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Molecular Structure of [2](2,5)(7,7,8,8-Tetracyanoquinodimethano)-[2](1,4)naphthalenophane[†]

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Molecular structure of [2.2](1,4)naphthalenophane containing 7,7,8,8-tetracyanoquinodimethan moiety as an electron acceptor has been determined by means of X-ray diffraction. Crystals belong to monoclinic system, space group Cc with four molecules per unit-cell; $a=9.770(1)$, $b=15.176(2)$, $c=13.299(2)$ Å, $\beta=98.43(1)°$. The structure was established by the direct method and refined by the full-matrix least-squares to $R=0.035$ for 1217 non-zero reflections. The [2.2]paracyclophane skeleton has the usual structure; a half of the naphthalene moiety has a boat-form, the six-membered ring of the TCNQ moiety also has a boat-form, and two $C(CN)_2$ portions in the TCNQ moiety are bent out and slightly twisted from the six-membered ring. The other half of the naphthalene ring free from the bridging is planar and are slightly bent out from the [2.2]paracyclophane skeleton.

As a part of a series of structural studies on layered cyclophanes, molecular structures of [2.2]paracyclophanes containing 7,7,8,8-tetracyanoquinodimethan (TCNQ) moiety as an electron acceptor have been determined;[1)] they are [2](2,5)(7,7,8,8-tetracyanoquinodimethano)[2]paracyclophane (TCNQ-X) and 14,17-dimethoxy[2](2,5)(7,7,8,8-tetracyanoquinodimethano)-[2]paracyclophane (TCNQ-X$(OMe)_2$). In relation with these structures, this paper will deal with the molecular structure of [2](2,5)(7,7,8,8-tetracyanoquinodimethano)[2](1,4)naphthalenophane (TCNQ-$N^{1,4}$), in which a TCNQ and a naphthalene moieties are contained as an electron acceptor and electron donor respectively.

Experimental

A dark violet, needle crystal of TCNQ-$N^{1,4}$ with approximate dimensions of $0.08\times0.15\times0.25$ mm^3 was used. The unit-cell dimensions were determined by the least-squares fit of 2θ values of high order reflections. The systematic absence of reflections showed that the corresponding space group is either Cc or C2/c. The value of calculated density of the crystal [$D_c=1.309$ g cm^{-3}] for $Z=4$ exclude the possibility of the space group C2/c, which was later confirmed by the structure determined.

Crystal Data. $C_{26}H_{16}N_4$, *F.W.* 384.44, monoclinic, space group Cc, $a=9.770(1)$, $b=15.176(2)$, $c=13.299(2)$ Å, $\beta=98.43(1)°$, $V=1950.5(3)$ Å^3, $D_c=1.309$ g cm^{-3} for $Z=4$.

Integrated intensities were measured on a Rigaku automated, four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The $\theta-2\theta$ scan technique was applied at a scan rate of 4° min^{-1} in 2θ; scan width was $\Delta2\theta=(2+0.30\tan\theta)°$. Backgrounds were counted for 7.5 s at both ends of a scan. A total of 1232 (1217 non-zero) reflections was collected. Usual Lp corrections were made but absorption correction was ignored [$\mu(\mathrm{Cu}\,K\alpha)=6.35$ cm^{-1}].

Structure Solution and Refinement

The structure was solved by the direct method (*MULTAN* 74).[2)] Twelve ring carbon atoms which consist of the [2.2]paracyclophane skeleton of the molecule could be located on the *E* map. The location of these atoms was confirmed to be consistent with the result of three-dimensional Patterson function. The Fourier synthesis revealed 28 carbon atoms out of 30, and the successive Fourier synthesis revealed the remaining carbon atoms.

The structure was refined isotropically by the block-diagonal least-squares method (*HBLS* V).[3)] When the *R* value reduced to 0.14, anisotropic thermal parameters were introduced for all the non-hydrogen atoms. Ten strong reflections, of which intensities were considered largely affected by the counting loss of the scintillation counter and/or affected by the extinction, were excluded from the subsequent refinement. The refinement was continued by the full-matrix least-squares procedure.[4)] At the later stage, all the hydrogen atoms located on a difference Fourier synthesis, were also included in the refinement, isotropic temperature factors being used. Finally, the *R* index converged to 0.035 ($R_w=0.045$) for 1217 non-zero reflections. The weighting schemes used at the final stage were $w=\{\sigma^2(F_o)+0.0523|F_o|+0.0025|F_o|^2\}^{-1}$ for $|F_o|>0$ and $w=2.2827$ for $|F_o|=0$. σ is the standard deviation obtained by the counting statistics of reflection intensities. Atomic scattering factors used for the C, N, and H atoms were taken from International Tables for X-Ray Crystallography, Vol. IV.[5)] Computations were carried out on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Final atomic parameters are listed in Table 1.**

Results and Discussion

Molecular Structure. Perspective and side views of the present TCNQ-$N^{1,4}$ molecule (*ORTEP* II)[7)] and those of TCNQ-X for comparison are shown in Figs. 1 and 2. Selected bond distances and bond angles are given in Fig. 3.

The [2.2]paracyclophane skeleton in the TCNQ-$N^{1,4}$ molecule has the similar structure as those in

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** Tables of observed and calculated structure factors and anisotropic thermal parameters are kept at the Chemical Society of Japan, Document No. 8236.

TCNQ-X and TCNQ-X(OMe)$_2$. Almost all of the bond distances and bond angles in the TCNQ-N^{1,4} molecule are equal to the corresponding distances and angles in the TCNQ-X within the limits of errors. The better coincidence is observed between two molecules in the TCNQ portion than in the other portions. A few exceptions are observed: the C(4)–C(9) and C(9)–C(10) distances [1.427(4) and 1.426(4) Å] are longer than the corresponding ones in the TCNQ-X[1.386(6) and 1.385(6) Å].

The upper six-membered ring of the [2.2]paracyclophane skeleton, which is a half of the naphthalene moiety, takes a boat form: the planes defined by the C(3), C(4), and C(12) atoms and by the C(9), C(10), and C(11) form angles of 12.7 and 11.8° respectively with the mean plane made by the C(4), C(9), C(11), and C(12) atoms. The other half of the naphthalene moiety, formed by the C(4) to C(9) atoms, is planar within 0.007 Å, and slightly bent up by 4.2° from the

Table 1. Fractional atomic coordinates of TCNQ-N^{1,4} with estimated standard deviations in parentheses

(a) C, N, and O atoms with equivalent temperature factors.[6)]

Atom	x	y	z	B_{eq}/Å^2
C (1)	0.2792 (4)	0.6500 (2)	0.1740 (3)	3.56
C (2)	0.2176 (4)	0.6213 (3)	0.2714 (3)	3.93
C (3)	0.3171 (4)	0.5608 (2)	0.3377 (3)	3.19
C (4)	0.4507 (4)	0.5918 (2)	0.3812 (2)	3.17
C (5)	0.4805 (5)	0.6821 (3)	0.3970 (3)	4.41
C (6)	0.6110 (5)	0.7111 (3)	0.4331 (4)	5.39
C (7)	0.7180 (5)	0.6502 (3)	0.4538 (4)	5.30
C (8)	0.6951 (4)	0.5622 (3)	0.4391 (3)	4.15
C (9)	0.5605 (4)	0.5295 (2)	0.4024 (3)	3.12
C (10)	0.5348 (4)	0.4380 (2)	0.3837 (3)	3.36
C (11)	0.3983 (4)	0.4110 (2)	0.3654 (3)	3.65
C (12)	0.2907 (4)	0.4726 (2)	0.3396 (3)	3.40
C (13)	0.6472 (4)	0.3762 (3)	0.3587 (3)	4.11
C (14)	0.6308 (4)	0.3571 (2)	0.2422 (3)	3.35
C (15)	0.5575 (3)	0.4306 (2)	0.1799 (3)	2.67
C (16)	0.4230 (3)	0.4189 (2)	0.1395 (3)	2.84
C (17)	0.3269 (3)	0.4907 (2)	0.1123 (3)	2.73
C (18)	0.3738 (4)	0.5579 (2)	0.1432 (3)	2.76
C (19)	0.5125 (4)	0.5913 (2)	0.1635 (3)	2.90
C (20)	0.6112 (3)	0.5200 (2)	0.1749 (3)	2.60
C (21)	0.1954 (3)	0.4708 (2)	0.0642 (3)	3.16
C (22)	0.1539 (4)	0.3826 (3)	0.0382 (3)	4.15
C (23)	0.0893 (4)	0.5340 (3)	0.0305 (3)	4.01
C (24)	0.7506 (4)	0.5402 (2)	0.1884 (3)	3.20
C (25)	0.7995 (4)	0.6287 (3)	0.1897 (3)	4.32
C (26)	0.8598 (4)	0.4761 (3)	0.2014 (3)	3.96
N (1)	0.1154 (4)	0.3128 (3)	0.0156 (4)	6.54
N (2)	0.	0.5794 (3)	0.	5.71
N (3)	0.8430 (4)	0.6991 (3)	0.1941 (4)	7.20
N (4)	0.9511 (4)	0.4278 (3)	0.2102 (4)	5.99

(b) H atoms with isotropic temperature factors.

Atom	x	y	z	B/Å^2
H (1A)	0.335 (4)	0.714 (3)	0.183 (3)	4.2 (8)
H (1B)	0.208 (4)	0.673 (3)	0.117 (3)	4.6 (8)
H (2A)	0.188 (4)	0.676 (3)	0.306 (3)	5.4 (9)
H (2B)	0.127 (5)	0.588 (3)	0.257 (3)	4.9 (8)
H (5)	0.410 (4)	0.723 (3)	0.384 (3)	4.8 (8)
H (6)	0.624 (5)	0.783 (3)	0.446 (3)	5.6 (9)
H (7)	0.809 (5)	0.672 (3)	0.479 (4)	5.9 (9)
H (8)	0.779 (4)	0.520 (3)	0.457 (3)	4.6 (8)
H (11)	0.380 (4)	0.349 (3)	0.350 (3)	4.1 (7)
H (12)	0.203 (4)	0.450 (3)	0.309 (3)	4.7 (8)
H (13A)	0.744 (5)	0.410 (3)	0.383 (4)	5.7 (9)
H (13B)	0.650 (5)	0.331 (3)	0.398 (4)	6.1 (9)
H (14A)	0.577 (4)	0.303 (3)	0.224 (3)	4.7 (8)
H (14B)	0.722 (4)	0.345 (3)	0.218 (3)	5.0 (8)
H (16)	0.382 (4)	0.355 (2)	0.139 (3)	2.9 (6)
H (19)	0.553 (4)	0.650 (2)	0.178 (3)	3.5 (6)

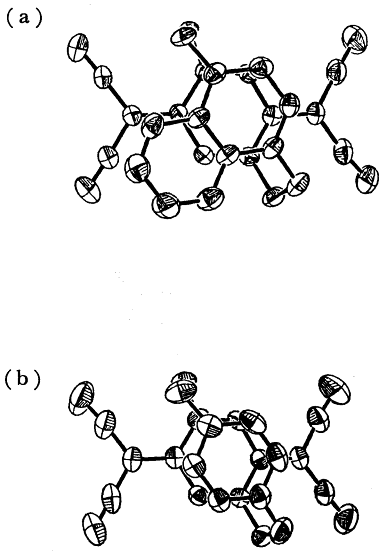

Fig. 1. A perspective view of the TCNQ-N^{1,4} molecule (a) compared with that of TCNQ-X (b). Non-hydrogen atoms are expressed as thermal ellipsoids with 50% probability level. Hydrogen atoms are omitted for clarity.

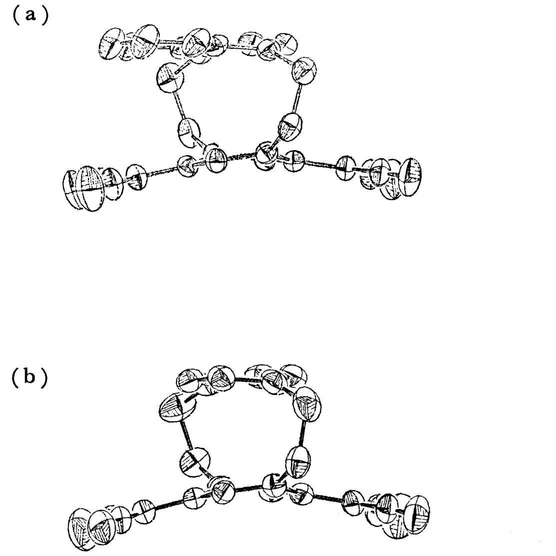

Fig. 2. A side view of the TCNQ-N^{1,4} molecule (a) compared with that of TCNQ-X (b).

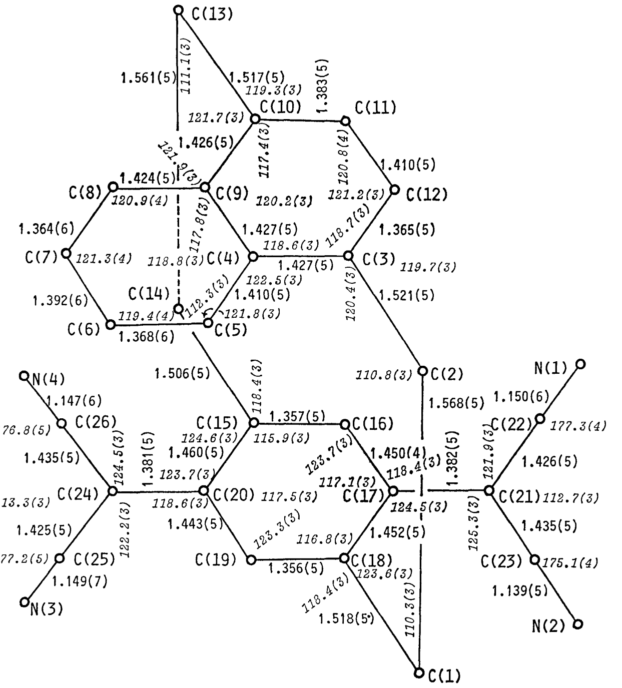

Fig. 3. Bond distances(l/Å) and bond angles(ϕ/°) in the TCNQ-N^{1,4} molecule (Estimated standard deviations in parentheses).

plane made by the C(4), C(9), C(11), and C(12). The C(3)–C(2) and C(10)–C(13) bonds are further bent down by 11.0 and 12.6° from planes defined by the C(3), C(4), and C(12) atoms and by the C(9), C(10), and C(11), respectively.

The TCNQ moiety has a twisted structure. The central six-membered ring is in a boat form, the planes formed by the C(17), C(18), and C(19) atoms and by the C(15), C(16), and C(20) are bent up from the mean plane defined by the C(16), C(17), C(19), and C(20) by 15.8 and 14.4°, respectively. On the other hand, both of the two C(CN)$_2$ portions slightly bent down from the mean plane. The C(17)–C(21) and C(20)–C(24) vectors respectively make angles of 10.7 and 9.2° with the mean plane formed by the C(16), C(17), C(19), and C(20) atoms. Two C(CN)$_2$ planes have tilt angles of 12.4 and 9.4° to the mean planes mentioned above. The deviations of C(14)–C(15)–C(20), C(15)–C(20)–C(24), C(20)–C(24)–C(26), C(1)–C(18)–C(17), C(18)–C(17)–C(21), and C(17)–C(21)–C(23) angles[av. 124.4°] from 120° are observed, which are considered as due to the repulsions between C(CN)$_2$ portions and –(CH$_2$)$_2$– bridges.

Two –(CH$_2$)$_2$– bridges are twisted: the torsion angles about their central C–C bonds are 29.8 and 26.2°.

As described above, the electron donor and electron acceptor moieties in the present molecule are no more planar after they were linked by two –(CH$_2$)$_2$– bridges: a half of the naphthalene moiety deformed into a boat form and the TCNQ moiety changed into a twisted structure. These deformations probably caused the electronic state in these moieties unfavorable to the charge-transfer interaction. In the similar manner little charge-transfer interaction between the benzene and TCNQ and p-methoxybenzene and TCNQ moieties respectively in the TCNQ-X and TCNQ-X-(OMe)$_2$ molecules can be explained well.

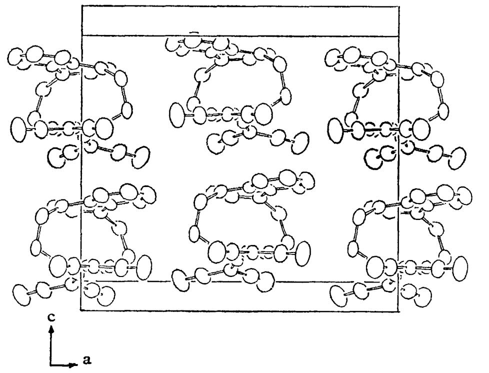

Fig. 4. A perspective view of the crystal structure of TCNQ-N^{1,4}.

Table 2. Short intermolecular atomic contacts (l/Å) less than 3.5 Å, with estimated standard deviations in parentheses

C(25)···N(2)^{a}	3.495(5)	C(21)···C(12)^{c}	3.368(4)
N(4)···C(21)^{a}	3.355(5)	C(3)···C(22)^{c}	3.412(5)
N(4)···C(22)^{a}	3.311(5)	C(4)···C(16)^{c}	3.489(4)
N(4)···C(23)^{a}	3.328(6)		
N(3)···N(1)^{b}	3.465(7)	Key: a, $1+x$, y, z;	
C(16)···C(4)^{b}	3.489(4)	b, x, $1-y$, $-0.5+z$;	
C(21)···C(3)^{b}	3.430(4)	c, x, $1-y$, $0.5+z$.	

Crystal Structure. A perspective view[7)] of the crystal structure is shown in Fig. 4. Short intermolecular atomic contacts less than 3.5 Å are given in Table 2. Most of them are involved between the neighboring TCNQ moieties.

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