# Preparation and Properties of the Dianion and the Dihydro Derivative of the Bis[1,2,5]thiadiazolo Derivative of Tetracyanoquinodimethane

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The dianion of the bis[1,2,5]thiadiazolo derivative of tetracyanoquinodimethane (BTDA-TCNQ) was isolated as a stable sodium salt; the dihydro derivative of BTDA-TCNQ, containing the benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole skeleton, was found to be a strong dibasic acid.

Recently we have prepared the bis[1,2,5]thiadiazolo derivative of tetracyanoquinodimethane (BTDA-TCNQ),† a new acceptor which forms highly conductive complexes with donors.[1] The presence of thiadiazole rings enlarges the $\pi$-electron system and reduces Coulombic repulsion, which is reflected in the smaller log $K_{sem}$ value (8.10) as compared with that of TCNQ (9.31).[1] Therefore, the dianion of BTDA-TCNQ ($BTDA^{2-}$) was expected to be persistent, in contrast to the TCNQ dianion which has been isolated only when special metal complex ions are used as counter ions.[2] The redox cycle of BTDA-TCNQ, including hydrogen and proton transfer, is considered to be as shown in Scheme 1. Dihydro-BTDA-TCNQ ($H_2BTDA$) is a derivative of benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole (**1**), an interesting hypervalent sulphur–nitrogen heterocycle. In order to clarify the redox cycle to discover the effect of the novel heterocyclic skeleton of (**1**), we have prepared $BTDA^{2-}$ and $H_2BTDA$, and investigated their properties.

The dianion $BTDA^{2-}$ was isolated in high yield as a stable sodium salt by reduction of $Na^+BTDA^{\bullet-}$ with $Na_2S_2O_4$ in

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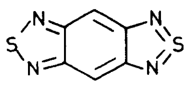
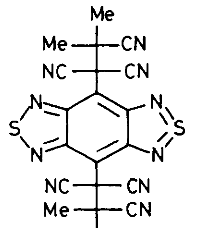
† Benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole-4,8-diylidenedi(malononitrile).



(1)



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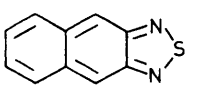

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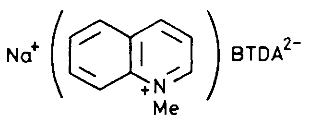

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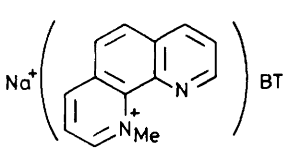

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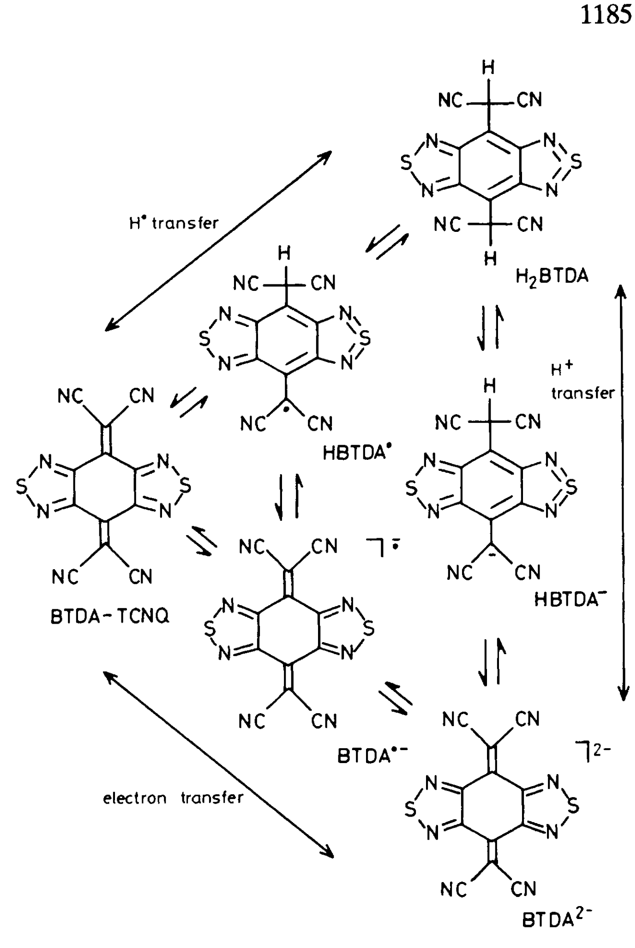

Scheme 1

ethanol [$Na^{+}{}_{2}BTDA^{2-}$: decomp. >380 °C, $\lambda_{max.}$ ($H_2O$) 596 (log ε 4.09), 402sh (4.27), 392sh (4.27), 337 (4.44), and 256 nm (4.02)]. The stability can be attributed to delocalization of the negative charge into the thiadiazole rings. This delocalization seems to be facilitated by the electron-withdrawing property of the thiadiazole rings as well as by the instability of the skeleton of (**1**) resulting from the presence of the hypervalent sulphur atoms. The nitrile stretching frequency of $Na^{+}{}_{2}BTDA^{2-}$ is 2205 $cm^{-1}$, higher than that of $Na^{+}BTDA^{\cdot -}$ (2185 $cm^{-1}$); that of neutral BTDA-TCNQ is 2225 $cm^{-1}$. Thus the nitrile stretching frequencies are not correlated with the degree of charge transfer, in contrast to the case of TCNQ.[3] This finding seems to be related to the strong S---N≡C interaction revealed by *X*-ray analyses of neutral BTDA-TCNQ[4] and an anion radical salt.[5]

Treatment of the dianion with dilute hydrochloric acid followed by extraction with benzene gave $H_2BTDA$ (decomp. 225—230 °C) in 87% yield; this substance is the first derivative of (**1**) to be isolated. Treatment of the anion radical of BTDA-TCNQ ($BTDA\text{-}TCNQ^{\cdot -}$) with acid resulted in disproportionation to give neutral BTDA-TCNQ and $H_2BTDA$. This finding indicates that the monoprotonated species $HBTDA^{\cdot}$ is unstable and readily undergoes disproportionation. The solution of $H_2BTDA$ in nonpolar solvents is yellow, but that in polar solvents is blue. The absorption spectrum in water was in complete agreement with that of $BTDA^{2-}$ in water. This suggests that $H_2BTDA$ dissociates into $BTDA^{2-}$ in polar solvents. In fact, the $pK_{a_2}$ value was determined to be −0.2 from measurement in water by an absorptiometric method, indicating that $H_2BTDA$ is a strong dibasic acid and that the mono-protonated species $HBTDA^{-}$ dissociates to $BTDA^{2-}$ in water. The acid strength is unexpected, involving C–H dissociation in this case. This novel property can be attributed to both the unusual skeleton of (**1**) and the stability of the dianion $BTDA^{2-}$. Owing to its hygroscopic nature in addition to its strong acidity, $H_2BTDA$ is unstable and turns blue on filter paper. For comparison, the heterocycle (**2**) (decomp. 240—243 °C), possessing no labile hydrogen atoms, was prepared by reaction of BTDA-TCNQ with azobisisobutyronitrile, in 50% yield. As expected, (**2**) was stable, in contrast to $H_2BTDA$, but the reduction potential of (**2**) was −0.89 V *vs.* standard calomel electrode (s.c.e.), higher than that of naphtho[1,2,5]thiadiazole (**3**) (−1.17 V *vs.* s.c.e.), indicating the high electron affinity of the benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole ring system.

Metathesis of $Na^{+}{}_{2}BTDA^{2-}$ with the organic cations *N*-methylquinolinium iodide and *N*-methyl-o-phenanthrolinium iodide gave the salts (**4**) and (**5**), respectively, in which only one $Na^{+}$ is replaced. This shows that one $Na^{+}$ is strongly bound to the dianion. The electrical resistivities of the dianion salts, $Na^{+}{}_{2}BTDA^{2-}$, (**4**), and (**5**) were $1.3 \times 10^{6}$, $1.9 \times 10^{10}$, and $4.5 \times 10^{11}$ Ω cm, respectively. These values are high as a result of Coulombic repulsion; however these are the first organic dianion salts to show conductive properties.

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