The temperature dependence of the ^{19}F resonance in isolated $F_2C = CFX$ molecules

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The ^{19}F nuclear magnetic shielding in a molecule of the type $F_2C = CFX$ in the zero-pressure limit is of particular interest since the shielding in three different electronic environments are averaged over the anharmonic motions described by a single force field. The temperature dependence of the nuclear shielding for the three ^{19}F nuclei in the molecules $F_2C = CFX$ (X = H, Cl, Br, I) are reported here. There are systematic changes in the temperature coefficient of the nuclear shielding upon X substitution. For these molecules, the values of $-(d\sigma_0/dT)_{300}$ decrease in the order X = I, Br, Cl, F, H for the F nuclei which are *gem* and *cis* to X. On the other hand, for the F nucleus which is *trans* to X, the values of $-(d\sigma_0/dT)_{300}$ are very similar for X = I, Br, Cl, F, and all are greater than for X = H. Comparison of the coupling constants obtained in the gas phase with values in various solvents provide support for Barfield and Johnston's theory of solvent effects on spin–spin coupling.

INTRODUCTION

Temperature-dependent chemical shifts in molecular systems in which intermolecular interactions and effects of conformational equilibria could be excluded were first noted for ^{59}Co in octahedral cobalt complexes and attributed to vibrational excitation.[1] Due to the very large chemical shift range of ^{59}Co these temperature-dependent shifts were of the order of 1.4–3.0 ppm deg^{-1}. Vibrational excitation was also cited as the possible mechanism for the observations of much smaller ^{1}H shifts with increasing temperature in HBr, C_2H_6, C_2H_4, and other gases.[2] Buckingham suggested that intermolecular effects and excitation of rotational states might also be important in the latter studies.[3] When temperature and density dependent chemical shift measurements are carried out in the gas phase, it is possible to separate out that part of the temperature dependence which is due to intermolecular effects in the equation

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots, \qquad (1)$$

leaving only the intrinsic temperature dependence of a rovibrationally averaged shielding, $\sigma_0(T)$ in the zero-pressure limit.[4] With the advantages provided by the Fourier transform technique, it has become possible to make measurements of $\sigma_0(T) - \sigma_0(300\ \mathrm{K})$ for ^{19}F, ^{15}N, ^{13}C, and ^{31}P in a variety of compounds.[5] For protons these shifts are still too small to separate out accurately from the accompanying temperature-dependent intermolecular shifts.[4,6,7]

In our previous studies we have interpreted the temperature dependence of nuclear shielding in the zero-pressure limit in terms of an expansion of the nuclear shielding in nuclear displacement coordinates[8,9]

$$\sigma_0(T) = \sigma_e + \sum_i (\partial\sigma/\partial\Delta r_i)_e \langle\Delta r_i\rangle^T + 1/2 \sum_{i,j} (\partial^2\sigma/\partial\Delta r_i\partial\Delta r_j)_e \langle\Delta r_i \Delta r_j\rangle^T \cdots. \qquad (2)$$

It has been shown[10] for diatomic molecules that the terms in the second and higher derivatives make relatively small contributions to the observed temperature dependence of nuclear shielding so that the experimental temperature dependence of shielding can provide good estimates of $(\partial\sigma/\partial\Delta r)_e$ when experiment is fitted to an Eq. (2) truncated after the linear term. The reason for the dominance of the linear term in the temperature dependence of σ_0 is the large contribution to $\langle\Delta r\rangle^T$ from centrifugal stretching, which is proportional to temperature in the classical limit. When this is combined with the anharmonic vibrational contribution to $\langle\Delta r\rangle^T$, the $(\partial\sigma/\partial\Delta r_e)\langle\Delta r\rangle^T$ term becomes the dominant term in the temperature dependence.[8,9] Thus, by observing the temperature dependence of the shielding $[\sigma_0(T) - \sigma_0(300\ \mathrm{K})]$ and fitting these experimental data to the temperature dependence of the mean bond displacements $\langle\Delta r_i\rangle^T$ which have been calculated with a suitable anharmonic force field, we have been able to obtain empirical values for the derivatives of nuclear shielding with respect to bond extension in small molecules. For example, for ^{19}F nuclei, we have determined empirical values of $(\partial\sigma^F/\partial\Delta r)_e$ in F_2, ClF, CF_4, BF_3, SiF_4, SF_6, and COF_2.[8,9] These empirical derivatives which are -4530, -2070, -1180, -1115, -1170, -2200, and -1140 ppm Å^{-1}, respectively, serve as chemical indices of the F–F, Cl–F, C–F, B–F, Si–F, and S–F bonds. These derivatives may be compared with one another although the quality of the anharmonic force fields varies from one molecule to the next. A more direct comparison is possible if we observe the effects at more than one nuclear site in the same molecule of the dynamical averaging over the anharmonic motions described by a single force field. We have done this for the two ^{15}N nuclei in NNO, where we found that the empirical values of the shielding derivatives $(\partial\sigma^N/\partial\Delta r_{NN})_e$ and $(\partial\sigma^N/\partial\Delta r_{NO})_e$ are remarkably different for the two nuclei.[9]

The ^{19}F nuclear magnetic shielding in the trifluoroethy-

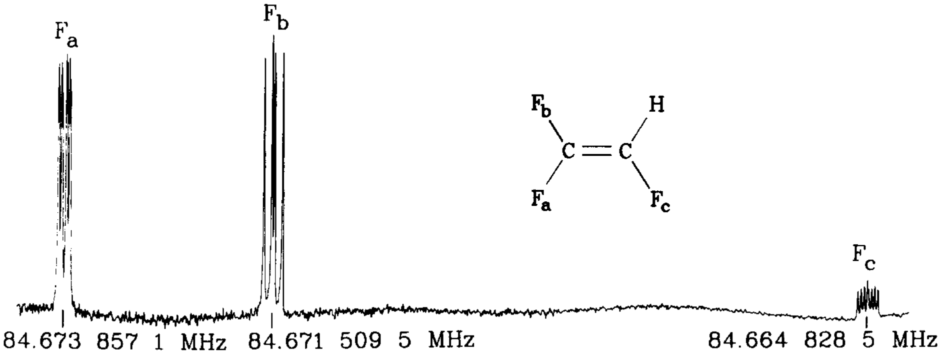

FIG. 1. A typical ^{19}F spectrum, showing that first-order spectral analysis is appropriate. This one is for a 17.96 amagat sample of $CF_2 = CFH$ at 301 K. The reduced intensities for the F_C multiplet are due to the limited filter bandwidth.

lenes are particularly interesting because the molecules are fairly simple and yet the three nuclei have very different electronic environments. We have chosen to study the series of related molecules $CF_2 = CFX$ for the following reasons. (1) There are three different nuclear sites for intermolecular interactions, all are $=$ C–F bonds but the F nuclei have inherently different electronic environments which might be affected differently by intermolecular interactions. (2) The three fluorine sites vary in their distances from the center of mass and thus in their relative exposure to intermolecular effects as X is varied through H, F, Cl, Br, I. (3) The effect of X substitution on the potential energy surface of the $CF_2 = CFX$ molecule leads to different vibrational averaging for the three C–F bonds. (4) The large chemical shifts between the three fluorines in these molecules permit a study of the correlation of shielding sensitivity to bond extension with the absolute shielding (which serves as a measure of the different electronic environments within the *same* molecule). (5) By varying X through H, F, Cl, Br, I, systematic trends in a particular shielding derivative, of the F nucleus *trans* to X for example, in these related compounds may be studied. (6) These molecules are sufficiently simple so that there is a reasonable expectation that F shielding tensors can be measured in these molecules using the same techniques as have been applied to ^{19}F shielding in CF_3X molecular types.[11] Correlation of shielding tensor components with the shielding sensitivity to bond extension can then be examined.

The first two of these reasons have provided a good account of the very interesting nuclear site effects in the intermolecular shifts.[12] In this paper we examine the experimental temperature dependence of ^{19}F nuclear shielding at the zero-pressure limit, with criteria (3)–(6) given above providing the rationale for the studies. The chemical shifts between the three fluorines in $CF_2 = CFH$ cover 100 ppm, a substantial part of the range of chemical shifts for this nucleus. In $CF_2 = CFX$ the F nuclei experience rovibrational averaging of the shielding at three sites; with a single anharmonic force field it will be possible to determine the effects of rovibrational averaging on the three mean C–F bond displacements. By comparison of this with the measured temperature dependence of ^{19}F nuclear shielding at the zero-pressure limit, it will be possible to determine empirical derivatives of the shielding $(\partial\sigma^F/\partial\Delta r_{CF})_e$ for all three nuclei. Furthermore, by studying the systematic trends in the related compounds, we expect to arrive at values of these derivatives which form an internally consistent set for each molecule and also follow systematic variations as X is changed through H, F, Cl, Br, I. With this, we hope to have a better understanding of the way in which the nuclear shielding changes with bond displacement for a molecule of this type.

EXPERIMENTAL RESULTS

^{19}F FT NMR spectra were taken at 84.7 MHz for sealed gas samples ($\sim$0.2 ml in volume) which could fit into a 5 mm sample tube with an annular space containing d_8-toluene as the heteronuclear lock substance. All compounds were obtained from PCR Chemicals and were used as obtained with degassing. Spectra were taken soon after preparation to minimize the effects of polymerization of photochemical decomposition. The spectrum at the lowest temperature at which the sample remained all gas was taken at the beginning and the end for each sample and was reproducible within our usual experimental variability. The temperature range for the data on each molecule is limited by the intrinsic vapor pressure of the sample at the low temperature end, while the upper limit of 380 K is governed by the boiling point of the lock substance. Further experimental details are given elsewhere.[13] All spectra were treated as first order spectra; this appeared to be satisfactory. All multiplets could be easily resolved even for the lowest density samples where broadening is commonly noticeable. A typical spectrum for $CF_2 = CFH$ taken in one sweep width (10 000 Hz, 2 K data points zero filled to 8 K) is shown in Fig. 1. No attempt was made to determine the coupling constants with exceptional accuracy since our primary interest is in the nuclear shielding. Our values of coupling constants for the gas phase are given in Table I, and compared with literature values obtained in condensed phase.

The density dependent parts of the shielding are a measure of the effects of intermolecular interactions on shielding. These were determined separately and are reported in a previous paper.[12] σ_1 appears to be temperature independent over the temperatures of the experiment except for C_2F_4 and $CF_2 = CFH$ while the density is small enough (under 40 amagat) that no deviation from linearity [due to $\sigma_2(T)\rho^2$ in Eq. (1)] could be observed. The remaining temperature dependence in the zero-density limit is characteristic of the thermal average shielding in an independent ("isolated") molecule and are shown in Figs. 2 and 3. These temperature-dependent ^{19}F resonance frequencies corrected for the temperature dependence of the lock substance can be described by quadratic functions of temperature, from which the

TABLE I. Coupling constants J/Hz in the fluoroethylenes in the dilute gas phase.[a] (See Fig. 3 for A, B, C designation of F nuclei.)

	F_AF_C [$^3J_{cis}$(FF)]	F_BF_C [$^3J_{trans}$(FF)]	F_AF_B [$^2J_{gem}$(FF)]
$F_2C=CFI$	54.6 ± 0.9 (52.2)	128.2 ± 1.0 (127)	70.4 ± 0.8 (65.3)
$F_2C=CFBr$	58.3 ± 0.7 (+57) (53.7–56.8)	122.2 ± 0.7 (−124) (121.9–123.4)	77.9 ± 0.4 (+75) (71.7–74.9)
$F_2C=CFCl$	58.0 ± 0.4 (+58)	117.0 ± 0.5 (−115)	81.4 ± 0.6 (+78)
$F_2C=CFH$	35.7 ± 0.5 (+33)	117.4 ± 0.5 (−119)	88.9 ± 0.6 (+87)
	F_BH [$^3J_{cis}$(FH)]	F_AH [$^3J_{trans}$(FH)]	F_CH [$^2J_{gem}$(FH)]
$F_2C=CFH$	<2.5 (−3) (−4.18 to −4.34)	9.8 ± 0.9 (+12) (12.52–14.01)	71.6 ± 0.7 (+72) (69.93–70.92)

[a] Data in various solvents, shown in parentheses, were taken from J. W. Emsley, L. Phillips, and V. Wray, Prog. NMR Spectrosc. **10**, 83 (1976).

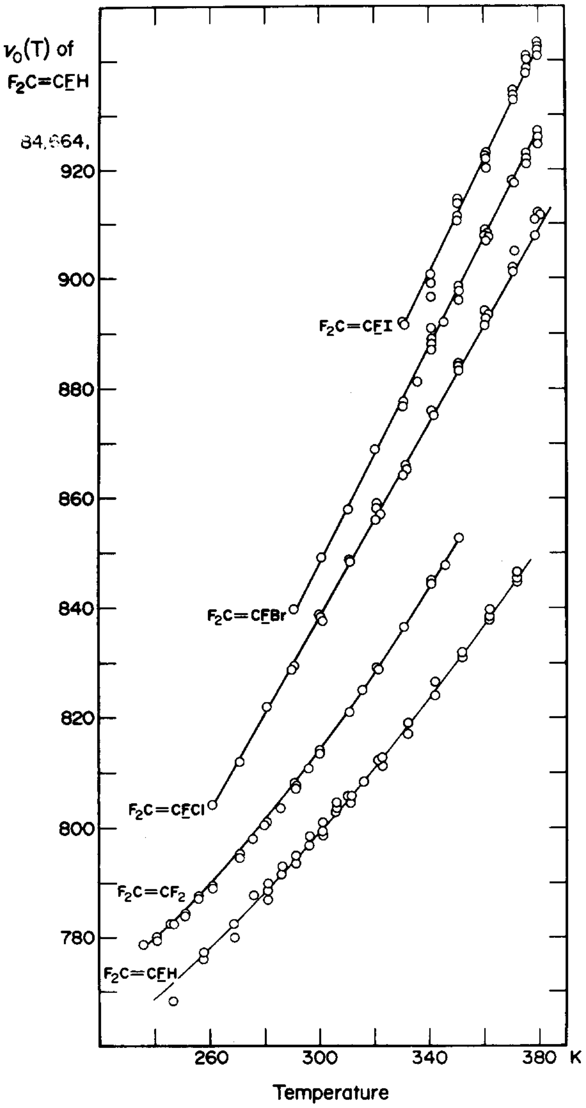

FIG. 2. The ^{19}F resonance frequencies in the zero-pressure limit for the fluorine nucleus which is *gem* to the substituent X in $F_2C=CFX$ molecules (F_C). The frequencies shown are for F_C in $F_2C=CFH$. The other curves have been arbitrarily shifted so as to compare relative slopes. The actual differences in the absolute shielding are shown in Fig. 4.

shielding functions [$\sigma_0(T) - \sigma_0(300\ \text{K})$] are calculated. The results are given in Table II where the previous results for $F_2C=CF_2$ are also shown for comparison.

DISCUSSION

Although the differences between our gas phase values and the condensed phase literature values for the *gem*, *cis*, and *trans* spin–spin coupling constants in these molecules are only 1 to 5 Hz, these are real differences. Our data indicates that for both HF and FF coupling the solvent contributions to $^2J_{gem}$ and $^3J_{cis}$ are negative, whereas that to $^3J_{trans}$ are positive. These may be compared with the theoretical model for the solvent effects on spin–spin couplings which has been discussed by Barfield and Johnston.[14] Their reaction field model predicts positive (wrong sign) solvent effects on $^2J_{gem}$ (HF) in $CF_2=CFH$ (+0.38 Hz in $CDCl_3$, +0.72 Hz in TFA), the correct sign for solvent effects on $^3J_{cis}$(HF) (although their −0.04 to −0.06 Hz values are too small), and the right magnitude and correct sign for solvent effects on $^3J_{trans}$(HF) (+1.60 to +3.04 Hz). All previous comparisons to support the theory had been made relative to a cyclohexane solution since no isolated molecule or dilute gas data had been available at the time. No calculations of solvent effects on J(FF) have been reported, but the similar trends which we find here in $^2J_{gem}$, $^3J_{cis}$, and $^3J_{trans}$ indicate that the mechanism of the solvent effects may be the same for HF and FF coupling.

The temperature dependences of σ_0 (^{19}F) in the fluoroethenes ($d\sigma_0/dT = -5.0$ to -12.8 ppb deg^{-1}) are comparable to the ethanes (-10.3 to -13.6 ppb deg^{-1})[15] and generally greater than the methanes (-1.5 to -11.6 ppb deg^{-1}),[16] in similar nuclear environments, i.e., for the same absolute shielding. We find a substituent effect which is common to all three classes of molecules: substitution of F with hydrogen atoms leads to a weaker temperature dependence, whereas substitution with Cl leads to a greater T dependence. For the fluoroethenes we see in Fig. 3 that for the ^{19}F nucleus which is geminal to the X (i.e., F_C), the curves are steepest for X = I and least steep for X = H, i.e., $-(d\sigma_0/$

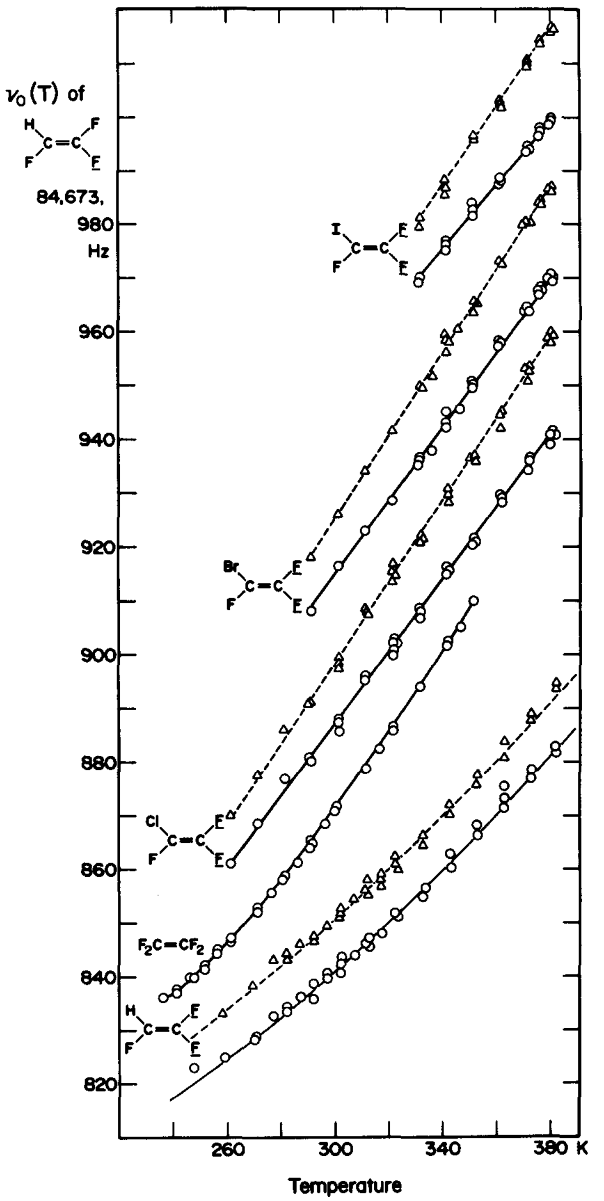

FIG. 3. The ^{19}F resonance frequencies in the zero-pressure limit for fluorine nuclei which are *cis* (F_B) and *trans* (F_A) to the substituent X in $F_2C = CFX$ molecules. The frequencies shown are for F_A in $F_2C = CFH$. The other curves have been arbitrarily shifted so as to compare relative slopes. The actual differences in the absolute shielding are shown in Fig. 4.

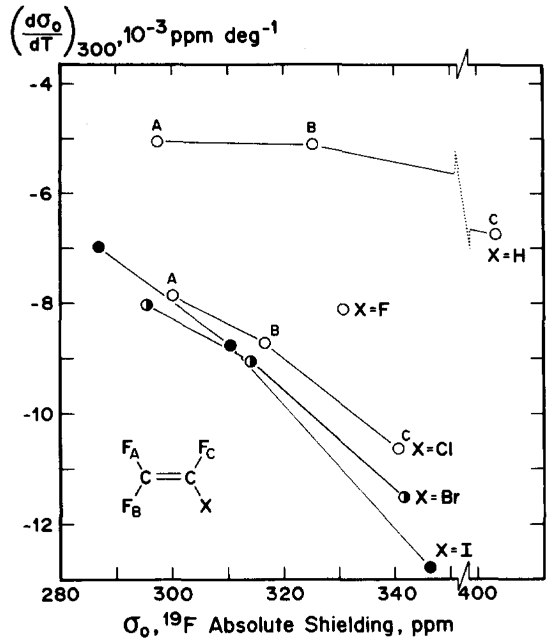

FIG. 4. Correlation between the temperature dependence of the ^{19}F nuclear shielding ($d\sigma_0/dT$) (this work) and the absolute shielding σ_0 (Ref. 17).

$dT)_{300}$ values for F_C are in the order I > Br > Cl > F > H. Similarly, in Fig. 2 we see that for the fluorine nucleus *cis* to X (F_B), $-(d\sigma_0/dT)_{300}$ values are in the order I ~ Br > Cl > F > H. On the other hand, for the fluorine nucleus *trans* to X (F_A), the $-(d\sigma_0/dT)_{300}$ values are more similar, I ~ Br ~ Cl ~ F > H. Within the same molecule we also find a clear trend, $-(d\sigma_0/dT)_{300}$ is in the order $F_C > F_B > F_A$ without exception. Of all the above trends this is the most pronounced correlation. The differences are greater between the three nuclear sites in the same molecule than for the same site in the different $CF_2 = CFX$ molecules. This holds for the absolute shielding, the less electronegative substituent X shields the fluorine in the *gem* position and deshields the fluorines in the *cis* and *trans* positions. This also holds for the temperature coefficients of the shielding. Under substitution of F with X, the magnitude of the temperature coefficient decreases somewhat for ^{19}F *trans* to X, increases for ^{19}F *cis* to X and increases markedly for ^{19}F *gem* to X.

An interesting and useful correlation is that between the ($d\sigma_0/dT$) values at 300 K and σ_0, the absolute shielding.[17] This is shown in Fig. 4 to be different from that which is observed for the fluoromethanes.[16] Unlike the methanes, the most shielded nucleus in a given $F_2C = CFX$ molecule has the greatest temperature dependence.

Calculations of the mean bond displacements with a suitable anharmonic force field were carried out for these

TABLE II. Temperature dependence of the ^{19}F nuclear magnetic shielding in the "isolated" fluoroethenes, $F_2C = CFX$.

			$[\sigma_0(T) - \sigma_0(300\ K)]$ ppb	
T	X	F_A (*trans* to X)	F_B (*cis* to X)	F_C (*gem* to X)
245–380	H	$-(5.06 \pm 0.14)(T-300)$ $-1.42\times10^{-2}(T-300)^2$	$-(5.11 \pm 0.12)(T-300)$ $-1.52\times10^{-2}(T-300)^2$	$-(6.76 \pm 0.12)(T-300)$ $-1.47\times10^{-2}(T-300)^2$
230–350	F[a]		$-(8.127 \pm 0.071)(T-300) - 2.09\times10^{-2}(T-300)^2$	
260–380	Cl	$-(7.87 \pm 0.12)(T-300)$	$-(8.73 \pm 0.12)(T-300)$	$-(10.64 \pm 0.40)(T-300)$
290–380	Br	$-(8.04 \pm 0.15)(T-300)$	$-(9.07 \pm 0.14)(T-300)$	$-(11.55 \pm 0.14)(T-300)$
330–380	I	$-(6.98 \pm 0.31)(T-300)$	$-(8.77 \pm 0.31)(T-300)$	$-(12.80 \pm 0.40)(T-300)$

[a] Reference 13(b).

molecules in order to determine whether the observed trends in $(d\sigma_0/dT)$ can be attributed to dynamic effects (i.e., systematic trends in $d\langle\Delta r_{\mathrm{CF}}\rangle/dT$). A plausible hypothesis is that the in-phase FCX bend affects the C–F_{gem} mean bond displacement, but this is shown to be insufficient to account for the greater magnitude of $(d\sigma_0/dT)_{300\,\mathrm{K}}$ for this fluorine. The observed trends in $(d\sigma_0/dT)_{300\,\mathrm{K}}$ are shown to be due to systematic trends in the electronic quantity $(\partial\sigma^{\mathrm{F}}/\partial\Delta r_{\mathrm{CF}})_e$. The theoretical interpretation of these data in the succeeding paper yields values of these derivatives. Their dependences on the absolute shielding and spin–spin coupling provides a useful correlation and leads to a better understanding of nuclear shielding as a fundamental molecular electronic property. Details of the theoretical interpretation are given in the following paper.

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