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2,2'-(5,8-Dihydroquinoxaline-5,8-diylidene)bis(1,3-benzodithiole)s. A New Type of Electron Donors

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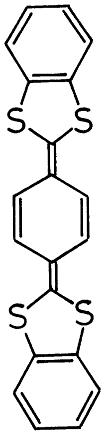
The title compounds were prepared from quinoxaline-5,8-diones by using a Wittig-Horner reaction of 2-dimethoxyphosphinyl-1,3-benzodithiole and a retro Diels-Alder reaction. They are stronger donors than dibenzo-TTF and formed conductive complexes with TCNQ and iodine.

Recently much attention has been focused on development of new organic conductors.[1)] In order to stabilize the metallic states, molecular design of new electron donors has been continuously done.[2)] One of the important strategies for the design is to extend conjugation to decrease on-site Coulomb repulsion.[3)] From this viewpoint, tetrathiafulvalene (TTF) analogues containing quinoid structures are interesting. Although dibenzo-TTF (DBTTF) analogues **1** and **2** were prepared with this aim, they were relatively unstable and readily decomposed in solvents.[4)] Therefore, we designed pyrazine-fused quinodimethane analogues **3**, in which the electron withdrawing heterocycle is expected to play a role in the stabilization. In addition, the pyrazine annelation has the following advantages. First, the nitrogen atoms in the pyrazine ring would increase intermolecular interactions.[5)] Second, the pyrazine ring can be easily functionallized to give various derivatives. Third, the polarization may result in interesting physical properties.[6)] We report here the preparation and properties of the promising electron donors **3**.



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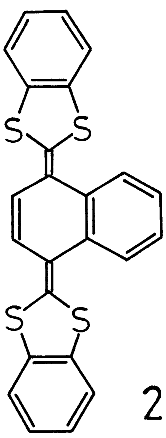

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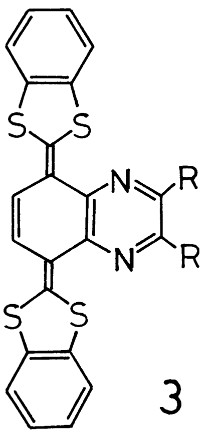

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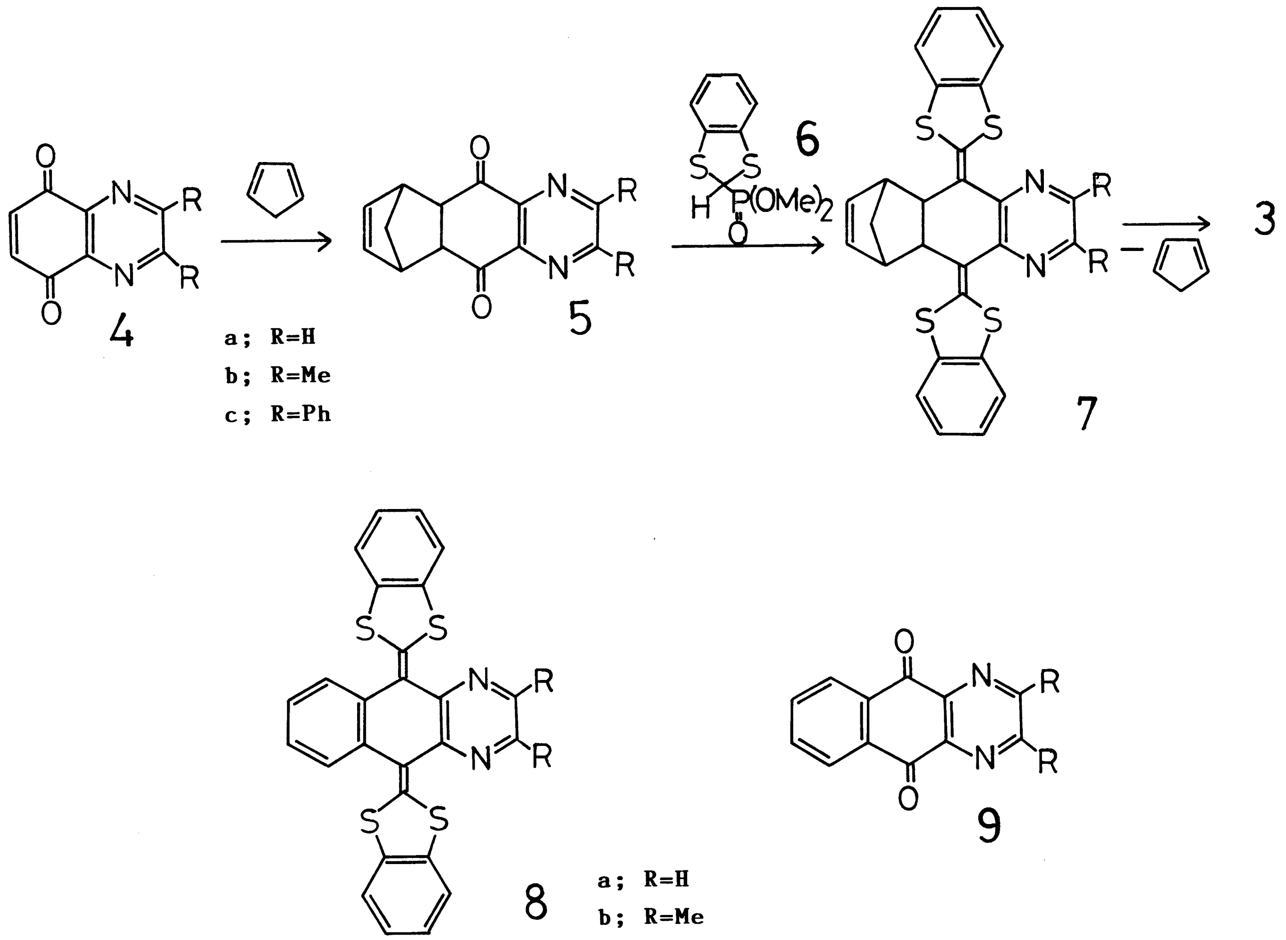

Scheme 1.

Table 1. Absorption maxima in the electronic spectra and oxidation potentials[a)] of donors

Compound	λmax/nm (logε) in CH_2Cl_2	E_1	E_2
3a	492(4.52), 462(4.38)	+0.37	+0.61
3b	489(4.90), 462(4.73)	+0.31	+0.56
3c	582sh(3.77), 500(4.84)	+0.44	+0.67
7a	394(4.71)	---b)	
7b	389(4.66)	---b)	
7c	490sh(4.18), 428(4.51)	+0.82c)	+0.94c)
8a	438(4.62), 370(4.18)	+0.66	
8b	439(4.66), 365(4.18)	+0.61	
2	468(4.74)	+0.40	
DBTTF	320(4.30)	+0.71	+1.13

a) 0.1 mol dm^{-3} Bu_4NClO_4 in CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}, V vs. SCE. b) Not measured. c) Irreversible. Calculated as Epa (anodic peak potential) - 0.03.

The donors **3** were synthesized according to the method shown in Scheme 1, in which a Wittig-Honor reaction of 2-dimethoxyphosphinyl-1,3-benzodithiole (**6**)[7] and a retro Diels-Alder reaction were used. First, quinoxaline-5,8-diones **4**[8] were reacted with cyclopentadiene[9] in order to protect the double bond since the direct Wittig-Honor reaction of **4** with **6** gave a complex mixture of products without formation of **3**. The reaction of cyclopentadiene adducts **5a-c** with **6** in the presence of n-BuLi gave bis(1,3-dithiole)s **7a-c** in 58, 80, and 54% yields, respectively.[10] Thermolysis of **7a-c** at 200 °C under reduced pressure gave **3a-c** by a retro Diels-Alder reaction in quantitative yields.[11] For comparisons, the benzo derivatives **8a,b** were synthesized by the Wittig-Horner reaction of **6** with the corresponding quinones **9a,b**[12] in 4% and 8% yields, respectively.[13]

The absorption maxima in the electronic spectra of the bis(1,3-dithiole) donors **3**, **7**, and **8** are shown in Table 1 along with those of **2** and DBTTF. Removal of the cyclopentadiene of **7** giving a quinoid structure makes the absorptions red-shift. The absorption maxima of pyrazino derivatives 3 are observed at longer wavelengths compared to that of **2**, indicating the contribution of the expected polarization effect.

The oxidation potentials of the donors **3a-c** and **8a,b** were measured by cyclic voltammetry in dichloromethane. These data are summarized in Table 1 along with those of **2** and DBTTF measured under the same conditions. The values of the oxidation potentials of **3a-c** and **8a,b** are lower than that of DBTTF although they contain an electron withdrawing heterocycle, indicating that the introduction of quinoid structures is very effective for strengthening electron donating properties. Another interesting feature is that two well-defined reversible one-electron oxidation waves are observed in **3a-c**, while benzo derivatives **2** and **8a,b** show two-electron oxidation waves. This fact indicates that the cation radical states of **3** are thermodynamically more stable than those of **2** and **8**. The instability of cation radicals of the benzo-derivatives **2** and **8** may be caused by their nonplanar structures due to steric interactions between the peri-hydrogen atoms of the benzene ring and the sulfur atoms. The differences between the first and the second oxidation potentials in 3 are smaller than that in dibenzo-TTF. This result can be attributed to the decreased on-site Coulomb repulsion due to the extended π-conjugation.

Table 2. Molar ratios[a] and electrical resistivities, ρ,[b] of complexes of donors with TCNQ and iodine

	TCNQ complex		I complex	
Donor	Ratio	ρ/Ω cm	Ratio	ρ/Ω cm
3a	1:1:H_2O	1.6	1:5	8.7×10^2
3b	1:1	2.1×10	1:3.5	2.0×10^2
3c	---[c]		1:7.5	1.0×10^2

a) Determined on the basis of elemental analyses.
b) Measured by a two-probe technique on compaction samples. c) Not obtained.

Pyrazine-fused donors **3a,b** gave 1:1 charge-transfer complexes with TCNQ[14)] although a complex of **3c** with TCNQ could not be obtained. The conductivities are good as shown in Table 2. The donors were also doped with iodine to give conducting materials.[15)] The iodine content is dependent on substituents as shown in Table 2. The preparation of cation radical salts by electrochemical oxidation is now in progress.

References

1) D. O. Cowan and F. M. Wlygul, Chem. Eng. News, 1986, July 21, 28.

2) T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann, and F. Wudl, J. Am. Chem. Soc., 111, 3108 (1989).

3) Y. Yamashita and T. Miyashi, Chem. Lett., 1988, 661; M. R. Bryce and A. J. Moore, Tetrahedron Lett., 29, 1075 (1988); K. Takahashi, T. Nihira, K. Takase, and K. Shibata, ibid., 30, 2091 (1989).

4) M. Sato, M. V. Lakshmikantham, M. P. Cava, and A. F. Garito, J. Org. Chem., 43, 2084 (1978); M. R. Bryce, Mol. Cryst. Liq. Cryst., 120, 305 (1985); Y. Yamashita, Y. Kobayashi, and T. Miyashi, Angew. Chem., in press.

5) G. C. Papavassiliou, S. Y. Yiannopoulos, and J. S. Zambounis, J. Chem. Soc., Chem. Commun., 1986, 820.

6) The conductivities of $TCNQ^{\overline{\cdot}}$ salts of cyanine dye increase with an increase in the polarizability of the cation. B. H. Klanderman and D. C. Hoesterey, J. Chem. Phys., 51, 377 (1969).

7) K. Akiba, K. Ishikawa, and N. Inamoto, Bull. Chem. Soc. Jpn., 51, 2674 (1978).

8) J. Adachi, Nippon Kagaku Zasshi, 76, 311 (1955).

9) W. F. Gum, Jr. and M. M. Joullie, J. Org. Chem., 30, 2583 (1965).

10) The synthetic procedure is as follows. A dry THF solution of **6** was treated with n-BuLi (1.1 equiv.) at -78 °C under nitrogen, and after stirring for 10 min, a dione 7 was added. The solution was stirred at -78 °C for 10 min and then gradually warmed to room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The organic extract was dried over Na_2SO_4 and removal of the solvent followed by column chromatography on SiO_2 (1:1 hexane-dichloromethane) gave **7**. Melting points of **7a-c** are the same as those of the corresponding bis(1,3-dithiole)s **3a-c** since the cyclopentadiene is eliminated during the measurements.

11) **3a**; mp 340-345 °C, **3b**; mp 315-318 °C, **3c**; mp 322-324 °C.

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

13) **8a**; mp 273-274 °C, **8b**; mp 270-272 °C.

14) The complexes were prepared by treatment of the donors in hot chlorobenzene with a boiling solution of 1 equiv. of TCNQ in chlorobenzene. After the solution was cooled to room temperature, the products were collected on a filter.

15) To a boiling solution of the donors in dichloromethane or chlorobenzene was added a boiling solution of 3 equiv. of iodine in dichloromethane or chlorobenzene, and the mixture was allowed to stand at room temperature for 30 min. Filtration gave the complexes. The iodine of the complexes was eliminated upon heating above 250 °C to give neutral compounds.

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