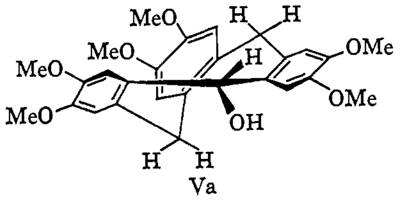
Table I. Nmr Spectra of Cyclotriveratrylene Derivatives[a]

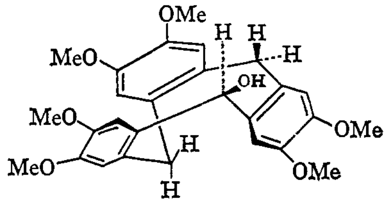
Ia	Ib	Id	III	III, Py[b]	II	II, Py[b]
					2.57 (2) s	
	3.07 (1) s	2.88 (2) s	2.83 (2) s			
3.21 (6) s	$\left.\begin{array}{l}3.21\\3.24\end{array}\right\}(6)$	3.22 (2) s			3.20 (2) s	
		3.26 (2) s	3.32 (4) s		3.46 (2) s	
		3.59 (1) s				
			3.92 (1) s			
	5.26 (1) OH[g]					
5.36 (2) d[c]	5.35 (2) d[c]	5.29 (2) d[c]		5.53 (2) d[f]		
			$\left.\begin{array}{l}5.96^{e}\\6.13\\6.24^{e}\end{array}\right\}(22)$			5.95 (4) s
				6.07 (2) d[f]	6.10 (12) s	
6.19 (18) s	$\left.\begin{array}{l}6.15\\6.18\end{array}\right\}(18)$	6.20 (18) s		$\left.\begin{array}{l}6.21\\6.28\end{array}\right\}(18)$	6.20 (10) s	6.17 (12) s
						6.34 (6) s
		6.46 (2) q[d]				
6.52 (2) d[c]	6.52 (2) d[c]	6.47 (2) d[c]				
		8.71 (3) t[d]				

[a] Figures show, respectively, position in τ (TMS = 10), number of protons, and multiplicity of absorptions (s = singlet, d = doublet, etc.). All spectra were run in deuteriochloroform except where indicated. [b] Py = pyridine solution. [c] AB quartet, J = 14 cps. [d] CH_2 and CH_3 of ethyl group, J = 7 cps. [e] Peaks 1, 2, and 4 of AB quartet visible, J = 15.5 cps. [f] AB quartet, J = 15.5 cps. [g] OH = hydroxyl resonance.

ial), on the basis of its stability and the occurrence of the methylene AB quartet in the nmr spectrum at almost the same position as that in I (see Table I). In the crown conformation of Ia and Ib the geminal coupling of the methylene protons is −14.0 cps (sign assumed), in fair agreement with the dihedral angle, estimated from Dreiding models, between the methylene groups and each adjacent p orbital of the benzene rings (110 ± 5°) after allowance for some opening of the C–CH_2–C angle.[6]



Va



VI

The conformation of the unstable α-cyclotriveratrylenol (III) is still subject to some doubt since two possibilities are open. Either it has the crown conformation Ic with the hydroxyl group "in" (*cf.* axial) (models show this to be an extremely crowded arrangement), or it could have a flexible conformation VI, like V, with the possibility of pseudorotation. Either of these could explain the observed data, but we favor VI as being derived more directly from reduction of V (V → Va → VI) and also on the ease of conversion of III to IV. (Nmr shows no evidence of inversion in cyclotriveratrylene at temperatures up to 200°.)

The sensitivity of the α-alcohol to acid also argues in favor of a flexible conformation; thus after 1 hr in chloroform–30% ethanol with a trace of hydrochloric acid the α-alcohol is converted completely into a mixture of α- and β-cyclotriveratrylenyl ethers (VII and VIII), together with a small amount of IV, whereas after 14 hr under the same conditions the β-alcohol is converted only partially into β-cyclotriveratrylenyl ethyl ether. (The α- and β-ethers exhibit the same behavior as the alcohols, the α being converted into the β form. The nmr spectra indicate that the conformational difference is analagous to that of the two alcohols.)

More conclusive evidence on the conformation of III could be obtained by isolation of a third conformer. We are pursuing this and other aspects of the chemistry of this interesting system.

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Received December 3, 1965

(6) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963); J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

Anomalous Temperature Dependence in the Electron Spin Resonance Spectrum of Bis(trifluoromethyl) Nitroxide[1]

Sir:

Recently a new stable neutral free radical, bis(trifluoromethyl) nitroxide (I), was prepared by Blackley and Reinhard.[2] They measured its electron spin resonance spectrum in $CFCl_3$ and determined the two hyperfine splittings: a^{N} = 8.2 gauss and a^{F} = 9.3 gauss. The unusual feature of this radical is its stability, which Blackley and Reinhard propose is due to the strong electronegative character of the CF_3 groups and possibly some delocalization of the unpaired electron onto the six fluorine atoms. In this note we present evidence which appears to confirm the delocalization mechanism for the fluorine hyperfine splittings. It has been found that both the fluorine and nitrogen hyperfine splittings change in an opposite manner between 163 and 277°K.

(1) This research was supported in part by the National Science Foundation through Grant No. GP-2836 and by the Graduate School, University of Minnesota.

(2) W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).

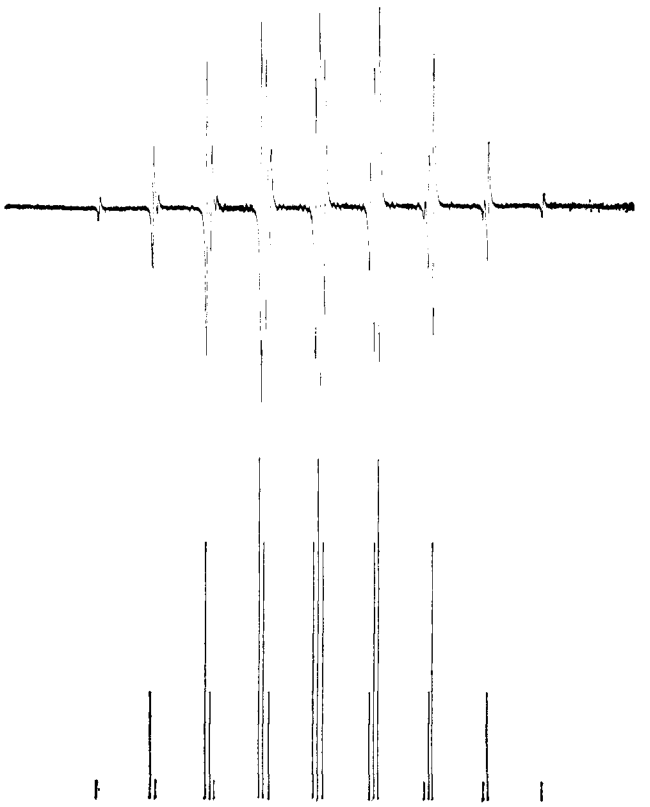

Figure 1. First derivative of the esr spectrum of bis(trifluoromethyl) nitroxide in $CFCl_3$ with reconstruction below.

Samples of I were prepared under vacuum using $CFCl_3$ as a solvent. The $CFCl_3$ (Du Pont) was thoroughly degassed in a 4-mm o.d. Pyrex tube and 0.025 mg (1.7×10^{-7} mole) of I added by vacuum transfer from a calibrated volume. The sample tube was then sealed off for the esr measurements.

Esr spectra were run on a modified Varian V-4560 100-kc spectrometer equipped with a 12-in. magnet, power supply, and "Field Dial" field control. Temperature control was achieved by connecting dewar tubing between a liquid nitrogen reservoir and a quartz dewar inserted in the cavity. The liquid nitrogen was boiled off at a constant rate by means of a heater. The temperature was monitored just below the cavity by means of a copper–constantan thermocouple. It was found possible to maintain the temperature to ±1° between −150 and −30° with this apparatus.

It was found necessary to calibrate the spectra directly with a proton resonance probe since the "Field Dial" sweep rate varies by about 1% from run to run. The calibration was made with a Varian Model F-8 Fluxmeter and Hewlett-Packard Model 524D frequency counter. The spectra were analyzed using the method of Bolton and Fraenkel[3] and computer programs developed by M. Kaplan.

Table I. Hyperfine Splittings for the Bis(trifluoromethyl) Nitroxide Radical in $CFCl_3$

Temp., °K	a^{N}, gauss	a^{F}, gauss
297	9.458 ± 0.018[a]	8.263 ± 0.010
236	9.328 ± 0.032	8.462 ± 0.020
210	9.276 ± 0.026	8.527 ± 0.014
193	9.231 ± 0.041	8.628 ± 0.018
163	9.140 ± 0.048	8.759 ± 0.020

[a] Errors determined from the least-squares analysis are given at the 95% confidence level (*i.e.*, $\pm 2\sigma$).

The results are tabulated in Table I. A typical spectrum is displayed in Figure 1. A least-squares fit of the data from 163 to 297°K shows that the fluorine and nitrogen hyperfine splittings can be fitted within experimental error to the equations

$$a^{\mathrm{F}} = (9.327 - 0.0036T)\text{ gauss}$$

$$a^{\mathrm{N}} = (8.776 + 0.0023T)\text{ gauss}$$

where T is the temperature in °K.

It is difficult to postulate a mechanism for this unusual temperature effect which does not involve partial conjugation of the fluorine p orbitals with the nitrogen $2p_z$ orbital. In fact, direct transfer of electron spin to β-fluorine atoms has been confirmed by Rogers and Whiffen[4] in their single crystal study of the perfluorosuccinic acid radical where they observed considerable anisotropy in the β-fluorine hyperfine tensors. This mechanism would result in partial double bonding between the nitrogen and the CF_3 groups leading to partially hindered rotation about the C–N bonds. The observation of six equivalent fluorines in the esr spectrum with line intensities having the expected binomial distribution requires that the CF_3 rotation rate be very much larger than the fluorine hyperfine splitting ($\sim 2.5 \times 10^7$ sec^{-1}). Nevertheless, a small energy barrier could lead to a nonuniform rotation with a heavier weighting of those configurations favorable to fluorine conjugation. The temperature dependence is entirely consistent with this model since as the temperature is decreased, a^{F} increases and a^{N} decreases. At the lower temperatures the favorable configurations are weighted more heavily, leading to a greater conjugation and hence a larger transfer of spin to the fluorine atoms. Additional evidence for such a transfer is provided by the nitrogen hyperfine splitting in this radical. In the di-*t*-butyl nitroxide radical a^{N} is 15.18 gauss,[5] whereas it is only ~9 gauss here. Such a decrease could be due to a transfer of spin to the oxygen atom. However, such a large decrease as this is more likely due to transfer to the fluorine atoms. Stock and Sukuki came to a similar conclusion in their study of the 2-trifluoromethylsemiquinone radical anion.[6]

It should be noted that the mechanism which we propose for the interaction of a CF_3 group with a π-electron system is a direct 1–3 conjugation between the fluorines and the π-electron system in the same sense as Sheppard's fluorine p–π interaction.[7] It is not a fluoride ion hyperconjugation mechanism.

It is interesting to note that in 1953 Bijl and Rose-Innes[8] observed a temperature dependence of the nitrogen hyperfine splitting in the diphenyl nitroxide radical with the nitrogen splitting decreasing to lower temperature. We are in the process of repeating this work to see if a similar spin-transfer mechanism is responsible. We are also continuing work on CF_3

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(3) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

(4) M. T. Rogers and D. H. Whiffen, *ibid.*, **40**, 2662 (1964).

(5) H. LeMaire, A. Rassat, and P. Servoz-Gavin, *J. Chim. Phys.*, **59**, 1247 (1962).

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(7) W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

(8) D. Bijl and A. C. Rose-Innes, *Phil. Mag.*, 1187 (1953).

groups in other radicals to see if the mechanism we propose here is general for CF_3 groups.

Acknowledgement. We wish to thank Dr. W. D. Blackley for his generous gift of I and for his helpful comments. We further wish to thank Dr. M. Kaplan for the use of his computer programs.

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Dependence of Rate Constants of an Electron-Transfer Reaction on the Optical Configuration of the Reactants

Sir:

We have used esr methods for determination of rates of electron-transfer reactions between the radical anion of the optically active hydrocarbon 1-(α-naphthyl)-1-phenylethane[1] and the neutral molecule.[2] Line breadths were measured in mixtures of radical anions and neutral molecules containing only the *d* enantiomer and in racemic mixtures.

Table I. Rate Constants and Energies of Activation for Electron Transfer between Potassium 1-(α-Naphthyl)-1-phenylethanide and 1-(α-Naphthyl)-1-phenylethane (25 ± 1°)[a]

	Solvent	$k_{dd} \times 10^{-8}$, M^{-1} sec^{-1}	$k_{dl} \times 10^{-8}$, M^{-1} sec^{-1} [b]	E_{dd}, kcal mole^{-1}	E_R, kcal mole^{-1} [c]
1	DME	0.68 ± 0.07	1.10 ± 0.34	1.6 ± 0.5	0.6 ± 0.5
2	THF	0.19 ± 0.04	0.20 ± 0.06	2.3 ± 0.06	1.7 ± 0.4

[a] Limits of uncertainty are standard deviations from the mean. [b] Calculated values. [c] E_R is obtained from the temperature dependence of k_R.

Standard methods for preparation of the anions by chemical reduction were used. Rates were determined from broadening of the lines at the low- and high-field extremes of the spectrum. The separation of these lines from their neighbors is large enough to eliminate complications from overlapping lines.

Partial reduction of the *d* enantiomer did not lead to racemization in a time long compared with the time required for each esr experiment. Measurements of the rates were carried out in dimethoxyethane (DME) and tetrahydrofuran (THF) with the sodium and potassium salts. Complications arise in interpretation of the data for the sodium salts because of contributions of ion-association phenomena to the line breadths. We therefore report here only the results for the potassium salts. The measurement of the rate for the pure enantiomer (**1**) leads directly to the rate constant k_{dd} for the reaction

$$[d\text{-}\mathbf{1}]^- + [d\text{-}\mathbf{1}]^0 \overset{k_{dd}}{\rightleftarrows} [d\text{-}\mathbf{1}]^0 + [d\text{-}\mathbf{1}]^-$$

Corresponding measurements for a racemic mixture yield an apparent rate constant k_R, which in turn is related to the rate constant k_{dl}, for the reaction

$$[d\text{-}\mathbf{1}]^- + [l\text{-}\mathbf{1}]^0 \overset{k_{dl}}{\rightleftarrows} [l\text{-}\mathbf{1}]^- + [d\text{-}\mathbf{1}]^0$$

by $k_{dl} = 2k_R - k_{dd}$. Table I lists the rate constants at 25° and apparent activation energies for the reaction of the potassium salts in DME and THF.

Our experiments bear directly on the applicability of the relation proposed by Marcus[3,4] $k_{AB} = (k_{AA}k_{BB}K_{AB} \cdot f)^{1/2}$, where k_{AA} and k_{BB} are the rate constants for the reactions $A^- + A = A + A^-$ and $B^- + B = B + B^-$, respectively; k_{AB} is the rate constant, and K_{AB} is the equilibrium constant for $A^- + B = A + B^-$; f is a function of K_{AB}, k_{AA}, k_{BB}, and the collision number which has the property $f \equiv 1$ when $K_{AB} = 1$. Since $k_{dd} = k_{ll}$ and $k_{dl} = 1$, the relation predicts $k_{dd} = k_{dl}$.

Our data indicate that at 25° in THF k_{dd} and k_{dl} are equal within limits of experimental error but that in DME they differ by almost a factor of 2. In each solvent the energies of activation are different.

The standard statistical criteria indicate that the confidence level for the difference in DME is about 85%. The differences in activation energies are statistically more reliable. Further, errors associated with measurements of concentrations do not appear in the activation energies, because only *ratios* of line broadenings for a given sample at various temperatures are used.

We believe that our results exhibit small, but real, deviations from the Marcus relation. Further work on other optically active systems is under way in order to assess the reasons for the deviations.

Acknowledgment. This work has been supported by the National Science Foundation under Grant GP 2676 and by the National Institutes of Health under Grant GM 13205, and NIH predoctoral fellowships to W. Bruning during 1963–1965.

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Received November 5, 1965

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(3) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

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