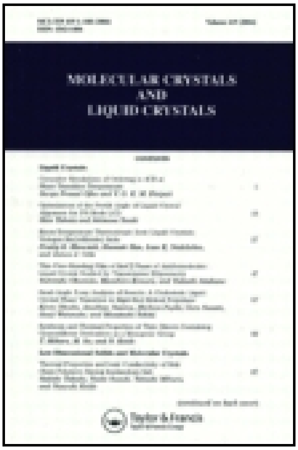

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Preparation and Properties of Biradicals and Related CT Complexes Based on 4-Substituted-Amino-TEMPO Radical

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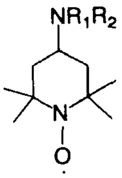
Several biradicals consisting of 4-substituted-amino-TEMPO were prepared from 4-oxo-TEMPO with certain diamines as piperazine, ethylenediamine, 1,2-trans- or cis-cyclohexanediamine by reductive amination reaction. A series of CT complexes derived from the biradicals and acceptors was then prepared and their magnetic behavior was investigated comparing with the original biradicals. Although the ferromagnetic behavior was observed in the biradical derived piperazine, antiferromagnetic behavior was predominantly observed in other biradicals or CT complexes derived therefrom.

Keywords: biradical; TEMPO radical; CT complex; ESR spectrum; magnetic property

INTRODUCTION

The search for new organomagnetic materials is continuously of current interest and a wide variety of spin systems for the materials has been proposed and developed recently.[1] In the course of our studies to develop new organomagnetic materials, we found that some TEMPO radicals as 4-substituted-amino-TEMPO radicals form CT complexes with appropriate acceptors to open a way to certain spin systems.[2] As an extension of the approach to develop new organomagnetic materials, we were interested in preparing biradicals derived from 4-amino TEMPO and the CT complexes derived therefrom and investigating their magnetic properties.

Here, we report on the preparation and the magnetic properties of the biradicals **2**-**5** consisting of 4-substituted-amino-TEMPO with piperazine, ethylenediamine, 1,2-trans- or cis-cyclohexanediamine as the bridging groups and a series of CT complexes derived from the biradicals with acceptors.



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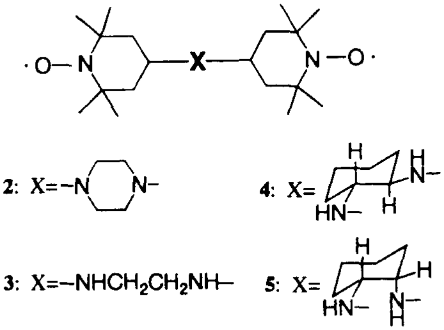

RESULTS AND DISCUSSION

Preparation of Biradicals Derived from 4-Amino-TEMPO and Their CT Complexes

The biradicals **2**-**5** consisting of 4-substituted-amino-TEMPO derivative were prepared from 4-oxo-TEMPO with certain diamines as piperazine, ethylenediamine, 1,2-trans- or cis-cyclohexanediamine by reductive amination reaction. Although the yield of each biradical was not sufficiently good in each case partially because of the contamination of corresponding mono-aminated radical, they could be easily isolated and purified by column chromatography and recrystallization. In the case of 1,2-trans-cyclohexanediamine, the biradical **4** was obtained by stepwise sequence through mono-aminated radical.

The corresponding CT complexes could be prepared from the biradicals with acceptors as $TCNQF_4$ or DDQ. It was of particular interest that both the complexes having the donor-to-acceptor ratio of 1:1 and 1:2 could be obtained for $TCNQF_4$ complexes of the biradicals. Almost twice as large extinction coefficients for the absorptions assigned to the $TCNQF_4$ radical anion were observed in each 1:2 complex as those of corresponding 1:1 complex. Although we further tried to prepare the mixed complexes such as biradical-$TCNQF_4$ with DDQ, no fruitful result has been obtained until now.

ESR Spectra of Biradicals 2-5 and their CT Complexes

ESR measurement on biradicals **2**-**5** and their CT complexes was carried out between the temperature range of 118 K - 300 K in 2-methyltetrahydrofuran. The data of zero field splitting parameters (|D|- and |E|-values) and the distances between the radical centers (r-values) estimated by point dipole approximation on biradicals **2**-**5** and $TCNQF_4$ complexes of **2** are summarized in TABLE 1.[3]

TABLE 1 Summary of ESR Data of Biradicals **2**-**5** and $TCNQF_4$ complexes of **2**

Compound	|D| (mT)	|E| (mT)	r (Å)[a]
2	3.75	0.10	9.1
3	3.78	0.61	9.0
4	4.08	0.43	8.8
5	4.95	0.68	8.3
2 • $TCNQF_4$ (1:1)	3.43	0.74	9.3
2 • $TCNQF_4$ (1:2)	3.46	0.92	9.3

[a]Estimated by point dipole approximation.

Although no large difference is observed in the three values listed in the TABLE 1 for the biradicals, the largest |D|-value is observed in **5** and the smallest |D|-value in **2** and the biradical has also the smallest |E|-value among them reflecting the small anisotropy of the biradical. As the result of their |D|-values, the smallest r-value (8.3 Å) estimated by point dipole approximation is assigned to the biradical **5** and the largest one (9.1 Å) to **2**. At the same time, the latter value of **2** appears to be reasonable from the structural point of view estimated by molecular model as well as X-ray analysis (*vide infra*). No large difference is also observed in |D|- as well as r-values by complexation of **2**, i. e., there is no marked difference in the two values of 1:1 or 1:2 $TCNQF_4$ complexes comparing with those of the biradical **2**. Only the increase of the |E|-values in the complexes is noticeable comparing with that of **2** suggesting the increase of anisotropy in the complexes.

Because no peak corresponding to Δ Ms=2 transition could be observed for the biradicals or their CT complexes at the above condition, we then carried out the ESR measurement for **2** as well as its CT complexes in acetonitrile at 4.2 K - 40 K to see if the peak could be observed. Actually, the peak corresponding to the transition was clearly observed at 4.2 K for **2** and which almost diminished at 40 K while the peaks observed at 4.2 K diminished above 10 K for the complexes of **2**. The observation indicates that ground state is singlet for both the biradical **2** and its CT complexes with thermally accessible low lying excited triplet state and the lower excited state is presumed for the biradical **2** than for the complexes.

Magnetic Susceptiblity of Biradicals 2-5 and their CT Complexes

The magnetic susceptibility of Biradical **2-5** and their CT complexes is measured with the polycrystalline samples in the temperature range of 2-300 K using a SQUID and the selected data are summarized in TABLE 2.

It was found from the results that ferromagnetic interactions were observed only for the biradical **2** being apparent from the positive value of its Weiss-temperature although the value was a small one. Weak antiferromagnetic interactions were predominantly observed for other biradicals **3-5** or the CT complexes of **2** being estimated by their negative Weiss-temperatures and it means that the spin-spin interactions between the radical centers are rather weak in these systems. No large decrease from two S=1/2 spins of their

TABLE 2 Summary of Magnetic Susceptibility Data of Biradicals **2**-**5** and CT complexes of **2**

Compound	C (emu·K/mol)[a]	Θ (K)	Magnetic Interaction
2	0.56	0.18	ferromagnetic
3	0.54	-0.30	Antiferromagnetic
4	0.74	-1.33	Antiferromagnetic
5	0.78	-2.27	Antiferromagnetic
2 • $TCNQF_4$ (1:1)	0.48	-0.67	Antiferromagnetic
2 • $TCNQF_4$ (1:2)	0.65	-0.67	Antiferromagnetic
2 • DDQ (1:1)	0.21	-2.89[b]	Antiferromagnetic

[a] Fitting for Curie-Weiss rule. [b] Short-range order is suggested.

susceptibility was apparent from their Curie constants except for DDQ complex of **2** and the tendency is consistent with earlier observation for the related mono-radicals.[2]

X-ray Analysis on Biradical 2

X-ray analysis on the biradical **2** was carried out with the single crystal grown from the n-hexane solution of the compound. It is apparent from the analysis that the molecule has a skewed conformation with almost perpendicular manner between central six-membered ring of piperazine and both six-membered rings of TEMPO radicals attached to it (FIGURE). The biradical molecules stack

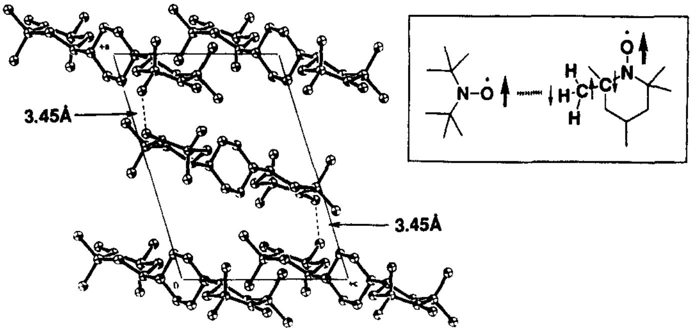

FIGURE Crystal structure of **2** viewed along b-axis.
Inset: spin polarization mechanism through hydrogen atom.

along the c-axis and a short contact is found between the oxygen atom of a nitroxide radical and one of the methyl groups of another biradical (C-O distance is 3.45 Å as depicted in FIGURE) and which is considered to be the contact based on the hydrogen bond between them. The ferromagnetic interactions observed in the biradical could then be well understood by taking the spin polarization effect into account.[4] The oxygen atom of another nitroxide radical of the same biradical molecule has, in turn, another contact with one of the methyl groups of another biradical which is placed in opposite direction from the biradical described above and thus the quasi-one-dimensional array of intermolecular hydrogen bond is formed in zig-zag manner between the biradical molecules as shown in FIGURE and which is relevant in ferromagnetic behavior of the biradical **2**.

Acknowledgments

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