

Peng-Fei Wang, Guang-Xiang Liu* and You-Cun Chen

Department of Chemistry, Anqing Normal College, Anqing 246003, People's Republic of China

Correspondence e-mail: njuliugx@yahoo.com

Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.056
 wR factor = 0.138
 Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

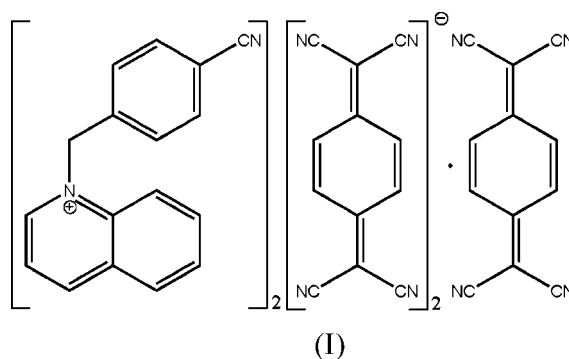
An ion-pair complex composed of two *N*-(4-cyanobenzyl)quinolinium cations, two 7,7,8,8-tetracyanoquinodimethane anions and one neutral 7,7,8,8-tetracyanoquinodimethane molecule

Received 23 June 2006
 Accepted 4 July 2006

In the title complex, $2\text{C}_{17}\text{H}_{13}\text{N}_2^+ \cdot 2\text{C}_{12}\text{H}_4\text{N}_4^- \cdot \text{C}_{12}\text{H}_4\text{N}_4$, a bound unit of two anions and one neutral TCNQ (TCNQ is 7,7,8,8-tetracyanoquinodimethane) molecule is formed and adjacent units are displaced relative to each other along the direction of the shorter molecular axis of TCNQ. Completely segregated columnar stacks of TCNQ anions/molecules and cations are observed. Within an TCNQ column, the benzene rings are parallel to each other, the neutral TCNQ molecules lying on inversion centres. The centroid-to-centroid distance between adjacent aromatic rings is less than 4.2 \AA and $\pi-\pi$ stacking interactions are found.

Comment

The charge-transfer (CT) salt approach has been one of the most successful strategies for producing magnetically ordered compounds based on molecular building blocks (Jeffrey *et al.*, 2005). One of the most extensively used radicals in these studies has been the planar organic molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ), since it shows a low reduction potential which makes it a suitable acceptor in charge-transfer processes. Another typical feature of this acceptor is its tendency to overlap its π -delocalised system with those of neighbouring molecules to form stacks with different degrees of electron delocalization (Alonso *et al.*, 2005).



Previous work has shown that molecular stacks of ion-pair complexes exhibit low-dimensional properties in some cases, which have interesting anisotropic magnetic, electronic and structural characteristics (Ren, Meng *et al.*, 2002; Ren, Ma *et al.*, 2003; Liu, Ren *et al.*, 2005). Furthermore, the size and shape of the counter-cations play an important role in determining the ground-state properties of the resulting materials (Ren, Chen *et al.*, 2002). As a result, ion-pair complexes consisting of the TCNQ anion and benzylquinolinium cations

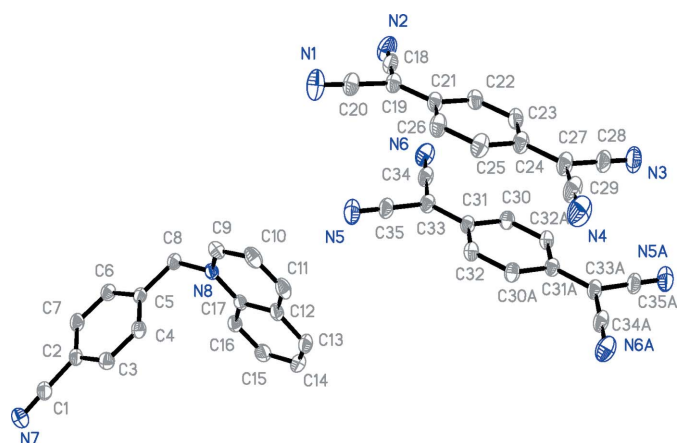


Figure 1
The The cation, anion and centrosymmetric neutral TCNQ molecule of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (A) $1 - x, 1 - y, -z$.]

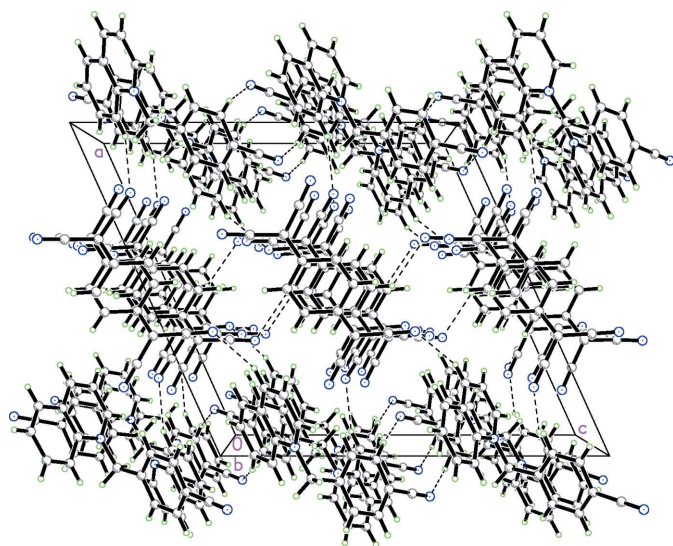


Figure 2
The cation, anion and centrosymmetric neutral TCNQ molecule of complex (I), viewed along the b -axis direction. Dashed lines indicate C–H...N hydrogen bonds

could offer the possibility of systematically studying the fundamental relationship between the stack structure and the size and steric properties of substituent groups. In this communication, we report the crystal structure of the title compound, (I).

The asymmetric unit of (I) is composed of one N -(4-cyanobenzyl)quinolinium cation, one TCNQ^- anion and one-half of a centrosymmetric neutral TCNQ molecule (Fig. 1). This complex stacks into completely segregated columns of TCNQ anions/molecules and cations, as illustrated by the projection along the crystallographic b axis in Fig. 2. The cation and anion columns are linked by hydrogen-bonding interactions (Table 1). Within an anionic column, a strongly bound unit of $[(\text{TCNQ})_3]^{2-}$ is formed, and adjacent units are displaced relative to each other along the direction of the shorter molecular axis of TCNQ. The benzene rings are

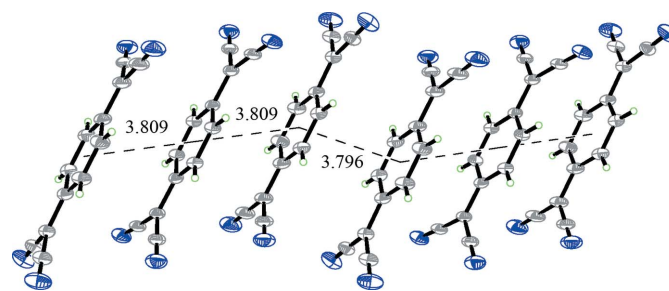


Figure 3
A side view of the one-dimensional anionic chain of (I). Distances are in Å.

parallel to each other. The centroid-to-centroid distances between adjacent aromatic rings are 3.809, 3.809 and 3.796 Å (Fig.3), indicating weak π – π stacking interactions.

The N -(4-cyanobenzyl)quinolinium cations have a Δ -shaped conformation, and the dihedral angles formed by the C5/C8/N8 plane with the benzene and quinolinium rings are 10.56 (10) and 73.81 (10)°, respectively.

Experimental

N -(4-Cyanobenzyl)quinolinium iodine was prepared by the direct combination of 1:1 molar equivalents of N -(4-cyanobenzyl)quinolinium chloride and NaI in a warm solution in acetone at 313 K. A white precipitate was formed (NaCl) which was filtered off, and a white microcrystalline product was obtained by evaporating the filtrate. 1:2 Molar equivalents of N -(4-cyanobenzyl)quinolinium iodide and TCNQ were mixed directly in a solution in methanol, and the mixture was refluxed for 12 h. The violet–red microcrystalline product which formed was filtered off, washed with MeOH and dried *in vacuo*. Single crystals of (I) suitable for structure analysis were obtained by diffusing diethyl ether into an MeCN solution of (I).

Crystal data

$2\text{C}_{17}\text{H}_{13}\text{N}_2^+ \cdot 2\text{C}_{12}\text{H}_4\text{N}_4^- \cdot \text{C}_{12}\text{H}_4\text{N}_4$
 $M_r = 1103.16$
 Monoclinic, $P2_1/c$
 $a = 16.083$ (3) Å
 $b = 10.8627$ (17) Å
 $c = 17.099$ (3) Å
 $\beta = 114.327$ (3)°
 $V = 2722.0$ (7) Å³

$Z = 2$
 $D_x = 1.346$ Mg m^{−3}
 Mo $K\alpha$ radiation
 $\mu = 0.08$ mm^{−1}
 $T = 293$ (2) K
 Block, dark green
 $0.20 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.983$, $T_{\max} = 0.988$

14142 measured reflections
 5321 independent reflections
 4175 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.138$
 $S = 1.05$
 5321 reflections
 388 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 0.5287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.21$ e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C32—H32···N1 ⁱ	0.93	2.58	3.220 (3)	126
C16—H16···N6 ⁱⁱ	0.93	2.46	3.346 (2)	160
C11—H11···N3 ⁱⁱⁱ	0.93	2.58	3.426 (3)	151
C4—H4···N8	0.93	2.51	2.856 (2)	102
C3—H3···N7 ^{iv}	0.93	2.58	3.435 (3)	154

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x, -y, -z + 1$.

All H atoms were placed in geometrically calculated positions, with C—H = 0.93 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

This work was funded by the National Natural Science Foundation of China (project No. 20371002) and the Natural Science Foundation of Anhui Province, China (project Nos. 2003kj253 and 2003jq153).

References

- Alonso, C., Ballester, L., Gutiérrez, A., Perpiñán, M. F., Sánchez, A. E. & Azcondo, M. T. (2005). *Eur. J. Inorg. Chem.* pp. 486–495.
- Bruker (2000). *SADABS, SMART, SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Jeffrey, A. C., Meredith, M. B., Hanusa, T. P., Wang, G. B., Brennessel, W. W. & Yee, G. T. (2005). *Inorg. Chem.* **44**, 172–174.
- Liu, G. X., Ren, X. M., Kremer, P. K. & Meng, Q. J. (2005). *J. Mol. Struct.* **743**, 125–133.
- Ren, X. M., Chen, Y. C., He, C. & Gao, S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3915–3918.
- Ren, X. M., Ma, J., Lu, C. S., Yang, S. Z., Meng, Q. J. & Wu, P. H. (2003). *Dalton Trans.* pp. 1345–1351.
- Ren, X. M., Meng, Q. J., Song, Y., Lu, C. S., Hu, C. J. & Chen, X. Y. (2002). *Inorg. Chem.* **41**, 5686–5692.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.