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A Twin-TCNQ-Type Acceptor. Synthesis of 11,11,12,12,13,13,14,14-Octacyano-1,4:5,8-anthradiquinotetramethane and Structures of the Tetraethylammonium Salts of Its Mono- and Dianion

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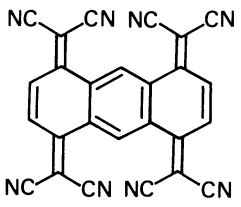
The title compound (OCNAQ) was synthesized. Treatment of 1,2,3,4,5,6,7,8-octahydroanthracene with *N*-bromosuccinimide (NBS) under irradiation using a 100-W light bulb in refluxing CCl_4 followed by dicyanomethylation with excess of $NaCH(CN)_2$ in Me_2SO gave an isomeric mixture of 1,4,5,8-tetrakis(dicyanomethyl) derivatives. The mixture was subjected by repetition of the successive bromination-dehydrobromination procedure giving OCNAQ in 20% overall yield. The cyclic voltammogram of OCNAQ exhibits four redox waves ($E_{1/2}^1$ 0.26, $E_{1/2}^2$ 0.05, $E_{1/2}^3$ −0.44, and $E_{1/2}^4$ −0.53 V vs. SCE in MeCN), indicating that OCNAQ is a stronger acceptor than tetracyanoquinodimethane (TCNQ, $E_{1/2}^1$ 0.17 V vs. SCE). Both 1:1 and 2:1 salts, (Et_4N)(OCNAQ) and $(Et_4N)_2$(OCNAQ), were obtained from reactions of Et_4NI with potassium and lithium salts of OCNAQ, respectively. The X-ray crystal analyses of these salts indicate that the TCNQ moieties are boat-shaped bent to opposite directions. With the 1:1 salt, which behaves as a semiconductor ($4\times10^{-4}\ \Omega^{-1}\,cm^{-1}$ at room temperature, E_a 0.22 eV), the OCNAQ molecules are arrayed in the segregated stacking mode, while the 2:1 salt ($10^{-7}\ \Omega^{-1}\,cm^{-1}$) has no columnar structure of the OCNAQ molecules.

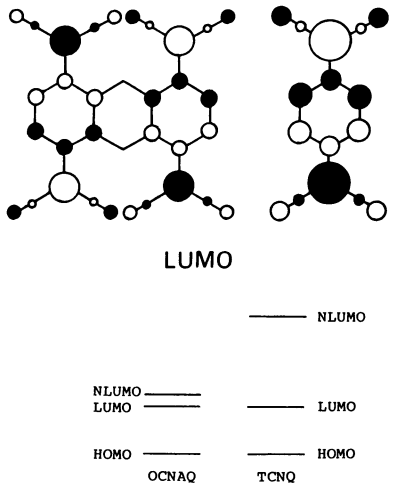
A large number of tetracyanoquinodimethane (TCNQ) derivatives have appeared in the past few decades; however, twin-TCNQ-type acceptors had not as yet been presented.[1] The compound **1** (abbreviated as OCNAQ) is one of the simplest examples of this



OCNAQ
1

type in which a pair of TCNQ nuclei are linked together through two methylidyne (-CH=) groups. The simple Hückel molecular orbital theory predicts that the lowest unoccupied molecular orbitals (LUMO) of OCNAQ and TCNQ are equal in energy and upon introduction of an electron into the OCNAQ molecule, the charge density is shared equally by both TCNQ nuclei.[2] Such charge dispersal would result in the reduction of on-site Coulomb repulsion and thus OCNAQ is expected to accept a second electron more easily than TCNQ.

Another factor that is not expected from TCNQ is the nonbonded interaction between cyano groups at positions 11 and 14 or 12 and 13 as well as that between a cyano group and a methylidyne group at position 9 or 10. Such a steric interaction



undoubtedly affects not only the molecular and crystal structures of the OCNAQ salts but also their electronic states.

In view of these considerations, it seems worthwhile to synthesize OCNAQ and to compare its physical and chemical properties with those of TCNQ which have been accumulated numerously since this intriguing acceptor was reported by Du Pont chemists.[3] This paper describes the synthetic route to OCNAQ and its fundamental properties obtained mainly from the mono- and dianion tetraethylammonium salts, a part of which has recently been reported in preliminary form.[4]

Results and Discussion

Synthesis. A number of synthetic strategies have been developed in order to construct the TCNQ-type-framework.[3,5-18] Survey of literature procedures suggested 1,4,5,8-tetrakis(cyanomethyl)anthracene and 1,4,5,8-tetrachloroanthraquinone to be most promising starting materials of the OCNAQ synthesis;[8] however, such approaches were unsuccessful. One of the key intermediates would be 1,4,5,8-tetrakis-(dicyanomethyl)-1,2,3,4,5,6,7,8-octahydroanthracene (**4**). It has been found that **4** is obtainable by simple substitution reactions and can be converted into OCNAQ by repetition of the successive bromination-dehydrobromination procedure in an overall yield of 20% as outlined in Scheme 1. The starting material, 1,2,3,4,5,6,7,8-octahydroanthracene (**2**), is readily available in one step from cheap, commercial compounds.[19] A mixture of **2** and *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride was irradiated with a 100-W unfrosted light bulb to afford an isomeric mixture of the 1,4,5,8-tetrabromo derivatives **3** as a white solid in 81% yield. The bromides **3** are unexpectedly stable at room temperature and can be stored in a freezer (−20 °C) without decomposition for a couple of days. Although **3** underwent dehydrobromination on treatment with sodium acetate in refluxing acetic acid to give anthracene in ca. 80% yield, the satisfactory dicyanomethylation of **3** was achieved by the use of a large excess of the sodium salt of malononitrile in Me_2SO to afford an isomeric mixture of **4** in 95% yield.

The active hydrogen atom of dicyanomethyl groups of **4** was easily replaced by bromine on treatment with NBS in MeCN in the presence of acetic acid. A difficulty with which the present procedure was confronted was the subsequent dehydrobromination, since even the action of such a weak base as pyridine led to the formation of polymerized products. One way out of the difficulty might be to carry out the dehydrobromination using a very weak base under slightly acidic conditions. A combination of *N*,*N*-dimethylformamide (DMF), acetic acid, and a small amount of ethanol was found to be suitable for the conversion of the bromination product from **4** into the tetrakis(dicyanomethylene) derivative **5** although the yield was moderate (35% based on **4**). The treatment of **5** with pyridine in MeCN followed by the addition of a solution of excess of bromine in 50% acetic acid gave OCNAQ as a yellow powder in 75% yield. The resulting crude product is sparingly soluble in MeCN but can be used directly for the preparation of charge-transfer complexes. OCNAQ reacted easily with potassium iodide in MeCN to afford the potassium salt of OCNAQ, which was then treated with tetraethylammonium iodide in refluxing MeCN giving the (Et_4N)(OCNAQ) salt (**6**) as black needles. Oxidation of **6** with bromine followed by recrystallization from MeCN gave an analytically pure sample of

$$\mathbf{1} \xrightarrow{KI} K^+OCNAQ^{\cdot-} \xrightarrow{Et_4NI} \underset{\mathbf{6}}{Et_4N^+OCNAQ^{\cdot-}} \xrightarrow{Br_2} \mathbf{1}$$

OCNAQ as fine golden yellow plates, which did not melt upon heating up to 400 °C but gradually turned brown above 180 °C. The infrared spectrum of OCNAQ as well as that of **5** exhibits a very strong absorption band due to the cyano stretching vibration at 2225 cm^{-1} indicating the presence of conjugated cyano groups.

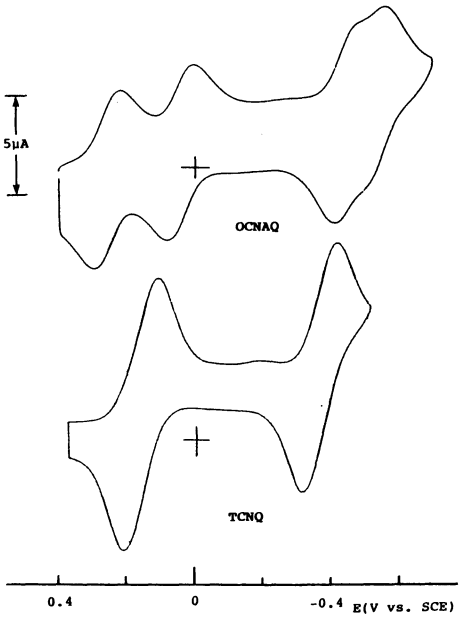
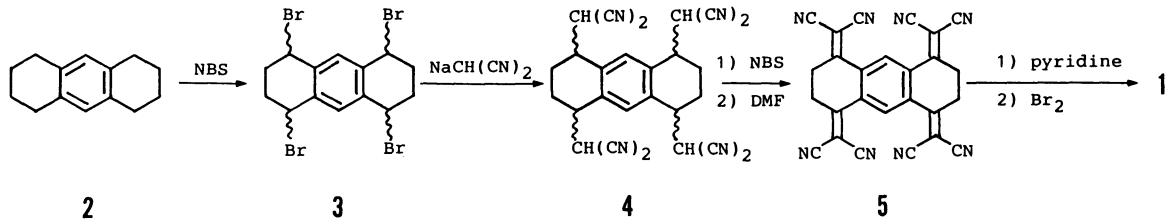


Fig. 1. Cyclic voltammograms of OCNAQ and TCNQ: solvent, MeCN; supporting electrolyte, Et_4NClO_4 (0.1 mol dm^{-3}); reference electrode, calomel; working electrode, platinum; sweep, 250 mV s^{-1}.



Scheme 1.

Electrochemical Studies. Figure 1 shows the cyclic voltammogram of OCNAQ with tetraethylammonium perchlorate as the supporting electrolyte in MeCN together with that of TCNQ measured under the same conditions. Four reversible redox waves appear at the potentials ($E_{1/2}$) 0.26, 0.05, −0.44, and −0.53 V vs. SCE. A comparison of the first redox potential of OCNAQ with that of TCNQ ($E_{1/2}$ 0.17 V vs. SCE)[20] reveals that OCNAQ is a stronger electron acceptor than TCNQ and thus the result is not exactly in accord with the expectation based on the simple Hückel molecular orbital calculation. Considerable deformation observed in the OCNAQ framework as described below as well as the stabilization due to charge dispersal present in the actual anion radical would result in such a discrepancy. Another interesting feature is that the second redox potential of OCNAQ is close to the first rather than the second redox potential of TCNQ ($E_{1/2}$ −0.36 V vs. SCE).[20] As mentioned in the introductory part, such a higher value of the second redox potential can be predicted by the simple Hückel MO theory combined with a consideration of Coulomb repulsive interaction.[21] In consequence, it is evident that the electron affinity of the anion radical $OCNAQ^{\cdot-}$ is stronger than that of $TCNQ^{\cdot-}$.

ESR Spectrum of the Radical Anion $OCNAQ^{\cdot-}$. A highly resolved ESR spectrum was obtained from the salt (Et_4N)(OCNAQ) **6** in MeCN with a *g*-factor of 2.0044. Figure 2 shows the observed spectrum and its simulation. The salt is completely ionic, because no hyperfine splitting due to the tetraethylammonium moiety has been observed. The hyperfine data derived from the spectrum together with the modified McLachlan calculation[22] provides the following coupling constants for the radical anion $OCNAQ^{\cdot-}$: a_H(2,3,6,7), 0.054±0.002 mT; a_H(9,10), −0.053±0.004 mT; a_N, 0.047±0.002 mT. Since a pair of acceptors are linked together through a conjugated system in OCNAQ, the charge in its anion radical $OCNAQ^{-\cdot}$ is expected to be highly delocalized. In fact, compared with the coupling constants for the radical anion $TCNQ^{\cdot-}$ [a_H (mT), 0.142[22] or 0.144;[23] a_N (mT), 0.099[22] or 0.102[23]], the value for the protons at positions 2,3,6,7 is about one-third and the value for the nitrogen atoms half as much.

X-Ray Structure of the (Et_4N)(OCNAQ) Salt (6). The structure of the OCNAQ framework was definitely confirmed by X-ray diffraction analysis of the salt **6** (Fig. 3). The crystal data are collected in Table 1. The final atomic parameters are listed in Table 2.[24] It is noteworthy that a quinonoid structure still remains in the OCNAQ framework of the salt, since the C–C distances between positions 2 and 3 and between positions 6 and 7 (1.33 Å) are shorter than those of aromatic rings and $TCNQ^{\cdot-}$ (1.38 Å;[25] 1.36 Å[26]) but are close to the corresponding distances of the neutral TCNQ (1.35 Å),[27] benzo-TCNQ (1.35 Å),[28] and $(Me)_4$TCNQ (1.34 Å)[17] in which the delocalization of π electrons of the bonds is depressed as a result of deformation from planarity. The result

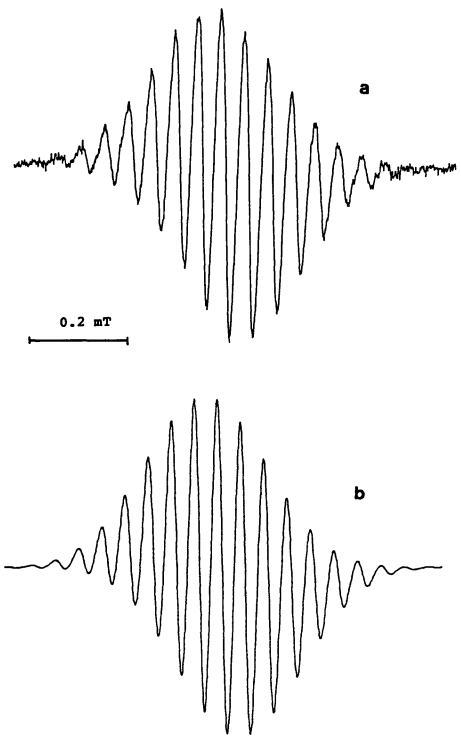


Fig. 2. ESR spectrum of $Et_4N^+OCNAQ^{\cdot-}$, **6**, in acetonitrile: (a) experimental; (b) computer simulation.

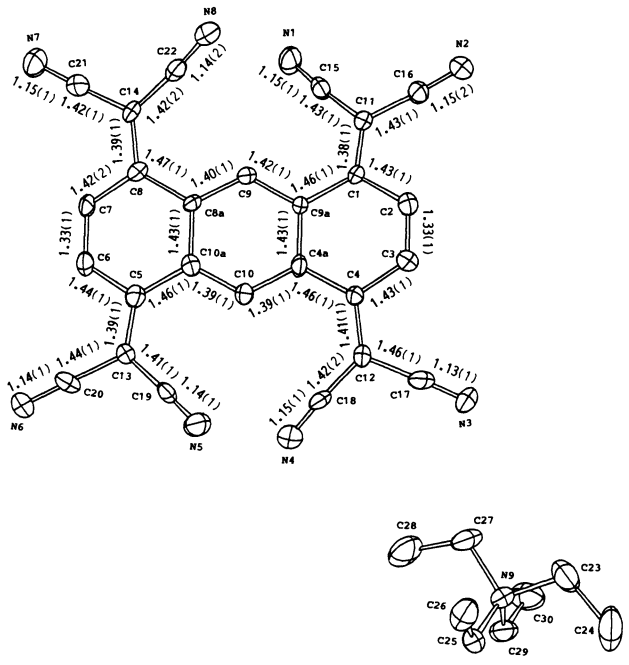


Fig. 3. ORTEP view of (Et_4N)(OCNAQ), **6**, showing the atom numbering scheme and bond lengths (Å).

Table 1. Crystal Data for $(Et_4N)(OCNAQ)$ (**6**) and $(Et_4N)_2(OCNAQ)$ (**7**)

	6	**7**
Molecular formula	$C_{34}H_{26}N_9$	$C_{42}H_{46}N_{10}$
M_w	560.65	690.91
Crystal size/mm	0.6×0.05×0.1	0.3×0.05×0.1
a/Å	7.800 (1)	12.383 (3)
b/Å	12.435 (1)	19.240 (5)
c/Å	16.004 (1)	9.090 (2)
α/deg	97.17 (1)	
β/deg	86.50 (1)	114.89 (2)
γ/deg	112.23 (1)	
U/Å^3	1425.5 (1)	1964.5 (9)
Z	2	2
D_c/g cm^{-3}	1.306	1.168
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
Absorption coeff/cm^{-1}	7.90	5.97

Table 2. Atomic Parameters (×10^4) and Their Equivalent Isotropic Temperature Factors for $(Et_4N)(OCNAQ)$ (**6**)

Atom	x	y	z	B_{eq}/Å^{2} [a]
C1	8373(11)	2467(7)	−680(4)	2.1(3)
C2	7793(13)	3142(8)	−16(6)	3.0(3)
C3	7343(14)	2826(8)	758(6)	3.1(3)
C4	7439(12)	1773(7)	977(5)	2.5(3)
C4A	7632(11)	926(7)	298(5)	2.5(3)
C5	7179(12)	−2236(7)	−79(5)	2.9(3)
C6	7654(13)	−2931(8)	−775(6)	3.1(3)
C7	7889(13)	−2627(8)	−1557(6)	3.0(3)
C8	7758(12)	−1593(7)	−1790(5)	2.7(3)
C8A	7689(11)	−742(6)	−1077(4)	2.4(3)
C9	8033(12)	411(7)	−1205(5)	2.6(3)
C9A	8060(11)	1270(6)	−531(4)	2.2(3)
C10	7345(13)	−218(8)	408(6)	2.7(3)
C10A	7379(11)	−1068(7)	−239(5)	2.7(3)
C11	9113(12)	2973(7)	−1409(5)	2.8(3)
C12	7350(12)	1648(7)	1841(5)	2.9(3)
C13	6521(12)	−2740(7)	663(5)	2.7(3)
C14	7646(12)	−1491(7)	−2639(5)	2.9(3)
C15	9986(13)	2514(7)	−2099(5)	3.0(3)
C16	9097(12)	4086(8)	−1534(5)	3.2(3)
C17	7110(15)	2561(8)	2451(6)	3.9(4)
C18	7692(13)	791(8)	2241(5)	3.2(3)
C19	5685(13)	−2309(7)	1358(6)	2.8(3)
C20	6534(12)	−3873(8)	768(5)	3.3(3)
C21	7923(14)	−2318(8)	−3272(6)	3.7(3)
C22	7207(13)	−619(8)	−2975(5)	3.5(3)
C23	5317(22)	3932(11)	5711(8)	5.7(5)
C24	4747(30)	4376(13)	6567(13)	8.3(7)
C25	4335(14)	1855(7)	6040(6)	3.3(3)
C26	2617(18)	1393(11)	5519(8)	4.7(4)
C27	6445(19)	2596(11)	4821(6)	4.9(4)
C28	7171(23)	1624(13)	4718(9)	6.3(6)
C29	7502(15)	3166(9)	6306(6)	4.0(4)
C30	9276(20)	4154(11)	6097(9)	5.7(5)
N1	10740(12)	2230(7)	−2668(5)	4.9(3)
N2	9020(13)	4956(7)	−1663(5)	5.1(4)
N3	6914(13)	3245(7)	2942(5)	5.0(3)
N4	8027(11)	174(7)	2625(5)	4.2(3)
N5	4932(11)	−2023(7)	1921(5)	4.1(3)
N6	6512(12)	−4769(7)	861(5)	4.5(3)
N7	8127(14)	−2977(7)	−3799(5)	5.6(4)
N8	6790(14)	7(7)	−3302(5)	5.4(4)
N9	5927(11)	2892(6)	5727(4)	3.3(2)

a) $B_{eq}=4/3(\sum_i\sum_j\beta_{ij}a_i\cdot a_j)$.

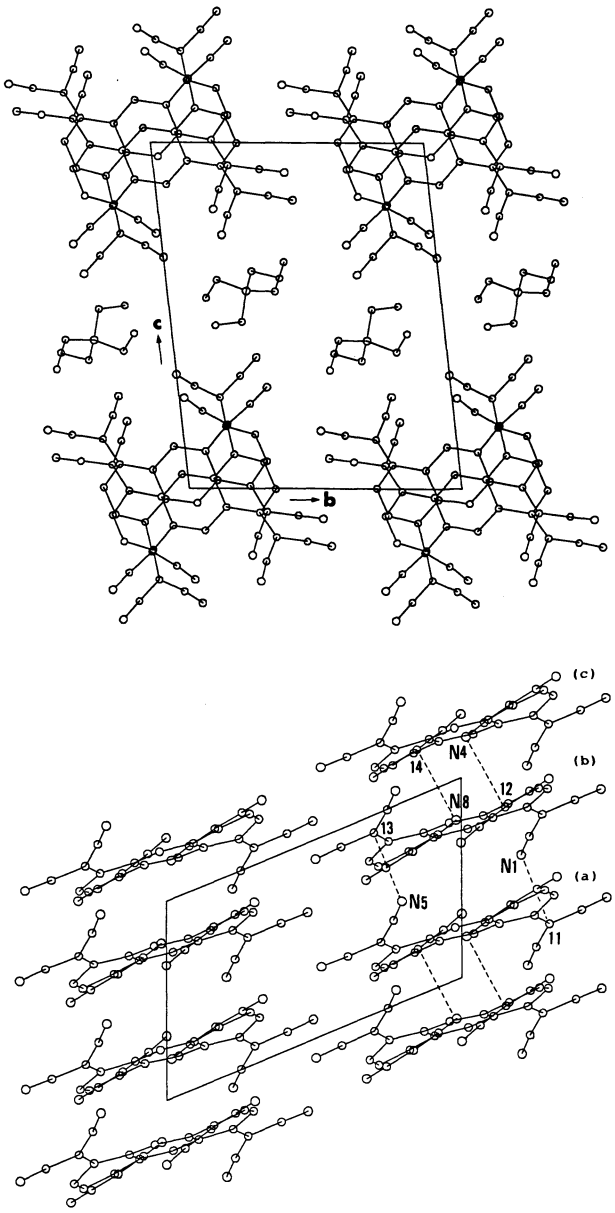


Fig. 4. Crystal structure of **6**: a-axis projection (upper) and drawing of the OCNAQ molecules projected on the [001] direction (lower).

Table 3. Dihedral Angles for Salts **6** and **7**

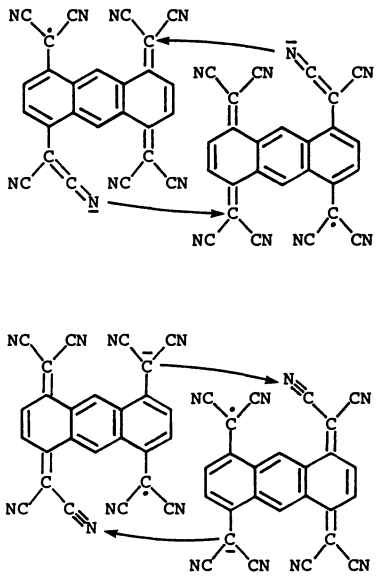
Plane I	Central benzene ring (e.g., C9, C9a, C4a, C10, C10a, C8a for **6**)		
Plane II	C2, C3, C4a, C9a	Plane III	C6, C7, C8a, C10a
Plane IV	C1, C2, C9a	Plane V	C3, C4, C4a
Plane VI	C7, C8, C8a	Plane VII	C5, C6 C10a
Plane VIII	C11, N1, N2	Plane IX	C12, N3, N4
Plane X	C14, N7, N8	Plane XI	C13, N5 N6

Angle between the planes A and B

Salt **6**			Salt **7**		
A	B	Angle (ϕ/°)	A	B	Angle (ϕ/°)
I	II	10.5(3)	I	II	10.4(4)
I	III	9.7(3)			
II	IV	12.0(9)	II	IV	12.4(13)
II	V	10.6(10)	II	V	10.6(14)
III	VI	10.3(9)			
III	VII	10.2(9)			
IV	VIII	10.2(4)	IV	VIII	9.8(12)
V	IX	9.7(8)	V	IX	14.3(10)
VI	X	10.5(6)			
VII	XI	11.0(7)			

suggests that OCNAQ has the ability to accept a second electron more easily than TCNQ, in agreement with a higher value of the second redox potential of OCNAQ. The benzene ring is essentially planar but the TCNQ nuclei are distorted into boat forms, and the bows and sterns of the two boats face in opposite directions. The $C(CN)_2$ groups are twisted about the exo CC axes (10—11°). The boat forms are bent by 10—12° and the dihedral angles between the plane of the benzene ring and that of the bottom of the boat form are ca. 10° (Table 3).[24]

Figure 4 shows the crystal structure. Clearly, the OCNAQ molecules stack nearly along a-axis to form a column with an alternate arrangement of slightly different interplanar spacings between the benzene rings of the adjacent molecules; the longer one (3.81 Å) appears between molecules (a) and (b) in Fig. 4, and the shorter (3.70 Å) between molecules (b) and (c), both of which are longer than the sum of the van der Waals radii (3.40 Å)[29] and thus much longer than those of the usual TCNQ columns (3.2—3.3 Å). In contrast, the shortest and the next shortest interatomic distances between nitrogens of the inside cyano groups of one molecule and exo-methylene carbons of the adjacent molecule, i.e., 3.05 (1) and 3.14 (1) Å, are shorter than the sum of the van der Waals radii (3.25 Å).[29] Interestingly the interatomic distances N(a)5···C(b)13 and C(a)11···N(b)1, which are placed between a pair of the molecules showing the longer interplanar spacing, are the shortest (3.05 Å), and hence the next shortest distance (3.14 Å) is allocated to the distances N(b)8···C(c)14 and C(b)12···N(c)4 belonging to a pair of the molecules with the shorter interplanar spacing.[30] This fact implies that the intermolecular charge delocalization in the column is



Scheme 2.

mainly caused by overlapping of orbitals of thses nitrogen and carbon atoms rather than that of the carbon atoms constituting anthracene nuclei, as can be illustrated by Scheme 2.

Solid State ESR Measurements of 6. Generally the ground state of the TCNQ salts is singlet and the singlet-triplet energy difference J ranges from 0.03 to 0.4 eV.[31-35] To evaluate the extent of intermolecular interaction in the OCNAQ column, the temperature dependence of ESR absorption intensity of the powdered salt was examined. As shown in Fig. 5, the intensity is increased by a factor of 10 on changing the temperature from −166 °C to −19 °C and the

equation[31,36] $I \propto [\exp(-J/kT)]/T$ holds in this temperature range, giving J=0.052 eV. The result suggests that there exist distinct intermolecular attractive forces other than those of the van der Waals type, which hold the columnar structure of the OCNAQ molecules and lead to the ground state singlet.

Electrical Conductivity of 6. The single crystal resistivity of **6** was measured with a two-probe technique. The room-temperature conductivity is ca. $4\times10^{-4}\,\Omega^{-1}\,cm^{-1}$. Unfortunately no information on the single crystal conductivities of 1:1 TCNQ ammonium salts is available. However, their compacted powder pellets exhibit much lower conductivities ($\sigma \leqq 10^{-6}\,\Omega^{-1}\,cm^{-1}$).[3,37] It seems reasonable to assume that the reduction of on-site Coulomb repulsion in $OCNAQ^{-}$ is responsible for the high conductivity of **6** as compared with those of simple TCNQ ammonium salts. The salt **6** behaves as a semiconductor. Figure 6 shows the temperature dependence of the resistivity. The conductivity is increased by a factor of 8 on changing the temperature from 300 to 400 K with an activation energy of 0.22 eV.

X-Ray Structure of the $(Et_4N)_2$(OCNAQ) Salt (7). The action of Et_4NI on the lithium salt of

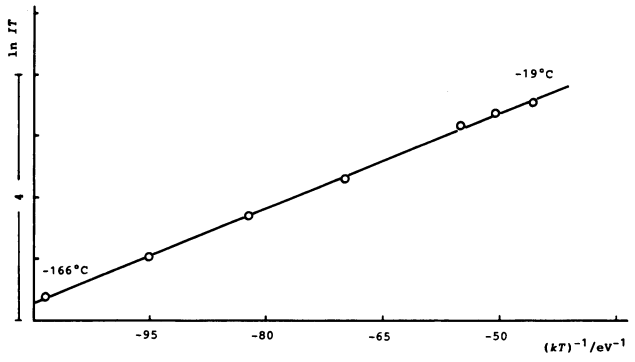


Fig. 5. Temperature dependence of ESR absorption intensity of powdered $Et_4N^{+}OCNAQ^{-\cdot}$, **6**.

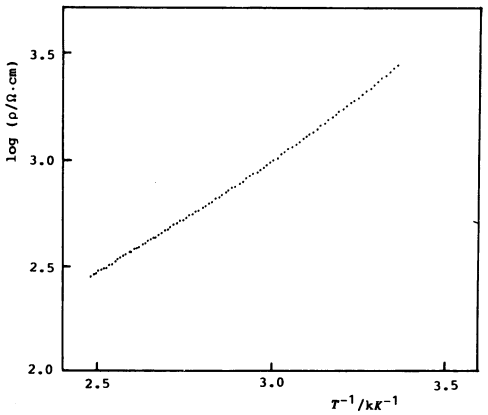


Fig. 6. Temperature dependence of the single-crystal resistivity of **6**.

Table 4. Atomic Parameters (×10⁴) and Their Equivalent Isotropic Temperature Factors for $(Et_4N)_2$(OCNAQ) (**7**)

Atom	x	y	z	B_{eq}/Å²[a]
C1	1109(7)	−1100(5)	−965(13)	5.1(4)
C2	551(9)	−1329(5)	−2577(14)	6.2(4)
C3	−340(8)	−949(4)	−3725(15)	5.7(4)
C4	−717(7)	−296(5)	−3352(15)	5.2(4)
C4A	−341(7)	−127(5)	−1712(14)	4.7(4)
C9	865(9)	−384(6)	1150(18)	4.9(4)
C9A	581(7)	−534(4)	−422(15)	4.5(4)
C11	2212(8)	−1434(5)	72(13)	5.7(4)
C12	−1399(7)	144(5)	−4694(14)	5.3(4)
C15	3007(10)	−1239(5)	1600(15)	6.9(5)
C16	2648(9)	−1993(7)	−567(15)	7.8(5)
C17	−1827(8)	−91(5)	−6290(14)	5.5(4)
C18	−1587(9)	863(7)	−4531(13)	7.3(5)
C23	6070(13)	−1701(9)	6625(22)	9.8(6)
C24	6579(16)	−1324(16)	5597(26)	13.3(8)
C25	5989(8)	−649(5)	8228(19)	8.0(6)
C26	4652(11)	−550(10)	7271(30)	12.2(7)
C27	5771(12)	−1852(9)	9096(30)	9.6(7)
C28	5928(18)	−1611(14)	10783(30)	12.6(8)
C29	7722(7)	−1367(6)	9299(21)	8.0(5)
C30	8340(12)	−2073(8)	9507(37)	13.7(10)
N1	3689(8)	−1067(5)	2872(14)	9.6(5)
N2	3024(8)	−2433(5)	−1085(15)	10.8(6)
N3	−2163(7)	−264(5)	−7596(11)	7.7(4)
N4	−1741(10)	1446(5)	−4463(15)	11.2(6)
N9	6371(6)	−1397(4)	8277(13)	6.7(4)

a) $B_{eq}=4/3(\sum_i\sum_j \beta_{ij} a_i \cdot a_j)$.

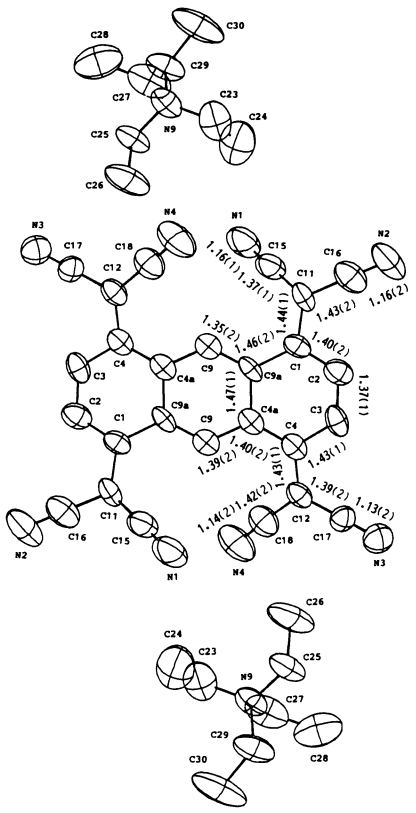


Fig. 7. ORTEP view of $(Et_4N)_2$(OCNAQ), **7**, showing the atom numbering scheme and bond lengths (Å).

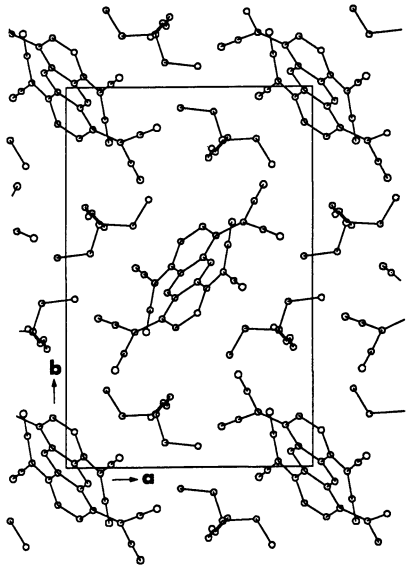


Fig. 8. Crystal structure of **7** (c-axis projection).

OCNAQ in hot methanol gave the 2:1 $(Et_4N)_2$-(OCNAQ) salt (**7**) as blue-black needles, reflecting a higher value of the second redox potential or the presence of a pair of TCNQ moieties. The salt **7** is readily soluble in hot methanol in which the salt **6** is insoluble. Its conductivity ($1.2\times10^{-7}\,\Omega^{-1}\,cm^{-1}$ at room temperature) is much lower than that of the 1:1 salt **6**. The crystal data and final atomic parameters of the salt are listed in Tables 1 and 4,[24] respectively. The salt has a center of symmetry in the OCNAQ molecule (Fig. 7). In contrast to the monoanion salt **6**, the C(2)–C(3) distance (1.37 Å) is within the range of the above-mentioned values of $TCNQ^-$ (1.35—1.38 Å), suggesting that the quinonoid geometry of the acceptor seems almost lacking. Such a geometrical change implies much difficulty in introducing a third electron into the OCNAQ molecule, in agreement with a considerably lower value of the third redox potential of OCNAQ, and would be responsible for a dramatic change in the crystal structure of the salt in which a columnar structure of the OCNAQ molecules is no longer present (Fig. 8). Deformation of the anthracene framework of **7** is, however, similar to that of **6**: The boat-shaped TCNQ nuclei in **7** are bent by 10—12° and the dihedral angle between the plane of the benzene ring and that of the bottom of the boat form is ca. 10° (Table 3).[24]

Experimental

Instruments. The following spectrometers were used: IR, Hitachi 260-30; ^1H NMR, Varian EM-390; ESR, Varian E-112/V 7800 for an MeCN solution, which was degassed in a quartz tube (4 mm o.d.) by three freeze-thaw cycles, and JEOL FE1X for a solid sample; Cyclic voltammograms were measured by a potentiostat (Yanaco V8-3010PG) equipped with a function generator (NF FG-121B) and an XY recorder (Watanabe WX 4401). MeCN (special grade) was distilled over P_2O_5 and subsequently over K_2CO_3. Resistivity measurements were performed by a two-probe (gold paste electrodes) technique.

X-Ray Structure Analyses. The structure analyses were made with a Rigaku Denki AFC-4 automatic four-circle diffractometer [Cu $K\alpha$ radiation (1.54184 Å), graphite monochromator, ω—2θ scan technique, $2\theta\leqq120°$, scan speed 4° min^{-1} (θ), scan range (1.1+0.5 tan θ)°]. Three standard reflections measured every 50 reflections showed no significant X-ray damage or crystal decay. Of 2595 (for **6**) and 2166 (for **7**) independent reflections observed, unique 1647 (for **6**) and 1007 (for **7**) reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure determination. The structure was solved by direct methods with MULTAN 78[38] (with atomic scattering factors from International Tables for X-ray Crystallography)[39] and refined by full-matrix least squares (UNICS III)[40,41] with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. **6**: $R=0.064$ and $R_w=0.074$, where $w=(4.155-0.274|F_{obs}|+0.006F_{obs}^2)^{-1}$. **7**: $R=0.072$ and $R_w=0.070$, where $w=(2.343-0.092|F_{obs}|+0.004F_{obs}^2)^{-1}$.

Elemental analyses were performed by Mses Toshiko Seki and Kimiyo Saeki of the analytical section of the Department of Chemistry, The University of Tokyo.

Preparation of 1,4,5,8-Tetrabromo-1,2,3,4,5,6,7,8-octahydroanthracenes (3). 1,2,3,4,5,6,7,8-Octahydroanthracene (**2**) was prepared by the action of $AlCl_3$ on a mixture of tetralin and 1,4-dichlorobutane (special grade) according to the literature procedure[19] and was recrystallized repeatedly from ethanol: mp 71.5 °C [lit,[19] mp 72 °C]. A solution of **2** (5.0 g, 26.8 mmol) in 250 ml of CCl_4 was placed in a 500-ml round-bottomed pyrex flask, and NBS (21 g, 117 mmol) was added. The flask was immersed in an oil bath preheated at 90 °C. The mixture was refluxed with stirring and was exposed to the light of an ordinary 100-W unfrosted bulb placed 1 cm from the flask. Vigorous reaction took place within 5 min. After irradiation for 45 min, the reaction mixture was cooled with water and filtered. The isolated solid mass was washed with CCl_4 and the washings were combined with the filtrate. The solid was then washed with water and ethanol to remove succinimide, and the residue was washed finally with hexane to give the first crop of the bromide **3** as a white solid (2.5 g, 19%), which was rather stable and decomposed only very slowly with loss of HBr at room temperature; IR (KBr, cm^{-1}) 2950 w, 2900 w, 1630 w, 1495 w, 1430 s, 1345 w, 1225 s, 1190 s, 1000 w, 985 w, 915 s, 895 m, 765 w, 740 m, 630 s, 520 m; ^1H NMR ($CDCl_3$) δ=2.3—2.8 (m, 8H), 5.4—5.8 (m, 4H), 7.33 (s, 2H). Found: C, 33.14; H, 2.57%. Calcd for $C_{14}H_{14}Br_4$: C, 33.50; H, 2.81%. The filtrate and the CCl_4 washings were concentrated under reduced pressure, and the viscous residue was triturated with 10 ml of $CHCl_3$, diluted with 10 ml of hexane, and cooled in a refrigerator. The resulting precipitate was isolated by filtration and washed with ethanol and hexane, affording the second crop of the bromide **3** as a white solid (8.3 g, 62%), which showed satisfactory elemental analysis after recrystallization from benzene. Found: C, 33.64; H, 2.60%. Calcd for $C_{14}H_{14}Br_4$: C, 33.50; H, 2.81%. These two crops of the crude bromide were combined, pulverized in a mortar, and used in the next step.

Preparation of 1,4,5,8-Tetrakis(dicyanomethyl)-1,2,3,4,5,6,7,8-octahydroanthracenes (4). To a mechanically stirred suspension of 20 g (0.5 mol) of sodium hydride (60% oil dispersion) in 60 ml of Me_2SO, which was placed in a 1000-ml three-necked flask, was added a solution of 35 g (0.53 mol) of malononitrile in 40 ml of Me_2SO at 25 °C under an atmosphere of nitrogen. After the addition was complete, stirring was continued for 15 min. To the resulting homogeneous solution was added 10.8 g (21.5 mmol) of the above powder of the bromide **3** in one portion and stirring was continued for 3 h. To the reaction mixture was added 500 ml of 10% aqueous acetic acid with stirring. The resulting light brown paste was collected, washed successively with water, benzene, and hexane and treated with 100 ml of hot acetic acid followed by addition of 500 ml of water. The resulting precipitate was isolated by filtration, washed with water and hexane, and dried in vacuo, affording a white solid (9.0 g, 19.2 mmol, 95%). The NMR spectrum in MeCN showed the solid to be an isomeric mixture of **4**. In a separate experiment under the same conditions, the bromide obtained as the first crop described above gave only one isomer of **4**: colorless needles from MeCN (dried at 80 °C in vacuo); mp 355 °C decomp; IR (KBr, cm^{-1}) 2900 s, 2245 m (CN), 2200 w (CN), 1620 m, 1510 m, 1440 m, 1400 w, 1320 m, 1260 w, 1230 m, 1145 m, 1040 w, 1000 w, 980 m, 920 m, 905 m, 795 m, 760 w, 720 m. ^1H NMR (Me_2SO-d_6) δ=1.5—2.6 (m. 8H), 3.6—3.9 (m, 4H), 5.56 (d, 4H, J=4.5 Hz), 7.52 (s, 2H). Found: C, 70.71; H, 4.04; N, 25.47%. Calcd for $C_{26}H_{18}N_8$: C, 70.57; H, 4.10; N, 25.33%. The second crop of the bromide afforded an isomeric mixture of **4**.

Preparation of 1,4,5,8-Tetrakis(dicyanomethylene)-1,2,3,4,5,6,7,8-octahydroanthracene (5). To a mixture of 60 ml of MeCN and 10 ml of acetic acid were added **4** (9.0 g) and NBS (20 g, 112 mmol), and the mixture was stirred at room temperature for 1 h and at 45 °C for 2 h and then filtered. To the well-stirred and water-cooled filtrate a mixture of 50 ml of DMF, 25 ml of acetic acid, and 3 ml of ethanol was added dropwise over a period of 1 h. The reaction mixture was stirred overnight and diluted with 100 ml of 50% aqueous acetic acid. The dark brown mixture was stirred for an additional 1 h. The product was separated by filtration and washed with MeCN until the filtrate became bright yellow. The yield of **5** was 3.1 g (7.1 mmol, 35%): mp 320—325 °C decomp, as yellow crystals from MeCN; IR (KBr, cm^{-1}) 3065 w, 2920 m, 2225 vs (CN), 1640 m, 1590 s, 1560 s, 1550 s, 1480 m, 1440 m, 1410 w, 1350 w, 1320 m, 1295 m, 1220 m, 1205 m, 1100 w, 980 w, 970 w, 915 m, 880 m, 800 s, 775 w. Found: C, 71.74; H, 2.44 N, 25.69%. Calcd for $C_{26}H_{10}N_8$: C, 71.88; H, 2.32; N, 25.80%.

Preparation of 11,11,12,12,13,13,14,14-Octacyano-1,4:5,8-anthradiquinotetramethane (1).[42] To a stirred suspension of 3.1 g of **5** in 100 ml of MeCN was added a solution of 3 g of pyridine in 50 ml of MeCN under an atmosphere of nitrogen. After 30 min, the dark blue-black mixture was ice-cooled and then an ice-cooled solution of 3.5 g of bromine in 250 ml of 50% aqueous acetic acid was added in one portion and stirred for 5 min. The product was separated by filtration and washed successively with 50% aqueous acetic acid, water, ethanol, and finally MeCN until the filtrate became bright yellow. The yield of **1** thus obtained was 2.3 g (5.3 mmol, 75%) as a yellow powder, and the overall yield starting from **2** was therefore 20%. This crude product was used without further purification. An analytical sample of **1** was obtained by two recrystallizations (from MeCN) of **1** regenerated from the bromine oxidation of the salt **6** as described below: fine golden yellow plates; mp>400 °C (its appearance gradually turned brown above 180 °C and dark brown above 380 °C); IR (KBr, cm^{-1}) 3060 w, 2930 vw, 2225 vs (CN), 1640 m, 1590 w, 1555 vs, 1480 w, 1335 w, 1300 m, 1260 vw, 1205 m, 1100 w, 970 w, 935 vw, 895 m, 800 m, 775 w. Found: C, 72.85; H, 1.40; N, 26.20%. Calcd for $C_{26}H_6N_8$: C, 72.56; H, 1.41; N, 26.04%.

Preparation of the Salt (Et_4N)(OCNAQ)(6) To a suspension of 0.5 g of OCNAQ in 40 ml of MeCN was added 0.5 g of potassium iodide and the mixture was stirred for 2 h. The black deposit was separated by filtration and washed with MeCN. A mixture of the crude potassium salt (0.55 g) and tetraethylammonium iodide (0.4 g) in 20 ml of MeCN was refluxed for 5 min. The resulting precipitate (0.58 g) was recrystallized twice from MeCN to give **6** as black needles. Found: C, 73.04; H, 4.43; N, 22.56%. Calcd for $C_{34}H_{26}N_9$: C, 72.84; H, 4.67; N, 22.49%. OCNAQ was regenerated upon addition of excess of an aqueous bromine solution to a suspension of **6** in MeCN.

Preparation of the Salt ($Et_4N)_2$(OCNAQ)(7). The crude lithium salt of OCNAQ, which was prepared analogously as described above, was dissolved in methanol and filtered. To the dark blue filtrate was added an excess of Et_4NI (more than 2.5 equiv) and the mixture was heated to boiling, filtered, and then the filtrate was cooled. The resulting precipitate was collected and recrystallized from methanol to give **7** as blue-black needles. Found: C, 73.02; H, 6.55; N, 20.42%. Calcd for $C_{42}H_{46}N_{10}$: C, 73.01; H, 6.71; N, 20.27%. A 1:1 mixture of **7** and OCNAQ was heated in MeCN to yield **6**.

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