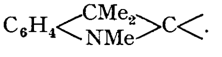
# 448. *The Thermotropy of Certain Benzonaphtho- and Dinaphtho-bis*spiro-2-*pyrans in Benzene Solutions.*

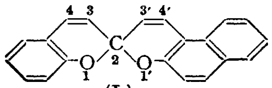
By A. A. Hukins and R. J. W. Le Fèvre.

Of the various explanations in the literature for the reversible colour changes shown by a number of *spiro*pyrans when successively heated and cooled, only those involving the production of, or increasing contributions to a mesomeride from, fully ionic forms seemed to accord with all recorded observations.

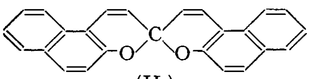
Such explanations may, however, be incorrect, since it is now found that the development of colour is not accompanied by any noticeable increase of dipole moment. Present measurements do not entirely eliminate possibilities that the thermally generated chromogens are of *o*-quinonoid type.

Senier and Shepheard, in a series of papers (*J.*, 1909—1912), obviously thought there was some connection between phototropy and thermotropy (cf. *J.*, 1909, **95**, 1943). Having previously (de Gaouck and Le Fèvre, *J.*, 1939, 1457) found that certain strongly phototropic crystalline anils ceased to be phototropic on dissolution, we thought it of interest to investigate a number of *spiro*pyrans which have been reported to exhibit *thermotropy in the dissolved condition.*

These substances are derivatives of benzonaphtho- and dinaphtho-bis*spiro*-2-pyrans (I and II) (Löwenbein and Katz, *Ber.*, 1926, **59**, 1377; Dilthey, Berres, Hölterhoff, and Wübken, *J. pr. Chem.*, 1926, **114**, 179; Dickinson and Heilbron, *J.*, 1927, 14, 1699; Heilbron and Irving, *J.*, 1933, 430), which, in *cold* solvents, form colourless solutions assuming, as their temperatures are raised, an intense violet-blue colour. The phenomenon, when it occurs, appears to be reversible, and after many repetitions the solutes can be recovered in their original purity. Heilbron *et al.* (*loc. cit.*) at first considered such behaviour to be limited to molecules having (*a*) at least one naphthalene nucleus, and (*b*) an unsubstituted 3′-carbon atom in the naphthopyran ring, but they later (1933) demonstrated that it could still occur if the 3 : 3′-positions were bridged by polymethylene chains. Since then, Wizinger and Wenning (*Helv. Chim. Acta*, 1940, **23**, 247) have also reported similar properties for a number of naphthopyrans in which the other component is heterocyclic, *e.g.*, $O(C_6H_4)_2C<$, $MeN(C_6H_4)_2C<$, or  $C_6H_4<\genfrac{}{}{0pt}{}{CMe_2}{NMe}>C<$.



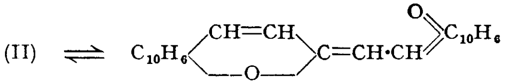
(I.)



(II.)

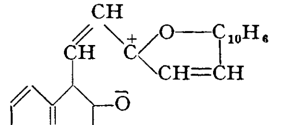
In the present work we have prepared di-β-naphtho- and benzo-β-naphtho-bis*spiro*-2-pyran, and the isomeric 3- and 3′-monomethyl derivatives, the last being chosen because it does not become coloured even in hot xylene. Further, Löwenbein and Dilthey have independently shown that the molecular weights of these compounds are normal both in the white and in the purple condition.

*Proposed Mechanisms.*—Dickinson and Heilbron, and Löwenbein and Katz initially attributed the production of colour to an intramolecular change from the *spiro*- (as I or II) to an *o*-quinonoid type (*e.g.*, III) :



$$(II) \rightleftharpoons \mathrm{C_{10}H_6}\left\langle\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{C{=}CH{\cdot}CH}\left\langle\begin{matrix}\mathrm{O}\\ \ \end{matrix}\right\rangle\mathrm{C_{10}H_6}$$

(III.)



(IV.)

Dilthey *et al.* (*loc. cit.*) rejected this hypothesis and suggested ionic dissociation as a cause, the coloured molecule being heteropolar, *e.g.*, as in (IV). Dickinson and Heilbron (*loc. cit.*, p. 1702) then wrote formulæ involving ionised chelates, but later withdrew them in the face of their own further experimental evidence (*loc. cit.*, 1933). The possibilities of free-radical formation have been considered by Heilbron, Löwenbein, and Dilthey, and by each found incompatible with observed chemical reactions, *e.g.*, prolonged oxygen treatment of hot solutions causing no diminution of colour, quinol being without effect, etc. Schönberg and Sina (*J.*, 1947, 175), by implication, regard these *spiro*pyrans as resonance hybrids between the neutral and the ionised structures (*e.g.*, between II and IV).

*Present Work.*—Explanations involving the intervention of ionised forms would require the development of colour to be accompanied by an increase of polarity. The dipole moment of, *e.g.*, (IV), when fully ionised, is clearly not less than *ca.* 10 D., while the original molecules (*e.g.*, I or II) will, from elementary vectorial principles, have moments lying around $(2\mu^2\cos^2 30°)^{\frac{1}{2}} = 1{\cdot}23\ \mu$ (where $\mu$ is the component moment acting roughly through each oxygen; regular hexagonal rings being assumed throughout). The calculation resembles that for 2 : 2′-disubstituted diphenyls (*J.*, 1938, 967) with an azimuthal angle of 90°. Plausible values for $\mu$ might be selected between those of coumarone (0·8 D.; Syrkin and Schott-Lvova, *J. Physical Chem. U.S.S.R.*, 1938, **12**, 479) and di-*p*-tolyl ether (1·4 D., Faraday Soc. List, 1934), whence the colourless *spiro*pyrans should show moments in the range 1—1·7 D.

## EXPERIMENTAL.

The *spiro*pyrans were prepared as indicated by Dickinson and Heilbron (*loc. cit.*), the m. p.s given by them being added in parentheses: Benzo-β-naphthobis*spiro*-2-pyran, from aqueous acetone, m. p. 167° (168°); 3-methyl-β-, from acetone, m. p. 149° (149°); 3′-methyl-β-, from absolute alcohol, m. p. 176° (177°); di-β-naphthobis*spiro*-2-pyran, from xylene, m. p. 160° (160°).

Measurements tabulated below have been made by means of the apparatus and techniques already reported (*J.*, 1948, 1949). They are set out under customary headings (explained in *J.*, 1937, 1805, wherein our method of calculation is also described). Refractive indices were observed with an Abbé refractometer. The solvent was benzene throughout—a preliminary test showing that it allowed a sufficient temperature range for the 3-methyl compound to develop a strong colour; AnalaR grade material was partly frozen, decanted, dried, and stored over sodium wire. The range of concentrations available was limited by the sparing solubilities of the *spiro*pyrans.

*Dielectric constant and density coefficients at* 25°.

| $100w_1$. | $\varepsilon^{25}_{1000}$. | $\alpha\varepsilon_2$. | $d^{25}_4$. | $\beta d_2$. | $100w_1$. | $\varepsilon^{25}_{1000}$. | $\alpha\varepsilon_2$. | $d^{25}_4$. | $\beta d_2$. |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 2·2725 | — | 0·87378 | — | 0 | 2·2725 | — | 0·87378 | — |
| Benzo-β-naphthobis*spiro*-2-pyran. | | | | | Di-β-naphthobis*spiro*-2-pyran. | | | | |
| 0·3604 | 2·2769 | 1·22 | 0·87474 | 0·2658 | 0·34503 | 2·2766 | 1 | 0·87477 | 0·2869 |
| 3-Methylbenzo-β-naphthobis*spiro*-2-pyran. | | | | | 3′-Methylbenzo-β-naphthobis*spiro*-2-pyran. | | | | |
| 0·93642 | 2·2832 | 1·14 | 0·87625 | 0·2637 | 0·3886 | 2·2774 | 1·25 | 0·87484 | 0·2725 |
| 1·2373 | 2·2853 | 1·03 | 0·87710 | 0·2683 | 0·8848 | 2·2828 | 1·16 | 0·87612 | 0·2641 |

A solution of the last compound ($100w_1 = 0{\cdot}62448$) in benzene ($n^{25}_{\mathrm{D}}$ 1·4971; $d^{25}_4$ as above) had $n^{25}_{\mathrm{D}}$ 1·4978 and $d^{25}_{\mathrm{D}}$ 0·87556. Its specific polarisation was therefore 0·33466 c.c., whence the molecular refraction of the solute was 90 c.c. From standard atomic and bond-refraction data the theoretical value was 91 c.c. This agreement justified the use, for the three other *spiro*pyrans, of $[R_L]_{\mathrm{D}}$ figures calculated from the tables of Roth–Eisenlohr (" Refraktometr. Hilfsbuch," Leipzig, 1911).

*Calculation of results.*

| $M_1$. | Mean $\alpha\varepsilon_2$. | Mean $\beta$. | $_\infty P_1$. | $[R_L]_D$. | $\mu$, D. | $M_1$. | Mean $\alpha\varepsilon_2$. | Mean $\beta$. | $_\infty P_1$. | $[R_L]_D$. | $\mu$, D. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzo-$\beta$-naphthobis*spiro*-2-pyran. | | | | | | Di-$\beta$-naphthobis*spiro*-2-pyran. | | | | | |
| 298·3 | 1·22 | 0·304 | 139·1 | 86·8 | $1{\cdot}4_2$ | 348·4 | 1·19 | 0·328 | 157·6 | 102·1 | $1{\cdot}6_4$ |
| 3-Methylbenzo-$\beta$-naphthobis*spiro*-2-pyran. | | | | | | 3′-Methylbenzo-$\beta$-naphthobis*spiro*-2-pyran. | | | | | |
| 312·4 | 1·09 | 0·316 | 136·4 | 91·4 | $1{\cdot}4_7$ | 312·4 | 1·20 | 0·307 | 144·4 | 91·4 | 1·6 |

The calculations showed that, at 25°, at which temperature the solutions were all colourless, the solutes had dipole moments of the orders to be expected for structures (I) and (II). Similar readings at higher temperatures were next taken, as shown in the following table.

*Polarisation and density measurements at higher temperatures.*

| Temp., $t$. | $d_4^t$. | $\beta d_2$. | $\beta$. | $\varepsilon_t$. | $\alpha\varepsilon_2$. | $P_1$. |
|---|---|---|---|---|---|---|
| 3-Methylbenzo-$\beta$-naphthobis*spiro*-2-pyran. | | | | | | |
| Solution (i) : $w_1 = 0{\cdot}006052$. | | | | | | |
| 30° | 0·87008 | 0·2645 | 0·3045 | 2·2693 | 1·074 | 138 |
| 40 | 0·85940 * | 0·2631 | 0·3067 | 2·2498 | 1·124 | 142 |
| 50 | 0·848743 | 0·2649 | 0·3127 | 2·2296 | 1·058 | 139 |
| 60 | 0·83807 | 0·2640 | 0·3156 | 2·2096 | 1·025 | 138 |
| Solution (ii) : $w_1 = 0{\cdot}015291$. | | | | | | |
| 30 | 0·87246 | 0·2605 | 0·3003 | 2·2781 | 1·001 | 134 |
| 35 | 0·86725 * | 0·2686 | 0·3112 | 2·2682 | 1·001 | 133 |
| 40 | 0·86187 | 0·2656 | 0·3096 | 2·2585 | 0·010 | 135 |
| 45 | 0·85665 | 0·2731 | 0·3204 | 2·2486 | 1·012 | 134 |
| 50 | 0·85127 | 0·2700 | 0·3187 | 2·2385 | 1·003 | 134 |
| 60 | 0·84074 | 0·2790 | 0·3335 | 2·2184 | 0·9816 | 133 |
| 3′-Methylbenzo-$\beta$-naphthobis*spiro*-2-pyran. | | | | | | |
| $w_1$ 0·0062448. | | | | | | |
| 30 | 0·87016 | 0·2697 | 0·3105 | 2·2702 | 1·190 | 144 |
| 35 | 0·86482 * | 0·2687 | 0·2319 | 2·2602 | 1·16 * | 143 |
| 40 | 0·85943 | 0·2597 | 0·3028 | 2·2500 | 1·121 | 142 |
| 45 | 0·85410 * | 0·2604 | 0·3054 | 2·2404 | 1·166 | 145 |
| 50 | 0·84886 | 0·2748 | 0·3244 | 2·2303 | 1·121 | 141 |
| 60 | 0·83815 | 0·2693 | 0·3220 | 2·2108 | 1·191 | 148 |

* Estimated by graphical interpolation.

The densities and dielectric constants recorded above were determined relatively to the standard figures (**) at 25° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **123**, *A*, 664). We have used the following data for evaluating the coefficients, $\alpha$ and $\beta$ :

| $t$. | $\varepsilon_t$. | $d_4^t$. | $t$. | $\varepsilon_t$. | $d_4^t$. | $t$. | $\varepsilon_t$. | $d_4^t$. |
|---|---|---|---|---|---|---|---|---|
| 25° | 2·2725 ** | 0·87378 ** | 40° | 2·2430 | 0·85781 | 50° | 2·2232 | 0·84714 |
| 30 | 2·2628 | 0·86848 | 45 | 2·2331 | 0·85247 | 60 | 2·2034 | 0·83647 |
| 35 | 2·2529 | 0·86314 | | | | | | |

## DISCUSSION.

The solutions of the 3-methylbenzo-compound began to show distinct colour at 40°. They were a deep violet at 60°. The 3′-isomer, however, remained without tint over the whole temperature range. Yet it will be noted that no change of polarisation accompanies the alteration of colour. The variations between the $P_1$ values for the thermotropic 3-methyl derivative are not more marked than between the corresponding values for the non-thermotropic 3′-isomer. Such irregularities as do occur are probably due to evaporation of solvent at the higher temperatures. It is relevant to mention that, on a basis of $\mu_{\text{solute}} = 1{\cdot}5$ D., a rise of 30° should cause $P_1$ to decrease about 4 c.c. On the other hand, a solute with $\mu = 10$ D. would require a $P_1$ of *ca.* 1600 c.c. We conclude, therefore, that our results show the negligible production of such fully ionised forms as (IV).

In the face of the recorded chemical evidence already cited, no convincing explanation for these cases of thermotropy seems to be available. Provisionally, the least unacceptable hypothesis is that indicated by (III) above, since it is possible for such structures to be disposed so that the C–O–C and the C=O component moments will oppose one another in the molecular resultant.

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