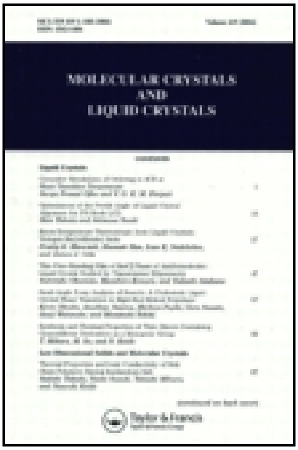

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Shin'ichi Nakatsuji [a] , Akari Kitamura [a] , Kazuyoshi Nishikawa [b] , Yukio Morimoto [b] , Noritake Yasuoka [b] , Haruki Kawamura [a] & Hiroyuki Anzai [a]

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

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

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Preparation and Properties of CT Complexes Derived from Verdazyl Radicals

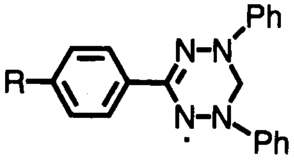
SHIN'ICHI NAKATSUJI[a], AKARI KITAMURA[a], KAZUYOSHI NISHIKAWA[b], YUKIO MORIMOTO[b], NORITAKE YASUOKA[b], HARUKI KAWAMURA[a] AND HIROYUKI ANZAI[a]
[a]Department of Material Science and [b]Department of Life Science, Faculty of Science, Himeji Institute of Technology, Kamigori, Hyogo 678-12, Japan

The charge-transfer (CT) complexes of a series of 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals with $TCNQF_4$ or DDQ were prepared and their magnetic properties were investigated. The X-ray crystal structural analyses on the CT complexes consisted of 3-(4-methoxyphenyl)-, 3-(4-tolyl)- as well as 3-(4-chlorophenyl)-verdazyl radicals and $TCNQF_4$ were carried out and correlated with their magnetic properties in which large decrease of magnetic susceptibility was observed in each complex.

Keywords: Verdazyl radicals; CT complexes; magnetic properties; X-ray analysis

INTRODUCTION

Along with the development of new organoconducting materials, it is of current interest to develop new organomagnetic materials with relevant solid state properties[1]. We have been interested in preparing such organic compounds that have eminent solid state properties and we found recently that several stable-radical molecules such as TEMPO and its derivatives act as donors for the CT complexes with appropriate acceptors[2].



1: R=H **4**: R=Cl
2: R=MeO **5**: $R=NO_2$
3: R=Me **6**: $R=NH_2$

Verdazyl radicals are also one of the well-known classes of stable radicals as well as nitroxide radicals having, however, differing from TEMPO radicals, delocalized spin structures of unpaired electrons[3], on several of which we found that the corresponding CT complexes could be formed with some acceptors. In this paper, we wish to report on the preparation and the magnetic properties of the CT complexes derived from 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals **1-6** with TCNQF4 or DDQ and on the results of the X-ray crystal structural analyses of three of the complexes to correlate with their magnetic properties.

PREPARATION, ELECTROCHEMICAL AND MAGNETIC PROPERTIES OF VERDAZYL RADICALS

We have been interested in the effect of p-substituents on formation of the corresponding CT complexes and their magnetic behavior to be regulated by the effect. The preparation of 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals was carried out by the standard method developed by Kuhn and Trischmann (Scheme) [4]. The amino derivative **6** was prepared by catalytic hydrogenation on Pd-$BaSO_4$ (5%) in 61% yield[5].

Because, to our knowledge, there is no report on the electrochemical behavior of verdazyl radicals, we investigated the donor ability of the radicals by an electrochemical method using cyclic voltammetry, and the results are summarized in TABLE. It was found from the results that the first oxidation potentials of the verdazyl radicals **1-6** were much lower compared with TEMPO radicals[2], thus showing their much higher donating ability. The values were, however, not so different within **1-6** suggesting that the donor ability is dominated mainly on the radical moiety. At the same time, gradual increase of the donating ability of the radicals was estimated with increase of

TABLE Cyclic voltammetric data for radicals **1-6**[a,b]

	1	**2**	**3**	**4**	**5**	**6**
E_1^{ox}	0.30	0.27	0.28	0.32	0.40	0.25

[a] Oxidation potentials (V) *vs.* SCE in CH_3CN with 0.1 M Bu_4NClO_4 at room temp.

[b] Irreversible. The first oxidation potentials are cited.

the electron-donating ability of substituents. Actually, corresponding CT complexes were found to be formed easily with acceptors as described below.

In their ESR spectra, typical quintet absorptions were observed in each radical with g-factor of 2.004 in benzene solution. The magnetic susceptibility measurement on the radicals was carried out on the polycrystalline sample by a SQUID susceptometer in the temperature range of 2-300 K It was found from the results that antiferromagnetic interactions were predominant for the verdazyl radicals, and short-range ordering was suggested in **1**[6], **2** and **4** in the very low temperature range[7].

PREPARATION AND MAGNETIC PROPERTIES OF THE CT COMPLEXES DERIVED FROM VERDAZYL RADICALS

According to the results from the electrochemical measurements on the verdazyl radicals, it was anticipated that they would form the corresponding CT complexes with an appropriate acceptor and, actually, several CT complexes were found to be formed from the radicals **1-6** with $TCNQF_4$ or DDQ. They were isolated as relatively stable crystalline solids, and the composition of donor-to-acceptor ratio was estimated from elemental analyses so far examined to be 1:1 in each case except **2**-$TCNQF_4$ complex, which included solvent molecules (ethyl acetate) in the crystal lattice as was evidenced also from X-ray analysis as described below.

Large decrease of magnetic susceptibility was observed in each complex examined, although the magnitude of decrease was dependent on the kind of complex, and rather weak antiferromagnetic interactions were observed in each complex estimated from their values of Weiss constants[8]. Similar large decrease of magnetic susceptibility was also observed in TEMPO-$TCNQF_4$ and its magnetic behavior was understood from X-ray analysis data[2]. To clarify the magneto-structure relationship on the class of charge-transfer complexes, we then carried out X-ray analyses on three of the complexes ($TCNQF_4$ complexes of **2**, **3** as well as **4**) for which single crystals were prepared by recrystallization using appropriate solvents.

X-RAY STRUCTURAL ANALYSES ON TCNQF4-COMPLEXES OF 2, 3 AS WELL AS 4

It was found that both **3**-TCNQF4 complex and **4**-TCNQF4 complex have rather similar molecular/crystal structures among the three complexes elucidated while **2**-TCNQF4 complex was somewhat different from them, taking solvent molecules (ethyl acetate) into a crystal lattice. As an example, the molecular as well as crystal structure of **3**-TCNQF4 is shown in FIG. 1 and FIG. 2. Some features are apparent from the analysis; the complex consisted of an equimolecular ratio of radical **3** and TCNQF4 and it is estimated from their molecular structures that verdazyl radical **3** is converted to a verdazylium ion by one-electron transfer to TCNQF4 because both N-N bond length, in the radical moiety (i. e., N5-N6=1.311 Å and N7-N8=1.313 Å) are clearly shortened compared with the normal bond length in the verdazyl radical (1.348-1.353 Å)[9] and the TCNQF4 molecule is converted to its radical anion owing to the one-electron transfer from the verdazyl radical with relatively small bond alternation in each TCNQF4 molecule of the complex, suggesting the delocalization of π-electrons on the whole molecule[10]. Very recently, Wudl et al. reported on the formation of the CT complex (salt) derived from a 2,4-diphenylbenzo-1,3,4-triazolyl radical and TCNQ with uncommon stoichiometry in which the radical is also converted to the corresponding cation transferring one electron to one dimer pair of TCNQ molecules[11]. In our complexes **3**-TCNQF4 as well as **4**-TCNQF4, normal stoichiometry is suggested from the X-ray analyses as well as elemental analyses and a segregated columnar structure along the c-axis for both radical molecules and TCNQF4 molecules is evident from their crystal

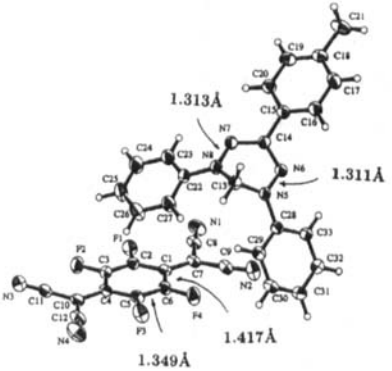


FIGURE 1 Molecular structure of **3**-TCNQF4.

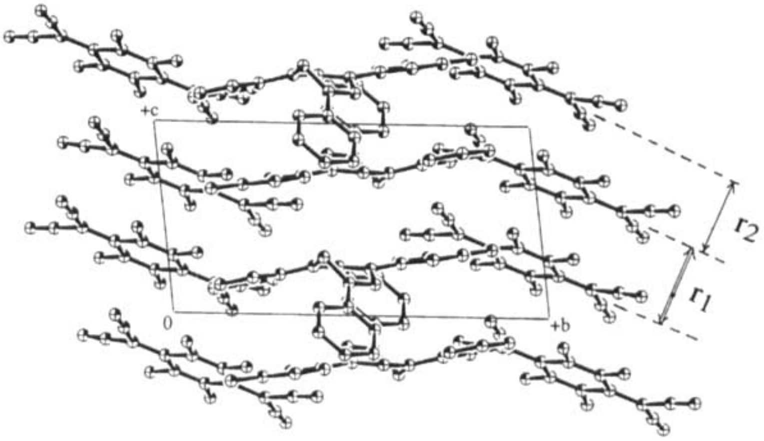


FIGURE 2 Crystal structure of **3**-$TCNQF_4$ viewed along the a-axis.

structures elucidated (e. g., FIG. 2 for **3**-$TCNQF_4$ complex). It is also apparent from the analyses that $TCNQF_4$ molecules in the complex form a dimer pair having intra-dimer distances of 3.21-3.23 Å (r_1) and inter-dimer distances of 4.78-4.80 Å (r_2) and the situation is quite similar to that in the **4**-$TCNQF_4$ complex. The large decrease of magnetic susceptibility in the complexes would then be considered to be due to the singlet formation between the dimer pairs of $TCNQF_4$ radical anions although the magnitude of the decrease is somewhat different between them. In **2**-$TCNQF_4$ complex, the molar ratio of the radical **2**, $TCNQF_4$ and ethyl acetate is found to be 2:3:1 to form the crystal lattice and in which the radicals as well as dimer pairs of $TCNQF_4$ molecules form a segregated column along the b-axis, but the remaining $TCNQF_4$ molecules with perpendicular molecular orientation to the dimer pairs form a sheet-like structure along the b-axis. Whereas the former $TCNQF_4$ molecules are considered to be radical anions estimated from their C-C bond length in their quinoid structures, the latter $TCNQF_4$ molecules appear to be neutral according to the bond length estimation. Therefore, the magnetic behavior of the complex could be understood eventually by similar consideration of the former complexes.

Because the segregated columnar structures were apparent in the $TCNQF_4$ complexes, some electrical conductivity was expected through the $TCNQF_4$

columns in the complexes but the room temperature conductivity of each complex was less than the order of 10^{-6} S/cm. Further studies on the measurement of the pressure dependence of their conductivities are now in progress.

References

[1.] Cf. H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179; O. Kahn, *Molecular magnetism*, VCH, Weinheim, 1993; J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 385.

[2.] S. Nakatsuji, A. Takai, K. Nishikawa, Y. Morimoto, N. Yasuoka, K. Suzuki, T. Enoki, and H. Anzai, *J. Chem. Soc., Chem. commun.*, **1997**, 275 and preceding paper.

[3.] Cf. F. A. Neugebauer, *Angew. Chem.*, 1973, **85**, 485.

[4.] R. Kuhn and H. Trischmann, *Monatsh. Chem.*, 1964, **95**, 457.

[5.] Cf. Y. Miura and M. Kinoshita, *Macromol. Chem.*, 1974, **175**, 23. We thank to Prof. Y. Miura of Osaka City University for his kind suggestion on the reduction.

[6.] E. Dormann, H. Winter, W. Dyakonow, B. Gotschy, A. Lang, H. Naarmann, and N. Walker, *Ber. Bunsenges. Phys. Chem.*, 1992, **96**, 922; S. Tomiyoshi, T. Yano, N. Azuma, M. Shoga, K. Yamada, and J. Yamauchi, *Phys. Rev. B*, 1994, **49**, 16031.

[7.] Weiss-constants of **1**, **2**, **4** are -9.9 K for **1**, -29 K for **2**, and -99 K for **4**, respectively.

[8.] For example, **3**-TCNQF4 complex showed very weak antiferromagnetic interactions with Weiss-constant of -0.1 K and its Curie-constant was as low as 0.0018 emu·K/mol. Details on magnetic behavior on CT complexes prepared will be reported separately together with the data on the radicals **1**-**6**.

[9.] Cf. D. E. Williams, *Acta Cryst B*, 1973, **29**, 96.

[10.] T. Sugimoto, K. Ueda, M. Tsujii, H. Fujita, N. Hosoito, N. Kanehisa, Y. Shibamoto, and Y. Kai, *Chem. Phys. Lett.*, 1996, **249**, 304.

[11.] K. A. Hutchison, G. Srdanov, R. Menon, J. C. P. Gabriel, B. Knight, and F. Wudl, *J. Am. Chem. Soc.*, 1996, **118**, 13081.