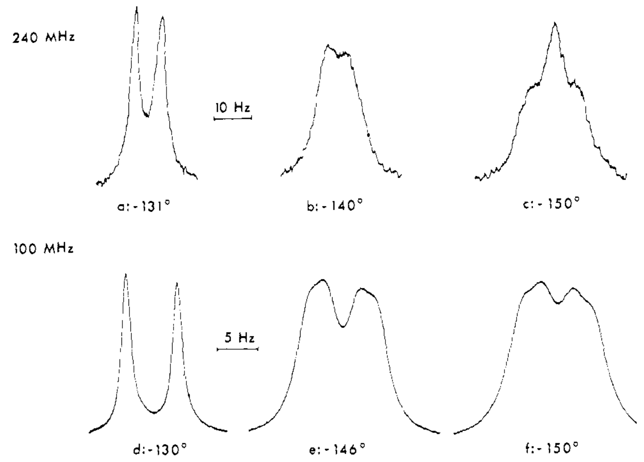

Figure 1. Spectra (240 and 100 MHz) of the methyl protons of diisopropylcarbodiimide at various temperatures.

line spectrum arising from two overlapping doublets with a chemical shift difference of about 6 Hz.

At 100 MHz the different chemical shifts could be seen through the appearance of inflection points (Figure 1f) only by a careful investigation of a more dilute sample in a solvent of lower viscosity, 1:1 vinyl chloride–chlorodifluoromethane.[10] These inflections disappear at −146° (Figure 1e) and a doublet with a coupling constant of 6.5 Hz is obtained at −130° (Figure 1d).

These results clearly demonstrate the dissymmetry of diisopropylcarbodiimide.[11] Chemical shift differences of similar magnitude have been reported for diastereotopic substituents on allenes.[12] The free energies of activation calculated from the coalescence temperature and the chemical shift differences are, at 240 MHz, 6.7 ± 0.2 kcal/mol, and at 100 MHz, 6.6 ± 0.3 kcal/mol; these values agree with theoretical predictions.[6,7,13]

Concerning the racemization mechanism, Gordon and Fischer[6] calculated that, for carbodiimide, rotation through the *trans* form, whereby the dihedral angle of the substituents increases from 90 to 180°, is favored over nitrogen inversion by 0.3 kcal/mol and suggested that the actual mechanism was probably a combination of rotation and inversion. Our present study does not give any information on the mechanism of racemization.

Acknowledgment. This work was supported by the U. S. Public Health Service.

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(10) Varian HA-100 spectrometer.

(11) Although the experimental results can be interpreted in terms of restricted rotation about the N–C single bond, we consider this possibility to be very unlikely.

(12) M. L. Martin, R. Mantione, and G. J. Martin, *Tetrahedron Lett.*, 4809 (1967).

(13) The errors given for the ΔF's are based on estimated maximal errors in the temperature of ±3° and an estimated uncertainty in chemical shift differences of ±1 Hz.

(14) On leave from Max-Planck-Institut für Medizinische Forschung, Heidelberg, Germany.

(15) Carbodiimides. V. For part IV see J. C. Jochims, *Chem. Ber.*, **101**, 1746 (1968).

F. A. L. Anet, J. C. Jochims,[14,15] C. H. Bradley
Contribution No. 2450, Department of Chemistry
University of California, Los Angeles, California 90024

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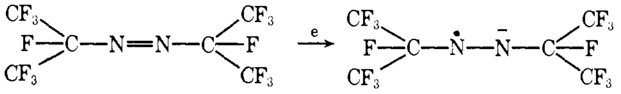
Electron Spin Resonance of Perfluoroazoalkane Radical Anions[1]

Sir:

Further investigations into the factors influencing the magnitude of β-fluorine hyperfine coupling in radical anions[2–5] have led to a study of the electron spin resonance (esr) spectra of perfluoroazoalkane radical anions. Perfluoroazoethane[6] is easily reduced on a platinum electrode at an applied voltage of −0.25 V in dry acetonitrile containing tetraethylammonium perchlorate.[7] An intense signal was produced immediately consisting of five groups of lines separated by approximately 35 G which could be further resolved into a total of 204 lines. Since first-order fluorine hyperfine coupling ($I = {}^1/_2$) can only account for 175 lines, support for second-order coupling was sought by inspection of a well-resolved spectrum produced at a very long time scan (250 G in 100 min) and recorded on a high gain recorder. Very good correlation was found with a second-order analysis[8] if the 35.25-G second-order coupling is assigned to four equivalent (β) fluorines and the 7.72- and 4.22-G first-order couplings are assigned to two equivalent nitrogen atoms and six equivalent (γ) fluorine atoms, respectively. In this analysis a total of 315 lines are predicted[8] ((5 × 7 × 1) + (5 × 7 × 2) + (5 × 7 × 3) + (5 × 7 × 2) + (5 × 7 × 1) = 315).

$$CF_3CF_2N{=}NCF_2CF_3 \xrightarrow{e} CF_3CF_2\dot{N}\bar{N}CF_2CF_3$$

The production of perfluoro-2-azopropane radical anion was also accomplished by electrolytic reduction of perfluoro-2-azopropane[9] at −3.0 V in acetonitrile. The spectrum consists of three groups of lines separated by approximately 60 G. Forty-five peaks in a symmetrical pattern were resolved in each side group. Approximately twice this number were resolved in the central group. The spectrum is consistent with a 62.45-G coupling from two equivalent fluorine atoms with a second-order splitting of 1.43 G. Further splitting of 7.81 G from two nitrogen atoms and 4.79 G from twelve (γ) fluorine atoms accounts for the splitting within each of the three groups of lines.



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(1) This work was supported by AFOSR(SRC)-OAR U.S.A.F. Grant No. 1069-66 and the Petroleum Research Fund administered by the American Chemical Society.

(2) E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **89**, 4902 (1967).

(3) E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967).

(4) J. L. Gerlock and E. G. Janzen, *J. Amer. Chem. Soc.*, **90**, 1652 (1968).

(5) J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

(6) Perfluoroazoethane was prepared by the reaction of silver difluoride with trifluoroacetonitrile according to J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967), and references therein.

(7) A platinum cathode inserted into the flattened region of a quartz vacuum electrolysis cell was used directly in an esr cavity.

(8) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

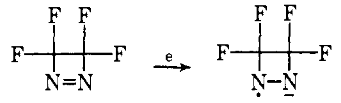
(9) Perfluoro-2-azopropane was prepared by allowing silver difluoride to react with hexafluoroacetone imine at room temperature in a closed system. This product was separated from the azine, $(CF_3)_2CNNC(CF_3)_2$, by slow vacuum line fractionation and identified by vapor density molecular weight measurement and fluorine-19 nmr and ir spectroscopy. The purity was checked by vpc. The esr spectrum of the tetrakis(trifluoromethyl)azine radical anion was also obtained. Further details will be reported at a later date.

Table I. Nitrogen and Fluorine Hyperfine Coupling in Perfluoroazoalkane Radical Anions[a]

Radical anion	A_N	$A_\beta{}^F$	$A_\gamma{}^F$	Solvent[b]	Θ, deg[c]
$CF_3CF_2N{=}NCF_2CF_3$	7.72	35.25	4.42	ACN	30
$CF_2{-}CF_2$ $\mid\quad\mid$ $N{=}N$	8.40	21.93		DMF	34–36.5
$CF_3N{=}NCF_3$	7.36[d]	18.26[d]		ACN	45
	7.38[d]	17.74[d]		DMF	
$(CF_3)_2FCN{=}NCF(CF_3)_2$	7.81	62.45	4.79	ACN	90

[a] In gauss. [b] ACN, acetonitrile; DMF, N,N-dimethylformamide. [c] Apparent dihedral angle. [d] Reference 4.

The cyclic tetrafluoroazoethylene[10] is also easily reduced under similar conditions in N,N-dimethylformamide. A second-order 21.93-G coupling due to four equivalent (β) fluorine atoms is easily recognized in this spectrum. A 8.40-G quintet is assigned to coupling from two equivalent nitrogens.

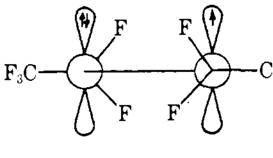


Other azo radical anions previously reported have similar nitrogen coupling constants: *e.g.*, dicyano,[11] 7.37; dicarbethoxy,[12] 5.9; diphenyl,[13] 4.84. The latter

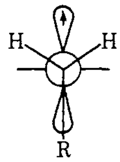
$$NC\dot{N}\bar{N}CN \qquad EtOOC\dot{N}\bar{N}COOEt \qquad C_6H_5\dot{N}\bar{N}C_6H_5$$

appears to have a nonlinear structure since nonequivalent *ortho*-hydrogen coupling constants have been extracted from the spectrum.[13] Zweig and Hoffmann[12] also favored a nonlinear structure for the dicarbethoxy derivative.

The second-order β-fluorine coupling in the perfluoroazoethane radical anion requires a highly equivalent magnetic environment[8] for the four β-fluorine atoms in the radical anion. The most probable conformation for this molecule fulfills this requirement (I) but is different from the most probable conformation suggested for previously studied radicals with substituted methylene groups[14] (II). In the most probable conformation for the perfluoroazoethane radical anion the average dihedral angle between the C–F bond and the p orbital on nitrogen is 30°, whereas in the substituted methylene derivatives[14] this angle is larger (60°).

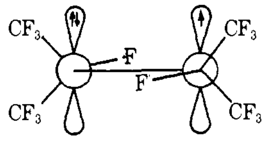


I

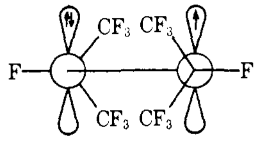


II

The most probable conformation of the perfluoro-2-azopropane radical anion is not obvious. Although the β-fluorine atoms are required to be in highly equivalent magnetic environments, because of the second-order splitting, this requirement can be met in an infinite number of conformations. However, the γ-fluorine atoms can only be in equivalent environments for conformations where the dihedral angle is 90° (III or IV). Insufficient data are available at this time concerning the factors influencing γ-fluorine coupling to assess the sensitivity of this coupling to slight differences in environment. However, the narrow line widths (0.3 G) and good intensity agreement with theory for the 13-line multiplets strongly support a highly equivalent environment for all 13-fluorine atoms in this radical anion.

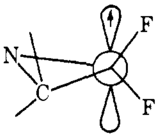


III



IV

In the cyclic tetrafluoroazoethylene radical anion the ring may be planar or the ring conformations must be interconverting rapidly on the esr scale. Since the FCF angle in perfluorocyclobutane[15] is found to be 107–112° (V) an average dihedral angle of 35–36.5° in the cyclic azo radical anion can be estimated.



V

Electrolytic reduction of hexafluoroazomethane[16] in acetonitrile or dimethylformamide gave high concentrations of a radical with the same spectrum as previously assigned to the bis(trifluoromethyl semidiazoxide)[4,17] obtained in the electrolytic reduction of CF_3NO. Extended purification of the azomethane to remove the trace amounts of CF_3NO possibly formed as a side product in the synthesis of the azomethane led to the same spectrum. Since the same results were also obtained upon rigorous exclusion of oxygen and water from the system no evidence could be found for the possible oxygenation of the azomethane radical anion to the semidiazoxide.[18] Moreover, the perfluoro-

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[10] Tetrafluoroazoethylene was prepared by the reaction of silver difluoride with cyanogen according to H. J. Emeleus and G. L. Hurst, *J. Chem. Soc.*, 3276 (1962). A Hestaloy bomb was used at room temperature.

[11] M. T. Jones, *J. Amer. Chem. Soc.*, **88**, 227 (1966); F. D. Marsh and M. E. Hermes, *ibid.*, **87**, 1819 (1965).

[12] A. Zweig and A. K. Hoffmann, *ibid.*, **85**, 2736 (1963).

[13] E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, **42**, 2033 (1965).

[14] D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967), and references therein.

[15] H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950); J. D. Dunitz and V. Schomaker, *ibid.*, **20**, 1703 (1952).

[16] Hexafluoroazomethane was synthesized by the reaction of silver difluoride with cyanogen chloride (V. O. Glemser, H. Schroeder, and H. Haeseler, *Z. Anorg. Allgem. Chem.*, **80**, 282 (1955)) or with hydrogen cyanide and purified according to literature methods.

[17] Note: inadvertently the row headings for the semidiazoxide in Table I of ref 4 were interchanged. The nitrogen and fluorine couplings are thus in the range 7.36–7.58 and 16.58–18.26 G, respectively, depending on solvent and water content.

[18] It should be noted that the spectra obtained from the reduction of hexafluoroazomethane always contained a second spectrum, sometimes

azoethane radical anion did not react with oxygen and/or small amounts of water to give new spectra. We are thus forced to the conclusion that the spectrum originally assigned to the semidiazoxide is due to the azo radical anion and that the electrolytic reduction of CF_3NO gives hexafluoroazomethane radical anion as the only esr detectable radical.[19] The magnitude of the nitrogen coupling[4,17] is also more in line with azo radical anions[11–13] than with the (probably larger) coupling expected from a semidiazoxide.

As can be seen from a comparison of the data reported (Table I), the β-fluorine coupling appears to go through a minimum as the dihedral angle is varied from 30 to 90° (if the conformational assignments are correct). Such a possibility was suggested in an earlier paper based on the comparison of the β-fluorine coupling in perfluoroalkylketyls[5] and nitroxides.[20] Both theoretical calculations[21–23] and experimental data indicate that β-fluorine coupling increases when the dihedral angle decreases from 45°. However, experimental results disagree on the extent of β-fluorine coupling when the dihedral angle is 90°. In triptycene semiquinone[24] the bridgehead fluorine coupling is approximately one-third of the value found for the freely rotating trifluoromethyl group, whereas in perfluoroisopropyl *t*-butyl nitroxide[22,25] the β-fluorine coupling is small (2.77 G at 25°) and decreases with decrease in temperature (0.76 G at $-$ 90°). In the perfluoroazoalkanes as shown in this work an unusually large β-fluorine coupling is observed when the dihedral angle is 90°. Clearly there is a need for data on systems where the dihedral angle *and* the spin density on the contiguous atom are known explicitly. Studies on perfluorobicycloazoalkane radical anions are planned.

It is of interest to note that no radicals were detected when hexafluoroazomethane (or hexafluoroacetone[3]) was reduced under ion-pairing conditions, *e.g.*, sodium or potassium in tetrahydrofuran.

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of equal intensity, consisting of two quintets, 8.51 and 21.89 G. Assignment to two equivalent nitrogens (2 N) and four equivalent fluorines (4 F) was not obvious from the intensities because of substantial overlap with peaks from the other spectrum. If the smaller coupling is assigned to 2 N and the larger to 4 F the structure could be assigned to cyclic tetrafluoroazoethylene radical anion (or some other azo radical anion with four fluorine atoms) obtained from impurities in the azomethane. Conversely if the smaller splitting is assigned to 4 F and the larger to 2 N we have considered the possibility of an azine radical anion structure produced from probable impurities. This possibility will be investigated.

$$\bar{C}F_2N{=}N\dot{C}F_2 \longleftrightarrow \bar{C}F_2\dot{N}N{=}CF_2 \longleftrightarrow \text{etc.}$$

(19) Studies with ^{17}O are planned to resolve this question.

(20) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966); see, however, E. T. Strom and A. L. Bluhm, *J. Phys. Chem.*, in press; E. G. Janzen, B. R. Knauer, J. L. Gerlock, and K. J. Klabunde, *ibid.*, in press.

(21) K. Morokuma, *J. Amer. Chem. Soc.*, **91**, 5412 (1969).

(22) G. R. Underwood, V. L. Vogel, and I. Krefting, unpublished; we acknowledge with appreciation the receipt of a preprint of this work.

(23) J. L. Meyer and E. G. Janzen, submitted for publication.

(24) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **92**, 409 (1970).

(25) K. J. Klabunde, *ibid.*, in press.

John L. Gerlock, Edward G. Janzen, John K. Ruff
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

Received November 1, 1969

Linkage Isomerization in Nitrogen-Labeled $[Ru(NH_3)_5N_2]Br_2$

Sir:

In other work, it was shown[1] that Cr(II) reacts readily and quantitatively with N_2O in the presence of $[Ru(NH_3)_5OH_2]^{2+}$ to form $[Ru(NH_3)_5N_2]^{2+}$. Since N_2O can be prepared[2] with the *exo* (or *endo*) nitrogen isotopically labeled, the possibility of preparing $[Ru(NH_3)_5N_2]^{2+}$ with the *endo* (or *exo*) nitrogen labeled suggests itself. The results to be presented show that the reaction does in fact take the indicated course, though there is some rearrangement of the specifically labeled complex during the time required to produce the salt of the complex. Approximate values for the rate of isomerization have been obtained, and these are of some use in assessing the stability of the π-bonded state.

Nitrogen-15-labeled N_2O was prepared by a modification of the method of Friedman and Bigeleisen.[2] Under the conditions described by them, we found ammonium nitrate to sublime virtually without decomposition. But by maintaining approximately 2 ml of degassed water open to the evacuated storage vessel and to the heated tube containing the ammonium nitrate, decomposition to N_2O did proceed smoothly. Water vapor was later removed by distilling the gaseous products through a glass wool trap kept at Dry Ice–acetone temperatures. Any NO formed as a side product was removed by pumping on the product gases condensed by liquid nitrogen. The conclusion[2] that $^{15}NH_4NO_3$ on decomposition leads to ^{15}NNO was confirmed by mass spectrometric analysis of the N_2O produced. Both NH_4^+- and NO_3^--labeled ammonium nitrate were used, each 95% enriched in ^{15}N; $^{15}NH_4NO_3$ was supplied by Bio-Rad and $NH_4{}^{15}NO_3$ by Mallinckrodt Nuclear.

The labeled $[Ru(NH_3)_5N_2]^{2+}$ was prepared by vacuum-line techniques.[3] $Ru(NH_3)_5Cl_3$ (50 mg) in 20 ml of a solution of 10^{-3} *M* in HCl was placed in a two-neck reaction flask. Air was removed by repetition of the freeze–pump–thaw cycle, and a fivefold excess of Cr^{2+} was then introduced into the reaction flask *via* a side arm. Approximately 3 mmol of the labeled N_2O was released into the reaction flask, and the reaction was allowed to proceed, with vigorous stirring, in the dark for 1 hr. To destroy residual Cr^{2+} and $[Ru(NH_3)_5OH_2]^{2+}$, oxygen was passed through the solution for a few minutes. Solid NaBr was added and the solid $[Ru(NH_3)_5N_2]Br_2$ which formed was separated, washed, and dried.

Nujol mulls of the solid were prepared and pressed between KBr disks, and the region[4] from 600 to 400 cm^{-1} was recorded on a Perkin-Elmer 421 grating ir spectrophotometer using the expanded wavelength scale.[5] All spectra were calibrated against water vapor, specifically at 502.3 cm^{-1} in the single-beam mode of

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(1) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6874 (1969).

(2) L. Friedman and J. Bigeleisen, *J. Chem. Phys.*, **18**, 1325 (1950).

(3) The authors wish to thank Mr. P. R. Jones for his assistance with the vacuum-line work.

(4) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967). These workers have concluded that the Ru–N stretching frequency appears at 499 cm^{-1}.

(5) The authors wish to thank Drs. L. Durham and M. Abe for their technical assistance with the ir phase of this work.