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N,N'-Diphenyl-1,4(5)-dimethoxyanthraquinone Diimines: "Butterfly" Inversion of Anthraquinone Diimines

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Model compounds for polyaromatic quinone imines were synthesized and characterized by variable-temperature ^{1}H NMR spectroscopy and X-ray single crystal structure determination. *N,N'*-Diphenyl-1,4(5)-dimethoxyanthraquinone 9,10-diimines were synthesized by condensing 2 equiv of aniline with 1,5-dimethoxyanthraquinone (**15DMAQ**) and 1,4-dimethoxyanthraquinone (**14DMAQ**), respectively, in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (**DABCO**). The X-ray single crystal structure determination of the diimine of **15DMAQ** is reported. The condensation of aniline with anthraquinones results in a buckling of the anthraquinone ring system, giving it a "butterfly" conformation while the diimine of **15DMAQ** has an anti configuration with the *N*-phenyl rings lying above the methoxy substituents. The diimine of **14DMAQ** has a syn configuration, again with these *N*-phenyl rings lying above the methoxy substituents. The symmetrical structural butterfly conformations of the diimines allowed for the observation of a dynamic butterfly inversion by variable-temperature ^{1}H NMR spectroscopy. The energy barriers for the butterfly inversion of *N*-phenyl **15DMAQ** and **14DMAQ** diimines are 9.5 kcal/mol. The implications of the crystal structure and molecular dynamics for the polymeric structures are discussed.

Introduction

We recently reported on the synthesis of a novel family of polymers, namely polyquinone diimines, by the polycondensation reaction of anthraquinones (AQ) with aromatic diamines.[1,2] These pernigraniline base analogs are similar in structure to the fully oxidized forms of undoped polyaniline and may display electrically conducting and optoelectronic properties.[3] Since the physical properties of the polymer are closely related to structure, model compounds were synthesized and fully characterized to give detailed structural information on the corresponding polymers.[4]

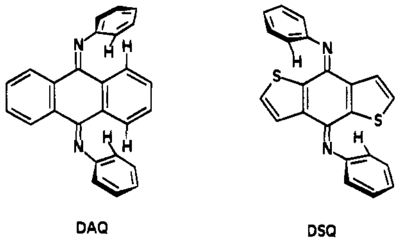

Figure 1. *N,N'*-Diphenylanthraquinone 9,10-diimine (**DAQ**) and dithiophenylbenzoquinone diimine (**DSQ**) drawn as the syn or anti configuration as determined by X-ray crystal structure.

The diimine model compound *N,N'*-diphenylanthraquinone 9,10-diimine (**DAQ**, Figure 1) was previously synthesized and characterized.[5] X-ray single crystal structure determination revealed that the anthracene ring system was not planar but buckled 26° to a "butterfly" conformation. In addition, the *N*-phenyl rings were twisted 54° out of the plane of the AQ ring system. This was believed to occur in part because of steric hindrance of the peri hydrogens of the AQ with ortho hydrogens of the *N*-phenyl substituent as shown in Figure 1. This steric repulsion caused the buckling and resulted in a butterfly conformation. The X-ray crystal structure also revealed that the diimine existed in the syn conformation. Similar butterfly conformations have also been reported for *N,N'*-dicyanoanthraquinone 9,10-diimine.[6]

X-ray single crystal structure determination of heterocyclic quinone diimine derivatives indicated that the steric interactions were eliminated and the quinone ring system remained planar. For example, the *N,N'*-diphenyl diimine of dithiophenylbenzoquinone (DSQ) had a planar central ring system and existed in the anti configuration with the *N*-phenyl rings residing over the sulfur atoms as drawn in Figure 1.[4] The resulting anti diimine model compound proved to be rather insoluble in common organic solvents, and no high polymer of dithiophenylbenzoquinone with aromatic diamines could be obtained, probably because the solubility of this type of system is so low.

The solubility of polymers is a critical factor in both characterization and processing. Therefore, we focused our attention on more soluble polymerizable quinones with anti configurations, such as 1,5-dialkoxyanthraquinones. In this paper, we report on the syntheses and NMR studies of the *N,N'*-diphenyl diimines from 1,5-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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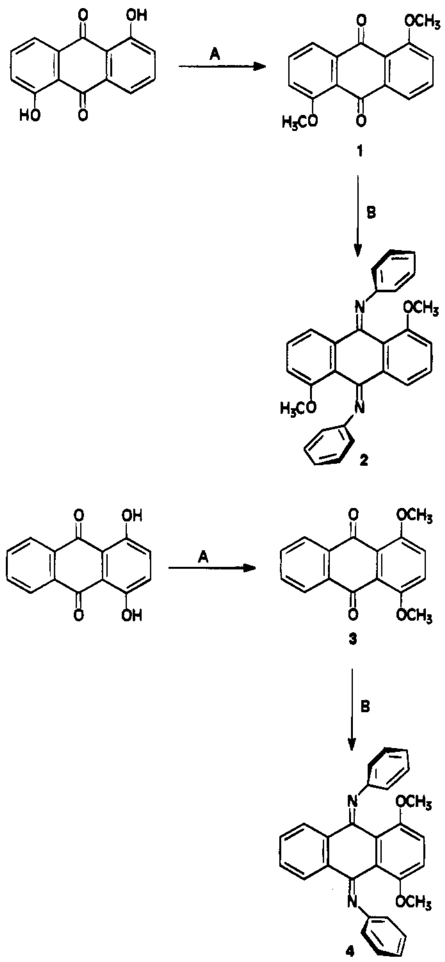
Scheme 1. Synthesis of *N,N'*-Diphenyl-1,5-dimethoxyanthraquinone 9,10-Diimine (2) and *N,N'*-Diphenyl-1,4-dimethoxyanthraquinone 9,10-Diimine (4)[a]



[a] (A) CH_3I, KF, Al_2O_3 (40%); (B) $TiCl_4$, DABCO, 2 equiv of aniline.

dimethoxyanthraquinone and 1,4-dimethoxyanthraquinone and an X-ray crystal structure of *N,N'*-diphenyl-1,5-dimethoxyanthraquinone-9,10-diimine.[14] The implications for polymer structure, dynamics, and solubility are discussed.

Results and Discussion

Synthesis and X-ray Study. 1,5-Dimethoxyanthraquinone (**15DMAQ 1**) was synthesized from 1,5-dihydroxyanthraquinone using slight modifications of a method described by Preston and co-workers.[7] 1,5-Dihydroxyanthraquinone was alkylated using methyl iodide and KF/alumina as a base in good yields. The resulting **15DMAQ 1** was condensed with 2 equiv of aniline in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) in refluxing chlorobenzene to give the *N,N'*-diphenyl diimine model compound **2** in good yield (Scheme 1). Characterization of the diimine **2** by ^{1}H NMR spectroscopy revealed a large 0.95 ppm upfield shift for the methoxy peak compared to that of the starting **15DMAQ 1**. This indicated that the chemical environment about the methoxy substituent had dramatically changed. The spectra suggest that the methoxy substituents lie in the *N*-phenyl ring's shielding region, giving an unexpected anti configuration. The ^{1}H NMR spectra of the starting **15DMAQ** and *N,N'*-diphenyl diimine **2** are shown in Figure 2.

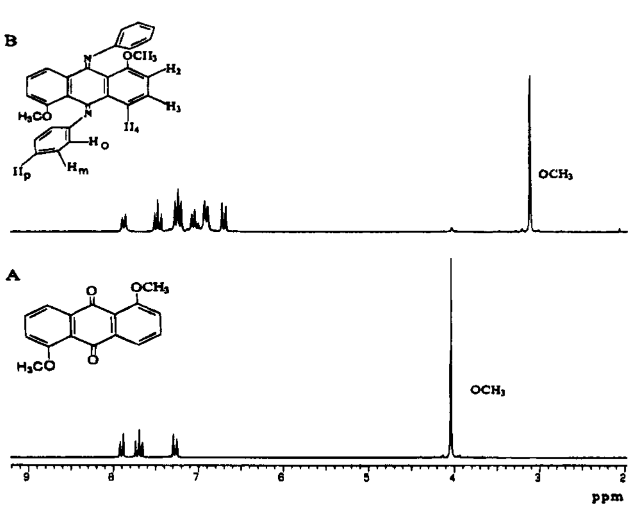


Figure 2. ^{1}H NMR spectra of (A) 1,5-dimethoxyanthraquinone (**1**) and (B) *N,N'*-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (**2**).

The X-ray single crystal structure of **2** confirmed that the proposed anti configuration was correct for the two crystallographically independent molecules (Figure 3). This is contrary to the syn conformation of the parent **DAQ** and to what was expected on the basis of steric reasoning. We postulate that repulsive interactions between the lone pair of electrons on the nitrogen and the lone pairs of electrons on the oxygen cause the *N*-phenyl ring to lie above the methoxy substituent. Thus, the *N,N'*-diphenyl diimine **2** exists in the anti configuration with the methoxy substituent located in the *N*-phenyl ring's shielding region, resulting in the large upfield shift observed in the NMR spectrum. The internuclear distance between the plane of the *N*-phenyl ring and the methoxy oxygen is 2.6 Å in the solid state.

The added steric interaction of the methoxy substituent with the *N*-phenyl ring results in an even larger buckling effect compared to that of the unsubstituted **DAQ**. The end-on-view of the crystal structure in Figure 3 reveals that the central anthraquinone ring system is buckled 34°. This is 8° larger than that of **DAQ** and 15° larger than that of the *N,N'*-dicyanoimine anthraquinones. The degree of buckling is consistent with steric arguments and increases with the size of the imine substituent and the AQ substituent in the peri position.[6,8] As in **DAQ**, the *N*-phenyl rings are twisted 54° out of the plane of the AQ ring system.

To confirm that this conformation was not an anomaly with *N*-phenyl diimines of **15DMAQ 1**, we investigated the *N,N'*-diphenyl diimine from 1,4-dimethoxyanthraquinone (**14DMAQ**) **3** (Scheme 1). **14DMAQ 3** was synthesized from 1,4-dihydroxyanthraquinone in a manner similar to that of **15DMAQ 1** using KF/ alumina and methyl iodide. **14DMAQ 3** was then condensed with 2 equiv of aniline using the standard $TiCl_4$/DABCO conditions previously developed to give the model compound *N,N'*-diphenyl-1,4-dimethoxyanthraquinone 9,10-diimine (**4**). ^{1}H NMR characterization revealed a large 0.99 ppm

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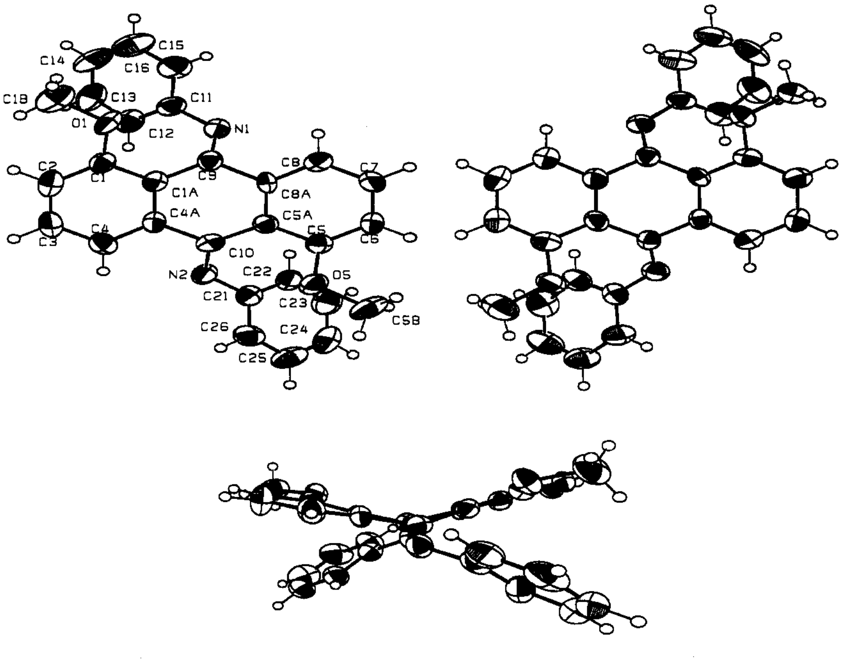

Figure 3. X-ray crystal structure of *N,N'*-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (**2**). The two independent molecules are plotted above as mirror images. The end-on-view of one molecule is given below to illustrate the buckling of the anthraquinone ring system.

upfield shift of the methoxy peak of **4** compared to that of the starting **14DMAQ 3** similar to the shift observed for the *N,N'*-diphenyl diimine **2** of **15DMAQ 1**. This confirmed that **4** existed as the syn stereoisomer with the *N*-phenyl rings located above the methoxy substituent. No suitable crystals of **4** could be grown for an X-ray study. Both model *N,N'*-diphenyl diimines **2** and **4** show that a strong interaction exists between the *N*-phenyl imine and the methoxy substituents, as shown by the large upfield shift of the methoxy signal compared to that of the parent quinoid compounds.

Variable-Temperature NMR Studies. The ^{1}H NMR spectrum of the unsubstituted model compound **DAQ** is complicated and difficult to interpret. The aromatic region is blurred with a combination of peaks from the AQ ring and the *N*-phenyl ring protons. This is not what would be expected if only the syn isomer were present as in the crystal structure. The ambient-temperature ^{13}C solution spectrum of **DAQ** is also complex with multiple peaks occurring for the AQ and phenyl ring carbons. We postulate that these complex spectra are due to both syn and anti conformers being present in solution. When **DAQ** was heated to 170 °C, ^{1}H NMR spectroscopy showed that the previously complex AQ ring proton signals coalesced to two peaks, very similar to the spectrum of AQ itself.[9] This can be assumed to be due to the syn/anti isomerization occurring quickly on the NMR time scale at these temperatures.

In contrast to the model compound **DAQ**, a variable-temperature NMR study of *N,N'*-diphenyl diimine **2** up to 180 °C showed no evidence for the syn stereoisomer, indicating that the molecule prefers the anti configuration by at least several kilocalories per mole. This attests to the strength of the repulsive interaction between the lone pair electrons on the nitrogen and the lone pairs of electrons on the oxygen in *N,N'*-diphenyl diimine **2** described above.

As shown in Figure 2, the spectrum of **2** at ambient temperature is much more straightforward and interpretable . The symmetrical structure of **2** makes the ortho (H_o), meta (H_m), and para (H_p) protons of the *N*-phenyl ring discernible along with H_2, H_3, and H_4 of the AQ ring system. The expanded aromatic regions of **2** at varying temperatures with peak integration for the spectra from 25 to −90 °C are shown in Figure 4. Low-temperature NMR revealed interesting molecular dynamics. As the temperature is lowered, the ortho (H_o) and meta (H_m) proton signals of the *N*-phenyl ring begin to broaden until they proceed through coalescence at −50 °C. At this temperature, the ortho proton peaks are completely averaged into the base line while the meta protons have become very broadened. At −70 °C, two peaks start to appear out of the base line at δ 6.4 and 7.3. The spectrum taken at −90 °C shows that this peak at δ 7.3 is now H_o and the peak at δ 6.4 is H_o'. The meta proton signals have now also split into two sets of peaks (H_m and H_m') which overlap H_p and H_3. Integration of the peak areas confirmed these assignments. Thus, the ortho and meta peaks exist in different chemical environments at lowered temperatures but are averaged at ambient temperatures, while the para proton remains in the same chemical environment at all temperatures. The mechanism most consistent with these NMR data is a butterfly flutter or inversion of the AQ system accompanying rotation about the N_1-C_{11} and N_2-C_{21} bonds. This mechanism is supported by identification of the two conformers of **2** in the crystal structure.

Interested in whether this was a general phenomenon with diimines of anthraquinones, we investigated **DAQ** and *N,N'*-diphenyl diimine **4** by low-temperature ^{1}H NMR spectroscopy. *N,N'*-Diphenyl diimine **4** exhibited behavior similar to that of **2** as the temperature was decreased. The spectra for **4** are nearly identical to those of **2** at all temperatures; the only difference is the overlap of H_m with H_6 at −90 °C due to the different substitution pattern on the AQ ring. The energy barriers for the butterfly inversion were calculated from the Eyring

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[9] Boone, H. W.; Hall, H. K., Jr. Unpublished results.

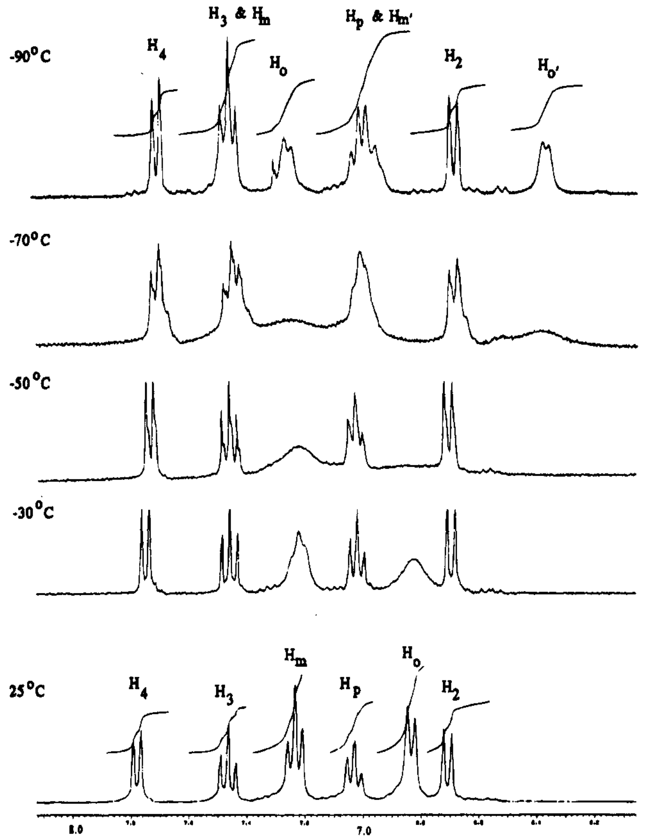

Figure 4. Variable-temperature ^1H NMR spectra of *N,N'*-diphenyl-1,5-dimethoxyanthraquinone 9,10-diimine (**2**) in CD_2Cl_2.

equation (eq 1) to be 9.5 kcal/mol for both **2** and **4**.[10] **DAQ**

$$K = \kappa k_b \frac{T}{h} \exp(-\Delta G/RT) \qquad (1)$$

was investigated at temperatures as low as −95 °C with no evidence for slowing of dynamic motion. We believe that the butterfly inversion is indeed occurring with **DAQ** and is a general phenomenon with all *N*-phenyl imines of AQ, but our temperature range is limited by the solubility of our compound and the freezing point of the NMR solvent (CD_2Cl_2). Thus, we could not measure the much lower barrier in the less sterically hindered **DAQ**.

Conclusion

The synthesis, structure, and molecular dynamics of novel diimines of 1,4- and 1,5-dimethoxy-substituted anthraquinones are reported. Both model compounds display the phenomenon of the *N*-phenyl ring lying above the methoxy substituent independent of the temperature. This indicates that a polyquinone imine formed from 1,5-dialkoxy-substituted anthraquinones will have regular anti repeat units that could possibly crystallize. The butterfly inversion of the model compounds indicates that the polymers will not be rigid rods but in dynamic motion in solution, thus enhancing their solubility. The added bulk of the methoxy substituent raises the energy barrier for a butterfly inversion and therefore decreases the solubility compared to that of the parent **DAQ**. In order to obtain polyquinone imines with anti configurations, longer alkoxy chains will be needed to overcome the decrease in solubility. This work is currently under investigation.

Experimental Section

General. NMR spectra were recorded on a Varian Unity 300 NMR spectrometer at 300 MHz. Temperatures were calibrated with 100% methanol. IR spectra were obtained on a Perkin-Elmer 960 infrared spectrophotometer. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Melting points were obtained on a Thomas-Hoover melting point apparatus and are corrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained by direct insertion probe at the University of Arizona Department of Chemistry mass spectrometry facility on a Hewlett-Packard 5988A apparatus with an RTE-6 data system at a source temperature of 200 °C.

Chlorobenzene was dried and distilled over P_2O_5 prior to use. DABCO was dried by azeotropic distillation of water with benzene. The benzene was removed *in vacuo*, followed by recrystallization from anhydrous ether. Aniline was distilled over potassium hydroxide prior to use. All other reagents were used as received from Aldrich.

1,5-Dimethoxyanthraquinone (1). Methyl iodide (33.2 mmol) was added dropwise to a stirred mixture of 1,5-dihydroxyanthraquinone (8.3 mmol) and potassium fluoride on alumina (40%, 166 mmol) in DMSO at 35 °C for 10 h.[11] The product was precipitated from cold water, isolated by filtration, and washed with 200 mL of water. Column chromatography on silica gel using $CHCl_3$ as eluent gave the product as a bright yellow solid: yield 71.4%; mp 236−237 °C (lit.[12] 236−237 °C); ^1H NMR δ (CD_2Cl_2, 25 °C) 4.00 (s, 6H), 7.3 (d, 2H), 7.7 (t, 2H), 7.91 (d, 2H); IR (KBr) 1661 (C=O) cm^{-1}.

***N,N'*-Diphenyl-1,5-dimethoxyanthraquinone 9,10-Diimine (2).** Aniline (2.4 mmol) and DABCO were dissolved in 6 mL of chlorobenzene at 90 °C. Titanium tetrachloride (1.8 mmol) in 3 mL of chlorobenzene was added dropwise over 15 min. The addition funnel was rinsed with 3 mL of chlorobenzene. **15DMAQ 1** (1.2 mmol) was added all at once via a powder addition funnel; the funnel was rinsed with 2 mL of chlorobenzene. The reaction mixture was heated in an oil bath at 125 °C for 24 h and then cooled to room temperature. All precipitates were filtered off, and the filter cake was rinsed with 200 mL of hot chlorobenzene. The solvent was removed *in vacuo*. Recrystallization from ethyl acetate gave the product as a bright yellow solid: yield 96.1%; mp 227−230 °C; ^1H NMR (CD_2Cl_2, 25 °C) δ 3.05 (s, 6H), 6.7 (d, 2H), 6.9 (d, 4H), 7.02 (t, 2H), 7.24 (t, 4H), 7.47 (t, 2H), 7.79 (dd, 2H); IR (KBr) 3009, 2932, 2835, 1615 (C=N), 1579 (C=C), 1465, 1260, 1103, 770 cm^{-1}; MS *m/z* (relative intensity) 418 (M^+), 326 (100), 297, 248, 221, 77, 51; UV−vis λ_{max} ($CHCl_3$) 368 nm, $\epsilon = 15\,133\ M^{-1}\ cm^{-1}$. Anal. Calcd for $C_{28}H_{22}O_2N_2$: C, 80.35; H, 5.30; N, 6.69. Found: C, 80.68; H, 5.36; N, 6.61.

1,4-Dimethoxyanthraquinone (3). Methyl iodide (33.2 mmol) was added dropwise to a stirring mixture of 1,4-dihydroxyanthraquinone (8.3 mmol) and potassium fluoride on alumina (40%, 166 mmol) in DMSO at 35 °C for 10 h. The product was extracted into CH_2Cl_2 and washed with 3 × 200 mL of water. The aqueous layer was back extracted with 3 × 30 mL of CH_2Cl_2. Column chromatography on neutral alumina using 90:10 hexane: EtOAc as eluent gave the product as a dull yellow solid: yield 58.5%; mp 168−170 °C (lit.[13] 170−171 °C); ^1H NMR (CD_2Cl_2) δ 3.99 (s, 6H), 7.34 (s, 2H), 7.72 (dd, 2H), 8.16 (dd, 2H); IR (KBr) 1668 (C=O) cm^{-1}.

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[14] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

***N,N'*-Diphenyl-1,4-dimethoxyanthraquinone 9,10-Diimine (4).** The method described for **2** was used to obtain **4**: yield 78.4%; mp 262–265 °C; ^{1}H NMR (CD_2Cl_2 , 25 °C) δ 3.0 (s, 6H), 6.66 (s, 2H), 6.9 (d, 4H) 7.02 (t, 2H), 7.3 (t, 4H), 7.53 (t, 2H), 8.16 (d, 2H); IR (KBr) 3001, 2967, 2835, 1615 (C=N), 1577 (C=C), 1483, 1267, 769 cm^{-1}; MS *m/z* (relative intensity) 418 (M$^+$), 326 (100), 297, 248, 221, 77, 51; UV–vis λ_{max} ($CHCl_3$) 372 nm, ϵ = 8350 M^{-1} cm^{-1}. Anal. Calcd for $C_{28}H_{22}O_2N_2$: C, 80.35; H, 5.30; N, 6.69. Found: C, 79.47; H, 5.23; N, 6.38.

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Supporting Information Available: Low-temperature ^{1}H NMR spectra for **4** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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