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Substituted Quinodimethans. IV. 7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan

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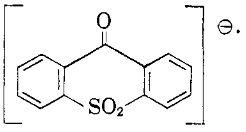
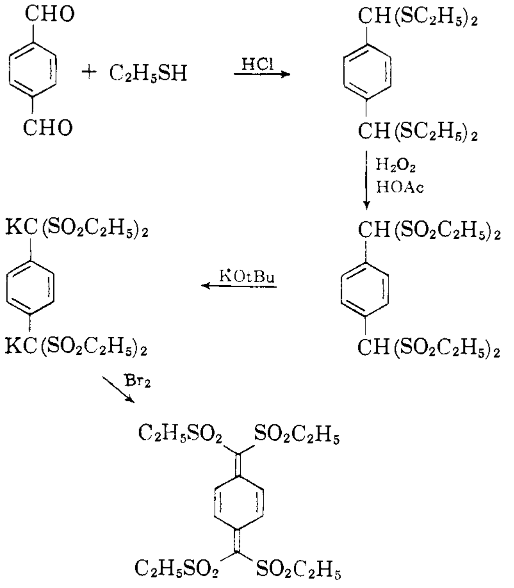
7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan (II) has been synthesized and found to be reducible to an anion-radical of limited stability. Halogens add to II readily in a 1,6-fashion. Ammonia and sodium methoxide react with II by an addition–elimination mechanism to give, respectively, a nitrile and a methyl orthoester.

The recent synthesis of 7,7,8,8-tetracyanoquinodimethan[1] (TCNQ) and the unusual solid state properties of its stable anion-radical salts[2] have prompted us to examine the effects of other electron-withdrawing groups on the quinodimethan nucleus. A quinodimethan bearing methoxycarbonyl groups, 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethan, has been shown to be moderately stable, but unlike TCNQ it fails to undergo one-electron reduction to give an anion-radical.[1] The diminished stability of 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethan relative to TCNQ has been attributed to the poorer electron-withdrawing ability of the ester group. Since the electron-withdrawing ability of the sulfonyl group is roughly comparable to that of the cyano group, it was decided to synthesize and study a quinodimethan with a multiplicity of alkylsulfonyl substituents. Additional incentive to undertake such a study was provided by the reported stability of the anion-radical of thioxanthene-9-one-10-dioxide (I).[3]



I

Synthesis and Properties.—7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan (II) was synthesized by the route outlined in Fig. A. Reasonable yields were obtained in all of the steps.



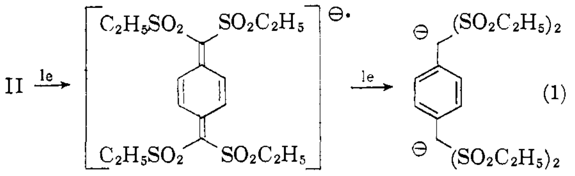
II

Fig. A.

7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan (II) is a yellow crystalline compound melting at 195.5–198° with decomposition. The infrared spectrum of II is consistent with the proposed structure. In addition to the strong absorption characteristic of the sulfonyl group, there is an absorption band at 1515 cm.$^{-1}$ which is assigned to the conjugated, sulfonyl-substituted, carbon–carbon double bond. Interestingly, the corresponding double bond stretching frequencies in TCNQ and tetrakis-(methoxycarbonyl)-quinodimethan occur at 1540 and at 1578 cm.$^{-1}$, respectively. The ultraviolet spectrum of II in methylene chloride solution in the absence of air has λ_{max} 372 mμ (ϵ 45,400). The quinodimethan II is diamagnetic as determined by electron paramagnetic resonance spectroscopy (E.P.R.).

Although II appears to be stable in the solid state, in solution it reacts slowly with oxygen. The only product from the reaction which was identified was terephthalic acid. In addition, the odor of sulfur dioxide was detected.

Polarographic reduction of II in dimethylformamide solution produced two one-electron reduction waves with half-wave potentials of +0.092 v. and +0.002 v. (*vs.* an aqueous saturated calomel electrode).[4] The first reduction wave corresponds to the reduction of the quinodimethan II to an anion-radical III, while the second wave represents further reduction to the dianion IV (eq. 1). The difference of only 0.09 v. between the first and second one-electron reduction steps is in marked contrast to



III IV

the spread of 0.42 v. between the corresponding reduction steps of TCNQ. The proximity of the two half-wave potentials is reflected in the propensity of the anion-radical III to disproportionate to the quinodimethan II and the dianion IV. The anion-radical III can be prepared chemically from the reaction of iodide ion with II. Thus, II and triphenylmethylarsonium iodide in acetonitrile

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(1) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

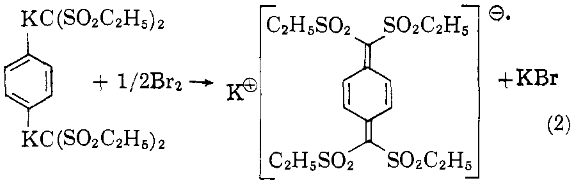
(2) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *ibid.*, **84**, 3374 (1962).

(3) H. Heymann, *ibid.*, **71**, 260 (1949).

(4) T. Berzins, unpublished results.

reacted in the absence of oxygen to give a deep green solution which contained a strongly paramagnetic species as determined by E.P.R. The anion-radical III is highly reactive toward oxygen, the green color of a solution containing III being discharged immediately on contact with air. Even in the absence of oxygen, III appears to have only limited stability, since a green solution of III retained its color for only a few hours under nitrogen. Disappearance of the green color was accompanied by loss of the E.P.R. signal.

A convenient method of preparation of a solution of the potassium salt of the anion-radical is to mix equimolar amounts of II and the dipotassium salt of IV in acetonitrile under nitrogen. A solution of the potassium salt of III could also be obtained by oxidation of the dipotassium salt of IV with 0.5 molar equivalent of bromine as shown in eq. 2. Indeed, during the final step in the synthesis of the quinodimethan II in which bromine is added dropwise to a stirred slurry of the dipotassium salt of IV in acetonitrile an intense green color which is attributable to the anion-radical III develops and is finally discharged as the last of the bromine is added.



(2)

An additional method of preparing a solution of the anion-radical is by reduction of the quinodimethan II with a metal. Thus, when a copper strip was immersed in a solution of II in acetonitrile in the absence of oxygen, the solution rapidly developed a deep green color attributable to the copper salt of the anion-radical III.

Concerning the autodecomposition of III, little can be said except that a complex mixture of products was obtained which contained not only sulfonyl groups but also hydroxyl and carbonyl groups as evidenced by the infrared spectrum.

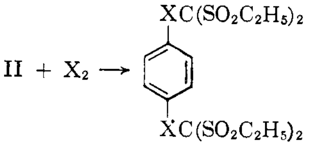
Tetrakis-(ethylsulfonyl)-quinodimethan (II) does not display the strong π-complexing propensity which was observed with TCNQ.[2] No visual evidence for complexing of II with such basic hydrocarbons as anthracene and xylene was obtained. This is surprising in view of the proximity of the reduction potentials of II (+0.092 v.) and TCNQ (+0.127 v.), but can be explained readily by the much greater steric requirement of the ethylsulfonyl group as compared with the cyano group which should tend to increase relatively the magnitude of the dissociation constant (K) of a π-complex (eq. 3).

$$\overset{\delta^-}{\mathrm{A}}\text{-}\overset{\delta^+}{\mathrm{D}} \rightleftharpoons \mathrm{D} + \mathrm{A} \qquad (3)$$

A = acceptor molecule; D = donor molecule

A similar steric effect was observed in complexes of tetracyanoethylene with aromatic hydrocarbons.[5] The dissociation constants for the TCNE-hexaethylbenzene complex and the TCNE-hexamethylbenzene complex are 0.196 and 0.0038, respectively, reflecting the greater steric requirement of the ethyl group as compared with the methyl group.

1,6-Addition Reactions.—Tetrakis-(ethylsulfonyl)-quinodimethan readily undergoes 1,6-addition reactions with halogens (eq. 4). Thus, treatment of II with bromine gave α,α'-dibromo-$\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-xylene (Va). Indeed, if the final step in the synthesis of the quinodimethan II is carried out with an excess of bromine, only the dibromide Va is isolated. This is in marked contrast to the sluggish reaction of tetracyanoquinodimethan with chlorine which requires chloride ion as a catalyst.[1] Similarly, and less expectedly, II reacted with iodine to give α,α-diiodo-$\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-p-xylene (Vb), which is less stable than Va. An additional convenient method for the preparation of solutions of the anion-radical III thus became available through the reaction of the dianion IV with the dibromide Va according to eq. 5.

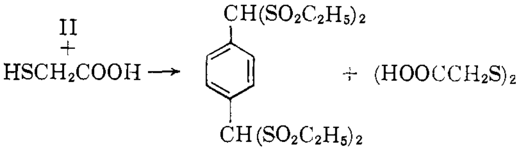


(4)

Va, X = Br
Vb, X = I

$$\mathrm{Va} + 3\mathrm{IV} \longrightarrow 4\mathrm{III} + 2\mathrm{KBr} \qquad (5)$$

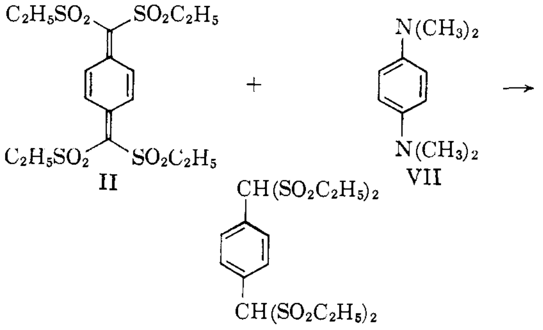
1,6-Addition of hydrogen to the quinodimethan II is illustrated by the reaction of II with mercaptoacetic acid to give $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-p-xylene (VI) according to eq. 6.



(6)

VI

Reduction of the quinodimethan II to the tetrakis-(ethylsulfonyl)-p-xylene VI was also brought about with tetramethyl-p-phenylene-diamine (VII). On mixing II and VII in methylene chloride solution, an intense purple color developed, and its gradual disappearance was accompanied by precipitation of VI. The purple color can be attributed



II VII VI

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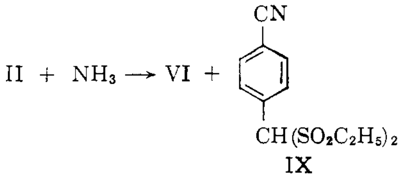
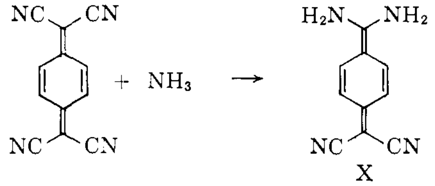
[5] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

to the cation-radical of tetramethyl-*p*-phenylenediamine, but the source of the α-protons of VI is at present unknown. A similar reduction of II to VI occurred with triethylamine. This reaction is reminiscent of the reaction of TCNQ with triethylamine to give a triethylammonium salt of the TCNQ anion-radical[2] and of the reaction between chloranil and triethylamine which gives, among other products, tetrachlorohydroquinone.[6] Unlike TCNQ,[1] II failed to react with the cyanoisopropyl free radicals generated thermally from azo-bisisobutyronitrile.

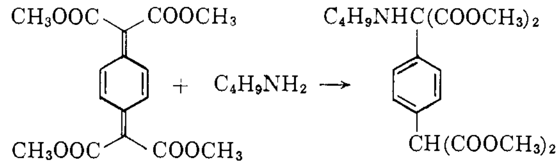
Reaction with Nucleophiles.—Tetrakis-(ethylsulfonyl)-quinodimethan has been found to undergo reaction with nucleophiles in a manner which differs from that of either TCNQ[7] or tetrakis-(methoxycarbonyl)-quinodimethan (VIII).[1] Thus, the reaction of II with ammonia gave in addition to the tetrakis-(ethylsulfonyl)-*p*-xylene (VI), α,α-bis-(ethylsulfonyl)-*p*-tolunitrile (IX) according to eq. 7. By contrast, TCNQ reacts with ammonia to give 7,7-diamino-8,8-dicyanoquinodimethan (X, eq. 8), and tetrakis-(methoxy-carbonyl)-quinodimethan with *n*-butylamine gives α-butylamino-$\alpha,\alpha,\alpha',\alpha'$-tetrakis-(methoxycarbonyl)-*p*-xylene (XI, eq. 9). The reaction of II with ammonia probably proceeds through two successive addition–elimination steps followed by loss of ammonia according to eq. 10. It is not certain by what mechanism the tetrakis-(ethylsulfonyl)-*p*-xylene (VI) was formed in the reaction of II with ammonia, but one possibility is that II was reduced by the ammonium ethylsulfinate which was formed when the ethylsulfonyl groups were displaced by ammonia. Sodium ethylsulfinate has, indeed, been found to react with II to give the green color characteristic of the one-electron-reduction product III, but further degradation occurred rapidly, and a complex mixture containing mercaptan was obtained.



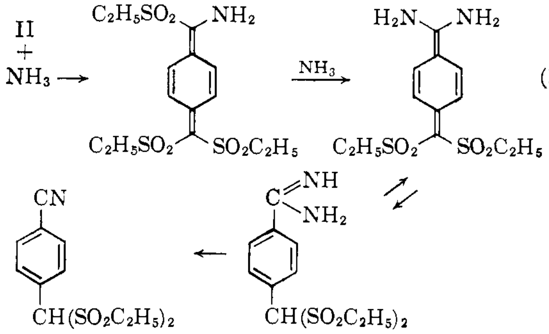
IX (7)



X (8)

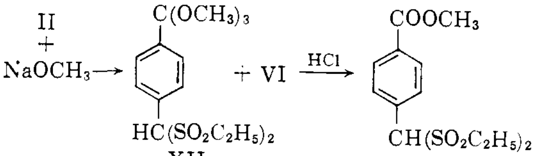


VIII XI (9)



(10)

In a somewhat analogous fashion, the quinodimethan II reacted with methanolic sodium methoxide to give methyl α,α-bis-(ethylsulfonyl)-*p*-orthotoluate (XII) along with some tetrakis-(ethylsulfonyl)-*p*-xylene (VI). Treatment of XII with dilute mineral acid gave methyl α,α-bis-(ethylsulfonyl-*p*-toluate (XIII).



XII XIII (11)

The formation of the orthoester XII probably proceeded through an intermediate dimethoxy-bis-(ethylsulfonyl)-quinodimethan which then underwent 1,6-addition of methanol.

Experimental

$\alpha,\alpha,\alpha',\alpha'$-Tetrakis-(ethylthio)-*p*-xylene.—Into a mixture of 13.4 g. of terephthalaldehyde and 30 g. of ethyl mercaptan was passed gaseous hydrogen chloride until the spontaneous refluxing ceased. The oily mixture was warmed *in vacuo* to remove residual ethyl mercaptan, and the resulting crystalline mass was washed with water and recrystallized from pentane giving 25.1 g. (73%) of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylthio)-*p*-xylene as white needles, m.p. 44.5°. Further recrystallization raised the m.p. to 44.5–46°.

Anal. Calcd. for $C_{16}H_{26}S_4$: S, 37.00. Found: S, 37.29.

$\alpha,\alpha,\alpha',\alpha'$-Tetrakis-(ethylsulfonyl)-*p*-xylene (VI).—A mixture of 100 g. of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylthio)-*p*-xylene, 2 l. of acetic acid and 600 ml. of 30% hydrogen peroxide was stirred under nitrogen at 10–15° for 6 hours and then at room temperature for 16 hours. The mixture was diluted with ice-water and filtered to give 111 g. (81%) of white crystalline VI, m.p. 255–265°. Recrystallization from pyridine-ether gave white crystals, m.p. 255–259°.

Anal. Calcd. for $C_{16}H_{26}S_4O_8$: C, 40.49; H, 5.52. Found: C, 40.88; H, 5.56.

When this compound was recrystallized from acetonitrile or methanol it was obtained as a crystalline 1:1 solvate.

Dipotassium *p*-Phenylene-bis-(diethylsulfonyl methide).—To a solution of potassium *tert*-butoxide prepared by dissolving 7.43 g. of potassium metal in 1.5 liters of *tert*-butyl alcohol was added 38 g. of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene. The resulting mixture was stirred at reflux under nitrogen overnight and then stirred at room temperature for 2 days. Filtration followed by washing of the filter cake with *tert*-butyl alcohol and then with ether gave 40.71 g. (92%) of pale yellow dipotassium *p*-phenylene-bis-(diethylsulfonyl methide). Neutralization of the dipotassium salt with mineral acid gave $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene (VI).

Anal. Calcd. for $C_{16}H_{24}S_4O_8K_2$: neut. equiv., 275.4. Found: neut. equiv., 278.

7,7,8,8-Tetrakis-(ethylsulfonyl)-*p*-quinodimethane (II).—To a stirred suspension of 136.2 g. of dipotassium *p*-phenylene-bis-(diethylsulfonyl methide) in 2.5 liters of acetonitrile

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[6] D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4880 (1957).

[7] W. R. Hertler, H. D. Hartzler, D. S. Acker and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3387 (1962).

under nitrogen was added dropwise over a period of 1 hour a solution of 39.7 g. of bromine in 250 ml. of acetonitrile. The green color which formed during the addition turned to yellow by the end of the addition. The mixture was cooled in an ice-bath and filtered. The filter cake was washed well with water and then with acetonitrile giving 87.5 g. (75%) of yellow 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan, m.p. 195–197°. Recrystallization from methylene chloride gave II as yellow microcrystals, m.p. 195.5–198° dec.

Anal. Calcd. for $C_{16}H_{24}S_4O_8$: C, 40.67; H, 5.12; S, 27.14. Found: C, 41.10; H, 5.20; S, 27.16.

The infrared spectrum of the product showed absorption at 1120 and 1325 cm.$^{-1}$ (sulfone) and 1515 cm.$^{-1}$ (sulfonyl-substituted conjugated double bond). The ultraviolet spectrum of the product in methylene chloride solution in the absence of air had λ_{max} 372 mμ (ϵ 45,500).

Reaction of II with Air.—Air was bubbled through a solution of 200 mg. of the quinodimethan II in 110 ml. of methylene chloride for 16 hours. Filtration gave 10 mg. of terephthalic acid. Evaporation of the filtrate gave an oily mixture which appeared to be evolving fumes of sulfur dioxide.

Reaction of II with Triphenylmethylarsonium Iodide.—Small amounts of the quinodimethan II, triphenylmethylarsonium iodide and acetonitrile were sealed in a small tube at Dry Ice temperature under nitrogen. On warming to room temperature and mixing, a green color formed and a strong E.P.R. signal was observed. After a brief period, the mixture turned yellow and the E.P.R. signal disappeared. The E.P.R. signal can be attributed to the triphenylmethylarsonium salt of the anion-radical of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan.

Reaction of Dipotassium *p*-Phenylene-bis-(diethylsulfonyl methide) with Bromine.—To a stirred mixture of 2.75 g. (5 mmoles) of dipotassium *p*-phenylene-bis-(diethylsulfonyl methide) and 80 ml. of dry acetonitrile under nitrogen was added over a period of 15 minutes a solution of 400 mg. (2.5 mmoles) of bromine in 15 ml. of acetonitrile. There resulted after filtration under nitrogen a deep green solution containing the anion-radical of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan.

α,α'-Dibromo-$\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene (Va). Method A. From Dipotassium *p*-Phenylene-bis-(diethylsulfonyl methide).—A mixture of 300 mg. of dipotassium *p*-phenylene-bis-(diethylsulfonyl methide) and 1:1 chloroform–acetonitrile was treated dropwise with bromine until a permanent bromine color remained. The mixture was filtered, and the filtrate evaporated under nitrogen until most of the solvent had been removed. The addition of ether gave 310 mg. of white microcrystals of Va, m.p. 173.5–175° dec. The infrared spectrum of the product shows absorption at 865 cm.$^{-1}$ typical of a 1,4-disubstituted benzene ring.

Anal. Calcd. for $C_{16}H_{24}S_4O_8Br_2$: C, 30.38; H, 3.83. Found: C, 30.75; H, 3.87.

Method B. From 7,7,8,8-Tetrakis(ethylsulfonyl)quinodimethan.—A mixture of 200 mg. of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan, 10 ml. of acetonitrile and 1 ml. of benzene was treated dropwise with bromine while warming gently until a permanent bromine color remained. The mixture was filtered, and the filtrate evaporated to dryness *in vacuo*. The residue was suspended in ether and filtered, giving 190 mg. of nearly white crystals of Va, m.p. 156.5–162°. Recrystallization from acetonitrile–ether raised the m.p. to 162–168°, and the infrared spectrum of the product was identical with that of the compound prepared by method A.

α,α'-Diiodo-$\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene (Vb).—A mixture of 472 mg. of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan, 250 mg. of iodine and 35 ml. of methylene chloride was stirred under nitrogen for 2 hours at which time most of the iodine color had disappeared. The solution was evaporated *in vacuo* until crystals began to form. Pentane was then added dropwise. Filtration gave 673 mg. (93%) of white crystalline Vb, m.p. 171–173° dec.

Anal. Calcd. for $C_{16}H_{24}I_2S_4O_8$: C, 26.45; H, 3.33; I, 34.94. Found: C, 26.25; H, 3.08; I, 34.69.

The infrared spectrum of the product shows absorption at 1504 and 1625 cm.$^{-1}$ (aromatic), 1325 and 1128 cm.$^{-1}$ (sulfone) and 862 cm.$^{-1}$ (1,4-disubstituted benzene). The ultraviolet spectrum shows absorption at 490 mμ (ϵ 44), 375 mμ (ϵ 254) and 262 mμ (ϵ 11,900).

On prolonged storage, samples of the diiodide Vb decomposed giving crystals of iodine.

Reduction of 7,7,8,8-Tetrakis-(ethylsulfonyl)-quinodimethan (II) with Tetramethyl-*p*-phenylenediamine.—To a solution of 330 mg. (2 mmoles) of N,N,N',N'-tetramethyl-*p*-phenylenediamine in a minimum of methylene chloride under nitrogen was added a solution of 945 mg. (2 mmoles) of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan in 100 ml. of methylene chloride. A deep purple color formed at once and gradually diminished in intensity as a white precipitate appeared. Most of the methylene chloride was removed in a stream of nitrogen, and the residue was suspended in ether and filtered giving 600 mg. of gray-white $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene monoacetonitrile solvate, m.p. 266–271.5° after crystallization from acetonitrile.

Anal. Calcd. for $C_{16}H_{26}S_4O_8 \cdot C_2H_3N$: C, 41.92; H, 5.67; S, 24.87; N, 2.72. Found: C, 41.97; H, 5.57; S, 24.15; N, 2.45.

Reduction of II with Mercaptoacetic Acid.—A mixture of 473 mg. of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan, 1 ml. of mercaptoacetic acid and 5 ml. of acetic acid was stirred at reflux under nitrogen for 15 minutes. The mixture was cooled and diluted with water. After adjusting to *p*H 5 with sodium bicarbonate, the mixture was filtered to give 385 mg. of white $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene monoacetonitrile solvate, m.p. 267–269° (from acetonitrile).

The solvent of crystallization could be removed by heating at 80° (0.1 mm.) for several hours. There was thus obtained white crystals of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene, m.p. 266–268°.

Anal. Calcd. for $C_{16}H_{26}S_4O_8$: C, 40.49; H, 5.52; S, 27.02; N, 0.00. Found: C, 41.12; H, 5.69; S, 27.06; N, 0.21.

Reduction of II with Triethylamine.—To a stirred mixture of 1 g. of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan and 50 ml. of acetonitrile under nitrogen was added 0.214 g. of triethylamine. A blue-green color appeared and was presumably attributable to formation of the anion-radical of the quinodimethan. The mixture was warmed until a clear solution formed, and the solution was then allowed to cool. A precipitate formed, and after 1 hour the dark brown mixture was cooled in an ice-bath and filtered to give 670 mg. of cream-colored $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene monoacetonitrile solvate, m.p. 261–268°, identified by comparison of its infrared spectrum with that of an authentic sample.

α,α-Bis-(ethylsulfonyl)-*p*-tolunitrile (IX).—To a stirred suspension of 1 g. of 7,7,8,8-tetrakis-(ethylsulfonyl)-quinodimethan in 30 ml. of acetonitrile under nitrogen was added 20 ml. of acetonitrile saturated with ammonia. The yellow color of the quinodimethan was discharged rapidly, and a precipitate gradually formed. After stirring for 30 minutes the mixture was filtered to give 520 mg. of white crystals of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene monoacetonitrile solvate, m.p. 258.5–260°. The filtrate was evaporated, and the residue was suspended in ether and filtered to give 300 mg. of white solid, m.p. 150–155°. Fractional crystallization of this material from acetonitrile–ether gave in the earlier fractions impure $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene monoacetonitrile solvate and finally 110 mg. of crystals, m.p. 161–164°. Recrystallization of the latter from acetonitrile–ether gave needles of α,α-bis-(ethylsulfonyl)-*p*-tolunitrile, m.p. 179–182°. The infrared spectrum of the product shows absorption at 2240 (aromatic nitrile), 1310, 1120–1140 (sulfone) and 860 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{12}H_{15}NS_2O_4$: C, 47.82; H, 5.02; N, 4.65. Found: C, 47.68; H, 4.91; N, 4.72.

α,α,α-Trimethoxy-α',α'-bis-(ethylsulfonyl)-*p*-xylene (XII).—A mixture of 472 mg. (1 mmole) of 7,7,8,8-tetrakis-ethylsulfonyl)-quinodimethan, 108 mg. (2 mmoles) of sodium methoxide and 25 ml. of methanol was stirred at reflux under nitrogen for 30 minutes during which time the quinodimethan dissolved while a precipitate formed, and a green color developed. After cooling, filtration gave 140 mg. of white crystals of $\alpha,\alpha,\alpha',\alpha'$-tetrakis-(ethylsulfonyl)-*p*-xylene, m.p. 255–260°. The pale green filtrate was evaporated *in vacuo*. The residue was treated with water and filtered to give 105 mg. (28%) of α,α,α-trimethoxy-α',α'-bis-(ethylsulfonyl)-*p*-xylene, m.p. 120–122.5°. Recrystallization from ether raised the m.p. to 122–123.5°. The infrared spectrum of the product shows no absorption due to a carbonyl group, but displays strong absorption characteristic of ether groups at 1040–1090 cm.$^{-1}$ in agreement with the assigned structure.

Anal. Calcd. for $C_{15}H_{24}S_2O_7$: C, 47.35; H, 6.36; S, 16.86. Found: C, 47.20; H, 6.21; S, 17.24.

Methyl α,α-Bis-(ethylsulfonyl)-*p*-toluate (XIII).—To a solution of 145 mg. of α,α,α-trimethoxy-α′,α′-bis-(ethylsulfonyl)-*p*-xylene in 2 ml. of methanol was added 3 drops of 10% aqueous hydrochloric acid. The resulting mixture was diluted with water and filtered to give 120 mg. (94%) of white crystals of methyl α,α-bis-(ethylsulfonyl)-*p*-toluate, m.p. 164–165.5°. Recrystallization from methanol gave crystals of m.p. 164–165°. The infrared spectrum of the product shows absorption at 1720 (ester carbonyl); 1600, 1500 (aromatic); 1280–1320, 1105–1140, (sulfone); and 850 cm.$^{-1}$ (1,4-disubstituted benzene).

Anal. Calcd. for $C_{13}H_{18}S_2O_6$: C, 46.69; H, 5.42; S, 19.17. Found: C, 46.84; H, 5.64; S, 19.43.

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Substituted Quinodimethanes. V.[1] *p*-Tricyanovinylphenyldicyanomethide and Related Anions

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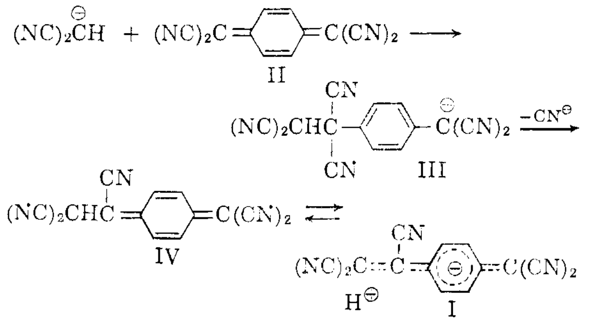
The deep-blue *p*-tricyanovinylphenyldicyanomethide (I) and two related anions have been prepared.

The deep-blue *p*-tricyanovinylphenyldicyanomethide ion (I) is the anion of a strong cyanocarbon acid[2] (pK_A 0.60) and owes its stability to the high degree of delocalization of its negative charge. It readily forms salts that are deep blue in solution (λ_{max}^{EtOH} 625, ε 52,200) and is best isolated as the tetramethylammonium salt.[3]

The most convenient method for preparing I (>90% yield) is to warm 7,7,8,8-tetracyanoquinodimethan[4] (II) with malononitrile in dimethylformamide solution. The steps leading to I probably involve the addition of the malononitrile anion to II to form the anion III. Elimination of cyanide ion from III can give IV, the conjugate acid of I.



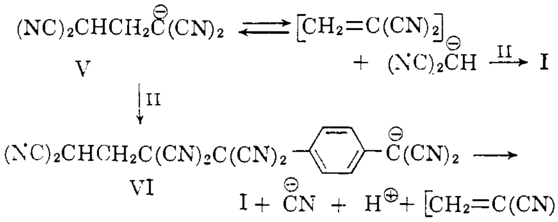
Two additional systems in which II is a reactant have been found to produce I, and in both the second component may function as a source of malononitrile. When II was allowed to react with tetracyanoethylene in moist dimethylformamide, compound I was formed in 45% yield. The formation of I in this system is analogous to the formation of the pentacyanopropenide anion[5] from tetracyanoethylene in moist dimethylformamide, a process that could involve the initial formation of the malonitrile anion as outlined below.

$$HO^{\ominus} + (NC)_2C{=}C(CN_2) \longrightarrow$$

$$HOC(CN)_2\overset{\ominus}{C}(CN)_2 \rightleftharpoons \overset{\ominus}{O}{-}C(CN)_2CH(CN)_2 \longrightarrow$$

$$\overset{\ominus}{C}H(CN_2) + [O{=}C(CN)_2] \xrightarrow{H_2O} 2HCN + CO_2$$

When II was allowed to react with 1,1,3,3-tetracyanopropane[6] in dimethylformamide, compound I was formed in 81% yield. In this system the anion V could be in equilibrium with vinylidene cyanide and malononitrile anion which would react with II to form I. Alternatively, V could add to II in an initial step to form the anion VI.



Elimination of cyanide ion, a proton and vinylidene cyanide from VI could then lead to I.

We have found another system that gives rise to I that does not include 7,7,8,8-tetracyanoquinodimethan. When phenylmalononitrile and potassium tetracyanoethylene anion radical (VII)[7] were allowed to react in dimethylformamide in the absence of moisture and oxygen, a 24% yield of I was obtained. Since no oxidizing agents were present it is unlikely that VII was converted to tetracyanoethylene, and thus the reaction cannot

$$\underset{\text{VII}}{K^{\oplus}(CN)_2CC(CN)_2\cdot^{\ominus}} + C_6H_5CH(CN)_2 \longrightarrow \text{I}$$

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(1) Paper IV, W. Hertler and R. Benson, *J. Am. Chem. Soc.*, **84**, 3474 (1962).

(2) We wish to thank Dr. R. H. Boyd for this spectrophotometric pK_A determination. Details of the technique used will be described by him elsewhere.

(3) An oxygen analog of I is the α,α-dicyano-*p*-toluoyl cyanide anion described in paper III of this series; W. R. Hertler, H. D. Hartzler, D. S. Acker and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3387 (1962).

(4) D. S. Acker, R. J. Hader, W. R. Hertler, W. Mahler, L. Melby, R. E. Benson and W. E. Mochel, *ibid.*, **82**, 6408 (1960).

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