Diazo liquid crystals for potential infrared applications

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Nine series of liquid crystals containing an electron-donating group at one end of a conjugated system and an electron-withdrawing group at the other end have been synthesized. The electron-donating group is 4-*n*-alkylpiperazine and the electron-withdrawing group is the nitro group; and the conjugated system is diphenyldiazene with zero, one or two substituents on the phenyl ring not containing the nitro group. The substituents are −F, −Cl, and −CH₃. Most of the compounds synthesized are nematogenic and exhibit rather broad liquid crystalline ranges. The effects of the lateral substituents on the optical absorption and phase transition temperatures are correlated with their nature and position of substitution. Dielectric anisotropy and birefringence measurements were made using mixtures containing 10 wt % of synthesized liquid crystals dissolved in commercial mixture E7.

1. Introduction

At present, liquid crystal displays (LCDs) are designed mainly for application in the visible region of the spectrum. However, some special operations require electro-optic devices specially designed to function in the IR for electronic sensing and communication. Although electro-mechanical IR modulators have been proven to be successful [1], LCDs operated in the near- and mid-IR ranges are a more desirable technological option because they have such advantages as small size and weight, low operating voltage and low power consumption. Commercial liquid crystals have been used to fabricate IR LCDs [2–6], but they suffer from such problems as insufficient birefringence (Δn) and high optical loss, because they are designed to be used in the visible range. Therefore, liquid crystals specially designed for use in the IR and with high dielectric anisotropy and birefringence need to be synthesized to overcome these problems.

Compounds with electron-donating and electron-withdrawing (push–pull) groups separated by a conjugated system, such as *N*,*N*-dimethyl-4-nitroaniline, are often used in non-linear optics applications. They have large molecular dipole moments, which result in optical absorption tailing into the near-IR region, high birefringence and large dielectric anisotropy ($\Delta \varepsilon$). Liquid crystal dyes bearing push–pull groups have been synthesized in this laboratory [7–9]; they exhibit high dielectric anisotropy and large birefringence which extends further into the IR than commercial liquid crystal mixtures.

However, their usage is limited to guest–host display since they are monotropic and have only narrow nematic ranges. Lengthening the mesogenic cores normally results in better liquid crystalline properties, and the introduction of lateral substituents can overcome the accompanying problem of an undesirable increase in the melting point [10–12]. Some four-ring nematic liquid crystals with a lateral alkoxy branch have been synthesized [13], and they have wide nematic ranges. Unfortunately, when used in guest–host display devices, they behaved differently from liquid crystal hosts, the reason for which is most likely the presence of the lateral alkoxy chain.

In this paper, we present the synthesis and mesomorphic properties of some new liquid crystalline compounds containing three rings with relatively small lateral substituents such as fluoro, chloro and methyl groups on the central phenyl ring. The core of these compounds bears an electron-withdrawing nitro group at one end and an electron-donating group in the form of a piperazine ring at the other. The properties of these compounds are compared with those of the parent (non-substituted) liquid crystals.

2. Results and discussion

Nine series of liquid crystals carrying push–pull groups were synthesized and studied in this work. Six of the series were synthesized using scheme 1, and the three others using scheme 2. For each series, four compounds having 5–8 carbon atoms in the alkyl chain were made.

The phase transition temperatures were determined with a Perkin Elmer DSC7 differential scanning calorimeter and the nature of the phases was examined

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Scheme 1.

Series a: X_1 = H, X_2 = H; Series b: X_1 = H, X_2 = F;
Series c: X_1 = H, X_2 = CH$_3$; Series d: X_1 = H, X_2= Cl;
Series e: X_1 = CH$_3$, X_2 = H; Series f: X_1 = F, X_2 =F.

Scheme 2.

Series a: X_1 = F, X_3 = F; Series b: X_1 = F, X_3 = H; Series c: X_1 = Cl, X_3 = H.
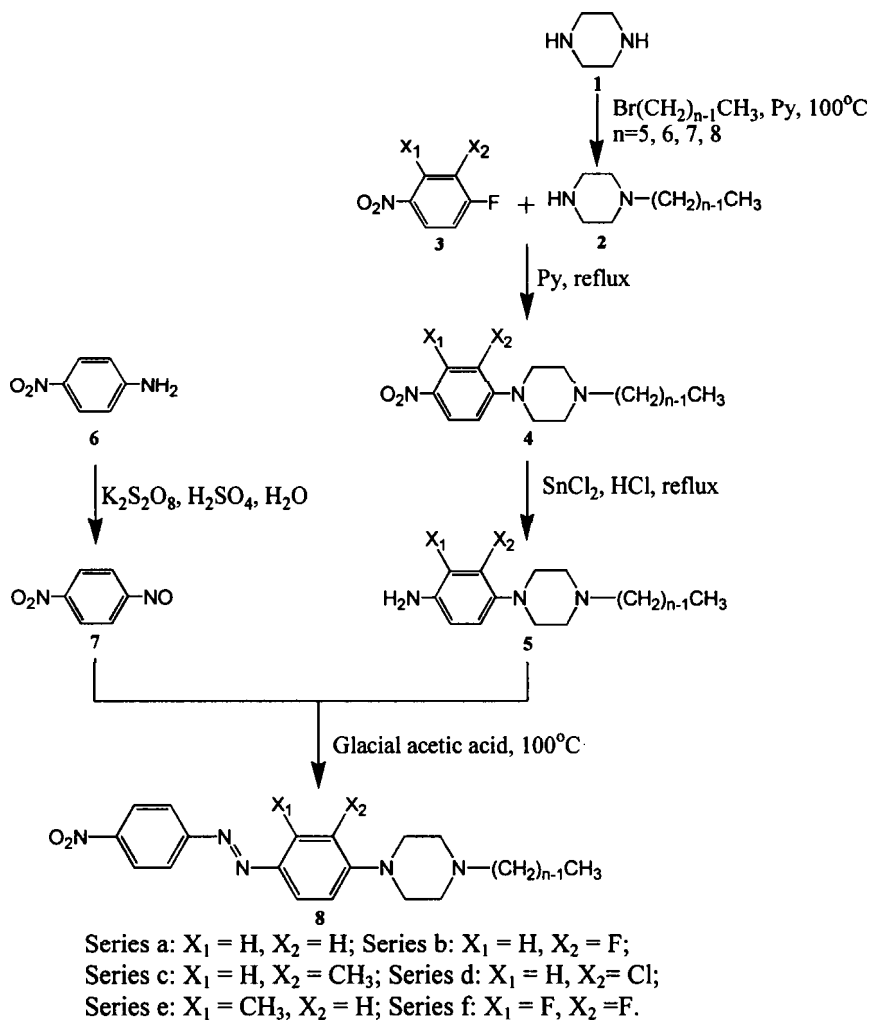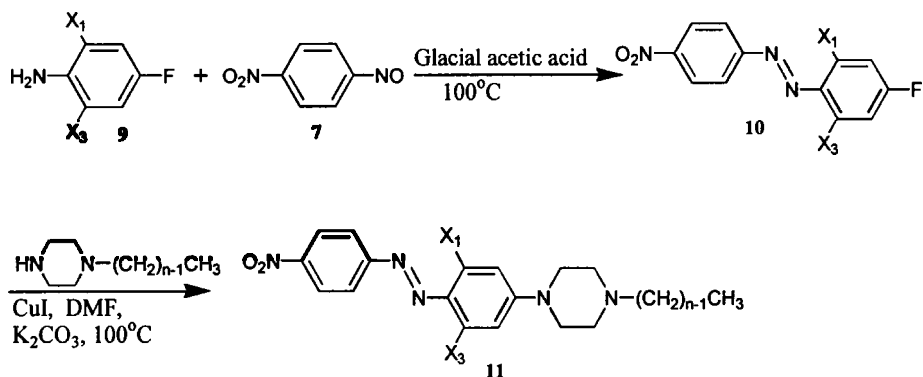
with an Olympus BH-2 polarized optical microscope. The results are summarized in table 1. As expected, the presence of lateral substituents depresses the melting and the clearing points of all the liquid crystals, because lateral substitution interferes with the packing of molecules in the crystalline and liquid crystalline phases. The position of substitution is important in affecting the phase transition temperature. When the substituents are *ortho*

Table 1. Phase transition temperatures for all the synthesized liquid crystals.

Compound	X_1	X_2	X_3	n	Cr	Sm	N	I
8a	H	H	H	5		—	148.2	194.8
				6		—	147.5	227.0
				7		—	145.1	230.9
				8		—	128.4	229.2
8b	H	F	H	5		—	98.6	194.2
				6		—	81.2	183.0
				7		—	91.9	180.7
				8	93.0	168.8		184.7
8d	H	Cl	H	5		—	91.3	154.4
				6		—	76.9	146.7
				7		—	74.0	148.6
				8		—	57.6	135.1
8c	H	CH_3	H	5		—	117.0	165.8
				6		—	86.7	154.9
				7		—	83.8	151.0
				8		—	87.7	149.0
11b	F	H	H	5	103.2	131.8		190.3
				6	82.9	154.4		184.2
				7	88.4	164.7		181.0
				8	81.8	175.8		181.2
11c	Cl	H	H	5		—	91.5	139.8
				6		—	84.2	127.5
				7		—	93.0	120.7
				8		—	77.7	128.3
8e	CH_3	H	H	5		—	124.5	146.8
				6		—	108.0	146.3
				7		—	102.3	131.2
				8		—	109.8	132.6
8f	F	F	H	5		—	132.9	191.6
				6	107.8	143.6		184.6
				7	127.5	173.3		181.0
				8	107.2	164.1		178.0
11a	F	H	F	5		—	115.2	175.2
				6	101.9	133.0		170.4
				7	100.2	153.1		175.9
				8	100.2	164.8		175.4

to the piperazine ring, the liquid crystals have lower melting points but higher clearing points (i.e. a broader LC range) than the corresponding *meta*-substituted liquid crystals. For substituents on the same position, the extent of melting point depression (compared with the non-substituted compound, **8a**) is Cl > CH_3 > F, while the extent of clearing point depression is CH_3 > Cl > F. Melting points are mainly determined by the packing of molecules as well as intermolecular interactions in the solid lattice; therefore, the melting point depression is a combinative effect of polar and steric factors. On the other hand, in the liquid crystalline phase, the steric interference plays a more important role in determining clearing points of these compounds.

As usual, the presence of one or two fluorine atoms favours the smectic A phase (table 1). When a second fluorine atom is introduced onto the aromatic ring, both the polar interaction between molecules and the steric crowding increase. Therefore, for the homologous series

8f and **11a** the melting points of the liquid crystals increase and the clearing points decrease in comparison with those for **11b**.

The optical absorption of the nine series of compounds was measured with a Shimadzu UV-160 UV-Visible spectrophotometer, using dimethyl sulphoxide as solvent. The λ_{max} values are listed in table 2. The data show that the substituents have considerable effect on the optical absorption of the liquid crystals. When they are located *meta* to the piperazine ring, the values of λ_{max} increase compared with the parent liquid crystals (**8a**) and the bathochromic effect is CH_3 > Cl > F. When the substituents are situated *ortho* to the piperazine ring, the values of λ_{max} decrease and the hypsochromic effect is CH_3 < Cl < F.

These results can be explained as follows. Because the piperazine ring prefers a chair conformation, the nitrogen atom directly bonded onto the phenyl ring cannot adopt sp^2 hybridization, but the conjugative stabilization

Table 2. λ_{max} values for the synthesized liquid crystals.

Compound	X_1	X_2	X_3	λ_{max}/nm
8a	H	H	H	480
8e	CH$_3$	H	H	493
11c	Cl	H	H	483
11b	F	H	H	482
8c	H	CH$_3$	H	406
8d	H	Cl	H	418
8b	H	F	H	435
8f	F	F	H	438
11a	F	H	F	444

will force the ring to adopt a certain conformation to allow partial overlapping of the lone pair on the nitrogen atom with the π electrons on the phenyl ring. The presence of a lateral substituent on the *ortho*-position (**8c**, **8d** and **8b**) would invoke strong steric interactions between the substituent and the piperazine ring, which would force the ring to rotate around the N–C bond connecting the piperazine ring to the phenyl ring, to relieve the steric repulsion. This would diminish the conjugation of the system, causing a broadening of the energy gap between n and π* orbitals and result in an increase of the n → π* excitation energy. An increase in the size of the substituent would increase the magnitude of steric interaction, so the hypsochromic effect shows the trend CH$_3$ > Cl > F.

When the substituents are neighbouring the azo linkage (*meta* to the piperazine ring; **8e**, **11c**, and **11b**), an opposite trend is observed. The steric interaction may force the 4-nitrophenyldiazene moiety to rotate away from the coplanar conformation with respect to the central phenyl ring. Quantum mechanical calculations by Forber [14] *et al.* showed that there is a strong antibonding interaction between the substituents and the azo linkage. It increases the energy of the n orbital on the nitrogen [14, 15], thus lowering the energy of the n → π* transition. Basically the effect of the substituent at the *meta*-position with respect to the piperazine ring is due to the steric factor, but it must also have an electronic component. This is manifested in two ways. First, the λ_{max} values for **8a**, **11c**, and **11b** are almost the same in spite of the large differences in the sizes of H, Cl, and F atoms. Second, the incorporation of another fluorine atom on the second *meta*-position causes λ_{max} to decrease significantly from **11b** to **11a**. Thus, the electronic interaction works against the steric factor in these compounds.

The two different kinds of substituent effects at the *ortho*- and *meta*-positions are both present in compound **8f**, for which a blue shift from **8a** was observed (table 2). This suggests that the deconjugation perturbation is larger in magnitude than the perturbation of increasing

nitrogen atom energy level in the azo linkage. This is confirmed by a comparison of the difference of λ_{max} values of the non-substituted and corresponding substituted compounds. For example, the difference between **8e** and **8a** is only 13 nm, while that between **8c** and **8a** is − 74 nm.

Since practical applications of LCDs are usually carried out at ambient temperature, we studied the electro-optic properties of the synthesized LCs by dissolving them in E7, a commercial LC mixture of biphenyls and terphenyls, to form 10 wt % room temperature LC mixtures.

The dielectric anisotropy of seven LC mixtures was measured with a Displaytech APT III liquid crystal tester, and the results are summarized in table 3. For the sake of comparison, the value for E7 is also listed. The values of dielectric anisotropy of the LC mixtures are very close to that of E7 because of the low concentration of diazo liquid crystals. It can be seen that the parent compound (**8a**) and two compounds with electronegative substituents neighbouring the diazo linkage (**8d** and **8b**) have smaller Δε values than E7, while other mono-substituted compounds have larger Δε values.

Birefringence measurements were also performed on the seven LC mixtures at two different wavelengths, 633 nm (visible) and 1060 nm (near IR), using a home-built optical path based on the principle discussed by Khoo and Wu [16]. The data are listed in table 3, which shows that, except for **11b**, all the LC mixtures possess large birefringence. Even for samples with only 10 wt % of the diazo LCs, the birefringence values of the samples are higher than that of E7. Therefore, the pure LCs are expected to possess much larger birefringence, making them good candidates for IR applications.

3. Synthetic procedures

Compounds with different chain lengths in each homologous series were synthesized using the same method. Therefore, the syntheses of the *n*-octyl homologues are shown below as examples.

Table 3. Dielectric anisotropy and birefringence values for 10% solutions of synthesized LCs in E7.

Compound	n	$\Delta\varepsilon$	Δn (633)	Δn (1060)
(E7		13.06	0.213	0.203)
8a	8	12.81	0.257	0.221
8e	8	14.16	0.257	0.220
11c	8	13.26	0.256	0.224
11b	8	16.28	0.217	0.200
8c	8	13.64	0.243	0.220
8d	8	12.76	0.242	0.217
8b	8	12.29	0.251	0.226

3.1. *N-Octylpiperazine (2)*

A round-bottom flask equipped with a reflux condenser was charged with 30.16 g (0.30 mol) piperazine (**1**), 13.52 g (0.070 mol) 1-bromooctane and 80 ml pyridine, and heated at reflux overnight. After cooling to room temperature, the flask was transferred to a freezer for further cooling. The precipitates (excess piperazine and resultant pyridinium salt) were then filtered off and washed with acetone. The acetone wash was combined with the previous filtrate and the solvents were removed in a rotary evaporator. The residue was heated at about 100°C under moderate vacuum overnight, and then fractionally distilled. The 115°C/20 mm Hg fraction was collected and 9.82 g of yellowish oil was obtained at a yield of 71%. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 2.93 (t, J = 4.8 Hz, 4H); 2.44 (sbr, 4H), 2.33 (m, 2H); 1.52 (m, 3H); 1.32 (br, 10H); 0.91 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 59.42 (CH$_2$); 54.62 (2 × CH$_2$); 46.06 (2 × CH$_2$); 31.72 (CH$_2$); 29.45 (CH$_2$); 29.15 (CH$_2$); 27.54 (CH$_2$); 26.59 (CH$_2$); 22.54 (CH$_2$); 14.00 (CH$_3$).

3.2. *1-(2-Chloro-4-nitrophenyl)-4-octylpiperazine (4d)* [17, 18]

A mixture of 0.64 g (3.65 mmol) 3-chloro-4-fluoronitrobenzene (**3d**), 0.72 g (3.65 mmol) *N*-octylpiperazine (**2**) and 20 ml pyridine was placed in a round-bottom flask fitted with a condenser and heated at reflux overnight. After cooling, the precipitate was filtered off. The solvent was then removed in a rotary evaporator, and the residue purified by column chromatography, eluent: ethyl acetate/hexane (1 : 4); yield 1.13 g (88%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.24 (d, J = 2.6 Hz, 1H); 8.09 (dd, J = 8.9 Hz, 2.6 Hz, 1H); 7.04 (d, J = 8.9 Hz, 1H); 3.25 (t, J = 4.7 Hz, 4H); 2.65 (t, J = 4.7 Hz, 4H); 2.41 (m, 2H); 1.53 (m, 2H); 1.32–1.28 (mbr, 10H); 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 154.86 (C); 141.94 (C); 127.35 (C); 126.61 (CH); 123.37 (CH); 119.21 (CH); 58.67 (CH$_2$); 52.96 (2 × CH$_2$); 50.61 (2 × CH$_2$); 31.80 (CH$_2$); 29.51 (CH$_2$); 29.22 (CH$_2$); 27.53 (CH$_2$); 26.84 (CH$_2$); 22.63 (CH$_2$); 14.07 (CH$_3$).

3.3. *1-(4-Amino-2-chlorophenyl)-4-octylpiperazine (5d)* [19]

A mixture of 1.13 g (3.2 mmol) 1-(2-chloro-4-nitrophenyl)-4-octylpiperazine (**4d**), 2.78 g (12.3 mmol) stannous chloride dihydrate (SnCl$_2$.2H$_2$O) and 54 ml hydrochloric acid was heated under reflux until a drop of the reaction mixture became clear when diluted with 1 ml distilled water. The reaction mixture was transferred to a flask and 100 ml chloroform added. After cooling, 35% ammonium hydroxide was added slowly

with stirring until the mixture was highly alkaline. The organic part was separated and the aqueous layer further extracted several times with chloroform. The organic portions were combined, dried over anhydrous potassium carbonate and filtered. After the removal of the solvent, the residue was purified by column chromatography, eluent: ethyl acetate; yield 1.03 g (~ 100%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 6.81 (d, J = 8.5 Hz, 1H); 6.73 (d, J = 2.6 Hz, 1H); 6.55 (dd, J = 8.5 Hz, 2.6 Hz, 1H); 3.53 (sbr, 2H); 2.98 (sbr, 4H); 2.61 (sbr, 4H); 2.39 (t, J = 7.8 Hz, 2H); 1.52 (sbr, 2H); 1.30 (mbr, 10H); 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 142.75 (C); 141.09 (C); 129.79 (C); 121.27 (CH); 117.09 (CH); 114.15 (CH); 58.89 (CH$_2$); 53.57 (2 × CH$_2$); 51.80 (2 × CH$_2$); 31.81 (CH$_2$); 29.54 (CH$_2$); 29.23 (CH$_2$); 27.64 (CH$_2$); 26.92 (CH$_2$); 22.64 (CH$_2$); 14.08 (CH$_3$).

3.4. *4-Nitrosonitrobenzene (7)* [20, 21]

To 3.5 ml pre-cooled concentrated sulfuric acid was added 5 g (18.5 mmol) potassium persulfate with continuous stirring. After the formation of a white paste, 50 g of ice was added. When the ice had completely melted, the resulting solution was adjusted to pH 3 with potassium carbonate. The white solid precipitated during the neutralization was filtered off and 0.207 g (1.5 mmol) *p*-nitroaniline was added to the collected filtrate at room temperature. After stirring for 3 h, the yellow solid formed in the mixture was filtered off and then purified by column chromatography, eluent: ethyl acetate/hexane (1 : 200); yield 0.164 g (72%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.52 (d, J = 8.8 Hz, 2H); 8.06 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 121.32 (2 × CH); 125.47 (2 × CH).

3.5. *1-(3-Chloro-4-octylpiperidylphenyl)-2-(4-nitrophenyl)diazene (8d)* [22]

A mixture of 0.38 g (1.17 mmol) 1-(4-amino-2-chlorophenyl)-4-octylpiperazine (**5d**), 0.178 g (1.17 mmol) 4-nitrosonitrobenzene (**7**) and 25 ml glacial acetic acid was heated at about 100°C with stirring; the progress of the reaction was monitored with TLC. The solvent was then removed under reduced pressure. The residue was first neutralized with saturated aqueous sodium bicarbonate and then extracted with ethyl acetate. The solvent was removed and the residue column chromatographed using ethyl acetate/hexane (1 : 3) as eluent; the product was then recrystallized from hexanes; yield 0.33 g (62%). MS spectrum: *m/e* = 459.3 (EI, 12 eV). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.36 (d, J = 5.0 Hz, 2H); 8.00 (d, J = 5.0 Hz, 2H); 7.98 (d, J = 2.4 Hz, 1H); 7.89 (dd, J = 8.5 Hz, 2.4 Hz, 1H); 7.15 (d, J = 8.5 Hz, 1H); 3.25 (sbr, 4H); 2.67 (sbr, 4H); 2.43 (t, J = 7.8 Hz, 2H);

1.54 (m, 2H); 1.32 (mbr, 10H); 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 155.71 (C); 152.87 (C); 148.50 (C); 147.71 (C); 128.30 (C); 125.06 (CH); 124.70 (2 × CH); 124.43 (CH); 123.25 (2 × CH); 119.90 (CH); 58.77 (CH$_2$); 53.14 (2 × CH$_2$); 50.86 (2 × CH$_2$); 31.81 (CH$_2$); 29.53 (CH$_2$); 29.23 (CH$_2$); 27.58 (CH$_2$); 26.86 (CH$_2$); 22.64 (CH$_2$); 14.08 (CH$_3$).

3.6. *1-(2-Chloro-4-fluorophenyl)-2-(4-nitrophenyl)diazene (10c)*

The procedure to make this compound is similar to that for making **8d**. A mixture of 1.00 g (6.87 mmol) 2-chloro-4-fluoroaniline (**9c**), 1.04 g (6.87 mmol) 4-nitro-sonitrobenzene (**7**) and 35 ml glacial acetic acid was heated at 100°C with stirring and the reaction monitored with TLC. After the removal of glacial acetic acid, neutralization with sodium bicarbonate solution, extraction with ethyl acetate and distillation of the ethyl acetate, the residue was subjected to column chromatographic separation, eluent: ethyl acetate/hexane (1 : 20); yield: 1.65 g (85%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.40 (d, $J = 8.3$ Hz, 2H); 8.07 (d, $J = 8.3$ Hz, 2H); 7.83 (dd, $J = 9.1$ Hz, 6.0 Hz, 1H); 7.35 (dd, $J = 9.1$ Hz, 2.8 Hz, 1H); 7.11 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 166.0 (C); 163.44 (C); 151.86 (C); 143.50 (C); 138.38 (C); 124.78 (2 × CH); 123.87 (2 × CH); 118.95 (CH); 118.11 (CH); 115.01 (CH).

3.7. *1-(2-Chloro-4-octylpiperidylphenyl)-2-(4-nitrophenyl)diazene (11c)* [23]

A flask was charged with 0.77 g (2.73 mmol) 1-(2-chloro-4-fluorophenyl)-2-(4-nitrophenyl)diazene (**10c**), 0.60 g (3.01 mmol) octylpiperazine (**2**), 0.57 g (3.01 mmol) cuprous iodide, 0.42 g (3.04 mmol) potassium carbonate and 30 ml dry DMF; the vessel was then sealed and heated at 100°C with stirring overnight. After cooling, the solvent was distilled off under reduced pressure and the residue purified with column chromatography, eluent: ethyl acetate/hexane (1 : 10) followed by ethyl acetate/hexane (1 : 3); yield: 0.35 g (28%). MS spectrum: *m/e* = 459.3 (EI, 12 eV). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.35 (d, $J = 7.0$ Hz, 2H); 7.99 (d, $J = 7.0$ Hz, 2H); 7.82 (d, $J = 9.4$ Hz, 1H); 6.99 (d, $J = 2.6$ Hz, 1H); 6.81 (dd, $J = 9.4$ Hz, 2.6 Hz, 1H); 3.44 (t, $J = 5.0$ Hz, 4H); 2.59 (t, $J = 5.0$ Hz, 4H); 2.39 (t, $J = 7.6$ Hz, 2H); 1.53 (m, 2H); 1.31 (mbr, 10H); 0.89 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 169.41 (C); 156.48 (C); 154.10 (C); 139.96 (C); 124.68 (2 × CH); 123.19 (2 × CH); 118.50 (CH); 114.22 (CH); 112.56 (CH); 58.64 (CH$_2$); 52.73 (2 × CH$_2$); 47.14 (2 × CH$_2$); 31.80 (CH$_2$); 29.50 (CH$_2$); 29.22 (CH$_2$); 27.49 (CH$_2$); 26.84 (CH$_2$); 22.63 (CH$_2$); 14.07 (CH$_3$).

4. Conclusion

The syntheses of nine series of liquid crystals carrying push–pull groups were carried out in this work. The effects of the substituents on phase behaviour, phase transition temperatures, and optical absorption were studied. The presence of lateral substitution depresses both melting and clearing points of the liquid crystals. Compounds with *ortho*-substitution (with respect to the piperazine ring) have broader nematic ranges than the corresponding *meta*-substituted compounds. For optical properties, *ortho*-substitution causes red shifts, while *meta*-substitution causes blue shifts. This effect originates from the steric and electronic interactions between the substituents and certain segments of the liquid crystals. Measurements of birefringence and dielectric anisotropy of seven compounds dissolved in E7 were carried out; satisfactory dielectric anisotropy and birefringence were obtained, which indicates that these diazo liquid crystals with push–pull structures are good candidates for potential IR applications. The results also provide useful information to guide future structural design of liquid crystals with similar structures.

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