covery, defined as for Table I, tended to decrease from about 0.88 to about 0.72 as the reaction temperature increased.

To determine the effect of varying the amount of fluorene, 1.00, 2.00 and 4.00 g. of fluorene were mixed with the 50.0 g. of alumina in a group of three experiments. The remainder of the procedure followed that given above for the experiments of Tables I and II. The resultant yields of fluorenone were 31, 34 and 40%. Comparison of the 31% yield obtained in the first experiment of this group with the 30% yield obtained in the second experiment of the preceding series indicates that it makes no significant difference whether the fluorene is adsorbed onto the alumina or merely mixed with it.

Study of Free Radical Promotors.—The spontaneous reactions using both a base and a copper salt were carried out: Fifty grams of alumina was added to 0.001 mole of cupric chloride dihydrate in absolute methanol, the slurry was swirled and filtered and the filter cake was added to a solution prepared from 120 ml. of anhydrous methanol and 12 g. of sodium. The mixture was swirled intermittently for 5 min., filtered with suction and the filtrate poured over the filter cake four times. The filter cake was then heated in an oil-bath at 200 ± 2° at 15 mm. pressure for 30 min. with occasional shaking. After the cooled powder was rapidly and thoroughly mixed with 0.01 mole of the pulverized organic compound to be oxidized the mixture was placed in the modified Allihn condenser and dried air was passed through in the standard fashion.

With fluorene a spontaneous reaction occurred after the air was passed through for 25 min. with no external heating; after 8 min. more the temperature rose to 119°. The temperature soon dropped and the air stream was stopped after a total of about 70 min. A 35% yield of fluorene was isolated and from the mother liquors a 5% yield of di(biphenylene)-ethylene which melted at 187.5–189° (lit. m.p. 189–190°) was obtained. *Anal.* Calcd. for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.02; H, 5.19. The isolation of this symmetrical product strongly indicates fluorenyl free radicals were formed.

With fluorenol little heat was apparent after air was passed through for 30 min. The base of the condenser was therefore heated for 30 sec. with a microburner whereupon reaction began as evidenced by heat evolution which continued for 20 min.; after 8 min. the temperature was 122°. Air was passed through a total of 80 min. and the yield of fluorenone was 75%.

The procedure followed with 2-naphthylamine was essentially the same as for fluorenol and the temperature reached was also about the same. A 23% yield of dibenzo-[*ah*]phenazine was obtained.

In two experiments to determine whether benzoyl peroxide had any effect the 50 g. of alumina containing 1.06 ± 0.02 g. of adsorbed fluorene was well mixed with 0.002 mole of benzoyl peroxide. With a reaction time of 24 hr. a 30% yield of fluorenone was obtained at a temperature of 120° while a 24% yield was obtained at a temperature of 148°. The corresponding yields obtained without benzoyl peroxide, as described above, were 8 and 13%.

Supplementary Experiments.—In an experiment to determine how much oxidation ocurred if air was not passed through the system 1.40 g. of fluorenol adsorbed onto the 50 g. of alumina was employed. The reaction time was 48 hr. and the temperature 120°. Except that no air was passed through the system the procedure was exactly like that described above for the time and temperature studies. The yield of fluorenone was 20% as compared to the 54% yield obtained when an air stream was used.

Fluorene was used in place of fluorenol in a similar experiment carried out according to the standard procedure for the experiments of Tables I and II (without sodium methoxide) except that no air was passed through the heated mixture of alumina and fluorene. The yield of fluorenone was 17% as compared to the tabulated value of 35% produced when an air stream was used.

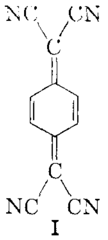
COMMUNICATIONS TO THE EDITOR

7,7,8,8-TETRACYANOQUINODIMETHANE AND ITS ELECTRICALLY CONDUCTING ANION-RADICAL DERIVATIVES

Sir:

7,7,8,8-Tetracyanoquinodimethane (TCNQ) has been synthesized and found to yield a series of stable anion-radical derivatives. Certain of these derivatives have the lowest electrical resistivities yet reported for organic compounds. This report describes the synthesis of TCNQ and its anion-radical derivatives.

TCNQ (I) is a strong pi-acid[1] and forms two series of salt-like crystalline complexes, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical $TCNQ^{\overline{\cdot}}$ (II). The first series is represented by the formula $M^+TCNQ^{\overline{\cdot}}$ and is generally characterized by relatively high electrical resistivity (10^4–10^{12} ohm cm.). The second series, represented by the formula $M^+(TCNQ^{\overline{\cdot}})(TCNQ)$, contains a molecule of formally neutral TCNQ in addition to $TCNQ^{\overline{\cdot}}$ and is characterized by exceptionally low electrical resistivity (0.01–100 ohm cm.).[2,3] In addition, the electrical resistivity is highly anisotropic along the three principal crystal axes.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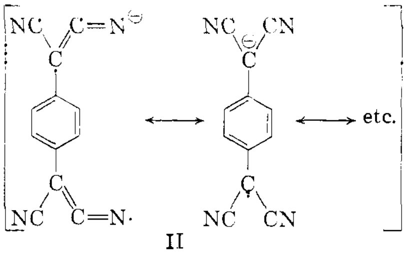

II

TCNQ, m.p. 293.5–296°, was synthesized in high yield by the bromine–pyridine dehydrogenation of 1,4-bis-(dicyanomethylene)-cyclohexane obtained by condensation of malononitrile with 1,4-cyclohexanedione.[4] *Anal.* Calcd. for $C_{12}H_4N_4$:

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[1] The equilibrium constant for π-complex formation between TCNQ and pyrene is 78.4 as compared to 29.5 for the complex between tetracyanoethylene and pyrene; see R. E. Merrifield and W. D. Phillips, THIS JOURNAL, **80**, 2278 (1958).

[2] For comparison, the resistivity of hyperpure silicon is about 1000 ohm cm., graphite about 10^{-3} ohm cm., and most organic compounds, 10^{10}–10^{14} ohm cm. The lowest resistivity previously reported for an organic compound appears to be 8 ohm cm. for the metastable iodine/perylene complex (J. Kommandeur and F. R. Hall, *Bull. Am. Phys. Soc.*, Series II, **4**, 421 (1959).

[3] Detailed physical study of the anion-radical derivatives has been carried out. Data on electrical and magnetic properties (R. G. Kepler, P. E. Bierstedt, and R. E. Merrifield, *Phys. Rev. Letters*, in press) and on EPR studies (D. B. Chesnut, H. Foster, and W. D. Phillips, *J. Chem. Phys.*, in press) will appear shortly.

C, 70.6; H, 1.97; N, 27.4. Found: C, 71.0; H, 1.94; N, 27.4.

TCNQ readily undergoes a one electron reduction with a variety of reagents, including metal iodides, onium iodides, and metals to give stable salts, $\mathrm{M}^{x+}(\mathrm{TCNQ}^{\overline{\cdot}})_x$. In this respect it resembles tetracyanoethylene.[5] The reaction of LiI with TCNQ in acetonitrile provides a convenient synthesis of $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$, which undergoes metathetical reactions in water or ethanol to yield a wide variety of $\mathrm{TCNQ}^{\overline{\cdot}}$ compounds containing metallic, organometallic, and onium ions. Specifically, reaction of $\mathrm{Li}^+\mathrm{TCNQ}^{\overline{\cdot}}$ with triethylammonium chloride in water has given $(\mathrm{C_2H_5})_3\mathrm{NH}^+(\mathrm{TCNQ}^{\overline{\cdot}})$ (III) as a blue powder, m.p. ~180° dec., resistivity (powder) = 10^9 ohm cm. *Anal.* Calcd. for $\mathrm{C_{18}H_{20}N_5}$: C, 70.6; H, 6.54; N, 22.9. Found: C, 70.4; H, 6.27; N, 23.1.

Surprisingly, the addition of neutral TCNQ to an acetonitrile solution of III yields purple-black crystals identified as the anion-radical complex $(\mathrm{C_2H_5})_3\mathrm{NH}^+(\mathrm{TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$ (IV), m.p. ~ 195°, resistivity (powder) = 20 ohm cm. *Anal.* Calcd. for $\mathrm{C_{30}H_{24}N_9}$: C, 70.7; H, 4.55; N, 24.7. Found: C, 70.8; H, 4.89; N, 24.8. The anion-radical complex is stable, and TCNQ cannot be recovered from it by crystallization techniques. In addition, IV can be sublimed (200° at 0.1 mm.) with only slight decomposition.

The triethylammonium anion-radical complex IV has also been synthesized by methods 2, 3, and 4.

$$(\mathrm{C_2H_5})_3\mathrm{NH}^+\mathrm{I}^- + 2\mathrm{TCNQ} \longrightarrow \mathrm{IV}\ (50\%) + {}^1/_2\mathrm{I_2} \qquad (2)$$

$$2(\mathrm{C_2H_5})_3\mathrm{N} + \mathrm{H_2TCNQ} + 3\mathrm{TCNQ} \longrightarrow \mathrm{IV}\ (87\%) \qquad (3)$$

$$(\mathrm{C_2H_5})_3\mathrm{N} + 2\mathrm{TCNQ} \longrightarrow \mathrm{IV}\ (77\%) \qquad (4)$$

In the second preparation the electron is furnished by the iodide ion. In the third preparation the acid *p*-phenylenedimalononitrile ($\mathrm{H_2TCNQ}$, m.p. 244–245°) is converted to its anion which transfers an electron to TCNQ. Reaction 4 is of special interest in that it occurs at room temperature in acetonitrile in the absence of added catalyst. The source of the ammonium proton has not been established but most probably it is derived from the amine.[6] The four reaction products have been shown to be identical by elemental analyses, absorption spectroscopy, polarography, and X-ray diffraction.

The above methods usually are applicable to synthesis of ion-radical complexes of the type IV, and a variety of products derived from aliphatic, aromatic, and heterocyclic amines have been prepared. However, in a few cases compounds lacking neutral TCNQ have been formed. For example, 5,8-dihydroxyquinoline with TCNQ gave the anion-radical salt, $\mathrm{C_9H_7NO_2H^+TCNQ}^{\overline{\cdot}}$, m.p. 167–168° dec., resistivity (powder) = 14 ohm cm. However, quinoline with TCNQ gave $\mathrm{C_9H_7NH^+(TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$, m.p. ~ 220° dec., resistivity[3] (single crystal) = 0.01 ohm cm.

Reactions of one mole of phosphonium and arsonium iodides with two moles of TCNQ in acetonitrile have given the corresponding onium anion-radical complexes. Both $(\mathrm{C_6H_5})_3\mathrm{PCH_3}^+[\mathrm{TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$ (V), (m.p. 231–233° dec., *Anal.* Calcd. for $\mathrm{C_{43}H_{26}N_8P}$: C, 75.3; H, 3.8; N, 16.3; P, 4.5. Found: C, 75.4; H, 3.9; N, 16.3; P, 4.7) and $(\mathrm{C_6H_5})_3\mathrm{AsCH_3}^+(\mathrm{TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$ (VI) (m.p. 224–227° dec., *Anal.* Calcd. for $\mathrm{C_{43}H_{26}N_8As}$: C, 70.8; H, 3.6; N, 15.4; As, 10.3. Found: C, 70.9; H, 3.6; N, 15.4; As, 10.3) crystallized as large prisms. The triethylammonium derivative IV also was obtained in macrocrystalline form by slow crystallization from acetonitrile.

In solution the above compounds are dissociated to the cation, neutral TCNQ, and $\mathrm{TCNQ}^{\overline{\cdot}}$. Thus, the ultraviolet absorption spectrum of $(\mathrm{C_2H_5})_3\mathrm{NH}^+(\mathrm{TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$ (ϵ_{395} = 85,800 and ϵ_{842} = 43,400) is essentially a composite of that of $(\mathrm{C_2H_5})_3\mathrm{NH}^+\mathrm{TCNQ}^{\overline{\cdot}}$ (ϵ_{394} = 21,500 and ϵ_{842} = 43,500) and TCNQ (ϵ_{395} = 63,600). Furthermore, the molecular weight determination of IV in acetonitrile showed dissociation into three fragments (mol. wt. found, 147), and the compound is a strong electrolyte in acetonitrile. In the solid state, however, it is believed that there is complete electron delocalization between $\mathrm{TCNQ}^{\overline{\cdot}}$ and TCNQ.

The relationship between a π-complex and an anion-radical complex derived from TCNQ has been illustrated dramatically in the case of diaminodurene. This amine with TCNQ in tetrahydrofuran gives the purple π-complex, whereas its hydroiodide with TCNQ yields the blue-black anion radical complex.

DIAMINODURENE-TCNQ DERIVATIVES

Product	Composition	Resistivity (powder) ohm cm.	Magnetic character
π-Complex	$\mathrm{C_{10}H_{16}N_2(TCNQ)}$	10^9	Diamagnetic
Anion radical complex	$\mathrm{C_{10}H_{16}N_2H^+}$ $(\mathrm{TCNQ}^{\overline{\cdot}})(\mathrm{TCNQ})$	8	Paramagnetic

Other quinodimethanes bearing electron-withdrawing substituents, *e.g.*, 7,7,8,8-tetrakis-(methoxycarbonyl)-quinodimethane, m.p. ~ 147°, and 7,7,8,8 - tetrakis - (ethylsulfonyl) - quinodimethane m.p. 195.5–198° dec., have been synthesized, and our studies in this area are continuing. A complete description of this work will be published shortly.

Acknowledgment.—We wish to thank Dr. D. C. Blomstrom for helpful suggestions.

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THE EFFECT OF CHAIN LENGTH UPON HYPOCHROMISM IN NUCLEIC ACIDS AND POLYNUCLEOTIDES

Sir:

The hypochromic effect is well known in nucleic acids and polynucleotides. It is a lowering of the

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(4) J. R. Vincent, A. F. Thompson and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

(5) O. W. Webster, W. Mahler and R. E. Benson, *ibid.*, **25**, 1470 (1960).

(6) D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4880 (1957). It was found that amines, including triethylamine, were dehydrogenated by chloranil at room temperature to give vinylamine intermediates together with the reduction product, tetrachlorohydroquinone.