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Shin'Ichi Nakatsuji [a], Nobutaka Akashi [a], Yoichiro Komori [a], Kazuya Suzuki [b], Toshiaki Enoki [c] & Hiroyuki Anzai [a]

[a] Department of Material Science, Faculty of Science, Himeji Institute of Technology, Kamigori, Hyogo, 678-12, Japan

[b] Department of Chemistry, Faculty of Engineering, Yokohama National University, 1-5-6 Tokiwadai, Hodogaya-ku, Yokohama, 240, Japan

[c] Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan

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PREPARATION AND PROPERTIES OF AROMATIC COMPOUNDS BEARING SUBSTITUENTS WITH UNPAIRED ELECTRON

SHIN'ICHI NAKATSUJI, NOBUTAKA AKASHI, YOICHIRO KOMORI, KAZUYA SUZUKI,† TOSHIAKI ENOKI††, AND HIROYUKI ANZAI
Department of Material Science, Faculty of Science, Himeji Institute of Technology, Kamigori, Hyogo 678-12, Japan
†Department of Chemistry, Faculty of Engineering, Yokohama National University, 1-5-6 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan
††Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract Preparation of some benzoquinones, pyridiniums, and benzenoid aromatics bearing subsitituents with unpaired electron as well as their properties, especially magnetic properties, are discussed.

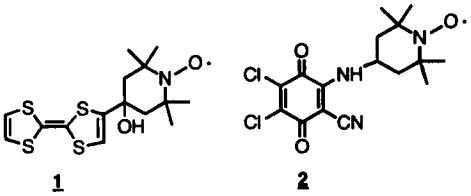
INTRODUCTION

It is of recent interest to search for new organomagnetic materials with relevant solid state properties. We are trying to prepare some organic compounds having such properities and we have been interested in the preparation of three types of stable-radical-substituted aromatic compounds indicated below and to arrange the unpaired electrons in their column structures. In this paper, we wish to report on the preparative studies and some properties of them obtained so far.

PREPARATION AND PROPERTIES

TEMPO-SUBSTITUTED BENZOQUINONE DERIVATIVES

For the construction of CT complexes bearing substituent (s) with unpaired electron, we have tried and succeeded to prepare hydroxy-TEMPO-substituted **1** and phenoxyl-



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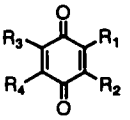


3: R_1=R_3=NH-TEMPO
R_2=CN, R_4=Cl
4: R_1=NH-TEMPO
R_2=R_3=R_4=Cl
5: R_1=R_3=NH-TEMPO
R_2=R_4=Cl
6: R_1=R_3=NH-TEMPO
R_2=R_4=Br
7: R_1=N^+H-TEMPO (Cl^-)
R_3=R_4=Cl, R_2=CN

substituted TTF derivatives as donor molecules and the CT complexes derived therefrom with several acceptors.[1] As acceptor molecule bearing substituent (s) with unpaired electron, we have prepared a series of TEMPO-substituted benzoquinone derivatives by the reaction of DDQ, chloranil or bromanil with amino-TEMPO.[2] It was found that mono-substituted derivative **2** was the major product in the reaction of DDQ with amino-TEMPO, whereas bis-substituted derivatives (**5**, **6**) were the major products in the reaction of chloranil or bromanil with amino-TEMPO. Compound **2** gave the salt of chloride (**7**) and **2** as well as **7** were found to give CT complexes with several donors as TTF, **1** or TMPD although others did not. Magnetic susceptibility of **2** as well as its CT complexes were measured on their polycrystalline samples by a SQUID susceptometer at temperatures between 2 K and 300 K. It was found from the susceptibility data that **2** had its susceptibility maxima around 3.8 K (Fig. 1) and the experimental data were well reproduced by theoritical data estimated by one-dimentional Heisenberg anti-ferromagnetic model with J = 3 K and χ_{max} = 0.037 emu/mol. In the CT complexes of **2**, the susceptibility data showed Curie-Weiss curve with Weiss temperature of as large as -1 K (cf. the data of TTF complex in Fig. 1) and apparent decrease of magnetic susceptibility was observed for each complex by CT formation resulting probably from the intra- and/or intermolecular singlet formation between unpaired electrons.

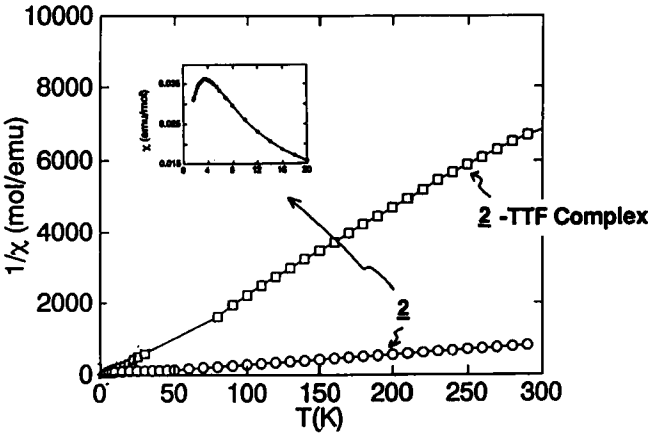
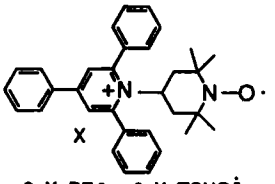


FIGURE 1 Temperature dependence of magnetic susceptibility of **2** and its TTF complex

TEMPO-SUBSTITUTED PYRIDINIUM DERIVATIVES



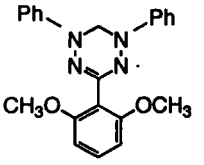
8: X=BF_4^- **9**: X=$TCNQ^-$

In recent papers, Awaga et al.[3] and Sugimoto et al.[4] have reported on the interesting magnetic properties in their pyridinium salts bearing substituent with unpaired electron. In the course of our studies to prepare radical salts with relevant magnetic property, we have been

interested in the preparation of N-TEMPO-substituted-pyridinium salts. Compound **8** was prepared by the reaction of corresponding pyrylium salt with amino-TEMPO and was transformed to **9** by the reaction with Li TCNQ. It was found from the susceptibility data that **8** as well as **9** showed Curie-Weiss behaviour with Weiss temperature of -1.5 K for **8** and as large as -0.2 K for **9** with no indication of parallel spin alignment between TEMPO-radicals and anion radicals of TCNQ. Further works on these and related compounds are now underway.

VERDAZYL-SUBSTITUTED AROMATICS

Along with the preparative studies of CT complexes or radical salts bearing substituent (s) with unpaired electron, we also have tried to prepare some radical compounds having possibly screwed conjunction between aromatic π-system and radical π-system and a series of verdazyl-substituted aromatics **10** - **13** were prepared to investigate their



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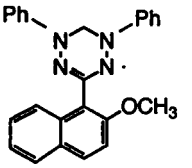

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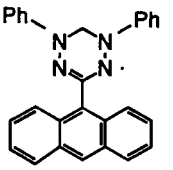

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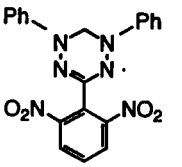

13

magnetic behaviour in connection with their molecular as well as crystal structures.[5,6] It was found from the susceptibility measuremants that each compound except **13** showed Curie-Weiss behavior with Weiss temperature of as large as -1 K. Compound **13** showed antiferromagnetic short range ordering (with Weiss temperature of -5 K) based possibly on one dimensionality of the system. Further studies including its X-ray crystallographic analysis are now in progress.

In summary, we have prepared three kinds of aromatic compounds bearing substituents with unpaired electron to investigate their magnetic properties, although we could see no ferromagtic or ferrimagnetic behaviour among them yet.

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