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A Theoretical Scale of Substituent Field Parameters[1]

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Abstract: It is shown that molecular orbital calculations at the ab initio level can provide a scale of field effects in good agreement with experimental values appropriate for the gas-phase or nonpolar solvents. The models employed involve simple molecules, thus allowing calculation for a wide range of substituents with a split-valence basis. The models employ either calculations of energy or of atomic electron population, but the preferred method is the polarization of HH by an isolated HX molecule, which is free from secondary polarizability effects. Values of σ_F are calculated for more than 50 substituents including many for which experimental values are not well defined. The impossibility of obtaining a universal scale of field parameters is discussed.

Much interest continues in the nature of transmission and the magnitude of electronic substituent effects in σ-bonded systems.[2-10] It is now well accepted[2,4,11] that the predominant transmission mechanism involves the field effect (designated F), a direct through-space transmission of the substituent dipole to the reaction or measurement site. However, some claims continue to be made[5,8,10,12] for alternative transmission mechanisms including effects (χ) originating in electronegativity differences between the substituent and the atom to which it is attached, transmitted via a progressive but diminishing relay along a chain of atoms. Less important but possible modes of transmission involve[4] the secondary effects caused by polarization of intervening bonds (particularly CH) and charge-transfer effects if the substituent is not far removed from the measurement site.

Scales of field and electronegativity effects differ markedly. Thus, the groups NH_2 and NO_2 have rather similar electronegativities but differ markedly in field effect as measured by σ_F values[2,13] reflecting the much higher effective dipole resulting from the introduction of a nitro rather than an amino group. The availability of extensive scales of both substituent electronegativity and field effects would thus allow a proper analysis of data sets to establish if the former are important. We have recently[3] established a theoretical method to generate substituent electronegativity parameters σ_χ for some 50 common substituents. However, experimental values of σ_F often depend quite markedly on the solvent employed, and values for either the gas-phase or nonpolar solvents are limited. Some such values are given in Table I where data are available from three recent compilations of values for hydroxylic solvents,[14] nonpolar solvents,[15] or the gas phase (inherent best values).[16] Clearly there are considerable differences for some substituents such as NMe_2, COMe, and CO_2Me. A recent tabulation[15] of results from six sources shows that for those substituents included from the first two rows of the periodic table only CF_3 (0.42), NO_2 (0.65), and Cl (0.45) have almost identical values. For most substituents not on these lists, there is considerable uncertainty about the appropriate value of σ_F.

Table I. Literature Values of σ_F for a Variety of Conditions

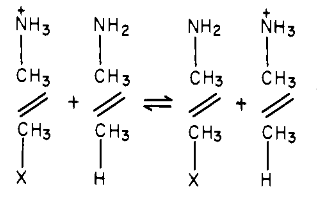
	gas phase[a]	nonpolar solvents[b]	polar solvents[c]
$SiMe_3$	−0.10	−0.04	−0.11
Me		0.03	−0.01
t-Bu		0.04	−0.01
C_2H_3	0.02		0.11
NMe_2	0.06	0.10	0.17
NH_2	0.10	0.14	0.17
C_2H	0.20		0.29
COMe	0.22	0.23	0.30
CO_2Me	0.17	0.21	0.32
OMe	0.25	0.24	0.30
SMe		0.23	0.30
CF_3	0.43	0.42	0.40
Cl	0.46	0.45	0.47
F	0.50	0.45	0.54
CN	0.58	0.60	0.57
SO_2Me	0.58		0.59
NO_2	0.65	0.65	0.67

[a] Reference 16. [b] Reference 15. [c] Reference 14.

It would thus be extremely valuable to have a scale of σ_F values for a wide variety of substituents produced under the same conditions and free from solvent effects. We have noted earlier[4,17] that theoretical calculations should be able to supply such inherent σ_F values. Thus, the effect of substituents on the calculated $\Delta E°$ values for the proton exchange equilibria of β-substituted ethylamines (eq 1) follows[17] the σ_F values. Such results probably

$$XCH_2CH_2NH_3^+ + CH_3CH_2NH_2 \rightleftharpoons XCH_2CH_2NH_2 + CH_3CH_2NH_3^+ \quad (1)$$

include a contribution from indirect polarization. An alternative is to use equilibrium 2. This process involves isolated molecules



(2)

and so avoids any χ effects, but a rather poor goodness of fit is found[4,18] against literature σ_F values because of indirect effects

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[1] Part IV of the series Theoretical Studies of the Inductive Effect. For Part III, see ref 13.

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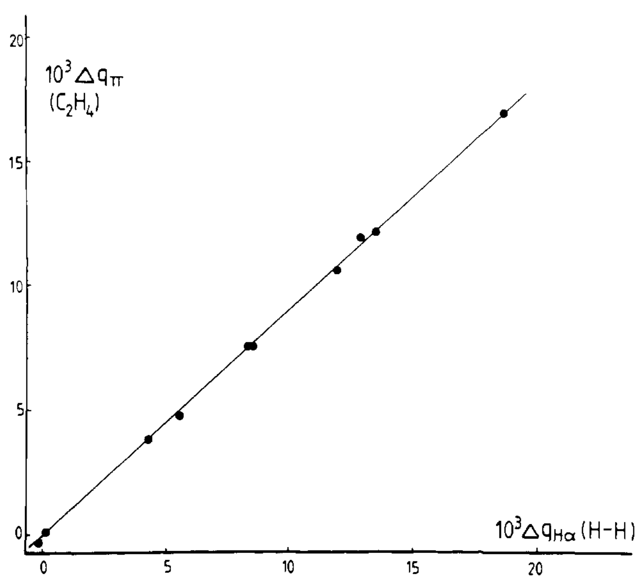
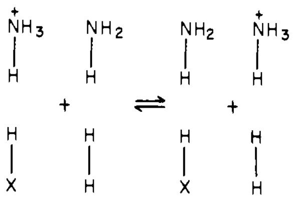


Figure 1.

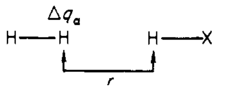
transmitted via charges induced in the methyl groups.

In a preliminary communication,[13] we pointed out that two very simple processes offer the best chance of establishing a theoretical scale of σ_F values. These are firstly equilibrium 3. This avoids



$$\begin{array}{ccccc} \overset{+}{N}H_3 & NH_2 & & NH_2 & \overset{+}{N}H_3 \\ | & | & & | & | \\ H & H & & H & H \\ & + & \rightleftharpoons & + & \\ H & H & & H & H \\ | & | & & | & | \\ X & H & & X & H \end{array} \qquad (3)$$

the possibility of indirect polarization effects. An alternative method (eq 4) is the relative polarization of the electron population in hydrogen molecules by an isolated HX molecule.



$$H-\underbrace{\overset{\Delta q_\alpha}{H}\qquad H}_{r}-X \qquad (4)$$

We have also recently shown[19] that the polarization of the π system of ethylene by molecules HX follows the substituent σ_F values.

Here we examine the utility of these three models and give theoretical σ_F values for more than 50 substituents.

Calculations

All calculations were made at the ab initio molecular orbital 3-21G (ethylene) or 4-31G level by using the GAUSSIAN 80 program.[20] The calculations were mostly[21] performed by using standard geometries.[22] It has earlier been shown[23] that geometry optimization at the 4-31G level makes little difference to electron populations in simple molecules, these being the conditions used here to define theoretical σ_F values. Such 4-31G results have also been shown[23] to be linear vs. 6-31G* values.

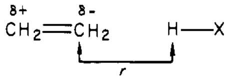
Table II. Theoretical and Experimental σ_F Values [Method A as Eq 3[a] in Text, Method B[b] as Eq 4 (ΔE in kcal mol^{-1}, $\Delta q_H(\alpha)$ in 10^3 electrons)]

	method A		method B		
	ΔE	σ_F	$\Delta q_H(\alpha)$	σ_F	lit.[c] σ_F
H	0.00	0.00	0.00	0.00	0.00
Me	0.29	−0.02	−0.24	−0.01	−0.04[d]
t-Bu	0.45	−0.03	−0.18	−0.01	
Ph	0.09	−0.01	1.75	0.06	
CF_3	−5.64	0.42	11.74	0.42	0.43
$CHCH_2$	−0.08	0.01	1.00	0.04	0.02
CCH	−1.47	0.11	4.88	0.17	0.20
COMe	−2.69	0.20	5.42	0.19	0.22
CN	−6.39	0.47	12.62	0.45	0.58
NH_2	−2.04	0.15	4.13	0.15	0.10
NMe_2	−1.62	0.12	4.11	0.15	0.06
NO_2	−8.92	0.66	18.48	0.66	0.65
OH	−3.71	0.27	8.51	0.30	
OMe	−3.29	0.24	8.12	0.29	0.25
F	−6.22	0.46	13.33	0.47	0.50

[a] Distance from N to H (of HX) is 4.5 Å. [b] Distance from H_α to H (of HX) is 4.0 Å. [c] Reference 16 (inherent best values). [d] Value for nonpolar media quoted in ref 16.

Results and Discussion

We consider first the polarization of the π system of ethylene as shown in (5). This has been shown[19] to follow σ_F values.



$$\overset{\delta+}{CH_2}=\underbrace{\overset{\delta-}{CH_2}\qquad H}_{r}-X \qquad (5)$$

Figure 1 shows a plot of Δq_π at the α carbon atom (r = 4 Å) for system 5[24] vs. the Δq values for the α hydrogen of H_2 (r = 4 Å) in system 4. The excellent linearity obtained shows that there is little point in using the larger ethylene system compared to the polarization of a hydrogen molecule. Similarly, in other work,[18] we have found that the ΔE values for proton transfer equilibria of isolated molecule systems such as $^{+}NH_3CH_3/CH_3X$, $^{+}NH_4/CH_3X$, and $^{+}NH_3CH_3/HX$ are less suitable than NH_4^{+}/HX to define σ_F values because of indirect effects transmitted via polarization of the methyl groups.

Thus, systems 3 and 4 were chosen for more detailed investigation. Table II lists the $\Delta E°$ for (3) and the $-\Delta q_H(\alpha)$ values for process 4 for some common substituents which are free from conformational ambiguity. (The latter values are relative to the small effect, at the chosen distance of 4 Å, caused by X = H.) The values obtained are proportional[13] to σ_F values from the literature, but one scale factor is required to afford an identity. We used the results for the CF_3 and NO_2 substituents for this purpose since, as discussed above, their σ_F values agree well on various scales. The average[25] of the proportionality factors obtained from the calculated results and σ_F values of CF_3, 0.42, and NO_2, 0.65, affords relationships 6 and 7.

$$\sigma_F = -0.074\Delta E° \qquad (6)$$

$$\sigma_F = -35.5\Delta q_H(\alpha) \qquad (7)$$

The resulting values of σ_F(theoretical) are listed in Table II. In general, the agreement between the two methods is excellent. However, it is seen that in comparisons where a difference in polarizability is involved, for example, NMe_2 compared to NH_2, or *t*-Bu compared to Me, method 3 gives a lower value of σ_F for the more polarizable substituent than method 4. This is doubtless because the charged ammonium ion polarizes the HX group to some extent and thus diminishes the measured field effect. Thus, we chose method 4 as the standard. A plot of such $\sigma_{F(\text{theor})}$ values

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(21) For the less common, or second row, substituents (X = Li, BeH, BH_2, BMe_2, BF_2, PH_2, PMe_2, SH, SMe, SOMe, SO_2Me, SCN, SCF_3, and Cl), the geometries of HX were obtained from optimized calculations at the 4-31G or 6-31G* level. The GAUSSIAN 80 program did not include parameters for Si at the 4-31G level.

(22) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(23) Marriott, S.; Topsom, R. D. *J. Mol. Struct.* **1982**, *89*, 83.

(24) The $\Delta q(\pi)\alpha$ values for the ethylenes polarised by HX (r = 4 Å) were (ref 19) as follows in 10^3 electrons: F, −122; CN, −120; NH_2, −37; Me, 2; OMe, −75; CF_3, −106; COMe, −47; NO_2, −171; OH, −75; CHO, −47.

(25) The two values are very similar, for example, being 35.8 (CF_3) and 35.2 (NO_2) for process 4.

Table III. Theoretical σ_F Values (as Eq 4 and Eq 7, See Text)

X	σ_F	X	σ_F	X	σ_F
H	0.00	NH_2	0.15	PH_2	0.05
Me	−0.01	NHMe	0.15	PMe_2	−0.03
Et	−0.01	NMe_2	0.15		
i-Pr	−0.01	NHCOMe	0.25[a]	SH	0.23
t-Bu	−0.01	$NHNH_2$	0.16[a]	SMe	0.16
CH_2CN	0.25	NHOH	0.27[a]	SCN	0.49
CH_2NH_2	−0.01[a]	NCO	0.38	SCF_3	0.42
CH_2OH	0.11[a]	NCS	0.53	SOMe	0.37
CH_2F	0.13	NO	0.55	SO_2Me	0.60
CHF_2	0.28	NO_2	0.66		
CF_3	0.42			Cl	0.44
$C(CN)_3$	0.63	OH	0.30		
$CHCH_2$	0.04	OMe	0.29		
Ph	0.06	OCOMe	0.41[a]		
CCH	0.17	OCF_3	0.50		
CHO	0.22				
COMe	0.19	F	0.47		
COCN	0.43				
$COCF_3$	0.40	Li	−0.94		
$CONH_2$	0.28				
CO_2H	0.27	BeH	−0.23		
CO_2Me	0.23				
COF	0.43	BH_2	−0.08		
CN	0.45	BMe_2	−0.15		
CNO	0.52	BF_2	0.13		
CNS	0.63				

[a] Average of two conformations, see text.

from Table II vs. a set of σ_F values derived from a single source in the literature[26] gives

$$\sigma_{F(\mathrm{theor})} = 0.93\sigma_F + 0.03 \tag{8}$$

with a correlation coefficient of 0.986. (The cyano substituent is excluded, see below.)

A difficulty is provided by substituents having a first atom from the second row of the periodic table. It is possible that a different scaling factor is needed here[3] to convert the electron populations into σ_F values. Accordingly, we used the accepted σ_F value of 0.45 for the chlorine substituent to derive a scaling factor of 44.0 (compared with the 35.5 in eq 7 for first-row elements). Confirmation of this value is provided in the close agreement of the σ_F values derived for the substituents SOMe (0.37) and SO_2Me (0.60) with the inherent best values in the literature[16] of 0.36 and 0.58, respectively.

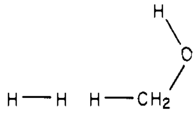
In Table III we list the $\sigma_{F(\mathrm{theor})}$ values for more than 50 substituents. These represent inherent σ_F values, that is values not affected by intermolecular interactions. We feel that these will serve alongside the recently determined σ_χ values[3] in the analysis of experimental data.

Individual Values. The values for simple alkyl groups are all −0.01. Earlier values in the literature[26] were in the range −0.01 to −0.05, but it has been suggested[27] that positive values of this magnitude may apply. Other authors consider that values for alkyl groups are constant[28] and probably zero.[29,30] It would seem best to take the σ_F values here as being effectively zero.

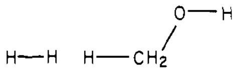
The values obtained for COX substituents such as COMe support the much lower values recently claimed[16,31] for nonpolar media than those listed[14] as appropriate for hydroxylic solvents. Our value for CHO (0.22) is only slightly above that for COMe (0.19) and maybe more appropriate than the values of 0.32[16] or 0.27[31] given elsewhere for nonpolar media. The value of 0.23 for the CO_2Me substituent given in Table III is that applying to the 3-cis conformer which is known[32] to be favored.

Only in the case of the CN substituent do we seem to get an unexpected result. The values in the literature are generally in the range 0.54 to 0.60 compared to our value of 0.45. We have repeated a few of the calculations at the 6-31G* level. Here, the value for the cyano substituent is only slightly larger (0.48) compared to the fluoro or nitro groups as standards. It may well be that the higher values in the literature reflect not only the effect of the simple dipole related to the cyano substitution but also the charge transfer (hyperconjugation) that can occur between the cyano group and CH or CC bonds if the atom of attachment is sp^3 hybridized. This effect is seen in the atomic electron populations[23] of the hydrogen atoms in methyl cyanide (0.820 electron at the 6-31G**/6-31G* level) compared to higher values in compounds such as methyl fluoride (0.893, 6-31G**/6-31G*). This would also lead to the enhanced effect of the CH_2CN group compared to a CH_2F group as seen in Table III. Such an effect would also explain the apparent resonance interaction[33] between substituents and the cyano group in molecules XCH_2CN. It should be of less importance where the atom of attachment is sp^2 hybridized, and it is interesting that the F-19 substituent chemical shifts for meta-substituted benzenes are almost identical for the cyano and fluoro substituents. Thus, the behavior of the cyano substituent may vary from system to system. A similar situation may arise to some extent with COX groups.

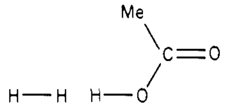
Another interesting feature is the effect of conformational changes in substituents such as CH_2OH, CO_2Me, and OCOMe.



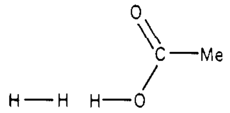
1a



1b



2a



2b

The calculated σ_F values are as follows: 1a, 0.21; 1b, 0.00; 2a, 0.60; 2b, 0.21. Similarly, the two corresponding values for CH_2NH_2 are 0.08 and −0.11, for NHOH 0.40 and 0.14, for $NHNH_2$ 0.26 and 0.05, for NHCOMe 0.41 and 0.08, and for CO_2Me 0.41 and 0.23. Such important conformational effects have some experimental support[34] but are not generally recognized.

The Impossibility of a Completely Universal Scale of σ_F Values

It is not generally appreciated that a completely universal scale of σ_F values is not possible for several different reasons even in the absence of specific solvent effects. First, dipolar substituents and poles (such as $^+NH_3$) cannot be included in the same set. This is because the effect of a dipole varies as $1/r^2$ while that of a pole varies as $1/r$. Thus, in comparing processes having different values of r it is not possible[35] to have the same direct proportionality of substituent effects for poles and dipoles. Second, for quite a few dipolar substituents, the preferred conformation may differ from one system to another. This is possible not only for molecules such as meta-disubstituted benzenes[36] but also because of changes such as shown in structures **1** and **2** above. The matter is even more complicated than this since the substituent effect will depend on the dipole, the distance (r), and the angle subtended by the line from the measurement site to the axis of the dipole. This angle will not vary uniformly in going from one system to another, for example, from para- to meta-disubstituted benzenes, if one

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[26] See, for example: Exner, O. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972.

[27] See, for example, ref 15.

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[32] Perrin, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 2839.

[33] Butt, G.; Cilmi, J.; Hoobin, P. M.; Topsom, R. D. *Spectrochim. Acta, Part A* **1980**, *36A*, 521.

[34] See, for example: Aue, D. H.; Bowers, M. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, **1979**; Vol. 2, p 21. Friedl, Z.; Hapola, J.; Exner, O. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2928.

[35] Reynolds, W. F.; Topsom, R. D., submitted for publication.

[36] See, for example: Katritzky, A. R.; Topsom, R. D. *Chem. Rev.* **1977**, *77*, 639.

compares a substituent having a dipole directed along the CX axis, such as F, with one such as COX. Third, even if the point dipole assumption holds, even for a linear substituent, the value of r does not change completely uniformly from one system to another. Thus, the distance from a probe site in the case of a fluorine substituent is to the midpoint of the CF bond while that to a cyano substituent is significantly greater. Thus, if the system is changed, the incremental increase in r is constant, but the relative change will alter from one substituent to another. We can readily illustrate this with system 4 using the F and CN substituents. At $r = 3.44$ Å, the effect of the F is 12% greater than that of the CN, at $r = 4.0$ it is only 5% greater, while at $r = 7$ Å it is 7% *less*. Fourth, as discussed with the cyano group above, substituent electronic effects may change somewhat depending on the substrate.

Conclusions

A simple theoretical method has been devised to calculate inherent σ_F values with a wide variety of substituents. These are in good agreement with values, where known, for nonpolar media and provide reliable values for many other substituents. The method shows the significance of conformational and distance effects on σ_F values that are not generally recognized.

Acknowledgment. We are grateful to the Australian Research Grants Scheme and The Ian Potter Foundation for financial assistance.

Spin-Echo ^{13}C NMR Spectroscopy for the Analysis of Deuterated Carbon Compounds

J. R. Wesener, P. Schmitt, and H. Günther*

Contribution from Fachbereich 8, Organic Chemistry II, University of Siegen, D-5900 Siegen 21, Germany. *Received June 15, 1983*

Abstract: J modulation of ^{13}C spin-echo signals is used to develop a strategy for the analysis of deuterated carbon compounds, with the aim to distinguish ^{13}C NMR signals of quaternary carbons, CH, CH_2, CH_3, CHD, CH_2D, CHD_2, CD, CD_2, and CD_3 groups. Three different experimental approaches are discussed: (1) spin-echo modulation by $^1J(^{13}C,^1H)$ (^{1}H-SEFT) without ^{2}H decoupling as the simplest method available; (2) spin-echo modulation by either $^1J(^{13}C,^1H)$ or $^1J(^{13}C,^2H)$ with simultaneous ^{1}H and ^{2}H decoupling [these experiments use ^{1}H- and ^{2}H-decoupling facilities and gated decoupling on one decoupler channel]; (3) the combination of two ^{13}C spin-echo sequences with gated ^{1}H as well as ^{2}H decoupling finally leading to TANDEM-SEFT, a pulse sequence that provides the most general approach to the analysis of labeled carbon sites in organic molecules.

Analytical methods that allow a quick and unambiguous characterization of labeled carbon sites are of vital importance for deuterium labeling studies in organic and bioorganic chemistry. It was shown recently that modern pulse techniques in connection with ^{2}H decoupling can be employed successfully for this purpose.[1-3] Rinaldi and Baldwin[1] proposed a $^{13}C\{^2H\}$-INEPT pulse sequence for the selective detection of deuterated carbons, while we showed[2,3] that the experimentally less demanding spin-echo sequence allows fully and partially deuterated carbons to be recognized if ^{2}H decoupling is used to control J modulation of transverse ^{13}C magnetization by one-bond ^{13}C,^{2}H spin-spin coupling.[2] It was further demonstrated that the analysis can be considerably improved by difference spectroscopy[3] and that two-dimensional J-resolved ^{13}C spectra can be used to unravel overlapping multiplets.[2]

Since ^{2}H decoupling and ^{19}F field/frequency lock facilities are normally not available with standard FT-NMR equipment, it seemed of interest to investigate an alternative approach that uses the well-known SEFT sequence[4] which is based on ^{1}H broadband decoupling and can be performed with most of the FT-NMR spectrometers presently in use, which are equipped with ^{1}H decoupler and ^{2}H lock channel:

^{13}C: 90°(x) — τ — 180°(x) — τ — acquisition (I)

^{1}H: decoupler — on —→|← off —→|← on —

At the same time it was desirable to study further the potential of pulse sequences that use ^{1}H as well as ^{2}H decoupling.

Results

The time dependence of transverse ^{13}C magnetization modulated by ^{13}C,^{1}H as well as ^{13}C,^{2}H spin-spin coupling, respectively, has been worked out,[2,4,5] and the following relations for the signal intensity I can be derived if relaxation effects are neglected ($\tau \ll T_2$):

CH: $$I = I_0 \cos (\pi J_{CH} \tau_1) \quad (1)$$

CH_2: $$I = I_0 \cos^2 (\pi J_{CH} \tau_1) \quad (2)$$

CH_3: $$I = I_0 \cos^3 (\pi J_{CH} \tau_1) \quad (3)$$

CD: $$I = I_0(^1/_3 + {}^2/_3 \cos (2\pi J_{CD} \tau_2)) \quad (4)$$

CD_2: $$I = I_0(^1/_3 + {}^2/_3 \cos (2\pi J_{CD} \tau_2))^2 \quad (5)$$

CD_3: $$I = I_0(^1/_3 + {}^2/_3 \cos (2\pi J_{CD} \tau_2))^3 \quad (6)$$

If ^{1}H decoupling is used, eq 1-3 apply, and in principle, two experiments should distinguish between the various ^{13}C resonances expected for partially deuterated compounds due to the presence

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[1] Rinaldi, P. L.; Baldwin, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5791.

[2] Schmitt, P.; Wesener, J. R.; Günther, H. *J. Magn. Reson.* **1983**, *52*, 511.

[3] Wesener, J. R.; Günther, H. *Org. Magn. Reson.* **1983**, *21*, 433.

[4] (a) Rabenstein, D. L.; Nakashima, T. T. *Anal. Chem.* **1979**, *51*, 1465A. (b) Brown, D. W.; Nakashima, T. T.; Rabenstein, D. L. *J. Magn. Reson.* **1981**, *45*, 302. (c) For a review, see: Benn, R.; Günther, H. *Angew. Chem.* **1983**, *95*, 381; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350. SEFT = spin-echo Fourier transform.

[5] The compact notation for eq 1-3 is due to the following Radeglia, R. *Z. Chem.* **1982**, *22*, 252. Blunt, J. W.; Steel, P. J. *Aust. J. Chem.* **1982**, *35*, 2561.

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