and proved to be identical in all respects with the methyl ester of authentic IIC,[4] m.p. and mixed m.p. 153.0–154.5°.

Oxidation of VB to VI.—A 0.502-g. sample of VB (0.00155 mole) was heated on the steam-bath for 6 hr. in a solution of 20 ml. of 1% potassium permanganate, 0.5 ml. of 20% sodium hydroxide and 40 ml. of water and the manganese dioxide was filtered from the hot solution. The pink filtrate was acidified with hydrochloric acid and treated with a little sodium sulfite to decolorize it. A white solid separated and was filtered off; 0.309 g. (61.8%), m.p. 259.5–269.0° dec. After three recrystallizations from acetone-benzene, and one recrystallization from nitromethane VI melted at 268–270° dec. A distinct depression in the melting point of a sample mixed with authentic VII (267–268°[4] dec.) was observed.

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found[13]: C, 70.45; H, 4.38.

The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 188–191°.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found[13]: C, 71.61; H, 5.09.

A 10-mg. sample of VI was oxidized in boiling 70% sulfuric acid[4] to give a few mg. of 3,3′-spirobiphthalide, identified by mixed m.p. with an authentic sample,[4] m.p. 205.5–207.0°, which was undepressed. Upon solution of VI in concd. sulfuric acid an intense yellow color was produced, and VI was reprecipitated unchanged on dilution of the solution with water.

ANN ARBOR, MICHIGAN

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

New Types of Thermochromic Substances. The Stereochemical Aspect of Thermochromism; Thermochromism and Vinylogy

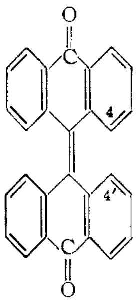
BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND WAFIA ASKER

RECEIVED JANUARY 26, 1954

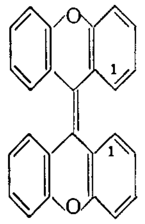
The discovery of thermochromic organic substances has been accidental. A working hypothesis, based on the connection between thermochromism and stereochemistry has led to the discovery of the thermochromic properties of the compounds listed in Table I. The relationship between vinylogy and thermochromism is discussed.

It is known that the color of solutions of colored organic substances in inert solvents changes with temperature and that these changes are strictly reversible provided that no reactions occur during heating and cooling; these changes of color are usually slight. However, some substances exhibit in solution striking changes observable with the naked eye; the term "thermochromism" in this paper is limited to such striking changes occurring between 0° and higher temperatures.

Thermochromism and Changes in Planarity of the Molecules of Thermochromic Substances.—This relationship has been discussed previously in connection with spirans,[1] bianthrones[2] (I) and dixanthylenes[3] (II); in all three cases substances which were colorless at low temperatures developed vivid colors with a rise of temperature. The chemical evidence suggested: (a) that thermochromism is due to a change of planarity of the molecules, the "colored molecules" having a greater degree of planarity, and (b) that since the thermochromic substances are thermostable, the phenomenon is not due to the formation of radicals or biradicals. The yellow color exhibited by the melt of 9,10-diphenylanthracene (m.p. 249–250°), a thermostable compound, cannot be explained by the formation of biradicals. On the other hand, when the solutions of many thermochromic substances are exposed to light, photo-activated molecules are formed which behave chemically like biradicals (disproportionation)[4]; thus I undergoes dehydrogenation with the loss of the two hydrogen atoms attached to positions 4 and 4′ and the formation of a new linkage.



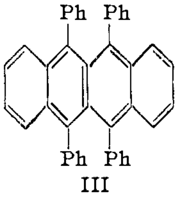
I



II

New Thermochromic Substances.—Up to now the discovery of thermochromic organic substances has been accidental. On the basis of the relationship between thermochromism and changes of planarity shown by the spirans, I and II, we have attempted to develop a general theory, by which the thermochromism of substances could be predicted. The value of our hypothesis has been proved by the discovery that the substances listed in Table I have thermochromic properties; the molecules of these substances are overcrowded to such a degree that planarity is hindered.

This working hypothesis may be formulated as follows: 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. If the molecules absorb in the visible region, thermochromism may be observed with the naked eye.



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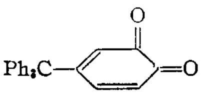

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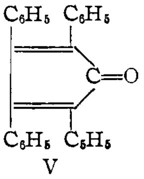

V

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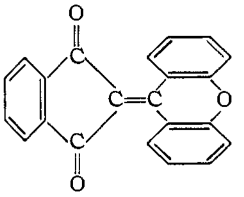
(1) *Cf.* C. F. Koelsch, *J. Org. Chem.*, **16**, 1362 (1951); A. Schönberg, A. Mustafa and W. Asker, *J. Chem. Soc.*, 847 (1947).

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

(3) A. Schönberg, A. Mustafa and M. E. D. Sobhy, THIS JOURNAL, **75**, 3377 (1953).

(4) A. Schönberg, A. Ismail and W. Asker, *J. Chem. Soc.*, 442 (1946); A. Schönberg and A. Mustafa, *ibid.*, 884 (1949).



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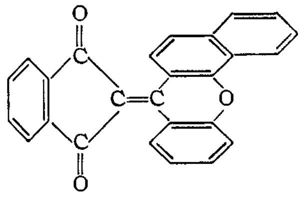

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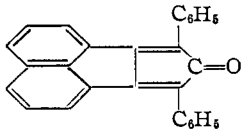

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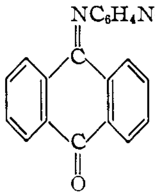

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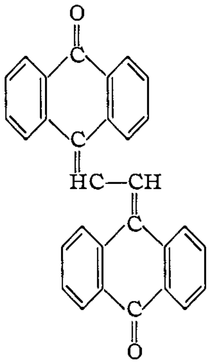


X

TABLE I

NEW THERMOCHROMIC SUBSTANCES

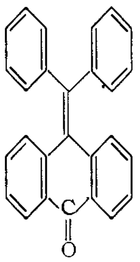
The color changes which are all reversible refer to very dilute ethyl benzoate solutions; in the case of IV anisole was used as a solvent. The arrow points to the color of the hot solution (boiling point).

Name	Formula	Thermochromic changes
Rubrene	III	Orange → deep red
4-Triphenyl-1,2-quinone	IV[a]	Orange → brownish-green
Tetracyclone[g]	V[b]	Violet → violet-red, fading of color
Acecyclone	VI[c]	Blue → violet, fading of color
2-(9-Xanthylidene)-indan-1,3-dione	VII[d]	Deep violet → brownish-red, marked fading of color
2-[9-(3,4-Benzo)-xanthylidene]-indan-1,3-dione	VIII	Deep violet → brownish-red, marked fading of color
Anthraquinone-mono-*p*-dimethylaminoanil	IX[e]	Deep violet → violet-red, marked fading of color
1,2-Bis-(9,9′-anthronylidene)-ethane[h]	X[f]	Yellow → orange

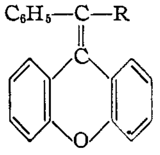
[a] Th. Zincke and E. Wugk, *Ann.*, **363**, 284 (1908). [b] W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930). [c] W. Dilthey, I. Horst and W. Schommer, *ibid.*, **143**, 189 (1935). [d] A. Schönberg, A. Mustafa and M. E. D. Sobhy, THIS JOURNAL, **75**, 3377 (1953). [e] E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929). [f] E. Clar, *ibid.*, **72**, 2134 (1939). [g] For hindered coplanarity of V, *cf.* E. L. Shapiro and E. I. Becker, THIS JOURNAL, **75**, 4773 (1953). [h] This experiment was carried out with Salah Mohamed Abdel Dayem Zayed.

Individual Gases of Thermochromism.—Our point of view and mode of reasoning are illustrated in the following discussion.

(a) **4-Triphenyl-1,2-quinone (IV).**—Benzil, phenanthraquinone and acenaphthenequinone are non-thermochromic; the molecules of these compounds are comparatively planar. In contrast IV is thermochromic; the molecules of this compound are pronouncedly non-planar.[5]



XI



XIIa, R = H;
b, R = C_6H_5

(b) **Diphenylmethyleneanthrone (XI).**—According to Grubb and Kistiakowsky[6] the thermochromism of XI is due to "a trivial cause, the broadening of a near-ultraviolet absorption region by changing distribution of molecules among vibrational states." This interpretation does not explain why other substances having a band in the near ultraviolet do not show thermochromic properties, comparable to that of XI; nor does it correlate thermochromism and constitution. Our hypothesis answers both questions.

(c) **1,2-Bis-(9,9′-anthronylidene)-ethane (X) and the Relationship between Thermochromism and Vinylogy.**—To determine whether the vinylene homologs[7] of thermochromic ethylenes are also thermochromic, we have investigated X, a vinylog of the strongly thermochromic I, and have found it to be thermochromic. In X as in I, planarity of the molecule is hindered by overcrowding. Strong reversible thermochromic effects were also observed with powdered X (orange at 0° → deep violet at 240°).

(d) **2-(9-Xanthylidene)-indan-1,3-dione (VII).**—The thermochromism of VII is remarkable because, in contrast to its analog I, a rise of temperature causes fading of the color.

Constitutional Changes in Thermochromic Substances Leading to Non-thermochromic Substances.—If our hypothesis is correct, the two following types of change in the structure of a thermochromic substance should lead to loss of thermochromic properties: (a) overcrowding of the molecule to such a degree that planarity is hindered even at high temperatures, and (b) a decrease in overcrowding which would permit the molecules to approach planarity at room temperature.

The effect of the first type of change has already been shown in the case of di-β-naphthospiropyran, the bianthrones (I) and the dixanthylenes (II)[1-3]; *e.g.*, II, a thermochromic compound, loses this property upon substitution at positions 1 and 1′.

Loss of thermochromism due to a decrease in the overcrowding of the molecule is illustrated in the following examples: Whereas VII (overcrowded molecule) is thermochromic, its analogs 2-(2-

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(5) Deca-1,3,7,9-tetraene-5,6-dione,1,10-diphenyl (XVII) (P. Karrer and Ch. Cochand, *Helv. Chim. Acta*, **28**, 1181 (1945)); a substance with no overcrowding exhibits as we found no thermochromic properties in ethyl benzoate solutions.

(6) W. T. Grubb and G. B. Kistiakowsky, THIS JOURNAL, **72**, 419 (1950).

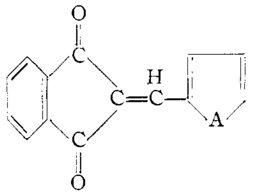
(7) R. C. Fuson, *Chem. Revs.*, **16**, 2 (1935).

furfurylidene)-indan-1,3-dione (XIIIa) and 2-(2-thienylidene)-indan-1,3-dione (XIIIb) show no thermochromic properties. I is strongly thermochromic, while 9-benzylideneanthrone is yellow and non-thermochromic, and anthronylidenephthalide (XVI) is yellow and weakly thermochromic. Similarly, II is thermochromic, while diflavylene (XV) (deep yellow), with less overcrowding, does not form thermochromic solutions in dekalin[8]; however, in the crystalline state this substance is thermochromic[9] and also shows piezochromic properties.[4] 9-Benzylidenexanthen (XIIa) which is non-thermochromic may be compared with diphenylmethylenexanthen (XIIb) which is thermochromic. Tetracyclone (V), an overcrowded molecule which displays thermochromism, may be compared with diphenylindone (XIV) which is less overcrowded and non-thermochromic. IX is thermochromic, 9-benzylideneanthrone is non-thermochromic; this difference may be explained by the fact that the latter compound is less overcrowded, since the C=C bond is longer than the C=N bond.[10]

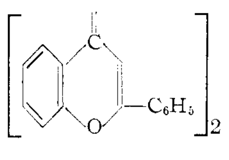
TABLE II

SUBSTANCES WHICH SHOW NO STRIKING THERMOCHROMISM IN ETHYL BENZOATE SOLUTION

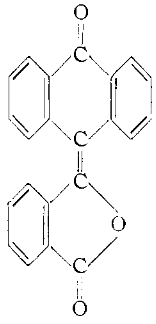
XV was dissolved in dekalin.



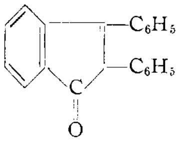
XIIIa, A = O; b, A = S



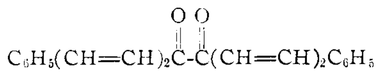
XV



XVI



XIV



$C_6H_5(CH{=}CH)_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}(CH{=}CH)_2C_6H_5$

XVII

Experimental

The color changes, which are all reversible, were observed in layers of solution 1 cm. in depth. The solutions were heated nearly to the boiling point (heating lasted only for a few seconds) and then cooled immediately. Since solutions of III are strongly fluorescent at low temperature, the observations were made in such a way that light could enter the tube only in the direction of the main axis. The expansion of the volume of the solutions with temperature was taken into consideration.

2,9-(3,4-Benzo)-xanthylidene-indan-1,3-dione (VIII).—3,4-Benzoxanthone[11] (2 g.) was refluxed (calcium chloride tube) with 10 g. of oxalyl chloride (or with 15 ml. of thionyl chloride) for 10 hours; the excess oxalyl chloride (or thionyl chloride) was distilled off, and the residual oil dissolved in 30 ml. of dry benzene. When 2 g. of 1,3-diketohydrindene[12] was added to the benzene solution, a vigorous reaction took place with strong evolution of hydrogen chloride. After the reaction mixture had been refluxed for three hours on a water-bath (calcium chloride tube) until no further evolution of hydrogen chloride occurred, the dark brown crystals which separated were filtered, washed with benzene and recrystallized from xylene as deep bronze-red crystals; yield 78%, m.p. 296° (intense red-violet melt).

Anal. Calcd. for $C_{26}H_{14}O_3$: C, 83.4; H, 3.7. Found: C, 83.3; H, 3.6.

VIII gives a deep 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.

Acknowledgment.—The authors are indebted to Dr. G. O. Schenck (University of Göttingen, Germany) for the gift of rubrene.

GIZA, CAIRO, EGYPT

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[8] W. Theilacker, G. Körtum and G. Friedheim, *Chem. Ber.*, **83**, 508 (1950).

[9] A. Schönberg and S. Nickel, *ibid.*, **64**, 2323 (1931).

(10) *Cf.* W. Hückel, "Theoretische Grundlagen der Organischen Chemie," 2nd Vol., 1948, p. 388.

(11) W. Knapp, *J. prakt. Chem.*, **146**, 116 (1936).

(12) W. O. Teeters and R. L. Shriner, THIS JOURNAL, **55**, 3027 (1933).