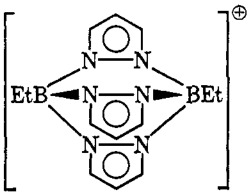
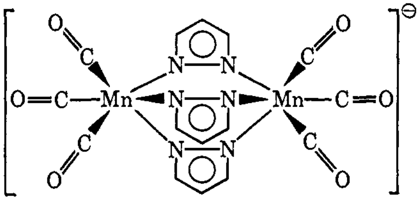


I



II

at τ 2.14, a triplet (J = 2.5 cps) at τ 3.89, and a distorted B-ethyl multiplet around τ 9 in 6:3:10 ratio. These data are consistent with structure I where both borons are tetrahedral and the ion is of local D_{3h} symmetry.[8] The ion I is also of interest in that it provides, formally at least, the first example of a boronium ion containing a formal charge of $+^1/_2$ per boron. Boronium ions with integral charges of +1 to +3 have been reported previously.[9,10]

The anion II was prepared in 69% yield by the reaction of $BrMn(CO)_5$ with 1.5 equiv of pyrazolide ion, and it was isolated as the yellow, fairly air-stable tetraethylammonium salt, mp 380–382°, the salt turning red around 290°. Elemental analysis (*Anal.* Calcd for $C_{23}H_{29}Mn_2N_7O_6$: C, 45.2; H, 4.77; Mn, 18.0; N, 16.1. Found: C, 45.2; H, 4.60; Mn, 17.7; N, 16.1) and the nmr spectrum [d (J = 1.9 cps) τ 2.55, t (J = 1.9 cps) 4.20, quartet (J = 7.0 cps) 7.27, and triplet of triplets (J = 7.0 and 1.8 cps) 9.21 in the correct 6:3:8:12 ratio] supported the assigned structure. In particular, the nmr spectrum not only showed the three pyrazolyl groups present to be identical, but also indicated equivalence of the 3 and 5 positions as would be anticipated on the basis of octahedral coordination for Mn and over-all D_{3h} symmetry for the ion. The ν_{CO} at 2016 and 1917 cm^{-1} reflects a higher M–C bond order as compared with the related uncharged species[11] HB(1-pyrazolyl)$_3$Mn(CO)$_3$ which has ν_{CO} at 2041 and 1941 cm^{-1} and the cation[12] [HC(1-pyrazolyl)$_3$Mn(CO)$_3$]$^+$ with ν_{CO} at 2059 and 1961 cm^{-1}.

The above examples underscore the versatility of pyrazolide ion as a ligand in organometallic chemistry, and the usefulness of the pyrazolide hydrogens for nmr probing of molecular symmetry.

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[8] This does not exclude an equilibration, fast on the nmr time scale, between instantaneous structures of lesser symmetry containing one of the B–N bonds detached, although this is regarded as unlikely. Some ring opening may be indicated from the fact that prolonged boiling in alcohol degrades this cation. The salt may, nevertheless, be recrystallized from ethanol.

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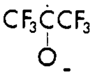
The Structure of Ketyl Radicals. Carbon-13 Splitting in Electron Spin Resonance Spectrum of Hexafluoroacetone Ketyl[1]

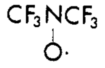
Sir:

Recently Janzen and Gerlock[2] reported an electron spin resonance spectrum of the hexafluoroacetone ketyl I. Their results are very unusual in that a very large (~35 G) fluorine hyperfine splitting (hfs) was observed. This is in contrast to a fluorine hfs of ~8 G for the isoelectronic bis(trifluoromethyl)nitroxide radical II.[3]



$\underset{\displaystyle O^-}{CF_3\dot{C}CF_3}$

I



$\underset{\displaystyle O\cdot}{CF_3NCF_3}$

II

The carbonyl ^{13}C hyperfine splittings in ketyl radicals have recently been discussed in terms of the structure of ketyl radicals.[4] The large ^{13}C carbonyl splitting in hexamethylacetone ketyl ($a^C_{C=O}$ = 49–53 G)[5] cannot be predicted by the Karplus–Fraenkel theory[6] if the unpaired electron is in a pure p orbital, *i.e.*, if the radical has a planar structure. Assuming a spin density of ρ^π_C = 0.8 on the carbonyl carbon, a maximum splitting of 20.3 G is calculated for a planar hexamethylacetone ketyl.[4] Thus it has been proposed that this radical is distorted out of the plane. We originally thought that the large difference between the fluorine hfs of I and II could be due to a difference in structure. Thus, we investigated the ^{13}C splittings for both the carbonyl and trifluoromethyl carbon atoms of I.

The ketyl I was generated by *in vacuo* electrolysis *intra muros*[7] with acetonitrile as the solvent.[2] The spectrum was recorded on a Varian E-3 spectrometer using Wurster's blue to calibrate the field sweep.[8] The assignments of the ^{13}C splittings were made on the basis of the intensities of the lines; the lines of the trifluoromethyl carbon splitting are about twice as intense as those of the carbonyl carbon splitting. Because the radical is unstable and the concentration was slowly changing while the spectrum was recorded, it was not possible to obtain the sign of the ^{13}C splitting by line-width variation.[9] The spectrum (Figure 1) was recorded over a period of 45 min. The ^{13}C hyperfine splittings are $a^C_{C=O} = 23.3 \pm 0.3$ G and $a^C_{CF_3} = 8.0 \pm 0.3$ G. No temperature dependence of the fluorine splitting was observed in acetonitrile in contrast to the temperature dependence found for the nitroxide.[3]

For a carbonyl carbon bonded to two carbon atoms that each have negligible π-spin density, the Karplus–Fraenkel theory predicts that

$$a^C_{C=O} = (S^C + 2Q^C_{CCF_3} + Q^C_{CO})\rho^\pi_C + Q^C_{OC}\rho^\pi_O \quad (1)$$

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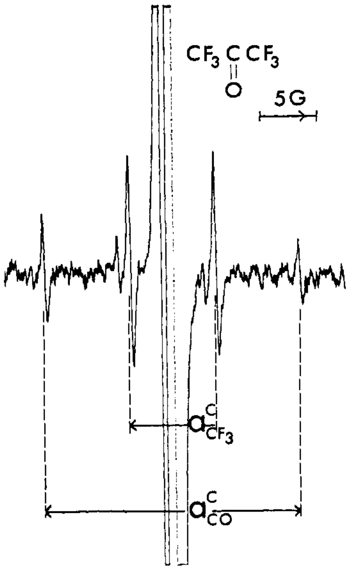

Figure 1. The spectrum of the low-field $\tilde{M}_{\mathrm{F}} = -2$ lines.

where $S^{\mathrm{C}} = -12.7$ G,[4] and $Q^{\mathrm{C}}_{\mathrm{CO}} = 17.7$ and $Q^{\mathrm{C}}_{\mathrm{OC}} = -27.1$ G.[10] $Q^{\mathrm{C}}_{\mathrm{CCF_3}}$ is taken to be the same as $Q^{\mathrm{C}}_{\mathrm{CCH_3}}$ in the ethyl radical. $Q^{\mathrm{C}}_{\mathrm{CCH_3}}$ may be calculated from the α-^{13}C splitting in the ethyl radical[11] ($a^{\mathrm{C}} = 39.07$ G)[12] by applying the Karplus–Fraenkel theory (assuming negligible π-spin density on the methyl carbon)

$$a^{\mathrm{C}} = (S^{\mathrm{C}} + 2Q^{\mathrm{C}}_{\mathrm{CH}} + Q^{\mathrm{C}}_{\mathrm{CCH_3}})\rho^{\pi}_{\mathrm{C}} \qquad (2)$$

where $Q^{\mathrm{C}}_{\mathrm{CH}} = 19.5$ G and $\rho^{\pi}_{\mathrm{C}} = 0.919$.[13] $Q^{\mathrm{C}}_{\mathrm{CCH_3}}$ is then calculated to be 16.3 G. Using this value in (1) and assuming $\rho^{\pi} = 0.5$–0.8, a carbonyl carbon splitting of 5.3–24.7 G is calculated. Our measured value of 23.3 G is within this range. Significant deviations from planarity would be expected to increase $a^{\mathrm{C}}_{\mathrm{C=O}}$ markedly. Thus we conclude that I is close to planar. Similar arguments indicate that II is also close to planar in structure. Hence, we must seek another explanation for the large change in the fluorine hfs. It is instructive to compare the available hyperfine splittings for I and II which are collected in Table I. Using the theoretically calculated splitting[14] for an electron in a 2s orbital on a carbon atom (1110 G) and a nitrogen atom (550 G), the ratio of the 2s orbital spin densities on the central atom in the isoelectronic species is calculated to be $\rho_{\mathrm{C}}/\rho_{\mathrm{N}} = 1.23$. This increase in spin density as the electronegativity of the central atom decreases in an isoelectronic family has been observed in inorganic radicals.[15] Thus the marked change in a^{F} between the bis(trifluoromethyl)nitroxide and the hexafluoroacetone ketyl cannot be explained in terms of large spin density changes on the central atom.

Table I. Comparison of the Hyperfine Splittings (G) in I and II

I	II
$a^{\mathrm{F}} = 34.94^{a}$	$a^{\mathrm{F}} = 8.26$
$a^{\mathrm{C}}_{\mathrm{CF_3}} = 8.0$	$a^{\mathrm{C}}_{\mathrm{CF_3}} = 5.1$
$a^{\mathrm{C}}_{\mathrm{CO}} = 23.3$	$a^{\mathrm{N}}_{\mathrm{NO}} = 9.46$

[a] Splitting determined by correcting observed second-order spectrum to first order and using a least-squares fit of data; see R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 3704 (1965).

The large fluorine splitting in hexafluoroacetone ketyl as compared to the isoelectronic nitroxide has now been interpreted in terms of an interaction between the lowest antibonding orbital on the carbonyl group and the lowest unoccupied antibonding orbital on the trifluoromethyl group.[16] This interaction is significantly greater than the corresponding interaction in the nitroxide radical because the energy difference between the interacting molecular orbitals is smaller in the hexafluoroacetone ketyl. This mechanism of spin transfer differs from that proposed by Scheidler and Bolton[3] since the electron transfer is in the opposite direction. However, the polarization of the fluorine 2s electrons by the net spin density in the trifluoromethyl group antibonding orbital is still the same. These calculations were made assuming that hexafluoroacetone ketyl is planar.

The larger fluorine splitting in I as well as the results of the INDO calculations by Morokuma are consistent with the double bond–no bond resonance scheme of Hine[17] insofar as both schemes predict electron transfer to the trifluoromethyl group.

Acknowledgments. The authors thank Dr. Morokuma for helpful discussions concerning this work.

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Molecular Orbital Interpretation of Fluorine Hyperfine Splitting in the Trifluoromethyl Group

Sir:

Recently an esr fluorine hyperfine splitting in hexafluoroacetone ketyl, $[\mathrm{OC(CF_3)_2}]^-$ (**1**)[1] has been reported to be $a_{\mathrm{F}} = 34.94$ G, which is 4.2 times larger than $a_{\mathrm{F}} = 8.26$ G in the isoelectronic bis(trifluoromethyl)-nitroxide (**2**).[2] This enormous change cannot be explained in terms of larger π spin density on the carbonyl carbon than on the nitroxide nitrogen.[1b]

In this communication we present an MO interpretation of this large splitting change. Numerical calculations are carried out with the unrestricted SCF method[3] in the INDO approximation.[4] The annihilation of the quartet component was then carried out with Amos and Snyder's scheme.[5] The bond distances used are NO and [CO]$^-$, 1.28 Å; CN, 1.47 Å; CC, 1.54 Å;

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