CHEMISTRY LETTERS, pp. 445-448, 1990.

Benzo[g][1,2,5]thiadiazolo[3,4-b]quinoxaline-5,10-dione and Its Selenium Analogue. An Unusual Type of Quinones

Yoshiro YAMASHITA,* Yoshiaki TSUBATA,† Takanori SUZUKI,† Tsutomu MIYASHI,† Toshio MUKAI,† and Shoji TANAKA
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

The title compounds, which were prepared from 2,3-diamino-1,4-naphthoquinone, are stronger acceptors than the related naphthoquinones. The studies of the cyclic voltammogram and MO calculation revealed that upon reduction electrons are first accepted at the heterocyclic part.

Quinones fused with heterocycles have recently attracted considerable interests because of the interesting redox properties.$^{1)}$ [1,2,5]Thiadiazolo[3,4-b]pyrazine-fused quinones are expected to be strong electron acceptors because the heterocycle has a high electron affinity.$^{2)}$ The interaction between the heterocyclic part and the quinone part is also interesting. From these viewpoints, we have prepared the title compound **1a** and its selenium analogue **1b**, and investigated their properties.

Quinone **1a** was prepared as follows. Reaction of 2,3-diaminonaphthoquinone$^{3)}$ with oxalyl chloride afforded a tetraone **2** (mp >400 °C) quantitatively, which was converted to a dichloride **3** [mp 200 °C (dec)] in 78% yield by reaction with thionyl chloride. 2,3-Diaminobenzo[g]quinoxaline-5,10-dione (**4**) (mp >400 °C) was obtained from **3** in 65% yield according to a Gabriel method. Reaction of **4** with thionyl chloride gave **1a** in 87% yield.$^{4)}$ Quinone **1b** was also prepared in 67% yield by reaction of **4** with selenium oxychloride.$^{5)}$

The first and second half-wave reduction potentials of **1a,b** measured by cyclic voltammetry, and their semiquinone formation constants (K_{sem}) are

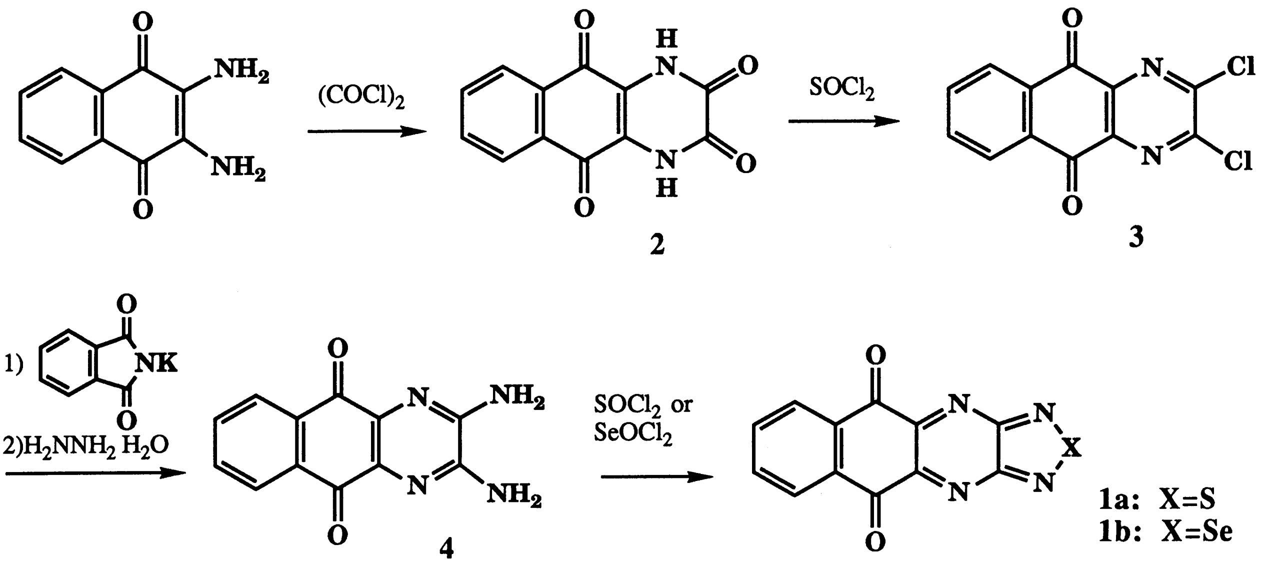
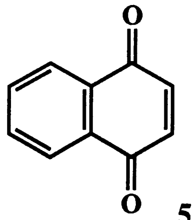
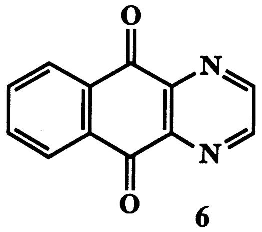


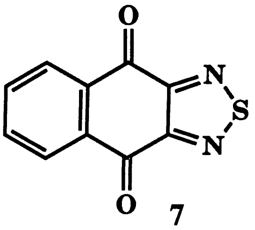
Table 1. Reduction Potentials[a)] and Semiquinone Formation Constants

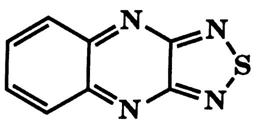
Compound	1a	1b	5	6	7	8
E^1	-0.25	-0.20	-0.71	-0.74	-0.76	-0.46
E^2	-1.18	-1.03	-1.38	-1.34	-1.36	-1.38
log K_{sem}[b)]	16.03	14.31	11.55	10.34	10.34	15.86

a) V vs. SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode. b) Calculated as $(E^1-E^2)/0.058$.


5

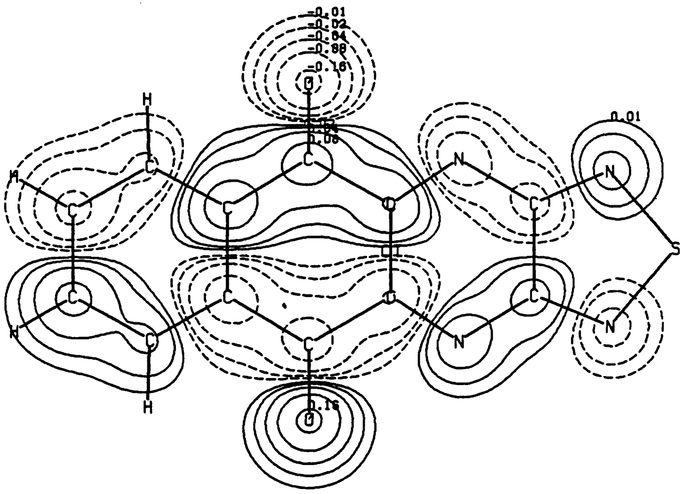

6


7


8

summarized in Table 1 along with those of the related compounds **5**, **6**,6) **7**,7) and **8**.8) The reduction potentials of **1a,b** are considerably higher than those of naphthoquinones **5**, **6**, and **7**, indicating that **1a,b** are stronger acceptors than the other quinones. The lower values of E^1 of **1a** compared with that of **1b** can be attributed to the fact that the electron affinity of a 1,2,5-thiadiazole ring is lower than that of a 1,2,5-selenadiazole ring.9) The semiquinone formation constants of **1a,b** are significantly larger than those of quinones **5**, **6**, **7**, while close to that of thiadiazoloquinoxaline **8**.10) This fact seems to indicate that both the first and second steps of reduction of **1a,b** occur at the thiadiazolopyrazine ring. In order to clarify this point, ab initio calculations using the STO-3G basis set were carried out.11) Figure 1 depicts the LUMO and next LUMO of **1a**, showing that the atoms in the heterocyclic ring have large coefficients in the

Next LUMO



LUMO

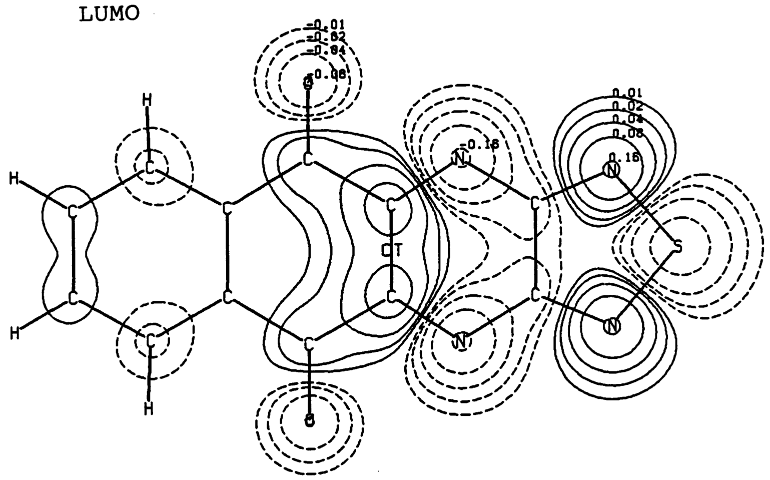


Fig. 1. Contour maps for the LUMO and the next LUMO of **1a**.

LUMO, while the dione part has large coefficients in the next LUMO. This result indicates that the heterocyclic ring first accepts electrons upon reduction.

References

1) M. A. Fox and T. A. Voynick, J. Org. Chem., 46, 1235 (1981); R. Neidlein, D. Tran-Viet, A. Gieren, M. Kokkinidis, R. Wilckens, H. Geserich, and W. Ruppel, Chem. Ber., 115, 2898 (1982); Y. Yamashita, T. Suzuki, G. Saito, and T. Mukai, J. Chem. Soc., Chem. Commun., 1986, 1489.

2) P. Camilleri, B. Odell, and P. O'Neill, J. Chem. Soc., Perkin Trans. 2, 1987, 1671.

3) E. Winkelmann, Tetrahedron, 25, 2427 (1969).

4) **1a**: mp 300-315 °C (dec); IR (KBr) 1680 cm^{-1}; UV (MeCN) 231 nm (logε 4.16), 255 (4.17), 284 (4.03), 341 (4.09), 356 (4.09).

5) **1b**: mp 360-362 °C (dec); IR (KBr) 1675 cm^{-1}; UV (MeCN) 235 nm (logε 4.06), 270 (4.30), 382 (4.39).

6) G. A. Efimova and L. S. Efros, Zh. Org. Kim., 2, 531 (1966).

7) R. Neeff and O. Bayer, Chem. Ber., 90, 1137 (1957).

8) A. P. Komin and M. Carmack, J. Heterocyclic Chem., 13, 13 (1976).

9) T. Suzuki, C. Kabuto, Y. Yamashita, and T. Mukai, Chem. Lett., 1987, 1129.

10) The smaller K_{sem} of **1b** compared with that of **1a** can be attributed to the large polarizability of selenium atom. The ESR studies of the radical species have been carried out by Prof. M. Hirayama of Ibaraki University. The result will be reported elsewhere.

11) Ab initio MO calculations were performed with MNDO-optimised geometries, using program packages MOPAC, JAMOL4, and JAPIC2. MOPAC [J. J. P. Stewart, Q. C. P. E. Bull. 3, 43 (1983)]. JAMOL4 [H. Kashiwagi, T. Takada, E. Miyoshi, S. Obara, and F. Sasaki, the Computer Center of the Institute for Molecular Science, Okazaki, (1987)]. JAPIC2 [H. Kashiwagi, E. Miyoshi, M. Sano, and Y. Watanabe, the Computer Center of the Institute for Molecular Science, Okazaki, (1980)].

(Received December 19, 1989)