into the tropylium iodide solution. The blue color of the anion radical was immediately discharged on contact and addition was stopped when the blue color persisted. The yellow precipitate was collected on a filter, washed with water, and dried to give 1.33 g. of organic product (98% of theory for TCNQ + α,α'-ditropyl-α,α,α',α'-tetracyano-*p*-xylene). No material was extracted from this product by boiling pentane (20 ml.), indicating the absence of ditropyl, which would be an expected product if tropyl radicals had been formed in the reaction.[31]

Treatment of the aqueous filtrate with 1.5 g. of silver nitrate in 10 ml. of water gave 1.07 g. (99% yield) of silver iodide.

The organic product was dissolved in methylene chloride, and the solution was concentrated until 0.39 g. of TCNQ had precipitated. Further removal of solvent gave an intermediate fraction weighing 0.09 g., which was not examined further. Complete removal of solvent then gave 0.80 g. of pale yellow prisms corresponding to 90% of theory for α,α'-ditropyl-α,α,α',α'-tetracyano-*p*-xylene, m.p. 200–206°. Recrystallization from benzene gave 0.96 g. of bright yellow leaflets which lost occluded solvent at about 100° and melted at 201–202°. The crystals were dried at 110° (1 hour) for analysis; the resulting buff-colored solid had m.p. 201–202°. The infrared spectrum had nitrile absorption at the same wave length (4.43 μ) as H_2TCNQ, and the aromatic ring absorption bands were also similar to those of H_2TCNQ.

Anal. Calcd. for $C_{26}H_{18}N_4$: C, 80.8; H, 4.7; N, 14.5. Found: C, 80.9; H, 4.8; N, 14.8.

Decomposition of $Et_3NH^+(TCNQ)^{-\cdot}_2$ with Hydrochloric Acid.—To 30 ml. of 2.4 *N* hydrochloric acid was added 2.10 g. (4.1 mmoles) of powdered $Et_3NH^+(TCNQ)_2$. The dark suspension became yellow-green on stirring at room temperature. After 16 hours, the solid was collected on a filter and washed with 2 ml. of 2.4 *N* hydrochloric acid in two portions. The combined filtrate and acid washings were retained for the isolation of triethylamine (see below). The solid was then washed with water and dried to give 1.66 g. of yellow-green crystals corresponding to 99% of theory for the TCNQ–H_2TCNQ mixture. The infrared spectrum of the crystals was very similar to that of an authentic 3:1 mixture of TCNQ and H_2TCNQ and was distinctly different from that of a 1:1 mixture. Treatment of an aqueous suspension of the product with dilute aqueous potassium hydroxide gave the purple color characteristics of mixtures of TCNQ and H_2TCNQ.

To the retained filtrate and acid washings was added 35 ml. of 10% aqueous sodium hydroxide, and the clear solution was extracted with 75 ml. of ether in three portions. Removal of solvent from the combined, dried ether extracts gave 0.27 g. (65%) of triethylamine, identified by infrared analysis and by mixed m.p. of its picrate with an authentic sample.

Oxidation of $TCNQ^{-\cdot}$ with Iodine—To 0.2 g. (0.37 mmole) of $Et_4N^+(TCNQ)^{-\cdot}_2$ and 10 ml. of acetonitrile was added 1.0 g. (4 mmoles) of iodine, and the mixture was warmed on a steam-bath whereupon the green solution turned red and deposited yellow crystals. Water (5 ml.) was added, and the mixture was filtered to obtain 0.12 mg. (79%) of TCNQ, m.p. 287–298° dec. Recrystallization from acetonitrile raised the m.p. to 293–294° dec. When one or two equivalents of iodine was used in similar experiments, no apparent change occurred.

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[31] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

[CONTRIBUTION NO. 739, FROM THE CENTRAL RESEARCH DEPARTMENT EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

Substituted Quinodimethans. III. Displacement Reactions of 7,7,8,8-Tetracyanoquinodimethan

BY W. R. HERTLER, H. D. HARTZLER, D. S. ACKER AND R. E. BENSON

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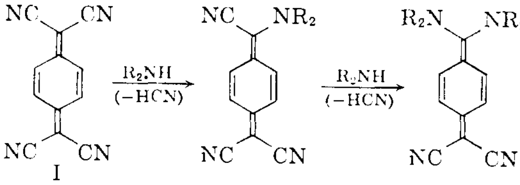
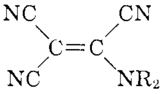
7,7,8,8-Tetracyanoquinodimethan (TCNQ) reacts with primary and secondary amines to give 7-amino-7,8,8-tricyanoquinodimethans or 7,7-diamino-8,8-dicyanoquinodimethans. Addition–elimination products also result from the reaction of TCNQ with nitrite ion or nitrogen dioxide.

7,7,8,8-Tetracyanoquinodimethan (TCNQ, I) has recently been synthesized[1] and shown to undergo facile reduction to an anion-radical[2] with a variety of reagents including aliphatic amines. It has now been found that certain primary and secondary amines react with TCNQ to give products in which one or two cyano groups are replaced by the amine according to eq. 1. This behavior is reminiscent of the reaction of tetracyanoethylene with amines to give tricyanovinylamines (II) or 1,1-diamino-2,2-dicyanoethylenes (III).[3] TCNQ reacts with one equivalent of pyrrolidine to give an intensely purple, crystalline, diamagnetic compound which is assigned the structure 7-pyrrolidino-7,8,8-tricyanoquinodimethan (IV) on the basis of infrared and ultraviolet spectra and elemental analysis. The dramatic bathochromic shift observed in going from TCNQ (λ_{max} 395 mμ) to IV (λ_{max} 567 mμ) has a precedent in the bathochromic shift observed in passing from tetracyanoethylene to a tricyanovinylamine.[3]

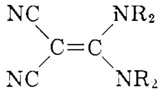


I

(1)



II



III

Reaction of either TCNQ or IV with an excess of pyrrolidine gives the same product, 7,7-dipyrrolidino-8,8-dicyanoquinodimethan (V), a pale yellow, high-melting mono-acidic base. In a similar fashion, TCNQ reacts with an excess of ammonia to give 7,7-diamino-8,8-dicyanoquinodimethan (VI).

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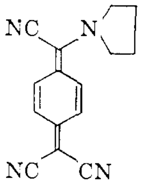
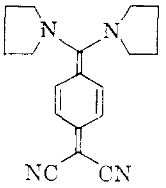
(1) (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Benson and W. E. Mochel, *ibid.*, **82**, 6408 (1960).

(2) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *ibid.*, **84**, 3374 (1962).

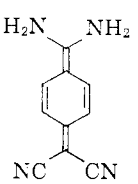
(3) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).



IV

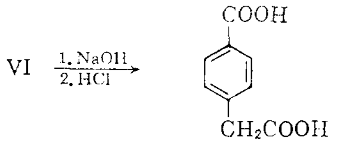


V

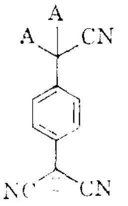


VI

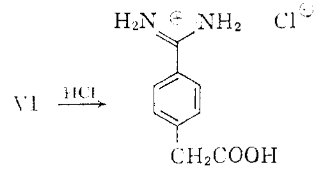
The possibility of a structure isomeric with VI for diaminodicyanoquinodimethan was ruled out by the observation that hydrolysis of VI with aqueous alkali followed by acidification gave homoterephthalic acid (VII) which proved to be identical with an authentic sample prepared by hydrolysis of methyl α-cyano-*p*-toluate. Clearly, homoterephthalic acid could readily arise from VI but not from an isomeric structure. Furthermore, from mechanistic considerations, it would be expected that nucleophilic attack by both the first and second amine molecules would occur on the same carbon atom to allow maximum delocalization of a transient carbanion by two adjacent cyano groups as in VIII. Hydrolysis of 7,7-diamino-8,8-dicyanoquinodimethan (VI) with hydrochloric acid gives a salt which elemental analysis and infrared spectroscopy indicate to be *p*-toluamidine-α-carboxylic acid hydrochloride (IX).



VII

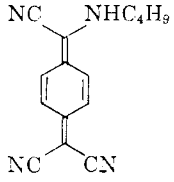


VIII

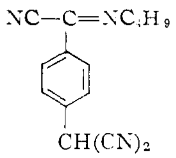


IX

The reaction of TCNQ with one equivalent of *n*-butylamine, rather than forming a single substitution product as was the case with pyrrolidine, leads to a poorly crystalline, purple material which appears to be a mixture of the tautomers Xa and Xb. The absorption in the visible spectrum, which is presumably attributable to Xa, is very weak compared to the absorption at 262 mμ which is due to Xb. This material is soluble in dilute alkali and precipitates unchanged upon acidification.

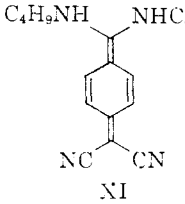


Xa



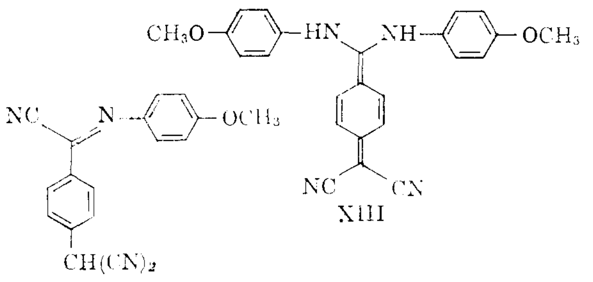
Xb

TCNQ and compound X both react with excess *n*-butylamine to give 7,7-bis(*n*-butylamino)-8,8-dicyanoquinodimethan (XI). Although in theory this compound is capable of existing in two tautomeric forms also, the similarity of its ultraviolet spectrum to that of 7,7-dipyrrolidino-8,8-dicyanoquinodimethan indicates that it is a quinodimethan.



XI

TCNQ reacts with excess *p*-anisidine to give 7,7-bis-(*p*-anisylamino)-8,8-dicyanoquinodimethan (XIII). With a limited amount of *p*-anisidine it is possible to isolate the intermediate α-(*p*-anisylimino)-α,α′,α′-tricyano-*p*-xylene (XII). There is no evidence for formation of the tautomeric quinodimethan.



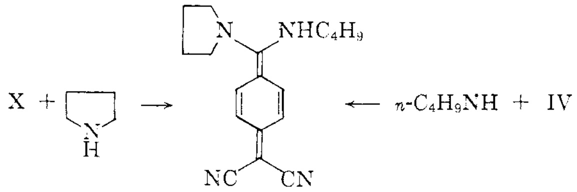
XIII

XII

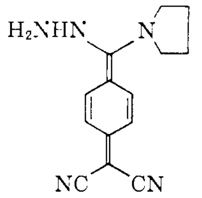
The position of equilibrium between tautomeric structures such as Xa and Xb would be expected to depend upon two factors. First, increasing the basicity of the amino nitrogen would be expected to provide additional stability to the quinodimethan Xa through increased resonance interaction of the amino nitrogen with the electron-deficient π-electron system. Second, with an aromatic, rather than an aliphatic, substituent on the amino nitrogen it would be expected that the stability of the imino tautomer (corresponding to Xb) would be enhanced through delocalization of electrons over both of the aromatic rings. The results obtained with X and XII are completely consistent with these concepts without, however, permitting assessment of the relative importance of either factor.

The infrared spectra of all of the diaminodicyanoquinodimethans show an intense absorption band in the region 1602–1607 cm.$^{-1}$ which has been useful for preliminary characterization. While the origin of the band cannot definitely be assigned, it may be the stretching vibration of the cyano-substituted carbon–carbon double bond.

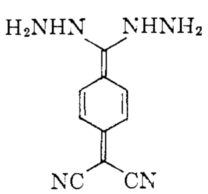
Reaction of X with pyrrolidine or of IV with *n*-butylamine gives the same mixed quinodimethan, 7-pyrrolidino-7-*n*-butylamino-8,8-dicyanoquinodimethan (XIV). In a similar manner, pyrrolidinotricyanoquinodimethan (IV) reacts with one equivalent of hydrazine hydrate to give 7-hydrazino-7-pyrrolidino-8,8-dicyanoquinodimethan (XV). However, with an excess of hydrazine hydrate the pyrrolidino group is replaced, giving 7,7-dihydrazino-8,8-dicyanoquinodimethan (XVI). Hydrazine is the only amine which has been observed to replace another amino substituent. It is not possible to prepare XVI directly from the reaction of hydrazine and TCNQ, since hydrazine reduces TCNQ to *p*-phenylenedimalononitrile.



XIV

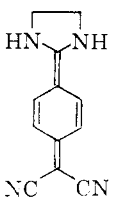


XV

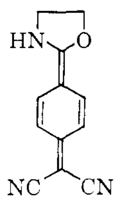


XVI

With certain bifunctional amines, cyclic substitution products are obtained. Thus, the reaction of TCNQ with ethylenediamine gives as the only isolated product 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-imidazolidine (XVII).



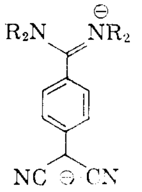
XVII



XVIII

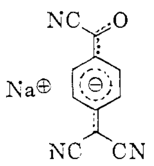
In an analogous manner, ethanolamine reacts with TCNQ to give 2-(4-dicyanomethylenecyclohexadienylidene)-oxazolidine (XVIII). In the latter reaction it is believed that displacement of a cyano group by the more basic amino group occurs first and that, because of a proximity effect, the intermediate undergoes an intramolecular cyanide-displacement by the hydroxyl group faster than it reacts with another molecule of ethanolamine.

The diaminodicyanoquinodimethans appear to be stable toward nucleophilic reagents. Indeed, when titrated with acid, they behave as monoacidic bases, much like amidines. Since the diaminodicyanoquinodimethans carry the strongly electron-attracting cyano groups at one end of the molecule and the electron-rich amino substituents at the opposite end, they would be expected to be highly polarized molecules with a significant contribution by canonical forms, such as XIX, to the ground state. It is probably this electronic distribution which gives rise to an infrared spectrum in which the nitrile absorption appears as an intense doublet near 2130 and 2175 cm.$^{-1}$ which is characteristic of a monosubstituted malonitrile anion.[4] The monoaminotricyanoquinodimethans in contrast do not retain any basic properties. In fact, as has been mentioned, 7-butylamino-7,8,8-tricyanoquinodimethan (X) is a weak protoacid indicative of the very powerful electron-withdrawing effect of the three cyano groups upon the single amino group.

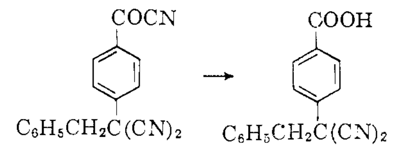


XIX

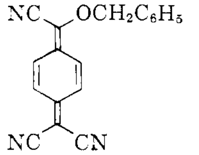
In addition to the displacement of cyano groups of TCNQ with amines, it has been found that a cyano group can be displaced by nitrite ion to give an orange-red salt.[5] Thus, the reaction of TCNQ with sodium nitrite in aqueous acetone gives a solid product in good yield having the composition $NaC_{11}H_4N_3O$, and displaying a λ_{max} in acetonitrile of 480 mμ (ϵ 38,800). These data, together with the infrared absorption spectrum which shows conjugated nitrile (2150 and 2200 cm.$^{-1}$), carbonyl (1645 cm.$^{-1}$) and conjugated cyanosubstituted double bond (1590 cm.$^{-1}$), suggest that the product is the sodium salt of α,α-dicyano-*p*-toluoyl cyanide (XX). Although XX could not be recrystallized satisfactorily, the corresponding tetramethylammonium salt, prepared from tetramethylammonium chloride and XX in acetonitrile solution, crystallized readily from methylene chloride as red needles. Alkylation of XX with benzyl bromide in acetone proceeded smoothly to give α,α-dicyano-α-benzyl-*p*-toluic acid (XXII) which



XX



XXI XXII



XXIII

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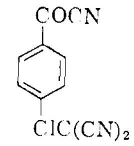
[4] O. W. Webster, W. Mahler and R. E. Benson, *J. Am. Chem. Soc.*, in press.

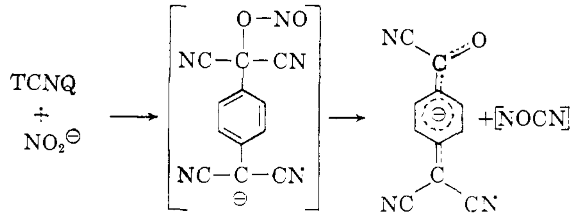
[5] We wish to thank Dr. L. Plambeck, Jr., for calling our attention to the reaction of TCNQ with sodium nitrite.

presumably was formed by hydrolysis of the intermediate acyl cyanide XXI. None of the O-alkylated product 7,8,8-tricyano-7-benzyloxyquinodimethan (XXIII) was observed. Chlorination of XX gave α,α-dicyano-α-chloro-*p*-toluoyl cyanide (XXIV).



XXIV

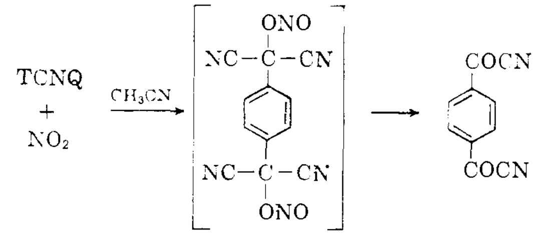
The formation of XX from TCNQ and nitrite ion most probably occurs by way of an adduct such as XXV. The nitrite would be expected to be unstable and to decompose directly to the anion of the acyl cyanide. The decomposition of nitrite esters substituted with electron-withdrawing groups has been observed in the addition of nitrogen dioxide to polyhaloölefins.[6] Thus, the formation of difluoronitroacetyl fluoride from the addition of nitrogen dioxide to chlorotrifluoroethylene is rationalized by assuming the formation of the nitronitrite as an intermediate



XXV

$$CF_2{=}CFCl + NO_2 \longrightarrow [O_2NCF_2CFClONO] \longrightarrow O_2NCF_2COF + NOCl$$

Another analogous reaction is the formation of terephthaloyl cyanide from the reaction of nitrogen dioxide and TCNQ. The bis-acyl cyanide may be obtained in a yield as high as 75% and an intermediate may be isolated, albeit not as a pure substance. The reaction occurs in acetonitrile at 0°, and may be followed by the gradual solution of the TCNQ. The intermediate adduct begins to decompose upon isolation. Nitrogen dioxide fumes quickly form above stored samples, even when chilled. The formation of the bis-acyl cyanide is conveniently effected by decomposing the crude adduct at 130° in an evacuated sublimation apparatus. The formation of the intermediate adduct could occur by addition of nitrite ion or the neutral NO_2 radical. The latter mode of reaction appears preferable, for the addition of silver nitrite to the reaction had (qualitatively) no effect on the reaction rate. A previous instance of radical addition to TCNQ has been reported.[1]



Terephthaloyl cyanide has previously been reported[7] as the product obtained from the reaction of terephthaloyl chloride, hydrogen cyanide and pyridine. The material obtained was a brown powder which did not melt, but became viscous around 300°. The material was insoluble in organic solvents and must be assumed to be polymeric. Monomeric terephthaloyl cyanide melts at 148–149°, may be crystallized from benzene, and gives dimethyl terephthalate upon warming in methanol.

Experimental

7-Pyrrolidino-7,8,8-tricyanoquinodimethan (IV).—To a warm solution of 1 g. of TCNQ in 100 ml. of tetrahydrofuran was added 0.25 ml. (less than 1 equivalent) of pyrrolidine. The initially green solution turned to a gray-purple color. After standing for 17 hours at room temperature the solution was cooled in an ice-bath and filtered to give 360 mg. of fine, purple needles, which began to melt at 233°, but did not melt completely up to 300°. Recrystallization from acetonitrile (purple solution) gave IV as fine purple needles. This product does not appear to melt up to 405°, although blackening occurs. Recrystallization of the product removed small amounts of anion-radical salts of TCNQ which were formed[2] as determined by electron paramagnetic resonance spectroscopy.

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57; mol. wt., 248.3. Found: C, 72.87; H, 4.67; N, 22.54; mol. wt., 225 (f.p., dimethyl sulfoxide).

The ultraviolet spectrum of this compound in methylene chloride solution shows intense absorption in the visible region at 532 mμ (ϵ 32,300), 567 mμ (ϵ 41,500) and 613 mμ (ϵ 31,300). The infrared spectrum (KBr wafer) shows no absorption attributable to NH. There is absorption at 2175 and 2200 cm.$^{-1}$ (conjugated nitrile) and additional weak nitrile absorption at 2240 cm.$^{-1}$.

7,7-Dipyrrolidino-8,8-dicyanoquinodimethan (V). A. From TCNQ.—To a warm solution of 1 g. (4.9 mmoles) of TCNQ in 100 ml. of tetrahydrofuran was added 2 ml. of pyrrolidine. After a few minutes a yellow crystalline compound began to precipitate. After 3 days the solution was cooled and filtered. The filter cake was washed with cold tetrahydrofuran and then with ether to give 1.2 g. (84%) of yellow crystalline 7,7-dipyrrolidino-8,8-dicyanoquinodimethan, m.p. 292–300° dec., with preliminary darkening at about 252°. Two recrystallizations from methanol gave pale yellow crystals of m.p. 304–307° dec.

Anal. Calcd. for $C_{18}H_{20}N_4$: C, 73.94; H, 6.89; N, 19.17; neut. equiv., 292.37 (for monoacidic base). Found: C, 73.87; H, 6.97; N, 18.98; neut. equiv., 290.

The ultraviolet absorption spectrum of this compound in methanol solution shows bands at 227 mμ (ϵ 19,900) and 367 mμ (ϵ 16,500). The infrared spectrum of the product (KBr wafer) shows absorption at 2175 and 2130 cm.$^{-1}$ (conjugated nitrile), 1330 cm.$^{-1}$ (possibly vinyl C–N) and 1607 cm.$^{-1}$. There is no N–H absorption.

B. From 7-Pyrrolidino-7,8,8-tricyanoquinodimethan.—A mixture of 500 mg. (2 mmoles) of 7-pyrrolidino-7,8,8-tricyanoquinodimethan and 40 ml. of tetrahydrofuran was treated with 1 ml. of pyrrolidine. The solution turned green and gradually deposited yellow crystals. After 5 hours the product was collected and washed with ether to give 465 mg. (80%) of yellow crystals of 7,7-dipyrrolidino-8,8-dicyanoquinodimethan, m.p. 276–281 (uncor.). Recrystallization from methanol gave pale yellow crystals, m.p. 289.5–311.5° dec. The infrared spectrum of the product confirmed its identity as authentic 7,7-dipyrrolidino-8,8-dicyanoquinodimethan.

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(6) I. L. Knunyants and A. V. Fokin, *Proc. Acad. Sci., U.S.S.R., Chem. Sec.*, **111**, 731 (1956); *Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci.*, 1462 (1957).

(7) G. Blackstock, *J. Am. Chem. Soc.*, **34**, 1080 (1912).

7,7-Diamino-8,8-dicyanoquinodimethan (VI).—To a solution of 4 g. (19.6 mmoles) of TCNQ in 350 ml. of tetrahydrofuran was added 200 ml. of tetrahydrofuran containing 74 mmoles of ammonia. The dark solution was stored at room temperature for 69 hours. Filtration of the mixture gave 3.02 g. (82%) of 7,7-diamino-8,8-dicyanoquinodimethan as a yellow-brown solid. A small portion of the product was twice recrystallized from a mixture of dimethylformamide and tetrahydrofuran to give yellow microcrystals which turned brown at 368° but did not melt up to 400°.

Anal. Calcd. for $C_{10}H_8N_4$: C, 65.20; H, 4.38; N, 30.42. Found: C, 65.38; H, 4.65; N, 30.46.

The infrared absorption spectrum of this product (KBr wafer) shows absorption bands at 3360 and 3160 cm.$^{-1}$ (N–H stretch), 1665 cm.$^{-1}$ (N–H deformation), 2175 and 2125 cm.$^{-1}$ (conjugated nitrile), 1340 cm.$^{-1}$ (possibly C–N of a vinylamine), and 1607 cm.$^{-1}$.

7,7-Diamino-8,8-dicyanoquinodimethan is insoluble in organic solvents of low to moderate polarity, but is soluble in dimethylformamide, dimethyl sulfoxide and dilute hydrochloric acid.

Alkaline Hydrolysis of 7,7-Diamino-8,8-dicyanoquinodimethan.—7,7-Diamino-8,8-dicyanoquinodimethan (1 g.), 6 g. of sodium hydroxide and 25 ml. of water were refluxed with stirring. During the period of refluxing the aminocyano compound gradually dissolved and gave a precipitate which, in turn, gradually dissolved. After a total reaction period of 5 hours, the solution was acidified with dilute hydrochloric acid and filtered to give 230 mg. of light tan solid, m.p. 225–230°. Recrystallization of a portion of this product from ether gave colorless homoterephthalic acid of m.p. 236-237° (uncor.); mixed melting point with authentic homoterephthalic acid (of m.p. 241.5–242°, uncor.), which was prepared by alkaline hydrolysis of methyl α-cyano-*p*-toluate,[8] was 239–241° (uncor.). The infrared spectrum is identical to that of authentic homoterephthalic acid.

Acid Hydrolysis of 7,7-Diamino-8,8-dicyanoquinodimethan.—7,7-Diamino-8,8-dicyanoquinodimethan (200 mg.) was dissolved in 15 ml. of 10% hydrochloric acid and heated on a steam-bath for 1 hour. The solution was concentrated *in vacuo* to pale yellow crystals. Crystallization from acetonitrile–methanol gave, in the first two crops, ammonium chloride. The third crop consisted of 80 mg. of well-formed, pale yellow crystals which, on recrystallization from acetonitrile–methanol, with the addition of a few drops of benzene to induce crystallization, gave fine white needles of *p*-toluamidine-α-carboxylic acid hydrochloride, m.p. 229–233° (some decomposition).

Anal. Calcd. for $C_9H_{11}N_2O_2Cl$: C, 50.35; H, 5.17; N, 13.05; Cl, 16.52. Found: C, 50.54; H, 4.91; N, 13.52; Cl, 16.80.

The ultraviolet spectrum of the product in methanol solution shows aromatic absorption at 240 mμ (ε 6250). The infrared absorption spectrum of the product shows a carbonyl stretching frequency at 1710 cm.$^{-1}$ characteristic of an amino acid hydrochloride where the amino group is not alpha to the carboxyl group. This absorption frequency is too high for a benzoic acid derivative.

Reaction of TCNQ with One Equivalent of *n*-Butylamine.—TCNQ (2 g., 9.8 mmoles) was dissolved in 250 ml. of tetrahydrofuran with gentle warming. To the warm solution was added 1.2 ml. (12.1 mmoles) of *n*-butylamine. The dark solution was stored at room temperature for 48 hours. The solution was concentrated *in vacuo* to give a dark solid which was dissolved in dilute sodium hydroxide and the resulting solution was filtered. The filtrate was washed with 1:1 pentane–ether. The aqueous layer (deep red) was acidified with dilute hydrochloric acid and the dark precipitate collected, washed with water, and dried in a desiccator. The dry, purple X (2 g., 82%) was dissolved in tetrahydrofuran and reprecipitated by addition of hexane to give 1.44 g. of purple powder, m.p. 159.5–169°.

Anal. Calcd. for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38; mol. wt., 246.3. Found: C, 71.55; H, 5.69; N, 21.81; mol. wt., 239.

The infrared spectrum of this compound shows NH absorption, a triplet in the nitrile region, and a shoulder in the imine region. The ultraviolet spectrum is complex with λ_{max} 262 mμ (ε 10,100) and a series of peaks from 425 to 617 mμ with ϵ_{570} 1010. The product is probably a mixture of the tautomers Xa and Xb.

The compound forms a silver salt. To a solution of 500 mg. of the purple compound X in a few ml. of tetrahydrofuran was added a solution of 390 mg. of silver nitrate in aqueous ethanolic tetrahydrofuran. An orange precipitate immediately formed. Water was added and the mixture filtered. The filter cake was washed with water to give 639 mg. of orange micro-crystals of silver salt, m.p. 157–161° with browning at 140°.

Anal. Calcd. for $C_{15}H_{13}N_4Ag$: Ag, 30.20. Found: Ag, 30.10.

7,7-Bis-(butylamino)-8,8-dicyanoquinodimethan (XI). A. From 7-Butylamino-7,8,8-tricyanoquinodimethan.—7-Butylamino-7,8,8-tricyanoquinodimethan (X, 125 mg.) was dissolved in 15 ml. of tetrahydrofuran, giving a deep purple solution. To this solution was added 0.15 ml. of *n*-butylamine. The solution immediately turned deep red and was stored under nitrogen at room temperature for 18 hours. At the end of that time the crystalline precipitate was collected and washed with a small amount of tetrahydrofuran to give 110 mg. of dull red crystals, m.p. 261–263° dec. This compound is soluble in dilute hydrochloric acid from which it can be recovered on treatment with sodium hydroxide. The compound was purified by boiling with Darco in methanol. Treatment of the filtrate with ether gave 7,7-bis-(butylamino)-8,8-dicyanoquinodimethan (XI) as pale yellow crystals, m.p. 264–266° dec. Recrystallization from methanol–water raised the melting point to 270–275° dec.

Anal. Calcd. for $C_{18}H_{24}N_4$: C, 72.93; H, 8.16; N, 18.91; neut. equiv., 296. Found: C, 72.66; H, 8.23; N, 18.79; neut. equiv., 300. The infrared spectrum of this compound shows NH absorption, a doublet in the nitrile region at 2175 and 2130 cm.$^{-1}$ (conjugated nitrile) and strong absorption at 1607 cm.$^{-1}$. The ultraviolet spectrum of this product in methanol solution shows absorption maxima at 224 mμ (ε 24,200) and 365 mμ (ε 21,600).

B. From TCNQ.—TCNQ (2 g., 9.8 mmoles) was dissolved in 300 ml. of tetrahydrofuran with warming. To the warm solution was added 3.95 ml. (40 mmoles) of *n*-butylamine. The dark, purple-green solution was allowed to stand at room temperature. After 1.25 hours a light-colored precipitate was noted. After 24 hours the mixture was filtered and the filter cake was washed with ether, leaving 2.35 g. of pale yellow crystals of XI, m.p. 270–273° dec. This material was identical to that described above as determined by mixed melting point and infrared spectroscopy.

α-(*p*-Anisylimino)-α,α′,α′-tricyano-*p*-xylene (XII).—To a warm mixture of 1 g. (4.9 mmoles) of TCNQ, 50 ml. of acetonitrile and 50 ml. of pyridine was added 628 mg. (5.1 mmoles) of *p*-anisidine. The red-colored mixture was refluxed under nitrogen for 1 hour and allowed to stand at room temperature for 22 hours. The solvent was removed *in vacuo*, and the residue was suspended in ether and filtered, giving 1.065 g. (72%) of red solid, m.p. 174–183° dec. The crude product was dissolved in a mixture of dimethylformamide and ether. The resulting solution was filtered and then extracted with 100 ml. of 5% sodium hydroxide. The alkaline extract was filtered and acidified, giving 550 mg. of dark-colored solid which was recrystallized twice from acetone–hexane, giving brown-green needles of α-(*p*-anisylimino)-α,α′,α′-tricyano-*p*-xylene, m.p. 179–182° dec.

Anal. Calcd. for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66. Found: C, 71.95; H, 3.99; N, 18.90.

The infrared spectrum of the product shows absorption at 2900 [ArC(CN)$_2$–H], 2270 (nitrile), 2215, 2180 and 2140 cm.$^{-1}$ (conjugated nitrile). There is no absorption which can be attributed to N–H. The ultraviolet spectrum of the product, determined in methylene chloride, shows absorption at 397 mμ (ε 11,200), 283 mμ (ε 11,100) and 258 mμ (ε 12,900). The absence of absorption above 397 mμ is evidence that there is no 7-(*p*-anisylamino)-7,8,8-tricyanoquinodimethan present.

7,7-Bis(*p*-anisylamino)-8,8-dicyanoquinodimethan (XIII).—A mixture of 1 g. (4.9 mmoles) of TCNQ, 3 g. (24.4 mmoles) of *p*-anisidine, 75 ml. of acetonitrile and 25 ml. of pyridine was refluxed under nitrogen for 1 hour and then allowed to stand at room temperature for 22 hours. The red solution was evaporated *in vacuo*, and the residue was suspended in ether and filtered, giving 1.41 g. (73%) of dark crystals, m.p. 292–298° dec. Repeated crystallization from

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[8] J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1035 (1952). We are indebted to Dr. Mosettig for supplying a sample of the ester.

dimethylformamide–ether gave yellow 7,7-bis-(*p*-anisylamino)-8,8-dicyanoquinodimethan, m.p. 288–294° dec.

Anal. Calcd. for $C_{24}H_{20}N_4O_2$: C, 72.71; H, 5.08; N, 14.11. Found: C, 72.92; H, 5.23; N, 13.78.

The ultraviolet spectrum of the product in dimethylformamide solution shows absorption at 353 mμ (ε 27,600) and 440 mμ (ε 2340).

7-Pyrrolidino-7-butylamino-8,8-dicyanoquinodimethan (XIV). A. From 7-Pyrrolidino-7,8,8-tricyanoquinodimethan.—To a mixture of 300 mg. (1.26 mmoles) of 7-pyrrolidino-7,8,8-tricyanoquinodimethan and 250 ml. of tetrahydrofuran was added 1 ml. of *n*-butylamine. The solution turned red and then green. After 4 hours, filtration gave 180 mg. of yellow solid, m.p. 105–135° dec. Recrystallization from acetonitrile gave pale yellow crystals of 7-butylamino-7-pyrrolidino-8,8-dicyanoquinodimethan, m.p. 267–269° dec.

Anal. Calcd. for $C_{18}H_{22}N_4$: C, 73.43; H, 7.53; N, 19.04. Found: C, 73.56; H, 7.41; N, 19.41.

The infrared spectrum of the product (KBr wafer) shows absorption at 3250 and 3200 cm.$^{-1}$ (N–H stretch), 1625 cm.$^{-1}$ (N–H deformation), 2175 and 2125 (conjugated nitrile), 1320 cm.$^{-1}$ (probably vinyl C–N) and 1603 cm.$^{-1}$. The ultraviolet spectrum of the product in methanol solution shows absorption at 224 mμ (ε 50,400) and 347 mμ (ε 34,400).

B. From 7-Butylamino-7,8,8-tricyanoquinodimethan.—To a mixture of 80 mg. of 7-butylamino-7,8,8-tricyanoquinodimethan in 10 ml. of tetrahydrofuran was added 0.1 ml. of pyrrolidine. An orange solution formed immediately. After 21 hours the precipitate was collected and washed with ether to give 70 mg. of impure yellow-red solid. Recrystallization from acetonitrile–ether gave 20 mg. of pale pink crystals, m.p. 261–262° dec. Mixed melting point with the product obtained by method A was 259.5–264° dec. The two products have identical infrared spectra.

7-Hydrazino-7-pyrrolidino-8,8-dicyanoquinodimethan (XV).—7-Pyrrolidino-7,8,8-tricyanoquinodimethan (250 mg.) was covered with a mixture of 5 ml. of acetonitrile and 1 ml. of dimethylformamide. Hydrazine hydrate was added to the suspension dropwise until a yellow homogeneous solution was obtained. Approximately 0.06 ml. of hydrazine hydrate was required. Addition of a large volume of ether caused an orange oil to separate. The supernatant liquid was decanted, and the oil was scratched in the presence of acetonitrile to give 182 mg. of orange-yellow solid, m.p. 205–210° dec. Recrystallization from acetonitrile–dimethylformamide–ether gave pale yellow micro-crystals of 7-hydrazino-7-pyrrolidino-8,8-dicyanoquinodimethan, m.p. 217–223° dec.

Anal. Calcd. for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65. Found: C, 66.23; H, 6.03; N, 28.11.

The infrared spectrum of the product shows absorption at 3450, 3320 and 3200 (N–H stretch), 3030 (Ar–H), 2900 (aliphatic C–H), 1660 (N–H deformation), 2125 and 2175 (conjugated nitrile) and 1607 cm.$^{-1}$. The ultraviolet spectrum of the product in acetonitrile solution has λ_{max} 375 mμ (ε ~ 17,700).

7,7-Dihydrazino-8,8-dicyanoquinodimethan (XVI).—To a mixture of 1 g. of 7-pyrrolidino-7,8,8-tricyanoquinodimethan and 15 ml. of acetonitrile was added 2 ml. of hydrazine hydrate. A homogeneous orange solution formed. Addition of ether caused an oil to separate which on scratching gave 560 mg. of orange solid. Recrystallization from dimethylformamide–ether gave 470 mg. of yellow 7,7-dihydrazino-8,8-dicyanoquinodimethan which did not melt up to 400°. A sample was recrystallized from dimethylacetamide–ether for analysis. The infrared spectrum of the product shows absorption which can be assigned to N–H and conjugated nitrile. There is no absorption due to aliphatic C–H.

Anal. Calcd. for $C_{10}H_{10}N_6$: C, 56.06; H, 4.71. Found: C, 56.43; H, 5.09.

2-(4-Dicyanomethylenecyclohexa-2,5-dienylidene)-imidazolidine (XVII).—To a warm solution of 1 g. (4.9 mmoles) of TCNQ in 60 ml. of acetonitrile was added 0.4 g. of ethylenediamine. A green color appeared, and a light-colored precipitate began to form immediately. After 1.5 hours at room temperature, filtration gave 927 mg. of yellow-green solid. Recrystallization from dimethylformamide–ether gave 235 mg. of yellow 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene-)imidazolidine, which did not melt up to 405°. The infrared spectrum of the product shows absorption characteristic of N–H and conjugated nitrile.

Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.66. Found: C, 68.46; H, 4.78; N, 26.22.

2-(4-Dicyanomethylenecyclohexa-2,5-dienylidene)-oxazolidine (XVIII).—To a warm solution of 1 g. (4.9 mmoles) of TCNQ in 60 ml. of acetonitrile was added 0.33 ml. (5.5 mmoles) of ethanolamine. A green color formed, and light-colored crystals began to precipitate almost at once. After 2.5 hours, filtration gave 570 mg. of yellow-green crystals which did not melt up to 400°. Recrystallization from dimethylformamide–ether with the help of Darco gave bright yellow microcrystals of 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-oxazolidine which did not melt up to 400°. The ultraviolet spectrum of the product in dimethylformamide solution has λ_{max} 368 mμ (ε ~ 39,000).

Anal. Calcd. for $C_{12}H_9N_3O$: C, 68.24; H, 4.29; N, 19.99. Found: C, 68.11; H, 4.23; N, 19.76.

Sodium Salt of *α,α*-Dicyano-*p*-toluoyl Cyanide (XX).—A solution of 200 mg. of TCNQ in 50 ml. of acetone was treated with a solution of 140 mg. of sodium nitrite in 5 ml. of water. The resulting orange solution was evaporated to dryness under reduced pressure at room temperature. The dry solid was then treated with acetone, which dissolved the orange compound and left behind an essentially colorless inorganic salt. The acetone solution was evaporated to dryness and the residue extracted with acetone as before. The resulting acetone solution was treated with an excess of methylene chloride and filtered to give 130 mg. of the orange-red sodium salt of *α,α*-dicyano-*p*-toluoyl cyanide. Further purification of the product was achieved by dissolving in acetone and reprecipitating by gradual addition of heptane.

Anal. Calcd. for $C_{11}H_4N_3ONa$: C, 60.84; H, 1.86; N, 19.35. Found: C, 59.55; H, 2.24; N, 19.49.

The ultraviolet spectrum of the product in acetonitrile solution shows absorption at 480 mμ (ε 38,800), 330 mμ (ε 1,100) and 287 mμ (ε 6,560). The infrared spectrum of the product shows absorption at 2150 and 2200 (nitrile), 1645 (carbonyl), 1590 (conjugated cyanosubstituted double bond) and 835 cm.$^{-1}$ (1,4-disubstituted benzene).

Tetramethylammonium Salt of *α,α*-Dicyano-*p*-toluoyl Cyanide.—A mixture of 600 mg. of XX, 200 mg. of tetramethylammonium chloride and 75 ml. of acetonitrile was warmed on a steam-bath for 10 minutes and filtered. The filtrate was evaporated to dryness, and the residue was recrystallized four times from methylene chloride to give 90 mg. of red needles of the tetramethylammonium salt of *α,α*-dicyano-*p*-toluoyl cyanide, m.p. 196.5–198.5°.

Anal. Calcd. for $C_{15}H_{16}N_4O$: C, 67.14; H, 5.96; N, 20.88. Found: C, 67.30; H, 6.12; N, 21.14.

The ultraviolet spectrum of the product in acetonitrile solution shows absorption at 480 mμ (ε 40,200), 330 mμ (ε 910) and 280 mμ (ε 6,540). The infrared spectrum of the product shows absorption at 2205, 2180 and 2150 (nitrile), 1640 (carbonyl of acyl cyanide), 1590 (conjugated cyano-substituted double bond) and 835 cm.$^{-1}$ (1,4-disubstituted benzene).

***α,α*-Dicyano-*α*-benzyl-*p*-toluic Acid (XXII).**—A mixture of 1.42 g. of XX, 5 ml. of benzyl bromide and 250 ml. of acetone was stirred at reflux for 24 hours and then filtered. The filtrate was evaporated and the residue extracted with ether, and the resulting solution was then filtered. The ethereal filtrate was evaporated and the residue was suspended in pentane and filtered, giving 1.05 g. of pale tan solid, m.p. 180–200°. Recrystallization from benzene-hexane followed by two recrystallizations from ether–hexane gave 100 mg. of pale yellow *α,α*-dicyano-*α*-benzyl-*p*-toluic acid, m.p. 224–226° (turning red). The infrared spectrum of the product shows absorption at 2700 and 2550 (OH of carboxylic acid), 2250 (weak, unconjugated nitrile), 1695 (aromatic carboxylic acid), 800 (1,4-disubstituted benzene) and 860 cm.$^{-1}$ (monosubstituted benzene).

Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.01. Found: C, 73.49; H, 4.44; N, 9.98.

***α,α*-Dicyano-*α*-chloro-*p*-toluoyl Cyanide (XXIV).**—Chlorine gas was passed into a slurry of 1.34 g. of XX in 100 ml. of acetonitrile until the orange color disappeared. The mixture was filtered, and the filtrate was evaporated under reduced pressure leaving an oily residue which was taken up in ether and filtered. The filtrate was boiled with Darco, filtered and concentrated. Treatment of the concentrate with hexane gave 714 mg. of gummy solid which was recrystallized twice from ether–hexane giving 80 mg. of white crystals of *α,α*-dicyano-*α*-chloro-*p*-toluoyl cyanide, m.p. 78–83°. The infrared spectrum of the product shows absorption at 3100 (Ar–H), 2225 (nitrile of acyl cyanide), 1695 (carbonyl of acyl cyanide), 1612 and 1503 (aromatic) and 816 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{11}H_4N_3OCl$: C, 57.53; H, 1.76; N, 18.30; Cl, 15.44. Found: C, 57.99; H, 1.93; N, 18.45; Cl, 15.02.

Terephthaloyl Cyanide.—A suspension of 20.5 g. of TCNQ in 200 ml. of acetonitrile was cooled to 0° under a nitrogen atmosphere. Nitrogen dioxide (10.9 g.) was added to the stirred mixture. The mixture was stirred for 16 hours during which time it became homogeneous. The solvent was removed under reduced pressure leaving a green oil as a residue. The oil evolved NO_2 on standing at room temperature and more rapidly on addition of a solvent. Decomposition of the oil is effected more advantageously by heating at 130° under vacuum in a sublimation apparatus. A near-white solid is deposited on the cold finger. Recrystallization from benzene gave crude terephthaloyl cyanide (13.8 g., 75%), m.p. 140–142°. Sublimation gave material of m.p. 148–149°.

Anal. Calcd. for $C_{10}H_4N_2O_2$: C, 65.22; H, 2.19; N, 15.22. Found: C, 65.89; H, 2.39; N, 14.76.

Upon standing the nitrogen content of the sample decreased, probably as a result of hydrolysis. The infrared spectrum of terephthaloyl cyanide is quite simple. It shows absorption at 2230 cm.$^{-1}$ (nitrile) and 1690 cm.$^{-1}$ (carbonyl). The aromatic absorption at 1500 cm.$^{-1}$ is moderate, but that at 1600 cm.$^{-1}$ is very weak. There is no absorption in the region 800–860 cm.$^{-1}$ normally cited for *p*-substituted aromatics, but this has also been noted previously for dimethyl terephthalate. Terephthaloyl cyanide does absorb at 875 cm.$^{-1}$, but this absorption is not as intense as that customarily due to a *p*-substituted aromatic compound.

Terephthaloyl cyanide was warmed in methanol solution and the odor of hydrogen cyanide was observed. Evaporation of the methanol left a solid residue which was sublimed to give dimethyl terephthalate, m.p. 142.5–143.5°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS., AND THE RESEARCH LABORATORIES OF CHAS. PFIZER AND CO., INC., GROTON, CONN.]

Structure and Synthesis of Flavocarpine

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The stem bark of *Pleiocarpa mutica* Benth. contains a yellow zwitterionic substance which we have named flavocarpine. Decarboxylation gave flavopereirine. The position of the carboxyl group was established from a study of the ultraviolet, infrared, mass and nuclear magnetic resonance spectra of a methyl ester prepared by reduction of flavocarpine methyl ester hydrochloride with sodium borohydride. The structure proposed was confirmed by a total synthesis.

Preliminary chemical analyses of *Pleiocarpa tubicina* Stapf[2] and *Pleiocarpa mutica* Benth.[3] (*Apocyanaceae*) revealed the presence of alkaloids and crude extracts of both plants were reported to exhibit considerable hypotensive activity.[2,4] A systematic search for alkaloids of *P. mutica* Benth. was initiated in several laboratories and the isolation of new indole bases has already been announced.[5-7]

In the present paper we outline our work on the isolation, structure elucidation and synthesis of a new alkaloid, m.p. 307° dec., $[\alpha]_D$ 0°, which we have isolated from the stem bark of *P. mutica* Benth. in 0.0005% yield. The most striking property of this substance is its brilliant yellow color and we have named it "flavocarpine" accordingly. Combustion analyses gave erratic results and the correct empirical formula ($C_{18}H_{14}N_2O_2$) had to be deduced from the composition of transformation products. The infrared spectrum posessed a broad carbonyl band at 1595 cm.$^{-1}$ ascribable to a carboxylate anion. This finding coupled with the extreme insolubility in common organic solvents indicated the presence of a zwitterionic structure. Flavocarpine exhibits complex ultraviolet light absorption (see Experimental) which is *p*H dependent. When measured in dilute hydrochloric acid the spectrum showed a vague resemblance to those of 7H-pyrido[2,3-c]carbazole (8)[8] and 7H-pyrido[4,3-c]carbazole (9)[9] in acid solution, but it was very similar to that of flavopereirine perchlorate.[10,11] The nuclear magnetic resonance spectrum[12] of the natural product in trifluoroacetic acid solution was even more revealing and the only bands appearing at field strengths above 2τ were a quartet centered at 6.58τ corresponding in intensity to two protons and a triplet centered at 8.45τ with an area of three protons. Consequently, five hydrogens are contained in an ethyl group while all other protons are attached to the aromatic system. In summary, the physical measurements discussed indicated that flavocarpine is a C- or N-ethylpyridocarbazolecarboxylic acid or, preferably, an ethyl-indolo[2,3,-a]pyridocolinecarboxylic acid. Reduction of N-alkylpyridocarbazole salts with sodium borohydride affords carbazoles[13] while reduction of indolopyridocoline salts with the same reagent furnishes derivatives with indole chromophores.[14] We have used this diagnostic test to ascertain the aromatic portion in the molecule.

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