) The experiments described above were repeated with solutions which were strongly illuminated by a mercury arc immediately before examination; again, no change was detected, showing that, if phototropy were occurring under these conditions, it decayed within a second or two.

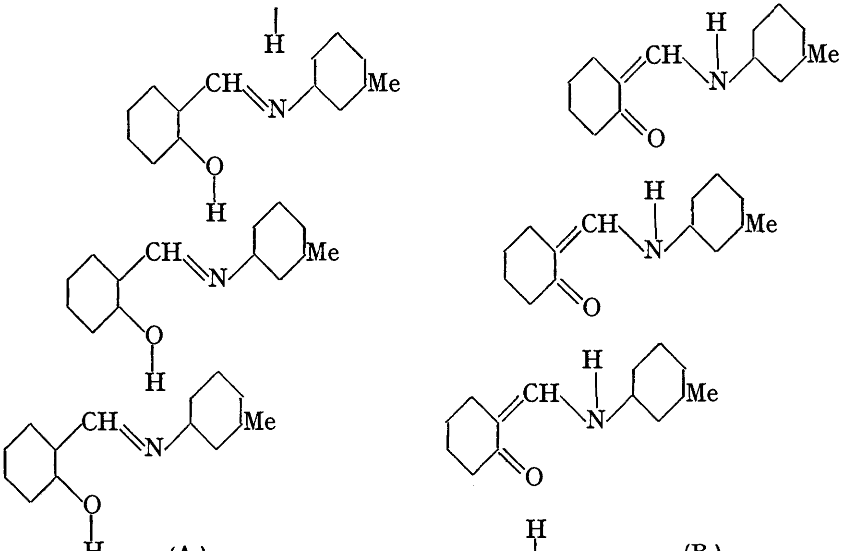
(3) Various solutions were placed in a parallel plate condenser, between the plates of which a condensed beam of light from a carbon arc could be passed This condenser was part of the circuit of a dynatron oscillator (see Experimental) and any change in its capacity would have caused a corresponding change of the frequency generated. If light were able to modify the solute molecules, such a capacity alteration on illumination of one or other of the solutions would have been likely, but this was never detected.

From these observations, therefore, we conclude that the phototropism of anils is a reaction which occurs *only* in the solid state and, being suppressed by the presence of a solvent (*i.e.*, a reversal of normal behaviour), must depend either upon some mutual molecular action or upon some alteration of the molecular arrangement in the crystal lattices.

Information on these possibilities was made accessible by the observation that the yellow forms of several of the phototropic anils were not darkened by *X*-rays; especially was this true of the most phototropic of all, *viz.*, salicylidene-*m*-toluidine. The two modifications of this substance were therefore examined by *X*-rays. Single-crystal and powder photographs of a yellow preparation of this substance were taken first, then—without otherwise disturbing the samples—darkening was effected by exposure to daylight, and finally, second *X*-ray photographs were taken. The corresponding films in both cases were identical.

Microphotographs of the same compound under analogous conditions similarly display no differences between the illuminated and the non-illuminated forms. Accordingly, since, except for the colour no other crystallographical property seems to be changed by light, it is concluded that the phototropic mechanism must consist in a mutual interaction of molecules in the lattice, and not in some rearrangement undergone by them therein.

A picture of such a mutual interaction would appear to be provided if, in the crystalline condition, the dispositions of the anil molecules in their lattices were such that the hydroxyl hydrogen of one molecule came near to the nitrogen atom of another. The whole solid could then be formulated as a hybrid between the states represented by (A) and (B),

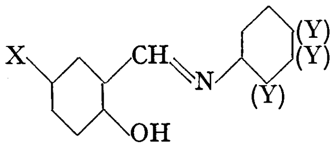


(A.) (B.)

in which the formulæ are to be imagined situated in parallel planes, one over the other. The extreme form of the anil molecule contained in (A) would presumably correspond to a colourless substance, since *o*-methoxybenzylidene-*m*-toluidine is itself colourless, whilst the form in (B)—*o*-quinonoid in structure—would be red to yellow. Illumination of the real form—intermediate between (A) and (B)—with light of suitable wave-length should cause activation, *i.e.*, the structure will become more like (A) or (B), a modification made manifest by alteration of colour but accompanied by no crystallographic change. The direction of this can be forecast by noting that the two characteristic units of structure in (A) and (B), *viz.*, OH·C:C·CH:N and NH·CH:C·C:O, differ in their energies (calculated from a table of heats of formation of covalent links; cf. Gooding and Sugden, private communication), the second being some 15 kg.-cals. per g.-mol. greater. Photoactivation of the solid anils will therefore correspond to an increase in the contribution which type (B) makes to the real form.

As mentioned on p. 1458, certain *p*-hydroxybenzylideneanils have been reported to be phototropic (Senier and Shepheard, *loc. cit.*; Senier and Foster, J., 1914, **105**, 2462; 1915, **107**, 452) and an analogous theory *mutatis mutandis* could obviously be stated for them. However, since we have made preparations of *p*-hydroxybenzylideneanils and *o*-anisidine which are *not* phototropic, the point will be further investigated.

The Influence of Substituents upon Phototropy.—A phenomenon occurring by the above mechanism should be influenced by factors tending to modify the hydrogen bond resonance. For instance, it would be expected: (1) that phototropic *o*- or *p*-hydroxyanils should lose this property if the hydroxylic hydrogen is blocked by methylation, and this is found to be so, for *methylation entirely destroys phototropy*; (2) the electrical influences of radicals substituted in the aryl nuclei should have considerable effect upon the phototropy. In the present work we have prepared examples, among others, of the following types of anils:



(*a*) where X = CH_3, Cl, Br, NO_2; Y = H.
(*b*) where X = H; 4-Y = H, CH_3, Cl, Br, NO_2.
(*c*) where X = CH_3; 4-Y = NO_2.
(*d*) where X = NO_2; 4-Y = CH_3.
(*e*) where X = H; 2-Y or 3-Y = CH_3.

At the outset it was planned to attempt to arrange these substances in a quantitative order with regard to their phototropism. The lighter-coloured forms were made into a paste with alcohol, smeared on to matt glass plates, and allowed to dry, in a dark-room. They were then exposed, leaving a masked section, at equal distances from a mercury-vapour lamp, and the time noted at which an impression of the mask upon the plate became definite. Salicylidene-*m*-toluidine underwent change most rapidly and was therefore adopted as a standard in these comparisons (accordingly, the θ values in the following text are, for a given anil, the time for definite darkening divided by the same time for salicylidene-*m*-toluidine).

Only three of these anils proved to be phototropic; nevertheless from these results certain general deductions can be drawn: (*a*) if X is any group other than hydrogen, phototropism does not occur; the electrical specification of X seems to be irrelevant—it may be either $+I$ or $\pm I \pm T$; (*b*) the influence of Y upon the phototropic process is very marked, for although salicylidene-*m*-toluidine, -aniline, and -*p*-bromoaniline gave θ values in the ratios 1 : 2 : 3, yet salicylidene-*o*- and -*p*-toluidines and -*p*-chloroaniline underwent no apparent colour changes.

These data bear no relation to any known order of action of the radicals involved, but this does not necessarily render invalid the picture of phototropy given above, since this requires that the substituents must neither reduce the electron density on the nitrogen atoms so that the tendency to "co-ordinate" a hydrogen atom is excessively repressed, nor facilitate this process so much that the real state of the compound is nearly that represented by a (B)-like structure. It is possible that the packing properties of these molecules are highly sensitive to the steric demands of substituents—perhaps more so than to their polarisations and polarisabilities (*e.g.*, the two crystalline modifications—plates and needles—of disalicylidene-*m*-phenylenediamine differ in their phototropic properties; Senier, Shepheard, and Clarke, *loc. cit.*)—so that in some of the lattices the -OH and N- groups of different molecules may not be close enough together.

Finally, it must be noticed that the results of such comparisons are dependent in some cases upon the light used. Salicylideneaniline, for instance, shows little colour development in sunlight, but if the light is first passed through a blue filter, a strong colour change—from light yellow to reddish-brown—is induced in the anil, which is thus evidently very sensitive to the reversing action of the longer waves.

EXPERIMENTAL.

Materials.—The anils were prepared by direct condensations between the appropriate aldehydes and primary amines. In most cases excellent preparations were secured by cooling an alcoholic solution saturated at about 30° to − 20°; after filtration, washing, and drying in a darkened room, the solids were stored in brown glass bottles. The solvents were purified as for dielectric-constant work (see Le Fèvre and Le Fèvre, J., 1935, 957).

Absorption Spectra.—These were obtained in the regions 2000—4500A for various anils in absolute alcohol by using a Hilger quartz spectrograph, a Spekker photometer, and Ilford Super Rapid Panchromatic plates. They are shown in Figs. 1—4, which represent $\log_{10}\varepsilon$ plotted against wave-length (the extinction coefficient ε being defined by $\log_{10} I_0/I = \varepsilon cl$, where c is the concentration in g.-mols./l., and l is in cm.).

The spectra show similarities of form, with two maxima of varying intensities in most cases around 2500—3000 A and 3500—4000 A. The nitro-anils and *o*-methoxybenzylideneaniline are rather different, the latter giving no indications of absorption in the shorter ultra-violet whereas the others all show sharp rises at 2500—3000 A. The steep right-hand parts of the curves correspond to the threshold of absorption noted for the *solid* forms in the next paragraph.

Absorption Spectrum of Solid Salicylidene-m-*toluidine.*—A paste of dilute alcohol and the finely ground anil was pressed into a wooden container, and set aside to dry in the dark. When hard, the surface was gently scraped to a matt finish. It was illuminated by light from a hydrogen discharge tube (continuous in the ultra-violet) impinging at 45°. The reflected light entered the slit of a large-aperture quartz Raman spectrograph (Hilger, E 420), where it was photographed on Ilford Special Rapid Panchromatic plates. In some experiments a mercury arc was used as the source of light. In all cases exposures of the anil and a reference layer of zinc oxide were made alternately every 20 minutes. No marked differences between the results were noticed when the yellow and the red form were interchanged; for both there is reflection at *ca.* 5000 A and a threshold of strong absorption at about 4050 A.

FIG. 1.

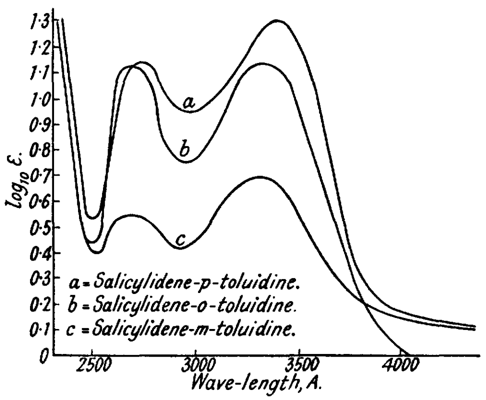


FIG. 2.

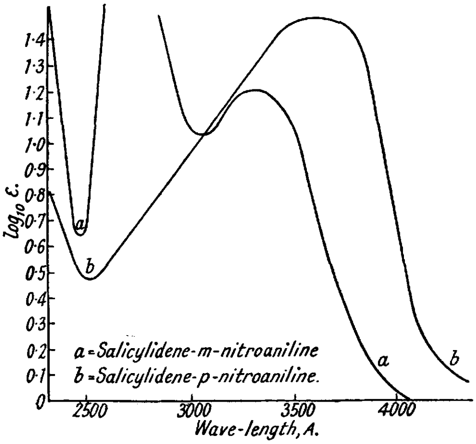


FIG. 3.

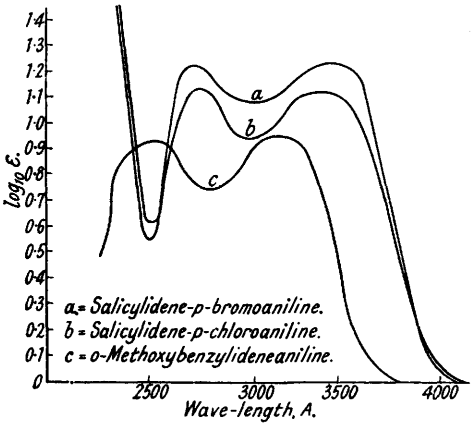
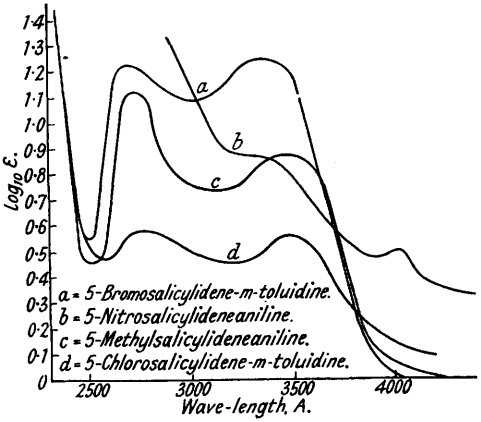


FIG. 4.

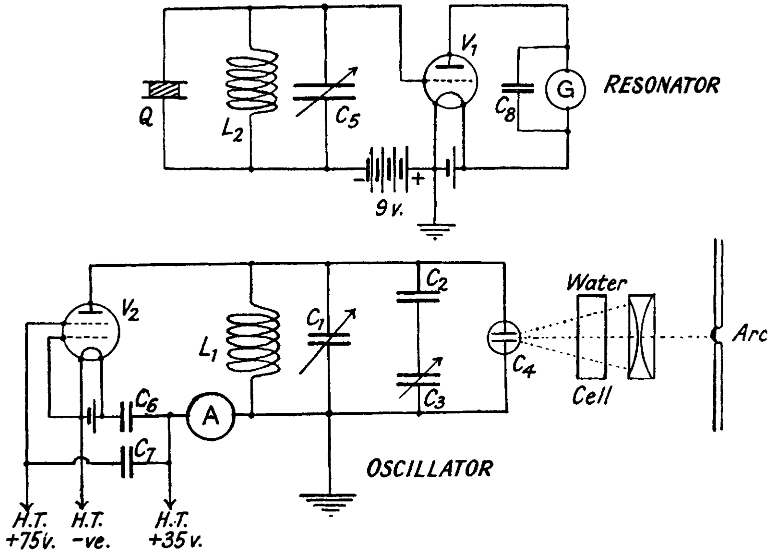


The Dielectrical Examination of Phototropic Changes in Solution.—The apparatus used is shown in Figs. 5 and 6.

The assembly was operated by setting condensers C_1 and C_3 in the oscillator so that the frequency radiated produced a galvanometer deflection in the resonator circuit about half-way down the wall of the crevasse caused in the ordinary tuning curve by the sharp resonance of the quartz (Q) : fuller details will be found in " Dipole Moments " (Methuen, 1938, pp. 25—27). This adjustment was very fine, the change caused by 0·1° alteration of temperature with pure benzene filling C_4 being of the order 50 galvanometer scale divisions. Since Hartshorne and Oliver (*Proc. Roy. Soc.*, 1929, *A*, **123**, 664) record ($\delta\varepsilon/\delta t$) benzene as — 0·0020, the actual capacity change under examination was *ca.* 0·0002 × 23 = 0·0046 μμF, so that a dielectric constant change of 1 in the fourth place was detectable.

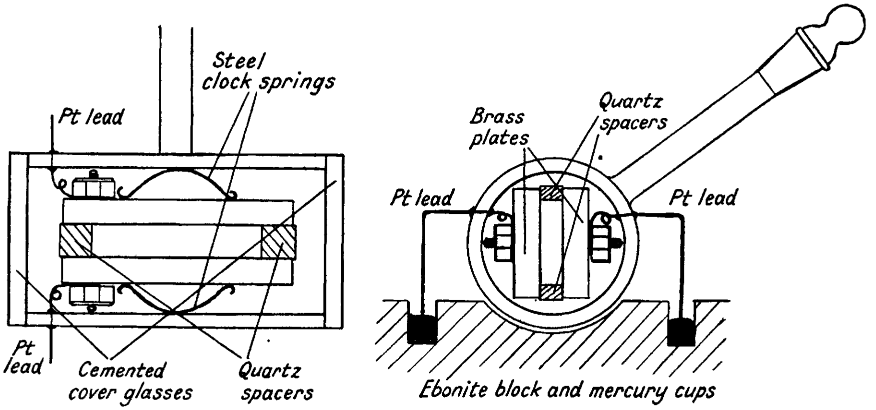
Illumination caused a slight deflection in *G* when pure benzene and other solvents were tested, but none of the anil and other solutions under comparable exposures showed any greater effects.

FIG. 5.



Apparatus for the detection of small changes of capacity.

FIG. 6.



Side view of cell. *End view of cell.*

Components.

V_1, *PM4DX Mullard valve.* V_2, *PM12 Screened-grid Mullard valve.* Q, *Quartz resonator,* 857 *kc. natural frequency.* L_1 *and* L_2, *about* 26 *turns No.* 18 *s.w.g. bare copper wire on* 3″ *diameter formers.* G, *Moll galvanometer.* C_1, 1200 *μμF Sullivan second-grade variable air condenser.* C_2, *Small fixed condenser about* 10 *μμF.* C_3, *Sullivan standard variable air condenser, maximum capacity* 250 *μμF.* C_4, *Special condenser (see Fig.* 6*), capacity about* 10 *μμF.* C_5, *Radio variable condenser, maximum capacity* 0·0005 *μF.* C_6, C_7, C_8, 2 *μF each.*

X-*Ray Photographs of Salicylidene*-m-*toluidine*.—A yellow specimen was finely powdered and packed into a lithium-glass tube. The *X*-ray spectrum was obtained in a Debye–Scherrer type of camera, a Philips Cu^{α} anode with 20 m.a. and 30 kW being used. The spacings obtained were very wide, but identical in intensity and position for the yellow and the red form of the anil. Use of a single crystal led to similar results which—because of the greater number of identically placed spots in the two films—were even more definite.

A preliminary experiment to ascertain whether *X*-rays could duplicate the effect of daylight was performed as follows: a yellow sample was mounted on a ground-glass plate by drying a coating of alcoholic paste in the dark, half-covered with ½″ lead plate, placed in a cardboard box, and exposed for 30 mins. at a distance of 50 cm. to a beam of *X*-rays from a Philips 180 kW, 4 m.a. copper anode with tungsten-tip, broad-focus, water-cooled treatment tube. No increase in the colour of the specimen was caused.

Microphotographs of Salicylidene-o-, m-, *and* -p-*toluidines*.—One drop of an absolute ethereal solution of the anil under investigation was allowed to crystallise on a microscope slide in the dark. The photographs were taken with a Vicker's "Transmitted Light Projection Microscope" used with an Abbé condenser and "Pointolite" source.

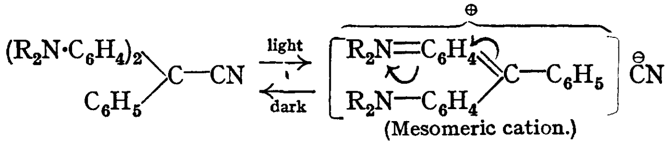
For the yellow forms, the illuminating beam was passed through a deep red-orange filter absorbing green, blue, violet, and ultra-violet (Ilford microfilter No. 5).

In the case of salicylidene-*m*-toluidine, the filter was then replaced by one transmitting ultra-violet, violet, and blue up to 4900 A (Ilford microfilter No. 6). A 30-min. exposure sufficed to darken the anil completely, and a second photograph was then taken.

The results for the yellow and the red modification were identical (see de Gaouck, Thesis, London, 1939, pp. 36*a*, *b*, and *c*, for the photographs).

A Note on the Phototropy of Solutions of the Leuco-cyanides of Malachite- and Brilliant-Greens.

In a search through the literature for cases of phototropy in solution it became obvious that in nearly all the instances where this phenomenon had been noticed it could be ascribed to ionisation induced by the illumination. For example, a colourless alcoholic solution of pararosaniline leuco-cyanide becomes red on exposure to ultra-violet light, and at the same time begins to show the characteristic absorption bands of pararosaniline salts, and the substances named in the above title give colourless solutions in alcoholic or aqueous media in the dark which become green in the light (Hantzsch and Osswald, *Ber.*, 1900, **33**, 278; Müller, *Ber.*, 1910, **43**, 2609); these colour changes are reversible and are accompanied by alterations in the electrical conductivities. The processes can therefore reasonably be formulated:



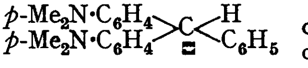
(R = Me and Et for malachite- and brilliant-green respectively.)

Similar schemes could be written for other leuco-derivatives.

On such a view no phototropy should occur in a non-ionising solvent. However, Joffe (Diss., Zürich, 1921) has stated that the leuco-cyanides of a number of triarylmethane dyes exhibit phototropy in benzene as well as in alcoholic and ethereal solutions. We have therefore prepared specimens of the leuco-cyanides of malachite- and brilliant-greens and re-examined these points experimentally.

Neither compound has shown in benzene solution any visible alteration under the influence of daylight or ultra-violet light from a mercury discharge tube. A similarly negative result has been obtained by testing the dielectric capacity [cf. method (3), p. 1462] of a condenser successively in the presence and absence of an intense illumination from a carbon arc source (the apparatus was that assembled for a similar experiment with salicylidene-*m*-toluidine).

Regarding the phototropy of alcoholic solutions, we confirm the increase of conductivity which accompanies illumination and colour development, yet in no case was the initial resistance ever recovered by long standing in the dark. Fig. 7 shows a typical result, the effect being quantitatively reversible *only after* the first exposure. This behaviour was possibly due to the hydrolytic action of the small amount of water present in ordinary "absolute" alcohol, by which the dye leuco-cyanides when dissociated tend to revert to the corresponding carbinol bases. The liberated hydrogen cyanide would then account for the permanent increase of conductivity.



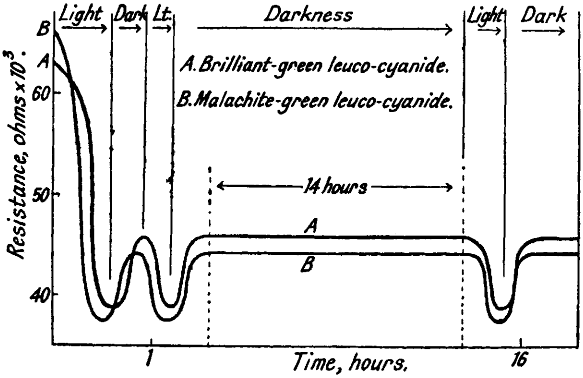
$$\begin{matrix} p\text{-}Me_2N{\cdot}C_6H_4 \\ p\text{-}Me_2N{\cdot}C_6H_4 \end{matrix} > C < \begin{matrix} H \\ C_6H_5 \end{matrix}$$

Incidentally, in this work we have determined the dipole moments of the two cyanides, together with that of the leuco-base of malachite-green (annexed formula).

The Leuco-cyanides of Malachite- and Brilliant-greens.—Commercial specimens of the dyes in 1% aqueous solution were treated with an excess of saturated potassium cyanide solution. The precipitates were collected, and recrystallised (charcoal) three times from alcohol in the dark. The preparations used had m. p. 176° and 160° respectively (compare Hantzsch and Osswald, *loc. cit.*).

The specimen of malachite-green leuco-base, after crystallisation from alcohol, had m. p. 102°. The form, m. p. 93—94°, said to be produced by the use of alcohol as solvent (cf. Beilstein, " Handbuch," 4th Edition, XIII, 275), was not observed.

FIG. 7.



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 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 $d_{4^\circ}^{25^\circ}$ for benzene = 0·87378; p, the specific polarisation of the solution; and ${}_{\mathrm{T}}P_\infty$, the total polarisation of the solute at infinite dilution. The last two quantities have been calculated on the assumption that the densities and dielectric constants of the solutions have a 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 ${}_{T}P_\infty = Mp$ c.c. The refractive

Results from Measurements recorded below.

	M.	Mean $\alpha\epsilon_2$.	Mean βd_2.	${}_{\mathrm{T}}P_\infty$.	$[R_L]_{\mathrm{D}}$.	μ, D.
Malachite-green leuco-cyanide	355	0·80	0·199	147·2	121	$1{\cdot}1_3$
Brilliant-green leuco-cyanide	411	1·00	0·191	186·7	126	$1{\cdot}7_2$
Malachite-green leuco-base	330	1·13	0·151	163·2	112	$1{\cdot}5_7$

Measurements.

$1000w_1$.	ϵ.	$\alpha\epsilon_2$.	d.	βd_2.	$n_{\mathrm{D}}^{25^\circ}$.	r_{12}.	$[R_L]_{\mathrm{D}}$.
0	2·2966	—	0·87378	—	1·49724	0·33503	—
			Malachite-green leuco-cyanide.				
3·125	2·2966	0·771	0·87431	0·170	1·49768	0·33510	120·9
4·235	2·3006	0·798	0·87456	0·184	1·49770	0·33501	120·9
5·012	2·3132	0·811	0·87539	0·221	1·49781	0·33472	120·9
7·584	2·3352	0·827	0·87547	0·223	1·49803	0·33471	120·9
			Brilliant-green leuco-cyanide.				
4·267	2·3162	1·02	0·87459	0·190	1·49760	0·33492	127·1
5·613	2·3276	0·98	0·87486	0·192	1·49774	0·33485	124·5
7·705	2·3439	0·93	0·87518	0·182	1·49794	0·33483	127·0
4·837	2·3242	1·07	0·87470	0·190	1·49762	0·33488	124·9
			Malachite-green leuco-base.				
2·433	2·2752	1·11	0·87413	0·144	1·49772	0·33517	112·4
4·242	2·2765	0·94	0·87440	0·146	1·49790	0·33517	112·4
5·420	2·2798	1·35	0·87467	0·164	1·49797	0·33510	112·4

indices and specific and molecular refractions respectively are given under $n_{\mathrm{D}}^{25^\circ}$, r_{12}, and $[R_L]_{\mathrm{D}}$, the last constant being calculated from $M[r_2 + (r_{12} - r_2)/w_1]$.

Marsden and Sutton (J., 1936, 599) have shown by dipole-moment measurements that the R_2N group greatly facilitates mesomerism in an aromatic system containing it (compare Ingold, *Ann. Reports*, 1926, **23**, 129), and the present results provide a further illustration. For, since the dipole moment of dimethylaniline is 1·6, that of chloro- or bromo-benzene about 1·6, and those of *p*-chloro- and -bromo-dimethylanilines 3·3 and 3·4 respectively (Marsden and Sutton, *loc. cit.*), it appears as if the two group moments of the p-$R_2N{\cdot}C_6H_4{\cdot}$ radicals in the dye derivatives should be taken as being *ca.* 1·6 D converging at 110°. The resultant, namely, 1·8 D, should then interact at 55°, with the vector appropriate to the CN groups (say 3·2), thus producing a resultant of 4·5 D. The actual experimental figures are considerably lower than this, suggesting that these are instances where the polarities arising from the opposing mechanisms, conventually formulated $\mathrm{R_2N} \overset{\curvearrowright}{\longleftarrow} \mathrm{C}$, roughly balance one another, so that the molecular resultants are the vectorial differences of the three $\mathrm{C}\rightarrow$Aryl components in each case and the $\mathrm{C}\rightarrow\mathrm{CN}$ component. As a rough assessment of the former factor, we may take the value for the leuco-base of malachite-green. This is found to be 1·6 D, which, subtracted from 3·2 D, gives a result of the order actually found.

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