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SPECTRAL POLARITY INDEX: A NEW METHOD FOR DETERMINING THE RELATIVE POLARITY OF SOLVENTS [1]

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SUMMARY

The relative polarity of a number of solvents, including perfluorocarbons, has been determined by measuring the bathochromic shift (as the solvent polarity increases) of the UV-visible λ_{max} of a new class of dyes, the (α-perfluoroheptyl-β,β-dicyanovinyl)aminostyrenes [2]. This new measure of polarity, which is defined as the Spectral Polarity Index, P_s, appears to be particularly useful in characterizing nonpolar solvents such as perfluorocarbons.

INTRODUCTION

Several criteria have been used to describe the polarity of a solvent: for example, dielectric constant, dipole moment, and the ability to dissolve polar or nonpolar solutes. However, these criteria appear to be inadequate in describing the ability of a solvent to solvate or complex with a solute, reactive intermediate, or transition state, and therefore do not always correlate well with the ability of a solvent to increase or retard the rate of a chemical reaction. For these reasons, a number of empirical polarity scales have been derived, based on kinetic [3] and equilibrium [4] measurements of solvent-sensitive reactions, and on the gas-liquid partition coefficients of various solutes [5]. While these polarity scales can be very useful, they all require an extensive amount of experimental work to obtain each value, and are usually limited in the types of solvents that can be classified. In particular, they are not suitable for measuring the polarities of the very nonpolar fluorocarbon solvents.

A possible way to overcome this experimental difficulty is to relate spectroscopic parameters of solvent-sensitive compounds to solvent polarity. This approach has been taken by a number of investigators [6]. The most comprehensive study of this nature to date utilizes the negative solvatochromic properties (hypsochromic shift as solvent polarity increases) of two pyridinium-*N*-phenoxide betaine dyes [6,7,8]. However, these polar (charged) dyes are not

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soluble in very non-polar solvents such as perfluorocarbons; therefore, the polarity of these solvents cannot be determined by direct measurements. Our goal was to develop a simple method of determining the relative polarity of solvents (particularly, very nonpolar solvents such as fluorocarbons) based on UV-visible spectral observations of a dye that is soluble in a wide variety of solvents ranging from the very nonpolar perfluorocarbons to very polar solvents such as dimethyl sulfoxide.

DISCUSSION AND RESULTS

The λ_{max} of an uncharged dyes would be expected to exhibit a bathochromic shift as the polarity of the solvent is increased because the ground state of the dye would be solvated less than the more polar excited state. This shift in λ_{max}, which can be related to energy differences, could form the basis for defining a new polarity index, P_s (Spectral Polarity Index), which could be determined very easily for any solvent or mixed solvent system in which the dye is soluble, and could be useful in studying the kinetics and mechanisms of reactions. In addition, this new polarity index could better relate the poorly documented polarity of perfluorocarbons to that of hydrocarbons and other more polar solvents.

For a meaningful polarity index to be developed along these lines, it is necessary to find a dye of sufficient tinctorial strength that is soluble in a wide range of solvents, from the very non-polar to the very polar. Recently, we have prepared a series of dyes, the (α-perfluoroheptyl-β,β-dicyanovinyl)aminostyrenes [2], that appear to fulfill this criterion. These compounds, because of the perfluoroheptyl group that they contain, are soluble in perfluorocarbons, among the least polar compounds known, and are also soluble in very polar solvents such as DMSO, possibly because of the two cyano groups that they contain.

In order that the Spectral Polarity Index, P_s, be related to differences in solvation energy, we have defined it in the following manner: the P_s of a given solvent is equal to the difference in transition energy between the ground state and the excited state of the unsolvated dye molecule and the solvated dye molecule, expressed as a fraction of the transition energy of the unsolvated dye molecule times a scaling factor, N_{dye}. This can be stated mathematically as

$$P_s = \frac{h\nu_{unsol} - h\nu_{sol}}{h\nu_{unsol}} N_{dye} = \left(1 - \frac{\lambda_{unsol}}{\lambda_{sol}}\right) N_{dye}$$

where λ_{unsol} = the λ_{max} of the unsolvated dye, λ_{sol} = the λ_{max} of the solvated dye, and the scaling factor, N_{dye}., is a constant for each dye, and is defined as 10 times the λ_{max} of a DMSO solution of the dye divided by the difference of the λ_{max} of the DMSO solution and the λ_{max} of the unsolvated dye. This scaling factor, which can be formulated as

$$N_{dye} = 10\left(\frac{\lambda_{max}^{DMSO}}{\lambda_{max}^{DMSO} - \lambda_{max}^{unsol}}\right)$$

was chosen so that the very polar solvent, DMSO, would always have the value, $P_s = 10$.

Because it is not practical to measure the λ_{max} of unsolvated dyes, we have approximated this value by determining the λ_{max} of the dye in the least polar solvent in our study — perfluorohexane; this approximation defines $P_s = 0$ for perfluorohexane. Using these values, we have determined the value of the scaling factor, N_{dye}, for several α-perfluoroheptyl-β,β-dicyanovinyl)aminostyrenes and related dyes (see **TABLE I**). As can be seen from the table, the values for N_{dye} range from 78.1 for 1,8-*bis*-(*N,N*-dimethylamino)-4-(α-perfluoroheptyl-β,β-dicyanovinyl)naphthalene (**10**) to 147.5 for 1-(*N,N*-dimethylamino)-4-(α-perfluoroheptyl-β,β-dicyanovinyl)naphthalene (**11**).

P_s scales for solvents constructed by the use of each of the dyes in **TABLE I** (that are soluble in perfluorohexane) show that each scale has the same relative order of polarity for the solvents, but the absolute values of P_s for specific solvents differ. For example, the scale constructed from dye **4** shows $P_s = 8.01$ for acetone, whereas the scale constructed from dye **1** shows $P_s = 7.62$ for acetone (see TABLE I). Because of these differences, extensive measurements were obtained on only one of the dyes. The dye of choice was **4**, because this compound was crystalline, was easy to prepare in high yield and purity, had good solubility in all solvents examined, had one of the longest wave lengths of absorption, and possessed a low scaling factor, N_{dye}. The lower the scaling factor, the more sensitive the dye is to changes in solvent; greater accuracy in measurement is therefore possible.

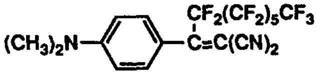
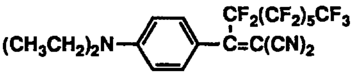
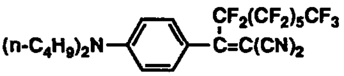
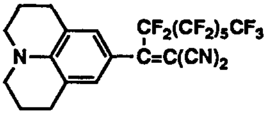
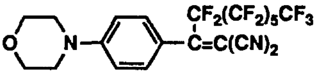
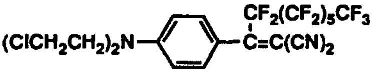
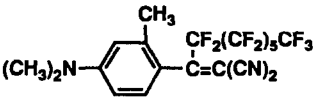
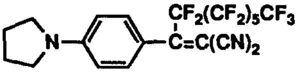
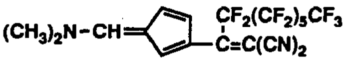
TABLE II contains a list of common solvents, and **TABLE III** a list of fluorine-containing solvents with their calculated Spectral Polarity Indices, P_s, obtained by using the dye, 9-(α-perfluoroheptyl-β,β-dicyanovinyl)julolidine (**4**).

Dye **4** was soluble in all solvents examined except water. An estimated value for water was obtained by determining the P_s values for various concentrations of aqueous solutions of acetone and 2-propanol, and extrapolating to find the value expected for pure water. Linear plots were obtained for acetone/water in the range of 0 to 60 % water, and for 2-propanol/water in the range of 20 to 60 % water (Fig. 1). In both cases, the extrapolated P_s value for water was determined to be 12.1. Aqueous solutions of ethanol, dimethylformamide, dimethyl sulfoxide, and dioxane did not give linear plots.

The intensity of the λ_{max} of **4** in anhydrous formic acid is very weak (λ_{max} 557 nm, ε = 177), indicating that most of the dye exists in a protonated form. When an equimolar amount of water is added to the formic acid solution of the dye, the intensity of the absorption greatly increases (λ_{max} 561 nm, ε = 6,090), indicating that a large percentage of the dye exists in an

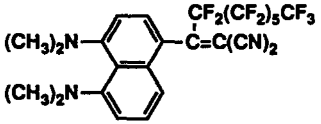
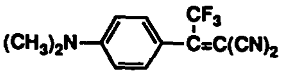
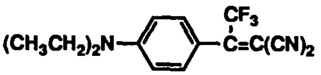
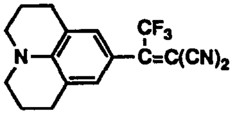
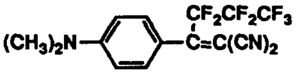
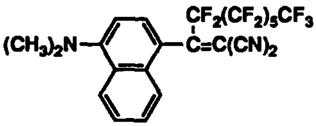
TABLE I

N_{dye} of α–Perfluoroalkyl-β,β–dicyanovinyl Dyes

Dyes		λ_{max}, nm			P_s	N_{dye}
No.	Structure	C_6F_{14}	Acetone	DMSO	Acetone	
1		450.5	493.0	508.0	7.62	88.3
2		464.5	503.5	517.5	7.56	97.6
3		469.2	508.0	519.8	7.85	102.7
4		490.4	541.7	556.2	8.01	84.5
5		419.0	445.0	463.5	6.09	104.2
6		414.5	467.0	480.0	8.24	73.3
7		447.5	488.4	499.4	8.06	96.2
8		463.0	495.0	506.0	7.61	117.7
9		452.6	487.8	489.4	9.60	133.0

(continued)

TABLE I (cont.)

Dyes		λ_{max}, nm			P_s	N_{dye}
No.	Structure	C_6F_{14}	Acetone	DMSO	Acetone	
10		490.0	546.5	562.0	8.07	78.1
11		---*	484.0	497.5	---*	---*
12		452.0	488.5	501.0	7.64	102.2
13		---*	536.0	541.5	---*	---*
14		448.5	490.0	504.0	7.69	90.8
15		438.5	465.0	470.5	8.38	147.0

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* Insoluble in perfluorohexane.

TABLE II

P_s Values* for Common Solvents

Solvent	λ_{max},nm	P_s	Solvent	λ_{max},nm	P_s
Pentane	504.8	2.41	Propyl Acetate	529.9	6.30
Tetramethylsilane (TMS)	505.0	2.44	Vinylidene Chloride	530	6.32
Hexane	505.7	2.56	Methyl Butyrate	531.1	6.48
2,2,4-Trimethylpentane	506.8	2.74	Propionic Acid	531.1	6.48
Heptane	507.0	2.77	*n*-Butyl Chloride	531.2	6.49
Octane	507.6	2.86	*o*-Xylene	531.5	6.54
Nonane	508.6	3.02	Toluene	531.8	6.58
Decane	509.0	3.09	Methyl Acetate	532.2	6.64
Undecane	509.4	3.15	Methyl Isobutyrate	532.3	6.65
Dodecane	509.7	3.20	*n*-Butyl Formate	532.7	6.71
1,3-Dimethylcyclohexane	510.4	3.31	Carbon Disulfide	533.4	6.81
Methylcyclohexane	510.6	3.34	1-Bromopentane	533.7	6.86
Tridecane	510.6	3.34	Ethylbenzene	533.8	6.87
Tetradecane	510.9	3.39	4-Methyl-2-pentanol	533.9	6.89
Pentadecane	511.0	3.41	Benzene	534.3	6.95
Hexadecane	511.4	3.47	Ethyl Acetate	534.4	6.96
Cyclohexane	511.5	3.49	Tetrahydrofuran	534.6	6.99
Heptadecane	511.5	3.49	Ethyl Formate	534.6	6.99
Tributylamine	514.3	3.93	Acetic Acid	534.9	7.03
Decalin	515.2	4.07	1,1,1-Trichloroethane	534.9	7.03
Cyclohexene	515.8	4.16	Chlorocyclohexane	535.6	7.13
Triethylamine	516.4	4.26	1-Bromopropane	536.6	7.28
Carbon Tetrachloride	518.9	4.64	2-Bromobutane	536.7	7.29
1,4-Dioxane	522.4	5.18	2-Bromopropane	537.1	7.35
Isopropyl Ether	523	5.27	Glyme	538.7	7.58
Ethyl Ether	526.3	5.77	1-Butanol	539.0	7.62
Butyric Acid	527.8	5.99	Pinacolone	539.6	7.71
Neopentyl Choride	527.8	5.99	1-Propanol	540.0	7.76
Ethyl Butryate	528.6	6.11	3-Methyl-2-butanone	540.5	7.84
p-Xylene	528.9	6.15	1,3-Dichlorobenzene	540.5	7.84
Isopropyl Acetate	529.1	6.18	2-Propanol	540.6	7.85
m-Xylene	529.7	6.27	Methyl Isobutyl Ketone	540.6	7.85

(continued)

TABLE II (cont.)

Solvent	λ_{max},nm	P_s	Solvent	λ_{max},nm	P_s
Glycerin	540.7	7.86	Trimethyl Phosphate	547.6	8.83
Propionitrile	541.0	7.91	1,2-Dichlorobenzene	548.4	8.94
2-Butanone	541.1	7.92	Methyl Salicyate	548.6	8.97
Chloroform	541.2	7.93	*N,N*-Dimethylformamide	550.4	9.21
3-Pentanone	541.2	7.93	Iodobenzene	550.4	9.21
2-Pentanone	541.3	7.95	*N,N*-Dimethylacetamide	550.5	9.23
Methanol	541.5	7.98	1,1,2,2-Tetrachloroethane	550.5	9.23
Acetone	541.7	8.01	Propylene Carbonate	551.4	9.35
Ethanol	542.0	8.05	1,2-Propanediol	551.6	9.38
Ethyl Benzoate	542.1	8.06	Benzonitrile	552.4	9.49
Diglyme	543.6	8.27	Nitromethane	552.5	9.50
Chlorobenzene	543.8	8.30	Acetophenone	552.6	9.51
Iodomethane	544.0	8.33	1-Methyl-2-pyrollidinone	553.8	9.68
Acetonitrile	544.5	8.40	Pyridine	555.6	9.92
Cyclohexanol	544.9	8.45	Diethylene Glycol	555.7	9.93
Methylene Chloride	545.0	8.47	Nitrobenzene	555.9	9.96
Bromobenzene	545.4	8.52	Triethylene Glycol	556.0	9.97
Cyclohexanone	545.5	8.54	Dimethyl Sulfoxide (DMSO)	556.2	10.00
Anisole	545.6	8.55	Formic Acid	557.1	10.12
1,2-Dichloroethane	546.0	8.61	1/1 molar Water-Formic Acid	561.0	10.64
Tetraethylene Glycol Dimethyl Ether	547.0	8.75	1,1,1,3,3,3-Hexafluoro-isopropanol	564.4	11.08
Allyl alcohol	547.6	8.83	Water	572.3[a]	12.10[a]

* Calculated from the λ_{max} of dye 4 in the indicated solvent. [a] Extrapolated value.

unprotonated form. Solutions of 4 in acids stronger than formic acid exhibit similar behavior. For example, the absorption of the unprotonated form of 4 in anhydrous trifluoroacetic acid was too weak to measure; a deep purple color devel-

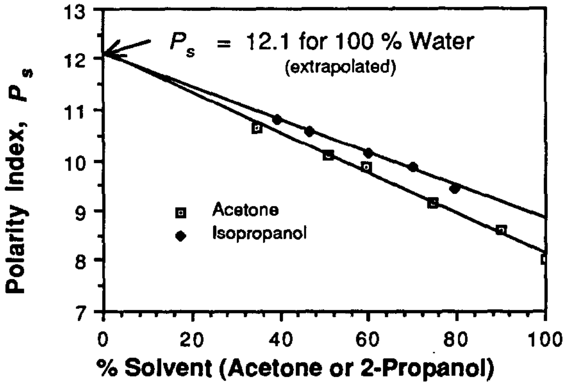

Fig. 1. **Acetone/Water and 2-Propanol/Water Mixtures.**

oped when water was added, but this color rapidly faded, presumably due to the hydration of the double bond of 4 in this strongly acidic media.

CONCLUSIONS

- Examination of TABLE II and TABLE III show that the organofluorine compounds are the most polar *and* the least polar organic compounds in these lists. The four least polar compounds are all polyfluorohydrocarbons, and the two most polar compounds are polyfluoroalcohols. This dichotomy of properties is not unusual for organofluorine compounds. For example, they are among the most reactive (*eg*, CF_3OF) and the least reactive (*eg*, CF_4), the most toxic (*eg*, perfluoroisobutylene) and the least toxic (*eg*, perfluorodecalin), of all organic compounds.

- The P_s scale is very useful for comparing the relative polarities of compounds normally considered nonpolar. The P_s scale appears to be greatly expanded in the nonpolar region, and greatly compressed in the polar region when compared to dielectric constant as a measure of polarity. For example, solvents less polar than benzene all have ε values for dielectric constant that are within one unit of each other, but have P_s values that range over almost 7 units. In contrast, solvents with polarities between benzene and propylene carbonate have ε values that range over 62 units, but have P_s values that lie within 0.7 of a unit of each other.

- In a relatively nonpolar homologous series, such as *n*-alkanes or perfluoro-*n*-alkanes, the P_s values increase as the size of the molecule increases. The same is also true to a lesser extent for the dielectric constant (see Fig. 2). These trends may show the effect of a greater degree of Van der Waals attractive forces present in the larger molecule because of their larger surface area (the same explanation given for their boiling points [9]).

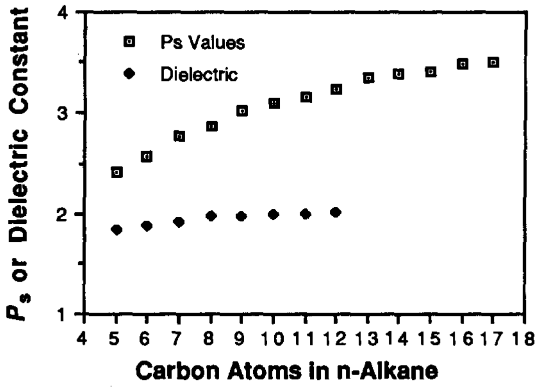

Fig. 2. Polarity of n-Alkanes.

- In every case, a perfluoro compound appears to be less polar than its fluorine-free ' normal ' analog (see Fig. 3). This is particularly true for nonpolar compounds, but is also true for polar compounds such as benzonitrile.

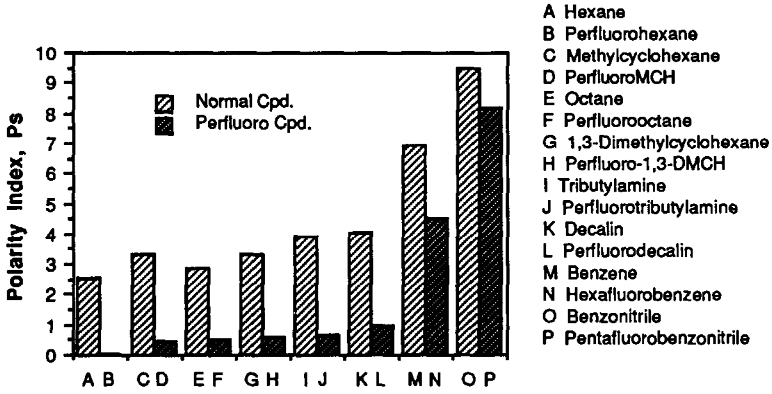

Fig. 3. Polarity (Ps) Comparison of Normal <u>vs</u> Perfluoro Compounds.

- The P_s scale correlates well with dipole moment when all other factors are equal (*eg*, the same number and kind of atoms and bonds). For example, *p*-xylene has the lowest P_s value and also the lowest dipole moment, while *o*-xylene has the highest P_s value and also the highest dipole moment of the three xylenes (Fig. 4). This correlation also holds true for the dichlorobenzenes (Fig. 4), and apparently for the difluorobenzenes (the dipole moment for 1,3-difluorobenzene was not found in the literature, but would be expected to be between that of 1,4- and 1,2-difluoro- benzene).

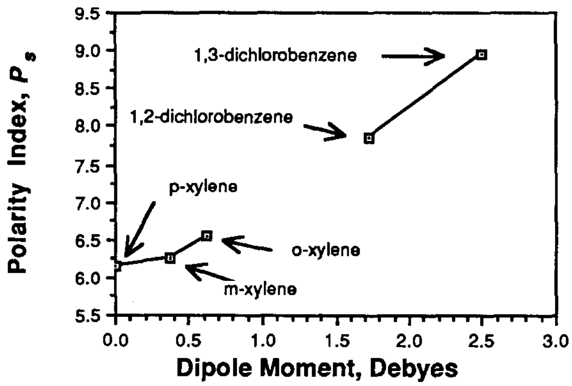

Fig. 4. Dipole Moment vs Polarity Index.

- Several factors influence the polarity of a solvent — dipoles, Van der Waals forces, ability to accept or donate hydrogen bonds and unbonded electron pairs, and polarizability. The P_s scale appears to be particularly sensitive to polarizability. This is evident in comparing the P_s values for the monohalobenzenes. The P_s values increase as the atomic weight of the halogen increases, with fluorobenzene having the lowest value and iodobenzene the highest. The previously devised spectral polarity scale based on betaine dyes, E_N^T, shows the opposite ordering, with fluorobenzene being the most polar and iodobenzene the least [6]. The dielectric constant shows little correlation with the nature of the halogen, with chlorobenzene having the highest value (TABLE IV).

TABLE III

P_s Values* for Fluorine-Containing Solvents

Solvent	λ_{max},nm	P_s	Solvent	λ_{max},nm	P_s
Perfluorohexane	490.4	0.00	Fluorotrichloromethane	513.0	3.72
Perfluoro(methylcyclohexane)	493.1	0.46	Hexafluorobenzene	518.2	4.53
Perfluorooctane	493.6	0.55	Ethyl Heptafluorobutyrate	523	5.27
Perfluoro-1,3,-Dimethyl-cyclohexane	493.8	0.58	1,4-Difluorobenzene	527.2	5.90
Perfluorotributylamine	494.4	0.68	Ethyl Trifluoroacetate	527.9	6.00
Mutltifluor™ 140 (avg. MW 468)	495.5	0.87	1,3-Bis(trifluoromethyl)benzene	528.1	6.03
Perfluorodecalin	496.2	0.99	1,3-Difluorobenzene	530.5	6.39
Multifluor™175 (avg. MW 570)	496.3	1.00	α,α,α-Trifluorotoluene	534.9	7.03
Multifluor™ 200 (avg. MW 620)	496.7	1.07	Fluorobenzene	538.3	7.52
Multifluor™ 215 (avg. MW 630)	497.0	1.12	2,2,2-Trifluoroethyl Trifluoroacetate	539.8	7.74
Perfluoro(tetradecahydro-phenanthrene	497.3	1.17	1,2-Difluorobenzene	540.7	7.86
Multifluor™ 240 (avg. MW 770)	497.5	1.21	Pentafluorobenzonitrile	543.1	8.20
HFP Trimer (C_9F_{18})~	498.5	1.37	1*H*,1*H*-Heptafluoro-1-butanol	554.4	9.76
HFP Dimer (C_6F_{12})^	501.1	1.80	1*H*,1*H*-Pentafluoro-1-propanol	556.5	10.0
1,1,2-Trichloro-1,2,2-trifluoro-ethane	509.8	3.22	2,2,2-Trifluoroethanol	558.2	10.2
1,2,4-Trifluorobenzene	511.0	3.41	1,1,1,3,3,3-Hexafluoro-isopropanol	564.4	11.08

* Calculated from the λ_{max} of dye 4 in the indicated solvent. ™ Multifluor is a Trademark of Air Products, Inc. These materials are saturated perfluorocarbons of the average molecular weight indicated. ~ Perfluoro(2,4-dimethyl-3-ethyl-2-pentene). ^ Perfluoro(2-methyl-2-pentene).

TABLE IV

Polarity of Halobenzenes

Halobenzenes	P_s Value	E_N^T Values	Dielectric
Fluorobenzene	7.52	0.194	5.42
Chlorobenzene	8.30	0.188	5.62
Bromobenzene	8.52	0.182	5.40
Iodobenzene	9.21	0.117	4.40

EXPERIMENTAL

All of the UV-visible spectra were obtained at ambient temperature (24 ± 1°) with a Hitachi model 200 uv/vis recording spectrophotometer. To obtain precise positions for λ_{max}, the spectrum was swept manually to give reproducibility of ± 0.1 nm. The spectral data obtained are listed in **TABLE I, TABLE II** and **TABLE III**. The fluorine containing solvents were obtained from PCR Inc., Gainesville, Florida, and from Air Products and Chemicals, Inc., Allentown, Pennsylvania. Spectrophotometric grade solvents were used when available; otherwise the highest purity solvent available was used. Nitrobenzene and diglyme were redistilled before use.

The (*α*-perfluoroheptyl-*β,β*-dicyanovinyl)aminostyrene dyes, including 9-(*α*-perfluoroheptyl-*β,β*-dicyanovinyl)julolidine (3), were prepared by the reaction of 1-perfluoroalkyl-1-chloro-2,2-dicyanoethylenes with aromatic amines, as described in an earlier paper [2]. The one new dye, **3**, used in this study was prepared by the following procedure:

4-(*N,N*-Dibutylamino)-*α*-(perfluoroheptyl)-*β,β*-dicyanostyrene (3)

A solution of 315 mg (1.5 mmol) of *N,N*-dibutylamine in 1.5 mL of dimethylformamide was added to a vial containing 721 mg (1.5 mmol) of 2-chloro-1,1-dicyano-2-(perfluoroheptyl)-ethylene [2], and the contents of the vial were throughly mixed. After a few minutes, an intense color developed. Fluorotrichloromethane, 50 mL, was added, and the resulting solution was thoroughly washed with water, dried ($MgSO_4$), and evaporated to dryness under reduced pressure to give 980 mg (100 %) of 3 as a purple oil, IR (neat) 2210 cm^{-1}. Anal. Calcd for $C_{25}H_{22}F_{15}N_3$: F, 43.88; N, 6.47. Found: F, 43.62; N, 6.40.

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