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Solvent and Temperature Dependence of Hydrogen–Hydrogen, Hydrogen–Fluorine, and Fluorine–Fluorine Coupling Constants in Difluoroethylenes[1]

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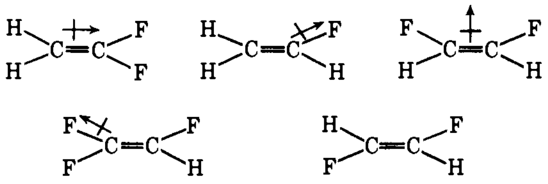
Abstract: Solvent- and temperature-induced variations of H–H, H–F, and F–F coupling constants in *cis*- and *trans*-1,2-difluoroethylene and 1,1-difluoroethylene are reported. These data, in conjunction with previous results, confirm that orientation of the solute dipole affects the magnitude of the solvent effect on geminal H–H and H–F coupling constants. Dipole orientation is not a factor in determining solvent effects on vicinal H–F and F–F coupling constants. The changes observed for vicinal H–F coupling constants are proportional to $\sqrt{{}^3J_{HF}}$. The dipole-induced solvent electric field is the primary causative factor producing the observed changes, but dispersion forces and specific interactions are also important. The best fit for a regression analysis of coupling constants against solvent parameters is of the form $J_{obsd} = J_0 + AR + BD$, where R and D represent reaction field and dispersion field terms. A and B are opposite in sign. Rough values of ΔH and ΔS are reported for weak solute–solvent complexes characterizing specific interactions effects. An apparent dichotomy is reported where one coupling constant in a molecule is solvent dependent but another is not, even though the same nuclei are involved in both couplings.

Solvent-induced variations of various coupling constants ranging from 0.30 Hz to 10.0 Hz have been reported in several hundred compounds.[2] The properties of the solute molecule and the solute–solvent interactions conducive to solvent-dependent coupling constants are the subject of much speculation. For the limited case of geminal H–H coupling constants, previous investigations[3,5] have implicated the solute dipole as a necessary condition for solvent dependency. The observation that ${}^2J_{HF}$ of vinyl fluoride increases while ${}^2J_{HF}$ of trifluoroethylene decreases under similar conditions confirmed that the solvent effect depends on the presence of the solute dipole, and on its orientation.[4] In these cases it is assumed that the dipole-induced solvent electric field (reaction field) alters the electronic distribution of the solute molecule, resulting in the observed changes in geminal coupling constants. However, reaction field effects are not the only mode of solute–solvent interaction. Laszlo[6] has demonstrated an excellent correlation between dispersion forces and coupling constant changes in symmetric molecules. Recently, Goldstein[7] has developed and tested a model involving both reaction field terms and equilibrium constants for collision complexes in order to explain discrepancies in extrapolating reaction field terms to high dielectric constant solvents. The difluoroethylenes provide a number of unique opportunities to clarify some of these problems.

The cis isomer possesses a permanent dipole whose orientation relative to the H–C–F group is intermediate to that of vinyl fluoride and trifluoroethylene, while the trans isomer contains the same H–C–F group but has no dipole moment. The dipole moment–solvent electric field concept predicts that ΔJ_{max}[8] for *cis*-1,2-difluoroethylene should be between the values observed for vinyl fluoride and trifluoroethylene, while ${}^2J_{HF}$ of *trans*-1,2-difluoroethylene should be solvent invariant.



All three isomers have a nice array of vicinal H–F couplings. Previous studies[4,9] indicate that solvent effects on vicinal H–F coupling constants are at least an order of magnitude larger than solvent effects on the corresponding vicinal H–H couplings (which are generally insensitive to solvent). The 1,2-difluoroethylenes present an excellent opportunity to compare the solvent-induced changes of vicinal H–F coupling constants with the corresponding changes in geminal

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[1] This work supported in part by DOD Project Themis Contract No. DAAB07-69-C-0366. A portion of this work was presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] References 3 and 4 contain many citations for early reports of solvent-dependent coupling constants.

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[8] A positive ΔJ is defined as a change for which J increases algebraically with enhanced solvent polarity.

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Table I. Nmr Parameters for *cis*-1,2-Difluoroethylene at 60 MHz in Various Solvents

Solvent	Solvent code	$J_{\mathrm{HH,cis}}$	$J_{\mathrm{HF,gem}}$	$J_{\mathrm{HF.trans}}$	$J_{\mathrm{FF.cis}}$	ν^a
n-Hexane	1	−2.05	71.70	19.63	18.74	365.49
Cyclohexane	2	−2.07	71.84	19.77	19.04	366.92
Benzene-d_6	3	−2.03	72.24	20.44	19.35	330.15
Carbon tetrachloride	4	−2.02	71.80	19.99	19.02	374.86
Carbon disulfide	5	−2.00	71.76	20.04	19.66	372.62
Propionic acid	6	−2.04	72.29	20.53	18.74	382.57
Diethylamine	7	−2.04	72.20	20.63	19.19	390.10
Diethyl ether	8	−2.02	72.12	20.43	18.98	382.96
Chloroform-*d*	9	−2.01	72.01	20.31	19.10	377.72
Chlorobenzene	10	−2.03	72.17	20.36	19.39	353.97
Ethyl acetate	11	−2.03	72.48	20.88	18.84	392.59
Tetrahydrofuran	12	−2.00	72.42	20.84	19.24	388.63
Methylene chloride	13	−2.02	72.73	20.51	18.94	380.29
Cyclopentanone	14	−2.00	72.56	21.06	19.35	395.35
Acetone-d_6	15	−2.03	72.73	21.08	18.89	397.45
2-Nitropropane	16	−1.97	72.56	20.85	18.89	387.43
Dimethylformamide	17	−1.99	72.76	21.49	19.45	408.88
Acetonitrile	18	−2.03	72.80	21.09	18.39	390.36
Nitromethane	19	−2.01	72.63	21.03	18.52	389.82
Trifluoroacetic acid	20	−2.03	72.50	20.34	17.77	376.69
Dimethyl sulfoxide	21	−1.93	72.67	21.94	20.59	407.78

[a] In hertz downfield from TMS.

Table II. Nmr Parameters for *trans*-1,2-Difluoroethylene at 60 MHz in Various Solvents

Solvent	Solvent code	ϵ	$J_{\mathrm{HH.trans}}$	$J_{\mathrm{HF.gem}}$	$J_{\mathrm{HF.cis}}$	$J_{\mathrm{FF.trans}}$	ν^a
Cyclohexane	2	2.02	9.53	75.10	2.80	−133.46	423.84
Benzene-d_6	3	2.26	9.53	75.14	3.04	−132.72	398.90
Carbon tetrachloride	4	2.38	9.51	75.05	2.83	−132.86	433.28
Carbon disulfide	5	2.64	9.53	75.06	2.84	−133.79	429.64
Propionic acid	6	3.30	9.55	75.17	3.15	−131.57	439.39
Diethylamine	7	3.60	9.51	72.20	3.17	−131.88	449.25
Diethyl ether	8	4.34	9.53	75.23	3.17	−131.94	441.96
Chloroform-*d*	9	4.80	9.51	75.14	2.96	−131.96	435.06
Chlorobenzene	10	5.94	9.51	75.13	2.99	−132.82	415.34
Ethyl acetate	11	6.40	9.52	75.15	3.33	−131.16	448.20
Tetrahydrofuran	12	7.40	9.49	75.23	3.25	−131.54	446.18
Methylene chloride	13	9.08	9.52	75.17	3.08	−131.54	437.59
Cyclopentanone	14	16.00	9.50	75.03	3.27	−131.42	449.71
Acetone-d_6	15	20.00	9.50	75.10	3.36	−130.77	452.79
Acetonitrile-d_3	18	35.10	9.56	75.30	3.33	−130.20	445.77
Trifluoroacetic acid	20	39.50	9.53	75.46	3.06	−130.37	434.41
Dimethyl-d_6 sulfoxide	21	46.00	9.48	75.03	3.57	−130.61	462.67

[a] In hertz downfield from TMS.

Table III. Nmr Parameters for 1,1-Difluoroethylene at 60 MHz in Various Solvents

Solvent	Solvent code	ϵ	$J_{\mathrm{HH.gem}}$	$J_{\mathrm{HF.cis}}$	$J_{\mathrm{HF.trans}}$	$J_{\mathrm{FF.gem}}$	ν^a
n-Hexane	1	1.96	−4.65	0.61	33.76	31.65	220.46
Cyclohexane	2	2.02	−4.60	0.64	33.90	30.93	221.03
Benzene	3	2.26	−4.97	0.79	34.58	32.76	202.70
Carbon tetrachloride	4	2.38	−4.69	0.63	33.99	31.09	228.60
Carbon disulfide	5	2.64	−4.72	0.67	34.01	30.01	225.13
Propionic acid	6	3.30	−4.99	0.90	34.99	34.84	231.49
Chloroform-*d*	9	4.80	−4.86	0.79	34.40	32.58	228.71
Methylene chloride	13	9.08	−4.97	0.88	34.85	33.86	230.66
Cyclopentanone	14	16.00	−5.28	0.98	35.39	35.27	239.30
Acetone	15	20.00	−5.19	1.07	35.42	36.51	238.23
2-Nitropropane	16	25.50	−5.21	1.04	35.28	35.65	234.38
Dimethylformamide	17	35.00	−5.38	1.19	36.15	36.92	248.78
Trifluoroacetic acid	20	39.50	−4.88	0.91	34.23	36.79	225.55
Dimethyl sulfoxide	21	46.00	−5.38	1.23	36.49	35.83	250.34

[a] In hertz downfield from TMS.

H–F coupling constants which appear to be dipole dependent. The symmetry of 1,1-difluoroethylene minimizes the differences in dipole orientation with respect to $^3J_{\mathrm{HF,cis}}$ and $^3J_{\mathrm{HF,trans}}$ and provides an excellent opportunity to determine the intrinsic differences in the sensitivity of cis and trans H–F coupling constants to solvent changes.

As an extra bonus, the difluoroethylenes present AA′XX′ spectra which permit an assessment of the F–F couplings directly from the proton spectra. Reports of solvent-dependent F–F couplings are very rare, and information gained from this study will represent a significant expansion of our knowledge in this area.

Finally, the study of two closely related series of compounds with and without dipoles in a variety of solvents and at several temperatures offers opportunities to clarify the relative roles of reaction fields, dispersion forces, and collision complexes as modes of solute–solvent interaction.

Experimental Section

Samples of 1,1-difluoroethylene and 1,2-difluoroethylene were purchased from Pierce Chemical Co., Rockford, Ill. Nmr analysis showed 1,1-difluoroethylene to be free of impurities. The 1,2-difluoroethylene sample was a 9:1 mixture of the cis and trans isomers. Bulb-to-bulb distillations with Dry Ice–acetone baths readily separated the cis and trans isomers. An iodine-catalyzed isomerization[10] was used to prepare sufficient quantities of *trans*-1,2-difluoroethylene.

Spectro and reagent grade solvents were used without further purification. No evidence of solvent impurities was encountered with the exception of dimethyl-d_6 sulfoxide (DMSO) which contained a detectable trace of water. Samples were prepared by adding a measured amount of liquified olefin to the proper volume of solvent containing approximately 3% tetramethylsilane to yield *ca.* 10 mol % solutions. All samples were degassed by the freeze–thaw technique and sealed under vacuum.

Proton spectra were run on a Varian Associates HA-60-IL spectrometer operating in the frequency sweep mode. In every case the final line positions represent the average of five or more independent scans in which the peak positions were counted directly.

The AA′XX′ spectra were analyzed with the procedure developed by McConnell, *et al.*[11] Computer analysis using LACN III[12] confirmed these parameters. In all cases, the probable errors in the calculated parameters are less than 0.05 Hz. Limitations in the experimental measurements were slightly greater, but the results given are certainly good to better than ±0.1 Hz. It is impossible to determine the absolute signs of the various coupling constants from the appearance of an AA′XX′ spectrum. Signs given in this paper are from the work of Flynn, *et al.*,[13] and are consistent with the results obtained from studies in the nematic phase.[14]

Statistical analyses of results were performed with the correlation–multiple regression program MULTR in the University of Kentucky Computing Center Statistical Library.

Results

Final results at ambient temperature for *cis*-1,2-difluoroethylene in 21 solvents, *trans*-1,2-difluoroethylene in 17 solvents, and 1,1-difluoroethylene in 14 solvents[15] are presented in Tables I–III. Tables IV and V summarize the results for *cis*-1,1-difluoroethylene and 1,1-difluoroethylene in a variety of solvents at *ca.* 25° intervals between 23 and −80°. A limited-temperature study for *trans*-1,2-difluoroethylene in three solvents at 23 and −65° is presented in Table VI.

Proton–Proton Coupling Constants. The geminal H–H coupling constant of 1,1-difluoroethylene decreases 0.73 Hz from −4.65 Hz in *n*-hexane to −5.38 Hz in DMSO, as expected from current theories.[3] Within experimental error, the vicinal H–H coupling constants of the cis and trans isomers are solvent and temperature invariant.

Table IV. Temperature Studies for *cis*-1,2-Difluoroethylene at 60 MHz[a] in Various Solvents

n-Hexane	23°	−2°	−43°	−64°	−84°
ν_H	365.49	366.31	367.31	367.98	368.70
$J_{HH\cdot cis}$	−2.05	−2.02	−2.06	−2.03	−2.03
$J_{HF\cdot trans}$	19.63	19.75	19.76	19.97	20.08
$J_{HF\cdot gem}$	71.70	71.81	71.58	71.77	71.78
$J_{FF\cdot cis}$	18.74	19.11	19.44	19.70	20.11
Carbon Disulfide	23°	−2°	−30°	−54°	−82°
ν_H	372.62	373.62	374.76	375.77	377.94
$J_{HH\cdot cis}$	−2.01	−1.93	−2.01	−1.96	−2.02
$J_{HF\cdot trans}$	20.04	20.14	20.20	20.14	20.20
$J_{HF\cdot gem}$	71.76	71.59	71.72	71.66	71.52
$J_{FF\cdot cis}$	19.66	20.41	20.14	20.72	21.34
Chloroform	23°	−2°	−30°	−61°	
ν_H	377.75	379.61	382.04	383.69	
$J_{HH\cdot cis}$	−2.02	−2.04	−2.03	−1.97	
$J_{HF\cdot trans}$	20.31	20.41	20.67	20.71	
$J_{HF\cdot gem}$	72.01	72.07	72.09	72.09	
$J_{FF\cdot cis}$	19.10	19.43	19.85	20.00	
Diethyl Ether	23°	−2°	−43°	−54°	−82°
ν_H	382.97	386.71	392.56	397.29	404.91
$J_{HH\cdot cis}$	−2.03	−2.02	−1.98	−2.05	−2.01
$J_{HF\cdot trans}$	20.43	20.65	20.92	21.20	21.52
$J_{HF\cdot gem}$	72.12	72.21	72.18	72.23	72.28
$J_{FF\cdot cis}$	18.98	19.37	20.00	20.34	20.90
Methyl Acetate	23°	−2°	−43°	−54°	−84°
ν_H	392.17	395.74	400.63	403.94	409.80
$J_{HH\cdot cis}$	−2.04	−2.00	−2.00	−1.99	−1.91
$J_{HF\cdot trans}$	20.36	21.05	21.29	21.39	21.68
$J_{HF\cdot gem}$	72.36	72.41	72.48	72.61	72.62
$J_{FF\cdot cis}$	18.70	19.02	19.46	19.67	20.15
Methylene Chloride	23°	−2°	−30°	−65°	−82°
ν_H	380.29	382.20	384.45	387.09	388.79
$J_{HH\cdot cis}$	−2.02	−2.01	−2.00	−1.98	−1.93
$J_{HF\cdot trans}$	20.37	20.70	20.81	20.95	21.11
$J_{HF\cdot gem}$	72.37	72.24	72.15	72.18	72.19
$J_{FF\cdot cis}$	18.94	19.22	19.59	19.87	20.23
Acetone	23°	−2°	−30°	−54°	−84°
ν_H	397.45	401.01	406.24	409.87	415.54
$J_{HH\cdot cis}$	−2.03	−2.01	−1.95	−1.99	−1.96
$J_{HF\cdot trans}$	21.08	21.19	21.44	21.56	21.74
$J_{HF\cdot gem}$	72.73	72.71	72.63	72.76	72.64
$J_{FF\cdot cis}$	18.89	19.25	19.71	19.97	20.41
Dimethylformamide	23°	−2°	−30°	−62°	
ν_H	408.88	413.53	420.29	425.03	
$J_{HH\cdot cis}$	−1.99	−1.98	−1.95	−1.95	
$J_{HF\cdot trans}$	21.49	21.75	21.94	22.09	
$J_{HF\cdot gem}$	72.77	72.78	72.63	72.67	
$J_{FF\cdot cis}$	19.45	19.88	20.38	20.70	

[a] Values for ν_H are in hertz downfield from TMS and the temperature is in °C.

Hydrogen–Fluorine Coupling Constants. The geminal H–F coupling constant of *cis*-1,2-difluoroethylene increases with increasing solvent polarity varying 1.10 Hz from a minimum of 71.70 Hz in *n*-hexane to a maximum of 72.80 Hz in dimethylformamide (DMF). The best correlation is observed with the Onsager reaction field term (χ = 0.89, 0.93) as illustrated in

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Table V. Temperature Studies for 1,1-Difluoroethylene at 60 MHz[a] in Various Solvents

	n-Hexane				
	23°	−2°	−43°	−65°	
ν	220.46	221.07	221.77	222.21	
$J_{\mathrm{HH.gem}}$	−4.65	−4.60	−4.67	−4.67	
$J_{\mathrm{HF.trans}}$	33.76	33.79	33.87	34.00	
$J_{\mathrm{HF.cis}}$	0.61	0.59	0.56	0.53	
$J_{\mathrm{FF.gem}}$	31.65	31.20	30.77	30.47	
	Carbon Disulfide				
	23°	−2°	−43°	−65°	
ν	225.13	226.02	227.11	227.91	
$J_{\mathrm{HH.gem}}$	−4.72	−4.70	−4.74	−4.66	
$J_{\mathrm{HF.trans}}$	34.01	34.04	34.25	34.26	
$J_{\mathrm{HF.cis}}$	0.67	0.66	0.68	0.57	
$J_{\mathrm{FF.gem}}$	30.01	29.55	29.07	28.93	
	Chloroform				
	23°	−2°	−43°	−61°	
ν	228.71	230.15	232.03	233.22	
$J_{\mathrm{HH.gem}}$	−4.86	−4.88	−4.90	−4.91	
$J_{\mathrm{HF.trans}}$	34.40	34.61	34.77	34.87	
$J_{\mathrm{HF.cis}}$	0.79	0.75	0.82	0.71	
$J_{\mathrm{FF.gem}}$	32.58	32.21	31.92	31.79	
	Methyl Acetate				
	23°	−2°	−43°	−54°	−84°
ν	238.42	241.26	244.89	247.61	252.22
$J_{\mathrm{HH.gem}}$	−5.10	−5.00	−5.29	−5.25	−5.25
$J_{\mathrm{HF.trans}}$	35.23	35.34	35.61	35.89	36.19
$J_{\mathrm{HF.cis}}$	1.04	1.10	0.96	1.11	1.11
$J_{\mathrm{FF.gem}}$	36.73	36.56	36.71	36.81	37.10
	Methyl Chloride				
	23°	−2°	−43°	−65°	−84°
ν	230.66	232.06	233.81	235.94	237.26
$J_{\mathrm{HH.gem}}$	−4.97	−5.00	−4.99	−5.07	−5.05
$J_{\mathrm{HF.trans}}$	34.85	34.74	35.01	35.31	35.36
$J_{\mathrm{HF.cis}}$	0.88	0.92	0.90	0.90	0.94
$J_{\mathrm{FF.gem}}$	33.86	33.69	33.43	33.27	33.27
	Acetone				
	23°	−2°	−43°	−54°	−82°
ν	238.23	240.87	244.38	247.25	252.63
$J_{\mathrm{HH.gem}}$	−5.19	−5.27	−5.29	−5.25	−5.37
$J_{\mathrm{HF.trans}}$	35.42	35.39	35.71	36.02	36.20
$J_{\mathrm{HF.cis}}$	1.07	1.05	1.06	1.08	1.15
$J_{\mathrm{FF.gem}}$	36.51	36.29	36.18	36.07	36.21
	Dimethylformamide				
	23°	−2°	−43°	−61°	
ν	248.78	252.26	256.92	259.99	
$J_{\mathrm{HH.gem}}$	−5.38	−5.38	−5.41	−5.41	
$J_{\mathrm{HF.trans}}$	36.15	36.23	36.21	36.59	
$J_{\mathrm{HF.cis}}$	1.19	1.27	1.30	1.27	
$J_{\mathrm{FF.gem}}$	36.92	36.83	36.87	36.78	

[a] Values for ν_{H} are in hertz downfield from TMS and the temperature is in °C.

Table VI. Temperature Studies for *trans*-1,2-Difluoroethylene at 60 MHz[a] in Various Solvents

	Carbon Disulfide	
	23°	−65°
ν_{H}	429.69	430.87
$J_{\mathrm{HH.trans}}$	9.53	9.51
$J_{\mathrm{HF.gem}}$	75.06	74.77
$J_{\mathrm{HF.cis}}$	2.84	2.82
$J_{\mathrm{FF.trans}}$	−133.79	−134.16
	Ethyl Ether	
	23°	−65°
ν_{H}	441.96	456.21
$J_{\mathrm{HH.trans}}$	9.53	9.50
$J_{\mathrm{HF.gem}}$	75.23	75.14
$J_{\mathrm{HF.cis}}$	3.17	3.50
$J_{\mathrm{FF.trans}}$	−131.94	−131.70
	Acetone	
	23°	−65°
ν_{H}	452.79	466.90
$J_{\mathrm{HH.trans}}$	9.50	9.55
$J_{\mathrm{HF.gem}}$	75.10	75.05
$J_{\mathrm{HF.cis}}$	3.36	3.49
$J_{\mathrm{FF.trans}}$	−130.77	−130.68

[a] Values for ν_{H} are in hertz downfield from TMS and the temperature is in °C.

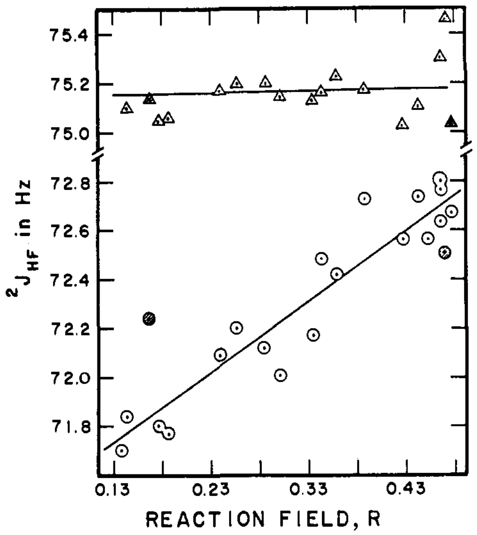

Figure 1. Plot of $J_{\mathrm{HE.gem}}$ of the cis (○) and trans (△) isomers of 1,2-difluoroethylene *vs.* the solvent reaction field *R*.

Figure 1. Generally, cyclohexane (or *n*-hexane) and DMSO provide extreme values for the solvent variations of $^2J_{\mathrm{HH}}$ and $^2J_{\mathrm{HF}}$. The insignificant change of 0.07 Hz for $^2J_{\mathrm{HF}}$ in *trans*-1,2-difluoroethylene for these solvents contrasts dramatically with the 1.87- and −0.58-Hz variations previously reported[4] for vinyl fluoride and trifluoroethylene and the change for $J_{\mathrm{HF.gem}}$ of *cis*-1,2-difluoroethylene described above. The meager solvent variation of $^2J_{\mathrm{HF}}$ in the trans isomer is obvious in Figure 1. The only significant changes for this coupling occur in solvents like trifluoroacetic acid and acetonitrile, which are expected to exhibit strong solute–solvent interactions. Both geminal H–F coupling constants are insensitive to temperature, with the 0.15-Hz/100° changes paralleling roughly the temperature effect on solvent dielectric constant.

Significant increases are observed for all vicinal H–F coupling constants with enhanced solvent polarity. In 1,1-difluoroethylene, changes of 0.62 and 2.73 Hz are observed for the cis and trans couplings, respectively. The trans H–F coupling constant of cis-1,2-difluoroethylene changes 2.31 Hz. The 0.77-Hz change for $^3J_{\mathrm{HF,cis}}$ of *trans*-1,2-difluoroethylene is in direct contrast to the solvent invariance of $^3J_{\mathrm{HH.trans}}$ and $^2J_{\mathrm{HF}}$ in this compound.

Large temperature variations are observed for all chemical shifts and the trans H–F coupling constants (20 Hz/100° for δ and 1.0 Hz/100° for $^3J_{\mathrm{HF.trans}}$) of 1,1-difluoroethylene and *cis*-1,2-difluoroethylene. In both instances, $^3J_{\mathrm{HF.trans}}$ increases with decreasing temperature. Temperature effects on $^3J_{\mathrm{HF.trans}}$ are more pronounced in solvents of higher dielectric constant and solvents with nonbonding electrons, *i.e.*,

Table VII. Simple Correlation Table for Solute Parameters *vs.* Solute Parameters[a]

	1,1-DFE					*trans*-1,2-DFE				*cis*-1,2-DFE			
	$^2J_{HH}$	$^3J_{HF}{}^c$	$^3J_{HF}{}^t$	$^2J_{FF}$	ν_H	$^2J_{HF}$	$^3J_{HF}{}^c$	$^3J_{FF}{}^t$	ν_H	$^2J_{HF}$	$^3J_{HF}{}^t$	$^3J_{FF}{}^c$	ν_H
cis-1,2-DFE													
$^2J_{HF}$	−0.8778	0.9075	0.8339	0.9059	0.5993	0.2833	0.8227	0.8790	0.5142		0.8491	0.0778	0.5821
$^3J_{HF}{}^t$	−0.9691	0.9644	0.9825	0.7863	0.7668	−0.0798	0.9628	0.7523	0.6851	*0.9154*		0.3455	0.7126
$^3J_{FF}{}^c$	−0.4028	0.3207	0.5266	0.1083	0.3747	−0.7703	0.1930	0.3186	0.1040	*−0.2858*	*−0.0922*		0.1178
ν_H	−0.6743	0.7394	0.7284	0.6277	0.9899	−0.0374	0.6794	0.6381	0.9945	*0.7389*	*0.8615*	*−0.1026*	
trans-1,2-DFE													
$^2J_{HF}$	0.2312	−0.1726	−0.2391	0.0220	−0.4538		0.0536	0.4742	−0.0258				
$^3J_{HF}{}^c$	−0.9701	−0.9942	0.9919	0.9272	0.6815	*0.3253*		0.8116	0.7233				
$^3J_{FF}{}^t$	−0.8848	0.9228	0.8940	0.9605	0.7051	*0.5433*	*0.9121*		0.6604				
ν_H	−0.6345	0.7248	0.7106	0.6513	0.9946	*0.2807*	*0.8254*	*0.7794*					
1,1-DFE													
$^2J_{HH}$		−0.9616	−0.9672	−0.8336	0.7166								
$^3J_{HF}{}^c$	*−0.9763*		0.9603	0.8975	0.7678								
$^3J_{HF}{}^t$	*−0.9815*	*0.9898*		0.7706	0.7832								
$^2J_{FF}$	*0.9465*	*0.9652*	*0.9558*		0.6139								
ν_H	*−0.9427*	*0.9290*	*0.9593*	*0.8735*									

[a] Values in italics are the correlations with values measured in benzene, DMSO and trifluoroacetic acid excluded.

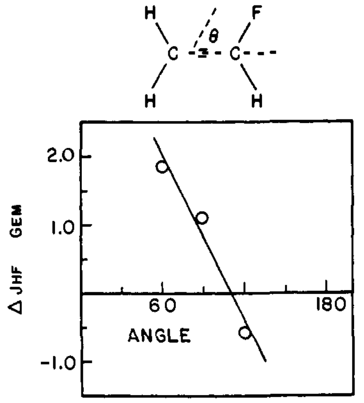

Figure 2. Plot of $\Delta^2J_{HF,max}$ *vs.* the angle between the solute dipole and a plane bisecting the geminal H–F group: vinyl fluoride, θ = 60°, ΔJ = +1.87 Hz; *cis*-12,-difluoroethylene, θ = 90°, ΔJ = +1.10 Hz; trifluoroethylene, θ = 120, ΔJ = 0.58 Hz.

diethyl ether and methyl acetate. Surprisingly, the cis H–F coupling constants in both *trans*-1,2-difluoroethylene and 1,1-difluoroethylene are essentially temperature invariant.

Fluorine–Fluorine Coupling Constants. Fluorine–fluorine coupling constants exhibit striking solvent and temperature variations which differ in detail from those observed for J_{HH} and J_{HF}. The 6.99-Hz change for $^2J_{FF}$ in 1,1-difluoroethylene (from 30.93 Hz in carbon disulfide to 36.92 Hz in DMF) is one of the largest solvent-induced changes ever observed for J_{FF} in a rigid system. A solvent-induced change of 2.82 Hz is observed for the vicinal F–F coupling constant of *cis*-1,2-difluoroethylene from 17.77 Hz in trifluoroacetic acid to 20.59 Hz in DMSO. The trans F–F coupling constant of *trans*-1,2-difluoroethylene changes by 3.26 Hz from −133.46 Hz in cyclohexane to −130.20 Hz in acetonitrile.

Both $^2J_{FF}$ and $^3J_{FF,trans}$ exhibit their best correlations with the reaction field term (χ = 0.80 and 0.87, respectively). The cis F–F coupling constant does not correlate with any common solvent parameter.

Temperature and solvent parameters for $^2J_{FF}$ show conflicting trends. Since solvent dielectric constant increases with decreasing temperature, $^2J_{FF}$ might be expected to increase at lower temperatures, as observed for other coupling constants. However, $^2J_{FF}$ decreases with decreasing temperature. Furthermore, the temperature effect is larger in solvents of low dielectric constant (*ca.* −1.50 Hz/100°), diminishing to within experimental error for high dielectric constant solvents such as DMF. The temperature-induced variations of $J_{FF,cis}$ exhibit an entirely different pattern. Despite the wide variety of solvents, the magnitude of the temperature effect remains essentially constant (0.80 Hz/100° for each solvent). Temperature effects for the trans F–F coupling are much smaller than those observed for the other F–F coupling constants.

Discussion

The results presented here and their interpretation are arbitrarily but conveniently divided intotwo sections, internal factors (primarily associated with the solute molecule) and the nature of the solute–solvent interactions. The results for *cis*- and *trans*-1,2-difluoroethylene present overwhelming evidence that the solute dipole is a necessary but insufficient condition for solvent-dependent geminal H–H and H–F coupling constants. The solvent variation of 0.83 Hz observed for $^2J_{HF}$ of *cis*-1,2-difluoroethylene in cyclohexane and DMSO is intermediate to the 1.87- and −0.58-Hz values reported for vinyl fluoride and trifluoroethylene in these two solvents.[4] These results are substantiated in Figure 2, which illustrates a nearly linear relation between $\Delta^2J_{HF,max}$ and the angle which the solute dipole makes with the plane bisecting the H–C–F group. Since *trans*-1,2-difluoroethylene does not possess a dipole, the solvent invariance of $^2J_{HF,gem}$ is consistent with the above premise.

The most striking internal result is presented in Table VII, which summarizes the correlations obtained when coupling constants of the same or different compounds are plotted *vs.* each other in corresponding solvents. All three bonded H–F coupling constants, even in different molecules, have correlation coefficients of 0.9 or better, as illustrated in Figure 3 for a plot of the trans H–F coupling constants in 1,1-difluoroethylene and *cis*-1,2-difluoroethylene *vs.* the cis H–F coupling constant of 1,1-difluoroethylene (χ = 0.96 and 0.98, respectively).

The obvious conclusion is that the same kinds of changes in electronic distribution, rotational or vibrational states, etc., are responsible for the observed

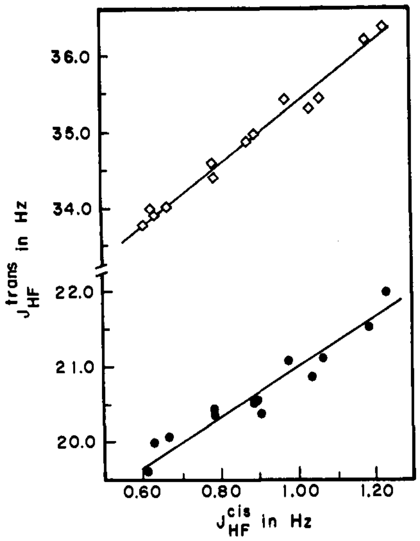

Figure 3. Plot of $J_{\mathrm{HF,trans}}$ of 1,1-difluoroethylene (◇) and *cis*-1,2-difluoroethylene (O) *vs.* $J_{\mathrm{HF,cis}}$ of 1,1-difluoroethylene.

changes in vicinal H–F coupling constants. Additional support for this hypothesis is shown in Figure 4, where a plot of $\Delta^3J_{\mathrm{HF,max}}$ *vs.* $\sqrt{J}$ demonstrates an excellent proportionality between the observed change in $^3J_{\mathrm{HF}}$ and the magnitude of the square root of the coupling constant. The plot also includes values for $\Delta^3J_{\mathrm{HF,max}}$ from trifluoroethylene and vinyl fluoride. The only significant deviation is $^3J_{\mathrm{HF,trans}}$ of vinyl fluoride. Presumably, this proportionality reflects the relative contribution of various orbital energies to the vicinal H–F coupling constant (*vide infra*).

There does not appear to be any relationship between the solute dipole and the solvent variations of vicinal H–F coupling constants. The most surprising observation supporting this conclusion is the significant change of 0.77 Hz observed for $^3J_{\mathrm{HF,cis}}$ of *trans*-1,2-difluoroethylene.

While each of the arguments for solvent dependence in geminal and vicinal H–F coupling constants is reasonable when considered as a separate entity, a dichotomy appears when they must be considered together. This is precisely the case for *trans*-1,2-difluoroethylene, where it would be expected that the solvent effects on the geminal and vicinal H–F coupling constants exhibit the same behavior. This problem might be resolved by an argument used previously in another context.[3]

Assuming that H–F coupling constants arise primarily or exclusively from Fermi contact interactions, the theoretical expression for a coupling constant is given by[16]

$$J_{\mathrm{AB}} = KS_{\mathrm{A}}(0)^2S_{\mathrm{B}}(0)^2\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}(\epsilon_j - \epsilon_i)^{-1}C_{i\mathrm{A}}C_{i\mathrm{B}}C_{j\mathrm{A}}C_{j\mathrm{B}}$$

where K is a collection of constants, $S_{\mathrm{n}}(0)$ represents the amplitude of a valence-shell s function at the nucleus, $(\epsilon_j - \epsilon_i)$ is the energy difference between molecular orbitals j and i, and $C_{k\mathrm{N}}$ is the coefficient of $S_{\mathrm{n}}(0)$ in orbital k. It is conceivable that either $(\epsilon_j - \epsilon_i)$ or the product of the coefficient does not change for the orbitals contributing to the geminal coupling but does vary for the orbitals contributing to the vicinal coupling or *vice versa*.

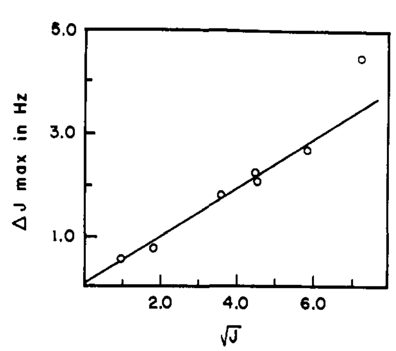

Figure 4. Plot of $^3J_{\mathrm{HF.max}}$ *vs.* $\sqrt{J}$ for the fluoroethylenes; from left to right, the points correspond to $^3J_{\mathrm{HF}^c}$ of 1,1-DFE, $^3J_{\mathrm{HF}^c}$ of *trans*-1,2-DFE, $^3J_{\mathrm{HF}^t}$ of trifluoroethylene, $^3J_{\mathrm{HF}^c}$ of vinyl fluoride, $^3J_{\mathrm{HF}^t}$ of *cis*-1,2-DFE, $^3J_{\mathrm{HF}^t}$ of 1,1-DFE, and $^3J_{\mathrm{HF}^t}$ of vinyl fluoride.

Turning to the question of solute–solvent interactions, several mechanisms must be considered. If the solvent is assumed to be a homogeneous continuum surrounding a solute molecule, then either the solvent reaction field, R, or dispersion interactions, D, are possible. The Onsager model for the reaction field assumes that the solute molecule is a point dipole in a spherical cavity. The reaction field is then given by[17]

$$R = \frac{\mu}{r^3}\frac{2(n^2 + 2)}{3}\frac{(\epsilon - 1)}{(2\epsilon + n^2)}$$

where μ is the dipole moment of the solute molecule in the gas phase, r is the radius of the solute cavity, n is the refractive index of the solute molecule, and ϵ is the dielectric constant of the solvent. For the three isomeric difluoroethylenes, r and n should be approximately the same. We assume n to be in the range of 1.3–1.35. The best expression for dispersion interactions is that given by McRae[18] as

$$D = (n - 1)/(2n^2 + 1)$$

where n is the refractive index of the solvent. Unlike R, the dispersion interaction is not expected to show any directional correlation.

Table VIII reports the results of simple correlations between the nmr parameters of the difluoroethylenes and ϵ, R, and D. With the exception of $^3J_{\mathrm{FF,cis}}$ of *cis*-1,2-difluoroethylene, all the solvent-dependent coupling constants exhibit the best correlation (0.8 or better) with R. If solvents most likely to show specific interactions, such as benzene, trifluoroacetic acid, and acetonitrile, are removed, the correlations with R improve to 0.9 or better. The relation with R is best for 1,1-difluoroethylene and worst for *trans*-1,2-difluoroethylene; on the other hand, D correlates best with the solvent-dependent coupling constants of *trans*-1,2-difluoroethylene. These results indicate that both reaction field and dispersion interactions are contributing to the observed changes in the coupling constants. This hypothesis is supported by results of a regression analysis. For every solvent-dependent cou-

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[16] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965); $K = (64/9)h\beta^2\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}$, where h is Planck's constant, β is the Bohr magneton, and γ_{N} is the magnetogyric ratio of nucleus N.

[17] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960); A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[18] E. G. McRae, *J. Phys. Chem.*, **61**, 502 (1957); N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

Table VIII. Simple Correlation and Regression Analysis of Solute Parameters *vs.* Solvent Parameters

		Simple correlation			Regression analysis[a]	
	ΔJ	ϵ	R	D	Best fit	Standard error
1,1-DFE						
$^2J_{\mathrm{HH}}$	−0.78	−0.7161	−0.8266	0.1312	R	0.1572
			−0.9481	*0.1943*	*R*	*0.0922*
$^3J_{\mathrm{HF}}{}^{\mathrm{c}}$	+0.62	0.8335	0.8903	−0.1079	R	0.0963
	+0.59		*0.9392*	*−0.2200*	*R + D*	*0.0716*
$^3J_{\mathrm{HF}}{}^{\mathrm{t}}$	+2.73	0.7157	0.7673	−0.1316	R	0.5670
	+2.39		*0.9182*	*−0.1860*	*R*	*0.3245*
$^2J_{\mathrm{FF}}$	+6.91	0.8094	0.8930	−0.2252	R + D	0.9852
			0.8871	*−0.4323*	*R + D*	*0.8213*
ν_{H}	47.64	0.6705	0.7418	−0.1690	R	8.448
	28.32		*0.8711*	*−0.0897*	*R*	*4.25*
cis-1,2-DFE						
$^2J_{\mathrm{HF}}$	+1.10	0.7287	0.8954	−0.2266	R + D	0.1584
			0.9324	*−0.3413*	*R + D*	*0.1299*
$^3J_{\mathrm{HF}}{}^{\mathrm{t}}$	+2.31	0.7224	0.8077	−0.1365	R	0.3375
			0.9163	*−0.2436*	*R*	*0.2089*
$^3J_{\mathrm{FF}}{}^{\mathrm{c}}$	−2.82	−0.0496	−0.0906	0.3414	D	0.5245
	−1.27		*0.1803*	*0.7500*	*D*	*0.2187*
ν_{H}	78.73	0.5650	0.6713	−0.3544	R + D	12.79
	43.39		*0.6816*	*−0.3933*	*R + D*	*9.68*
trans-1,2-DFE						
$^2J_{\mathrm{HF}}$	+0.41	0.3222	0.3237	−0.1579	R	0.1054
	+0.25		*0.3300*	*−0.6054*	*R + D*	*0.0624*
$^3J_{\mathrm{HF}}{}^{\mathrm{c}}$	+0.77	0.6147	0.7427	−0.4952	R + D	0.1293
	+0.53		*0.8121*	*−0.7195*	*R + D*	*0.0801*
$^3J_{\mathrm{FF}}{}^{\mathrm{t}}$	+3.59	0.7622	0.8733	−0.4878	R + D	0.4032
			0.8337	*−0.7924*	*R + D*	*0.2968*
ν_{H}	64.77	0.4786	0.6203	−0.5049	R + D	11.134
	37.45		*0.5548*	*−0.6845*	*R + D*	*7.892*

[a] Values in italics represent correlation with values measured in benzene, DMSO and trifluoroacetic acid excluded.

pling except $^3J_{\mathrm{FF,cis}}$, the best least-squares fit is obtained by the expression

$$J_{\mathrm{obsd}} = J_0 + AR + BD$$

In all cases the coefficients A and B are of opposite sign. For 1,1-difluoroethylene, A is large and B is small, reflecting the expected primacy of the reaction field effects. For *trans*-1,2-difluoroethylene, A and B are of the same order of magnitude.

Even with the improved fit obtained with a combination of R and D, there are many indications of specific interactions. Solvents containing nonbonding electrons such as diethyl ether, tetrahydrofuran, diethylamine, and ethyl acetate consistently deviate in the same direction, behaving as if they have a higher dielectric constant. Similarly, values for the cis F–F coupling constant of *cis*-1,2-difluoroethylene are found to fall in three groups corresponding to the shape of the solvent molecule. Values measured in roughly cyclic planar solvents as cyclohexane, benzene, chlorobenzene, and tetrahydrofuran are between 19.04 and 19.39 Hz. Values measured in approximately linear or cylindrical solvents such as *n*-hexane, propionic acid, ethyl acetate, 2-nitropropane, ethyl ether, and diethylamine fall in the range of 18.74–18.98 Hz. Values obtained in small, approximately spherical solvents are randomly distributed.

Further indications of specific solvent–solute interactions are supported by temperature-dependence studies. Using the approach of Abraham,[19] a series of equilibrium expressions were calculated for the difluoroethylenes in various solvents. For simplicity, it was assumed that values for J (or ν) in *n*-hexane could be used for the uncomplexed solute and values for J (or ν) extrapolated to absolute zero could be used for the complexed species. Arrhenius plots of ln K *vs.* $1/T$ for either chemical shifts or $^3J_{\mathrm{HF,trans}}$ are surprisingly linear. The calculated values for ΔH and ΔS are consistent with those of other investigations[20] for similar interactions. Some representative values are given in Table IX. Given the nature of the approximations used and experimental difficulties involved in handling gaseous solutes, not much significance can be attached to the absolute values of the thermodynamic parameters obtained. However, the very existence of linear Arrhenius plots, the general trends in values for ΔS, and the intuitive correlation between chemical structure and solvent-induced changes leaves little doubt that specific interactions play an important role in producing solvent-induced changes of coupling constants.

An anomalous result is the opposing temperature and solvent effects on F–F coupling constants. The good correlation (χ = 0.89) for R *vs.* J_{FF} of 1,1-difluoroethylene would predict a large increase for J_{FF} at subambient temperatues. Exactly the opposite behavior is observed. This coupling constant decreases dramatically in nonpolar solvents with diminishing temperatures but becomes temperature invariant under the same conditions in polar solvents. Ramey and Brey[21] proposed that changes in the distribution of vibrational and torsional states of the solute molecule may influence J_{FF}. Changes in the distribution of these molecular vibrations could cause $^2J_{\mathrm{FF}}$ to decrease at lower temperatures for nonpolar solvents, while a

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(19) R. J. Abraham, *Mol. Phys.*, **4**, 369 (1961).

(20) I. D. Kuntz and M. D. Johnston, *J. Amer. Chem. Soc.*, **89**, 6008 (1967); T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1224 (1965).

(21) K. C. Ramey and W. S. Brey, Jr., *ibid.*, **40**, 2349 (1964).

Table IX. Enthalpy and Entropy of Complex Formation from the Temperature Dependence of J_{HF} Trans and Proton Chemical Shift of *cis*-1,2-Difluoroethylene in Various Solvents

		Chemical shift			Coupling constant		
Solvent	ϵ	$\Delta\nu^a$	H^b	S^c	ΔJ^a	H^b	S^c
n-Hexane	1.96	2.56	−1.67	−9.80	0.42	−1.96	−10.67
Carbon disulfide	2.64	4.80	−0.93	−4.97	0.12	−0.79	−2.53
Diethyl ether	4.34	18.05	−1.01	−5.54	1.01	−1.09	−5.73
Chloroform	4.80	8.37	−0.89	−3.94	0.56	−0.97	−4.72
Methyl acetate	6.50	18.03	−0.97	−4.55	0.86	−0.95	−4.50
Methylene chloride	9.08	8.00	−0.83	−3.18	0.57	−0.87	−3.94
Acetone	20.00	18.00	−0.83	−3.56	0.63	−0.99	−3.95
Dimethylformamide	35.00	22.60	−0.95	−3.95	0.84	−0.77	−3.14

[a] All data at 60 MHz, Hz/100°. [b] H, kcal mol^{-1}. [c] S, cal deg^{-1}.

competing effect, probably arising from temperature-dependent increases in the reaction field, could nullify the former effect in polar solvents. The same competitive effect might be envoked to rationalize the constant magnitude of the temperature variation for $^3J_{FF,cis}$ in polar and nonpolar solvents. The trans F–F coupling constant is essentially temperature invariant, at least in the limited number of solvents in which it was examined. Ng, Tang, and Sederholm[22] found large temperature-induced changes in the geminal and cis F–F coupling constants but small temperature effects for trans F–F in a study of trifluorobromoethylene. They postulated that the temperature effects on the cis and geminal coupling constants were due to large contributions from through-space mechanisms that are solvent and temperature sensitive. The meager temperature effect on $^3J_{FF,trans}$ was interpreted as evidence that the trans F–F coupling arose primarily from temperature-insensitive contact interactions. The large temperature effect on the trans H–F coupling constants which are more likely to arise primarily from contact interactions makes it apparent that perhaps another explanation is needed to justify the small temperature effect on $^3J_{FF,trans}$.

Conclusions

Solvent-induced changes of geminal and vicinal coupling constants apparently arise from various changes within the solute molecule and from a multitude of different solute–solvent interactions.[23] These results provide almost overwhelming evidence that the solute dipole orientation and its reaction field are controlling factors for solvent-dependent geminal H–H and H–F coupling constants in polar solutes. In contrast, specific interactions appear to affect vicinal H–F and F–F coupling constants, support for which is found in the apparent existence of calculated thermodynamic values of solute–solvent complexes. The excellent correlations between vicinal H–F coupling constants of the same or different compounds suggest that the solvent effect stems from a common origin.

Acknowledgments. Financial support by the University of Kentucky Computing Center is gratefully acknowledged. A. M. I. expresses his appreciation to the Haggen Foundation for a research fellowship.

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(22) S. Ng, J. Tang and C. H. Sederholm, *J. Chem. Phys.*, 42, 79 (1965).

(23) W. T. Raynes, *Mol. Phys.*, 15, 435 (1968).