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An Anion Radical Salt of a Quinone Fused with 1,3-Dithiole Units. Crystal and Molecular Structure of a Tetraethylammonium Salt of 2,6-Dithioxobenzo[1,2-*d*:4,5-*d'*]-bis[1,3]dithiole-4,8-dione

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Synopsis. Crystal structure of the title salt was determined by the X-ray analysis. Segregated columnar stacks of anion radicals are formed along the c axis, in which quinone molecules are not spaced equally but forming dyads with short contacts between sulfur atoms.

We have recently found that the quinones fused with sulfur heterocycles such as 1,3-dithiole rings possess strong electron affinities to give highly conductive CT complexes with tetrathianaphthacene (TTN) or tetrathiafulvalene (TTF) derivatives.[1)] For example, quinone **1** formed CT complexes with TTN and tetramethyltetraselenafulvalene (TMTSF) whose electrical resistivities measured on compaction samples at room temperature are 9.9 Ω cm and 2.4 Ω cm, respectively. It is expected in these highly conductive complexes that the quinone molecules may form segregated columnar stacks with some interheteroatom interactions which can stabilize the metallic state by forming two-dimensional networks. However, unfortunately the crystallization of these complexes have still been unsuccessful. On the other hand, the anion radicals of quinone **1** have been isolated as stable salts.[1)] To investigate the possible interheteroatom interactions in the negatively charged quinone molecules, we carried out the X-ray structural analysis of the title salt which was obtained as suitable single crystals. The role of the 1,3-dithiole rings which enhance the electron affinity of the quinone skeleton is discussed from the view point of the molecular structure.

Experimental

Material. Quinone **1** was prepared according to the literature.[2)] The title 1:1 anion radical salt was prepared by the reaction of quinone **1** (64 mg) with tetraethylammonium iodide (514 mg, 10 equivalents) in hot dry acetonitrile (40 ml). Black needles of the salt thus obtained (85 mg, decomp. 240—241 °C) show the following analytical values, Calcd for $C_{16}H_{20}NS_6O_2$: C, 42.64; H, 4.47; N, 3.11%. Found: C, 42.43; H, 4.43; N, 3.11%. Its electrical resistivity (ρ_{RT}) measured on a compaction sample at room temperature was 1.2×10^7 Ω cm. Single crystals were obtained when the hot acetonitrile solution was cooled slowly. When four equivalents of the iodide were used, green-black needles (mp > 400 °C) were obtained whose molar ratio was determined to be 1:2 on the basis of the elemental analysis. Calcd for $C_{24}H_{20}NS_{12}O_4$: C, 37.38; H, 2.61; N, 1.82%. Found: C, 37.30; H, 2.54; N, 1.93%. The resistivity (ρ_{RT}) of the 1:2 salt was 8.7×10^3 Ω cm.

Table 1. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Factors (Å^2)

Atom	*X*	*Y*	*Z*	B_{eqv}[a)]
S 1	8676(1)	531(2)	3282(3)	4.2
S 2	1370(1)	590(2)	1066(3)	4.0
S 3	7675(1)	2034(1)	2206(2)	3.1
S 4	2439(1)	−820(1)	1998(2)	2.9
S 5	6163(1)	−882(1)	3279(2)	3.0
S 6	3930(1)	2093(1)	917(2)	3.0
O 1	6472(3)	3370(3)	1033(6)	3.5
O 2	3704(3)	−2072(3)	2777(6)	3.7
C 1	7574(5)	569(5)	2938(8)	3.0
C 2	2525(4)	634(5)	1297(8)	2.8
C 3	6248(4)	1315(5)	2000(8)	2.4
C 4	3917(4)	−32(4)	1903(7)	2.4
C 5	5540(4)	−67(4)	2481(7)	2.4
C 6	4618(4)	1339(4)	1417(7)	2.3
C 7	4337(4)	−834(5)	2408(8)	2.7
C 8	5841(4)	2121(4)	1422(7)	2.4
N	1976(4)	4051(4)	5543(6)	2.7
C 11	1071(5)	3330(5)	7670(9)	3.4
C 12	1020(6)	4251(7)	8322(11)	5.1
C 21	3241(5)	5099(6)	5473(9)	3.8
C 22	3676(6)	4530(8)	7022(12)	5.5
C 31	1842(6)	2920(6)	5178(9)	4.1
C 32	2661(8)	3423(8)	3135(12)	6.6
C 41	1734(5)	4853(5)	3842(8)	3.3
C 42	487(6)	4029(7)	3741(11)	4.7

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

Structural Analysis. A needle-like crystal with the dimensions of $0.15\times0.15\times0.25$ mm^3 was used for the data collection on a Rigaku AFC-5R automated four-circle diffractometer. A total of 4366 reflections within $2\theta=52°$ was collected using graphite monochromated Mo *Kα* radiation ($\lambda=0.71069$ Å). Crystal data are as follows: MF $C_{16}H_{20}NS_6O_2$, MW 450.72, triclinic, $P\bar{1}$, $a=14.300(1)$, $b=13.243(1)$, $c=7.251(1)$ Å, $\alpha=69.58(1)$, $\beta=86.73(1)$, $\gamma=124.56(1)°$, $V=1000.2(3)$ Å^3, $Z=2$, $D_{calcd}=1.50$ g cm^{-1}. The structure was solved by the direct method using RANTAN 81[3)] with some modification whereby only quinone molecule appeared in the Fourier map. After the block-diagonal least-squares refinement for these atoms, the remaining atoms of the ammonium ion were located in the difference Fourier map. After the refinement with anisotropic temperature factors, all the hydrogen atoms were successively picked up from the difference Fourier map. The final R value is 4.36% for the 2636 reflections with $|F_o|>3\sigma|F_o|$. The final atomic coordinates are given in Table 1.

The atomic scattering factors from the International Tables for X-Ray Crystallography[4] were used. All the computation were carried out by an ACOS 1000 computer at Tohoku University using the applied library programs of UNICS III system.[5]

Results and Discussion

The crystal structure viewed along the b axis and the c axis are shown in Figs. 1 and 2. The quinone molecules form segregated columnar stacks along the c axis. These columns are linearly arranged to the a axis and separated by the ammonium ions along the b axis. In the column, the anion radicals are not equally spaced but pairing to form dyads. So there are two different modes of overlapping, and the quinone molecules are stacked parallel to each other in both overlapping. In the dyad, the overlapping is a well-known "ring-double bond" type[6] of a high symmetry with the short interplanar distance of 3.21 Å. There exist some short contacts such as C(7)-C(7) (3.13 Å) and O(2)-C(8) (3.11 Å) in this dyad, and particularly the S(4)-S(5) contact (3.42 Å) is quite shorter than the sum of van der Waals radii (3.70 Å)[7], indicating the strong interactions between sulfur atoms which may contribute to the dyad formation with "ring-double bond" type overlapping. Although the quinone molecule is nearly planar, slight deviations of atoms from the molecular plane are observed. These deviations afford the dihedral angles of 4.5° for the planes containing S(1)-S(3)-S(5) and C(3)-S(3)-S(5)-C(5), 2.5° for the planes containing C(3)-C(5)-C(4)-C(6) and O(2)-C(4)-C(5), and 2.3° for the planes containing C(4)-C(6)-(8)-C(7) and C(3)-C(5)-C(7)-C(8). Since molecules bow in the opposite direction in the dyad, this slight molecular defomation is considered to be accompanied by the short interplanar distance in the dyad which is formed in the crystal. Between the dyads, the interplanar distance (molecule C and D in Fig. 1) is 3.65 Å which is much longer than that in the dyad (molecule A and B), and the distances among the inner sulfur atoms are also long [S(3)-S(4) 3.90 Å, S(5)-S(6) 3.91 Å]. This type of segregated stack accompanied by the dyad formation is also observed in

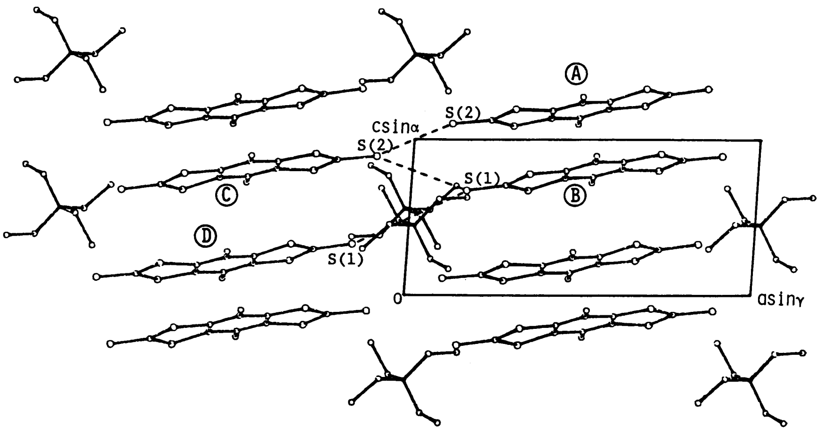


Fig. 1. Crystal structure viewed along the b axis. Molecules A—D are related by the following symmetry operations: A (x, y, z), B (1−x, −y, −z), C (−x, −y, −z), D (−1+x, y, −1+z). Intercolumn S-S contacts are indicated by broken line: 3.95 Å for molecule A and C, 4.04 Å for molecule B and C, 5.21 Å for molecule B and D.

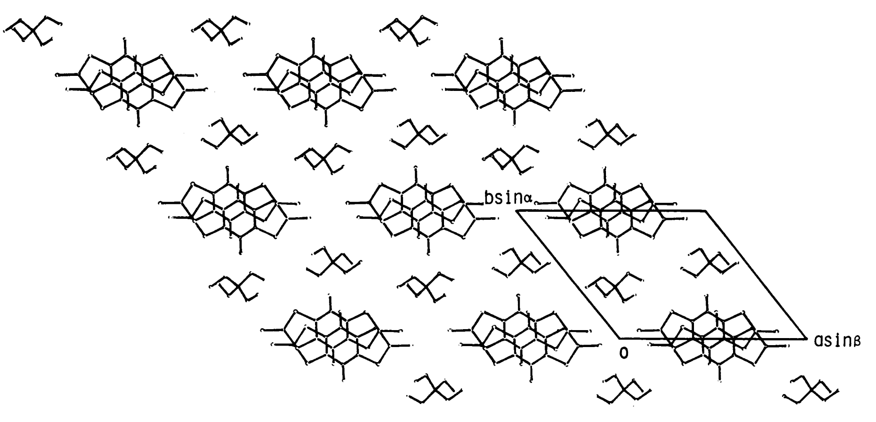


Fig. 2. Crystal structure viewed along the stacking c axis. Nitrogen atom of the ammonium ion is located on the same plane of the quinone molecule.

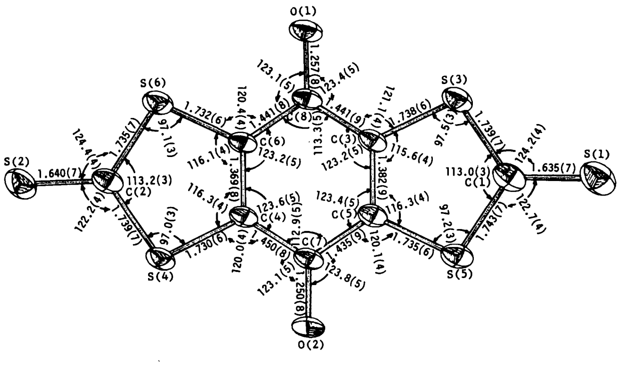
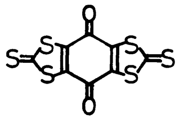


Fig. 3. Molecular geometry of quinone anion radical with bond lengths and angles.

the Et_4N^+ $(BTDA\text{-}TCNQ)_2^{\overline{\cdot}}$ anion radical salt which shows low electrical conductivity.[8] Therefore, the low conductivity of the present salt is accounted for by this dyad formation. However, it is noted that the segregated columnar stacks are formed with "ring-double bond" type overlapping, and this stacking motif is facilitated by the interaction between the sulfur atoms. This finding suggests that the highly conductive CT complexes of quinone **1** may have the segregated columnar stacks[9] which are facilitated by the S–S contacts observed here. Although the intercolumn interactions were also expected by the contacts between the terminal sulfur atoms, the distances among S(1) and S(2) are too long (3.95—5.21 Å, Fig. 1) to undergo such interactions.

The molecular geometry of the quinone anion radical is shown in Fig. 3. It is apparent that the C(8)=O(1) (1.257 Å) and C(7)=O(2) (1.250 Å) bonds are elongated than the corresponding bonds of ordinary neutral quinones (ca. 1.22 Å)[10] although those for the quinone **1** are not available. This means that the negative charge is largely localized on the carbonyl moieties, indicating that the anion radical mainly exists as the semiquinone form **2a**. The possibility of **2c** was excluded by considering the molecular overlapping in the dyad and the location of counter cation which may reflect the charge density of the anion radical species. However, the six-membered ring of **1** takes a quinoid structure and the bond lengths of S(1)=C(1) (1.635 Å) and S(2)=C(2) (1.640 Å) are longer than those of ordinary thiocarbonyl bonds (1.61 Å). This fact can be attributed to the contribution of the structure **2b**, in which aromatic 1,3-dithiolium cations are formed. This result leads to the conclusion that the electron affinity of the quinone **1** fused with 1,3-dithiole units is enhanced inductively by the contribution of the polarized form in the 1,3-dithiol-2-ylidene moieties.

Tables of observed and calculated structure factors, atomic positional parameters, anisotropic temperature factors, and bond lengths and angles are kept at the Chemical Society of Japan, Document No. 8755.



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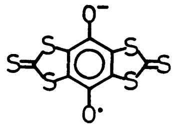
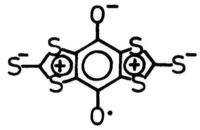
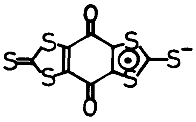


2a



2b



2c

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1) Y. Yamashita, T. Suzuki, G. Saito, and T. Mukai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1489.

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7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y. (1960), p. 260, Tables 7—20.

8) BTDA-TCNQ: bis[1,2,5]thiadiazolotetracyanoquinodimethan. T. Suzuki, C. Kabuto, Y. Yamashita, T. Mukai, T. Miyashi, and G. Saito, submitted for publication.

9) Generally, CT complexes of quinones tend to form mixed stacks with alternated overlapping of donors and acceptors which leads to low electrical conductivity.

10) The C=O bond lengths of quinones are as follows: 1.218 Å for benzoquinone (J. Trotter, *Acta Crystallogr.*, **13**, 86 (1960); 1.21 and 1.22 Å for naphthoquinone (J. Gaultier and C. Hauw, *Acta Crystallogr.*, **18**, 604 (1965)); 1.213 Å for anthraquinone (A. Prakash, *Acta Crystallogr.*, **22**, 439 (1967)).