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学位論文題目 Studies on Novel Organic Redox Systems
Containing Fused 1,2,5-Thiadiazole Rings

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Recently much attention has been focused on development of organic conductors and superconductors. For this purpose, syntheses of new electron donors and acceptors are very important. One of the important points for the molecular design is to extend π -conjugation in order to reduce on-site Coulombic repulsion. The other is to form highly dimensional crystal structures. From these viewpoints, 1,2,5-thiadiazole rings are of interest since they have extended π -conjugation and polarized heteroatoms resulting in strong intermolecular interactions by heteroatom contacts. Furthermore, since thiadiazoles are electron-withdrawing heterocycles, compounds with both thiadiazole rings and electron-donating ones are expected to have a high polarizability, intramolecular charge transfer (CT) interaction, and an enhanced amphoteric redox ability. In this research work, He designed some new types of redox systems containing thiadiazole moieties and investigated their electronic properties and crystal structures. Chapter 1 describes the purpose and some attractive previous works as introduction of this thesis.

Chapter 2 describes preparation, properties, and an X-ray crystal structure analysis of 7-(1,3-dithiol-2-ylidene)-4-methyl-4,7-dihydro[1,2,5]-thiadiazolo[3,4-b]pyridine. The compound and its derivatives were characterized by intramolecular CT bands around 510 and 490 nm and stronger electron-donating abilities than tetrathiafulvalene (TTF) in the cyclic voltammetry (CV) study, indicating that they are of interest as novel electron donors which have no TTF skeleton. The crystal analysis revealed that the molecules make columnar stacks and the overlapping is in accord with an effective interaction between the HOMO and the LUMO. The crystal structure is composed of a set of four columns interacted with each other through short S...S contacts. Although the net atomic charges calculated by the MNDO-PM3 method show that the molecule is highly polarized, S...N contacts arising from an electrostatic effect were not observed. The compounds formed conducting CT complexes with tetracyanoquinodimethane. One of them showed a high electrical conductivity (1 S cm^{-1}) as a compressed pellet, and the degree of CT was evaluated as 0.67 according to the C=N stretching frequency. The cation radical salts were prepared by an electrochemical oxidation, and the ClO_4 salt of the ethylenedithio-derivative showed a semiconducting behavior with $\sigma_{300} = 4.4 \times 10^{-2} \text{ S cm}^{-1}$ and $E_a = 0.15 \text{ eV}$.

Nonplanar donors or acceptors giving organic conductors are very few. Chapter 3 describes a novel nonplanar donor molecule containing fused benzene and fused thiadiazole rings. The unique butterfly-shaped structure and intramolecular short S...N contacts were revealed by an X-ray crystal structure analysis, and a uniform columnar stacking was also observed.

Although many organic conductors are known, they are composed of multi-components such as CT complexes. Usual organic compounds are insulators as single components. However, molecules containing both donor and acceptor units are expected to exhibit unusual electrical properties owing to intramolecular CT interaction. *4H, 8H*-4,8-Bis(1,3-dithiol-2-ylidene)benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole (BTQBT) is one of the most electrical conducting materials as a single component. Its electrical behavior is ascribable to strong intermolecular interactions in the crystal. He have now replaced one of the 1,3-dithiole groups by a carbonyl group to give BTQT, which is considerable to be more polarized than BTQBT. Chapter 4 deals with an X-ray crystal structure analysis and an electrical behavior of BTQT. In the crystal the molecular overlapping is close to that of BTQBT, suggesting intermolecular CT interaction. The overlap mode is caused from the most effective interaction between the HOMO and the LUMO. On the other hand, the crystal structure is in sharp contrast with that of BTQBT, which makes a sheet-like network with short S...S contacts. BTQT molecules are three-dimensionally connected with each other through short S...S, S...N, and S...O contacts. These S...N and S...O contacts are attributed to an electrostatic effect due to the highly polarized structure. The electrical conducting behavior fails to obey Ohm's law. The current increased approximately in proportion to the third power of the voltage. The non-ohmic behavior observed here is an unprecedented one as organic crystals.

Chapter 5 is concerned with novel heterocycles, benzo[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole)s and the monoselenium analogues, which contain a tetravalent sulfur atom. They are characterized by higher electron affinities and longer absorption maxima compared with those of a related Kekule-type isomer. The high electron affinities are owing to the unique 14π -electron ring system containing a tetravalent sulfur atom, which generates a more stable Kekule-type thiadiazole ring upon accepting an electron. Their electron-accepting abilities are comparable to that of *p*-benzoquinone. They showed strong fluorescence emission. Their electronic properties and reactivities are explained by the MNDO-PM 3 calculations. In the X-ray crystal structure analysis of the dibromoderivative, the molecular structure demonstrates the hypervalency on the sulfur atoms and the 14π -electron ring moiety. The crystal structure is composed of a set of two ribbon columns linked by short S...N and N...N contacts, and these columns interact with each other through short Br...N contacts resulted in a dense crystal packing. The donor- π -acceptor molecules were also synthesized by introduction of electron-donating groups into the skeleton. Their redox potentials were determined by the CV study. The molecules substituted by amine groups show good amphoteric redox properties. The electron-donating ability of the dimethylaminobenzene derivative is similar to that of TTF, indicating that it is

a promising electron donor for organic conductors.

At the end of the thesis, this research work is summarized and makes some suggestions. Introduction of 1,2,5-thiadiazole rings into electron donors results in large polarization, which is helpful to stabilize the ring systems. Highly polarized molecules show interesting physical properties. Unique molecular assemblies are constructed by intermolecular interactions between polarized heteroatoms. Control of physical properties and crystal structures of such molecules seems possible by changing the polarizability affected by the charge densities on the heteroatoms.

審査結果の要旨

有機電導体などの物性分野の研究の発展には新規化合物の開発が不可欠である。本論文では1, 2, 5-チアジアゾール環が縮合した新しいドナー類やドナー-アクセプター型の特異な分子が合成されており、それら新分子の構造ならびに酸化還元特性を始めとする物性が明らかにされている。

ドナー類としては1, 3-ジチオール環とアミノ基を有する4-メチル-7-(1, 3-ジチオール-2-イリデン)-4, 7-ジヒドロ[1, 2, 5]チアジアゾロ[3, 4-b]ピリジンが合成されている。この分子は電子受容性のチアジアゾール環が縮合しているにもかかわらず強力なドナー性を示し、TCNQと高電導性の電荷移動錯体を生成している。中性分子は分子内電荷移動により分極しており、結晶構造はカラム構造を取っていて短いS...S接触によってカラム間に相互作用が見られる。このドナーはTTF骨格を持たない新タイプのドナーとして評価できる。また、通常のドナー分子はほとんど平面分子であるが、バタフライ型の非平面構造であるにもかかわらず、分子の重なりがよく、単一成分で半導体的電気伝導を示すビス(1, 3-ジチオール)ドナーの合成にも成功している。この分子は1段階2電子酸化を行う分子内クーロン反発の小さい系としても注目される。

分子内にドナー部とアクセプター部を有する分子としてはビス[1, 2, 5]チアジアゾロ-p-キノ-1, 3-ジチオール-を合成している。この分子は大きく分極しており、電流が電圧のほぼ3乗に比例するような非線型電気伝導を示している。この物性は有機結晶としては初めての例である。結晶構造はヘテロ原子接触と電荷移動相互作用で特異な3次元構造をしている。さらにドナー-アクセプター系分子としてビスチアジアゾロベンゼン誘導体を合成しているが、非古典的構造のヘテロ環骨格は高い電子親和性を持ち、アリアル置換基との間に分子内電荷移動を起こしている。また、ジフェニルおよびジブロム体はp-ベンゾキノンと同程度のアクセプター性を持ち、強い蛍光を示すことからエレクトロルミネセンスなどの応用面も期待される。結晶構造解析はジブロム体で行われており、非古典的構造およびヘテロ原子接触に基づくリボン構造が明らかにされている。

このように小野君の論文では電導体の成分分子となる新しいドナー分子や特異な物性を示すドナー-アクセプター系分子が合成されている。ヘテロ原子接触に基づく結晶構造も特異的であり、分子集合体の構築の観点から興味深い。これらの内容は電導体の分野のみならず、有機固体化学の分野にも貢献しており、本論文は博士論文に値すると判断した。また、50分間の論文発表に続く約80分の質問時間の中で有機化学と物理化学の基礎的な知識についての質問を数多く行った。小野君は有機電導体の分野の研究の背景をよく理解していると同時に、有機化学に加えて電気化学、固体物性の基礎知識についても十分に修得していると判断された。また、学位論文を平易な英文でまとめており、英語に関する学力については問題ないと判断された。

以上、小野克彦君は博士論文を中心としてその周辺分野まで含めて幅広い学識を有していると判断した。また、公開発表による最終審査でも明解な発表をし、質問にも明確に答え、合格した。