ethanol and charcoaled to give 1.20 g. (52.2%) of product as thin white needles, m.p. 170–172°. Further recrystallization twice from ethanol increased the melting point to 173° (lit.[21] m.p. 170°); λ_{max}^{KBr} 6.1 μ (C=N).

1-Amino-3-selena-4-thiatetradecane Hydrochloride.—Sodium hydroxide (1.20 g., 0.03 mole) was dissolved with stirring in 30 ml. of methanol through which nitrogen was slowly bubbled. Then 4.08 g. (0.02 mole) of finely powdered I was added with stirring. When solution was complete, the temperature of the reaction mixture was lowered to near 0° by external cooling and 1.72 g. (0.01 mole) of freshly distilled 1-decanethiol was added in one portion. Sodium sulfite immediately precipitated from solution, and, when an aliquot of the reaction mixture was centrifuged, the supernatant liquid reacted negatively to sodium nitroprusside indicating complete uptake of the mercaptan. The reaction mixture was filtered with the aid of Celite and the filtrate, still maintained near 0°, was acidified with ethanolic hydrogen chloride. The sodium chloride and unreacted I which precipitated were filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from isopropyl alcohol to give 1.15 g. (34.6% yield) of product as pale yellow, waxy crystals, m.p. 107–108°.

Anal. Calcd. for $C_{12}H_{28}ClNSSe$: C, 43.30; H, 8.48; N, 4.21; Se, 23.72. Found: C, 43.43; H, 8.23; N, 4.45; Se, 24.50.

Selenocystamine (II).—Compound I (10.2 g., 0.05 mole) was dissolved in 50 ml. of 10% aqueous sodium hydroxide and permitted to remain at room temperature for 2 hr. The yellow solution was then extracted with three 30-ml. portions of chloroform and the combined extracts were dried with anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator under reduced pressure giving a moderately viscous, yellow-orange oil as a residue; yield, 3.14 g. (51.1%). About 80% of the product could be vacuum distilled (0.1 mm.) using a Hickman still before the onset of decomposition.[22]

The dihydrochloride (yellow crystals from methanol) softened at 179° and melted at 186–188° (lit. m.p. 188°,[11] 177–179° dec.[23]).

The picrate (from ethanol) melted at 179–181° (lit.[11] m.p. 178°).

Selenocysteamine (2-Aminoethaneselenol) Hydrochloride.—To a solution of 0.615 g. (0.025 mole) of II in 5 ml. of water into which nitrogen was slowly bubbled was added 0.052 g. (0.014 mole) of sodium borohydride in 5 ml. of water. The yellow color of II was dispelled after about 22 min. At the end of 0.75 hr. the solvent was removed on a rotary evaporator at reduced pressure at 50° to give a white residue. (Atmospheric pressure was restored to the evaporator system by allowing nitrogen, rather than air, to enter.) The residue was acidified with *ca.* 30 ml. of ice-cooled ethanolic hydrogen chloride. The mixture was agitated for 0.5 hr. under nitrogen to dissolve the selenocysteamine hydrochloride and was then filtered. The filtrate was taken down to dryness under reduced pressure to give 0.64 g. (80.0%) of the product as white, slightly hygroscopic crystals, m.p. 108–110°. Titration of 0.1699 g. of the compound with 10.70 ml. of 0.0965 *N* iodine solution indicated a purity of 97.5%.

Anal. Calcd. for C_2H_8ClNSe: C, 14.96; H, 5.02; N, 8.73; Se, 49.19. Found: C, 15.11; H, 4.91; N, 8.77; Se, 49.60.

Selenohypotaurine (2-Aminoethaneseleninic Acid).—To an ice-cooled solution of 2.46 g. (0.01 mole) of II in 5 ml. of water was added 5.0 ml. of 30% hydrogen peroxide in small portions over 1 hr. with stirring. The solution, which turned from yellow to colorless, was stirred an additional hour at room temperature. Isopropyl alcohol was added to the solution until the appearance of cloudiness and it was then cooled. Selenohypotaurine, which separated as white needles, 2.56 g. (82.1% yield), darkened at *ca.* 125° and melted at 150–151° dec. (lit.[14] m.p. 150–152° dec.). Further recrystallization from water–ethanol gave a sample which darkened at *ca.* 135° and melted at 155–156° dec.

Cystamine[24] (1.52 g., 0.01 mole), if oxidized in the manner described above, gave 1.72 g. (68.8% yield) of taurine, which darkened at *ca.* 280°, m.p.[25] 325° dec. The infrared spectrum was identical with that of an authentic sample of taurine.

If 0.01 mole of the dihydrochloride of either II or cystamine was used as the starting material in the above procedure, it was dissolved in 4 ml. of water and 1 ml. of 28% ammonia solution. Selenohypotaurine and taurine were obtained in 66.3 and 60.2% yields, respectively.

(21) W. Baringer, *Ber.*, **23**, 1003 (1890).

(22) It was found that cystamine could similarly be distilled despite a report to the contrary [J. von Braun, A. Bahn, and H. Munch, *Ber.*, **62**, 2766 (1929)].

(23) W. H. H. Gunther and H. G. Mautner, *J. Am. Chem. Soc.*, **82**, 2762 (1960).

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(25) The melting point was determined on an Electrothermal melting point apparatus.

2-Benzhydryl-7,7,8,8-tetracyanoquinodimethan

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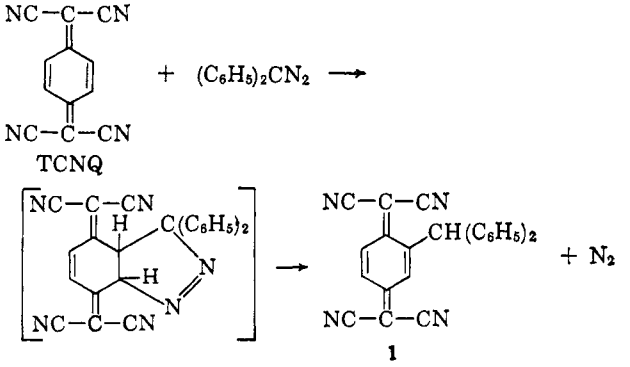
The remarkable electrical properties of salts of the anion radical of 7,7,8,8-tetracyanoquinodimethan (TCNQ)[1] have prompted investigations of related systems. Direct substitution on the ring of TCNQ proved difficult because nucleophiles generally displaced cyano groups (by an addition–elimination mechanism),[2] free radicals usually added across the 7 and 8 carbon atoms to give aromatic systems,[3] and TCNQ was inert to most electrophilic reagents. This paper describes the behavior of TCNQ with diazoalkanes. The properties of 2-benzhydryl-7,7,8,8-tetracyanoquinodimethan (1), in which the quinodimethan system is nonplanar, are contrasted with those of TCNQ.

Diphenyldiazomethane and TCNQ in acetone, acetonitrile, or tetrahydrofuran react slowly at 60 to 80° to release nitrogen and form 1 in 58% yield. The reaction occurred considerably more rapidly than the unassisted thermal decomposition of the diazoalkane. The rate of reaction as well as the absence of products of reaction of diphenylmethylene with the solvents[4] suggest that the reaction occurs by way of electrophilic attack of the diazo compound on TCNQ.



1

Diphenyldiazomethane apparently reacts similarly with *p*-benzoquinone,[5] but the intermediate enolizes to give the aromatic system 2.

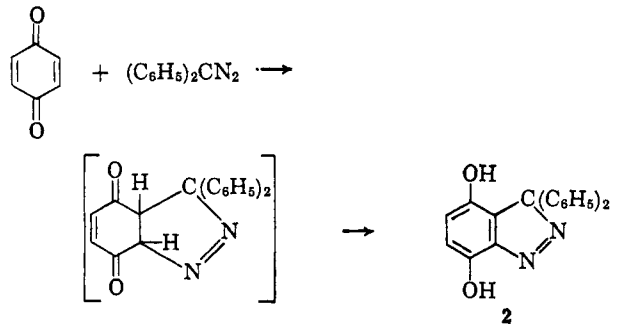
(1) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

(2) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *ibid.*, **84**, 3387 (1962).

(3) D. S. Acker and W. R. Hertler, *ibid.*, **84**, 3370 (1962).

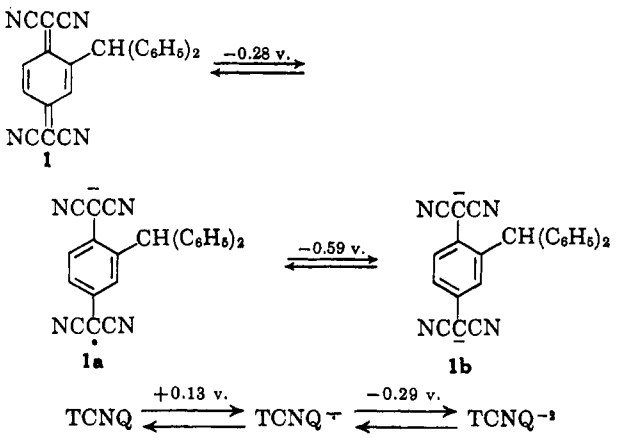
(4) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

(5) H. von Pechmann, *Ber.*, **28**, 885 (1895).



TCNQ formed a solid π complex with 9-diazofluorene at room temperature. In acetone at reflux the complex decomposed with nitrogen evolution. The reaction product, however, was not soluble enough to allow purification and characterization. Ethyl diazoacetate underwent thermal decomposition with no attack on TCNQ.

The quinodimethan system of **1** cannot be planar because of the bulky benzhydryl substituent. This is reflected in the absorption spectrum of **1**: λ_{max} 361 mμ (ϵ 25,600), 258 (6650), 221 (17,700). This differs greatly from that of TCNQ: λ_{max} 395 mμ (ϵ 63,600). A marked change in the ease of reduction was also observed. Compound **1** undergoes polarographic reduction in acetonitrile solution with 0.1 *M* lithium perchlorate as supporting electrolyte. Two well-defined one-electron waves occurred at −0.28 and −0.59 v. *vs.* the standard calomel electrode. Both reductions were reversible and are assumed to be indicative of formation of radical anion **1a** and dianion **1b**. The corresponding one-electron reductions of



TCNQ occur at +0.13 and −0.29 v.[3] The greater difficulty of reduction of **1** *vs.* TCNQ is evidence that the lack of planarity destabilizes the anion radical and dianion more than the parent quinodimethan, which is certainly in accord with expectation.

The anion radical **1a** can be prepared by controlled electrochemical reduction of **1**. Air immediately oxidized **1a**. Solutions of **1a** in acetonitrile gave a strong, but broad electron spin resonance signal. Fine structure has not been resolved. Upon standing at room temperature under nitrogen the electron spin resonance signal of **1a** slowly changed to that of TCNQ anion radical. A similar transformation occurred in an attempt to form a salt of **1a**. The reaction of an acetonitrile solution of **1** with metallic copper yielded the copper(I) salt of TCNQ anion radical. This reaction may also proceed by way of **1a**. The remarkable elimination of the benzhydryl group (probably as a radical) is additional evidence of the instability due to nonplanarity of the anion radical **1a**.

Experimental

2-Benzhydryl-7,7,8,8-tetracyanoquinodimethan (1).—A solution of 19 g. (0.09 mole) of diphenyldiazomethane in 25 ml. of acetone was added to a stirred slurry of 17.3 g. (0.085 mole) of tetracyanoquinodimethan in 300 ml. of acetone. The system was connected to a wet-test meter through a reflux condenser. The mixture was heated at reflux, and gas (2.12 l., 100%) was evolved. The mixture was filtered, and the solid was rinsed with acetone. A yellow, crystalline solid (18.3 g., 58%, m.p. 343–348°) was obtained. Recrystallization from acetonitrile (very slightly soluble) gave **1**, m.p. 350–353° dec.

Anal. Calcd. for $C_{25}H_{14}N_4$: C, 81.06; H, 3.81; N, 15.13. Found: C, 81.03; H, 3.83; N, 15.14.

The infrared spectrum of **1** showed absorption at 3.29 (saturated CH), 4.50 (conjugated nitrile), 6.27, 6.35, 6.45, 6.57, and 6.71 (conjugated C=C), and 13.25 and 14.06 μ (monosubstituted aromatic). The insolubility of **1** precluded an n.m.r. spectrum.

Anion Radical of 1.—Compound **1** was reduced by applying a voltage of from −0.31 to −0.33 v. *vs.* the standard calomel electrode to a slurry of **1** in acetonitrile containing 0.1 *M* lithium perchlorate. The solution of the anion radical was a deep violet, and it decolorized immediately upon exposure to air.

Reaction of 1 with Copper.—A strip of copper was suspended in a stirred slurry of 0.74 g. of **1** in 300 ml. of acetonitrile. A purple solid formed on the copper surface and was periodically removed by scraping. The solid was identical in infrared and ultraviolet spectra with the cuprous salt of TCNQ anion radical.

Anal. Calcd. for $C_{12}H_4CuN_4$: C, 53.9; H, 1.50; N, 20.9. Found: C, 53.7; H, 1.84; N, 21.2.

TCNA with Ethyl Diazoacetate.—A mixture of 20.4 g. of TCNQ and 14 g. of ethyl diazoacetate in 500 ml. of acetone was heated at reflux for 17 hr. at which time 2.7 l. of nitrogen had been evolved. From the reaction mixture there was recovered 19.5 g. (95%) of TCNQ, m.p. 290–295°.

The Structure of 2-(D-*arabino*-Tetrahydroxybutyl)quinoxaline

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The oxidative condensation of 2-amino-2-deoxy-D-glucose hydrochloride with *o*-phenylene diamine in the presence of cupric acetate yields a crystalline quinoxaline derivative[1] identical with the product formed in the reaction of *o*-phenylene diamine with D-glucose,[2] D-fructose,[3] and D-*arabino*-hexosulose.[4] This derivative has long been formulated[5] as 2-(D-*arabino*-tetrahydroxybutyl)quinoxaline (I), with the sugar residue in the acyclic form, and this structure is supported by glycol cleavage[6] and ultraviolet spectroscopic[7] studies. An alternative cyclic formulation (II) has, however, been

(1) R. Lohmar and K. P. Link, *J. Biol. Chem.*, **150**, 351 (1943).
(2) P. Griess and G. Harrow, *Ber.*, **20**, 281, 2205 (1887).
(3) H. Ohle, *ibid.*, **67**, 155 (1934).
(4) E. Fischer, *ibid.*, **22**, 87 (1889).
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(6) A. Müller and I. Varga, *Ber.*, **72**, 1993 (1939); G. Henseke and K.-J. Bähner, *ibid.*, **91**, 1605 (1958).
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