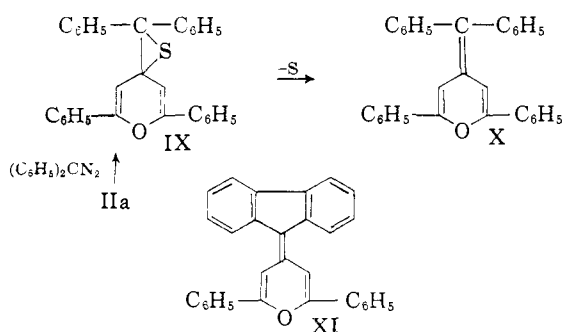


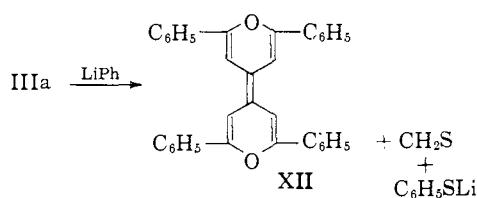
on thioketones, *e.g.*, thiobenzophenones, xanthenes and 4-thiochromones,⁵ proceeds with the formation of ethylenesulfides, thermolabile compounds which form the corresponding ethylenes by losing sulfur. In some cases the ethylenes and not the ethylene sulfides were obtained.⁵

The action of diphenyldiazomethane on 2,6-diphenyl-4-thiopyrone (IIa) yields X *via* IX, and XI was obtained in the case of 9-diazofluorene; XI is red while X is yellow. The mother substance of X (the two phenyl groups attached to the ring in X replaced by hydrogen) is also yellow.⁶

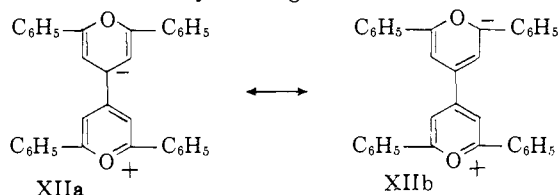


Synthesis and Properties of 2,2',6,6'-Tetraphenyl-4,4'-dipyrylene (XII).—When IIIa was treated with lithium phenyl, XII was obtained. Similarly the deep violet 2,2'-distyryldichromylene (VIb) was obtained from Vb. By a similar method dixanthylene (XIII) and diflavylene (VIa)⁴ were prepared previously.

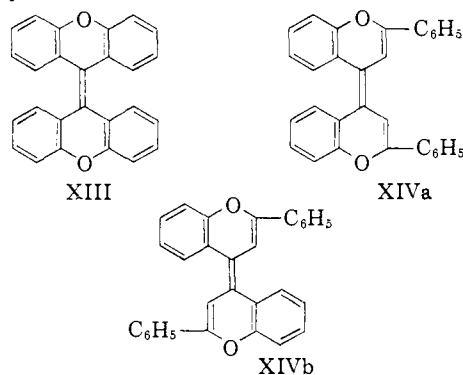
2,2',6,6'-Tetraphenyl-4,4'-dipyrylene has been obtained previously by a different method by Arndt,² who drew attention to the great stability of this substance toward aqueous acids and alkalis which we confirmed. The substance is also very



stable when treated with (a) potassium permanganate (in acetic acid as well as in pyridine), (b) hydrochloric acid and activated zinc, (c) sodium hydroxide, (d) sodium amalgam in the presence of amyl alcohol and (e) diazomethane. The chemostability of this substance cannot be explained by XII (which shows the formula of a vinyl ether), but by regarding the substance as a resonance hybrid with strong contributions from structures characterized by separation of charges (compare *inter alia* XIIa ↔ XIIb). The intense color of the substance as well as its thermostability are in accordance with this conception. Resonance XII ↔ XIIa ↔ XIIb should stabilize coplanarity of the two heterocyclic rings.



We regard 2,2',6,6'-tetraphenyl-4,4'-dipyrylene as an analog of dixanthylene (XIII) (green form), the two heterocyclic rings being coplanar or nearly so, and we shall report on the importance of the chemistry of this dipyrylene derivative for the theory of thermochromism of XIII in a later paper.



Piezochromic Properties of Diflavylene (VIa).—Compound VIa (yellow crystals in the cold, yellow-orange at room temperature which turn red on heating, forming a deep red melt) shows piezochromic properties: the crystals, when pressed in a mortar at room temperature, turn red.⁷ After some hours or days the red color is replaced by the original color; this change takes place within a few seconds when the crushed crystals are exposed to diethyl ether vapors.

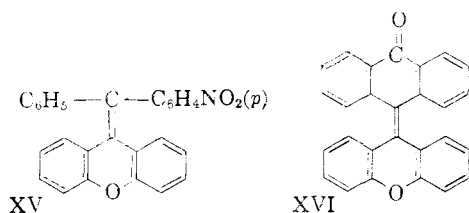
According to Kortüm,⁸ *et al.*, the piezochromism of VIa is due to the reversible formation of *cis-trans* isomers (XIVa ↔ XIVb).

(5) A. Schönberg, A. Fateen and M. Sammour, *THIS JOURNAL*, **78**, 4689 (1956).

(6) H. Staudinger and N. Kon, *Ann.*, **384**, 38 (1911).

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

(8) G. Kortüm, W. Theilacker and G. Schreyer, *Z. physik. Chem., Neue Folge*, **11**, 182 (1957).



However 9-(*p*-nitrophenyl phenylmethylene)-xanthene⁹ (XV) and 10-(9'-xanthylene)-anthrone¹⁰ (XVI) (these substances are related to VIa as they all may be regarded as γ -pyran derivatives) show piezochromic properties similar to diflavylene. Here the formation of *cis-trans* isomers is impossible and we find it difficult to accept a theory which explains the piezochromic properties of VIa, but not of XV and XVI.

Experimental

2,6-Diphenyl-4-thiopyrone (IIa).—2,6-Diphenyl-4-pyrone (1 g.) was refluxed with 15 g. of thionyl chloride for 5 hours, and the resulting solution was evaporated to dryness under reduced pressure. The residue was suspended in 30 ml. of dry benzene and 2 ml. of thioacetic acid and the mixture was refluxed for 5 hours in a carbon dioxide atmosphere. Removal of the solvent under reduced pressure gave a crystalline solid which was recrystallized from ethyl alcohol. Red crystals of IIa (0.5 g.), identical with a sample obtained from 2,6-diphenyl-4-pyrone and phosphorus pentasulfide² (identification was carried out by m.p. and mixed m.p.) were obtained. When these crystals were exposed to the ultraviolet light no striking change of color was observed, whereas 2,6-diphenyl-4-pyrone gave an intense blue fluorescence.

2,6-Di-(*p*-methoxyphenyl)-4-pyrone (Ib).—To dianisalacetone tetrabromide¹¹ (28 g.) suspended in 228 ml. of boiling absolute alkyl alcohol a solution of 10 g. of potassium hydroxide in absolute alcohol was added portionwise. The reaction mixture was refluxed (one hour), cooled and filtered from the deposited potassium bromide. The solvent was distilled off under reduced pressure leaving an oil. It was extracted with ether, the ether washed with water, dried and evaporated leaving an oil (15 g.).

A mixture of 15 g. of the oil and 1000 ml. of concentrated hydrochloric acid (sp. gr. 1.19) was boiled for 6 hours under reflux. The cooled acid solution containing the pyrone was decanted from the oil (A) and diluted with water. 2,6-Di-(*p*-methoxyphenyl)-4-pyrone was precipitated. On repeatedly boiling (A) with hydrochloric acid small amounts of fairly pure Ib were obtained, total yield 1 g. The product was crystallized from benzene-petroleum ether (60–90°) in yellowish crystals of m.p. 189–190°. It dissolves in concentrated sulfuric acid giving a yellow color with strong green fluorescence, and also exhibits green fluorescence in the ultraviolet light; Ib is easily soluble in cold methyl and ethyl alcohol.

Anal. Calcd. for C₁₉H₁₆O₄: C, 74.0; H, 5.2. Found: C, 73.7; H, 5.2.

2,6-Di-(*p*-methoxyphenyl)-4-thiopyrone (IIb). (1) **Phosphorus Pentasulfide Method.**—To a solution of Ib (0.5 g.) in 25 ml. of dry benzene, 1.5 g. of pure phosphorus pentasulfide was added and the reaction mixture was boiled under reflux for one hour then filtered hot. The residue was washed with a strong solution of ammonium sulfide then added to the dark reddish-brown solid obtained upon evaporation of the filtrate to dryness and the whole crop was crystallized from ethyl alcohol to give 0.15 g. of IIb as reddish-brown crystals, m.p. 180°. It gives a yellow color with green fluorescence when treated with concentrated sulfuric acid.

Anal. Calcd. for C₁₉H₁₆O₃S: C, 70.2; H, 4.9; S, 9.9. Found: C, 70.1; H, 5.1; S, 10.0.

(9) A. Schönberg, A. Fateen and M. Sammour, *THIS JOURNAL*, **79**, 6022 (1937).

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

(11) D. Vorländer and E. Mumma, *Ber.*, **36**, 1470 (1903).

(2) **Thionyl Chloride Method.**—2,6-Di-(*p*-methoxyphenyl)-4-pyrone (0.2 g.) was refluxed with 5 g. of thionyl chloride for 5 hours, then the excess thionyl chloride was removed by distillation. The solid residue was suspended in 10 ml. of dry benzene and 1 ml. of thioacetic acid was added. The reaction mixture was refluxed in dry carbon dioxide atmosphere, then the solvent was distilled off under reduced pressure whereby crystals were obtained which were recrystallized from ethyl alcohol; IIb (0.12 g.) was obtained in reddish-brown crystals melting at 178°. It gave a yellow color with green fluorescence when treated with concentrated sulfuric acid.

Anal. Calcd. for C₁₉H₁₆O₃S: S, 9.9. Found: S, 9.6.

Action of Mercuric Chloride on IIa and IIb.—To the red solution of the thiopyrone in benzene at room temperature a few crystals of mercuric chloride were added. After some hours the surface of the crystals became yellow in the case of IIa and orange in the case of IIb, while the solution was practically colorless in both cases.

Action of Diazomethane on 2,6-Diphenyl-4-thiopyrone (IIa).—To a solution of IIa (1 g.) in dry benzene (30 ml.) an excess of diazomethane in dry ether was added. The reaction mixture was allowed to stand for 4 days at room temperature with a further amount of diazomethane solution added each day. The total volume of the solution was 250 ml. containing diazomethane generated from 25 g. of nitrosomethylurea. An almost colorless crystalline solid deposited which was collected by filtration and washed with ether (0.5 g.). Compound IIIa gave a red-brown color with concentrated sulfuric acid and the crystals were orange-red when viewed in the ultraviolet light. This substance in a capillary tube when immersed in a heating bath at 150° became red-brown in color within 40 seconds.

Anal. Calcd. for C₂₀H₁₆O₂S₂: C, 77.4; H, 4.8; S, 11.7. Found: C, 77.2; H, 5.1; S, 11.6.

Treatment of 2,6-Diphenyl-4-pyrone (Ia) with Diazomethane.—The treatment of Ia with diazomethane in the same way as described under 2,6-diphenyl-4-thiopyrone led to the recovery of the starting material (m.p. and mixed m.p. 140°).¹²

Action of Diazomethane on: (a) 2-Styryl-4-thiochromone (IVb).—One gram of IVb¹³ was treated with an ethereal solution of diazomethane (from 6 g. of nitrosomethylurea). The reaction vessel was kept in the ice-chest overnight, then left at room temperature for 2 days. The ethereal solution which was reddish-brown in color became pale brown and pale yellow crystals separated. The crystals were collected, washed with ether, and crystallized from benzene-petroleum ether (50–70°) as pale yellow crystals of Vb, m.p. 180° dec., violet color with concentrated sulfuric acid; yield ca. 0.8 g.

Anal. Calcd. for C₂₀H₁₆O₂S₂: C, 77.5; H, 4.8; S, 11.7. Found: C, 77.5; H, 4.6; S, 11.8.

(b) **2-(4'-Methoxystyryl)-4-thiochromone (IVc).**—The same procedure as with IVb was followed. Yellow crystals of Vc, separated, crystallized from benzene-petroleum ether (50–70°) as yellow crystals, m.p. 176° dec.; violet color with concentrated sulfuric acid; yield ca. 0.8 g.

Anal. Calcd. for C₂₁H₂₀O₄S₂: C, 73.7; H, 5.0; S, 10.6. Found: C, 73.8; H, 5.2; S, 10.4.

(c) **2-Styryl-4-thio- α -naphthopyrone (VIIa).**—One gram of VIIa⁵ was treated with an ethereal solution of diazomethane (from 6 g. of nitrosomethylurea), and left at room temperature for 3 days. The brown crystals of VIIa were transformed into an amorphous yellow substance which was collected and washed with ether. Compound VIIIa was crystallized from chloroform-petroleum ether (50–70°) as yellow crystals, m.p. 188° dec. It gave a violet color with concentrated sulfuric acid; yield ca. 0.7 g.

Anal. Calcd. for C₂₃H₂₀O₃S₂: S, 9.9. Found: S, 10.0.

(d) **2-(4'-Methoxystyryl)-4-thio- α -naphthopyrone (VIIb).**—The experiment was carried out as in the case of VIIa. After 2 days a second amount of ethereal diazomethane solution (prepared from 4 g. of nitrosomethylurea) was added and the reaction mixture was left at room temperature of 2 days. Pale yellow crystals of VIIIb separated, which were collected and crystallized from benzene-petro-

(12) D. Vorländer and G. A. Meyer, *ibid.*, **45**, 3355 (1912).

(13) A. Schönberg, M. Sidky and G. Aziz, *THIS JOURNAL*, **76**, 5115 (1954).

leum ether (50–70°), m.p. 175° dec. It gave a deep violet color with concentrated sulfuric acid; yield *ca.* 0.7 g.

Anal. Calcd. for $C_{45}H_{34}O_4S_2$: C, 76.9; H, 4.8; S, 9.1. Found: C, 77.0; H, 5.3; S, 9.2.

Action of Diphenyldiazomethane on 2,6-Diphenyl-4-thiopyrone (IIa).—A benzene solution of diphenyldiazomethane (2 g.) was added to a solution of IIa (0.5 g.) in about 20 ml. of dry benzene at room temperature. The reaction mixture was left overnight and then refluxed for 3 hours. The oily residue, which remained after the removal of benzene under reduced pressure, solidified on treatment with methyl alcohol to give yellow crystals of X (0.25 g.), m.p. 193–194° (deep red melt); X produces a yellow greenish coloration with concentrated sulfuric acid. Hardly any change of color was observed when a solution of this substance in dimethyl phthalate was heated. Compound X exhibited a green fluorescence when exposed to the ultraviolet light.

Anal. Calcd. for $C_{30}H_{20}O$: C, 90.4; H, 5.5. Found: C, 90.3; H, 5.6.

Action of 9-Diazofluorene on 2,6-Diphenyl-4-thiopyrone (IIa).—To IIa (1 g.) 9-diazofluorene (1.2 g.) dissolved in 25 ml. of dry benzene was added. The reaction mixture was refluxed for 5 hours and then allowed to stand overnight. The solvent was driven off under reduced pressure whereby a crystalline solid was obtained, which on further crystallization from benzene gave deep red crystals (0.4 g.), m.p. 265°; XI was red when viewed in ultraviolet light, and its dimethyl phthalate solution showed hardly any thermochromic change. It gives a red color with concd. sulfuric acid.

Anal. Calcd. for $C_{30}H_{20}O$: C, 90.9; H, 5.1. Found: C, 91.1; H, 5.1.

2,2',6,6'-Tetraphenyl-4,4'-dipyrylene (XII).—Lithium phenyl was prepared from 0.1 g. of lithium and 1 ml. of bromobenzene in 15 ml. of dry ether. Compound IIIa (0.5 g.) was added and the reaction mixture was refluxed for 4 hours and then left to stand overnight. The solid product which deposited was collected and crystallized from xylene to give XII (0.3 g.), m.p. and mixed m.p. 313°. The product gave the characteristic olive-green coloration with concentrated sulfuric acid.

2,2'-Distyrylene-dichromylene (VIb).—1.2 g. of Vb was dissolved in 30 ml. of benzene (thiophene-free, dried over sodium) and treated with a solution of lithium phenyl (prepared from 1 g. of lithium and 9 g. of bromobenzene in about 50 ml. of dry ether). The reaction mixture (deep violet) was refluxed gently for 2 hours in a nitrogen atmosphere, then decomposed (ice-cold ammonium chloride solution). The solid substance obtained was crystallized from xylene as deep violet crystals of VIb, m.p. 285°. It gave a red-orange color with concentrated sulfuric acid; yield *ca.* 0.5 g.

Anal. Calcd. for $C_{34}H_{24}O_2$: C, 88.0; H, 5.1. Found: C, 88.2; H, 5.4.

Experiments Showing the Stability of 2,2',6,6'-Tetraphenyl-4,4'-dipyrylene (XII) toward Various Chemical Agents.¹⁴ (1) Potassium Permanganate. (a) In Acetic

Acid.—0.4 g. of XII was partially dissolved in 8 ml. of boiling acetic acid. To the boiling solution 0.08 g. of potassium permanganate in 1 ml. of water was added during 8 minutes and the mixture was refluxed for 3 hours. The solution was then filtered while hot and the residue washed with water and dried at 100° (0.12 g.). The filtrate was allowed to cool and then diluted with water yielding crystals (0.28 g.).

(b) In Pyridine.—To XII (0.3 g.) dissolved in 30 ml. of boiling pyridine (previously distilled over potassium permanganate), a solution of 0.2 g. of potassium permanganate in 10 ml. of water was added and the mixture after being refluxed for 40 minutes was filtered while hot (filtrate A). The residue was washed with dilute hydrochloric acid and then dried at 100° (0.27 g.). Filtrate A was concentrated to dryness under diminished pressure and the solid residue treated with cold water. On standing colorless crystals (0.03 g.) of 2,6-diphenyl-4-pyrone were obtained (m.p. and mixed m.p. 140°).

(2) Hydrochloric Acid. (a) In Alcohol.—A suspension of XII (0.2 g.) in ethanol (10 ml.) was treated with 2.5 ml. of hydrochloric acid (sp. gr. 1.19) and the mixture was refluxed for 10 hours. The solvent was then distilled off under reduced pressure whereby the starting material was recovered.

(b) In Glacial Acetic Acid.—A mixture of 0.2 g. of XII and 10 ml. of hydrochloric acid (sp. gr. 1.19), was refluxed for 9 hours. The cold mixture yielded a solid which was crystallized from xylene (0.17 g.).

(3) Hydrochloric Acid and Zinc.—To a mixture of 20 ml. of glacial acetic acid and 1 ml. of concentrated hydrochloric acid was added 2 g. of zinc powder (activated with copper sulfate). A vigorous evolution of gas took place and 0.2 g. of XII was added. After about 45 minutes the evolution of gas slowed down and the reaction mixture was refluxed for 5 minutes, cooled and filtered. A deep violet crystalline product was obtained which was dried and extracted with xylene. From the xylene solution, 0.08 g. was obtained.

(4) Sodium Hydroxide.—To a solution of 0.3 g. of XII in 25 ml. of acetone, a solution of sodium hydroxide in 25 ml. of water was added, and the mixture was refluxed for 9 hours. After cooling, the solid was filtered off, washed with water and recrystallized from xylene (0.25 g.).

(5) Sodium Amalgam.—To 0.5 g. of XII in amyl alcohol was added sodium amalgam (prepared from 0.5 g. of sodium and 34 g. of mercury). After 5 minutes reflux, the reaction mixture developed a red color and refluxing was continued for 3 hours. Upon filtration while hot, crystals were obtained which were recrystallized from xylene (0.4 g.).

(6) Diazomethane.—To XII (0.25 g.) suspended in 65 ml. of dry benzene, 80 ml. of diazomethane in ether (prepared from 25 g. of nitrosomethylurea) was added in the cold. After 2 days a further amount of about 30 ml. of the same diazomethane solution was added. The reaction mixture was kept in the ice-chest for another 2 days and then filtered (0.2 g.). The filtrate was brought to dryness and a further amount of the starting material was obtained (0.05 g.).

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green) with concentrated sulfuric acid, the grams in parentheses indicate the yield.

(14) In the following experiments XII (recovered) was identified by the m.p. and the mixed m.p. test and by the color reaction (olive