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Crystal Structure of 2-Bromo-5-hydroxyethoxy-7,7,8,8-tetracyanoquinodimethane, BHTCNQ*

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Abstract

2-Bromo-5-(2'-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane [*Chemical Abstracts* name: 2-bromo-5-(2'-hydroxyethoxy)-2,2'-(2,5-cyclohexadiene-1,4-

diylidene)bispropanedinitrile, 58268-31-8], $C_{14}H_7BrN_4O_2$, $M_r = 343.14$, monoclinic, $P2_1/n$ (No. 14), $a = 9.258$ (5), $b = 13.618$ (5), $c = 10.947$ (2) Å, $\beta = 92.14$ (4)°, $V = 1379.1$ Å³, $Z = 4$, $D_x = 1.65$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 31.7$ cm⁻¹, $F(000) = 680.0$, $T = 295$ (3) K, $R = 3.9\%$ for 1395 observed reflections. The molecule has an approximate quinoid structure, but there are significant deviations from the *mmm* symmetry of TCNQ; the hydroxyethoxy group is extended away from the molecule. There are two stacks of 'dimers' of BHTCNQ molecules along [001]; these stacks, mutually related by the glide-plane operation, form a 'herringbone' pattern. The least-squares six-membered ring in the first stack is tilted by 56° to [001] (and tilted by 95° to the equivalent plane in the second stack), with interplanar distances of 3.500 and 3.831 Å

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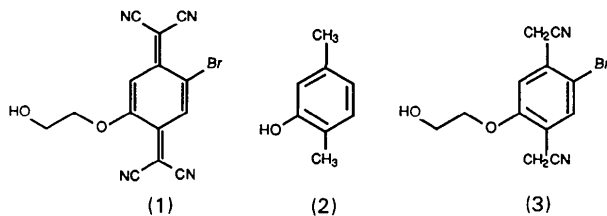
and no π - π overlap. The terminal H atom of the hydroxyethoxy moiety of one BHTCNQ along the first stack is close to the malononitrile end of the BHTCNQ on the second stack; this is confirmed by 'hydrogen-bonding' satellites of the crystal infrared O-H band. The gas-phase electron affinity of BHTCNQ is estimated as 2.9 ± 0.2 e V from cyclic voltammetry.

Introduction

The structure of BHTCNQ (1) has been examined during a systematic study of several D - σ - A (organic one-electron donor/ σ bridge/organic one-electron acceptor) molecules whose potential electrical rectification properties may enable the assembly of ultrathin (5 nm) but fast (<1 ns) $M_1|D$ - σ - $A|M_2$ rectifiers, where M_1 and M_2 are metallic thin films (Metzger *et al.*, 1986). In particular, D would be a one-electron donor such as tetrathiafulvalene (TTF) or N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD), σ would be a carbamate bridge, and A would be the excellent acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Metzger & Panetta, 1983). Since all such molecules studied to date depend on the previous synthesis of BHTCNQ (Hertler, 1976), it is of some interest to probe its molecular structure. A preliminary report was made, for instance, of the structure of phenyl carbamate-TCNQ (Panetta, Baghdadchi & Metzger, 1984).

Synthesis

2-Bromo-5-(2'-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane [BHTCNQ (1)] was first synthesized (Hertler, 1976) in six steps from 2,5-dimethylphenol (2); its melting temperature is 494–495 K (lit. 486–490 K dec.). The synthesis of (1) has one very inefficient step: in the protective carboxymethylation of intermediate (3) (prior to its treatment with cyanogen chloride) the yields vary randomly from 0% to a maximum of 13%, despite efforts to improve the reaction conditions [using cyanogen bromide (Baghdadchi, 1983), or a tetrahydropyranyl protecting group (Day, 1984)].



X-ray crystallography and structure determination

From a batch of red acicular crystals, a relatively equant specimen was mounted on an Enraf-Nonius

CAD-4F automated diffractometer at the University of Alabama, using graphite-monochromatized Mo $K\alpha$ radiation. The experimental conditions are summarized in Table 1. Of 2082 unique data measured, 687 were unobserved, and 1395 were measured above background. The data were corrected for Lorentz and polarization factors, and also by an absorption factor, ranging from 0.81 to 1.00, obtained by scanning reflection $30\bar{1}$ (at $\chi = 85^\circ$) for $\psi = 0$ – 180° . The structure was solved by direct methods and refined by full-matrix least squares on F , using anisotropic thermal parameters for all non-H atoms, riding positions and variable isotropic thermal parameters for the H atoms, and unit weights, to a final unweighted R index of 3.9% (1395 observations, 197 parameters). The largest peak in the final difference Fourier map is close to the Br(21) atom position, with density 0.262 e \AA^{-3} .

During structure refinement, all H atoms were forced to 'ride' at a fixed position from the C or O atom to which they were bonded; an effort was made to refine the alcohol H(20) atom as an independent atom, using two candidate difference Fourier peaks; however, neither position refined reasonably, and disorder models did not help either.

The programs used were *DATRDN* (Hunter, 1982), *MULTAN80* (Main *et al.*, 1980), *SHELX76* (Sheldrick, 1976), *ORTEPII* (Johnson, 1976), *SYBYL* (Tripos Associates, 1986), *CNINDO* (Pople & Beveridge, 1970), and, for least-squares planes and Madelung energies, programs *CELMAP* (Metzger & Bloch, 1975) and *EWALD* (Metzger & Bloch, 1975). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Infrared spectra of BHTCNQ microcrystals were measured with a Mattson Sirius 100 Fourier transform spectrophotometer equipped with a Bach-Scheerer IR microscope. Cyclic voltammetry was performed with an Amel potentiostat.

Crystal structure: results and discussion

The final atom coordinates are given in Table 2,* the bond distances and bond angles within the molecule are given in Table 3. Significantly short intermolecular contacts are H(20)···C(2) (2.216 Å) and H(20)···C(3) (2.488 Å), and the distances O(20)···C(2) and O(20)···C(3) are 3.137 and 3.287 Å, respectively; other contacts and least-squares planes for selected groups have been deposited.* The molecular structure is displayed in Fig. 1; the unit-cell packing can be seen in Fig. 2; the overlap between four BHTCNQ molecules

* Lists of structure amplitudes, anisotropic temperature factors, least-squares planes, and intermolecular close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44456 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of experimental conditions of data collection and crystal structure determination

Crystal color	Red
Crystal size (mm)	0.3 × 0.4 × 1.1
Orientation matrix from	24 reflections, $\theta = 9-18^\circ$
Scan mode	$\omega-2\theta$
Scan speed ($^\circ \text{ min}^{-1}$)	0.78-21
Scan-width parameters $\Delta\omega_a, \Delta\omega_b$	0.80, 0.20
Scan range (θ_{min} to θ_{max}) ($^\circ$)	1-30
Scan range	h 0-15, k 0-12, l -10-10
Intensity control reflections	134 and 400
Fluctuation of control reflections	< 1%
Total reflections measured	2082
Reflections observed	1395 [$F_{\text{obs}} > 1.67\sigma(F_{\text{obs}})$]
Number of parameters	197
Weighting scheme	Unit weights
R index (unweighted) (%)	3.9
Final max. (shift/e.s.d.)	0.014
Final largest difference Fourier peak ($e \text{ \AA}^{-3}$)	0.262

Table 2. Atomic coordinates for all atoms, and equivalent isotropic thermal parameters (\AA^2)

For non-H atoms, U_{eq} = one-third of the trace of orthogonalized U tensor. For space group $P2_1/n$, the symmetry operations are x, y, z ; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z, -x, -y, -z$; $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$.

	x	y	z	U_{eq}
Br(21)	0.26450 (7)	0.09237 (7)	0.37025 (8)	0.063 (21)
N(1)	0.6170 (5)	-0.1040 (5)	0.0246 (6)	0.055 (23)
C(2)	0.4987 (7)	-0.1250 (5)	0.0183 (6)	0.040 (9)
C(3)	0.3469 (6)	-0.1488 (5)	0.0075 (6)	0.036 (9)
C(4)	0.3177 (6)	-0.2101 (6)	-0.0948 (7)	0.043 (15)
N(5)	0.3040 (6)	-0.2566 (6)	-0.1803 (6)	0.064 (21)
C(6)	0.2472 (5)	-0.1080 (5)	0.0885 (5)	0.032 (10)
C(7)	0.0904 (6)	-0.1291 (5)	0.0808 (6)	0.035 (9)
C(8)	-0.0047 (6)	-0.0794 (5)	0.1519 (5)	0.036 (11)
C(9)	0.0346 (6)	-0.0104 (5)	0.2422 (5)	0.034 (7)
C(10)	0.1930 (6)	0.0053 (5)	0.2542 (5)	0.035 (7)
C(11)	0.2874 (6)	-0.0413 (5)	0.1815 (5)	0.034 (10)
C(12)	-0.0714 (6)	0.0343 (5)	0.3141 (6)	0.039 (12)
C(13)	-0.0582 (6)	0.0995 (6)	0.4149 (6)	0.043 (13)
N(14)	-0.0661 (6)	0.1477 (5)	0.5001 (6)	0.061 (15)
C(15)	-0.2220 (7)	0.0147 (6)	0.2921 (6)	0.050 (9)
N(16)	-0.3421 (6)	0.0031 (6)	0.2785 (7)	0.076 (33)
O(17)	0.0630 (4)	-0.1994 (4)	0.0007 (4)	0.049 (20)
C(18)	-0.0839 (6)	-0.2244 (6)	-0.0204 (6)	0.051 (19)
C(19)	-0.0838 (8)	-0.3059 (7)	-0.1087 (7)	0.063 (22)
O(20)	-0.0255 (5)	-0.2779 (5)	-0.2235 (5)	0.067 (28)
H(8)	-0.1184 (6)	-0.0948 (5)	0.1371 (5)	0.087 (25)
H(11)	0.4011 (6)	-0.0260 (5)	0.1965 (5)	0.087 (25)
H(181)	-0.1312 (6)	-0.2475 (6)	0.0636 (6)	0.048 (18)
H(182)	-0.1435 (6)	-0.1626 (6)	-0.0580 (6)	0.076 (25)
H(191)	-0.1937 (8)	-0.3306 (7)	-0.1250 (7)	0.129 (36)
H(192)	-0.0195 (8)	-0.3652 (7)	-0.0701 (7)	0.072 (25)
H(20)	-0.0087 (5)	-0.2792 (5)	-0.3185 (5)	0.707 (142)

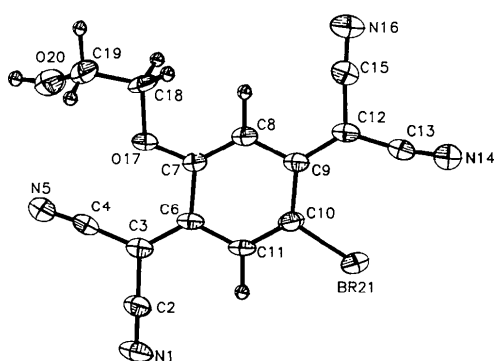


Fig. 1. ORTEPII (Johnson, 1976) drawing of the molecule. The thermal ellipsoids of vibration are depicted at the 50% probability level.

Table 3. Bond distances (\AA) and bond angles ($^\circ$) within the BHTCNQ molecule

C(2)—N(1)	1.131 (8)	C(2)—C(3)	1.443 (8)
C(3)—C(4)	1.414 (9)	C(3)—C(6)	1.417 (8)
N(5)—C(4)	1.133 (8)	C(6)—C(7)	1.480 (7)
C(6)—C(11)	1.404 (8)	C(7)—C(8)	1.375 (8)
H(8)—C(8)	1.080	C(8)—C(9)	1.402 (8)
C(9)—C(10)	1.483 (7)	C(9)—C(12)	1.418 (8)
C(10)—C(11)	1.361 (8)	H(11)—C(11)	1.080
C(12)—C(13)	1.418 (9)	C(12)—C(15)	1.431 (9)
N(14)—C(13)	1.146 (8)	N(16)—C(15)	1.128 (8)
O(17)—C(7)	1.317 (7)	C(18)—O(17)	1.412 (6)
C(18)—C(19)	1.47 (1)	O(20)—C(19)	1.437 (9)
H(20)—O(20)	1.057	Br(21)—C(10)	1.843 (6)
H(181)—C(18)	1.080	H(182)—C(18)	1.080
H(191)—C(19)	1.080	H(192)—C(19)	1.080
C(3)—C(2)—N(1)	178.1 (7)	C(2)—C(3)—C(4)	110.8 (5)
C(2)—C(3)—C(6)	121.0 (6)	C(4)—C(3)—C(6)	128.1 (5)
N(5)—C(4)—C(3)	174.7 (7)	C(3)—C(6)—C(7)	123.3 (6)
C(7)—C(6)—C(11)	123.1 (5)	C(7)—C(6)—C(11)	113.5 (5)
O(17)—C(7)—C(6)	110.1 (5)	C(6)—C(7)—C(8)	121.3 (6)
O(17)—C(7)—C(8)	128.6 (5)	H(8)—C(8)—C(7)	117.5 (3)
C(9)—C(8)—H(8)	117.5 (3)	C(7)—C(8)—C(9)	125.1 (5)
C(8)—C(9)—C(10)	112.9 (5)	C(8)—C(9)—C(12)	120.8 (5)
C(10)—C(9)—C(12)	126.3 (6)	Br(21)—C(10)—C(9)	118.8 (5)
C(9)—C(10)—C(11)	122.4 (6)	Br(21)—C(10)—C(11)	118.8 (4)
H(11)—C(11)—C(6)	117.7 (3)	C(6)—C(11)—C(10)	124.6 (5)
H(11)—C(11)—C(10)	117.7 (3)	C(9)—C(12)—C(13)	131.3 (5)
C(9)—C(12)—C(15)	121.1 (6)	C(13)—C(12)—C(15)	107.6 (5)
N(14)—C(13)—C(12)	170.6 (7)	N(16)—C(15)—C(12)	176.5 (8)
C(7)—O(17)—C(18)	116.4 (5)	H(181)—C(18)—O(17)	110.5 (4)
H(182)—C(18)—O(17)	110.5 (4)	C(19)—C(18)—O(17)	105.4 (5)
C(19)—C(18)—H(181)	110.5 (5)	H(181)—C(18)—H(182)	109.472 (1)
C(19)—C(18)—H(182)	110.5 (5)	H(191)—C(19)—C(18)	108.7 (4)
H(192)—C(19)—C(18)	108.7 (5)	O(20)—C(19)—C(18)	112.6 (7)
O(20)—C(19)—H(191)	108.7 (3)	H(191)—C(19)—H(192)	109.471 (1)
O(20)—C(19)—H(192)	108.7 (4)	H(20)—O(20)—C(19)	158.3 (4)

along the stacking direction is shown in Figs. 3 (face-on view) and 4 (end-on view); the packing of four cells (showing the 'dimers' of BHTCNQ along the [001] axis) is given in Fig. 4.

BHTCNQ is fairly flat, but with a slight helical twist of the two malononitrile moieties, which are twisted 7.19° relative to each other, and 9.66 and 5.15° relative to the central six-carbon-atom ring. The hydroxyethoxy substituent is extended away from the TCNQ ring. The central six-membered ring is not as

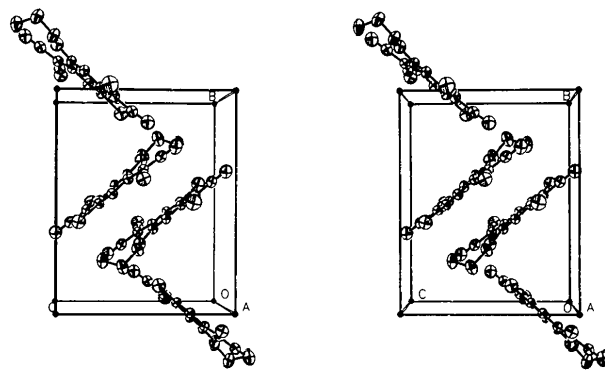


Fig. 2. Stereoscopic ORTEPII (Johnson, 1976) drawing of the molecular packing within the unit cell. H atoms are omitted for simplicity.

planar or as quinoidal as one would expect from a TCNQ structure: the ideal mmm (D_{2h}) symmetry of TCNQ is seriously distorted in the six-membered ring, in that the bond distances C(6)–C(7) and C(9)–C(10) are 0.076 (8) and 0.061 (8) Å longer than the bond distances C(6)–C(11) and C(8)–C(9), respectively: the longer bonds are to the atoms bearing the hydroxyethoxy and the bromo substituents, respectively. Furthermore, the six-membered ring is not very flat; rather, there are paired deviations from the least-squares plane that are largest for atoms C(6) and C(7), medium for C(9) and C(10), and smallest for C(8) and C(11); alternatively, if one uses atoms C(7), C(6) and C(11) to define a plane exactly, then atoms C(10), C(9) and C(8) deviate -0.076 , -0.165 and -0.120 Å, respectively, from it. The C(10)–Br(21) bond distance (1.843 Å) is close to the sum of the C (0.772 Å) and Br (1.14 Å) single-

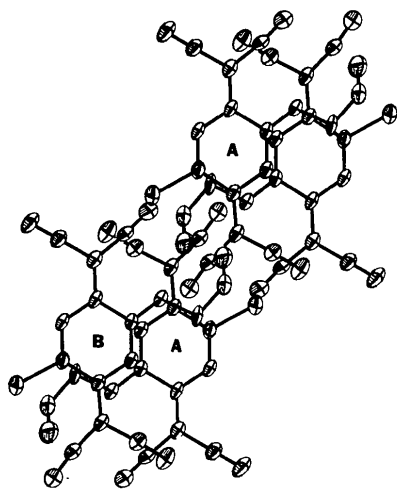


Fig. 3. ORTEPII (Johnson, 1976) drawing of four nearest-neighbor molecules ('dimers') along [001], projected onto the six-membered ring plane. Molecules *A* and *B* are 3.500 Å apart (perpendicular distance between least-squares six-membered ring planes); molecules *A* and *A'* are 3.831 Å apart. There is no noticeable π - π overlap between the molecules.

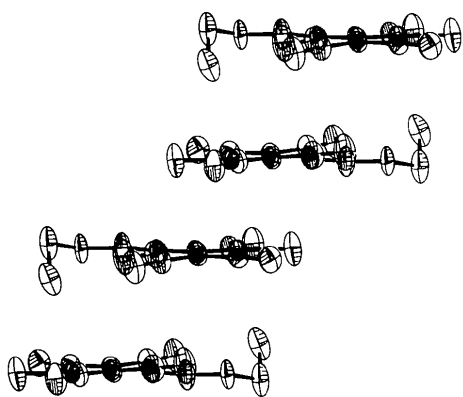


Fig. 4. ORTEPII (Johnson, 1976) drawing of the four nearest-neighbor BHTCNQ molecules along [001].

bond covalent radii (Pauling, 1960). The bond angle C(4)–C(3)–C(6) is larger than the bond angle C(2)–C(3)–C(6) by 7.1° , and also the bond angle C(9)–C(12)–C(13) is larger than the bond angle C(9)–C(12)–C(15) by 10.2° , presumably because of the 7.19° twist of the two malononitrile moieties with respect to each other.

One of the BHTCNQ molecules is oriented so that the unit normal to the six-membered quinoid ring has Miller indices 0.64, 10.04 and 7.32; the angle of this normal with the [001] axis is 56.35° . Thus the molecules are stacked, with a large slant, along [001] as approximate 'dimers' related by an inversion center; the glide plane then generates another stack (least-squares six-membered rings of the molecules in the second stack are inclined by 94.9° to the six-membered rings of the molecules of the first stack), so that a herringbone pattern (Fig. 5) is obtained. The dimer stacking motif is evident in Figs. 3–5. The BHTCNQ molecules do not show much π - π perpendicular intermolecular overlap, but are 'side-slipped' (Fig. 3); however, the molecules stacked along [001] are dimers (Figs. 3, 4) in the usual sense that they have alternating intermolecular distances between the least-squares planes of the six-membered rings of 3.500 Å (molecules *A* and *B*) and 3.831 Å (molecules *A* and *A'*). However, while in TCNQ and in TCNQ salts there is usually some perpendicular overlap between the six-membered rings, here the overlap between *A*, *A'* and *B* does not bring the six-membered rings over each other at all. Rather, the pair *A*, *B* is displaced away from eclipsed perpendicular overlap along an axis approximately parallel to the vector C(8)–C(10) (close to [100]) so that the six-membered rings are only accosted towards each other. Similarly, the pair *A*, *A'* is slipped away from eclipsed perpendicular overlap along a vector C(7)–C(9) so that the propanedinitrile end of molecule *A* is 'close' to the propanedinitrile end of molecule *B*.

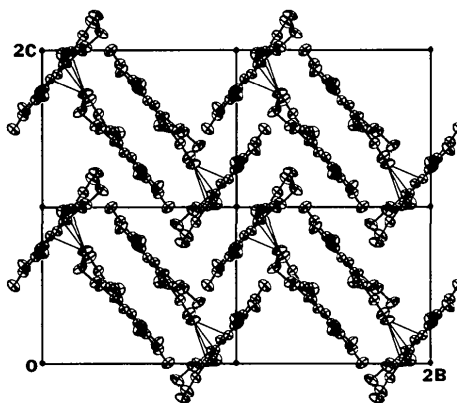


Fig. 5. ORTEPII (Johnson, 1976) drawing of four unit cells, showing the motif of 'dimers'. The short intermolecular contacts between O(20) and C(2), C(3), C(6) and C(11) are shown as thin lines.

However, there is a close van der Waals interaction between the molecules in the stack along [001] and the molecules related to them by the glide-plane symmetry operation: there are some abnormally short intermolecular contacts discussed above. The hydroxyl H(20) atom approaches atoms C(2), C(3) and (less strongly) C(6) of the BHTCNQ molecule related to it by the glide-plane operation: the term 'hydrogen bonding' is traditionally not applied to such a case. The calculated H(20) position is oriented more or less towards atom C(2), to which O(20) is closest, but other alternate positions are possible: this suggests a rotameric equilibrium between several close sites.

Table 4 compares significant structural features of BHTCNQ with those of related neutral TCNQ structures. The symmetry lowering from *mmm* (D_{2h}) for TCNQ to 1 (C_1) for BHTCNQ, and the lack of intermolecular π - π bonding along the stack set BHTCNQ apart from the other TCNQ structures given. (To avoid the difficult distinction between Mulliken charge-transfer complex and crystal-packing contributions to molecular structure, all crystal structures containing salts and complexes of derivatized TCNQ's were avoided in the comparison.)

Infrared spectrum and lattice energy

The infrared spectrum of a BHTCNQ crystal shows O-H stretch bands at 3564 cm^{-1} (non-hydrogen bonded) and satellite peaks between 3482 and 3500 cm^{-1} (hydrogen bonded). The spectrum confirms that the H(20) atom is 'hydrogen bonded' to some other atom or atoms [e.g. C(2), C(3), C(6), or C(11)], as is suggested by the crystal structure.

Table 5 gives the CNDO/2 atom-in-molecule charges (Pople & Beveridge, 1970; Hase & Schweig, 1973), which resemble those of TCNQ (Metzger, 1981; Metzger & Bloch, 1975). Using the CNDO/2 charges, the Madelung energy of BHTCNQ is $E_M = -9.230\text{ kJ mol}^{-1}$, which is fairly typical for a neutral crystal.

Cyclic voltammetry and electron affinity of BHTCNQ

It would be of great interest to obtain the electron affinity of BHTCNQ by direct experiment, but this is not easy. We must content ourselves here with a measurement of relative half-wave potentials ($E_{1/2}$) in solution. The cyclic voltammogram of BHTCNQ in acetonitrile solution using 0.1 M tetrabutylammonium perchlorate electrolyte, measured with a Pt disc electrode, shows two reversible waves: a one-electron reversible reduction (to TCNQ^-) with $E_{1/2} = 0.305\text{ V}$ versus SCE (SCE = standard calomel electrode), and a two-electron reversible reduction (to TCNQ^{2-}) at $E_{1/2} = -0.170\text{ V}$ versus SCE. This is compared with the available data for TCNQ and for DHTCNQ

Table 4. Comparison of bond distances (\AA , uncorrected for libration), bond angles ($^\circ$) and intra-stack intermolecular distances (\AA) between selected TCNQ structures (atom numbering of BHTCNQ)

	BHTCNQ	TCNQ	2,5-TCNQF ₂	TCNQF ₄
N(1)-C(2)	1.131 (8)	1.137 (3)	1.145 (3)	1.139 (2)
C(4)-N(5)	1.133 (8)	1.135 (9)	1.143 (3)	1.142 (2)
N(14)-C(13)	1.146 (8)	—	—	—
C(15)-N(16)	1.128 (9)	—	—	—
C(2)-C(3)	1.443 (8)	1.440 (4)	1.431 (3)	1.435 (2)
C(3)-C(4)	1.414 (9)	1.441 (4)	1.437 (3)	1.439 (2)
C(12)-C(13)	1.418 (9)	—	—	—
C(12)-C(15)	1.431 (9)	—	—	—
C(3)-C(6)	1.417 (9)	1.373 (3)	1.400 (3)	1.372 (2)
C(9)-C(12)	1.418 (8)	—	—	—
C(6)-C(7)	1.480 (7)	1.440 (4)	1.443 (2)	1.436 (2)
C(6)-C(11)	1.404 (8)	1.406 (9)	1.439 (2)	1.438 (2)
C(8)-C(9)	1.402 (8)	—	—	—
C(9)-C(10)	1.483 (7)	—	—	—
C(7)-C(8)	1.375 (8)	1.344 (3)	1.328 (2)	1.334 (2)
C(10)-C(11)	1.361 (8)	—	—	—
N(1)-C(2)-C(3)	178.1 (7)	179.4 (2)	177.6 (1)	174.7 (1)
N(5)-C(4)-C(3)	174.7 (7)	179.6 (2)	179.9 (1)	175.8 (1)
N(14)-C(13)-C(12)	170.6 (7)	—	—	—
N(16)-C(15)-C(12)	176.5 (8)	—	—	—
C(2)-C(3)-C(4)	110.8 (5)	115.9 (2)	114.6 (1)	112.4 (1)
C(13)-C(12)-C(15)	107.6 (5)	—	—	—
C(8)-C(9)-C(10)	112.9 (5)	118.1 (2)	115.3 (1)	113.5 (1)
C(7)-C(6)-C(11)	113.5 (5)	—	—	—
C(6)-C(7)-C(8)	121.3 (6)	120.8 (2)	120.5 (1)	123.2 (1)
C(7)-C(8)-C(9)	125.1 (5)	121.0 (2)	124.1 (1)	123.2 (1)
C(6)-C(11)-C(10)	124.6 (5)	—	—	—
C(9)-C(10)-C(11)	122.4 (6)	—	—	—
Intermolecular spacing	3.831	3.45	3.013	NC

References: TCNQ (Long, Sparks & Trueblood, 1965), 2,5-TCNQF₂ (Wiygul, Ferraris, Emge & Kistenmacher, 1981), TCNQF₄ (Emge, Maxfield, Cowan & Kistenmacher, 1981).

Table 5. CNDO/2 atom-in-molecule charges ($|e|$)

The computed molecular dipole moment is 4.3722 debye; its orientation is close to the C8-C9 vector, but is tilted 16° out of the least-squares plane, in the direction of O20.

Br(21)	-0.1355	C(10)	0.0343	O(20)	-0.3673
N(1)	-0.1296	C(11)	0.0422	H(8)	0.0107
C(2)	0.0938	C(12)	-0.0138	H(11)	-0.0125
C(3)	0.0570	C(13)	0.1092	H(181)	-0.0082
C(4)	0.1034	N(14)	-0.1586	H(182)	0.1216
N(5)	-0.1290	C(15)	0.1048	H(191)	-0.0258
C(6)	0.0114	N(16)	-0.1650	H(192)	-0.0141
C(7)	0.2055	O(17)	-0.1939	H(20)	0.2078
C(8)	-0.1129	C(18)	-0.0056		
C(9)	0.1005	C(19)	0.2446		

(Hertler's dihydroxyethoxyTCNQ) in Table 6. The $E_{1/2}$ values are solvent-dependent, and it is dangerous to compare the reduction potentials for different molecules even in the same solvent (Bechgaard & Anderson, 1980); nevertheless, one can say safely that BHTCNQ seems to be as good a one-electron acceptor (within 0.1 eV) as TCNQ itself. The experimental gas-phase electron affinity of TCNQ, measured by a caesium-beam collisional ionization, is $A_A = 2.8 \pm 0.1\text{ eV}$ (Compton & Cooper, 1977); if it is safe to add $E_{1/2}$ shifts among closely related molecules to obtain A_A for

Table 6. Half-wave reduction potentials for BHTCNQ, DHTCNQ (2,5-dihydroxyethoxyTCNQ) and TCNQ in various solvents at room temperature

Species	Solvent	Supporting electrolyte	Working electrode	$E_{1/2}^1$ 0 → -1 (V vs SCE)	$E_{1/2}^2$ -1 → -2 (V vs SCE)	Ref.
BHTCNQ	CH ₃ CN	0.1 M TBAP	Pt disc	0.305	-0.170	This work
DHTCNQ	CH ₃ CN	0.1 M TEAP	Pt disc	0.080*	-0.370*	Inzelt, Day, Kinstle & Chambers (1983)
TCNQ†	CH ₃ CN	0.1 M LiClO ₄	DME	0.127†	-0.291†	Acker & Hertler (1962)
TCNQ	CH ₃ CN	TPrAP	Pt	0.23‡	-0.33‡	Rieger, Bernal, Reinmuth & Fraenkel (1963)
TCNQ†	H ₂ O	0.1 M LiClO ₄	Pt	0.115†	-0.133†	Sharp (1976)
TCNQ	CH ₃ CN	0.1 M TBABF ₄	Pt button	0.17	-0.35	Bechgaard & Anderson (1980)
TCNQ	CH ₃ CN	0.2 M TBABF ₄	Pt	0.20	-0.35	White, Ricco & Wrighton (1983)
TCNQ	CH ₃ CN	0.1 M TEAP	Pt disc	0.14*	-0.31*	Inzelt, Day, Kinstle & Chambers (1983)
TCNQ	CH ₃ CN	0.1 M TBABF ₄	Pt button	0.19	-0.35	Anderson & Jorgensen (1979)

* Assuming that 'V versus Ag | 0.1 M AgNO₃; 0.1 M LiClO₄' + 0.320 = 'V versus SCE' (Larson, Iwamoto & Adams, 1961).

† In Li⁺-containing supporting electrolyte, it is assumed that (TCNQ)₂ is formed instead of TCNQ⁻ (Sharp, 1976; Bechgaard & Anderson, 1980).

‡ Assuming that 'V versus Ag | 0.1 M AgClO₄ (DMF solvent); 0.1 M (C₂H₅)₄NClO₄' + 0.42 = 'V versus SCE' [in analogy with 'V versus Ag | AgClO₄ (0.001 M, CH₃CN); 0.1 M Et₄NClO₄ (CH₃CN)' + 0.42 = 'V versus SCE(aq)'] (Larson & Iwamoto, 1960).

a new molecule (Emge, Maxfield, Cowan & Kistenmacher, 1981), then one can estimate that the gas-phase electron affinity of BHTCNQ is 2.9 ± 0.2 eV. Given the presence of the bromine in BHTCNQ, this increase of A_4 relative to TCNQ is reasonable.

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