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Thermochromism of Dixanthylenes¹

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Dixanthylene (I) is thermochromic; substitution in the positions 1 and 1' is detrimental to the development of color. The significance of thermochromism for the correct interpretation of the relationship between color and constitution and of chemical reactions is stressed. When VIa and VIb were treated with thionyl chloride followed by water, xanthone and thioxanthone were obtained, respectively.

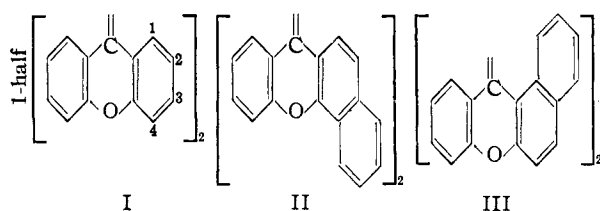
Dixanthylene (I) is a strongly thermochromic substance, the crystals are colorless in liquid air, blue-greenish on heating and the melt is deep blue-green.² The authors have tried to show how substitution affects the thermochromic properties of dixanthylenes; the results are shown in Table I; the substances were tested in boiling diphenyl ether solutions.

TABLE I

Dixanthylenes	
2,2'-Dichloro	Strongly thermochromic
4,4'-Dichloro	Strongly thermochromic
1,1'-Dichloro-4,4'-dimethyl	Not thermochromic
Di-1,2:1',2'-dibenzo ³ (III)	Weakly thermochromic
Di-3,4:3',4'-dibenzo ³ (II)	Strongly thermochromic

Discussion of the Results

Dixanthylenes may be divided into two halves (*cf.* I) and substitution which hinders the planarity of the whole molecule is detrimental to the development of the thermochromic properties; from this, we conclude that the green forms of dixanthylene and its analogs are (relatively) planar; the experiments with thermochromic bianthrone have led Hirshberg, Loewenthal, Bergmann and Pullman⁴ to similar conclusions.⁵



Color is related to the electronic structure of the molecule and in strongly thermochromic substances the electronic structure must change considerably with changes of temperature. Therefore, it seems not admissible, as is now the practice, to make use of physical data (dipole moments, etc.) obtained

(1) For previous work on thermochromic substances, see A. Schönberg and Asker, *Chem. Revs.*, **37**, 1 (1945); A. Mustafa, *ibid.*, **43**, 509 (1948); A. Schönberg and Asker, *Science*, **113**, 56 (1951); A. Schönberg, A. Mustafa and Asker, *THIS JOURNAL*, **73**, 2876 (1951); A. Schönberg, A. Mustafa and Asker, *ibid.*, **74**, 5640 (1952).

(2) A. Schönberg and Schütz, *Ber.*, **61**, 478 (1928).

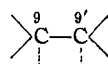
(3) A. Mustafa and Hilmy, *J. Chem. Soc.*, 1343 (1952).

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

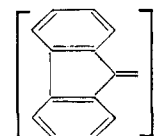
(5) The relationship between color and planarity of the molecule in the case of thermochromic substances has recently, *inter alia*, been discussed by Grubb and Kistiakowsky (*THIS JOURNAL*, **72**, 419 (1950)) who investigated the thermochromic bianthrone. Koelsch (*J. Org. Chem.*, **18**, 1362 (1951)) and Knott (*J. Chem. Soc.*, 3038 (1951)) have investigated thermochromic spirans from this point of view. The importance of the stereochemical aspect of thermochromism was first stressed by A. Schönberg, A. Mustafa and Asker (*ibid.*, 847 (1947)).

from experiments which were carried out at room temperature, for the explanation of the course of reactions proceeding at high temperature. This is only admissible if and when it is established that none of the reactants is strongly thermochromic.

When comparing the constitution and the color of the substances, it seems arbitrary to draw conclusions from optical experiments carried out at room temperature only, *e.g.*, it seems doubtful whether the colorless form of dixanthylene is the analog of the red $\Delta^{9,9'}$ -bifluorene (V); the possibility that it is the green form should be taken into consideration.



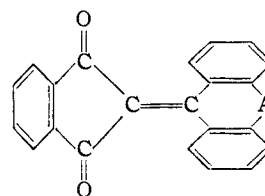
IV



V

At first Schönberg and co-workers⁶ believed that the great reactivity of the central double bond of dixanthylene together with the green color might be explained best by assuming the green form to be the di-radical (*cf.* IV abbreviated formula); later on, however, this theory was abandoned.⁷ Recently, however, Bergmann⁸ and Theilacker, Kortüm and Friedheim⁹ have commented favorably on it. Dixanthylene is a thermostable substance, which fact, in our opinion, is not in accordance with the supposed di-radical character of the green form. Organic free radicals are not thermostable,¹⁰ *e.g.*, triphenylmethyl and diphenylnitrogen.

Action of Thionyl Chloride on Some Analogs of Dixanthylene.—Dixanthylene shows remarkable behavior toward thionyl chloride, followed by the action of water.¹¹ Fission of the central ethylene bond occurs and xanthone is formed. The authors found that VIa and VIb behaved analogously, yielding xanthone and thioxanthone, respectively.



VIa, A = O; VIb, A = S

(6) *Cf.* A. Schönberg and Nickel, *Ber.*, **64**, 2323 (1931).

(7) A. Schönberg, Ismail and Asker, *J. Chem. Soc.*, 442 (1946).

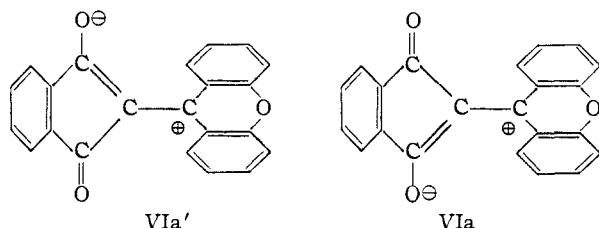
(8) Bergmann, "Isomerism and Isomerization of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 47.

(9) W. Theilacker, G. Kortüm and G. Friedheim, *Chem. Ber.*, **83**, 508 (1950).

(10) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 889 (1949).

(11) A. Schönberg and Asker, *ibid.*, 725 (1942).

The formulas (VIa) and (VIb) show planar molecules (classical chemistry). It is, however, not probable that the molecules are planar in consequence of steric interference. We believe that the central double bond has single bond character (*cf.* the identical resonance structures VIa' and VIa'') which also explains the abnormal behavior of the "central double bond" toward thionyl chloride.



Methods of Preparations.—The dioxanthylene derivatives listed in Table I were prepared by treating the corresponding xanthenes with thionyl chloride, followed by the action of copper bronze.¹² The first two listed in Table I have also been prepared by the action of zinc dust, acetic acid and a few drops of hydrochloric acid.²

(VIa) has been prepared by allowing 1:3-indanone to react with the product obtained by the action of thionyl chloride on xanthone. (VIb) was obtained in an analogous way using thioxanthone.

Experimental

Dioxanthylene Derivatives. General Procedure.—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 g. of copper bronze for 6 hours with occasional shaking. The xylene solution was filtered while hot and concentrated; on cooling the dioxanthylene derivative crystallized.

1,1'-Dichloro-4,4'-dimethyldioxanthylene (*cf.* I) was obtained in 72% yield from 1-chloro-4-methylxanthone¹³ (as described above) as pale yellow crystals from xylene, m.p. about 330° (red-brown melt).

Anal. Calcd. for C₂₂H₁₈O₂Cl₂: C, 73.5; H, 3.9; Cl, 15.5. Found: C, 73.4; H, 4.0; Cl, 15.3. It shows a deep green fluorescence in the solid state, it sublimes readily at 300° and gives no color with sulfuric acid in the cold, but at 100° a light-violet solution is obtained. When to this solution, after cooling, a drop of concentrated nitric acid is added a very deep violet solution is produced at once. It dissolves in diphenyl ether (at boiling point and at room temperature) and shows no thermochromism to the naked eye.

4,4'-Dichlorodioxanthylene (*cf.* I) was obtained in 68% yield from 4-chloroxanthone¹⁴ as almost colorless crystals from xylene, m.p. 280° (deep blue-green melt). *Anal.* Calcd. for C₂₀H₁₄O₂Cl₂: C, 72.7; H, 3.3; Cl, 16.6. Found: C, 72.5; H, 3.1; Cl, 16.0. Its dilute solution in diphenyl ether at room temperature is almost colorless, the boiling solution is bluish-green; the color phenomenon is reversible.

2,2'-Dichlorodioxanthylene was obtained from 2-chloroxanthone¹⁴ as very light yellow crystals from xylene, m.p. 304° (yield; *ca.* 63%) (deep bluish-green melt). *Anal.* Calcd. for C₂₀H₁₄O₂Cl₂: C, 72.7; H, 3.3; Cl, 16.6. Found: C, 73.0; H, 3.2; Cl, 16.3. It shows reversible thermochromic properties as in the case of 4,4'-dichloro derivative. The substance sublimes at about 290° at ordinary pressure.

Reduction of 4-Chloro- and 2-Chloroxanthenes.—One gram of 4-chloroxanthone, 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, after 10 minutes boiling, 0.2 g. of 4,4'-dichlorodioxanthylene (identified by m.p. and thermochromic behavior).

Similarly, 1 g. of 2-chloroxanthone gave *ca.* 0.15 g. of 2,2'-dichlorodioxanthylene (identified as mentioned above).

Action of Thionyl Chloride.—One gram of each of 2,2'-dichloro-, 4,4'-dichloro- and 1,1'-dichloro-4,4'-dimethyldioxanthylenes was refluxed with 30 ml. of thionyl chloride, respectively, for 6 hours, the excess of thionyl chloride distilled off completely (pump) and the residual oil 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-chloro-, 4-chloro- and 1-chloro-4-methylxanthenes, respectively (identified by m.p. and mixed m.p. and color reaction with sulfuric acid). Yield is exceeding 60%.

2-(9-Xanthylidene)-indan-1,3-dione (VIa).—To a solution of the orange oil, obtained by the action of 30 ml. of thionyl chloride on 5 g. of xanthone as previously described, in 40 ml. of benzene, was added 2 g. of 1,3-diketohydrindene.¹⁵ A vigorous reaction took place with strong evolution of hydrogen chloride. The reaction mixture was refluxed for three hours on a water-bath (calcium chloride tube) until no more evolution of hydrogen chloride took place, when dark brown crystals separated which were filtered, washed with benzene and recrystallized from xylene as deep bronze-red crystals (yield 80%), m.p. 230°. *Anal.* Calcd. for C₂₂H₁₂O₃: C, 81.5; H, 3.9. Found: C, 81.4; H, 3.8. (VIa) gives a brown-red color when treated with sulfuric acid; it is difficultly soluble in hot alcohol and benzene and practically insoluble in petroleum ether (b.p. below 40°). It dissolves in hot benzene with a violet color.

Action of Thionyl Chloride.—One gram of (VIa) was refluxed with 30 ml. of thionyl chloride for five hours; the excess of thionyl chloride was distilled off and the oily residue was dissolved in benzene and shaken with water at 30° for half an hour. The benzene layer was separated, dried and concentrated when pale-yellow crystals were obtained, which proved to be xanthone (m.p. and mixed m.p. and color reaction with sulfuric acid, yield 40%). Resinous material, which was also found in the reaction, did not dissolve in the benzene layer; the former has so far not been identified.

2-(9-Thioxanthylidene)-indan-1,3-dione (VIb).—To a solution of the oil obtained, as in the case of VIa by the action of 30 ml. of thionyl chloride on 5 g. of thioxanthone in 40 ml. of dry benzene, was added 2 g. of 1:3-diketohydrindene¹⁵ and the reaction mixture was refluxed for three hours. The benzene solution on concentration and cooling, gave brownish-orange crystals which were recrystallized from acetic acid, m.p. 225° (red-melt) (yield *ca.* 65%). *Anal.* Calcd. for C₂₂H₁₂O₂S: C, 77.6; H, 3.5; S, 9.4. Found: C, 77.5; H, 3.5; S, 9.2. (VIb) is easily soluble in benzene (red solution) and difficultly soluble in alcohol and gives a violet-red color with sulfuric acid.

(VIb) when treated with thionyl chloride, as described in the case of (VIa), gave, after treatment with water, thioxanthone (identified by m.p. and mixed m.p.).

CAIRO, EGYPT

(12) A. Schönberg and Asker, *J. Chem. Soc.*, 272 (1942).

(13) Mauss, *Chem. Ber.*, **81**, 24 (1948).

(14) Dahr, *J. Chem. Soc.*, **117**, 1053 (1920).

(15) Teeters and Shriner, *THIS JOURNAL*, **55**, 3027 (1933).