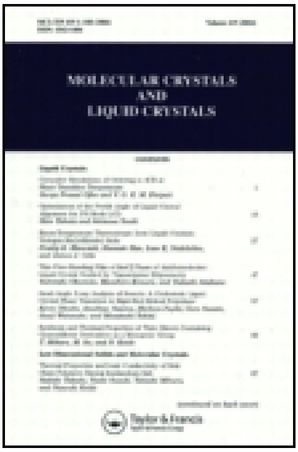

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EFFECT OF SUBSTITUENTS ON DIPOLAR COUPLING IN ALKALI METAL KETYL RADICAL PAIRS

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Abstract: A series of substituted alkali metal benzophenone ketyls was prepared and studied by ESR at low temperature. These species form triplet radical pairs in THF solution. Zero-field splitting parameters show that the high-spin behavior of these systems is unaffected by a variety of electronically and sterically perturbing substituents. The use of ketyl radical pairs as building blocks in the construction of molecular magnetic materials is suggested.

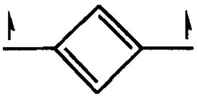
INTRODUCTION

A significant challenge in the field of molecular magnetic materials is the introduction of reliable high-spin coupling interactions between paramagnetic centers. Our interest in using ion binding as a means of organizing radical ionophores led us to reexamine the behavior of alkali metal benzophenone ketyl pairs. These radical anion salts are familiar in organic chemistry laboratories as the characteristic blue species that signal dry, anaerobic solvent stills. Though they are among the earliest recognized examples of high-spin coupling through metal ions, these established intermolecular ferromagnetic coupling units surprisingly have been ignored as building blocks for extended magnetic structures. As a first step toward their potential development as self-assembling, high-spin coupling subunits of molecular magnetic systems, we have examined a series of aryl ring-substituted alkali metal benzophenone ketyls and made systematic measurements of their triplet zero-field splitting (ZFS) parameters.

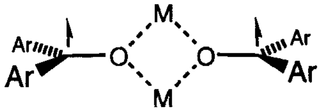
In 1891, Beckmann and Paul observed that aromatic ketones react with sodium in anhydrous ether to give dark blue compounds that we now understand as ketyl radical salts.[1] Gomberg, in 1927, introduced a pinacolate-ketyl free radical equilibrium.[2] After the advent of ESR methods, these equilibria were examined and clarified by Hirota,[3] and Mathias and Warhurst.[4] Hirota and others made the presumption that the paramagnetic dimers must have triplet ground states.[5]

Structural insights followed: McClelland[6] was the first to suggest that the metal ions are positioned over the carbonyl π-system in the fluorenone radical anions. Hirota's detailed ESR and UV-vis absorption studies of diarylketyls indicated that in polar solvents a complex series of equilibria are set up between monomeric and dimeric ion-pairs, solvated ion-pairs, and free ions. He proposed a diamond-shaped ion tetrad as the species responsible for the observed dipolar couplings. Other structural hypotheses have been published, but the recent crystal structure of $[\{\text{fluorenone}^{\bullet-}\}\{\text{Na}^{+}(\text{dme})_2\}]_2$ by Bock and coworkers, the only ketyl X-ray structure reported to date,[7] strongly supports Hirota's original Na-O-Na-O diamond arrangement. Moreover, this intermolecular coupling motif bears a strong topological resemblance to the known covalent high-spin coupling framework in dimethylenecyclobutadiene.[8]

One notable exception to the general lack of interest in high-spin (S>1) ketyl radical pairs has been preliminarily mentioned[9] and has been beautifully articulated at this Conference. Baumgarten and coworkers showed that diaroylbenzenes may be twice reduced to triplet biradicals that associate to form S=2 species. This is a key finding that points the way to the use of ketyls in extended magnetic structures.



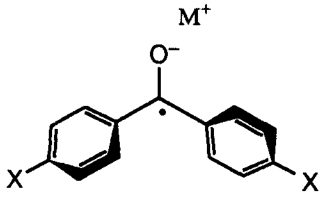
Dimethylenecyclobutadiene



Alkali Metal Ketyl Ion Tetrad

RESULTS

We have examined the ketyls **1** of a series of *para*-substituted benzophenones as well as **2**, the ketyl of the *ortho*-substituted bis(2,6-dimethoxy)phenylketone,[10] which is an intermediate in our triarylmethyl radical chemistry.[11] Diarylketyls were generated by reduction of the benzophenone with an alkali metal (Li, Na, or K) in THF solution. From the ESR spectra, zero field splitting parameters for associated ion tetrads were measured; they are listed in Table 1. The D values are systematically affected by the metal's identity and by the electronic characteristics of the aryl ring substituents; the variation of the E values, however, shows no recognizable pattern. Strong half-field transitions were seen for all but the *para*-nitro substituted case, indicating high-spin coupling.



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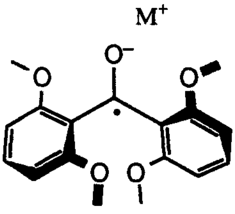

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TABLE 1: ESR ZFS Parameters for Alkali Metal Ketyls

Ketyl	Metal	D/hc (cm^{-1})	E/hc (cm^{-1})	Temp (K)
1, X=H	Li	0.0126	0.00024	100
	Na	0.0111	0.00020	100
	K	0.0093	0.00052	100
1, X=Me	Li	0.0122	0.00033	5
	Na	0.0112	0.00032	5
	K	0.0089	0.00034	100
1, X=OMe	Li	0.0140	0.00034	5
	Na	0.0112	0.00016	100
	K	0.0096	0.00024	100
1, X=NMe_2	Li	0.0117	0.00032	100
	Na	0.0106	0.00022	100
	K	0.0089	0.00018	100
1, X=Ph	Li	0.0109	0.00017	100
	Na	0.0093	0.00031	100
	K	0.0080	0.00013	100
1, X=NO_2	Li,Na,K	No ZFS measurable; weak half-field transition		
2	Li	0.0140	0.00031	6
	Na	0.0121	0.00031	100
	K	0.0089	0.00037	100

DISCUSSION

In order to prepare solid molecular magnetic materials from ketyls by self-assembly, it is necessary to prepare ketyl radicals that tolerate concentration to the point of total solvent removal. The familiar ketyl-pinacolate equilibrium therefore must be prevented in some manner, either by electronic stabilization of the ketyls, or by steric inhibition of bond formation.[12] Such modifications might be expected to adversely affect the coupling in ketyl radical pairs; the data in Table 1 provide tests of this hypothesis.

With the exception of the strongly electron withdrawing NO_2 group, *para*-substituents do not significantly affect the ZFS parameters, suggesting that they have little effect on the basic ion tetrad structure. The literature on the effects of substituents on ZFS parameters in biradicals is scant. Adam and coworkers recently analyzed the effect of *para*-substituents on the ZFS parameters of 1,3-diaryl-1,3-cyclopentanediyls.[13] They report a modest correlation with σ, the electron withdrawing ability of the *para*-substituents. Moreover, such a correlation would seem more likely in molecular triplets, with their covalently defined frameworks, than in ketyl ion tetrad radical pairs. In the present case, no simple variation with σ is evident; other possible correlations are still under investigation.

In the case of the *para*-nitro substituted benzophenone ketyl, a strong doublet ESR signal was observed, but essentially no half-field transition; we interpret this finding to indicate that the NO_2 group delocalizes the negative charge so strongly that the aggregation of ion pairs into tetrads is obviated. This interpretation is supported by the results of our electrochemical studies in addition to those of others,[14] which find the reduction potential of *para*-nitro benzophenone to be cleanly reversible and substantially (0.9 volts) less negative than that of benzophenone.

Steric hindrance of dimerization by addition of bulky *ortho* substituents might be expected to interfere with formation of the ion tetrads. However, the ketyls derived from bis(2,6-dimethoxyphenyl)ketone by alkali metal reduction give ZFS parameters that are not significantly different from those of the *para*-methoxy benzophenone ketyl. Evidently the triplet coupling structure is retained, despite the availability of potential ligating OMe sites.

An additional requirement for the eventual assembly of high-spin coupled materials is that the ketyl radical pairs have triplet ground states. In his earlier work, Hirota very reasonably assumed this to be true. As shown in Table 1, this assumption is supported by our observation of strong triplet spectra for several of these ketyl radical pairs at liquid helium temperatures. In more detailed studies of unsubstituted systems, Baumgarten et al. have positively confirmed the triplet ground state for ketyl dimers.[15]

In summary, we have shown that the magnetic coupling of benzophenone ketyls is a robust and predictable phenomenon. Variation of *para* substituents does not significantly affect the strength of magnetic coupling, nor do changes in the alkali metal's identity. The coupling also survives addition of bulky groups in all *ortho* positions, a common strategy for preventing dimerization of di- and triarylmethyl radicals. Liquid helium ESR spectra indicate triplet ground states in these systems. With their high-spin coupling motif, ketyls may now be added to the armamentarium of radicals with real potential as building blocks for the construction of high-spin organic magnetic materials.

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