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Spectroscopic and Magnetic Resonance Elucidation of the Structure of the Polymer Derived from 1,2-Dihydro-4-(4-Hydroxyphenyl)-1-oxo-(2H)-Phthalazine and Bis(4-Fluorophenyl)Sulfone

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SPECTROSCOPIC AND MAGNETIC RESONANCE ELUCIDATION OF THE STRUCTURE OF THE POLYMER DERIVED FROM 1,2-DIHYDRO-4-(4-HYDROXYPHENYL)-1-OXO-(2*H*)-PHTHALAZINE AND BIS(4-FLUOROPHENYL)SULFONE

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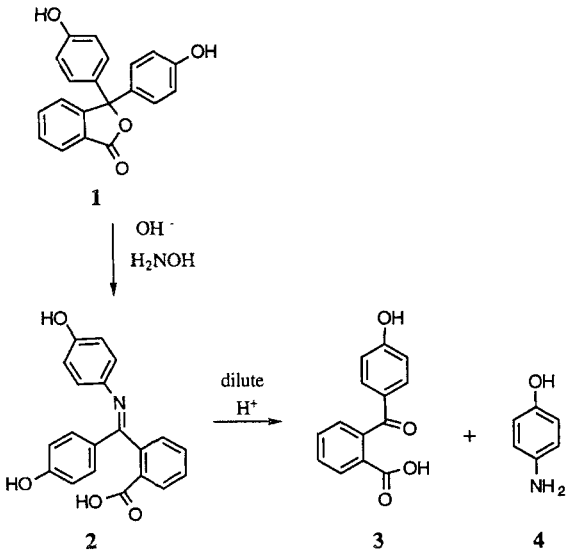
ABSTRACT

Two model compounds 4,4′-[sulfonylbis(4′-phenyleneoxy-4-phenylene)]-bis[1,2-dihydro-1-oxo-2-phenyl-(2*H*)-phthalazine] (**13**) and 4-(4-methoxyphenyl)-1-(4-methylphenoxy)phthalazine (**17**) for the respective lactam and lactim forms of 1,2-dihydro-4-(4-hydroxyphenyl)-1-oxo-(2*H*)-phthalazine (**5**) were synthesized. They were used as guides in the structural analysis of polymer **9** resulting from the reaction of **5** with bis(4-fluorophenyl)sulfone (**8**) carried out in *N*-methyl-2-pyrrolidinone at 170°C for 6 hours utilizing K_2CO_3 as the basic catalyst. The interpretations were largely done by ^1H and ^{13}C NMR and, qualitatively, by FT-IR and UV spectroscopy. For the key model compounds **13** and **17** and polymer **9**, all of the carbons were conclusively assigned aided by H-COSY, H-C HETCOR, HMQC, and HMBC NMR techniques. The results reveal that species **5** bonds with **8** at the 2-aza-nitrogen atom of the phthalazine moiety with its lactam tautomer as the only detectable form in polymer **9**. The multiple lines shown by several carbons in the ^{13}C-NMR spectrum of **9** and their similar geometrical shapes strongly indicate that there are perhaps four magnetically different environments of the repeat unit which are randomly arranged in the chain of polymer **9**.

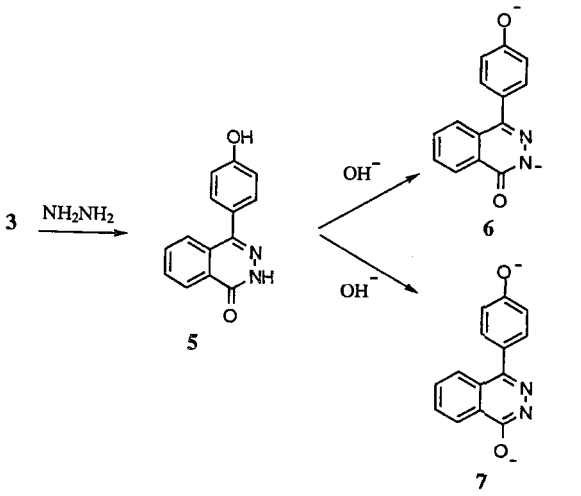
INTRODUCTION

Our laboratory research focuses in part on the synthesis of amorphous polymers with very high glass transition temperatures, which are soluble and hence can be readily fabricated. They may be applicable, for instance, as adhesives, coatings, or in composite matrices for the automotive and aerospace industries to be used under stringent high temperature conditions for prolonged periods of time.

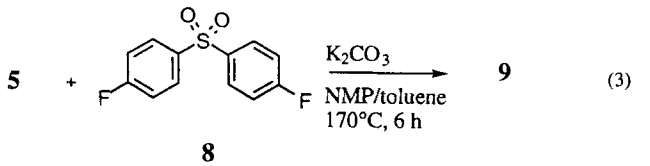
Phenolphthalein (**1**), hydroxylamine, and hydrazine are readily available starting materials. The reaction of **1** and hydroxylamine gives the keto acid **3** (Eq. 1)

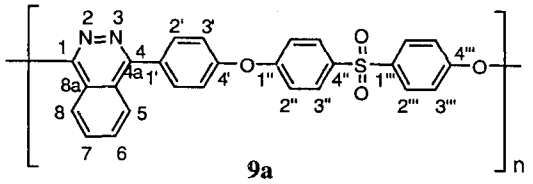


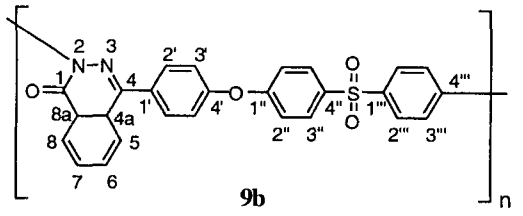
and 4-aminophenol (**4**), another useful bifunctional monomer, in a two-step reaction. The keto acid **3** reacts with hydrazine to yield the phthalazinone derivative **5** (Eq. 2)



which when reacted with bis(4-fluorophenyl)sulfone **8** gives the title polymer **9** (Eq. 3).







These syntheses were outlined in our previous reports [1].

The phthalazinone monomer **5** is a high-melting compound (310°C) deriving this property from the aromatic substituent and fused heteroaromatic ring. Polymer **9** derived from **5** has a high glass transition temperature ($T_g \approx 300$°C) and high thermooxidative stability as indicated by the 5% weight loss under a 200 mL/min flow of air at 500°C as measured by thermogravimetric analysis [1]. Yet polymer **9** is readily soluble in common solvents such as chloroform and methylene chloride, and processable into a tough, colorless, and transparent flexible film.

We were initially unsure of the structure of polymer **9**. We expected that **5** would react as a divalent phenoxide **7**, and reaction of **7** with **8** would then give a polymer with structure **9a**. However, spectral evidence presented herein points to **9b** as the structure, which means that the polymerization reaction proceeds via **6**.

This paper describes IR, UV, and more powerful NMR techniques which demonstrate conclusively that the dianion tautomeric form of the phthalazinone moiety, lactam **6**, reacts with **8** to give the polymer represented in **9b**. A single polymer strand is best explained as a random arrangement of four magnetically different subunits. To our knowledge, this is the first reported polymerization marked by an aza-nitrogen-anion displacement of fluorine from an activated aryl-fluoride.

EXPERIMENTAL SECTION

Measurements

^{1}H, ^{13}C, H-C HETCOR, and H-decoupling NMR experiments were recorded at room temperature on Varian XL-200, XL-300, and Unity-500 NMR or JOEL-270 spectrometers. Usually 30–50 mg of sample was dissolved in 1.0 mL $CDCl_3$ and the solvent resonance was used as the internal lock. For the ^{1}H-NMR determinations,

tetramethylsilane was used as the internal standard. The HMQC spectra were obtained using a Bird pulse sequence [2–4] followed by a null delay of 0.5, 0.7, and 0.7 s for **9**, **13**, and **17**, respectively. The $^{1}J_{C,H}$ used was 160.0 Hz for all experiments.

For polymer **9** other HMQC parameters were: number of points (np) 512, 1483.0 Hz sweep width, 0.98 ms pulse delay, 16 transients with 512 increments (ni). The spectral width along F1 (carbon) was 2229.5 Hz starting at 10,136.8 Hz, and 795.2 Hz along F2 (proton) starting at 3476.6 Hz.

For species **13** other HMQC parameters were: number of points (np) 512, 1088.4 Hz sweep width, 0.99 ms pulse delay, 4 transients with 256 increments (ni). The spectral width along F1 (carbon) was 2939.8 Hz starting at 10,121.5 Hz, and 884 Hz along F2 (proton) starting at 3499.4 Hz.

For species **17** other HMQC parameters were: number of points (np) 1024, 1046 Hz sweep width, 0.900 ms pulse delay, 16 transients with 256 increments (ni). The spectral width along F1 (carbon) was 7209.8 Hz starting at 10,121.5 Hz, and 884.3 Hz along F2 (proton) starting at 3439.7 Hz.

Processing was done with zero filling by setting fn1 = 4(ni) and fn = 2(np) using a standard Varian Unity 500 microprogram.

The HMBC experiments for **9**, **13**, and **17** were carried out using the same parameters used in the corresponding HMQC experiments but with 0 second null delay and 0.05 second coherence transfer time (*taumb*) allowing for enhancements of signals whose J couplings are $4 < {}^{2\text{ or }3}J < 10$ Hz [3, 4]. Processing was done with the same zero filling parameters as for the HMQC experiments. Carbon traces at a particular proton chemical shift were plotted and analyzed (for example, see Fig. 8).

No HMBC experiments were run when the XL-200, XL-270, or XL-300 instruments were employed for the precursors species, thus assignments for precursors are less definitive.

The IR spectra (32 scans) were recorded on an Analect Instruments AQS-18 FT-IR spectrometer at a resolution of 2 cm^{-1} in $CDCl_3$ solution of ~0.01 M concentration at room temperature in a KBr cell of ~0.05 mm path length. All IR absorbances reported are normalized relative to the strongest peak in the spectrum.

The UV measurements were made on a Unicam SP800 spectrophotometer in $CHCl_3$ solution at 25°C.

Traces for figures in this paper were digitized from analog spectra using the Macintosh software FlexiTrace by Adam Treister which is available from Tree Star Inc.

Materials

Polymer **9** and compounds **3** and **5** were synthesized and obtained from Berard [1]. Common reagents such as the sulfone **3**, dimethylsulfate, hydrazine, *N*,*N*-dimethylacetamide (DMAc), NMP, *N*-phenylhydrazine, and sulfolane were Aldrich products, anhydrous K_2CO_3 and $POCl_3$ were ACP products, and all were used without purification.

1,2-Dihydro-4-methoxy-2-methyl-1-oxo-(2*H*)-phthalazine (**10**)

Prepared by H. Ghassemi in our laboratory following a literature preparation [5], mp 93°C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 3 H, NCH_3), 3.97 (s, 3 H, OCH_3), 7.72–7.79 (m, 2 H, H6 and 7), 7.92–7.97 (m, 1 H, H5), 8.36–8.42 (m, 1 H, H8); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 38.70 (NCH_3), 54.09 (OCH_3), 123.33 (C5 or C8), 124.73 (C4a or C8a), 126.91 (C5 or C8), 128.96 (C4a or C8a), 131.70 (C6 or C7), 132.45 (C6 or C7), 150.06 (C4), 158.78 (C1).

Poly[(1,2-dihydro-1-oxo(2*H*)phthalazine-2,4-diyl)-1,4-phenyleneoxy-1,4-phenylene sulfonyl-1,4-phenylene) (**9b**): as a Representation of Polymer **9** [1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (br d, J = 8.5 Hz, 2 H, H2″), 7.19 (br d, 2 H, H3′), 7.65 (d, J = 7 Hz, 2 H, H2′), 7.79 [within a m, 1 H, H5 (see text)], 7.83 (m, 2 H, H6 and H7), 7.92 (m, 2 H, H3″), 7.98 (m, 2 H, H3‴), 8.01 (m, 2 H, H2‴), 8.57 (br s, 1 H, H8); IR (absorbance at ν_{max}, assignment) 1108 (0.72), 1157 (0.80), 1246 (1.00), 1324 (0.67), 1490 (0.75), 1507 (0.31), 1588 (0.67), 1667 (0.79 C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}(log ϵ): 257 (4.26), 306 (4.02).

1,2-Dihydro-4-(4-hydroxyphenyl)-1-oxo-(2*H*)phthalazine (**5**) [1]

^{1}H NMR (300 MHz, DMSO-d_6) δ 6.91 (d, $J_{2',3'}$ = 7.2 Hz, 2 H, H3′), 7.38 (d, 2 H, H2′), 7.70 (d, $J_{5,6}$ = 7.4 Hz, 1 H, H5), 7.80–7.88 (m, 2 H, H6 and 7), 8.30 (d, $J_{7,8}$ = 7.7 Hz, H8), 9.81 (s, 1 H, O*H*), 12.74 (s, 1 H, N*H*); ^{13}C NMR (75.4 MHz, DMSO-d_6, reference solvent middle line at 39.70 ppm), δ 115.45 (C3′), 125.95 (C4a or C8a), 126.19 (C5 or C8), 126.86 (C5 or C8), 128.10 (C4a or C8a), 129.40 (C1′), 130.80 (C2′), 131.54 (C6 or C7), 133.56 (C6 or C7), 146.63 (C4), 158.25 (C4′ or C1), 159.35 (C4′ or C1).

1,2-Dihydro-4-(4-hydroxyphenyl)-1-oxo-2-phenyl-(2*H*)-phthalazine (**11**)

The keto acid **3** (2.42 g, 0.01 mol) and phenylhydrazine (1.08 g, 0.01 mol) were heated in sulfolane (7 mL) at 110°C for 1.5 hours, precipitating the title compound. The mixture was cooled and water (50 mL) was added. The precipitate was filtered and washed with MeOH (10 mL). The orange precipitate was recrystallized from EtOH obtaining 2.21 g (70%) of the title compound, mp 285–287°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.93 (d, $J_{2'',3''} \approx$ 8.3 Hz, 2 H, H3″), 7.40 (br t, $J \approx$ 8.1 Hz, 1 H, H4′), 7.48 (d within a t, 2 H, H2″), 7.51 (t, 2 H, H3′), 7.67 (d, $J_{2',3'} \approx$ 7.7 Hz, 2 H, H2′), 7.78–7.84 (m, 1 H, H5), 7.90–7.98 (m, 2 H, H6 and H7), 8.42 (d, $J_{7,8}$ = 8.4 Hz, H8), 9.86 (s, 1 H, O*H*); ^{13}C NMR (75.4 MHz, DMSO-d_6, reference solvent middle line at 39.70 ppm), δ 115.48 (C3″), 125.39 (C1″), 126.19 (C2′), 127.10 (C5 and C8), 127.62 (C4′), 128.30 (C4a or C8a), 128.67 (C3′), 128.85 (C4a or C8a), 131.00 (C2″), 132.12 (C6 or C7), 133.91 (C6 or C7), 142.11 (C1′), 146.99 (C4), 158.06 (C4″), 158.53 (C1). MS (EI) 314 (100, M$^+$); HRMS calculated for $C_{20}H_{14}N_2O_2$ 314.1055, found 314.1067.

1,2-Dihydro-4-(4-methoxyphenyl)-1-oxo-2-phenyl-(2*H*)-phthalazine (**12**)

A mixture of compound **11** (0.525 g, 0.00167 mol), K_2CO_3 (0.69 g, 0.0050 mol), Me_2SO_4 (0.315 g, 0.0025 mol), and DMAc (10 mL) was heated under reflux for 12 hours, cooled, and added to H_2O (50 mL). The aqueous solution was extracted with $CHCl_3$ (3 × 10 mL). The organics were combined and evaporated. The liquid residue gave a solid precipitate by treatment with ether. This was filtered and recrystallized from MeOH, mp 145–147°C (80% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.88 (s, 3 H, OMe), 7.04 (d, $J_{2'',3''}$ = 8.6 Hz, 2 H, H3″), 7.22–7.82 (m, 10 H, H5-H7 and H2′-H4′ and H2″), 8.55-8.62 (m, 1 H, H8); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 55.40 (OMe), 114.03, 125.81, 126.88, 127.62 (C4′), 127.38, 127.57, 127.68, 128.66, 128.80, 129.24, 130.81, 131.53, 133.07, 141.98, 147.35, 158.90, 160.35; IR (absorbance, assignment) 1033 (0.24), 1139 (0.20), 1176 (0.38), 1206 (0.12), 1251 (0.72), 1297 (0.19), 1312 (0.22), 1334 (0.43), 1460 (0.14), 1492 (0.23), 1516 (0.50), 1580 (0.18), 1611 (0.33), 1664 (1.00, C=O) cm^{-1}. MS (EI) 328 (100,

M^+); HRMS calculated for $C_{21}H_{16}N_2O_2$, 328.1212; found, 328.1204; UV ($CHCl_3$) λ_{max}(log ϵ): 265 (3.99), 310 (4.01).

4,4′-[Sulfonylbis(4′-phenyleneoxy-4-phenylene)]-bis[1,2-dihydro-1-oxo-2-phenyl-(2*H*)-phthalazine] (**13**)

The mixture of compound **11** (1.57 g, 0.005 mol), bis(4-fluorophenyl)sulfone (0.6356 g, 0.0025 mol), K_2CO_3 (0.380 g, 0.00275 mol), NMP (12.93 g), and toluene (5 mL) was heated at 140°C under nitrogen with azeotropic removal of water for 1.5 hours and then heated at 170–175°C for 2 hours, cooled to 100°C, and added dropwise to water/methanol 1:1 (200 mL) to give a sticky precipitate. This material was filtered, dissolved in acetone adsorbed on silica gel, and chromatographed ($CHCl_3$). After evaporation of the eluant the residue solidifies into a white material. This was dissolved in a minimum of $CHCl_3$ and flooded with 20-fold of petroleum ether to give a white powder, 1.70 g (81%). This powder does not melt but becomes clear in the range of 168–175°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, $J_{2'',3''}$ = 9.0 Hz, 4 H, H2″), 7.20 (d, $J_{2',3'}$ = 8.0 Hz, 4 H, H3′), 7.38 (t, $J_{3''',4'''} \approx$ 7.8 Hz, 2 H, H4‴), 7.49 (t, $J_{2''',3'''} \approx J_{3''',4'''} \approx$ 7.5 Hz, 4 H, H3‴), 7.69 (d, $J_{2',3'}$ = 8.0 Hz, 4 H, H2′), 7.73 (d, $J_{2''',3'''}$ = 7.5 Hz, 4 H, H2‴), 7.78–7.86 (m, 6 H, H5-7), 7.94 (d, $J_{2'',3''}$ = 9.0 Hz, 4 H, H3″), 8.63 (d, $J_{7,8}$ = 6.5 Hz, 2 H, H8); IR (absorbance, assignment): 1109 (0.35), 1480 (0.40), 1170 (0.24), 1245 (1.00), 1296 (0.15), 1330 (0.38), 1489 (0.68), 1508 (0.28), 1587 (0.54), 1665 (0.77, C=O) cm^{-1}. Analysis calculated for $C_{52}H_{34}N_4O_6S$ (842.925): C 74.10, H 4.07, N 6.65. Found: C 72.26, H 4.37, N 6.28. MS (FAB) calculated for 842.9 (M^+); found, 844 (MH^+); UV ($CHCl_3$) λ_{max}(log ϵ): 264 (4.56), 306 (4.32).

2-[(4-Methoxyphenyl)oxomethyl][methylbenzoate] (**14**)

The keto acid **3** (10 g, 0.0413 mol), dimethylsulfate (15.6 g, 0.124 mol), K_2CO_3 (12.5 g, 0.091 mol), and DMAc (40 mL) were heated at 160°C for 4 hours. The mixture was cooled and water (150 mL) was added. The resulting precipitate was filtered, dissolved in $CHCl_3$, and dried over $MgSO_4$. The $CHCl_3$ solution was filtered and evaporated to give an oil which crystallizes on standing. The yield of the title compound is quantitative. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.60 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, OCH_3), 6.86 (d, J = 8.5 Hz, 2 H, H-3′), 7.34 (d, J = 7 Hz, 1 H, H-3), 7.54 (m, 2 H, H-4 and 5), 7.68 (d, J = 8.5 Hz, 2 H, H-2′), 7.99 (d, J = 7.6 Hz, 1 H, H-6); ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 52.10, 55.37, 113.65, 127.55, 128.95, 129.26, 129.98, 130.12, 131.51, 132,22, 141.92, 166.35, 195.70. This compound was not characterized further and used as such below.

1,2-Dihydro-4-(4-methoxyphenyl)-1-oxo-(2*H*)-phthalazine (**15**) [6]

To a solution of **14** (11.2 g, 0.0413 mol) in sulfolane (50 mL) was added hydrazine monohydrate (5 mL), and the solution was heated at 110°C for 1 hour. Then it was poured into water (200 mL) and the resulting precipitate was filtered and dried to give 8.7 g (82% yield) of the title compound, mp 241°C (MeOH): ^{1}H NMR (200 MHz, DMSO-d_6) δ 3.83 (s, 3 H, OCH_3), 7.09 (d, 2 H, H-3′), 7.52 (d, J = 8.5 Hz, 2 H, H-2′), 7.70 (m, 1 H, H-5), 8.32 (m, 2 H, H-6 and 7); MS (EI) *m/e* 252 (16.8), 147 (22.1), 129 (100).

4-Chloro-1-(4-methoxyphenyl)phthalazine (16) [7]

Compound **15** (1 g, 0.00396 mol) and phosphorus oxychloride ($POCl_3$, 3 mL) were heated at reflux temperature in N_2 atmosphere for 30 minutes, poured onto ice (25 g), and the solution was extracted with $CHCl_3$ (3 × 10 mL). The organic layer was combined, dried (Na_2SO_4), filtered, and evaporated to give the title compound (1 g, 95% yield), mp 147°C; ^{1}H NMR (200 MHz, DMSO-d_6), δ 3.87 (s, 3 H, OCH_3), 7.17 (d, J = 8.5 Hz, 2 H, H-3′), 7.68 (d, J = 8.5 Hz, 2 H, H-2′), 8.19–8.04 (m, 3 H, H-5,6,7), 8.33 (m, 1 H, H-8); MS (EI) *m/e* 269 (100), 270 (79.7), 271 (44.5), 272 (26.2).

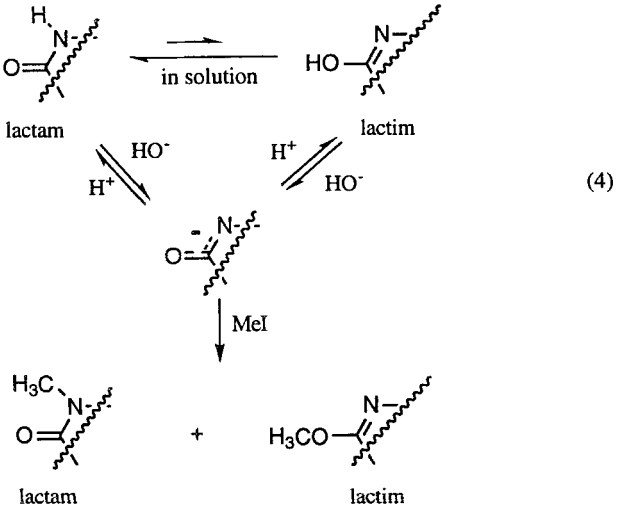
4-(4-Methoxyphenyl)-1-(4-methylphenoxy)phthalazine (17)

To DMAc (8 mL) and toluene (4 mL) was added 4-chloro-1-(4-methoxyphenyl)phthalazine (1 g, 0.0037 mol), *p*-cresol (0.8 g, 0.0074 mol), K_2CO_3 (1 g, 0.074 mol), and the reaction mixture was heated under N_2 with azeotropic removal of H_2O for 1 hour. Some toluene was bled from the Dean–Stark trap until the temperature rose to 160°C where it was maintained for 15 minutes. The reaction mixture was cooled and poured into H_2O (50 mL). The precipitate was filtered and recrystallized to give the title product (0.80 g, 63% yield): mp 192–193°C (MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3 H, $PhCH_3$), 3.87 (s, 3 H, OCH_3), 7.07 (d, J = 8.0 Hz, 2 H, H3′), 7.26 (s, 4 H, H2″ and H3″), 7.69 (d, J = 8.0 Hz, 2 H, H2′), 7.88 (t, 1 H, H6), 7.93 (t, 1 H, H7), 8.09 (d, $J_{5,6}$ = 8.0 Hz, 1 H, H5), 8.49 (d, $J_{7,8}$ = 8.0 Hz, 1 H, H8); IR (absorbance at ν_{max}, assignment) 1032 (0.28), 1175 (0.46), 1210 (0.79), 1250 (1.00), 1365 (0.80), 1387 (0.40), 1513 (0.78), 1610 (0.36) cm^{-1}. MS (EI) 342 (100, M$^+$); HRMS calculated for $C_{22}H_{18}N_2O_2$, 342.1368; found, 342.1362; UV ($CHCl_3$) λ_{max}(log ϵ): 299 (4.02).

RESULTS AND DISCUSSION

Synthesis of Tautomeric Models

The lactam–lactim tautomer problem explored in this report is exemplified in Eq. (4)

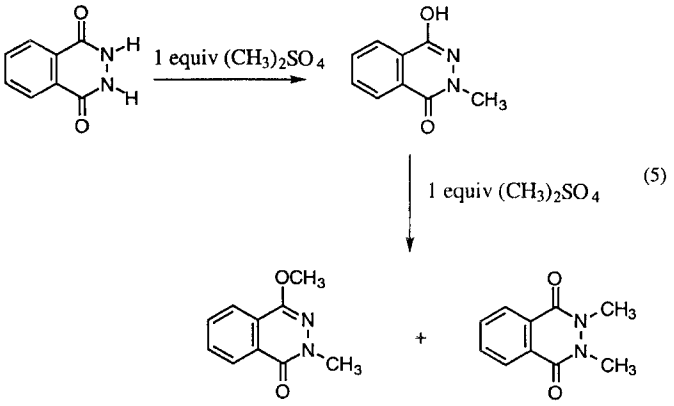


(4)

and is analogous to the keto-enol tautomerism associated with carbonyls. To probe

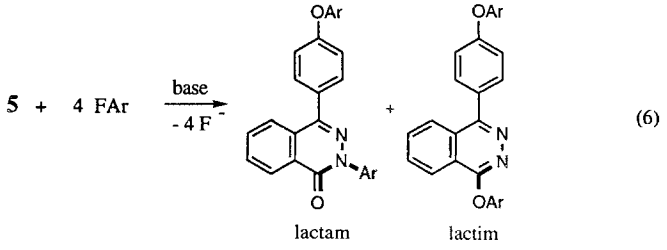
which tautomer is favored under specific conditions for a heterocycle, the chemist often turns to the unambiguous synthesis of model compounds; usually methyl derivatives. Utilizing a specific or a combination of techniques (NMR, UV, IR, etc.), tautomeric ratios have been determined or estimated for many heterocyclics [8]. The model compound serves as the anchor, devoid of prototropic equilibrium (shown in Eq. 4).

The first question we wished to answer was which tautomer was formed or favored for the phthalazine moiety during the polymerization of **5** and **8** reported earlier [1]. For a polymer such as **9** the task is more difficult compared to a monomer because there will be many phthalazine moieties within one polymer chain. The dimethylation of 1,2,3,4-tetrahydro-1,4-phthalazinedione shown in Eq. (5),



from the work of Elvidge and Redman [5], emulates more closely what may be happening during the polymerization of **5**. This example illustrates inter alia that both the lactam and lactim tautomers may form as in species **10** together with the all-lactam alkylated product 1,2,3,4-tetrahydro-2,3-dimethyl-1,4-phthalazinedione (Eq. 5). Compound **10** is also a model for the lactim and lactam functionalities on the phthalazine ring, and useful information has been extracted from it.

A better model reaction for the synthesis of polymer **9** is the arylation of **5** (Eq. 6).

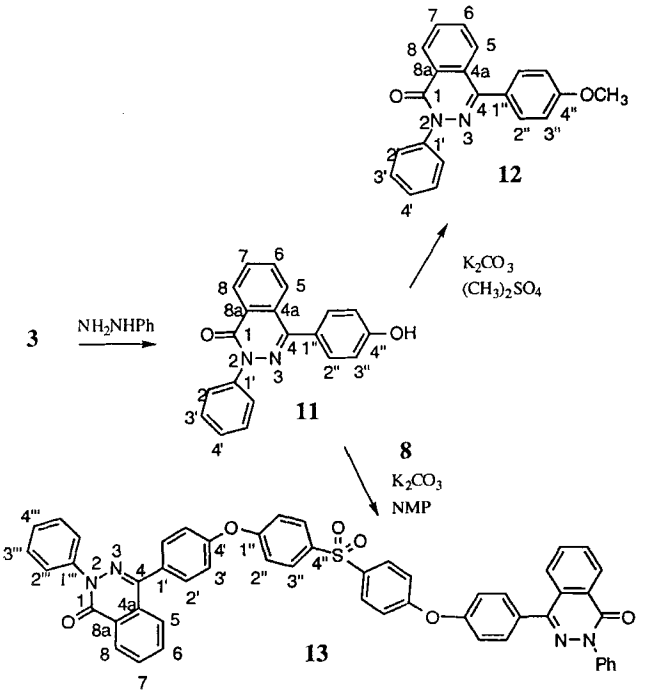


Aside from our reports on the phthalazine-containing polymers, no examples of arylation of phthalazinone derivatives has to our knowledge been reported. The

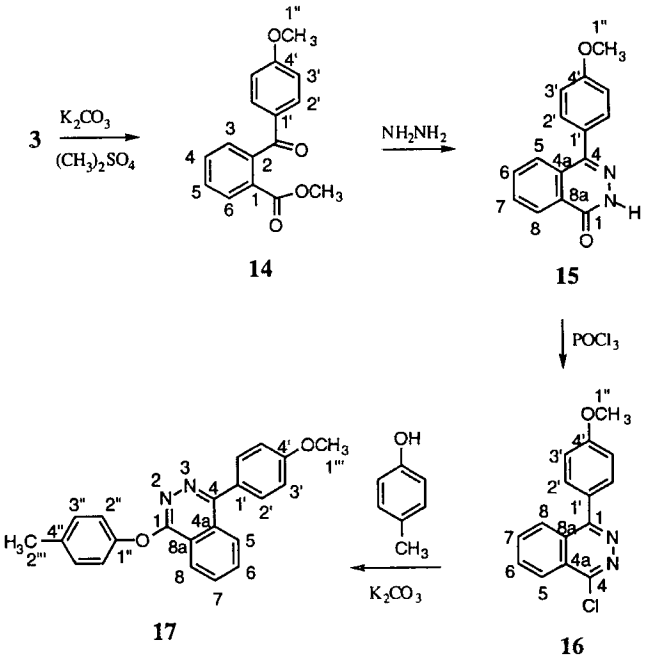
arylation of **5** by displacement of fluorine from an activated arylmonofluoride might produce both the lactam and lactim tautomers (illustrated by boldfaced lines in Eq. 6). We have synthesized the appropriate model compounds in order to unambiguously determine the course of the reaction.

We have synthesized compound **13** as a model for the lactam form **9b** and compound **17** for the lactim form **9a**. Their unambiguous syntheses are shown in Schemes 1 and 2. In Scheme 1 is also shown the synthesis of compound **12** by methylation of **11** with dimethylsulfate in the presence of K_2CO_3, as another model of the lactam tautomer of the phthalazinone, and employed in the assignments and discussion below. Compound **12** also serves to compare how the reduced number of functionalities of the model affect the interpretation of the spectra. Compound **13** is closer in architecture and functionalities to **9b** and in this respect is a better model than **12**.

The second model was made through a more tortuous route shown in Scheme 2. The phenolic hydroxyl group was blocked to prevent reaction at a later stage with the 1-chlorophthalazine derivative. Thus the keto acid **3** was methylated to give the ether ester **14**. This was reacted with hydrazine, as for the preparation of **5** [1], to give **15** which was converted to **16** after warming with $POCl_3$. The reaction of **16** with 4-methylphenol gave **17**, which is a model for the lactim form of the phthalazine.



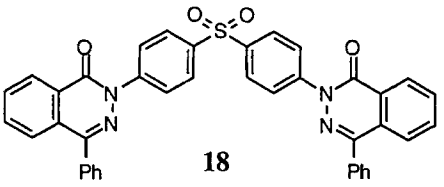
SCHEME 1.



SCHEME 2.

IR and UV

The infrared spectrum in Fig. 1 of the model compound **13** is very similar to that of the polymer. For example, strong C=O stretching frequencies are present at 1665 cm^{-1} for **13** and 1667 cm^{-1} for the polymer, respectively. Imai et al. [9] reported the C=O stretching frequency for 2,2′-sulfonyl-di-1,4-phenylenebis-(4-phenyl-1-phthalazinone) (**18**)



at 1660 cm^{-1}, which compares favorably to **13** and **9**. In Fig. 1 the dotted vertical lines are drawn from the ν_{max} for **9** and these correspond to ν_{max} for both **12** and **13**. On the other hand, the lactim model **17** shows a different pattern with higher wavenumbers for the C=C or C=N absorption at 1610 cm^{-1}. Another reported [5] example is 1,4-dimethoxyphthalazine which has no amidic C=O stretch in the 1600–1700 cm^{-1} range but it does exhibit C=N and C=C stretch in the 1434–1600 cm^{-1} range. The 1,4-dimethoxyphthalazine, like model **17**, is in the lactim form. Figure 1 presents the tautomeric form of the phthalazine moiety in polymer **9** resembling that of **13**, and therefore the polymer is predominantly linked at the 2-aza nitrogen of the phthalazine.

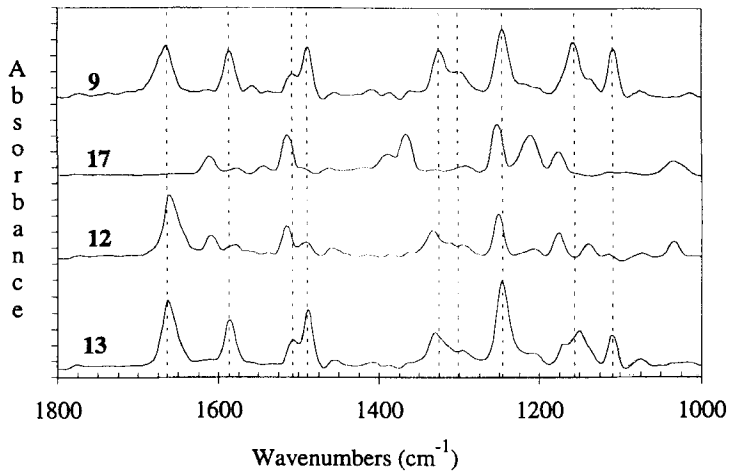


FIG. 1. Selected FT-IR region of polymer **9** and model compounds **12**, **13**, and **17** (~ 0.01 M in $CDCl_3$ in KBr cell ~ 0.05 mm).

The UV spectra for **9**, **12**, **13**, and **17** are shown in Fig. 2. As can be seen, model **13** is very similar to the polymer whose repeat unit molecular weight was taken as 452.48 g/mol. The smaller monomers **12** and **17** contain no diphenylsulfone units, but the phthalazine chromophore is clearly perceptible. The wavelength maxima (λ_{max}) for lactim **17** and lactam **12** are 291 and 310 nm, respectively. The shift in λ_{max} to a higher wavelength for the lactam form is consistent with other lactam–lactim tautomers. For instance, 1-methoxyphthalazine (pH = 7.0 in H_2O at 20°C): $\lambda_{max}(\log \epsilon)$ = 265 (3.74), 291 (3.41), 304 (3.39); and 1,2-dihydro-2-methyl-1-oxo-(2*H*)-phthalazine: $\lambda_{max}(\log \epsilon)$ = 250 (3.79), 284 (3.81), 299 (3.70), 301 (3.54) (pH = 7.0 in H_2O at 20°C) [10]. In ethanol the picture is similar. For instance, for the lactim tautomer 1,4-dimethoxyphthalazine, $\lambda_{max}(\log \epsilon)$ = 245 (5.32), 280

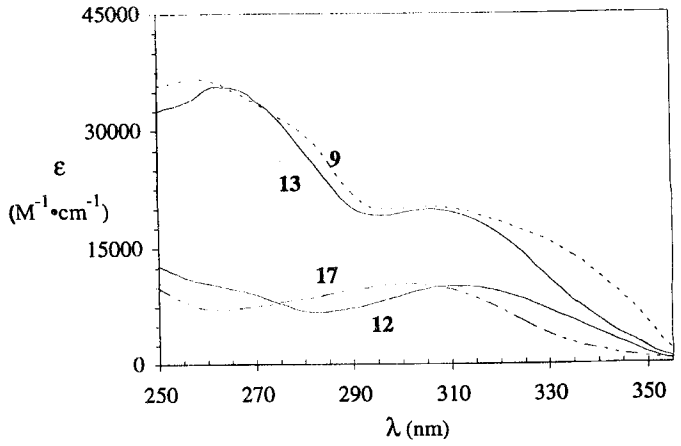


FIG. 2. UV spectra of polymer **9** and model compounds **12**, **13**, and **17** in $CHCl_3$.

(4.75), whereas the lactam 1,2,3,4-tetrahydro-2,3-dimethylphthalazine-1,4-dione has $\lambda_{max}(\log \epsilon) = 302$ (4.84) [5]. The wavelength maximum of the polymer (λ_{max} = 300 nm) falls between that for the lactam and lactim forms of the phthalazines **17** and **12**. The similarity of the UV spectrum of **9** with the dimer **13** and a bathochromic shift for the phthalazine moiety of **9** compared to the lactim **17** or 1,4-dimethoxyphthalazine [5] heavily favors the lactam form of the phthalazine group in the polymer.

The NMR Scheme and Arrangement of Repeat Units

An attempt has been made in this report to resolve the way in which the repeating units of polymer **9** are linked together since the resulting properties of the material are directly related to this. Examples of the literature have shown that ^{13}C-NMR resonances can be influenced by groups separated by as much as four aromatic rings [11]. For the determination of linkages we utilized ^{13}C NMR, which is the most powerful tool for probing the microstructure [12]. We employed the heteronuclear multiple quantum correlation (HMQC) [2, 3] which gives the same information as a heteronuclear correlation (HETCOR), but it is a more sensitive technique and experiments are completed within a shorter period. Its complementary technique, the hetero multiple bond correlation (HMBC) [3, 4, 13, 14], analogous to the COLOC, gives the correlation between a hydrogen (bonded to ^{12}C) and distant carbons (^{13}C) through the much smaller $^{2}J_{C-H}$ and $^{3}J_{C-H}$ couplings [4]. The HMBC experiments finalized the assignments and the connectivities of two model compounds **13** and **17** and the title polymer **9**.

The ^{1}H-NMR spectra for **9**, **13**, and **17** are illustrated in Fig. 3. The depicted assignments were derived from knowledge of carbon and hydrogen resonances of

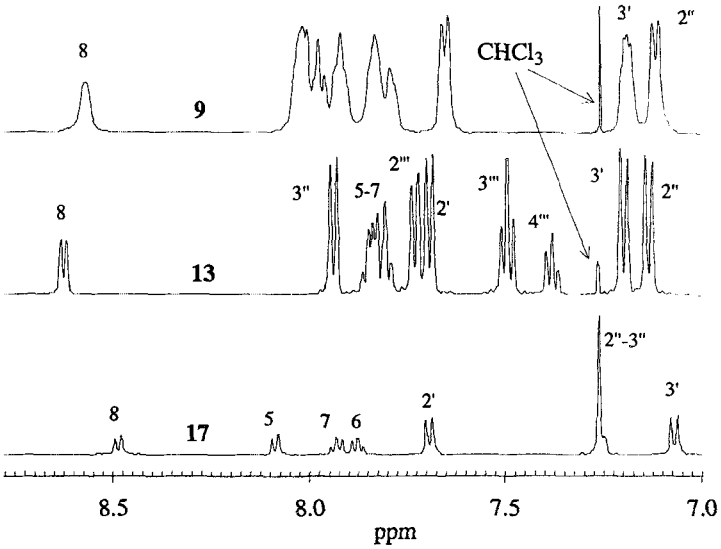


FIG. 3. The 500 MHz ^{1}H-NMR spectra of polymer **9** and models **13** and **17** in $CDCl_3$.

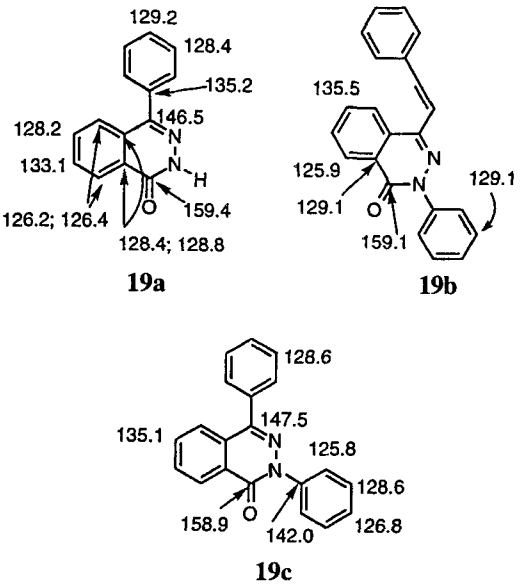


FIG. 4. Structures showing a partial ^{13}C-NMR assignment in ppm values: **19a** [15a], **19b** [15b], **19c** [15c].

model compounds **19** shown in Fig. 4 [15], structure **20** [16] in Fig. 5, from tables [17a] to calculate chemical shifts, and from COSY and HMQC experiments of **9** and **13**.

For model **17** we were unable to find suitable literature data to be able to unambiguously assign 8.09 δ and 8.49 δ to H5 and H8. From the assignment of structures **10** and **20** in Fig. 5, which contain the two similar bonding elements of

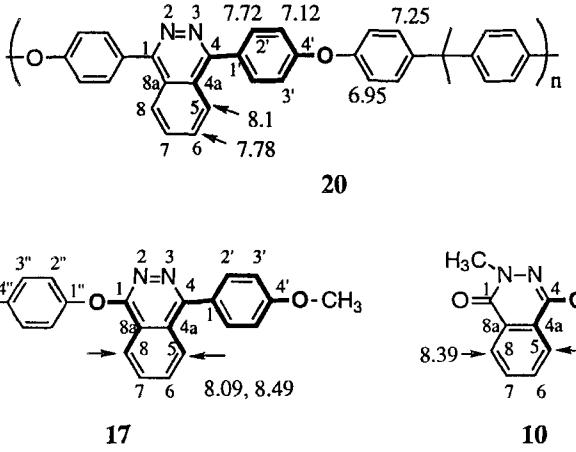


FIG. 5. Structures showing partial ^{1}H-NMR assignments. Boldfaced bonds illustrate the similarity existing in **10** and **20** relative to model **17**. Assignments to polymer **20** are from Ref. 16.

species **17**, illustrated by the boldfaced lines, we conclude that the resonance of H5 in **10** is at 7.95 ppm and should be closer to the lactim arrangement in **17**, and therefore H8 in **17** should resonate at 8.09 ppm. The resonance of H5 is 8.10 ppm in **20**, implying that the resonance of H5 in **17** should also be 8.09 ppm.

This ambiguity was resolved with a difference NOE on **17**. Positions 2′ and 3′ of **17** may be assigned with relative ease by comparison of the cognates of **15** in Fig. 5 and by contrasting the values calculated [17a] for 4-phenoxytoluene and 4-methoxy-[1,1′]biphenyl in Fig. 6, which imply that for **17** the resonances of H2″ and H3″ should be close in chemical shift whereas H2′ and H3′ should be well-separated in chemical shifts. In compound **12**, H2″ and H3″ coincidentally resonate at ~7.26 ppm and are not coupled with any other proton signal in the spectrum. For the difference NOE experiment, protons 2′ may come in closest proximity to H5 by rotation and the latter may, when irradiated to saturation, enhance, through the dipolar coupling, the resonance intensity of H5 on the phthalazine ring. From experiment, irradiation of H2′ enhances the intensity of the signal at 8.09 ppm and that at 7.07 ppm (H3′). Irradiation of the signal at 8.49 ppm enhances but more weakly (longer distance) the signal at ~7.26 ppm (H2″). Thus for **17**, H5 resonates at 8.09 ppm and H8 at 8.49 ppm. Therefore for all the phthalazine derivatives presented here H8 is the most downfield signal and a good starting point to the assignments of the other atoms.

However, because H8 appears to resonate over a relatively wide range (cf. 8.57 ppm for **9**, 8.49 ppm for lactim **17**, 8.63 ppm for lactam **13**, or 8.39 ppm for lactam **10**) and, in general, this range overlaps with the H5–7 resonances of both the lactam and lactim tautomers, ^{1}H NMR is not a good diagnostic tool to distinguish between the lactam and lactim forms.

We have attempted to run ^{15}N-NMR experiments which would be a more direct approach to resolve the problem of the lactim and lactam forms of the phthalazine moiety. However, due to the insensitivity of this technique, we failed to obtain a spectrum within 24 hours.

But from Table 1, and as argued below, C8 (also C1, C4, and C8a) is markedly different in chemical shift for the two different tautomeric forms of the phthalazine in **13** and **17** such that carbon resonances may be used as a probe. For this and to illustrate the linkage of the repeat unit, we elected to assign the carbon chemical shifts of the polymer and model species.

The ^{13}C assignments are listed in Table 1. The phthalazine atoms (namely C1, C4, C8, and C8a) are the key because this group should contain the most pronounced NMR chemical shift changes from one tautomer to the other. At the same time this group should experience minimal magnetic chemical shifts changes from the distal bonding atoms (i.e., carbons not within the phthalazine moiety).

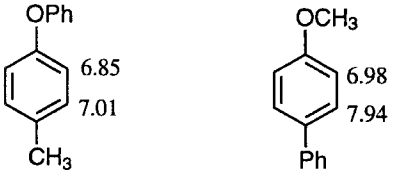


FIG. 6. Structures showing calculated [17a] partial ^{1}H-NMR assignments.

TABLE 1. ^{13}C-NMR Assignments for **9**, **13**, and **17**[a] in ppm

C[b]	**9**[c]	**13**	**17**
1	158.74, 158.82	158.79	160.37[d]
4	147.53, 147.58, 147.68, 147.72	146.56	156.89
4a	128.65, 128.73, 128.75, 128.79, 128.80[e]	128.93[e,f]	128.12
5	126.81, 126.86, 126.92	126.53	126.29
6	133.74, 133.81	133.23	132.28
7	132.14, 132.17, 133.22, 132.24	131.78	131.75
8	127.98	127.86	123.24
8a	128.65, 128.73, 128.75, 128.79, 128.80[e]	128.90[e,f]	120.30
1′	131.05, 131.13, 131.21	131.67	128.71
2′	131.39, 131.40, 131.44	131.47	131.23
3′	120.16	120.15	113.84
4′	156.27, 156.33, 156.38, 156.44	155.99	160.30[d]
1″	161.15, 161.18, 161.19, 161.22, 161.30, 161.32, 161.34, 161.36	161.32	151.21
2″	118.43, 118.45, 118.60	118.27	130.00
3″	129.92, 130.14	129.87	121.33
4″	135.72, 135.74, 135.77, 135.80, 136.07, 136.10, 136.14, 136.17	136.00	134.66
1‴	139.64, 140.21, 140.23	141.86	55.30
2‴	128.16, 128.27	125.76	20.84
3‴	125.98, 126.13	128.74	
4‴	145.66, 145.83	127.73	

[a]Acquired at 125.7 MHz in $CDCl_3$. Assignments are relative to $CDCl_3$ (middle line at 77.0 ppm) made on the basis of HMQC, H-COSY, and HMBC techniques.

[b]Carbon number in structures **9b**, **13**, and **17**. Underlined positions emphasize the critical resonances to distinguish the lactam and lactim tautomers of the phthalazine.

[c]Multiple chemical shifts for carbons are explained in the text.

[d]Assignment of carbons 1 and 4′ may be interchanged.

[e]Carbons 4a and 8a resonate in the same region.

[f]Assignment of carbons 4a and 8a may be interchanged.

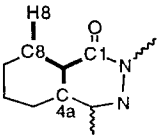
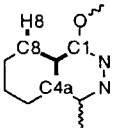
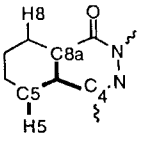
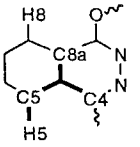
The most downfield atom (H8) is used as a starting point for all the assignments. From the known H8 resonance the HMQC experiments were used to assign the C8 atoms whereas the HMBC experiments lead, inter alia, to the assignment of C1 and C4a. Atom H5 was assigned from H-COSY and its *J*-splitting pattern, which ought to be close to a doublet, and for **17**, H5 was assigned through difference NOE. From the H5 resonance the assignments of C5, C4, and C8a are then possible by HMQC and HMBC experiments. This reasoning is outlined in Scheme 3.

The Carbon Assignments

The ^{13}C-NMR spectrum of polymer **9** is given in Fig. 7. The method for the assignment of these carbons is described below.

Some ^{13}C resonances for substituted phthalazines [15] are given in Fig. 4. These served as the basis for the carbon assignments, because it is possible to build

Highlighting Key Atoms from H8

Relevant Atom to Assign in Polymer	Method (Atom Resonance)	Lactam Model **13**	Lactim Model **17**
C8	HMQC (H8)		
C1, C4a	HMBC (H8)		
H5	H-COSY and *J* pattern (H8)		
C5	HMQC (H5)		
C4, C8a	HMBC (H5)		

SCHEME 3.

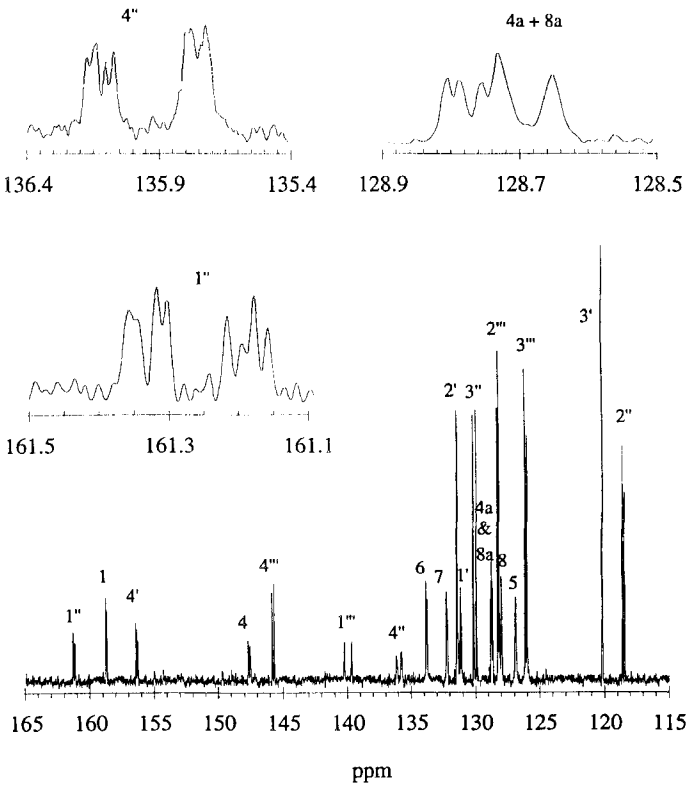


FIG. 7. The 125.7-MHz ^{13}C-NMR spectrum of polymer **9** and selected expansions in $CDCl_3$. Numbers refer to the carbon positions illustrated in **9b**.

on the resonances shown in **19** to obtain other carbon chemical shifts by using listed values in the literature tables [17a] and applying linear additivity relationships [17a, 18]. The resonance assignment for models **13** and **17** were first worked out. These assignments may then be used, in turn, as better estimates to calculate the chemical shifts for **9a** and assign those for **9b**.

For instance, the position of C4′ in polymer **9b** may be obtained as follows. In structure **19a** (Fig. 4), the carbon corresponding to C4′ of **9b** is substituted by a hydrogen and has a resonance at 129.2 ppm. A hypothetical substitution of —OPh [17a] instead of hydrogen on this carbon should shift its resonance to 156.8 ppm [i.e., 129.2 (base) + 27.6 (—OPh)] (cf. Table 1: middle position for C4′ ≈ 156.35 ppm). The chemical shift for C2‴ in polymer **9b** may be computed from the value of 129.1 from structure **19b** by placing a hypothetical $-SO_2CH_3$ substituent [17a] on the ortho carbon, thus giving a resonance of 127.7 ppm [i.e., 129.1 (base) − 1.4 ($-SO_2CH_3$)] for C2‴ (cf. Table 1: middle position for C2‴ ≈ 128.2 ppm). These examples illustrate the substitution groups listed [17a] which we used for estimating specific chemical shifts.

From the previous section, the ^{1}H-NMR spectrum of **9**, and H-COSY of **9** we determine that protons 2″, 3′, and 8 resonate at 7.12, 7.19, and 8.57 δ, respectively. The HMQC defines the 2″, 3′, and 8 carbon positions resonating at 118.4–118.6, 120.2, and 128 ppm, respectively.

To interpret the HMBC traces presented in Fig. 8, one must be reminded that our parameter for the coherence transfer time of 0.05 second ensures that connectivity three bonds away gives a larger response (intensity) than atoms connected two bonds away ($^2J_{C-H}$: 1–4 Hz) [17b], and often the latter effect is not discernible [4]. In addition, the connectivity three bonds away and in a *trans* arrangement ($^3J_{C-H}$ *trans*: 7–10 Hz) is greater than in a *cis* arrangement ($^3J_{C-H}$*cis*: 4–6 Hz) [17b].

As shown above, H8 of **9** resonates at 8.57 δ and C8 has a chemical shift at 127.98 ppm. Focusing on the proton resonance at ~8.59 δ (H8) of the HMBC experiment (plot **a** of Fig. 8), the carbon resonances, which are of lower resolution and may not be numerically identical to those of the individual ^{1}H- or ^{13}C-NMR experiments, at 133.8, 158.8, and 128.7 ppm are correlated through the coupling constant of this hydrogen. The more intense peak resonating at 133.8 ppm is followed by those at 128.7 and 158.8 ppm. Thus C6, which is *trans* to H8, is the atom resonating at 133.8 ppm, and C1 is resonating at 158.8 ppm (lower intensity for *cis* arrangement). The latter assignment may also be derived from other known compounds (see Fig. 4) [15, 17a]. The remaining carbon C4a resonates at 128.7 ppm.

The resonance position of H3′ for **9** at 7.19 δ is estimated from the cognates doublets in the spectra of **13** and **20** resonating at 7.20 and 7.12 δ, respectively. H2′ (7.65 δ) is assigned by a decoupling or H-COSY experiment from the position of H3′ (7.19 δ). From HMQC, C2′ resonates at 131.4 ppm. The HMBC trace at 7.66 δ is shown in Fig. 8, plot **b**. The peak of intermediate intensity at 131.4 ppm corresponds to C2′, the equivalently positioned atom in a *trans* arrangement. The other peak is that for C4′ at 156.3 ppm, recognizable because this is the typical region of resonance for this quaternary carbon [15, 17a]. The peak at 147.7 ppm corresponds to C4 in a *cis* configuration with H2′.

The H5 proton in **9** could not be assigned definitively using H-COSY experiment since H5–7 are very close in chemical shifts in the range 7.79–7.83 δ. The trace

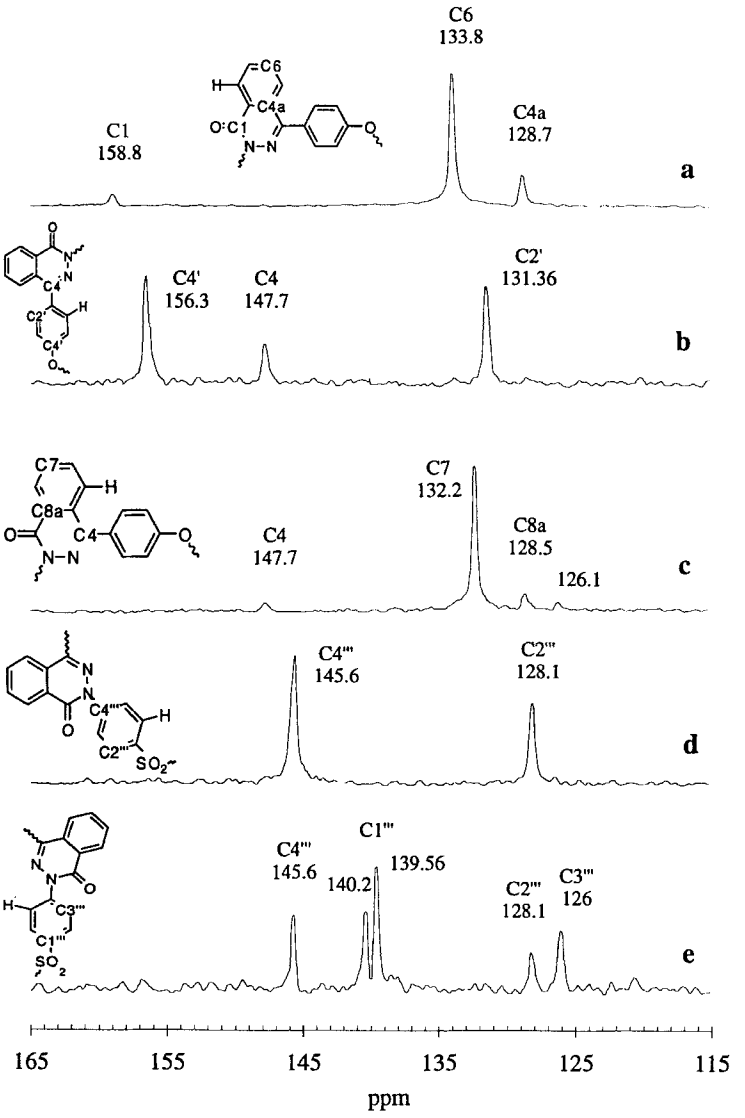


FIG. 8. Partial HMBC traces (^{13}C) for **9** in $CDCl_3$ at different ^1H resonances: **a** at 8.59 δ; **b** at 7.66 δ; **c** 7.80 δ; **d** at 8.05 δ; **e** at 8.01 δ.

denoted as **c** in Fig. 8 is for a hydrogen chemical shift at 7.80 δ. There is a correlation with a peak at 147.7 ppm which, in the explanation of plot **b**, was assigned to the quaternary carbon C4 for polymer **9**. The weak intensity suggests that this carbon is in a *cis* arrangement with the hydrogen at 7.80 δ, which appears to indicate the resonance of H5. The peak at 132.2 ppm therefore likely corresponds to C7 in a *trans* arrangement to H5. The peak at 128.5 ppm then corresponds to the quaternary carbon C8a which is also in a *trans* arrangement to H5. The smaller peak at 126.1 ppm corresponds to C3''' arising because of the overlap of the H3''' resonance with H5 at 8.0 δ in the ^1H-NMR spectrum (see Fig. 3). From the HMQC, C5 resonates at ~126.9 ppm.

From HMQC and HMBC experiments on model compound **13**, C1‴, C2‴, C3‴, and C4‴, which resonate at 141.8, 125.8, 128.7, and 127.7 ppm, were assigned, respectively (see Table 1).

From the assignment of C1‴ and C4‴ in model compound **13**, using additivity we can estimate that C4‴ and C1‴ of **9** resonate at 146.9 and 137.9 ppm, respectively. In Fig. 8, plot **d** for the ^{1}H region of ~8.05 δ is likely the resonance of H2‴ with the quaternary carbon C4‴ at 145.6 ppm in a *trans* arrangement and C2‴ resonating at 128.2 ppm (128.1 ppm in Fig. 8 **d**). The agreement between a calculated value of 146.9 ppm and the spectral value of 145.6 ppm for C4‴ is quite good.

Overlap of resonances of H2‴ and H3‴ in the proton spectrum of **9** gives rise to a mixed HMBC trace of **9** at ~8.01 δ (Fig. 8 **e**). The peaks due to C4‴ and C2‴ in trace **d** repeat. Thus the quaternary carbon C1‴, in a *trans* arrangement to H3‴, shows two resolved lines (see below for a discussion of multiple lines) at 139.6 and 140.2 ppm but due to a single carbon. Carbon 3‴ then resonates at 126.0 ppm.

The elegance of the HMBC experiments is that some carbons may be assigned by convergence from several differently located hydrogens of known chemical shift. This procedure also serves as an internal check where the approach is from two or more hydrogens and also as a starting point to get at the position of more distant atoms of hydrogen or carbon.

The quaternary carbon resonances that cannot be fully resolved are C4a and C8a for both polymer **9** and model **13** due to quasi-overlapping resonances. But the expanded inset for **9** between 128.90 and 128.55 ppm shows two geometrically different patterns, one of three lines and the other of two lines (see Fig. 7), suggesting that there are two different sets of resonances.

From inspection of the data (Table 1) we can see very similar resonance values for the carbons in polymer **9** and model compound **13**, and therefore **9** is more likely represented by the repeating unit **9b** which is closer in structure to **13**.

If part of the polymer had a phthalazine moiety in the lactim form (i.e., like **9a**), the resulting calculated carbon resonances using the additivity relationships and the values for models **13** and **17** are listed in Table 2. Thus for **9** in the form **9a** there should have been resonances for C8a at 120.3 ppm, C4a at 128.1 ppm, C4 at 156.9 ppm, and C8 at 123.2 ppm. Carbons 4 and 8 show the greatest difference in chemi-

TABLE 2. Calculated ^{13}C-NMR Chemical Shifts for **9a**[a] in ppm

C[b]	δ	C[b]	δ	C[b]	δ	C[b]	δ
1	160.4	7	131.8	3′	117.0	4″	136.0
4	156.9	8	123.2	4′	156.5	1‴	137.8
4a	128.1	8a	120.3	1″	161.3	2‴	119.2
5	126.3	1′	129.5	2″	118.3	3‴	130.9
6	132.3	2′	129.9	3″	129.9	4‴	159.3

[a]Assignments are calculated from model compounds **13** and **17** in $CDCl_3$ and using the tabulated chemical shifts [17a].

[b]Atom numbers refer to those depicted in structure **9a**.

cal shift, ~8–9 ppm between the lactam (modeled by **13**) and lactim (modeled by **17**) forms (cf. Table 1) of the phthalazine moiety. All these carbon atoms should have been distinguishable with the NMR techniques described above. The expected ^{13}C-NMR spectrum for the mix of entities **9a** and **9b** possible in **9** should have shown more than 20 sets of lines, but only 19 sets of lines appear in the spectrum (Fig. 7). We conclude that the polymer is linked exclusively at the 2-aza nitrogen atom of the phthalazinone group.

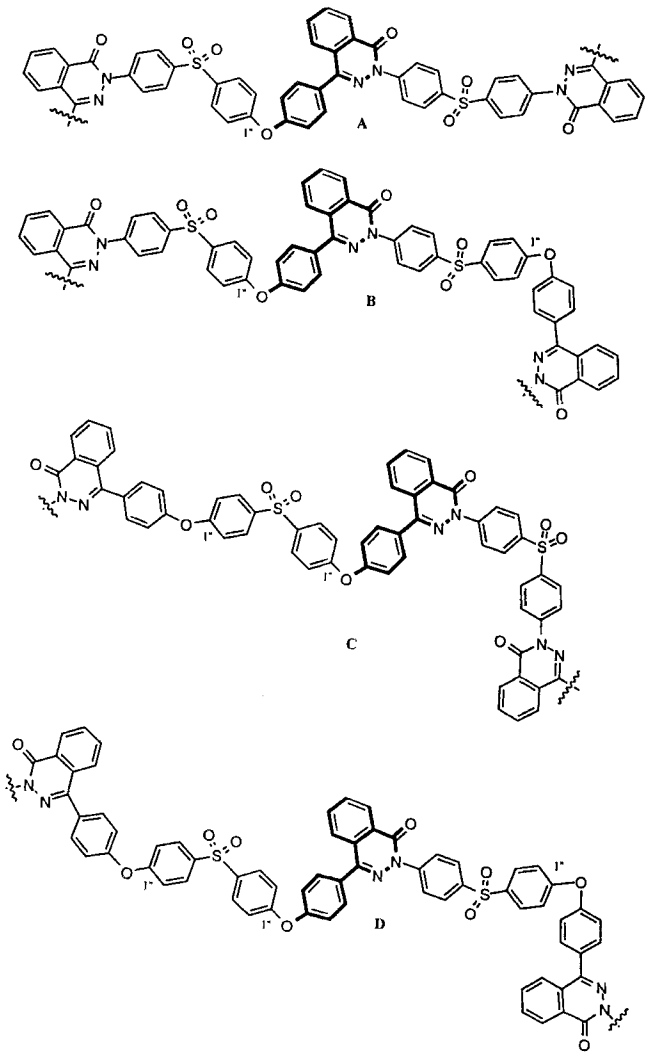
Multiple Lines within a Set

At this point we can conclude that the repeat unit contains the phthalazine unit in the lactam form **9b**, as detected by IR, UV, and NMR. In this section we offer an interpretation of the multiple lines seen in the carbon spectrum (Fig. 7 and Table 1) of polymer **9**.

Because monomer **5** is not symmetric, a further complication is introduced. Scheme 4 attempts to illustrate that a large number of different arrangements of repeating units is possible when considering the lactam form of the phthalazine and asymmetry of **5**. For an internal phthalazine moiety illustrated in boldface in **A–D**, only four arrangements of repeat units may be present with two flanking phthalazine moieties. Thus, any of the atoms in the central phthalazine moiety may show four resonances associated with the **A–D** arrangements. Eight may be possible (see next paragraph) but not observed, probably because these chemical shifts are too close together. Small differences in chemical shift are shown by several carbons in Table 1 or by inspection of Fig. 7. These differences are of the same order of magnitude as those purported to be due to the distant group effect of aromatic ether sulfone copolymers [11]. Multiple resonance lines which have been reported for poly(ether ketone sulfone)s [19] also show differences of the same order of magnitude as listed in Table 1 for **9b**.

There appears to be at least eight resonance lines of carbons 1″ and 4″ (expanded scale views are inset in Fig. 7). This more complex definition is reminiscent of quaternary carbons in some other polymers. However, two research groups [14, 19] have not discussed the observation of multiple lines for some quaternary carbons. The possibility of eight magnetically different atoms may also be explained by **A–D** by labeling the appropriate atoms corresponding to **9b**; see Scheme 4 where eight magnetically different carbons 1″ are labeled as an example. The same can be shown for C4″ and all other carbons labeled in **9b**. Many of these resonance lines are too close to be resolved at 125.7 MHz, so that any number of resonance lines (from 1 to 8) may appear for a specific carbon. Thus the multiple resonance lines associated with some carbons (Table 1 or Fig. 7) may be explained by the way in which the repeating units are linked together and illustrated as **A–D** in Scheme 4.

We reasoned that perhaps variable temperature experiments might show changes in the number or shapes of the resonance lines in the NMR spectra. Surprisingly, at temperatures between 50 and 60°C, polymer **9** precipitates from $CDCl_3$ solution, a phenomenon usually due to lower critical demixing [20]. The solvent 1,1,2,2-tetrachloroethane (TCE) with DMSO-d_6 (10%) dissolves the polymer at temperatures from 20 to 130°C; unfortunately, both the proton and carbon spectra failed to show the same definition as for the $CDCl_3$ spectra at 21°C. Pairs of lines are observed for both C1″ and C4″. Interestingly, the effect of changing the temperature from 21.6 to 130°C in this solvent shows delomorphic variation for



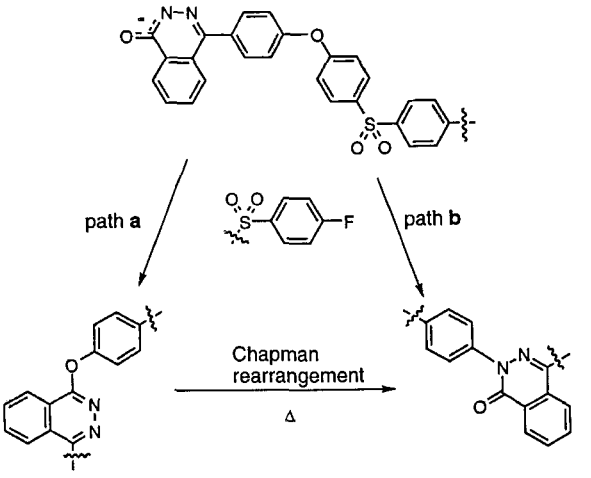
SCHEME 4.

hydrogens 2‴ and 3‴. Smaller variations are also noticeable for the other hydrogens in solution (30 mg of polymer per 1 mL of solvent). More concentrated solutions broaden the peaks, and the demarcations disappear.

Thus, we cannot discriminate between solvent or temperature effect as another probable cause for the manifestation of multiple line resonances (greater than the four for each of **A–D**) in the carbon spectrum of polymer **9** for C1″ and C4″.

MECHANISM

Two pathways for the polymerization reaction are illustrated in Scheme 5. To test to see if the Chapman rearrangement [21] is operative (path **a**), the lactim **17**



SCHEME 5.

(125 mg) was heated in NMP (1 mL) at 160°C in the presence of K_2CO_3 (25 mg) and KF (30 mg) under a nitrogen atmosphere. Some hydrolysis of compound **17** occurs due to the presence of some water in the NMP (the reaction was monitored by reversed phase high performance liquid chromatography); however, **17** and other products persist in the same ratio over 30 hours at 160°C. The lactim is stable in NMP in the absence of water for over 48 hours at 160°C, indicating no rearrangement is taking place. This observation indicates that path **b** is the one that likely operates in the polymerization. We speculate that amide-nitrogen-anion displacement of fluoride takes place, which leads to the thermodynamically more stable lactam form of the phthalazinone.

CONCLUSIONS

There is a very close similarity of the IR spectrum of polymer **9** with that of **13** and less with that of **12** whereas the spectrum of the lactim form **17** is completely different. The UV spectrum of **9** parallels that of **13**, and the NMR chemical shifts for the carbons of **9** and **13** are virtually identical (see Table 1), leading to the conclusion that in **9** the phthalazinone group is found in the lactam form (*N*-aryl linked as in **9b**) with no detectable lactim present (as in **9a**). The multiple lines of similar geometries within the same set (i.e., similar peak height or area) appear to indicate a random arrangement of the repeat units **9b**. In the polymerization reaction of **5** and **8** the aromatic fluoride ion is displaced by an aza-nitrogen anion. To our knowledge, polymer **9** is the first reported material where the polymerization apparently occurs exclusively through aza-nitrogen arylation.

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