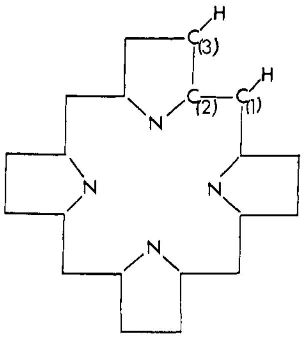
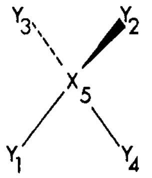
(the notation $T_d[T_d(\mathrm{X}),C_{3v}(\mathrm{Y})]$ is actually sufficient). The notation for CH_2F_2 would be $C_{2v}[C_{2v}(\mathrm{C}),C_s(\mathrm{H}),C_s'(\mathrm{F})]$. That for the porphine dianion (**1**) would be $D_{4h}[C_{2v}(\mathrm{N}),C_{2v}'(\mathrm{C(1)H}),C_s(\mathrm{C(2)},\mathrm{C(3)H})]$. Tables II–V of ref 1 have their original meaning with the obvious substitution of the new definitions.



1

For an illustration of the computational utility of site symmetry and interchange groups, consider the construction of symmetry adapted functions from an s and p basis set on each atom of the tetrahedral XY_4 system (**2**). Let the reference Cartesian axes



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be parallel to the C_2 axes. Call the basis functions s_i, x_i, y_i, and z_i. The orientation of the x_i on the Y atoms should be such that they are interchanged by the operations of the interchange symmetry group and similarly for the y_i and z_i. The site symmetry of X is the full T_d and that for Y_i is C_{3v}. The respective interchange groups are C_1 and S_4. A correlation diagram[4] of C_{3v} and S_4 with T_d is useful. This is given in Table III. This tells us that, for example, a function transforming as the A_1 representation in the C_{3v} site symmetry and as E under the interchange spans the T_2 representation of T_d.

For the X atom, s_5 transforms as A_1 within T_d, while x_5, y_5, and z_5 together transform as T_2. For Y_1, s_1 transforms as A_1, while x_1, y_1, and z_1 span $A_1 + E$. By using the projection operators, P^Γ, from C_{3v}, the symmetry adapted combinations of x_1, y_1, and z_1 are

$$P^{A_1}x_1 = (1/\sqrt{3})(x_1 + y_1 + z_1) \equiv a_1 \tag{1}$$

$$P^{E}x_1 = (1/\sqrt{6})(2x_1 - y_1 - z_1) \equiv e_1 \tag{2}$$

$$P^{E'}x_1 = (1/\sqrt{2})(y_1 - z_1) \equiv p_1 \tag{3}$$

(where eq 2 and 3 are the two orthogonal components of the E function.) The symmetry adapted functions in T_d can be obtained by applying the appropriate S_4 projection operators to s_1, a_1, e_1, and p_1. We have for the A_1 functions

$$P^{A}s_1 = N(s_1 + s_2 + s_3 + s_4) \equiv \lambda_1^{\mathrm{A}_1} \tag{4}$$

$$P^{A}a_1 = N(a_1 + a_2 + a_3 + a_4) = N(x_1 + x_2 + x_3 + x_4 + y_1 + y_2 + y_3 + y_4 + z_1 + z_2 + z_3 + z_4) \equiv \lambda_2^{A_1} \tag{5}$$

where the N's are normalizing constants. Several combinations are possible for the degenerate E, T_1, and T_2 functions. Unique combinations should be chosen. The combinations EB for E, EE for T_1, and $\mathrm{A_1B}$ and EE for T_2, where the first listed representation is from the site symmetry and the second from the interchange, are suitable choices. The two components of the E representation of S_4 acting on the same component of the E from C_{3v} give the T_1 and T_2 functions. We have for one component of the E functions

$$P^{B}e_1 = N(e_1 - e_2 + e_3 - e_4) = N[2(x_1 - x_2 + x_3 - x_4) - (y_1 - y_2 + y_3 - y_4) - (z_1 - z_2 + z_3 - z_4)] \equiv \lambda^{E} \tag{6}$$

For one component of the T_1 function

$$P^{E}e_1 = N(e_1 - e_3) = N[2(x_1 - x_3) - (y_1 - y_3) - (z_1 - z_3)] \equiv \lambda^{T_1} \tag{7}$$

And for one component of each of the T_2 functions

$$P^{\mathrm{B}}s_1 = N(s_1 - s_2 + s_3 - s_4) \equiv \lambda_1^{T_2} \tag{8}$$

$$P^{B}a_1 = N(a_1 - a_2 + a_3 - a_4) = N(x_1 - x_2 + x_3 - x_4 + y_1 - y_2 + y_3 - y_4 + z_1 - z_2 + z_3 - z_4) \equiv \lambda_2^{T_2} \tag{9}$$

$$P^{E}e_1N(e_2 - e_4) = N[2(x_2 - x_4) - (y_2 - y_4) - (z_2 - z_4)] \equiv \lambda_3^{T_2} \tag{10}$$

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[4] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955, p 122.

Radical Anion of 1,1-Difluoroethylene. EPR Evidence for a Perpendicular Geometry

Jih Tzong Wang and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Received December 22, 1980

Fluorine substitution is known to have a profound effect on the geometry and electronic structure of alkyl radicals.[1-3] Also, it has been demonstrated that increasing fluorination of the benzene and pyridine radical anions brings about a π^*–σ^* crossover in the electronic structure of these radicals.[4,5] Since previous work has provided strong evidence that the tetrafluoroethylene radical anion is a σ^* radical,[6] we have sought to generate the 1,1-difluoroethylene radical anion in the solid state and compare the structures of these two radicals. We find that the EPR spectrum of $CF_2{=}CH_2^-$ can be uniquely interpreted in terms of a 90° twisted (perpendicular) molecular geometry, the unpaired electron occupying an orbital which can be designated as σ^* (or π'^*)[7] for the CF_2 group and π for the CH_2 group.

The lower spectrum (c) in Figure 1 obtained from a γ-irradiated solution of $CF_2{=}CH_2$ in methylcyclohexane-d_{14} (MCHD) glass shows a pair of broad anisotropic features positioned just inside the lines of atomic hydrogen. Careful studies at 77 K established that these signals were produced to the exclusion of the narrow singlet from the matrix-trapped electron[8] for 1,1-difluoroethylene solutions in both MCHD and 2-methyltetrahydrofuran[9] glasses, thereby proving that these outer features result from electron capture by the solute. Thus, the features are assigned to the outer lines of a triplet spectrum resulting from hyperfine interaction with the two fluorines[10] in $CF_2{=}CH_2^-$, the center line being

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(8) (a) Lin, J.; Tsuji, K.; Williams, F. *J. Am. Chem. Soc.* **1968**, *90*, 2766. (b) Tsuji, K., Williams, F. *J. Phys. Chem.* **1968**, *72*, 3884.

(9) McNeil, R. I.; Ph.D. thesis, University of Tennessee, 1978.

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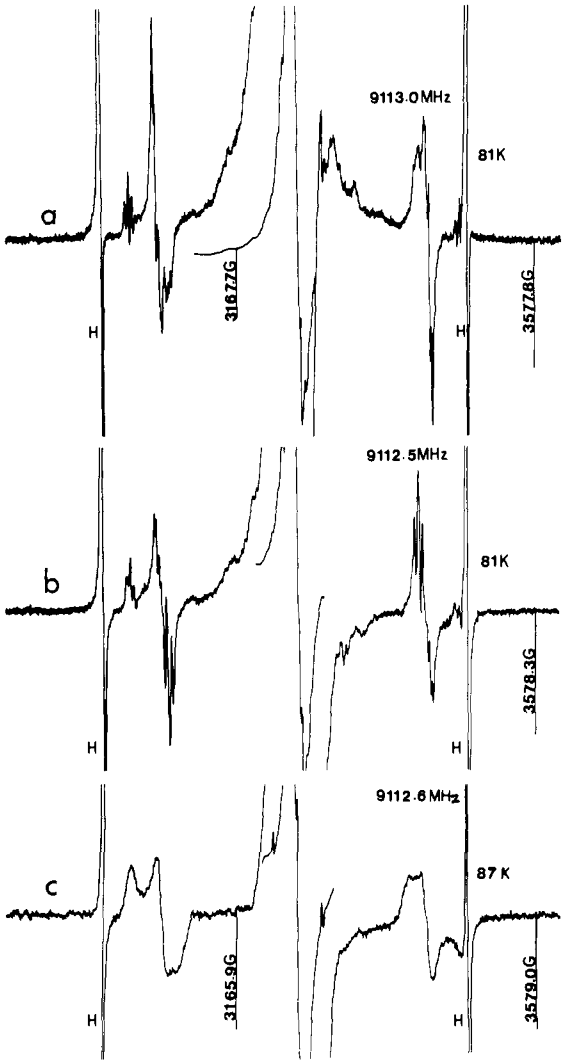

Figure 1. First-derivative EPR spectra of solid solutions containing 4 mol % 1,1-difluoroethylene in methylcyclohexane-d_{14} after γ irradiation at 77 K for a dose of ca. 1 Mrad. Spectra a and b were obtained at different orientations from a crystalline sample, and spectrum c was obtained from a sample in the glassy state.

Table I. EPR Parameters[a] for the 1,1-Difluoroethylene Radical Anion

source	g	hyperfine couplings, G	
		^{19}F(2)	^{1}H(2)
Figure 1a	2.0000	228.6	5.3
Figure 2	2.0027	188.3	3.7
Figure 1b	2.0031	172.3	5.3
av values	2.0019	196.4	4.8

[a] These parameters were derived from the high-resolution spectra in Figures 1 and 2, and they define the main resonances in the absorption envelope of the powder spectrum.

masked by the much stronger signals of the matrix radicals.

Although the spectra from the glassy state provide qualitative evidence for the formation of the 1,1-difluoroethylene radical anion,[9] the lack of spectral resolution provides few clues about its structure. We resorted, therefore, to EPR studies in partially ordered, crystalline MCHD solutions prepared by slow cooling, since recent studies have demonstrated the usefulness of this technique for discriminating between parallel and perpendicular features in powder spectra.[11,12] The results are illustrated by the spectra labeled (a) and (b) in Figure 1. In contrast to the structureless outer features of spectrum c from the glassy sample, these spectra obtained from partially ordered crystalline MCHD samples at optimized orientations show a well-defined hyperfine structure. In particular, the outer and inner singularities of the absorption envelopes are seen in spectra a and b, respectively, to be resolved into narrow 1:2:1 triplets which can be assigned to

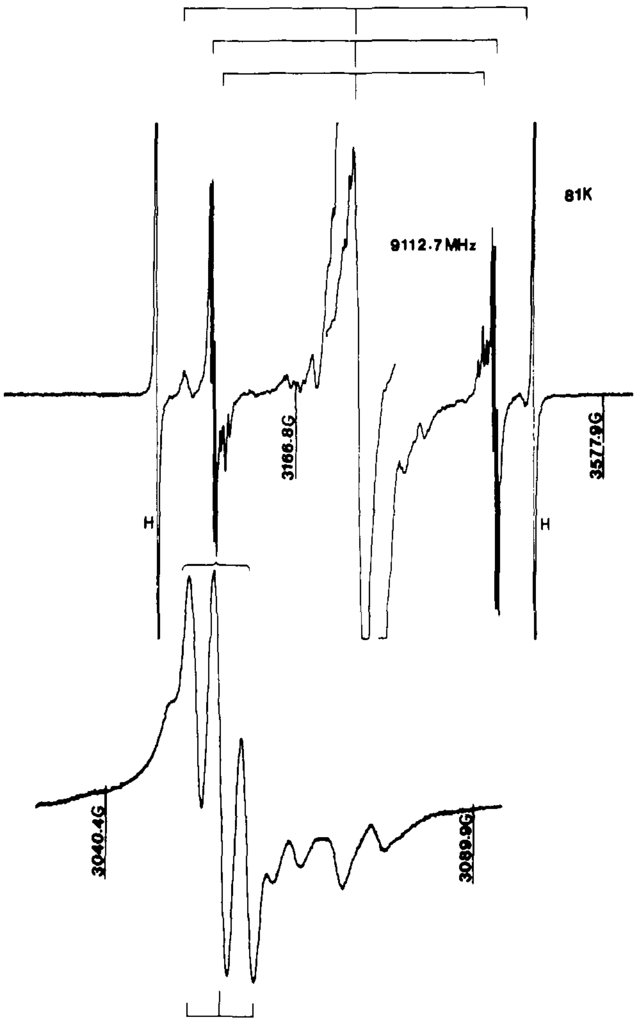

Figure 2. First-derivative EPR spectrum of a γ-irradiated ordered solution of 1,1-difluoroethylene in crystalline methylcyclohexane-d_{14} at a selected orientation. The low-field portion of the spectrum is also shown in expanded form for greater clarity. These spectra expose the 1:2:1 triplet substructure in the wing lines of the central ^{19}F triplet indicated in the upper stick diagram.

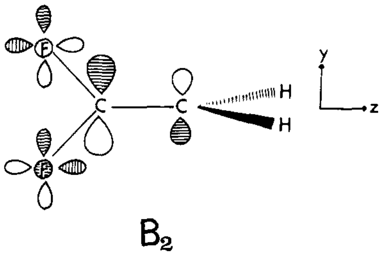

Figure 3. A schematic drawing showing the approximate composition of the 5B$_2$ singly occupied molecular orbital for perpendicular 1,1-difluoroethylene in C_{2v} symmetry.

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(10) The alternative possibility that the large hyperfine couplings result from interaction with the two hydrogens can be rejected, since this would require that almost all the spin density be concentrated in the hydrogen 1s orbitals.

(11) McNeil, R. I.; Williams, F.; Yim, M. B. *Chem. Phys. Lett.* **1979**, *61*, 293.

(12) Morton, J. R.; Preston, K. F.; Wang, J. T.; Williams, F. *Chem. Phys. Lett.* **1979**, *64*, 71.

hyperfine interaction with two equivalent hydrogens. Futhermore, another orientation was found to give a well-resolved triplet substructure in the center of the absorption envelope, as shown in Figure 2. As well as providing important structural information, these details clearly verify the radical anion assignment.

The hyperfine and *g* parameters deduced from the spectra obtained at the three canonical orientations are collected in Table I. These are unlikely to be the principal tensor components, since the magnetic field directions corresponding to these canonical orientations are limited to those for which the two hydrogens (and the two fluorines) are magnetically equivalent. Despite this restriction, the values of the ^{19}F and ^{1}H hyperfine parameters so obtained are diagnostic for the structural analysis given below.

If we assume that the 1,1-difluoroethylene radical anion adopts a planar geometry as in the case of the neutral molecule,[13] it is difficult to reconcile the combination of large ^{19}F and small ^{1}H couplings in Table I. Thus, the uniformly large ^{19}F couplings appear to rule out a π^* radical and are strongly indicative of a σ^* configuration as in $C_6F_6^-$ (ref 4) [$^{19}a(6)$ = 134 G[14,15]] or $C_2F_4^-$ (ref 6 and 12) [$^{19}a(4)$ = 94 G], whereas the very small ^{1}H couplings would not be expected for a σ^* radical but are typical of a π^* configuration as in $C_6H_6^-$ (ref 16) ($^{1}a(6)$ = 3.75 G). There is also a serious problem in explaining the results in terms of a slightly pyramidal radical with most of the spin density concentrated on the carbon of the CF_2 group, since the average fluorine couplings are much larger than the range of values (68–94 G) reported for isotropic ^{19}F couplings in CF_2X radicals.[1-3]

On the other hand, the results are readily accommodated by the assumption of a perpendicular geometry for the radical anion, and the $5B_2$ orbital shown in Figure 3 satisfies the requirements for the singly occupied molecular orbital (SOMO) imposed by the ^{19}F and ^{1}H hyperfine parameters. INDO calculations[17] show that this orbital is built primarily from the σ^* (or π'^*) group orbital in the (*yz*) plane of the CF_2 group which is antibonding with a smaller contribution from the p_y orbital of the CH_2 group. This is just the combination demanded by the experimental results, as mentioned earlier. While the ordering of antibonding molecular orbitals predicted by INDO calculations for $CF_2{=}CH_2^-$ gives the sequence, in increasing energy, $3B_1 < 6A_1 < 7A_1 < 5B_2$, the $3B_1$ and the two A_1 orbitals can be ruled out as candidates for the SOMO on the basis of their unsuitable compositions. Thus, each of these molecular orbitals possesses a direct contribution from the 1s orbitals of the two hydrogens, suggesting a much larger ^{1}H coupling than that which is observed. Also, it should be noted that the ordering of antibonding molecular orbitals predicted by INDO calculations is also incorrect for both $C_6F_6^-$ (ref 4) and $C_2F_4^-$.[18]

Finally, the present assignment for $CF_2{=}CH_2^-$ makes good sense if $C_2F_4^-$ is a σ^* radical[6] and $C_2H_4^-$ is a π^* radical. Although the EPR spectrum of the ethylene radical anion has not been reported,[19] a π^* assignment would be expected from the results of optical spectroscopy.[20] Also, the σ^* assignment for $C_2F_4^-$ (ref 6) is consistent with the results of electron transmisssion spectroscopy which show that the temporary π^* anions of the fluoroethylenes are increasingly destabilized by fluorination relative to the π^* anion of ethylene.[21] We conclude, therefore, that the perpendicular geometry of the 1,1-difluoroethylene radical anion enables it to avoid the π^*–σ^* crossover problem[4,5] by adopting the π configuration at the CH_2 group and σ^* configuration at the CF_2 group.[22,23]

Acknowledgment. This research has been supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Report DOE/ER/02968-133).

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[19] Attempts to generate $C_2H_4^-$ in solid matrices at 77 K have been unsuccessful.

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[22] It is interesting to note that the average ^{19}F coupling of 196 G (Table I) for the 1,1-difluoroethylene radical anion is approximately twice the isotropic ^{19}F coupling of 94 G for $C_2F_4^{-}$.[6,12] Also, the average ^{1}H coupling of 4.8 G (Table I) indicates a spin density of 4.8/22.5 = 0.21 in the p orbital of the CH_2 carbon. These results suggest that most of the spin density in $CF_2{=}CH_2^-$ is located in the σ^* (π'^*) CF_2 group orbital, in qualitative agreement with the composition of the $5B_2$ orbital (Figure 3).

[23] The cis–trans isomerization of 1,2-substituted ethylene radical anions is well-known (see, e.g., for the stilbene radical anions: Gerson, F.; Ohya-Nishiguchi, H.; Szwarc, M.; Levin, G. Chem. *Phys. Lett.* **1977**, *52*, 587), but in such cases the perpendicular form of the the radical anion is nonisolable and possibly corresponds to the transition state for the reaction.

Condensation of Enolates with Hexachlorobutadiene

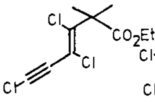
Andrew S. Kende,* Pawel Fludzinski, and John H. Hill

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

Received November 17, 1980

The formation of carbon–carbon bonds by uncatalyzed condensation of enolates with halo olefins is sufficiently unusual to merit synthetic exploitation and mechanistic scrutiny.[1-3] We have recently described an unprecedented dichlorovinylation of certain enolates as a route to α- and γ-ethynylated carbonyl compounds.[4] We now report novel and synthetically useful direct condensation reactions of enolates with hexachlorobutadiene (HBD) and propose a mechanistic rationale for our observations.

Reaction of 2 equiv of the lithium enolate of ethyl isobutyrate (from 2 equiv each of the ester, LDA, and HMPA at -78 °C in THF) with HBD (from -78 °C to room temperature, 6 h) gave, after kugelrohr distillation at 87–90 °C (0.1 mm), a 63% yield of a $C_{10}H_{11}O_2Cl_3$ oil having intense UV absorption at λ_{max} (MeOH) 245 nm (ϵ 13 500) and 251 nm (ϵ 13 800), ν_{max} (neat) 1740, 1560 cm^{-1}, and MS, ^{1}H NMR and ^{13}C NMR spectra consistent with either structure **1** or **2**.[5] Catalytic hydrogenation of the product (5% Pd/C, H_2, EtOH–Et_3N) to ethyl 2,2-dimethylhexanoate confirmed its carbon skeleton, and hydration of the product under vigorous conditions (saturated $HgSO_4$ in 1% H_2SO_4, EtOH, 75 °C, 21 h) to the highly reactive trichloro enone **3**[5] [λ_{max} (MeOH) 260 nm (ϵ 5500)] established the correct regiochemistry as **2**.[5]



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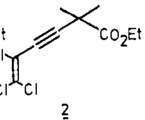

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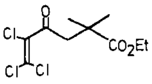

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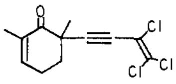

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The kinetic C-6 lithium enolate of 2,6-dimethyl-2-cyclohexenone reacted with HBD under the above conditions to give in 56% yield the condensation product **4**[5] having spectroscopic properties entirely analogous to the isobutyrate product **2**. In contrast, the sodio derivative (NaH, THF, room temperature, HMPA) from diethyl methylmalonate underwent negligible reaction with HBD. However, in THF at reflux for 35 h a condensation proceeded

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[1] For examples of nickel-catalyzed vinylation and arylation of enolates by bromides and iodides, see: Millard, A. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 4833.

[2] For examples of nickel- and palladium-catalyzed arylation and vinylation of Reformatsky reagents, see: Fauvarque, V. F.; Jutand, A. *J. Organomet. Chem.* **1978**, *177*, 273.

[3] For examples of iron-assisted vinylation of enolates, see: Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930.

[4] Kende, A. S.; Benechie, M.; Curran, D. P.; Fludzinski, P.; Swenson, W.; Clardy, J. *Tetrahedron Lett.* **1979**, 4513.

[5] UV, MS, ^{1}H NMR, and ^{13}C NMR spectra and elemental analyses are submitted as supplementary information.

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