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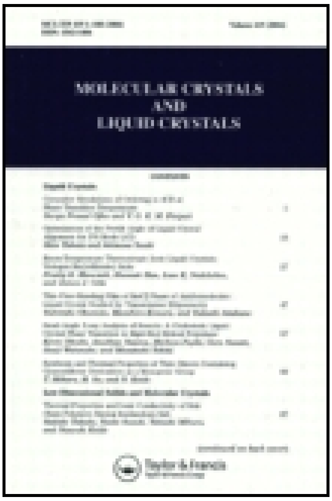

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Synthesis and Characterization of Some Azo-Anil Dyes

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SYNTHESIS AND CHARACTERIZATION OF SOME AZO-ANIL DYES

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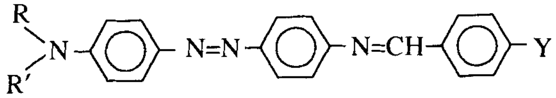
Abstract A number of azo-anil dyes of the type



with Y=CN or NO_2 and R,R′=Me, Me; Me,C_6H_{13}; Et,Pr and C_6H_{13},C_6,H_{13} were synthesized by reactions of the aminosubstituted nitrosoamine with phenylene diamine followed by condensation of the resulting aniline with the appropriate 4–substituted benzaldehyde. Mesomorphic properties were determined both by hot-stage polarizing microscopy and DSC. A nematic phase was observed only when R=R′=CH_3 while smectic A phases occurred in the other homologs. Melting temperatures were greater than 130°. All had colors ranging from red to orange with UV λ_{max} ranging from 448–459 nm and ϵ 2.20–3.67 E+4. The ΔH melting values ranged from 16.8 to 30.7 KJ/mole and solubilities in a BDH-E7 liquid crystal mixture were low.

INTRODUCTION

Pleochroic dyes have been used in nematic and cholesteric guest-host[1,2] type display systems to improve viewing angle, increase the image brightness by eliminating the polarizers and produce optically reversible surface alignment.[3] The development and wide use of guest-host liquid crystal (LC) displays are primarily dependent on the stability of the dye; its solubility and degree of order in the host liquid crystal mixture. Evaluation of the photostability of azo and anthraquinone dyes for display applications in the visible range[4] have shown that the monoazo- and bis azo-dyes are

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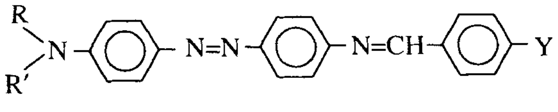
less stable than the anthraquinone dyes. The azo dyes, however, may be suitable for infrared (IR) or millimeter wave (MMW) applications where only the electrochemical and thermal stability issues need to be considered.

We have been exploring several methods for increasing the birefringence of the LC mixture in the IR and MMW range. The use of high birefringence liquid crystals should improve the performance of LC-MMW devices by increasing the phase shift per unit optical path length resulting in a larger modulation angle and a more compact device physical dimension. To obtain a larger effective LC-MMW birefringence, we used diacetylene backbone liquid crystals[5] with a longer π–electron conjugation length and selected LC dyes in LC hosts. Our preliminary results indicated that both liquid crystals with a longer conjugation length[6] and dye doped liquid crystals[7] contribute to higher birefringence values.

We now are seeking pleochroic dye materials having a nematic phase with a moderate melting temperature, a small heat of fusion enthalpy and a reasonable (+) dielectric anisotropy to include in the formulation of wide temperature range LC mixtures for low voltage IR or MMW phase modulation. Our goal is to design highly conjugated pleochroic LC dye structures such as anils, dianils and azo-anils, synthesize these, determine their mesomorphic properties, and then select the best candidates based on their solubility properties and order parameters for high birefringence eutectic LC mixture formulation. In this paper, we discuss the synthesis and properties of the azo-anil series *1*:



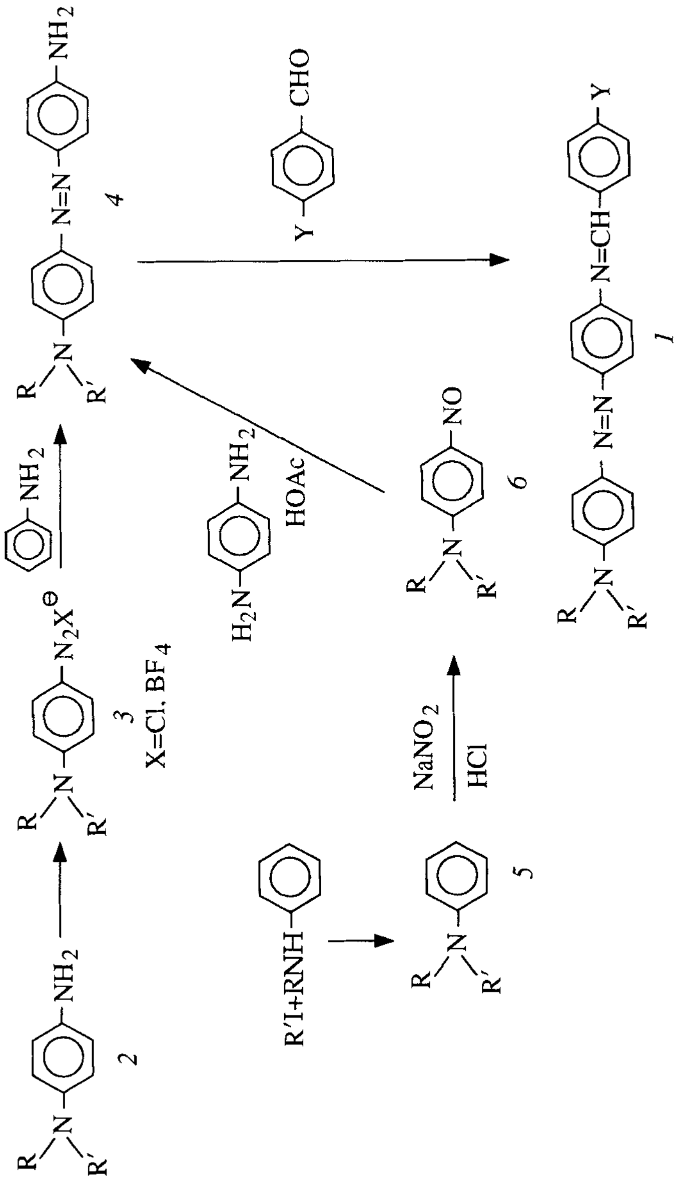
1 Y=CN or NO_2

SYNTHESIS

Such azo-anil compounds are not new; several were previously reported.[8,9] Since the reported syntheses involved reaction of the diazonium salt *3* with aniline to give the diamino-azo compound *4* followed by reaction with a 4–substituted aldehyde to give the azo-anil *1* (Scheme 1), this was our first approach to the synthesis of these compounds. We were, however, unable to achieve any appreciable coupling using the chlorodiazonium salt despite repeated attempts. Since this could be due to either the diazonium salt not being formed or that it had not coupled, the tetrafluroborate salt was synthesized since it could be isolated and characterized. However, this salt did not couple even with aniline. Only starting material was recovered. Apparently the electro-donating dialkylamino group increases the stability of the diazonium salt making it less reactive in a coupling reaction.

Considerably better results were obtained by converting the disubstituted aniline *5* to the nitroso compound *6*, reacting this with phenylenediamine to obtain the azo compound *4* and continuing this on to the azo-anil *1*. Yields ranged from 34.1–44.8% for the formation of the nitrosoamine, 39.5–44.1% for the azo coupling, and 73.6–82.6% for condensation with the aldehyde.

Problems were encountered in the synthesis of the disubstituted anilines *5* from either the monosubstituted anilines or aniline itself. Complete dialkylation was never achieved requiring separation of the di- from the mono-substituted aniline. Using an alkyl iodide gave a better yield than an alkyl bromide. Separation of the two anilines was accomplished by distillation at atmospheric pressure with the ease of separation depending on the difference between the boiling points of the two amines. Separation of the R-Et, R′=Pr from the R′=H aniline was particularly difficult since their boiling points were similar. Separation was achieved by two careful distillations through a Vigeraux column and sacrificing a mixed aniline fraction. In retrospect, separation would have probably been better achieved using the literature method of preparing the acetamide of the secondary amine and separating this from the tertiary amine.[10] Additionally, the dialkyl anilines seemed to be more unstable on exposure to air than the monoalkylated anilines requiring that the purification and subsequent reaction be done as quickly as possible. Otherwise, impurities that were difficult to separate were found in the product *4* from the next reaction.


R
R′
N
NH2
2
N2X⊖
3
X=Cl, BF4
N=N
4
Y
CHO
N=CH
1
R′I+RNH
5
NaNO2
HCl
NO
6
H2N
HOAc

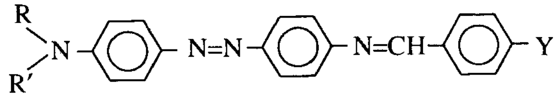
Scheme 1

All compounds synthesized were purified using the standard methods of recrystallization, distillation and flash chromatography until they showed only one spot on TLC, sharp melting temperatures and NMR spectra indicated the absence of any impurities.

PROPERTIES

Transition temperatures determined by hot stage polarizing optical microscopy for the azo-anils synthesized are given in Table I. A nematic phase was observed only when R=R′=Me while the other homologs showing only smectic A phases. Two chains longer than a methyl group but of nearly similar chain lengths (R=Et, R′=Pr) gave lower transition temperatures and a wide range smectic A phase. A long and a short chain (R=Me, R′=C_6H_{13}) gave a smectic A phase with nearly twice the phase range

Table I
Transition Temperatures (°) for



Dye No.	R	R′	Y	K[a]	A	N	I
1	CH_3	CH_3	CN	216.2		248.0-250.7[b]	>300°
2	C_2H_5	C_3H_7	CN	158.0	177.7-178.7		233.5-235.3
3	C_2H_5	C_3H_7	NO_2	161.7	179.8-180.5		238.5-240.1
4	CH_3	C_6H_{13}	CN	110.1	140.1-142.0		247.2-248.2
5	C_6H_{13}	C_6H_{13}	CN	119.8	(123.0-124.7)		133.0-133.6

a. K=crystallization temperature obtained by cooling the melt 2°/min, A=smectic A phase, N=nematic phase, I=isotropic liquid. Data were determined by hot stage optical microscopy.

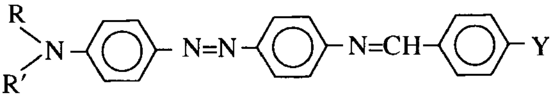
b. Previously reported (ref. 9) values 88.5° (C-N), 129° (N-I). Our sample melted to what appeared to be a nematic phase with a clearing temperature >300°, the limit of our equipment.

(106.2° versus 56.6°) but two long chains ($R=R'=C_6H_{13}$) gave the lowest transition temperatures and only a monotropic smectic A phase. Transition temperatures for the nitro compound were similar to those for the analogous cyano compound.

Absorption maxima (λ_{max}), bandwidth at half height (FWHM) and extinction coefficients (ϵ) are summarized in Table II. The absorption wavelength appeared to be dominated by the conjugated core showing only small shifts with changes in alkyl chain lengths. The largest shift to longer wavelength occurred on going from the R=R′=Me to the R=Et, R′=Pr compound. A comparison of the absorption data for the azo-anils with Y=CN and NO_2 showed only a small increase in the extinction coefficient for the nitro dye (Fig. 1). The observed increase in the λ_{max} for the nitro compound is within the accuracy of the measurement.

Table II

Absorption Properties in Acetonitrile for



Dye No.	λ_{max} (nm)	FWHM (nm)	ϵ	color
1	448	108	3.20E+4	burnt orange
2	460		2.22E+4	orange
3	463	105	3.39E+4	bronze
4	459	106	3.26E+4	orange
5	462	110	3.67E+4	red

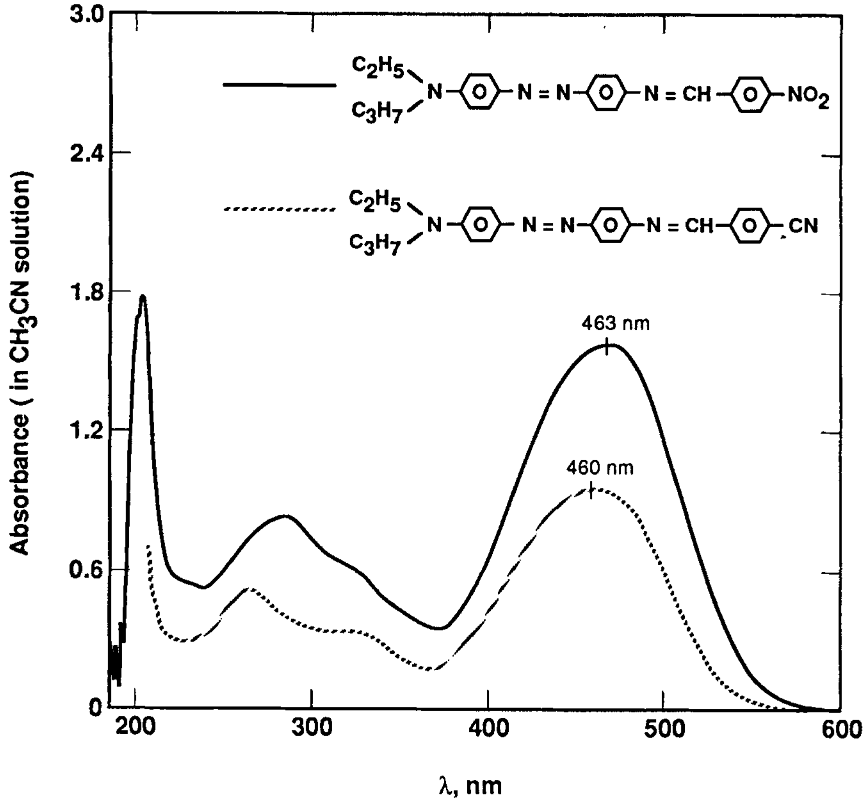


Figure 1. A Comparison of Absorption Spectra for the Azo Anils with Y = CN and NO_2.

The solubility of these dyes were determined by dissolving each candidate, at an elevated temperature, in a BDH-E7 liquid crystal mixture having a positive dielectric anisotropy. These dye-LC mixtures were checked for dye precipitation after cooling to room temperature. Since the solubility characteristics of LC-dyes and eutectic mixture formation are governed by their melting temperature and heat of fusion enthalpy, these were measured by DSC at a heating rate of 5°/min. These DSC scans also provided confirmation of the transition temperatures determined by microscopy. The observed ΔH values are given in Table III. A combination of very high melting temperatures

Table III
DSC Data (Heating Rate 5°/min) and Azo-anil Dye Solubility in BDH-E7 Liquid Crystal Mixture

	melting		clearing		solubility	calculated eutectic
Dye No.	temp (°C)	ΔH[a]	temp (°C)	ΔH	in E7(%)	in E7(%)
1	258.5°	29.7			2.5	
2	180.3	16.8	240.2	7.1	3.9<S<4.8	6.6
3	161.6[b]	7.06	246.8	7.9	<4.8	2.1
	180.7	23.6				
4	142.1	19.0	252.3	5.4	>5.6	7.4
	158.8[c]	1.6				
5	91.8[b]	2.7			5.2-5.5	
	132.4	25.7				
5+BDH-D2[d]					4.3+2.7	

a. ΔH in kj/mole.

b. These compounds showed crystal-to-crystal changes below the melting transition.

c. The observance of this peak only on heating indicated this is due to a crystal-to-crystal change.

d. Commercially available BDH-D2 azo dye has the structure $C_6H_5N{=}N{-}C_6H_4N{=}N{-}C_6H_4\ NMe_2$.

and moderate heat of fusion enthalpies (in the range of 16–30 KJ or 4–7 kcal/mole) resulted in very low dye solubilities in the cyanobiphenyl LC mixture (Table III and Fig. 2). According to the well-known Schroeder-van Laar relationship used for eutectic LC mixture calculations,[11] the mole fraction of each component in the eutectic is dependent on its crystal to nematic melting temperature and its molar heat of fusion. The calculated eutectic composition of BDH-E7 with dyes nos. 2,3 and 4 listed in Table III are similar to the experimentally obtained solubility values. From the measured solubility of these dyes in the BDH-E7 liquid crystal mixture, it is estimated that a melting temperature of 83–52°C would be required to obtain a desired 10–15% solubility, respectively.

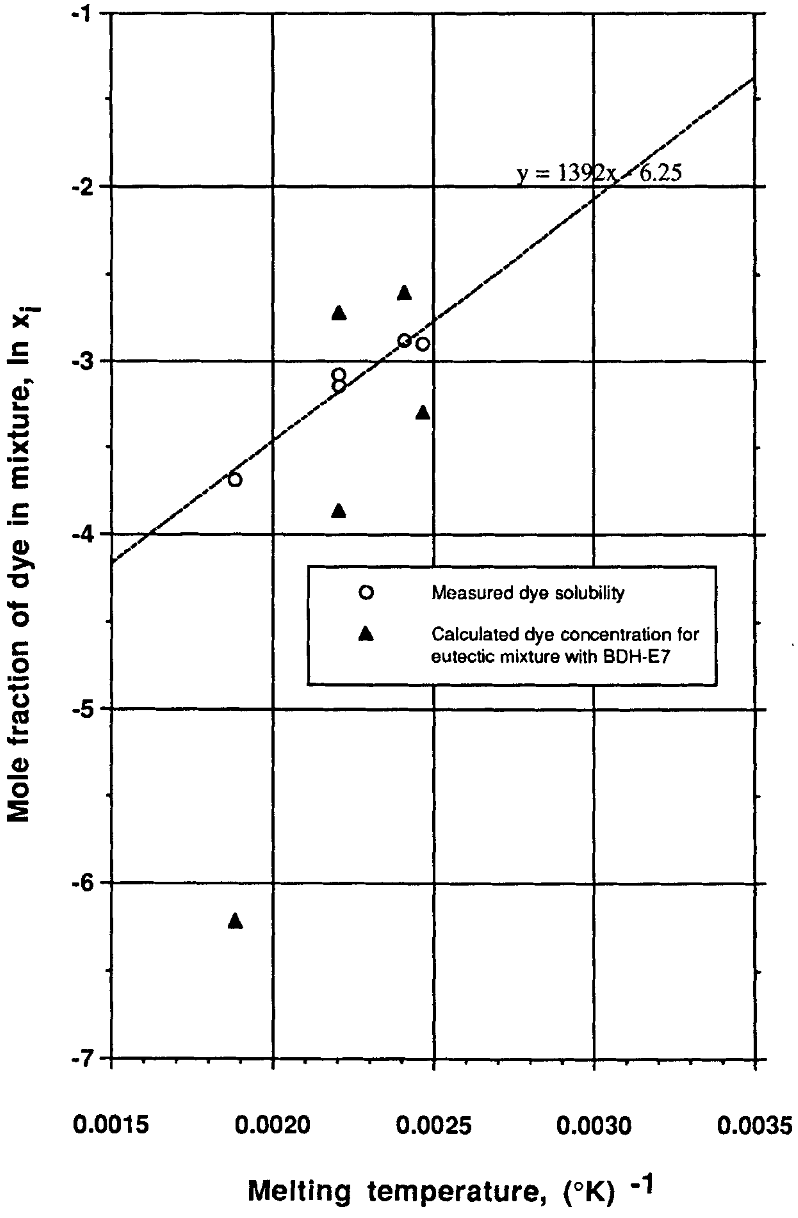


Figure 2. Azo Anil Dyes Solubility in BDH-E7 LC Mixture.

CONCLUSIONS

Several azo-anils of the type *1* were synthesized. Most of these showed wide range enantiotropic smectic A phases. Two long chains on the amino group decreased the transition temperatures but also gave poor mesomorphic properties as shown by the presence of only a monotropic smectic A phase. However, the high melting temperatures combined with moderate enthalpies of fusion gave too low of solubilities in BDH-E7 LC mixtures for these dyes to be useful in IR or MMW applications.

EXPERIMENTAL

The N-alkylanilines and N,N-dimethyl-4–nitroso aniline were purchased from Aldrich Chemical Co. and used without further purification. The BDH-E7 liquid crystal is a mixture of 4′–alkyl-4–cyanobiphenyls obtained from EM Industries, Inc.

TLC data were collected from Anal-Tech silica gel GHLF Uniplates using $CHCl_3$ as the solvent and UV light and I_2 as the detectors. Flash chromatography was done on E. Merck or Mallinchrodt silica gel (230–400 mesh) under N_2 (10–15 psi).[12] IR spectra were obtained using a Nicolet Magna FT-IR Spectrometer 550 and ^1H NMR spectra were run in $CDCl_3$ with TMS as the internal standard using a Varian Gemini 200 MHz instrument.

Transition temperatures (°C) in Table I and mesophase identification were determined using a Leitz-Laborlux 12 POL polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min as previously described.[13] Temperatures for the monotropic phase (one that occurs below the melting temperature) were obtained by reheating this phase immediately before crystallization occurred to obtain the more accurate heating temperature. Samples were cooled at 2°/min until they crystallized so that no monotropic phases before this temperature were missed. The textures observed were typical of those previously reported for the nematic and smectic A phases.[14]

DSC scans were run using a Mettler differential scanning calorimeter and a heating rate of 5°C/min. Data from these scans are given in Table II. Dye absorptions were measured using a Perkin-Elmer Lambda 9 spectrophotometer with spectral grade acetonitrile as both a reference and solvent in 1cm path length cells.

N,N-Dialkylanilines, *5*

The anilines with R=R′ were prepared by alkylating aniline with 2 equiv of alkyl bromide whereas those with R $\neq$ R′ were synthesized by alkylating the shorter chain alkylaniline with the longer chain alkyl bromide or iodide. Since the nitroso aniline for R=R′=Me was commercially available, it was not necessary to prepare this aniline. A general alkylation procedure is described here.

To a stirred solution of the alkylaniline (0.60 mole) in 384 ml of DMF was added dropwise the alkyl bromide (0.66 mole). The reaction mixture was refluxed for 17 hr, cooled to RT, poured into an equal volume of H_2O and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over anhyd Na_2SO_4, filtered and the filtrate rotovaped to give the crude product. Purification either by two careful consecutive vacuum distillations or flash chromatography on silica gel (hexane-CH_2Cl_2) gave the dialkylaniline *5* (R=CH_3, R′=C_6H_{13}): 41.2%* b.p. 90° (0.7 mm) lit[15] b.p. 94–98° (0.3 mm) TLC (1:1 hexane, CH_2Cl_2) R_f=0.88 (R_f for starting material=0.62); IR (film) 1600 (str Ar), 1580 (wk Ar and 1509 cm^{-1} (str Ar) and no NH and ^1H NMR ($CDCl_3$) for R=CH_3, R′=C_6H_{13}: δ7.29, 7.25 (dd, 2, J=7.00, 7.08 Hz, ArH meta to NRR′), 6.73 (d, 2, J=8.9 Hz, ArH ortho to NRR′), 6.67 (t, 1, J=8.0 Hz, ArH para to NRR′), 3.34 (t, 2, J=7.51 Hz, NCH_2), 2.96 (s, 3, NMe), 1.61 (quint, 2, J=5.70 Hz, $NCH_2\underline{CH_2}$), 1.52–1.25 (m, 6, $3CH_2$) and 0.94 (t, 3, J=6.41 Hz, CH_3).

R=C_2H_5, R′=C_3H_7 b.p. 65° (0.4 mm) lit[10] b.p. 111° (13 mm); NMR indicated this material contained some impurity.

R=R′=C_6H_{13} purified by chromatography.

These anilines tended to darken quickly showing impurities by TLC. Best results in the next reaction were achieved when they were used immediately.

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[*] A yield of 82.1% was obtained during the first distillation. We feel the yield on the second distillation was low due to formation of impurities on standing for 48 hr. Immediate distillation at atmospheric pressure would probably give a higher yield.

N,N-Dialkyl-4-nitroso anilines, *6*

To a stirred solution of the aniline *5* (0.07 mole) in 50% HCl (140 ml) at 0°C was added dropwise a solution of $NaNO_2$ (0.14 mole). After stirring for 30 min, the reaction mixture was made basic by the addition of 5% aq KOH. The resulting oil was extracted unto Et_2O (3×) washed with H_2O, dried over anhyd Na_2SO_4, filtered and the filtrate rotovaped to give the crude product. Purification by flash chromatography on silica gel using CH_2Cl_2 as the eluate solvent gave the purified nitroso amine *6* (34.1–44.8%) that was easily detected on the column by a change in color of the eluate from orange to green. $\underline{R=CH_3, R'=C_6H_{13}}$: TLC ($CH_2Cl_2$) $R_f=0.11$; IR (film) 1610, 1530 (str, Ar) and 1555 cm^{-1} (wk, NO) and ^1H NMR ($CDCl_3$) δ6.,62 (d, 2, J=7.49 Hz, ArH ortho to NRR′), 3.40 (t, 4, J=7.84 Hz, NCH_2), 1.80–1.55 (m, 4, $NCH_2\underline{CH_2}$), 1.50–1.20 (m, 12, $3CH_2$) and 0.91 (t, 6, J=6.06 Hz, $2CH_3$). We were unable to obtain a peak for the protons ortho to the nitroso group in either the nitroso amines synthesized or in the commercially available R=R′=Me even when the relaxation time was increased to 10 sec and the aromatic region was expanded. Aldrich's NMR spectrum show a broad doublet at 7.8δ.[16]

4–Amino-4′–(N,N-dialkylamino)azobenzene, *4*

A mixture of the nitroso amine *6* (5.86 mole), 4–phenylenediamine (5.86 mmole) in benzene (60 ml) containing glac HOAc (0.5 ml) was refluxed for 35–48 hr using a Dean-Stark trap. The reaction mixture was cooled to RT, filtered and the filtrate rotovaped to give the crude product (54–94%). This material was purified by flash chromatography on silica gel. Elution with CH_2Cl_2 gave first a red oil with $R_f=0.96$ (21.2–34.8% of the total material isolated) followed by the azo compound *4* as a red-orange liquid (39.5–44.1%): TLC (CH_2Cl_2) $R_f=0.49$; IR (film) 3461, 3373, 3215 (wk, NH_2) and 1598 cm^{-1} (str, Ar) and ^1H NMR for R=Me, $R'=C_6H_{13}$: δ7.80 (d, 2, J=8.46 Hz, ArH meta to NH_2), 7.72 (d, 2, J=8.58 Hz, ArH meta to NRR′), 6.74 (d, 2, J=8.06 Hz, ArH ortho to NRR′), 6.72 (d, 2, J=8.79 Hz, ArH ortho to NH_2), 3.91 (s, 2, NH_2), 3.39 (t, 2, J=7.32 Hz, NCH_2), 3.03 (s, 3, CH_3), 1.70–1.50 (m, 2, $NCH_2\underline{CH_2}$), 1.40–1.20 (m, 6, $3CH_2$) and 0.90 (t, 3, J=0.90 Hz, CH_3).

R=R′=Me crystallized mp 186–188° (lit[17] mp 191–191.3°); R=Et, R′=Pr also crystallized after standing at RT for a long time but was not recrystallized.

4″–Cyanobenzylidene-4′–(N,N-dialkylamino)-4–aminoazobenzene, *1* (Y=CN)

A mixture of the aniline *4* (2.2 mmol) and 4–cyanobenzaldehyde (2.5 mmol) in abs EtOH (35 ml) containing Linde molecular sieves #4A (250 mg) was refluxed for 4 hr. The reaction mixture was cooled to RT, filtered, the insoluble material washed thoroughly with CH_2Cl_2 and the filtrate rotovaped to give the crude product (~90%). Recrystallization of this material from abs EtOH gave the highly colored dyes *1* (73.6–82.6%): transition temperatures are given in Table I: IR 2218 (wk, CN) and 1605 cm^{-1} (med, Ar); ^1H NMR ($CDCl_3$)* for R=CH_3, R′=C_6H_{13}: δ8.56 (s, 1, CH), 8.04 (d, 2, J=8.42 Hz, ArH ortho to CH), 7.91 (d, 2, J=8.62, ArH meta to N=CH), 7.85 (d, 2, J=9.07 Hz, ArH meta to NRR′), 7.77 (d, 2, J=8.22 Hz, ArH ortho to CN), 7.35 (d, 2, J=8.67 Hz, ArH ortho to N=CH), 6.74 (d, 2, J=9.16 Hz, ArH ortho to NRR′), 3.42 (t, 2, J=7.51 Hz, NCH_2), 3.07 (s, 3, NMe), 1.80–1.50 (m, 2, $NCH_2\underline{CH_2}$), 1.50–1.20 (m, 6, $3CH_2$ and 0.90 (t, 3, J=6.43 Hz, CH_3) and ^{13}C NMR ($CDCl_3$) δ157.55, 152.06, 151.49, 151.32, 143.34, 139.86, 132.48, 129.12, 125.15, 123.23, 121.69, 118.43, 114.32, 111.20, 52.63, 38.56, 31.63, 26.90, 26.71, 22.60 and 14.00. These ^{13}C chemical shifts agree within 6.1δ with those calculated using a Softshell ^{13}C NMR Module.

The azo-anil with Y=NO_2 and R=Et, R′=Pr was prepared in the same manner. Yield=65.5%. NMR ($CDCl_3$: δ8.62 (s, 1, CH), 8.34 (d, 2, J=8.75 Hz, ArH ortho to CH), 8.10 (d, 2, J=8.79 Hz, ArH ortho to NO_2), 7.91 (d, 2, J=8.71 Hz, ArH meta to N=CH), 7.86 (d, 2, J=9.52 Hz, ArH meta to NRR′), 7.37 (d, 2, J=8.71 Hz, ArH ortho to N=CH), 6.72 (d, 2, J=9.08 Hz, ArH ortho to NRR′), 3.48 (q, 2, J=7.04 Hz, $N\underline{CH_2}CH_3$), 3.34 (t, 2, J=6.10 Hz, NCH_2), 1.80–1.60 (m, 2, CH_2), 1.23 (t, 3, J=7.04 Hz, $CH_2\underline{CH_3}$) and 0.98 (t, 3, J=7.24 Hz, $(CH_2)_2\underline{CH_3}$).

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* Proton assignments were confirmed by 2D-NMR.

ACKNOWLEDGMENTS

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