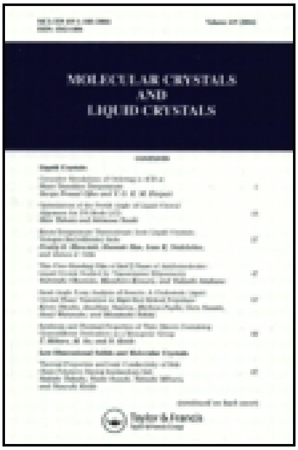

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Improvements in the Method for Preparing *bis*-(4′-*n*-Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines†

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An improved synthetic procedure for the preparation of *bis*-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines has been developed. A detailed procedure for the isolation of the starting diamine, 2-chloro-1,4-phenylenediamine, from its sulfate salt and its purification is presented. Condensation of this diamine with the 4-alkoxybenzaldehydes in the presence of a catalytic amount of acetic acid and refluxing in ethanol for 18 hours gave high yields of the desired dianils. A shorter reflux time of 5 hours gave a mixture of the dianil **5** and monoanil **3**. The use of molecular sieves in place of the acetic acid yielded primarily the monoanil.

The synthesis and mesomorphic properties of *bis*-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamines, **5** (scheme 1) have already been described in the literature.[1,2] However, our interest in preparing a deuterated analog of **5** ($R{=}C_8D_{17}$) for broad line NMR studies[3] as well as large quantities of the undeuterated materials for a variety of physical measurement studies required a synthetic procedure which would produce these dianils in high yields and purity. Yields were not reported in either of the literature procedures which we found to be inadequate and lacking sufficient details to achieve good results.

Two problems were encountered in the preparation of these compounds. One involved the isolation and purification of the free diamine **2** from its sulfate salt **4**. The diamine is commercially available either as the monosulfate salt (Aldrich) or as the dihydrochloride (Eastman Kodak) but both materials were found to be impure. The sulfate salt could be purified by

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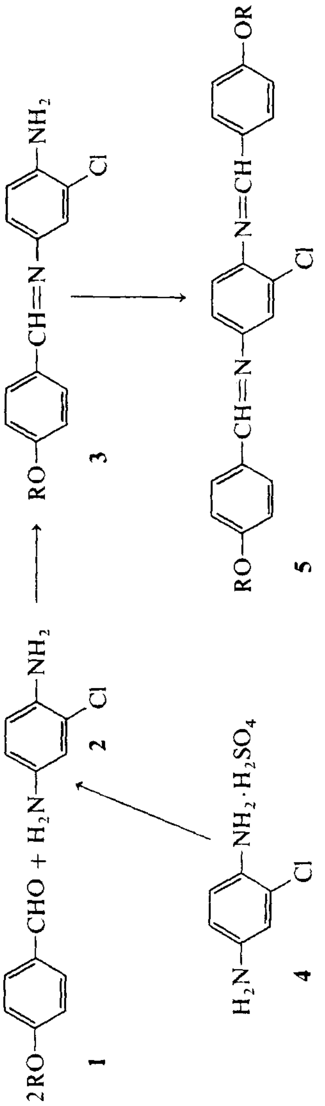
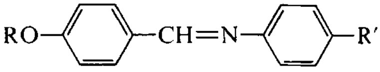

2RO
CHO + H_2N
Cl
NH_2
1
2
H_2N
Cl
$NH_2 \cdot H_2SO_4$
4
RO
CH=N
Cl
NH_2
3
RO
CH=N
Cl
N=CH
OR
5

SCHEME 1

recrystallization from water but the diamine isolated by an extraction of the neutalized salt solution was impure and obtained in low yields. Attempts to purify the hydrochloride salt by recrystallization were unsuccessful. The use of impure diamine to prepare the dianils gave material which was difficult to obtain pure in good yields by recrystallization.

We found that the best method for obtaining the pure diamine was to isolate it by neutralizing a hot aqueous solution of the sulfate salt, removing the water under a vacuum at *ca.* 40° and extracting the diamine into chloroform from the dried solid residue. The brown solid isolated from the chloroform extract was distilled under a vacuum to a colorless liquid which solidified on cooling. This material could be kept essentially color free for long periods of time by storing under a vacuum whereas it gradually darkened when exposed to atmospheric conditions.

The second problem encountered in the preparation of these dianils involved the conditions required to achieve a good yield of the dianil in the condensation reaction (scheme 1). Both literature procedures used absolute ethanol as the solvent and refluxed for 30 minutes[2] or 5–6 hours[1] without the addition of an acid catalyst. Initially, we used molecular sieves as a water scavenger in our reaction since we had successfully prepared the simple anils **6**



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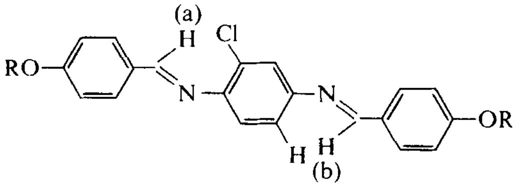
and the homologs of TBBA[4] using this method. However, when a reflux time of 5 hours was employed with our purified diamine, the material isolated consisted primarily of a monoanil rather than the dianil. Apparently, there is steric hindrance to the condensation of the aldehyde with the amino group adjacent to the chlorine atom in the diamine **2** so that the monoanil isolated probably has the structure **3**. The NMR chemical shifts for the anil protons provide evidence that it is this anil rather than the one in which the anil is adjacent to the chlorine atom. Only one singlet occurs at 8.44δ for the anil proton in the monoanil whereas the dianil shows two singlets at 8.44 and 8.40δ. The angle between the aromatic rings on the anil function closest to the chlorine atom would be expected to be larger due to steric hindrance between the chlorine atom and the anil proton (a) (structure **7**) than the angle between the aromatic ring substituents of the other anil function. This would be expected to decrease the aromatic deshielding effect of the aromatic ring on the anil proton closest to the chlorine atom (a) giving it a lower chemical shift value i.e., 8.40δ than that observed for the proton not influenced by an *ortho* chlorine substitutent (b).



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When a small amount of acetic acid was added to the reaction solution instead of molecular sieves, a mixture of mono- and dianils was isolated. Some separation of these two compounds by recrystallization was possible since the dianil is less soluble in ethanol than the monoanil but obtaining pure dianil was difficult and the yield low (~25%). The dianil could be isolated free of monanil and in high yields when the reflux time was extended to 18 hours. No evidence of the presence of the monoanil could be found in the filtrates obtained from the dianil.

A careful study of the transition temperatures for the dianil where $R{=}C_8H_{17}$ by hot stage polarizing microscopy showed the presence of a short range monotropic smectic C phase below the nematic phase. Since the crystal to nematic, the nematic to smectic C and the smectic C to crystal transition temperatures all occur within a range of *ca.* 4°, it was initially difficult to determine if this phase was enantiotropic or not. We now believe that it is not. Some textural changes seemed to occur in the crystal structure before the melting point. These appeared to be more noticeable in the C_6 and C_{10} homologs than in the C_8 compound. We have not yet done purity studies on these compounds to determine if this is an impurity effect. Some decomposition of these compounds seemed to occur near the nematic to isotropic transitions when the materials were heated repeatedly at the higher temperatures. No such effect was observed on repeated heating near the smectic C to nematic transition but the temperature of this transition seems to be more sensitive to impurities.

Since the monoanil **3** isolated from the reaction containing molecular sieves using two equivalents of aldehyde seemed to contain small amounts of the dianil which made it difficult to obtain a pure sample for identification purposes, better material was prepared using only one equivalent of the aldehyde. The crude yield was lower but the monoanil could be purified easier. No mesophases were observed in the monoanil ($R{=}C_8H_{17}$).

No attempt was made to repeat the literature method of using ethanol as the solvent in the absence of either an acid catalyst or a water scavenger. It is conceivable that the presence of water in the ethanol or of small amounts of the acid salt in the impure diamine could provide the acid catalyst necessary to obtain the dianil. This might explain the literature results but since yields and adequate details were not provided no conclusion can be reached. Our results with the addition of acetic acid indicate that a longer reaction time is required than that reported in the literature and that it is unlikely that the literature procedures gave complete conversion to the dianil.

Knowing that the monoanil **3** can be isolated creates the temptation to try to prepare a dianil **5** which would contain two different R groups. However, since the synthesis of these dianils involves an equilibrium reaction between the anil and the starting materials, the product would undoubtedly consist of a mixture of four dianils.

EXPERIMENTAL

4-*n*-Octyloxybenzaldehyde was prepared by a procedure which we have reported earlier.[5] No difficulties were encountered in using the commercially available C_6 and C_{10} alkoxybenzaldehydes without purification. Melting points and approximate transition temperatures were determined using a Thomas–Hoover apparatus and are corrected. Instruments used as analytical tools were a Perkin Elmer model 700 (ir) and a Varian A-60 model (nmr) with chloroform as the solvent. Mesomorphic transition temperatures and textures were determined using a Leitz–Wexler Ortholux polarizing microscope equipped with a modified and calibrated Mettler FP-2 heating stage. The elemental analysis was obtained from Spang Microanalytical Laboratories, Ann Arbor, Michigan.

2-Chloro-1,4-phenylenediamine (2)

The sulfate salt of this diamine, **4** (100 g, 0.415 moles, Aldrich) was dissolved in *ca.* 2.0 l of boiling H_2O,[6] a concd aq soln of NaOH added cautiously until the soln was basic[7] and the H_2O removed *in vacuo* at 40–45°. The remaining residue was dried over P_2O_5 *in vacuo* to give a tan solid. This was pulverized, extracted with $CHCl_3$ (2 × 250 ml), filtered to remove insoluble materials and the filtrate concentrated (Rotovap) at 40–45° to a brown solid. Distillation at 150° (3.4 mm) gave a colorless liquid which crystallized to the white solid diamine, **2** (43.3 g, 73.1%): mp 65–68.5° [lit.[8] mp 63–64°] and ir broad triplet at 3400, 3350, 3200 (NH_2) and 1600 cm^{-1} (Ar). This material was stored under a vacuum in order to preserve its purity.

Bis-(4′-*n*-Octyloxybenzal)-2-chloro-1,4-phenylenediamine (5, $R = C_8H_{17}$).

To a soln of the diamine **2** (10.0 g, 70.1 mmoles) and glacial HOAc (0.8 ml) in abs EtOH (400 ml) was added 4-*n*-octyloxybenzaldehyde (33.8 g, 0.140

moles) and the yellow soln refluxed for 18 hr. The yellow crystals formed on cooling the reaction soln in an ice bath were collected by filtration, washed with abs EtOH and dried *in vacuo* to give 34.6 g (90.3 %) of the crude dianil **5** ($R{=}C_8H_{17}$): mp 57–61° (C → N), 179–180° (N → I). Trituration of the residue obtained from the filtrate with abs EtOH gave an additional 5 g of impure dianil with mp 54–59.5, 146–150°. Recrystallization gave 4.1 g of material with mp 53–59, 168–170° resulting in an essentially quantitative total crude yield. These two materials were combined, dissolved in hot $CHCl_3$ (200 ml), filtered over hard paper (Whatman no. 50) and the $CHCl_3$ gradually replaced with EtOH by adding abs EtOH as the $CHCl_3$ was boiled off until the cloud point was almost reached. Cooling this soln to room temperature followed by filtration gave 37.2 g of yellow crystals. Another recrystallization yielded 34.6 g (90.3 %) of the purified dianil, **5** ($R{=}C_8H_{17}$): transition temperatures 60.0–61.7° (C → N), 178.1–178.5° (N–I), 60.0–60.2° (monotropic, S_c → N), 56.4–53.4° (S_c → C); ir triplet at 3020, 2940, 2870 (CH) and 1620, 1600 cm^{-1} (ArCH=NAr)[9] and nmr δ8.45 (*s*, 1, $C_6H_4CH{=}N$), 8.40 (*s*, 1, $C_6H_3CH{=}N$), 8.10–6.80 (*m*, 11, ArH), 4.05 (*t*, 4, J = 6.0 Hz, $ArOCH_2$) and 2.20–0.80 (*m*, 30, C_7H_{15}).

Also, prepared in this manner, were the dianils **5** where $R{=}C_6H_{17}$ (87.1 %); transition temperatures 98.3–99.2° (C → N),[10] 197.6–198.1° (N → I) and 89.9° (N → C) and where $R{=}C_{10}H_{21}$ (96.8 %); transition temperatures 56.4° (crystal change), 63.4–64.4° (C → S_c), 108.6–109.7° (S_c → N), 165.7–166.1° (N → I), 52.5° (S_c → C). These values compare favorably with those found in References 1 and 2.

4′-*n*-Octyloxybenzal-2-chloro-1,4-phenylenediamine, 3 ($R{=}C_8H_{17}$)

To a soln of the diamine **2** (1.0 g, 7.0 mmoles) in abs EtOH (40 ml) containing no. 4A molecular sieves (1.64 g, 7.00 mmoles, Linde $\frac{1}{16}$″ pellets) was added 4-*n*-octyloxybenzaldehyde (3.28 g, 14.0 mmoles) and the mixture stirred at reflux for 3 hr. The yellow precipitate formed on cooling to room temperature was collected by filtration, washed with abs EtOH and dried to give 1.16 g (46.2 %) of the crude monoanil **3**: mp 92.5–98.0°: Recrystallization twice from EtOH gave an analytical sample; mp (microscope) 91.7–95.6° (C → I), 57.7° (I → C); ir weak broad 3180 (NH_2), doublet at 2940 and 2860 (CH) and doublet at 1620 and 1600 cm^{-1} (ArCH=NAr) and nmr δ8.44 (*s*, 1, $C_6H_4CH{=}N$), 8.10–6.68 (*m*, 7, ArH), 4.30–3.90 (*t*, 2, J = 6 Hz, $ArOCH_2$), 3.90–3.42 (broad peak, 2, NH_2) and 2.20–0.68 (*m*, 15, C_7H_{15}).

Anal. Calcd. for $C_{21}H_{27}ClN_2O$: C, 70.27; H, 7.58; N, 7.81. Found: C, 70.39; H, 7.66; N, 7.82.

Acknowledgements

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4. M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, in press.
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6. It is much easier to dissolve the salt by a gradual addition to boiling water than to try to dissolve it by heating a suspension of the salt in water to the boiling point.
7. The boiling solution was actually treated with Norit in this case but this was later found to serve no useful purpose and led to the loss of the material during filtration due to crystallization of the salt in the funnel.
8. P. Cohn, *Chem. Zentralbl. I*, 752 (1902).
9. This absorption is typical for the simple diarylanils, see K. Murase, *Rev. Electr. Commun. Labs.*, **20**, 1125 (1972).
10. Changes within the crystalline phase began to occur at *ca.* 91.6°.