LIQUID-CRYSTAL COMPOUNDS

II.* REACTION OF p-(N-ALKYL)BENZALDEHYDES WITH p-AMINOBENZONTRILE

V. V. Titov, E. I. Kovshev,
L. A. Karamysheva, G. V. Purvanetskas,
and V. K. Daukshas

UDC 532.783+547.832.5

An attempt to obtain Schiff bases of p-(n-alkyl)benzaldehydes with p-aminobenzontrile in the presence of boron trifluoride etherate unexpectedly gave mixtures of 2-[p-(n-alkyl)-phenyl]-6-cyanoquinolines and p-(n-alkyl)benzyl-p-aminobenzontrile; the former have liquid-crystalline properties. Unstable Schiff bases can be obtained only when catalytic amounts of piperidine or p-toluenesulfonic acid are used.

Although Schiff bases of p-(n-alkyl)benzaldehydes with p-aminobenzonitrile (I) have liquid-crystal properties and can be used for the creation of low-temperature mixtures with high dielectric anisotropies [21], no information regarding the synthesis and physical constants of these compounds is available. We therefore accomplished a series of experiments for the selection of the optimum conditions for their preparation. Azomethines I, which, according to IR spectroscopy, contain admixtures of the starting amine, were actually obtained in ~30% yields in toluene in the presence of catalytic amounts of piperidine or p-toluenesulfonic acid. These compounds are unstable in air and decompose under the influence of moisture and during chromatography on aluminum oxide or silica gel. They have the properties of nematic liquid crystals, but have a meso phase with low thermal stability (T_i) and a broad temperature range over which it exists (ΔT) (Table 1).

We hoped to increase the yields of imines I and obtain purer products using boron trifluoride etherate as the catalyst. According to the results of thin-layer chromatography (TLC), no less than five reaction products and the starting imine were detected in the mixtures after the reactions in the presence of this catalyst; we were able to isolate and identify two basic products.

The first of these basic products proved to be 2-aryl-6-cyanoquinolines II, which contain two more carbon atoms than the starting compounds, as confirmed by mass-spectrometric determination of the molecular weights (m/e 272 for IIb). The IR spectrum of IIb contains the absorption band of a nitrile group at 2230 cm^{-1} but the absorption of an NH group is not detected; there is a series of bands characteristic for vibrations of 2- and 6-substituted quinoline rings (1620, 1425, and 1377 cm^{-1}). In addition the IR spectra contain bands characteristic for the CH bonds of a quinoline ring containing hydrogen atoms in the 5, 7, and 8 positions (1165, 1115, 896, and 848 cm^{-1}) and at 1145, 945, and 814 cm^{-1} characteristic for the vibrations of the CH bonds of a quinoline ring containing hydrogen atoms in the 3 and 4 positions [3]. The PMR spectrum of IIe contains signals of the protons of a hexyl group [0.86 t (2H), 1.30 m (8H), and 2.61 t (3H) ppm] and a multiplet of protons of an aromatic ring at 7.1-8.2 ppm. The absence of the signal at 8.8 ppm peculiar to unsubstituted quinoline proves the presence of a substituent in the 2 position.

Hydrogenation of quinoline IId and subsequent hydrolysis gave 2-[p-(n-amyl)phenyl]-6-formylquinoline, the structure of which was confirmed by the IR and PMR spectral data. Nitrile IId is hydrolyzed to 2-[p-(n-amyl)phenyl]quinoline-6-carboxylic acid.

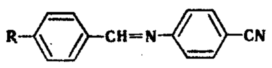
Compounds II, like p-substituted p-cyanodiphenyl [4], have liquid-crystal properties (Table 2).

---

*See [1] for communication I.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1364-1367, October, 1975. Original article submitted December 11, 1974.

TABLE 1. Temperatures of the Phase Transitions of N-p-(n-Alkyl)benzylidene-p-cyanoanilines



I

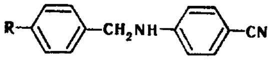
Compound	T_n,* °C	T_i, °C	$\Delta T(T_i-T_n)$
Ia	63,0	73,9	10,9
Ib	64,7	75,5	10,8
Id	46,4	73,6	27,2
Ie	45,8	68,0	22,2

*Symbols: T_n is the temperature of formation of the nematic liquid-crystal phase, and T_i is the temperature of conversion to the isotropic liquid.

TABLE 2. 2-[p-(n-Alkyl)phenyl]-6-cyanoquinolines (II)

Compound	T_n, °C	T_i, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
IIa	123,5—124,5	137,5—138,0	$C_{18}H_{14}N_2$	83,8	5,4	11,1	83,7	5,5	10,9	8
IIb	106,0—107,0	146,0—146,5	$C_{19}H_{16}N_2$	83,9	6,1	10,3	83,8	5,9	10,3	14
IIc	96,0—97,0	109,0—110,0	$C_{20}H_{18}N_2$	84,1	6,4	9,8	83,9	6,3	9,8	17
IId	91,0—91,8	135,0—135,5	$C_{21}H_{20}N_2$	83,8	6,6	9,4	84,0	6,7	9,3	23
IIe	85,7—86,3	123,5—124,0	$C_{22}H_{22}N_2$	83,8	7,1	9,0	84,0	7,0	8,9	36

TABLE 3. N-(p-Alkylbenzyl)-p-aminobenzonitriles (III)

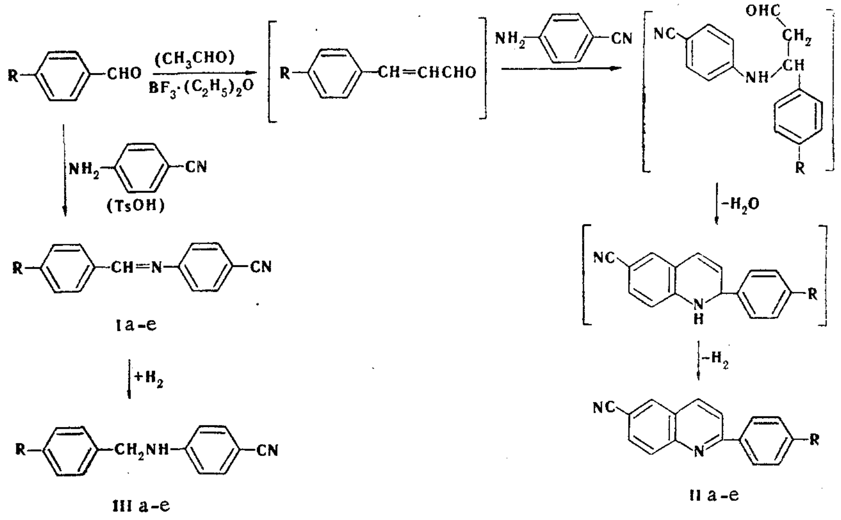


Compound	mp, °C (solvent)	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
IIIa	129,7—130,0 (hexane–dichloroethane)	$C_{16}H_{16}N_2$	81,4	6,7	11,9	81,3	6,8	11,9	27
IIIb	141,5—142,3 (hexane–dichloroethane)	$C_{17}H_{18}N_2$	81,9	7,1	11,1	81,6	7,2	11,2	37
IIIc	103,0—103,8 (hexane)	$C_{18}H_{20}N_2$	81,9	7,5	10,6	81,8	7,6	10,6	38
IIId	57,2—58,0 (hexane–ether)	$C_{19}H_{22}N_2$	81,9	8,0	10,2	82,0	8,0	10,1	39
IIIe	47,5—48,5 (cyclohexane)	$C_{20}H_{24}N_2$	81,9	8,2	9,7	82,2	8,3	9,6	59

The second group of basic products isolated from the reaction mixtures are N-[p-(n-alkyl)benzyl]-p-aminobenzonitriles III, the structure of which was confirmed by mass spectrometric determination of the molecular weight (m/e 250 for IIIb) and by spectroscopic data for IIIe [CO group at 2200 and NH group at 3350 cm^{-1} in the IR spectrum; 0.85 t (3H), 1.27 m (8H), and 2.52 m (2H) for aromatic ring CH_2, 4.12 d (2H) for CH_2N, 4.99 s (1H) for NH, and 6.35-7.35 m (8H) for the aromatic protons]. Compounds III (Table 3) do not have liquid-crystal properties.

Acetaldehyde is evidently formed initially in the reaction of disproportionation of the aldehyde and ethanol [5, 6], after which quinolines II are formed via the usual Doebner–Miller reaction, during which, as previously shown in another case [7], the liberated hydrogen is consumed in the reduction of the simultaneously formed Schiff bases to amines III.

p-Aminobenzonitrile reacts similarly with 3,4-ethylenedioxybenzaldehyde to give 2-(3,4-ethylenedioxyphenyl)-6-cyanoquinoline in 10% yield, while the same aldehyde reacts with p-(n-butyl)aniline to give a Schiff base – 3,4-ethylenedioxybenzylidene-p-(n-butyl)aniline.



I–III a $R = C_2H_5$; b $R = C_3H_7$; c $R = C_4H_9$; d $R = C_5H_{11}$; e $R = C_6H_{13}$

EXPERIMENTAL

The temperatures of the phase transitions of I were determined with a Mettler FP-5 optical recording apparatus with an FP-51 heating block. The PMR spectra were recorded with a Tesla BS-487C spectrometer. The mass spectra were recorded with an MKh-1303 spectrometer. The IR spectra were recorded with a UR-20 spectrometer. Thin-layer chromatography was carried out on activity II aluminum oxide with elution by petroleum ether–diethyl ether (4 : 1).

N-[p-(n-Alkyl)benzylidene-p-aminobenzonitrile (I). A mixture of 15 mmole of p-(n-alkyl)benzaldehyde, 9 mmole of p-aminobenzonitrile, and two to three drops of piperidine (or a solution of 0.001 g of p-toluenesulfonic acid in 0.5 ml of dioxane) was refluxed in 40 ml of anhydrous toluene for 3 h, after which it was cooled and filtered. The solvent was removed from the filtrate by distillation, and the residue was recrystallized from 20 ml of n-hexane. The condensation product (30% yield) was purified to remove the starting amine by recrystallization from petroleum ether, heptane, and benzene–heptane (1 : 10) and filtration in absolute benzene through a layer of silica gel (Table 1). The IR spectra of all of the compounds (in KBr pellets) contained bands at 1635-1640 (CH=N) and 2230-2234 cm^{-1} (CN). In addition to signals of aliphatic and aromatic protons, the PMR spectra of CCl_4 solutions of the compounds contained a singlet of an azomethine group at 8.20-8.24 ppm.

2-[p-(n-Alkyl)phenyl]-6-cyanoquinolines (II) and N-[p-(n-Alkyl)benzyl]-p-aminobenzonitriles (III). A mixture of 100 mmole of p-(n-alkyl)benzaldehyde, 135 mmole of p-aminobenzonitrile, 10 ml of absolute ethanol, 75 ml of anhydrous toluene, and 16 mmole (2 ml) of boron trifluoride etherate was refluxed with a Dean–Stark trap for ~30 h (until the starting aldehyde had vanished according to TLC), after which the mixture was cooled to 20°, and the resulting precipitate was filtered through a small layer of aluminum oxide. The solvent was removed from the filtrate by distillation, the residue was dissolved in the minimum volume of benzene, and the benzene solution was chromatographed with a column filled with activity II aluminum oxide by elution with petroleum ether–diethyl ether (4 : 1). Two basic fractions of the reaction products were isolated, the solvent was removed by distillation, and the reaction products were additionally purified by crystallization. The results of analysis and the physical constants of II and III are presented in Tables 2 and 3.

2-(3,4-Ethylenedioxyphenyl)-6-cyanoquinoline. A mixture of 73 mmole of 3,4-ethylenedioxybenzaldehyde [8] and 99 mmole of p-aminobenzonitrile was dissolved in 60 ml of anhydrous toluene, after which 12 mmole of boron trifluoride etherate and 20 ml of absolute ethanol were added, and the mixture was refluxed for 70 h with a Dean–Stark trap, during which another 30 ml of alcohol was added in portions in order to dissolve the precipitated complex of the catalyst with the starting amine. The cooled reaction mixture was filtered through a small layer of aluminum oxide, the filtrate was concentrated, and the concentrated residue was chromatographed on aluminum oxide with elution initially with benzene and then with benzene–ether (1 : 1) to give 2 g (10%) of a product with mp 191-192° (from isopropyl alcohol). UV spectrum, λ_{max} (alcohol) (log ε), nm: 234 (4.46), 265-270 (shoulder), 353 (1.19). IR spectrum: 2220 cm^{-1} (CN). Found: C 74.7; H 4.3; N 9.8%. $C_{18}H_{12}N_2O_2$. Calculated: C 75.0; H 4.2; N 9.7%.

3,4-Ethylenedioxybenzylidene-p-(n-butyl)aniline. A mixture of 61 mmole of 3,4-ethylenedioxybenzaldehyde and 97 mmole of p-(n-butyl)aniline was dissolved in 65 ml of anhydrous toluene, 9.7 mmole of boron trifluoride etherate was added, and the mixture was refluxed for 25 h with a Dean–Stark trap. The mixture was then worked up as described above, and the reaction product obtained after chromatography and removal of the solvent by distillation was vacuum dried at 70-80° to give 10 g (50%) of a viscous liquid with n_D^{20} 1.1620. UV spectrum, λ_{max}, nm (log ε): 232 (4.32), 283 (3.96), and 317 (3.85) in alcohol. Found: C 77.3; H 7.2; N 4.4%. $C_{19}H_{21}NO_2$. Calculated: C 77.2; H 7.2; N 4.7%.

2-[p-(n-Amyl)phenyl]-6-formylquinoline. A 0.3-g sample of Raney nickel was added to a solution of 1.3 g of IId in 25 ml of moist toluene, after which the mixture was hydrogenated in a long-necked hydrogenation flask. The catalyst was then removed by filtration, and the solvent was evaporated to give 0.35 g (65%) of a product with mp 71-72° (from hexane). IR spectrum: 1710 cm^{-1} (CO). PMR spectrum (CCl_4), δ, ppm: 1.20 t (3H) for CH_3, 1.48-2.17 m (6H) for the CH_2 groups, 2.97 t (2H) for the aromatic ring CH_2 groups, 7.52 d (J = 8 Hz, 2H) for the aromatic protons adjacent to the C_5H_{11} group, 8.05-8.55 m (7H) for the aromatic protons, and 10.35 s (1H) for the CHO groups. Found: C 83.0; H 6.9; N 4.7%. $C_{21}H_{21}NO$. Calculated: C 83.1; H 7.0; N 4.6%.

2-[p-(n-Amylphenyl]quinoline-6-carboxylic Acid. A mixture of 1 g of IId and 50 ml of hydrochloric acid (1 : 1) was refluxed for 30 h, after which it was cooled, and the resulting precipitate was recrystallized from alcohol to give 0.8 g (80%) of a product with mp 245-247°. IR spectrum (in mineral oil): 1700 cm^{-1} (CO). PMR spectrum (CF_3COOH), δ, ppm: 0.77 t (3H) for the CH_3 group, 1.0-1.75 m (6H) for the CH_2 groups, 2.68 t (2H) for the aromatic ring CH_2 groups, and 7.45-9.03 m (9H) for the aromatic protons. Found: C 78.6; H 6.3; N 4.5%. $C_{21}H_{21}NO_2$. Calculated: C 79.0; H 6.6; N 4.4%.

LITERATURE CITED

1. V. V. Titov, E. I. Kovshev, A. I. Pavluchenko, V. T. Lazareva, and M. F. Grebenkin, J. Phys. (Paris), 36 (1975), Colloq., C-1, Cl-393.
2. M. Boller, H. Scheffer, and M. Schadt, Proc. IEEE, 60, 1002 (1972).
3. A. R. Katritzky (editor), Physical Methods in the Chemistry of Heterocyclic Compounds, Academic Press (1963).
4. G. W. Gray, K. J. Harrison, and J. A. Nash, Electron Letters, 9, 130 (1973).
5. J. M. Zander and G. Vries, Rec. Trav. Chim., 67, 962 (1946).
6. J. M. Zander and G. Vries, Rec. Trav. Chim., 70, 600 (1951).
7. R. Elderfield (editor), Heterocyclic Compounds, Vol. 4, Wiley (1950-1967).
8. V. Daukshas and G. Mil'videne, Nauchnye Trudy Vuzov Lit. SSSR, Ser. Khim. i Khim. Tekhnol., 7, 83 (1965).

HETARYLATION OF CYCLOPENTADIENE, INDENE, AND AZULENE

A. K. Sheinkman, G. V. Samoilenko,
S. N. Baranov, and N. R. Kal'nitskii

UDC 547.821.831–835

The direct hetarylation of cyclopentadiene, indene, and azulene with several benzopyridines in the presence of acyl halides was studied. It is shown that the most electrophilic N-benzoylisoquinolinium salt is capable of hetarylating CH acids with $pK_a < 21$.

Donetsk State University. Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1368-1375, October, 1975. Original article submitted July 17, 1974.