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Dichalcogen-Bridged Acenaphthenes as New Electron Donors

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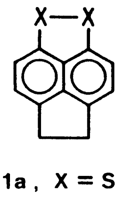
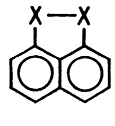
Three new electron donors, 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole (**1a**), -diselenole (**1b**), and -ditellurole (**1c**) have been prepared with a view to developing new electron donors for low-dimensional molecular complexes. Their donor characters are markedly enhanced as compared with the corresponding dichalcogen-bridged naphthalenes. They formed charge-transfer complexes with tetracyanoquinodimethane (TCNQ). Their electrical conductivities increase in the order of polarizable chalcogen. The crystal structures of **1a**–TCNQ complex and neutral **1c** were determined by X-ray analyses. In the crystal, **1a** and TCNQ form a unique mixed stack, that is, a pair of donors and a pair of acceptors make an alternately stacking column. Neutral **1c** takes an almost planar conformation and molecules are connected to each other with strong Te–Te interactions.

Polycyclic aromatic compounds bearing peri-dichalcogen bridges, as represented by tetrathiotetracene (TTT), have been recognized as good electron donors for the formation of low-dimensional molecular complexes.[1] Although a number of tetrathiafulvalene (TTF) derivatives possessing alkyl or heteroatom substituents have been synthesized and have attracted much attention, there have been known few examples of chemical modifications of TTT-type donors. Meinwald et al. reported that even simple 1,8-dichalcogen-bridged naphthalenes **2a**—**c**, when the chalcogen was replaced by heavy element such as tellurium, could form a conducting charge-transfer (CT) complex with tetracyanoquinodimethane (TCNQ),[2] and they and we extended its study to acenaphthylene[3] and fluoranthene[4] system, respectively. In both cases, a donor character of peri-dichalcogenonaphthalene was rather reduced by the expansion of the π-system at another peri-position. We have recently reported the syntheses and some physical properties of 1,8:4,5-bis(dichalcogeno)-2,3,6,7-tetramethylnaphthalenes as the first example of alkyl-substituted TTT-type donors.[5] However, a marked enhancement of their donor characters, predicted by an electron-releasing effect of the methyl groups, was not observed for the sulfur nor selenium derivatives.[6] This is presumably a result of a lowering of the molecular planarity caused by steric repulsion.

Now we wish to report the syntheses of 5,6-dichalcogen-bridged acenaphthenes **1a**—**c** and their properties as electron donors. The introduced methylene groups are not only located in opposite peri-positions of dichalcogen bridge but also bound together so as not to bring about steric repulsion, therefore being capable of increasing the donor character.



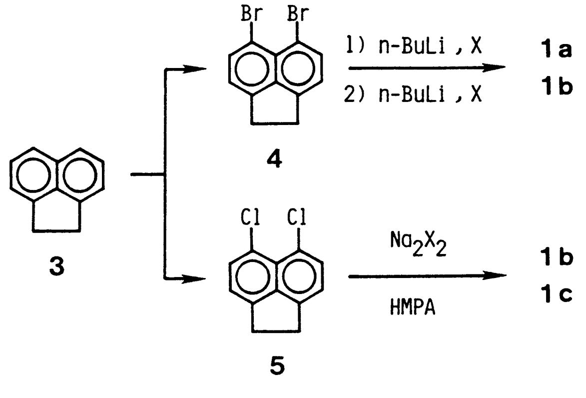
1a, X = S
1b, X = Se
1c, X = Te



2a, X = S
2b, X = Se
2c, X = Te

Results and Discussion

Syntheses and Properties. 5,6-Dichalcogen-bridged acenaphthenes **1a**—**c** were synthesized starting from acenaphthene (**3**) (Scheme 1). 5,6-Dibromoacenaphthene (**4**) was prepared by bromination of **3** according to a reported method.[3] A reaction of 5,6-dilithioacenaphthene, generated from **4** and 2 equiv of butyllithium, with elemental chalcogen gave a complex mixture. However, the sequential reactions of **4** with 1 equiv of butyllithium, 1 equiv of elemental chalcogen, second 1 equiv of butyllithium, and 1 equiv of elemental chalcogen and subsequent air-oxidation resulted in the formation of **1a** (17%) or **1b** (6%). The tellurium analogue **1c** could not be obtained by the same series of reactions. On the other hand, 5,6-dichloroacenaphthene (**5**), prepared by the chlorination of **3** with sulfuryl chloride in the presence of aluminium chloride,[7] was submitted to a reaction with Na_2Te_2 in hexamethylphosphoric triamide (HMPA) to yield **1c** (5%). Furthermore, treatment of **5** with Na_2Se_2 gave **1b** in an improved yield (16%).



Scheme 1.

In the electronic spectra of compounds **1a**—**c**, marked bathochromic shifts of the longest wavelength absorptions, which were assigned to π-σ^* transition,[8] were observed in the order of polarizable chalcogens, indicating an increased electronic interaction between the naphthalene chromophore and the heavy chalcogen, $\lambda_{\max}$ in tetrahydrofuran (THF); **1a**: 422; **1b**: 550; **1c**: 691 nm. This phenomenon is common to the dichalcogen-bridged arenes.[4,5] More interestingly, the corresponding absorptions of naphthalene series, $\lambda_{\max}$ (THF); **2a**: concealed behind a strong shorter wavelength absorption at 368 nm; **2b**: 512; **2c**: 685 nm,[9] are shifted to longer wavelength by introduction of the ethylene bridge, reflecting an elevated π-HOMO level due to its electron-releasing effect. Its magnitude, however, decreases with increasing polarizability of chalcogen. In the wavelength region of π-π^* transition, the absorptions of **1b** are quite similar to those of **1a** except for slight bathochromic shifts whereas those of **1c** are considerably different in shape (cf. experimental section). This specificity of the tellurium derivative, also observed in naphthalene series, may be attributed to geometrical as well as electronic perturbation of very large and polarizable ditelluro bridge on the π-system of naphthalene.

The cyclic voltammograms of compounds **1a**—**c** exhibited one reversible wave corresponding to apparent one-electron oxidation,[8] and the second one was not observed in the measurable region. Their half-wave potentials $E_{1/2}$ are given in Table 1, together with those of peri-dichalcogenonaphthalenes **2a**—**c**. The donor strength of **1a**—**c** increases with introduction of the heavy chalcogen. Moreover, the ethylene bridges evidently exert an electron-donating perturbation on the π-system. These results are consistent with the electronic interactions stated above. Once again the effect of ethylene bridge decreases in the order of chalcogen triad and, in other words, is proportional to the oxidation potential of the naphthalene derivative. This is understandable as follows: The π-HOMO level of dichalcogen-bridged naphthalenes is raised in the order of polarizable chalcogen, and accordingly the interaction of the HOMO with ethylene bridge (hyperconjugation) decreases in the same order due to an increasing energy gap between the two interactive orbitals. It is worth noting that the oxidation potential of tellurium compound **1c** is the quite same as the first one of TTF (+0.33 V under the same conditions listed in Table 1) which forms a metallic complex with TCNQ.

Table 1. Half Wave Oxidation Potentials of **1** and **2** (V vs. Ag/AgCl)[a]

X	S	Se	Te
1	0.68	0.57	0.32
2	0.94	0.77	0.43

a) Measured by cyclic voltammetry in 0.1 mol dm^{-3} Bu_4NClO_4/CH_2Cl_2 at a glassy-carbon working electrode.

Table 2. Physical Properties of CT Complexes

CT complex	**1a**-TCNQ	**1b**-TCNQ	**1c**-TCNQ
Crystal form	black needles	black needles	black powder
Composition[a]	1 : 1	1 : 1	1 : 1
ΔE[b]	0.43	0.32	0.07
$\nu_{CN}/\mathrm{cm}^{-1}$	2211	2216	2172
$\sigma/\mathrm{S\,cm}^{-1}$	1.0×10^{-8}[c]	1.0×10^{-5}[c]	1.8×10^{-1}[d]

a) Determined by elemental analysis. b) See text. c) Measured on a single crystal by two-probe method. d) Measured on a compressed pellet by four-probe method.

Compounds **1a** and **1b** readily formed black crystalline 1 : 1 CT complexes with TCNQ in THF. Tellurium compound **1c** was resistant to complexation with TCNQ (in THF or dichloromethane), and even if the complex was formed (in chloroform), its stoichiometry was rich in donor and lack of reproducibility. From chlorobenzene solution the 1 : 1 complex was eventually obtained under an atmosphere of nitrogen. Their physical properties are listed in Table 2. The difference between the half-wave potentials of donor and acceptor (TCNQ: +0.25 V under the same conditions listed in Table 1), ΔE, is known to be a measure to predict electrical properties of the complex.[10] From the ΔE value for each complex, therefore, it is predictable that **1a**-TCNQ and **1b**-TCNQ are non- or slightly ionic and **1c**-TCNQ is in incomplete CT state. Complexation with **1a** and **1b** caused slightly lower shifts in the nitrile stretching frequency of TCNQ, but with **1c** led to a great shift, supporting a large charge transfer in **1c**-TCNQ.[11] Electrical conductivities of **1a**-, **1b**-, and **1c**-TCNQ complexes increase in that order, reflecting the estimated degree of CT.

Crystal Structure. The crystal structures of **1a**-TCNQ complex and neutral **1c** were determined by X-ray analysis.

Complex 1a-TCNQ: The crystal composition is one donor and one acceptor, and both molecules take quite planar conformations. As shown in Fig. 1, they form unusual modified mixed stacking columns along [111] direction. A pair of donors and a pair of acceptors make an alternately stacking column.[12] A mixed stacking is often observed in low conductive CT complexes and, in such cases, the overlapping pattern is usually "direct" overlap or slightly "shifted" form so as to facilitate CT interaction.[13] As shown in Fig. 2, the donor and the acceptor overlapping of this complex is not of such type. The long molecular axis of TCNQ and **1a** are twisted to ca. 40°. The donors are overlapped head to tail, and there exist no short intrastack interactions of the S-S nor S-N type. On the other hand, there exist somewhat short interstack contacts; the shortest S-N distance of 3.39 Å is approximately equal to the van der Waals distance of S-N

(3.35 Å).[14] Applying the method of Kistenmacher et al.[15] to estimating the degree of CT based on TCNQ geometry, we calculated it at 0.12, a value which indicates a small CT.

Neutral 1c: In the crystal, **1c** maintains the almost planar molecular structure though substitution of very large and long (2.748 Å) ditelluro bridge considerably distorts bond length and angles of acenaphthene skeleton in its molecular plane, and this is consistent with the inference from the electronic spectrum. As shown in Fig. 3, the molecules are stacked along c axis, forming the tellurium columns, and also arranged side by side along a axis forming linear chains of tellurium atoms. Moreover, each column is arranged along b axis alternately with opposite orientation of ditelluro bridge, and hence there exist the tellurium layers in the ac plane. Intrastack Te–Te distances of 4.15 and 4.37 Å are somewhat longer than the sum of the corresponding van der Waals distance (4.12 Å).[14] A more interesting feature in the crystal is the strong interactions between adjacent columns caused by shorter Te–Te contacts; the shortest one goes down to 3.57 Å (Fig. 4). In adjacent columns along b axis, the positions of ditelluro bridges are shifted one another to c axis by one half of unit (Fig. 3, left). Therefore, each molecule is connected with other four molecules by strong Te–Te interactions (Fig. 4), that is, molecule A is connected with two molecules B and B′ by Te(2)–Te(2) (3.75 Å) and Te(2)–Te(1) (3.93 Å) interactions and also connected with two molecules C and C′ by Te(1)–Te(1) (3.57 Å) interaction. These situations result in the formation of a two-dimensional sheet-like tight network in the ac plane.

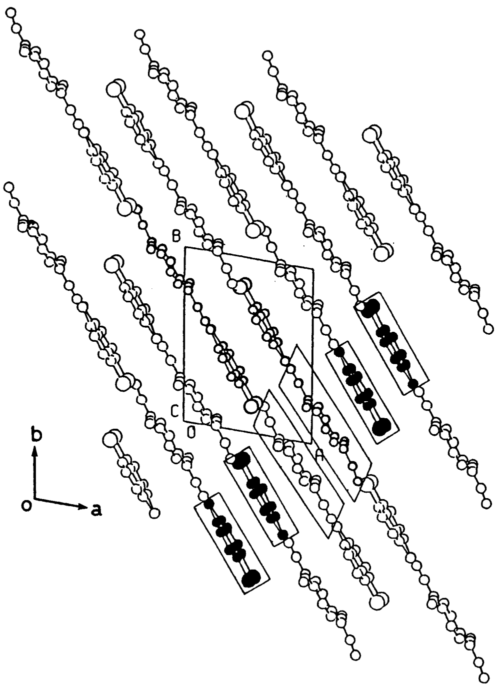


Fig. 1. Crystal structure of **1a**–TCNQ projected along c axis.

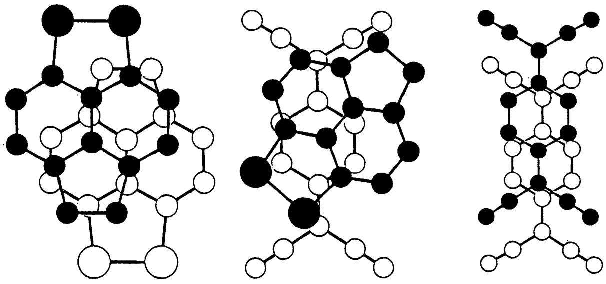


Fig. 2. Molecular overlapping patterns viewed perpendicular to the molecular plane.

Conclusion

The electron-donating character of dichalcogen-bridged naphthalene could be markedly enhanced by introduction of alkyl group without lowering the molecular planarity. Neither that of dithio- nor diseleno-bridged acenaphthene, however, was high enough to bring about an incomplete charge transfer in the TCNQ complex. Moreover, the result of X-ray analysis of **1a**–TCNQ indicated that the donor and the acceptor formed unusual mixed-staking columns probably due to the strong electronic and/or structural disorder of **1a**, and that this complex was characterized by a small CT, weak intrastack interactions, and tight interstack S–N interactions. The oxidation potential

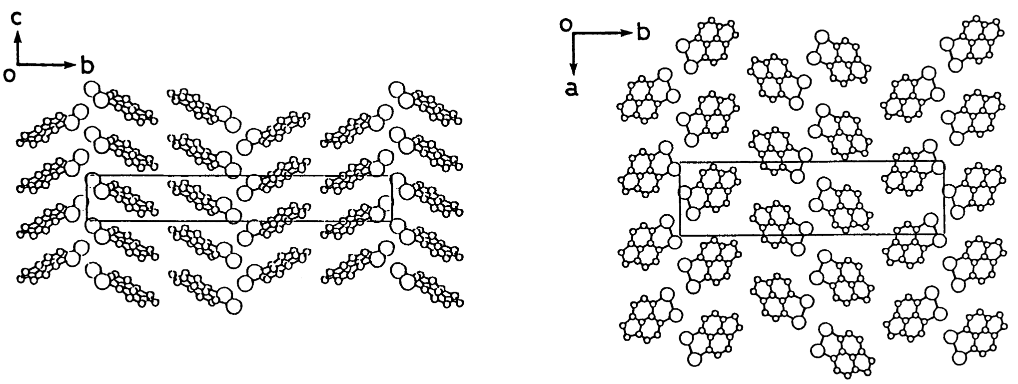


Fig. 3. Crystal structure of neutral **1c** projected along a axis (left) and c axis (right).

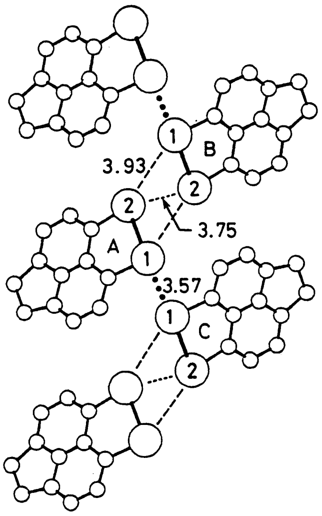


Fig. 4. The network of **1c** molecules projected along c axis. Close intermolecular Te–Te distances are illustrated. The symmetry operations are A (x,y,z), B ($-0.5-x,2.0-y,0.5+z$), B′ ($-0.5-x,2.0-y,-0.5+z$), C ($0.5-x,2.0-y,0.5+z$), and C′ ($0.5-x,2.0-y,-0.5+z$).

of **1c** was low enough, so that it formed a highly conducting TCNQ complex. In the crystal the molecules of **1c** associated to form densely packed tellurium layers resulting from the very strong Te–Te interactions. This marked tendency to aggregate seems to be reflected in low crystallinity of the CT complex and in its composition rich in donor. Such intermolecular strong interactions, however, are preferable for the enhancement of dimensionality of molecular complexes, especially for radical cation salts.[16] Finally, this study suggests that an enhancement of dimensionality of the CT complex as well as an increase in the donor strength may be achieved by the introduction of alkyl groups to a highly symmetrical doubly ditelluro-bridged arene without steric repulsion and a lowering of the symmetry. This is our target for future studies.

Experimental

General. All the melting points were uncorrected. Mass spectra were determined with a JEOL JMS-DX300 mass spectrometer. Proton NMR spectra were recorded with a JEOL JNM-PMX-60 spectrometer. Electronic spectra were measured with a JASCO UVIDEC-610A double beam spectrophotometer. Infrared spectra were recorded on a Hitachi infrared spectrophotometer, Model 260-30. The cyclic voltammetry was carried out at room temperature under nitrogen using a Hokuto Denko potentiostat/galvanostat HA-301 and a function generator HB-104. Gel-permeation liquid chromatography was carried out using a Japan Analytical Industry LC-08 liquid chromatograph, equipped with JAIGEL 1H and 2H columns, with chloroform as eluent.

Preparation of the Donors. 5,6-Dihydroacenaphtho[5,6-*cd*]-1,2-dithiole (1a): To a stirred solution of 5,6-dibromoacenaphthene (**4**)[3] (312 mg, 1.00 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (232 mg, 2.00 mmol) in THF (30 cm^3) was slowly added a 1.6 mol dm^{-3} hexane solution of butyllithium (0.64 cm^3, 1.0 mmol) at −78 °C under argon. After the mixture was stirred for 15 min at −78 °C, sulfur (32 mg, 1.0 mmol) was added, and stirring was continued at −40—−30 °C for 2 h. After the mixture was cooled again to −78 °C, it was treated with butyllithium (0.64 cm^3, 1.0 mmol) and then sulfur (32 mg, 1.0 mmol) in the same way as described above. The mixture was quenched with acetic acid (0.2 cm^3), followed by exposure to air stream for oxidation. The resulting solution was concentrated under reduced pressure. After water was added, the mixture was extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. After the solvent was removed under reduced pressure, the residue was purified by gel-permeation liquid chromatography and recrystallized from hexane to give 37 mg (17%) of **1a** as reddish brown prisms: mp 190.3 °C; MS (70 eV) m/z 216 (M^+); ^1H NMR (CCl_4) δ=3.25 (4H, s) and 6.90 (4H, s); UV (THF) 250 (ε 19600), 351 (11500), 369 (14000), and 422 nm (99.1); Anal. ($C_{12}H_8S_2$) C, H.

5,6-Dihydroacenaphtho[5,6-*cd*]-1,2-diselenole (1b): The title compound was prepared as described for **1a** (6%), and also as follows. To a solution of sodium diselenide, which was in situ prepared by heating sodium (308 mg, 13.4 mmol) and selenium (1.06 g, 13.4 mmol) at 120 °C for 2 h in HMPA (30 cm^3) under an argon atmosphere, was added a solution of 5,6-dichloroacenaphthene (**5**)[7] (1.00 g, 4.47 mmol) in HMPA (15 cm^3), and the mixture was stirred at 140 °C for 30 h. To the resulting solution were added brine (30 cm^3) and acetic acid (15 cm^3) with vigorous stirring. The resulting suspension was extracted with CS_2, and the extract was washed with water, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residual solid was recrystallized from CS_2-hexane (3/1 volume ratio), purified with gel-permeation liquid chromatography, and again recrystallized from benzene to give 220 mg (16%) of **1b** as deep violet prisms: mp 208—213 °C; MS (70 eV) m/z 312 (M^+); ^1H NMR (CS_2) δ=3.22 (4H, s), 6.90 (2H, d, J=7 Hz), and 7.12 (2H, d, J=7 Hz); UV (THF) 259 (ε 10000), 379 (15000), and 550 nm (73.1); Anal. ($C_{12}H_8Se_2$) C, H.

5,6-Dihydroacenaphtho[5,6-*cd*]-1,2-ditellurole (1c): To a solution of sodium ditelluride, which was in situ prepared by heating sodium (154 mg, 6.71 mmol) and tellurium (856 mg, 6.71 mmol) at 125 °C in HMPA (20 cm^3) for 2 h under an argon atmosphere, was added a solution of **5** (500 mg, 2.24 mmol) in HMPA (15 cm^3), and the mixture was stirred at 150 °C for 31 h. The mixture was poured into water and extracted with CS_2. The extract was washed with water, dried over anhydrous magnesium sulfate, and then concentrated under reduced pressure. To the residual oil was added water, and the precipitated solid was filtered off, washed with acetone-water (1/1 volume ratio), and recrystallized from CS_2-hexane (3/1 volume ratio) to give 46 mg (5%) of **1c** as greenish black needles: mp 231 °C (decomp); MS (70 eV) m/z 408 (M^+); ^1H NMR (CS_2) δ=3.29 (4H, s), 6.92 (2H, d, J=7 Hz), and 7.15 (2H, d, J=7 Hz); UV (THF under argon) 223 (ε 3920), 258 (sh, 4830), 302 (1570), 404 (10400), 498 (2500), and 691 nm (134); Anal. ($C_{12}H_8Te_2$) C, H.

Preparation of Charge-Transfer Complexes. Both **1a**-TCNQ and **1b**-TCNQ complexes were prepared by mixing THF solutions of the donor and the acceptor in the same flask and standing for a few days. In the case of **1c**-TCNQ, hot chlorobenzene solutions of **1c** and TCNQ were mixed

Table 3. Crystallographic Data

	1a-TCNQ	**1c**
Chemical formula	$C_{24}H_{12}S_2N_4$	$C_{12}H_8Te_2$
FW	420.15	407.40
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	9.647(1)	8.137(3)
b/Å	12.181(1)	29.241(12)
c/Å	8.797(2)	4.364(4)
α/°	93.96(1)	
β/°	109.32(1)	
γ/°	97.65(1)	
V/Å^3	959.7(2)	1038.4(10)
Z	2	4
D_m/g cm^{-3}	1.439	2.572
D_c/g cm^{-3}	1.456	2.606
R	0.038	0.065
$2\theta_{max}$/°	126	126
No. of non-zero unique data	3037	1003
Crystal size/mm	$0.21\times0.10\times0.50$	$0.06\times0.04\times0.60$

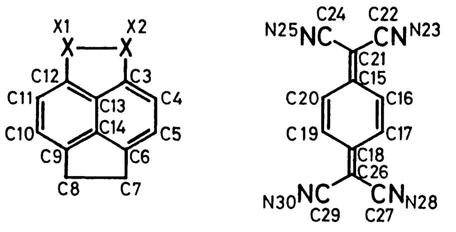


Fig. 5. Atomic numbering scheme of dichalcogen-bridged acenaphthene (left) and TCNQ (right).

under an atmosphere of nitrogen and stood at 0 °C for 15 min to give a black fine solid. The 1 : 1 stoichiometry of donor and acceptor was determined by elemental analyses which agreed with calculated values within ±0.3% for C, H, and N. Their properties are summarized in Table 2.

Table 4. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Thermal Parameters

1a-TCNQ	x	y	z	$B_{eq}/10^2$ Å^2 [a]
S1	5663(1)	1784(0)	7706(1)	380(1)
S2	5296(1)	1560(0)	9899(1)	420(1)
C3	4321(2)	2684(1)	9888(2)	311(4)
C4	3760(2)	3056(2)	11060(2)	376(4)
C5	2997(2)	3978(2)	10863(2)	378(4)
C6	2778(2)	4517(1)	9487(2)	322(4)
C7	2060(2)	5520(2)	8895(3)	380(5)
C8	2166(2)	5591(2)	7173(3)	419(5)
C9	3042(2)	4684(1)	6933(2)	334(4)
C10	3564(2)	4345(2)	5725(2)	397(5)
C11	4376(2)	3447(2)	5888(2)	388(5)
C12	4645(2)	2891(1)	7259(2)	317(4)
C13	4104(2)	3227(1)	8483(2)	290(4)
C14	3332(2)	4112(1)	8310(2)	295(4)
C15	10400(2)	1885(1)	7481(2)	292(4)
C16	11092(2)	958(2)	8136(2)	320(4)
C17	11767(2)	371(1)	7318(2)	313(4)
C18	11837(2)	658(1)	5777(2)	287(4)
C19	11138(2)	1581(1)	5116(2)	304(4)
C20	10454(2)	2160(1)	5930(2)	303(4)
C21	9699(2)	2475(2)	8315(2)	328(4)
C22	9639(2)	2220(2)	9863(3)	399(5)
N23	9594(3)	2018(2)	11102(3)	585(6)
C24	8980(2)	3378(2)	7669(2)	360(4)
N25	8422(2)	4107(2)	7141(2)	499(5)
C26	12538(2)	66(1)	4946(2)	313(4)
C27	13210(2)	−871(2)	5536(2)	359(4)
N28	13731(2)	−1637(2)	5964(3)	523(5)
C29	12583(2)	311(2)	3389(2)	366(4)
N30	12606(3)	477(2)	2129(2)	536(6)
1c	x	y	z	$B_{eq}/10^2$ Å^2 [a]
Te1	907(2)	9810(1)	3914(6)	291(10)
Te2	−1992(2)	9499(1)	1446(6)	300(10)
C3	−697(27)	8946(7)	−121(66)	201(56)
C4	−1422(39)	8619(10)	−2142(75)	303(76)
C5	−582(38)	8220(11)	−3339(91)	376(80)
C6	1059(38)	8162(9)	−2360(90)	327(80)
C7	2326(38)	7785(19)	−3069(105)	404(95)
C8	3911(50)	7944(11)	−1450(154)	570(127)
C9	3509(36)	8396(10)	4(108)	440(107)
C10	4348(28)	8690(11)	1806(97)	383(89)
C11	3615(32)	9093(11)	2985(119)	410(107)
C12	1955(28)	9212(7)	2505(65)	223(55)
C13	1050(29)	8886(8)	602(79)	246(69)
C14	1834(37)	8502(10)	−568(83)	324(77)

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$.

Crystal Structure Analysis. The X-ray diffraction data were collected by use of an automated four-circle diffractometer, Rigaku AFC-5, set on a rotating anode X-ray generator, Rigaku RU-200, with a graphite monochromated Cu radiation (Cu $K\alpha$=1.5418 Å). Crystallographic data are listed in Table 3. Crystal structures were solved by the Monte-Carlo direct method[17] using MULTAN 78 program system[18] and were refined on F^2 by the full-matrix least-squares program with the analytical absorption correction.[19] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[20] Anisotropic temperature factors were used for the refinement of the non-H atoms. The hydrogen atoms of **1a**-TCNQ complex were located from difference Fourier maps and were refined with the isotropic temperature factors equivalent to that of the bonded carbon atoms. In the case of neutral **1c**, the H atoms were not included in the refinement. The atomic numbering scheme and the final atomic parameters are listed in Fig. 5 and Table 4, respectively. All estimated standard deviations for intermolecular atomic distances mentioned in the text were 0.00, and that for the Te–Te bond length of **1c** was 0.002. All computations were carried out at the Computation Center of Nagoya University using the library program of CRYSTAN system. Tables of structure factors, anisotropic thermal parameters, coordinates of hydrogen atoms, bond lengths, and bond angles are deposited as Document No. 8797 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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