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SYNTHESIS OF TWO ISOMERIC TETRACYANOANTHRAQUINODIMETHANES

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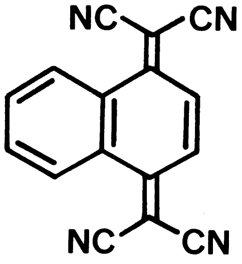
Synthesis of two new acceptors, i.e., dibenzo- and naphtho-TCNQ, is described. Their redox potentials suggest that benzo and naphtho annelations to TCNQ lower the acceptor strength. Both compounds gave no CT complex with TTT, TTF, etc.

It is well known that tetracyanoquinodimethane (TCNQ) forms highly conductive CT complexes with various donors such as tetrathiafulvalene (TTF). Much efforts have been paid so far to develop a more excellent π-acceptor than TCNQ. A number of substituted1) and cyclobutane-fused2) TCNQ derivatives have been prepared along this line, while the TCNQ analog fused with an aromatic ring has not been reported other than benzo-TCNQ **1**.3) We report here the synthesis of 11,11,12,12-tetracyanoanthraquinodimethane (TCNA) or dibenzo-TCNQ **2**4) and naphtho-TCNQ **3**. Both compounds are expected to offer instructive information about the effect of benzo and naphtho annelations upon the electronic nature of the acceptors as well as the conductive properties of their CT complexes.



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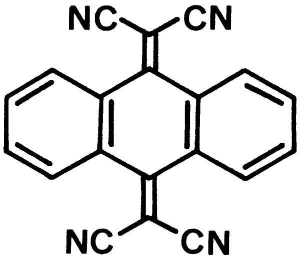

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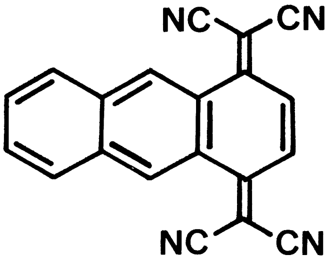

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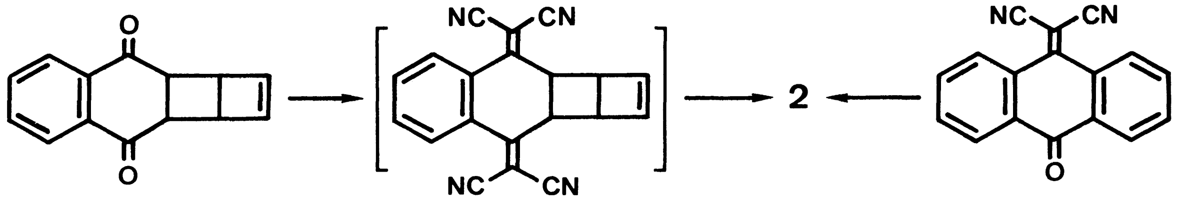
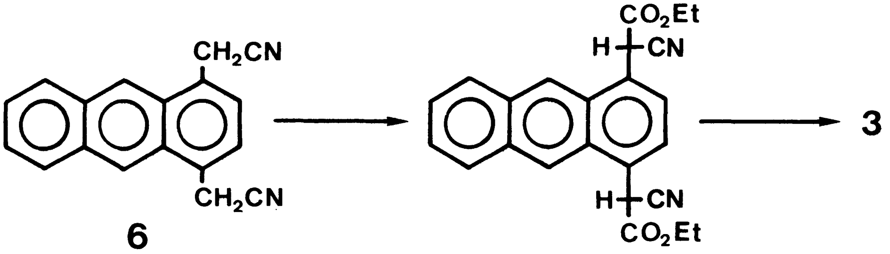
The synthetic routes of **2** and **3** are shown below. Considering the unfruitful results5) about dicyanomethylenation of anthraquinone and its 1,4,4a,5,8,8a,9a,10a-octahydro derivative, we chose **4** as a key intermediate for the synthesis of **2**. Diketone **4** was prepared in 44% yield by the Diels-Alder reaction of 1,4-naphthoquinone and cyclobutadiene, generated in situ from its iron tricarbonyl complex with ceric ammonium nitrate.6) Dicyanomethylenation of **4** was carried out with large excess (40 eq.) of malononitrile in the presence of β-alanine in DMF at 40-45 °C for 6 d to give **2** in 1% yield. The crude product was purified by column chromatography on silica gel, followed by gradient sublimation (230-240 °C/4x10^{-4} mmHg) [**2**7): orange prisms from acetonitrile, mp 350-353 °C with dec.; NMR (CDCl$_3$) δ 8.26, 7.74 ppm (AA'BB'); IR (KBr disk) 2224 cm^{-1}; UV (λ_{max}(ϵ) in CH$_3$CN) 279 (28,700), 302 (16,600), 342 nm (24,900); M$^+$ 304]. Owing to the extremely low and non-reproducible yield of the above reaction, an alternative synthesis of **2** was studied, and a moderate and reproducible yield (27%) of **2** was obtained by dicyanomethylenation of **5**8) under the same conditions as that for **4**. On the other hand, **3** was prepared via **6**7) from 1,4-bis(bromomethyl)anthracene9) in a total yield of 5.4% according to the Wheland and Martin's method.1) [**3**7): red crystals by gradient sublimation, dec>320 °C; NMR (CDCl$_3$) δ 7.80, 8.10 (AA'BB', 4H), 9.35 (s, 2H), 9.77 ppm (s, 2H); IR (KBr disk) 2225 cm^{-1}; UV(λ_{max} (ϵ) in CH$_3$CN) 237 (33,500), 250 (27,800), 339 (18,300), 387 (22,500), 489 (5,160), 668 nm (1,110)].



4 → [ ] → 2 ← 5



6 → 3

The half-wave redox potentials of **2**, **3**, and the related compounds are summarized in Table 1. The table shows that the strength of acceptors is lowered as the increasing number of the fused benzene ring., i.e., TCNQ > **1** > **2** and is weakened by naphtho annelation in greater extent than benzo annelation, i.e., TCNQ > **1** > **3**. The deviation of dicyanomethylene groups from the molecular plane as well as the change of the electronic state are probably responsible for the marked decrease in the redox potential of **2**.

Table 1. Redox Potential of Acceptors(V vs. SCE)$^{a)}$

Compound	$E^1_{1/2}$	$E^2_{1/2}$
TCNQ	0.08	-0.48
Benzo-TCNQ **1**	-0.04	-0.41
Naphtho-TCNQ **3**	-0.18	-0.48
TCNA **2**	-0.46	-0.65
5	-0.65	-0.80
Anthraquinone	-1.06	-1.58

a) 0.1M Et_4NCl_4-CH_3CN:glassy carbon electrode, scan rate: 100 mV/s.

Complexation was tested in acetonitrile and 1,2,4-trichlorobenzene for **2** with TTT,$^{10)}$ TTF, Ph_4BTP,$^{10)}$ $Bu_4N^+I^-$, and LiI and for **3** with TTT and TTF. All the attempts to prepare complexes were unsuccessful. No evidence for the complexation was observed even by color change and/or electronic spectra. The dominant cause of these results might be attributable to the low redox potentials of **2** and **3**.

References

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10) TTT: tetrathiotetracene; Ph_4BTP: tetraphenylbithiopyranylidene.

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