A Twin-TCNQ-type Acceptor: Synthesis of 11,11,12,12,13,13,14,14-Octacyano-1,4 : 5,8-anthradiquinotetramethane and the Structure of Its (1 : 1) Tetraethylammonium Salt

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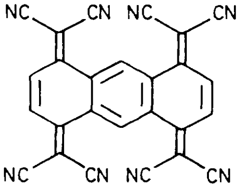
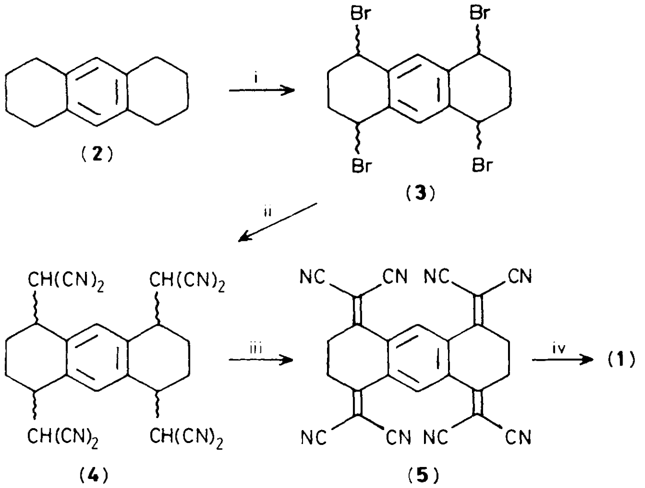
Bromination of octahydroanthracene with *N*-bromosuccinimide (NBS) followed by dicyanomethylation with excess of $NaCH(CN)_2$ followed by repetition of the successive bromination–dehydrobromination procedure gives the title compound (20%), the structure of which has been confirmed by *X*-ray analysis of its monoanionic semiconductor Et_4N^+ salt.

The title compound (**1**) (OCNAQ) has a pair of tetracyanoquinodimethane (TCNQ) nuclei which are linked together through two methylidyne groups. Upon introduction of an electron into the OCNAQ molecule, the charge density is shared equally by both TCNQ nuclei. Such charge dispersal would result in the reduction of on-site Coulomb repulsion and thus (**1**) is expected to accept a second electron more easily than TCNQ. Although a large number of TCNQ derivatives have appeared in the past few decades, twin-



(1)



Scheme 1. *Reagents and conditions:* i, NBS, CCl_4, reflux, hν; ii, $NaCH(CN)_2$, Me_2SO; iii, NBS, MeCN, AcOH, then DMF, AcOH; iv, pyridine, MeCN, then Br_2, 50% AcOH(aq).

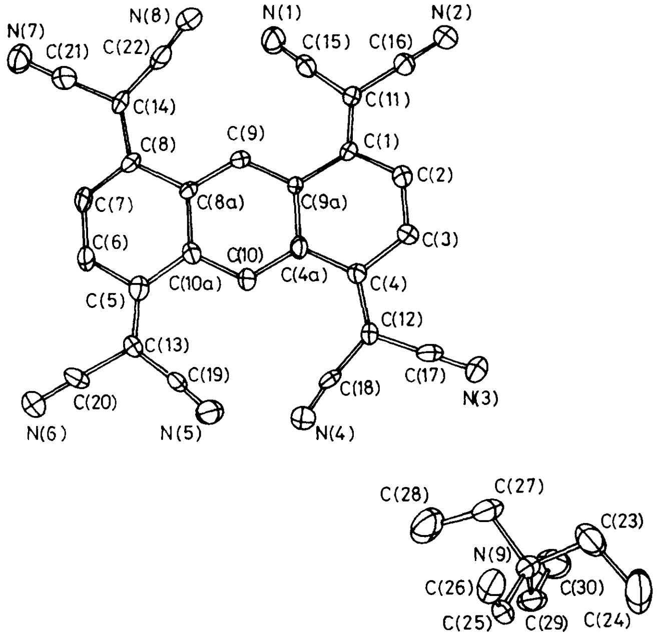


Figure 1. ORTEP view of $(Et_4N)(OCNAQ)$ (**6**) showing the atom numbering scheme. Selected bond lengths are: C(2)–C(3) 1.333 (13), C(6)–C(7) 1.334 (13), C(1)–C(11) 1.384 (11), C(4)–C(12) 1.405 (11), C(5)–C(13) 1.391 (11), C(8)–C(14) 1.390 (11) Å.

TCNQ-type acceptors such as (**1**) are unprecedented. This paper describes the synthetic route to (**1**) and its characterization.

After many futile efforts, the synthetic procedure outlined in Scheme 1, which we hesitated to attempt for fear of aromatization leading to anthracene, met with unexpected success.

A mixture of octahydroanthracene (**2**)[1] and *N*-bromosuccinimide (NBS) in refluxing CCl_4 was irradiated with a 100 W unfrosted light bulb to afford an isomeric mixture of tetrabromo derivatives (**3**) (81%). Dicyanomethylation of (**3**) with a large excess of the sodium salt of malononitrile in Me_2SO afforded an isomeric mixture of (**4**), the active hydrogen of which was replaced by bromine on treatment with NBS in MeCN in the presence of AcOH. To the reaction mixture was added dropwise a mixture of *N,N*-dimethylformamide (DMF) and AcOH to give (**5**) [33% based on (**3**)]. Treatment of (**5**) with pyridine in MeCN followed by the addition of a solution of excess of bromine in 50% acetic acid gave OCNAQ (**1**) as a yellow powder (75%) in an overall yield of 20%.† The cyclic voltammogram of (**1**) (in MeCN containing 0.1 M Et_4NClO_4) exhibits four reversible redox waves at $E_{\frac{1}{2}}$ 0.26, 0.05, −0.44, and −0.53 V *vs.* standard calomel electrode (s.c.e.), indicating that OCNAQ is a stronger acceptor than TCNQ ($E_{\frac{1}{2}}$ 0.17 V *vs.* s.c.e.);[2] the second potential of OCNAQ is close to the first rather than the second potential of TCNQ ($E_{\frac{1}{2}}$ −0.36 V *vs.* s.c.e.).[2]

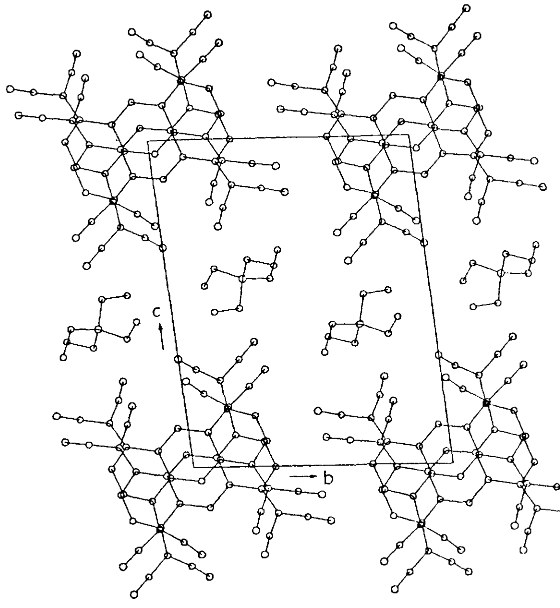


Figure 2. Structure of (**6**) as a projection along the *a*-axis.

The potassium salt of OCNAQ was treated with Et_4NI in hot MeCN giving the 1 : 1 (Et_4N) (OCNAQ) semiconductor salt (**6**) as black needles. A highly resolved e.s.r. spectrum was obtained from (**6**) in MeCN with a *g*-factor of 2.0044 ($4.3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 27 °C, E_a 0.22 eV). The hyperfine data derived from the spectrum provide the following coupling constants for the anion radical $OCNAQ^{-\bullet}$: $a_H(2,3,6,7)$, 0.054 ± 0.002 mT; $a_H(9,10)$, −0.053 ± 0.004 mT; a_N, 0.047 ± 0.002 mT.

The structure of the OCNAQ framework was confirmed by *X*-ray diffraction analysis of salt (**6**) (Figure 1).‡ The benzene

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† The crude product is sparingly soluble in MeCN but can be used directly for the preparation of salts. An analytically pure sample of OCNAQ was obtained by oxidation of (**6**) with bromine: fine golden yellow plates (from MeCN); m.p. >400 °C; ν_{CN} 2225 cm^{-1} (vs).

‡ *Crystal data* for (**6**): $C_{34}H_{26}N_9$, triclinic, space group $P\bar{1}$, a = 7.800 (1), b = 12.435(1), c = 16.004(1) Å, α = 97.17(1), β = 86.50(1), γ = 112.23(1)°, U = 1425.5(1) Å^3, Z = 2, $R(R_\omega)$ = 0.064 (0.074). Measurements were made with a Rigaku Denki AFC-4 autodiffractometer (Cu-K_α radiation, λ = 1.54184 Å, graphite monochromator ω–2θ scan technique, 2θ ≤ 120°). 1647 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were used for structure determination. The intensities were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods using MULTAN 78[4] and refined by full-matrix least-squares (UNICS III).[5] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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 boat form is bent by *ca.* 11° and the dihedral angle between the plane of the benzene ring and that of the bottom of the boat form is *ca.* 10°. The OCNAQ molecules stack along the *a*-axis (Figure 2) to form a column with an alternate arrangement of slightly different interplanar spacings between the benzene rings of the adjacent molecules (3.81 and 3.70 Å), which are longer than the sum of the van der Waals radii (3.40 Å).[3] 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 and 3.14 Å, are shorter than the sum of the van der Waals radii (3.25 Å).[3] To evaluate the extent of intermolecular interaction in the OCNAQ column, the temperature dependence of the e.s.r. absorption intensity of the powdered salt was examined and a J value of 0.052 eV was obtained. These results suggest 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.

OCNAQ was treated with tetrathiafulvalene (TTF) in hot MeCN to afford fine black needles with a TTF : OCNAQ ratio of around 1.15 : 1. Its compacted powder conductivity is *ca.* $10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$ at room temperature. This is a semiconductor with an activation energy of 0.2 eV.

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