4.0; Cl, 11.3; active H, 0.30. 9-Phenyl-2-chloroxanthydrol is easily soluble in cold benzene, ether and hot ethyl alcohol and gives an orange color with sulfuric acid.

Reduction of 9-phenyl-2-chloroxanthydrol was carried out as described by Ullmann and Engi[19] for phenylxanthene (VIIIa), *i.e.*, by means of zinc dust and acetic acid with platinum chloride as a catalyst. VIIIb was crystallized from ethyl alcohol as colorless crystals, m.p. 139°, in almost quantitative yield. *Anal.* Calcd. for $C_{19}H_{13}ClO$: C, 78.1; H, 4.5; Cl, 11.98. Found: C, 77.9; H, 4.4; Cl, 12.0. It is easily soluble in benzene, but sparingly soluble in cold ethyl alcohol and gives no color with sulfuric acid.

A solution of 1 g. of VIIIb was exposed to sunlight for 15 days (April). The colorless crystals that separated out during exposure were recrystallized from benzene (*ca.* 0.63 g.), m.p. 221° dec., brown-red melt. *Anal.* Calcd. for $C_{38}H_{24}Cl_2O_4$: C, 74.3; H, 3.9; Cl, 11.4. Found: C, 74.1; H, 3.8; Cl, 11.3. IXb is soluble in hot benzene and xylene, but difficultly soluble in ethyl alcohol and gives an orange-yellow color with sulfuric acid.

Thermal decomposition of 0.5 g. of IXb for half an hour at 270° (bath-temp.) afforded xanthone (*ca.* 0.18 g.) (m.p. and mixed m.p. and color reaction with sulfuric acid) as a pale-yellow sublimate.

GIZA, CAIRO, EGYPT

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[19] F. Ullmann and E. Engi, *Ber.*, **37**, 2371 (1904).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

# Thermochromism of Dixanthylenes. II[1]

BY AHMED MUSTAFA AND MOHAMED EZZ EL-DIN SOBHY

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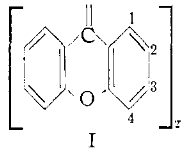
Substitution in dixanthylene (I) in positions 1 and 1′, which hinders the planarity of the whole molecule, is detrimental to the development of thermochromic properties (Table I). Fission of the central ethylene linkage in dixanthylenes Ia-d is brought about by the action of thionyl chloride followed by water to give the corresponding xanthone derivatives and by the action of sulfur at 270° to yield the corresponding xanthione derivatives. Three new xanthone derivatives Va-c, needed in this investigation, have been synthesized.

In continuation of the study of constitutional changes in thermochromic substances leading to non-thermochromic substances,[2] we now have extended our previous investigation[1] to show how substitution affects the thermochromic properties of dixanthylene (I); a strongly thermochromic substance, the crystals are colorless in liquid air, blue-greenish on heating and the melt is deep blue-green.[3] The results are shown in Table I; the substances were tested in boiling diphenyl ether solutions.



I

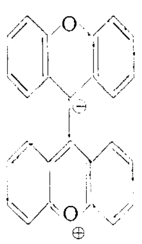
TABLE I

| | |
|---|---|
| 2,2′-Dibromo- (Ia) | Strongly thermochromic |
| 4,4′-Dibromo- (Ib) | Strongly thermochromic |
| 2,3,2′,3′-Tetramethyl- (Ic) | Strongly thermochromic |
| 2,4,2′,4′-Tetramethyl- (Id) | Strongly thermochromic |
| 1,4,1′,4′-Tetramethyl- (Ie) | Not thermochromic |
| 1,3,1′,3′-Tetramethyl- (If) | Not thermochromic |

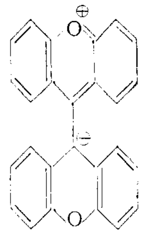
## Discussion of the Results

Recently, Schönberg, Mustafa and Asker[2] advanced a hypothesis that "in overcrowded molecules in which planarity is hindered, the degree of non-planarity changes with temperature. This is associated with change of color, one reason being that resonance is related to planarity." Dixanthylenes, *e.g.*, I, a thermochromic compound, lose this property upon substitution at positions 1 and 1′ (*cf.* Table I). The loss of the thermochromic properties is due to a constitutional change in I, overcrowding of the molecule to such a degree that planarity is hindered even at high temperatures. From this, it has been concluded that the green forms of I and its analogs, the "colored molecules" have a greater degree of planarity; the experiments of thermochromic bianthrones have led Hirshberg, Loewenthal, Bergmann and Pullman[4] to similar conclusions.

**Action of Thionyl Chloride on Dixanthylenes.** Dixanthylene shows remarkable behavior toward thionyl chloride, followed by the action of water.[5] Fission of the central ethylene bond, which has single bond character (*cf.* IIa and IIb), occurs and xanthone is formed. The authors have now found that Ia-d behaved analogously, yielding 2-bromo-, 4-bromo-, 2,3-dimethyl- (Vc) and 2,4-dimethylxanthones (Vd), respectively.

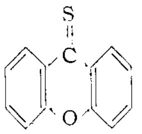


IIa



IIb

**Action of Sulfur on Dixanthylenes.**—Fission of the central ethylene linkage in dixanthylenes Ia-d is brought about by the action of sulfur[6] at 270° for a few minutes, with the formation of the corresponding xanthones III.



III

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[1] For part I *cf.* A. Schönberg, A. Mustafa and M. E. E. Sobhy, THIS JOURNAL, **75**, 3377 (1953).

[2] A. Schönberg, A. Mustafa and W. Asker, *ibid.*, **76**, 4134 (1954).

[3] A. Schönberg and O. Schütz, *Ber.*, **61**, 478 (1928).

[4] Y. Hirshberg, E. Loewenthal, E. D. Bergmann and B. Pullman, *Bull. soc. chim.*, [5] **18**, 88 (1951).

[5] A. Schönberg and W. Asker, *J. Chem. Soc.*, 725 (1942).

[6] A. Schönberg, A. Ismail and W. Asker, *ibid.*, 442 (1946).

TABLE II

SUBSTITUTED DIXANTHYLENES

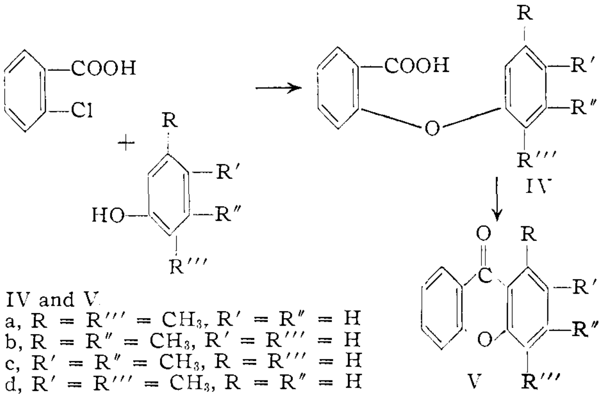
| Dixanthylene[c,d] | M.p.,[e] °C. | Method of prepn. | Yield, % | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Halogen, % Calcd. | Halogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 293[a] | A | 71 | | | | | | | |
| | | B | 32 | $C_{26}H_{14}Br_2O_2$ | 60.2 | 59.8 | 2.7 | 2.5 | 30.9 | 30.7 |
| | | C | 53 | | | | | | | |
| Ib | 278[a] | A | 72 | | | | | | | |
| | | B | 35 | $C_{26}H_{14}Br_2O_2$ | 60.2 | 60.1 | 2.7 | 2.3 | 30.9 | 30.5 |
| | | C | 53 | | | | | | | |
| Ic | 287[a] | B | 29 | | | | | | | |
| | | C | 57 | $C_{30}H_{24}O_2$ | 86.5 | 86.3 | 5.8 | 5.5 | .. | .. |
| Id | 285[a] | B | 27 | | | | | | | |
| | | C | 57 | $C_{30}H_{24}O_2$ | 86.5 | 86.1 | 5.8 | 5.7 | .. | .. |
| Ie | 267[b] | B | 38 | $C_{30}H_{24}O_2$ | 86.5 | 86.4 | 5.8 | 5.4 | .. | .. |
| If | 191[b] | B | 34 | $C_{30}H_{24}O_2$ | 86.5 | 86.0 | 5.8 | 5.7 | .. | .. |

[a] Deep bluish-green melt. [b] Yellow melt. [c] An orange-red color is developed when treated with sulfuric acid at 100°. [d] Xylene was used as a solvent for crystallization except for If petroleum ether (b.p. 100–110°) was used. Ia-f are easily soluble in hot anisole, but difficultly soluble in alcohol. [e] Melting points are uncorrected.

**Methods of Preparation.** (a) **Dixanthylenes.**—The dixanthylene derivatives Ia-f listed in Table I were prepared by treating the corresponding xanthone derivatives with zinc dust and acetic acid in the presence of concentrated hydrochloric acid.[7] Ia-b also have been obtained by treating the corresponding xanthones with thionyl chloride, followed by the action of copper bronze,[8] and by the action of copper bronze on the corresponding xanthiones[9] in the case of Ia-d.

(b) **Xanthiones.**—The xanthiones III listed in Table III were prepared by the action of phosphorus pentasulfide on the corresponding xanthones. The halogen-substituted xanthiones also have been obtained by the action of thiolacetic acid on the product obtained by the action of thionyl chloride on the coresponding halogen-substituted xanthones.[9]

(c) **Xanthones.**—The new xanthone derivatives needed in this work, namely, 1,4-dimethyl-(Va), 1,3-dimethyl-(Vb) and 2,3-dimethylxanthone (Vc), were prepared after Dahr method,[10] from 5-hydroxy-1,4-dimethylbenzene, 5-hydroxy-1,3-dimethylbenzene and 5-hydroxy-2,3-dimethylbenzene, respectively, and *o*-chlorobenzoic acid in the presence of sodium methoxide and copper powder followed by ring closure of the intermediate phenoxybenzoic acid IV with sulfuric acid.



IV and V

a, $R = R''' = CH_3, R' = R'' = H$

b, $R = R'' = CH_3, R' = R''' = H$

c, $R' = R'' = CH_3, R = R''' = H$

d, $R' = R''' = CH_3, R = R'' = H$

## Experimental

**Dixanthylene Derivatives** (**I**) (*cf.* Table II). **Method (A).**—Two grams of the xanthone was refluxed (using a calcium chloride tube) with 15 ml. of thionyl chloride (or with 10 g. of oxalyl chloride) for 10 hours; the excess of thionyl chloride (or oxalyl chloride) was distilled off, and the residual oil dissolved in 30 ml. of dry xylene and refluxed with 4.0 g. of copper bronze for 6 hours with occasional shaking. The xylene solution was filtered while hot and concentrated; on cooling the dixanthylene derivative crystallized out.

(**B**).—One gram of the xanthone after 30 minutes boiling with 0.5 g. of zinc dust and 10 ml. of glacial acetic acid in the presence of 2–3 drops of concentrated hydrochloric acid gave the dixanthylene derivative.

(**C**).—A solution of 1 g. of the xanthione in 20 ml. of dry xylene was refluxed with 0.5 g. of copper bronze for 6 hours. The filtered xylene solution, on concentration, gave the dixanthylene derivative.

Dilute solutions of the dixanthylenes Ia-d in diphenyl ether or anisole are almost colorless at room temperature; the boiling solutions are bluish-green; the color phenomenon is reversible.

Non-thermochromic dixanthylenes Ie-f dissolve in diphenyl ether or anisole and show no thermochromism to the naked eye both at room temperature and at the boiling point of the solvent.

**Action of Thionyl Chloride.**—One gram of each of Ia-d was refluxed with 30 ml. of thionyl chloride, respectively, for 6 hours; the excess of thionyl chloride was distilled off completely (pump) and the residual oil was dissolved in benzene and shaken with water at 30° for 30 minutes. The benzene layer was evaporated and the residual oil was crystallized from benzene–petroleum ether (b.p. 40–60°) and proved to be 2-bromo-, 4-bromo-, 2,3 dimethyl- (Vc) and 2,4-dimethylxanthones (Vd), respectively (identified by m.p. and mixed m.p. and color reaction with sulfuric acid); yield is 68, 71, 63 and 66%, respectively.

**Action of Sulfur.**—One gram of each of Ia-d was ground with 0.5 g. of sulfur and the mixture was heated at 270° (bath temp.) for 10 minutes, allowed to cool, powdered and extracted repeatedly with petroleum ether (b.p. 100–110°). The extract was concentrated, cooled, filtered from precipitated sulfur, and the bluish-green solution was concentrated further and cooled. 2-Bromo-, 4-bromo-, 2,3-dimethyl- and 2,4-dimethylxanthiones (III; *cf.* Table III) were obtained, respectively. Identification was carried out by m.p. and mixed m.p. determination with an authentic specimen (see below) and the formation of a reddish-brown colored surface on the crystals of mercuric chloride added to their benzene solutions.[11]

**Xanthiones. General Procedure.** (**a**).—One gram of the xanthone was mixed thoroughly with 1.2 g. of phosphorus pentasulfide. The mixture was heated for one hour and the solid mass, so obtained on cooling, was powdered and extracted several times with hot benzene (*ca.* 50 ml.). The benzene solution was evaporated and the solid residue was dissolved in petroleum ether (b.p. 60–80°) and concentrated on cooling, the xanthione derivative crystallized out.

(**b**).—The orange oil, obtained by the action of 15 ml. of thionyl chloride on 1 g. of the xanthone, as described above, was dissolved in 40 ml. of dry benzene and refluxed for 6 hours with 2 ml. of thiolacetic acid during which time a deep bluish-green color was developed. The excess of benzene and acid was removed by distillation and on addition

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(7) G. Gurgenjans and G. B. Kostanecki, *Ber.*, **28**, 2310 (1895).

(8) A. Schönberg and W. Asker, *ibid.*, 272 (1942).

(9) A. Schönberg, O. Schütz and S. Nickel, *ibid.*, **61**, 1375 (1928).

(10) S. N. Dahr, *J. Chem. Soc.*, **117**, 1053 (1920).

(11) For the formation of molecular compounds between xanthione and mercuric chloride, *cf.* A. Schönberg (*Ber.*, **58**, 1793 (1925)).

TABLE III

SUBSTITUTED XANTHIONES OBTAINED USING METHOD A

| Xanthione III | M.p.,[a] °C. | Temp. of reacn., °C. | Yield, % | Formula | Carbon, % |  | Hydrogen, % |  | Halogen, % |  | Sulfur, % |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| 2-Chloro- | 154 | 155 | 84 | $C_{13}H_7ClOS$ | 63.3 | 62.9 | 2.8 | 3.0 | 14.4 | 14.1 | 13.0 | 12.5 |
| 4-Chloro- | 137 | 115 | 76 | $C_{13}H_7ClOS$ | 63.3 | 63.1 | 2.8 | 2.5 | 14.4 | 14.3 | 13.0 | 12.7 |
| 2-Bromo- | 154 | 135 | 82 | $C_{13}H_7BrOS$ | 53.6 | 53.4 | 2.4 | 2.1 | 27.5 | 27.3 | 11.0 | 10.9 |
| 4-Bromo- | 141 | 125 | 77 | $C_{13}H_7BrOS$ | 53.6 | 53.2 | 2.4 | 2.3 | 27.5 | 27.1 | 11.0 | 10.6 |
| 1,3-Dimethyl- | 109 | 80 | 65 | $C_{15}H_{12}OS$ | 75.0 | 74.7 | 5.0 | 4.7 | .. | .. | 13.3 | 13.3 |
| 1,4-Dimethyl- | 105 | 110 | 68 | $C_{15}H_{12}OS$ | 75.0 | 74.6 | 5.0 | 4.5 | .. | .. | 13.3 | 13.0 |
| 2,3-Dimethyl- | 123 | 110 | 71 | $C_{15}H_{12}OS$ | 75.0 | 74.8 | 5.0 | 4.8 | .. | .. | 13.3 | 13.1 |
| 2,4-Dimethyl- | 134 | 135 | 79 | $C_{15}H_{12}OS$ | 75.0 | 74.8 | 5.0 | 4.7 | .. | .. | 13.3 | 12.9 |

[a] Melting points are uncorrected. The melt is green.

of light petroleum (b.p. 40–60°) to the residue, the xanthione derivative was deposited; it was recrystallized from petroleum ether (b.p. 60–80°).

The xanthiones (listed in Table III) are easily soluble in benzene giving a bluish-green solution, but sparingly soluble in light petroleum and give an orange-red color with sulfuric acid.

Method b was applied in the case of 2-bromo- and 4-bromoxanthiones; the yield was 73 and 81%, respectively.

**Preparation of:** (a) **1,4-Dimethylxanthone** (**Va**).—A procedure similar to that described by Dahr[10] for the preparation of 2-chloroxanthone was used.

A mixture of 5.3 g. of 5-hydroxy-1,4-dimethylbenzene, 3.5 g. of *o*-chlorobenzoic acid, 0.8 g. of metallic sodium, 20 ml. of methyl alcohol and a trace of copper powder was heated gradually (oil-bath) until all the alcohol evaporated. The reaction mixture was kept at 160° for half an hour and the temperature then was raised to 220°. It was cooled, powdered, and heated (steam-bath) with 30 ml. of sulfuric acid (70%) for 15 minutes. The cooled reaction mixture was poured onto water and the solid substance that separated was filtered off, washed thoroughly with water and crystallized from ethyl alcohol or petroleum ether (b.p. 60–80°) as colorless crystals (*ca.* 1.7 g.), m.p. 121°. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4. Found: C, 80.1; H, 5.2. Va is easily soluble in benzene, but difficultly soluble in cold ethyl alcohol and gives a yellow color with a green fluorescence when treated with sulfuric acid.

The above experiment was repeated and the powdered reaction product, before treatment with sulfuric acid, was extracted several times with dilute aqueous sodium hydroxide solution (8% *ca.* 60 ml.). The filtered alkaline extract was acidified with cold dilute hydrochloric acid and the solid so obtained was washed thoroughly with cold water, crystallized from dilute ethyl alcohol and finally from benzene. 1,4-Dimethyl-5-phenoxy-*o*-benzoic acid (IVa), m.p. 130°, is obtained in 78% yield. It is easily soluble in hot benzene and alcohol and gives a yellow color with sulfuric acid. *Anal.* Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.7. Found: C, 74.3; H, 5.5.

Va reacts with hydrazine hydrate to give the corresponding hydrazone under the same experimental conditions described in the case of xanthonehydrazone.[12] The hydrazone derivative forms pale yellow crystals from petroleum ether (b.p. 80–100°), m.p. 133°. *Anal.* Calcd. for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.9; N, 11.8. Found: C, 75.4; H, 5.7; N, 11.5. It gives yellow color with green fluorescence when treated with sulfuric acid; yield is almost quantitative.

(b) **1,3-Dimethylxanthone** (**Vb**) was prepared from 5-hydroxy-1,3-dimethylbenzene as described above. Vb forms almost colorless crystals from petroleum ether (b.p. 50–60°); m.p. 91°. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4. Found: C, 80.3; H, 4.9. The yield is *ca.* 53%. Vb is easily soluble in ordinary organic solvents, but difficultly soluble in light petroleum (b.p. below 40°) and gives the same color reaction with sulfuric acid as described in the case of Va.

(c) **2,3-Dimethylxanthone** (**Vc**).—The above procedure, using 5-hydroxy-2,3-dimethylbenzene, was applied. Vc is obtained in almost colorless needles from petroleum ether (b.p. 50–60°), m.p. 124°; yield is *ca.* 57%. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4. Found: C, 79.9; H, 5.4. The solubility of Vc in organic solvents and the color reaction with sulfuric acid is the same as described for Va.

2,3-Dimethyl-5-phenoxy-*o*-benzoic acid (IVc) is obtained, as described in the case of IVa, in colorless crystals from dilute ethyl alcohol or benzene, m.p. 106° (64% yield). *Anal.* Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.7. Found: C, 74.1; H, 5.7. IVc is soluble in aqueous sodium carbonate and recovered unchanged on acidification. It is easily soluble in benzene, but difficultly soluble in hot water.

(d) **2,4-Dimethylxanthone** (**Vd**) was prepared from 5-hydroxy-2,4-dimethylbenzene, as described above, and proved to be identical with a sample of Vd, prepared after Ullmann and Zlokasoff[13]; yield is 73%.

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[12] A. M. v. dem Knesebeck and F. Ullmann, *Ber.*, **55**, 306 (1922).

[13] F. Ullmann and M. Zlokasoff, *ibid.*, **38**, 2111 (1905).