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NOTE

Synthesis of a New Homologous Series of 4-*n*-Alkoxy-2,3,5,6-tetramethyl-phenyl-4′-nitroazobenzene

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4-n-Alkoxy-2,3,5,6-tetramethylphenyl-4′-nitroazobenzene where the number of carbon atoms in the alkoxy group varies from 2–8, were synthesised. The structures of the prepared liquid crystals were characterised on the basis of their UV-visible, IR spectral data and on their elemental analysis. Reversed phase high performance liquid chromatography analysis was used to check the degree of purity of the prepared liquid crystals.

Up to now there have been issued several thousands of patents and a great number of published papers were devoted to the preparation and application of liquid crystals in different technologies. Up to 1980 there were a limited real applications for liquid crystals. However, a recent review was published in which are given full details about the modern applications of different types of liquid crystals that have as yet been traced[1,2]. Furthermore there are many other applications including electronic industries[3–5], defense advance research projects[6], early diagnosis of breast cancer[7] and in display devices[8].

The present work concerns the synthesis of a new homologous series of some azo compounds of the type mentioned above in an attempt to introduce some new varieties in the field of liquid crystals, hoping that these new compounds will find applications in technology.

All chemicals and solvents used were of analytical grade; solvents were used without further purification. IR spectra were recorded using Philips infrared spectrophotometer Pu-2712. UV and visible spectra were recorded in ethanol using Schinadzu UV-visible spectrophotometer type UV-160. CHN analyses were done using Perkin-Elmer CHN analyser model 240 B.

Synthesis of 4-hydroxy-1,3,5,6-tetramethylphenyl-4′-nitroazobenzene

4-Nitrobenzene diazonium chloride was prepared by dissolving 10 g (0.0724 mole) of 4-nitroaniline in 25 mL of 50% HCl at 0°C. This solution was treated with sodium nitrite solution made of 6 g $NaNO_2$ in 12 mL distilled water, with stirring and cooling. The solution of diazonium salt was added under cooling and stirring to a solution of 2,3,5,6-tetramethylphenol (10.5 g, 0.07 mole) in 10 mL 20% NaOH. The resulting red-coloured solution was allowed to stand for 2 h at cold temperature. The solution was acidified with 30% hydrochloric acid. A red crystalline solid material was formed. Filtration gave a solid product which was washed with distilled water, and crystalized from ethanol (18 g, 87.8%, m.p. 169°C). The physical and spectral data are presented in Tables-1 and 2.

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TABLE-1
PHYSICAL AND ANALYTICAL DATA FOR COMPOUNDS 1 AND 2

Compound/n	m.p. (°C)	% Analysis, Calculated (Found)		
		C	H	N
1/0	169	64.21 (64.40)	5.68 (5.85)	14.04 (14.08)
2/2	155–156	66.05 (66.37)	6.42 (6.40)	14.67 (13.40)
2/3	130–132	66.86 (69.43)	6.74 (6.94)	12.36 (12.73)
2/4	114–116	67.61 (67.30)	7.04 (7.44)	11.83 (12.35)
2/5	106–108	68.29 (68.12)	7.32 (7.63)	11.38 (11.60)
2/6	72–74	68.93 (68.75)	7.57 (8.00)	10.96 (11.00)
2/7	60–62	69.52 (69.12)	7.81 (7.92)	10.58 (10.80)
2/8	54–56	70.07 (70.10)	8.03 (8.05)	10.22 (10.02)

TABLE-2
I.R. AND UV SPECRAL DATA OF COMPOUNDS 1 AND 2

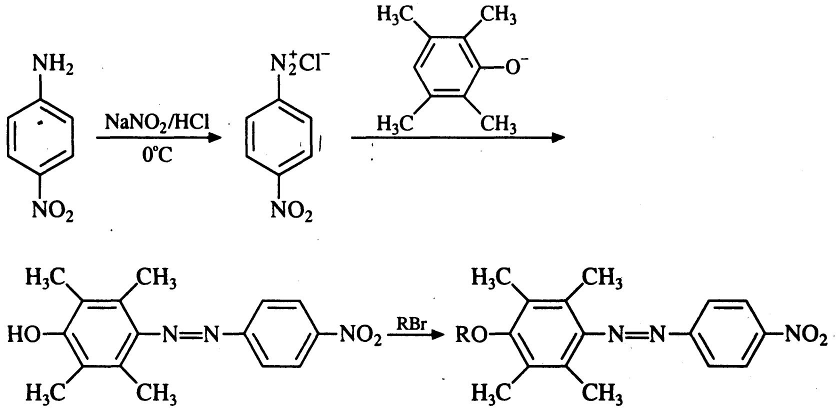
Compd/n	UV				IR (cm^{-1})			
	K band		R band					
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	ν(OH)	ν(N=N)	ν(NO_2)	ν(C—O—C)
1/0	382	1.990	477	0.362	3525	1570, 1440	1520, 1320	–
2/2	366	1.312	480	0.175	–	1450, 1420	1500, 1320	1300, 1010
2/3	363	1.023	484	0.130	–	1450, 1420	1490, 1310	1280, 990
2/4	363	0.980	475	0.106	–	1450, 1420	1500, 1320	1305, 1030
2/5	372	2.234	482	0.346	–	1450, 1410	1520, 1310	1310, 1000
2/6	365	1.399	482	0.192	–	1480, 1420	1520, 1310	1320, 995
2/7	370	2.299	485	0.263	–	1480, 1400	1520, 1310	1350, 1010
2/8	366	1.882	484	0.273	–	1490, 1410	1520, 1320	1360, 1010

Synthesis of 4-n-alkoxy-2,3,5,6-tetramethylphenyl-4′-nitro azobenzene

A solution of 1 g (0.0033 mole) of the hydroxy derivative was made in 50 mL potassium ethoxide solution (prepared by adding 48 mL of absolute ethanol to 8 g of potassium); the mixture was refluxed until all the potassium was consumed; after cooling the mixture, 0.0033 mole of the required alkyl bromide was added. The resulting mixture was refluxed for 2–5 days. The excess solvent was distilled off, then 100 mL of water was added. The resulting mixture was extracted with (3 × 100 mL) ether. The combined ether layer was washed with water, 10% $NaHCO_3$, then water and dried over anhydrous magnesium sulfate. Filtration and then evaporating the solvent afforded the desired product as a red colored solid.

The obtained product was purified by dissolving it in ethanol under reflux with active charcoal for 4 h, then after filtration and evaporating the solvent, the obtained solid product was crystallised five times from ethanol.

The following Scheme shows the steps used for these preparation.



1 **2**

R = CnH2n + 1 where *n* = 2–8.

The observed λ_{max} and ε_{max} for the K- and R-bands which represent the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transition respectively for the prepared compounds are represented in Table-2. It seems that the ε_{max} for the K band in compound 2 with n = 5 and 7 is higher than the others. Compound 1 shows a strong absorption at 3520 due to OH and two bands at 1570 and 1440 cm^{-1} due to the azo group. This clearly indicates that the coupling reaction between the diazonium salt and the phenolic compound has occurred. On the other hand the absence of the OH absorption and the presence of C—O—C band at 1360–1280 and 1010–990 cm^{-1} clearly indicate that alkylation reactions occurred between the phenolic compound and the alkyl halide to give the alkoxy compound **2**. All these assignment are in good agreement with the literature values[9].

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