Figure 1. The spectrum of the low-field $\hat{M}_F = -2$ lines.

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

$$a^C = (S^C + 2Q^C_{CH} + Q^C_{CCH_3})\rho^\pi_C \qquad (2)$$

where $Q^C_{CH} = 19.5$ G and $\rho^\pi_C = 0.919$.[13] $Q^C_{CCH_3}$ 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 $a^C_{C=O}$ 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 theoreti-

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

I	II
$a^F = 34.94^a$	$a^F = 8.26$
$a^C_{CF_3} = 8.0$	$a^C_{CF_3} = 5.1$
$a^C_{CO} = 23.3$	$a^N_{NO} = 9.46$

^{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).

cally 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 $\rho_C/\rho_N = 1.23$. This increase in spin density as the electronegativity of the central atom decreases in an iso-

(10) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).
(11) See reference 15 in footnote 4.
(12) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(14) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

electronic 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.

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.

(15) H. J. Bower, M. C. R. Symons, and D. J. A. Tinling in "Radical Ions," E. K. Kaiser and L. Kevan, Ed., John Wiley and Sons, Inc., New York, N. Y., 1968, p 422.
(16) K. Morokuma, *J. Amer. Chem. Soc.*, **91**, 5412 (1969).
(17) J. Hine, *ibid.*, **85**, 3239 (1963).

William R. Knolle, James R. Bolton
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455
Received June 26, 1969

Molecular Orbital Interpretation of Fluorine Hyperfine Splitting in the Trifluoromethyl Group

Sir:

Recently an esr fluorine hyperfine splitting in hexafluoroacetone ketyl, [OC(CF$_3$)$_2$]$^-$ (1)[1] has been reported to be $a_F = 34.94$ G, which is 4.2 times larger than $a_F = 8.26$ 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;

(1) (a) E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967); (b) W. R. Knolle and J. R. Bolton, *J. Amer. Chem. Soc.*, **91**, 5411 (1969).
(2) P. J. Scheidler and J. R. Bolton, *ibid.*, **88**, 371 (1966).
(3) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 57 (1954).
(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967). The program used is originally based on G. A. Segal, CNDO/2, distributed as Quantum Chemistry Program Exchange 91, Indiana University.
(5) A. T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964).

and CF, 1.33 Å. All the atoms except for fluorine are assumed to be planar (xy plane) and the bond angles are 120° and 109° 28'. Two presumably stable rotational isomers a and b are considered for each compound.

a   b
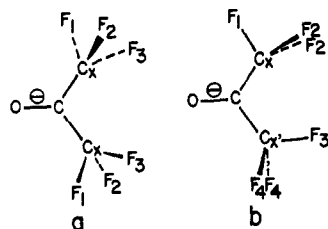
The fluorine 2s spin densities as well as the π spin density on CO and NO groups and other 2s spin densities are shown in Table I.[6] The ratio of the average

Table I. Calculated Spin Densities

Atomic orbital	1a	1b	2a	2b
F_1 2s	+0.00055	−0.00001	+0.00010	−0.00001
F_2 2s	+0.00239	+0.00178	+0.00050	+0.00038
F_3 2s	+0.00057	−0.00003	+0.00011	−0.00003
F_4 2s		+0.00174		+0.00035
F average	+0.00117	+0.00117	+0.00024	+0.00024
C_x and $C_{x'}$ 2s	−0.00181	−0.00183	−0.00105	−0.00105
C or N 2s	+0.00401	+0.00401	+0.00263	−0.00263
O 2s	+0.00454	+0.00454	+0.00439	+0.00439
C or N 2pπ	+0.3008	+0.3008	+0.1694	+0.1694
O 2pπ	+0.6394	+0.6394	+0.8156	+0.1857

fluorine 2s spin density is $\rho_F(1)/\rho_F(2) = +0.00117/+0.00024 = 4.9$, which is in good agreement with the above-mentioned experimental value of 4.2.[7] This large coupling in 1 can be qualitatively explained in that the half-occupied π MO φ_0 of [CO]⁻ group has such a high energy (+0.1038 au for [H₂CO]⁻ in INDO) that it interacts efficiently with the unoccupied π^* MO ψ_π^* of the CF₃ group which has a low energy (+0.2984 au in HCF₃) because of the large electronegativity of fluorine atoms. In 2, on the other hand, φ_0 of the NO group is of low energy (−0.4600 au for H₂NO) so that the interaction with ψ_π^* is small, but is not low enough to interact strongly with occupied π MO's ψ_{π_2} and ψ_{π_3} of the CF₃ group (−0.7126 and −0.7814 au in HCF₃).

Such an abnormality would not be expected in conjugated ketyls[9] in which φ_0 is stabilized by conjugation or in methyl compounds[10] in which the methyl unoccupied π level is of higher energy than the hexafluoro-

methyl level because of smaller electronegativity of the proton.

The calculated ratio of the trifluoromethyl carbon 2s spin density, $\rho_C(1)/\rho_C(2) = -0.00182/-0.00105 = 1.7$, compares very well with experimental ratio of the ¹³C coupling constant,[1b] $a_C(1)/a_C(2) = 8.0$ G/5.1 G = 1.6. In addition, the ratio of the calculated CO carbon 2s to the NO nitrogen 2s spin density, $\rho_C(1)/\rho_N(2) = +0.00401/+0.00263$, times the ratio of the theoretical splitting[8] for a 2s electron on a ¹³C atom (1110 G) to that on an ¹⁴N atom (550 G) gives the calculated ratio of the coupling constant $a_C(1)/a_N(2) = 3.1$, which again agrees well with the experimental value,[1b] 23.3 G/8.26 G = 2.8.

Scheidler and Bolton have proposed a hindered rotation of CF₃ groups to explain the temperature dependence of a_F in 2 between 163 and 297°K,[2] and on the other hand a_F in 1 is temperature independent.[1b] The difference of the INDO total energy between 1a and 1b gives a rotational barrier of 0.3 kcal/mole, while that between 2a and 2b gives 0.6 kcal/mole. This is in qualitative agreement with the hindered rotation mechanism in that the barrier for 2 is larger than for 1, but cannot explain the temperature dependence of the coupling constant a_F because the average ρ_F in the more stable isomer a is not different from that of b (cf. Table I).

Finally it is interesting to note in Table I that for both 1 and 2 the fluorine 2s spin density and therefore the coupling constant a_F can be expressed in good approximation by $a_F = A + B \cos^2 \theta$, where θ is the angle between the z axis and the projection of the CF bond to a plane perpendicular to the CF₃ axis. This is of the same form as the relationship known for CH₃ proton coupling.[11] A is near zero in both compounds, and B is a constant which depends on the molecule.

(11) C. Heller and H. M. McConnell, *J. Chem. Phys.*, 32, 1535 (1960).

Keiji Morokuma
Department of Chemistry, University of Rochester
Rochester, New York 14627

(6) From the anisotropic ¹⁴N hyperfine coupling constant, ρ^π_N in di-t-butyl nitroxide is considered to be approximately 0.5 (J. R. Bolton private communication). The calculated $\rho^\pi_N = 0.1694$ for 2 and $\rho^\pi_C = 0.3008$ for 1 seem to be too small, but their ratio qualitatively satisfies the experimental implication[1]: $\rho^\pi_C > \rho^\pi_N$.

(7) In INDO calculation of ethyl radical[4] the average CH₃ proton spin density after annihilation is +0.0347. To obtain the observed coupling constant of +26.87 G, a value of 778 G or 1.53 times 508 G has to be used as the conversion factor. If we use 1.53 times the theoretical value 1.71 × 10⁴ G for fluorine 2s orbitals,[8] the average spin densities 0.00117 and 0.00024 amount to the coupling constants 31.6 and 6.3 G, respectively, which turn out to be reasonably close to the experimental values 34.94 and 8.26 G.

(8) J. R. Morton, *Chem. Rev.*, 64, 453 (1964).

(9) L. M. Stock and J. Suzukui, *J. Amer. Chem. Soc.*, 87, 3909 (1965).

(10) G. Chapelet-Letourneux, L. Lamaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3283 (1965); J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc.*, A, 298 (1968).

Triplet Lifetimes of Benzophenone, Acetophenone, and Triphenylene in Hydrocarbons

Sir:

Aromatic ketones, such as benzophenone and acetophenone, are generally considered not to phosphoresce in normal solvents at room temperature,[1] although Parker[2] has recently observed phosphorescence at room temperature from benzophenone in a fluorocarbon solvent. However, the reasonably long lifetime[3] of benzophenone in benzene ($\tau_0 \sim 10^{-5}$ sec) led us to believe that we should be able to see emission in hydrocarbons. This is indeed the case, and in Figure 1 we show the

(1) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966).

(2) C. A. Parker, *Chem. Commun.*, 13, 749 (1968).

(3) J. A. Bell and H. Linschitz, *J. Am. Chem. Soc.*, 85, 528 (1963).