Texasin (III).—Hydrolysis of II with 5% HCl for 1 hr at 100° gave a white precipitate which crystallized from methanol: mp 285–287° (lit.[2] mp 291.5–292.5°); λ_{max} (CH_3OH) 227 shoulder, 254, 324 nm; λ_{max} ($NaOCH_3$) 252, 350 nm; λ_{max} (NaOAc), 251, 346 nm; λ_{max} (NaOAc–H_3BO_3) 250 shoulder, 333 nm; λ_{max} ($AlCl_3$)2 15, 232 shoulder, 250, 344 nm; λ_{max} ($AlCl_3$–HCl) 227 shoulder, 254, 322 nm; R_f values, 0.80 (TBA), 0.31 (HOAc), 0.4 (Bz); *cf.* formononetin, 0.87, 0.40, 0.6, and afrormosin, 0.85, 0.35, 0.9, in the same solvents, respectively.

Texasin was also isolated by paper chromatography of the crude *B. australis* methanol extract and by β-glucosidase hydrolysis of the glucoside in distilled water at 25°.

Sugar Analysis of Texasin 7-O-Glucoside (II).—The sugar–aglycone mixture obtained from acid hydrolysis of II was paper chromatographed using EtAc–pyridine–H_2O (12:5:4) as solvent. The sugar was detected using a *p*-anisidine hydrochloride spray reagent[10] and proved to be identical with glucose.

Synthesis of Afrormosin from Texasin 7-O-Glucoside (II).—Texasin 7-glucoside (4 mg) in methanol (2 ml) was treated with an ether solution of CH_2N_2 until an ultraviolet spectrum of the resultant solution showed no change on the addition of $NaOCH_3$. Acid hydrolysis of the product gave the methylated aglycone which was chromatograpically (TBA, HOAc, and Bz systems) and spectrally identical with afrormosin.

Registry No.—III, 897-46-1.

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Photodimerization. I. The *syn* and *anti* Photodimers of 1,4-Naphthoquinone

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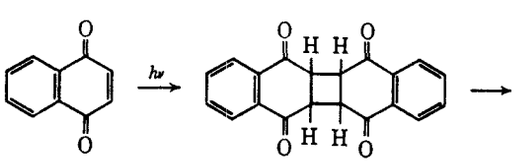
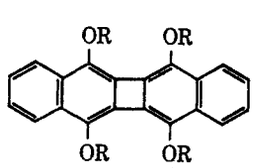
Schönberg, Mustafa, *et al.*,[1] reported, in 1948, the photolytic dimerization of 1,4-naphthoquinone (I) to II (mp 244–248°). Bruce[2] succeeded in converting II into the 2,3-binaphthylene derivatives III, IV, and V.



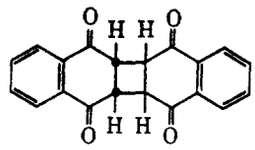
I II



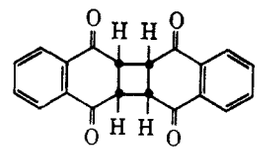
III, R = H
IV, R = Me
V, R = Ac

The symmetrical nature of the 2,3 double bond in I confines the possible number of C_4 photodimers of I to two, namely the *anti* dimer (IIa) and the *syn* dimer (IIb). Compound IIb will be by far the more strained

(1) A. Schönberg, *et al.*, *J. Chem., Soc.*, 2126 (1948).
(2) J. M. Bruce, *ibid.*, 2782 (1962).



IIa



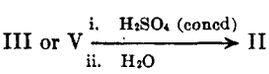
IIb

owing to its rather unsymmetrical all-*cis* structure and consequent steric repulsion.

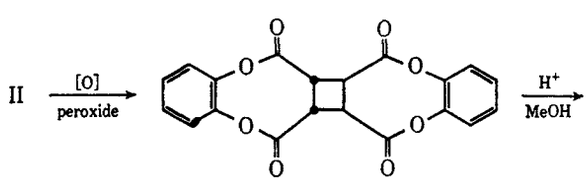
The *anti* Photodimer (IIa).—As a result of lower inherent strain in IIa compared with IIb, we expected that the *anti* dimer (IIa) will be formed preferably during photolysis of I.

The high degree of double-bond fixation of the four central π bonds in 2,3-binaphthylene[3] led us to the assumption that ketonization of III could be accomplished, leading to the thermodynamically more stable naphthoquinone dimer, namely, IIa.

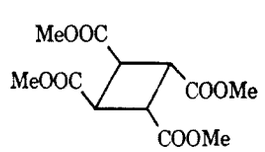
Both III and V dissolve easily in cold concentrated sulfuric acid. Subsequent dilution of the reddish solutions led to the quantitative formation of the Schönberg–Mustafa dimer (II), indicating that II must have an *anti* configuration. Proof of the *anti* configuration of II was obtained by the Baeyer–Villiger oxidation, which is known to proceed with retention of configuration,[4,5]



of II to VI. On refluxing VI in methanol containing sulfuric acid, *cis,trans,cis*-tetracarbomethoxycyclobutane (VII)[6,7] was obtained.



VI



VII

The *syn* Photodimer (IIb).—Several cases[8,9] are, however, known where both the *syn* and *anti* dimers were produced during photolysis of olefinic compounds. In the case of cyclohexadiene,[10] the *anti* dimer was shown to be the major product. The possibility that the *syn* dimer (IIb) could be formed in addition to IIa during the photolysis of I might therefore not be excluded. It was further argued that IIb, owing to its lesser degree of symmetry, should have a higher solubility than IIa. We therefore refluxed the crude photoproduct of I in methanol in which IIa is practically

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(10) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

insoluble. On concentrating the filtrate to a small volume and cooling the mother liquor to 0°, a small crop of off-white needles, melting with decomposition at 233–237,° was obtained.

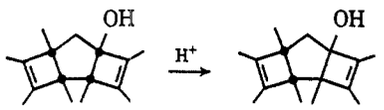
The mass spectrum (*m/e* 316) and microanalysis ($C_{20}H_{12}O_4$) indicated that the new compound is a dimer of I, with IIb as the most probable structure.

The infrared spectrum of IIb (as in the case of IIa) shows bands between 850 and 1000 cm^{-1} such as are usually associated with vibrations of cyclobutane rings. The spectrum of IIb is slightly more complex than (although strongly resembling) that of IIa as might be expected for *syn–anti* stereoisomeric pairs. The splitting of the carbonyl absorption (1682, 1672 cm^{-1}) is probably due to intercarbonylic electrostatic interaction.[11] The greater degree of splitting of the bands in the aromatic out-of-plane C–H deformation vibration region (820–700 cm^{-1}), and especially the splitting of the 750-cm^{-1} band,[12] is connected with steric interferences in the all-*cis* compound, IIb. The infrared spectra of IIa and IIb are shown in Figure 1.

The conversion of IIb into the 2,3-binaphthylene derivatives III, IV, and V should proceed with even more facility than that of IIa. The quantitative acetylation of IIb to V, when boiled with acetic anhydride containing sodium acetate, substantiates the correctness of the interpretation of the above-mentioned spectroscopic data, *i.e.*, that the new photodimer (IIb) of I must be a stereoisomer of the Schönberg–Mustafa dimer (IIa).

$$\text{IIa} \longrightarrow \text{V} \longleftarrow \text{IIb}$$

Isomerization of IIb to IIa.—Criegee[13] found that the *syn*-tricyclononadiene derivative VIII isomerizes rapidly to its *anti* isomer (IX) when treated with phosphoric acid. One might expect that the *syn*



VIII IX

dimer (IIb) would behave similarly under appropriate conditions in order to diminish its inherent strain. When IIb was dissolved in cold concentrated sulfuric acid, a reddish solution was obtained. When this solution was poured onto ice, IIa was precipitated in over 90% yield. This *syn–anti* rearrangement of a polynuclear *ortho*-condensed ring system is in itself novel in the cyclobutane series and must proceed *via* an enolic intermediate.

$$\text{IIb} \xrightarrow[\text{ii. } H_2O]{\text{i. } H_2SO_4 \text{ (concd)}} \text{IIa}$$

Photodimerization of Crystalline 1,4-Naphthoquinone (I).—Various compounds undergo C_4 photocyclization when irradiated in the solid state.[6,14–17]

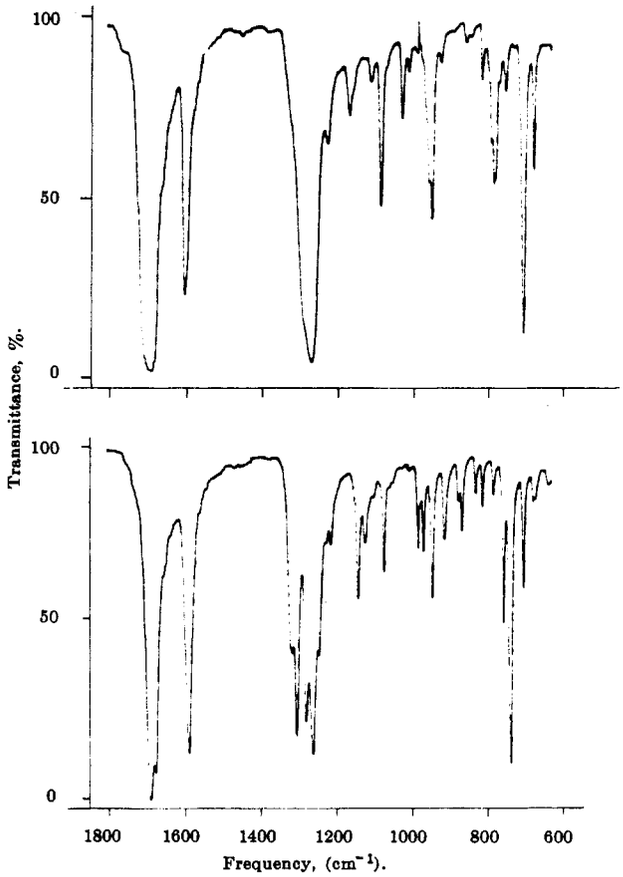


Figure 1.—Infrared spectra (in KBr) of the *anti* photodimer (top) and the *syn* photodimer (bottom) of 1,4-naphthoquinone.

Madinaveitia[18] found that 2-methyl-1,4-naphthoquinone, for example, dimerizes rapidly in sunlight. In view of these results, and despite Schönberg and Mustafa's[1] report on the stability of crystalline I toward sunlight, we decided to reinvestigate the influence of various light sources on solid I. When I (recrystallized from petroleum ether) was placed in a sealed Pyrex petri dish (glass thickness = 0.15 cm) and subjected to the irradiation of a medium-pressure ultraviolet lamp for a period of 2 weeks at room temperature, no reaction occurred. On repeating this procedure in direct sunlight, however, I gradually changes from yellow to light brown. The unchanged naphthoquinone (I) was extracted from the reaction product with boiling ether whereby the *syn* dimer (IIb) was obtained in 3% yield. An even higher yield (15%) of IIb was obtained when I was covered with a thick window glass plate (thickness = 1 cm) and subjected to direct sunlight.

$$\text{I (crystalline)} \xrightarrow{h\nu} \text{IIb}$$

It is interesting to note that a recent structure analysis by Gaultier and Hauw[19] showed that the 2,3 bonds in 1,4-naphthoquinone (I) do not make "short contacts." In view of Rabinovich and Schmidt's[20] suggestion that initiation of polymerization is topochemically controlled by the proximity of the initially formed diradical of a reaction partner implied in the infinite chain of short

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(17) A. W. K. de Jong, *ibid.*, **55**, 463 (1922).
(18) J. Madinaveitia, *Anales Real Soc. Espan. Fis. y Quim.* (Madrid), **31**, 750 (1933).
(19) J. Gaultier and C. Hauw, *Acta Cryst.*, **18**, 179 (1965).
(20) D. Rabinovich and G. M. J. Schmidt, *J. Chem. Soc., Sect. B*, 144 (1967).

contacts—the suggested reason for the "light stability" of solid 1,4-naphthoquinone (I)—we are now reinvestigating the crystal structure of I.

Experimental Section

Infrared spectra were recorded (in KBr) on a Perkin-Elmer 221 spectrophotometer. Mass spectra were obtained on an M.S.9 mass spectrometer. Melting points were determined on a Gallenkamp (design no. 889339) apparatus and are uncorrected.

Photodimerization of 1,4-Naphthoquinone. i. *anti* Dimer (IIa).—A solution of I (1 g) in acetic anhydride (12.5 ml) was sealed in a Pyrex test tube and irradiated with a medium-pressure ultraviolet lamp at room temperature for 2 weeks. The off-white precipitate (0.2 g) crystallized from glacial acetic acid in colorless plates melting with decomposition at 246–248° (lit.[1] mp 244–248°). The mass of molecular ion was *m/e* 316.

ii. ***syn* Dimer (IIb). a.**—The off-white precipitate (2 g), obtained in the previous experiment, was refluxed for 18 min in methanol (50 ml). The filtrate was concentrated (15 ml), allowed to stand for 1 hr at room temperature, filtered, concentrated (8 ml), and cooled to 0°, whereupon straw-colored crystals of IIb were obtained. Recrystallization from methanol yielded off-white needles (0.005 g), melting with decomposition at 235–237°.

Anal. Calcd for $C_{20}H_{12}O_4$: C, 75.92; H, 3.9; O, 20.26. Found: C, 75.9; H, 3.9; O, 20.2.

The mass of molecular ion was *m/e* 316.

b.—A thin layer of I (1 g), recrystallized from petroleum ether (bp 50–70°), was placed between two sealed window glass plates of 1-cm thickness and placed in direct sunlight for a period of 6 weeks. The set-up was turned over weekly. The pale brown material was refluxed for 15 min in ether, the mixture filtered, and the insoluble photoproduct (IIb) washed with ether (0.15 g).

1,4,5,8-Tetraacetoxy-2,3,6,7-dibenzobiphenylene (V). a. From the *anti* Dimer (IIa).—A mixture of IIa (0.03 g), acetic anhydride (10 ml), and anhydrous sodium acetate (0.1 g) was refluxed for 4 hr and cooled to room temperature. The crystalline product (V) was filtered off, washed successively with acetic acid and water, dried, and recrystallized from acetic anhydride. Yellow needles were obtained: yield, 0.041 g (90%); mp 358–360° (lit.[2] mp 358–360°).

b. From the *syn* Dimer (IIb).—Compound IIb (0.03 g) was refluxed with a mixture of acetic anhydride (10 ml) and anhydrous as above (0.041 g).

Ketonization of 1,4,5,8-Tetrahydroxy-2,3,6,7-dibenzobiphenylene (III).—Compound III (0.025 g) was dissolved in cold concentrated sulfuric acid (2 ml) and the reddish solution poured into ice water (20 ml). The mixture was filtered and the grayish precipitate washed with water. Recrystallization from glacial acetic acid led to colorless plates of the *anti* dimer (IIa) (0.02 g).

Sulfuric Acid Hydrolyses of 1,4,5,8-Tetraacetoxy-2,3,6,7-dibenzobiphenylene (V).—Compound IV (0.05 g) was dissolved in cold concentrated sulfuric acid (3 ml) and the reddish solution poured into ice water (25 ml). The grayish precipitate was treated as above (0.044 g, 88% of IIa).

Baeyer–Villiger Oxidation of the *anti* Dimer (IIa).—Trifluoroacetic anhydride (0.98 ml) was added slowly to an ice-cooled stirred dispersion of 85% hydrogen peroxide (0.17 ml) in methylene chloride (7 ml). This solution was slowly added to a vigorously stirred suspension of anhydrous disodium hydrogen phosphate (3 g) and the *anti* dimer (IIa) (0.1 g) in methylene chloride (17 ml). The mixture was refluxed with stirring for 30 hr and cooled. The undissolved material was filtered off and washed with water, whereby the tetralactone (VI) was obtained: yield, 0.059 g; mp 350°, ν_{max}^{KBR} 1765 (s), 1592 (w), 1485 (s), 1451 (sh), 1448 (w), 1266 (s), 1250 (s), 1177 (s), 1126 (m), 1100 (m), 1033 (m), 981 (w), 969 (w), 945 (w), 905 (m), 875 (m), 776 (s), 741 (m) cm^{-1}.

Compound VI was converted into *cis,trans,cis*-tetracarbomethoxycyclobutane (VII) by refluxing VI (0.1 g) for 12 hr in methanol (6 ml) containing concentrated sulfuric acid (0.1 ml). The cooled solution was poured into cold water (10 ml) and the precipitated product extracted with ether. The ethereal solution was washed with saturated sodium bicarbonate and water and dried ($MgSO_4$). Ether was removed on a water bath. The product was recrystallized from benzene to give colorless crystals, mp 144° (lit.[3] mp 145°). The infrared spectrum was identical with that of an authentic sample of VII.

Isomerization of the *syn* Dimer (IIb) to the *anti* Dimer (IIa).—Compound IIb (0.02 g) was dissolved in cold concentrated sulfuric acid (1.5 ml). Th solution was poured into ice water (20 ml) and a grayish precipitate was obtained. Recrystallization from acetic acid produced IIa in colorless plates (0.018 g).

Registry No.—IIa, 14734-19-1; IIb, 14734-20-4.

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Nucleosides. XLVI. Selectively Methylated Derivatives of Spongouridine

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In view of the biological activity recently found in nucleosides containing an arabino moiety,[2] it was of interest to prepare partially methylated derivatives of 1-β-D-arabinofuranosyluracil (spongouridine). The present paper reports the synthesis and properties of two dimethylated nucleosides, 1-(2-*O*-methyl-β-D-arabinofuranosyl)-3-methyluracil (IV) and 1-(3-*O*-methyl-β-D-arabinofuranosyl)-3-methyluracil (IX).

The synthesis of IV utilized the 3′,5′-di-*O*-trityl nucleoside II, which had been prepared in this laboratory by two routes,[3] namely, tritylation of the 5′-*O*-trityl nucleoside I to yield IIa and cleavage of the ditrityl anhydro nucleoside V to give IIb. Although the structure of IIb had been unequivocally established, there remained some incertitude regarding the structure of IIa. The assignment of a 3′,5′-di-*O*-trityl structure to IIa was based upon its physical properties, which were similar to those of IIb. Melting points, however, were over a 15° range, and infrared spectra, although identical, possessed broad peaks. Furthermore, it has been our experience that infrared spectra of some tritylated nucleosides of different structure are similar. Therefore, the possibility that the 2′,5′- and 3′,5′-di-*O*-trityl compounds would possess nearly identical properties could not be discounted. Fortunately, methylation of IIa by the method of Kuhn and coworkers[4] gave, after detritylation, colorless crystals which were shown to have a 2′-*O*-methyl structure IV, as described below, thus confirming the previously assigned 3′,5′-di-*O*-trityl structure for IIa.

The 3′-*O*-methyl isomer of IV, compound IX, was prepared in crystalline form from 2,2′-anhydro-1-β-D-arabinofuranosyluracil (VI) by the methylation procedure of Kuhn, *et al.*[4] It is of interest to note that

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(2) (a) M. R. Dollinger, J. H. Burchenal, W. Kreis, and J. J. Fox, *Biochem. Pharmacol.*, **16**, 689 (1967), and leading references therein; (b) S. S. Cohen, *Progr. Nucleic Acid Res. Mol. Biol.*, **5**, 1 (1966).

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