Synthesis and Structure of Heterocyclic Quinone Arylimines as Model Compounds for Polyaromatic Quinone Imines

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ABSTRACT: The structures of model compounds for the polyaromatic quinone diimine polymers were determined. These polymers were obtained by polycondensation of tricyclic quinones with aromatic diamines in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane. The *N*-phenyldiimine and monoimine derivatives of the following quinones were synthesized: naphthoquinone, 2-methyl- and 2-*tert*-butyloxazolonaphthoquinone, 2,2′-dimethylbis(oxazolo)benzoquinone, and bisthiophenobenzoquinone. X-ray single-crystal structure determinations are reported for the following derivatives: *N*,*N*′-bis(*p*-fluorophenyl)naphthoquinone 1,4-diimine, *N*-phenyl-2-*tert*-butylnaphtho[2,3-*d*]oxazole-4,9-dione 4-imine and 9-imine, *N*-(*p*-fluorophenyl)-2-*tert*-butylnaphtho[2,3-*d*]oxazole-9-one 4-imine, *N*-phenyl-2-isobutylnaphtho[2,3-*d*]oxazole-9-one 4-imine, and *N*,*N*′-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione diimine. The following common features are observed for these structures: the central ring systems are planar in contrast to the anthraquinone diimine derivatives in which the central ring system is buckled, the *N*-phenyl ring is twisted out of the plane of the central ring system, and the *N*-phenyl rings are twisted toward the ring with the heteroatom and away from the C−H group on the adjacent ring. Molecular modeling calculations are found to be in agreement with the X-ray structures. The implications of the crystal structures of the model compounds for the polymeric structures are discussed.

Introduction

We recently synthesized a series of poly(quinone diimines) by the polycondensation reaction of anthraquinone with aromatic diamines.[1,2] These polymers have a pernigraniline base backbone (fully oxidized form of undoped polyaniline) and thus have possible conducting and optoelectronic properties, but this requires coplanarity, at least to within 15°.[3] The coplanarity of these polymers is in doubt, based on the known X-ray single-crystal structure of the model compound of the anthraquinone polymers, namely, *N*,*N*′-diphenylanthraquinone 9,10-diimine (DAQ).[4] The *N*-phenyl rings in this structure are twisted out of the plane defined by anthraquinone, but, more importantly, the anthraquinone ring system itself is buckled in a butterfly form.

We also embarked on a study of the polycondensation reactions of heterocyclic benzoquinone derivatives with aromatic diamines.[2] These monomers were selected to eliminate the steric hindrance of the substituents on the imine nitrogen and the *peri*-hydrogens of the anthraquinone ring system. In this paper we will describe the synthesis of the model compounds for these polymers and their X-ray single-crystal structure in the cases where suitable single crystals could be obtained. In particular, we will be looking at naphthoquinone, oxazolonaphthoquinone, and bis(oxazolo)- and bisthiophenobenzoquinone derivatives. Molecular modeling calculations are also performed to try to attain a certain level of predictability in these systems. We will evaluate the relationship between the chemical structure and the conformation in the crystalline form and the implications of these structural properties on the polymer structure and properties.

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Results and Discussion

Syntheses. Quinone Syntheses (Scheme 1). The quinones, which will be derivatized to the diimines, are the following: naphthoquinone, which is commercially available, several oxazolonaphthoquinones **2a**−**c**, bis(oxazolo)benzoquinone **4**, and bisthiophenobenzoquinone (**5**).

The precursors to the oxazole-containing quinones, 2-(acylamino)-3-hydroxy-1,4-naphthoquinone (**1a**−**c**) and 2,5-bis(acylamino)-3,6-dihydroxy-1,4-benzoquinone (**3**), were prepared according to literature procedures,[5,6] starting from the readily available 2,3-dichloronaphthoquinone and chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone), respectively. Both reaction sequences proceed parallel, as shown in Scheme 1. Amination of one chlorine, followed by *N*-acylation and by amination of the second chlorine, and finally hydrolysis of this amine to a hydroxy substituent lead to the desired precursors **1a**−**c** and **3**. 2-Methyloxazolonaphthoquinone (**2a**) and 2,6-dimethylbis(oxazolo)benzoquinone (**4**) were easily formed by dehydration of **1** and **3** with acetic anhydride. The dehydration of 2-(*tert*-butylacylamino)-3-hydroxy-1,4-naphthoquinone (**1b**) to form the oxazole ring was first attempted with acetic anhydride, but amide interchange took place concomitant with the heterocycle ring formation, resulting in the isolation of methyloxazolonaphthoquinone (**2a**). The *C*-*tert*-butyl derivative **2b** and the *C*-iso-butyl derivative **2c** could only be obtained in fairly good yield when a mixture of phosphorus pentoxide and triethylamine was used as the dehydrating agent. We did not succeed in obtaining the 2,6-di-*tert*-butylbis(oxazolo)benzoquinone derivative due to the same amide interchange during the dehydration reaction, which always led back to the dimethyl derivative **4**. Other dehydrating agents proved unsuccessful.

The synthesis of bisthiophenobenzoquinone (**5**) was reported via a tandem-directed metalation starting from

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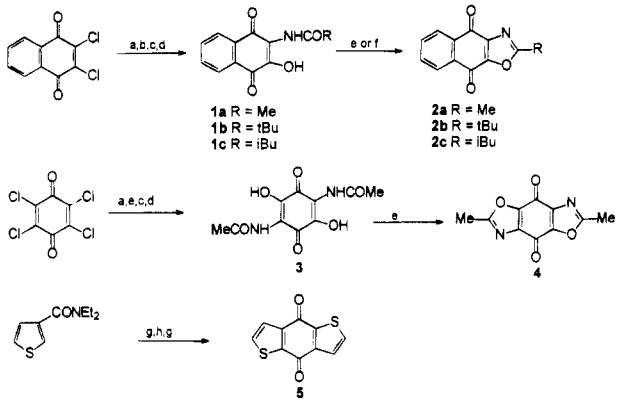
Scheme 1



a: NH_4OH, 95% EtOH, b: $(RCO)_2O$, H^+, c: $HNEt_2$, Et_3N, 95% EtOH, d: 2N HCl, e: $(MeCO)_2O$, f: P_2O_5, Et_3N, g: sec-BuLi, h: thiophene-3-carboxaldehyde

N,N-diethylthiophene-3-carboxamide.[7] In this procedure, the starting thiophenecarboxamide is treated with *s*-BuLi/TMEDA in THF, after which 3-thiophenecarboxaldehyde and a second equivalent of *s*-BuLi are added. The product **5** is obtained after acidification and air oxidation.

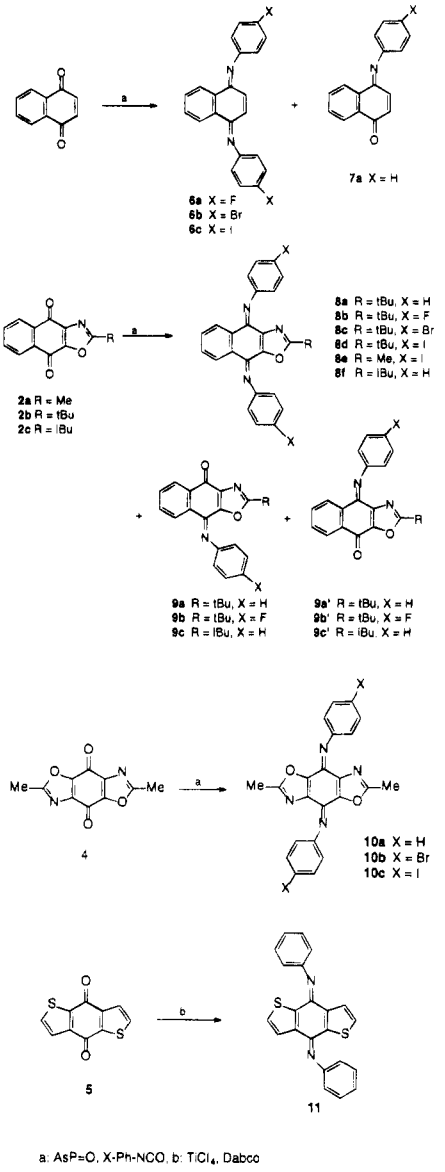
Imine Formation (Scheme 2). Numerous catalysts have been reported for the imine formation between amines and ketones. The most common are Lewis or protonic acids such as *p*-toluenesulfonic acid, aluminum trichloride, and titanium tetrachloride, but these failed to give the desired diimines in satisfactory yield. Quinonoid carbonyl groups are much less reactive toward amines than aliphatic ketones due to the conjugation. In our previous work, the anthraquinone diimine model compound was synthesized, but only in low yield, using $AlCl_3$ as a Lewis acid catalyst.[4]

Classical Wittig chemistry using phosphinimines on naphthoquinone led exclusively to the monoimine derivatives **7**. Extended conjugation by derivatization of the first carbonyl group is thought to reduce the reactivity of the second carbonyl group. For the other quinones, no diimine formation could be accomplished using the phosphinimines. The only exception was for 2-isobutyloxazolonaphthoquinone (**2c**), in which case the desired *N,N'*-diphenyldiimine **8f** was obtained in 50% yield using *N*-phenyltriphenylphosphinimine.

The diimine formation for naphthoquinone was achieved through the Wittig addition of triphenylarsinimines to the carbonyl functionality according to a method developed by Froyen.[8] *N*-Aryltriphenylarsinimines, which are readily formed from triphenylarsine oxide and arylisocyanates, were reactive enough to convert the quinonoid carbonyls to the corresponding imines. The yields were optimum when a 0.5 equiv of triphenylarsine oxide was used compared to the carbonyl groups. The yields greatly varied depending on the quinone derivative and the para-substitution of the *N*-aryltriphenylarsinimine. For example, the reaction of naphthoquinone with *N*-phenyltriphenylarsinimine led only to deep red tars. The ionic contribution to the arsinimine was reduced by using para-substituents with increasing σ_p values[9] (H, F, Br, I), and indeed the yields increased from 0 to 6, 29, and 36%, respectively (**6a–c**).

For the diimine formation of the oxazolonaphthoquinone derivatives **2a–b** and dimethylbis(oxazolo)benzoquinone (**4**), the Froyen reaction using triarylarsinimines was also utilized. The diimines **8a–f** and **10a–c** were very soluble, independent of the substitution. They even dissolved in hydrocarbons, such as pentane, hexane, and cyclohexane. Useful yields of the isomeric monoimines **9a–a'** and **9b–b'** were obtained along with the respective diimines **8a** and **8b** and could be isolated by means of column chromatography. In the case of **9a–a'**, the mixture could be resolved, the two isomers separated, and their respective structures assigned by single-crystal X-ray analysis (see below).

Scheme 2



a: AsP=O, X-Ph-NCO, b: $TiCl_4$, Dabco

Because the Froyen reaction was not satisfactory for the polymerization (see the preceding paper[2]), several Lewis acids and bases were reevaluated as to their ability to catalyze the imine formation of these quinone derivatives in different reaction conditions.[10] The Lewis acids included $SnCl_4$, $AlCl_3$, alkylaluminum chlorides, and $TiCl_4$. Several amines were also investigated, namely, triethylamine, ethyldiisopropylamine, DBN, DBU, and Dabco (1,4-diazabicyclo[2.2.2]octane), and these reactions were run in a series of solvents, including benzene, toluene, and chloro- and dichlorobenzene. The reaction conditions were optimized for the reaction of anthraquinone with aniline. $TiCl_4$ in chloro- or dichlorobenzene gave quantitative yields, and the use of Dabco turned out to be crucial as no black side products were formed with this base.[2] For bisthiophenobenzoquinone (**5**), the *N,N'*-diphenyldiimine **11** was

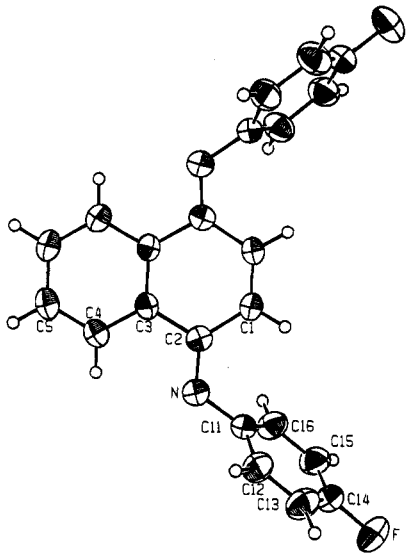


Figure 1. X-ray crystal structure of *N,N'*-bis(*p*-fluorophenyl)-naphthoquinone 1,4-diimine (**6a**).

synthesized using aniline, $TiCl_4$, and Dabco in chlorobenzene at reflux. The yield was quantitative, and this diimine too is very soluble. Only one isomer was obtained, as shown by NMR and by X-ray analysis (see below).

X-ray Single-Crystal Structure Determination. No suitable single crystals could be obtained from the oxazolonaphthoquinone diimines (**8a**–**f**) or from the bis(oxazolo)benzoquinone diimines **10a**–**c**, even though many different derivatives were synthesized by introducing halogen substituents in the para-position of the *N*-arylimine functionality. On the other hand, single crystals were successfully obtained from several of the monoimine derivatives. The X-ray single-crystal structures of **9a/a'**, **9b/b'**, and **9c/c'** are reported below. In addition, the structure of the *N,N'*-bis(*p*-fluorophenyl)-naphthoquinone diimine (**6a**) and of the *N,N'*-diphenylbisthiophenobenzoquinone diimine (**11**) are reported. The complete X-ray structure determinations are available as supplementary material.

***N,N'*-Bis(*p*-fluorophenyl)naphthoquinone 1,4-Diimine (6a).** This is the simplest diimine investigated in this study, and the result of the X-ray structure determination is shown in Figure 1. The molecule has a mirror symmetry element about the molecular axis. The bond distances in the naphthoquinone moiety agree with those for naphthoquinone itself. The bond distance C3–C3' is longer than C1–C1' (1.403 versus 1.338 Å), indicating that the C3-C3' bond is not participating in the quinonoid structure.

A small distortion of the phenyl ring on N is observed and is principally due to the electron-withdrawing character of the fluorine. The angle C15–C14–C13 is slightly larger than expected for a pure sp^2 hybridization at C14, namely, 122.6°. Aromatic substitution by electron-withdrawing groups generally leads to an increase in the internal angle at the position of substitution.[11] The bond distances in this aromatic ring are shorter than the r_g value for benzene (1.399 ± 0.001 Å), and this is also ascribed to the fluorine substituent.

The naphthoquinone residue in the molecule is found to be planar as expected. However, the two imine nitrogens are out of the plane of the naphthoquinone by about 5°. The phenyl groups on N and N' are twisted away from the naphthoquinone plane by 70.7°.

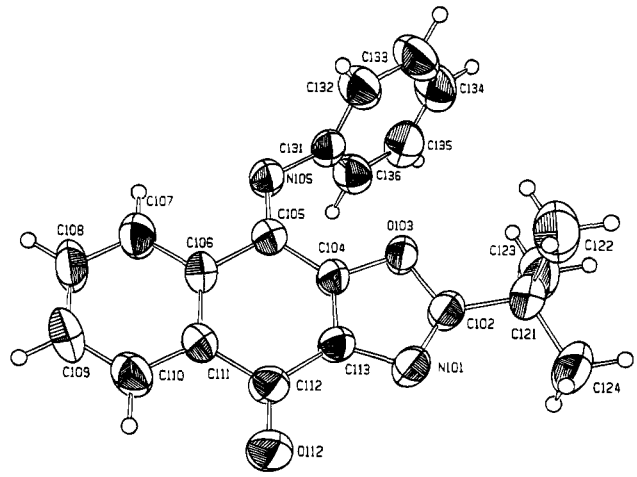


Figure 2. X-ray crystal structure of *N*-phenyl-2-*tert*-butylnaphth[2,3-*d*]oxazole-9-one 4-imine (**9a**).

As far as molecular packing is concerned, the *N*-phenyl rings of one molecule are stacking with the *N*-phenyl rings of the next molecule, with the naphthoquinone residues pointing in the opposite direction. The interesting feature of this crystal structure is that the naphthoquinone residue fits in a cavity formed by two *N*-phenyl rings of another molecule in such a way that the two naphthoquinone residues are perpendicular to each other.

***N*-Phenyl-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione 4-Imine (9a) and 9-Imine (9a').** The two isomers of this monomine were successfully separated by preparative flash column chromatography on silica-gel and completely characterized by standard methods. X-ray structure determinations were performed on both isomers. It was found difficult to distinguish the two isomers from each other. When the structures were fully refined with isotropic thermal parameters, a resonable data/parameter value was obtained. The refinement indices were high for **9a'**, indicating a poorly determined structure. When the structure was fully refined with anisotropic thermal parameters, the data/parameter ratios were poor, but the refinement indices were much better. In each case, attempts were made to refine the alternate isomer. The assignments given in this paper yielded the best thermal parameters and refinement indices and are consistent with each other. The structure determination of **9a** was of good quality, and this isomer is depicted in Figure 2.

Structure **9a** has two chemically equivalent, crystallographically independent molecules. The phenyl ring is placed above the oxygen of the oxazole ring in both structures. The buckling of the central ring system (angle β) is 4.25° and 2.36°, respectively, for the two different structures. In addition, the *N*-phenyl rings are rotated out of the central plane at a different angle too, namely, 79.3° and 109.9°, respectively. As far as the bond angles of interest are concerned, the angles in the two different structures are very close to each other, within 0.5°.

***N*-(4-Fluorophenyl)-2-*tert*-butylnaphtho[2,3-*d*]-oxazole-4,9-dione 4-Imine (9b).** Only one of the isomers crystallized in this case, namely, **9b**. The geometry of this crystalline isomer has the *N*-phenylimine on the side of the oxazole oxygen and is depicted in Figure 3.

The internal angles and the bond distances of the oxazole ring are the same as those obtained for an unsubstituted oxazole ring determined by microwave spectroscopy.[12] In analogy to the structure of **6a**, the

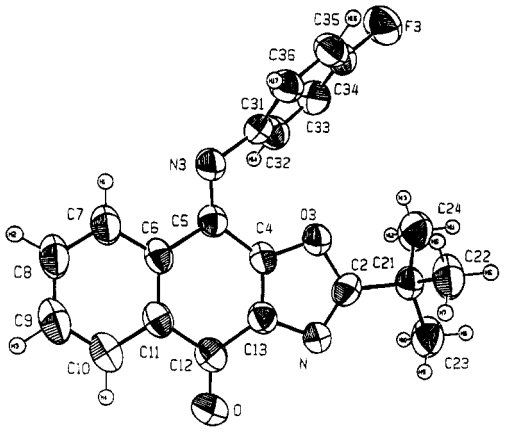
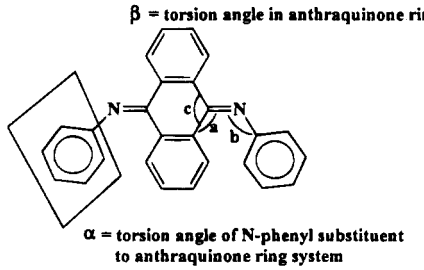


Figure 3. X-ray crystal structure of *N*-(*p*-fluorophenyl)-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione 4-imine (**9b**).

phenyl ring on N is distorted due to the influence of the electron-withdrawing fluorine substituent.

The three-ring fused system is not planar, but the molecule is slightly buckled. The dihedral angle β between the two outside rings is about 5.5°. The dihedral angle α between the main body and the phenyl ring on N3 is 113.5°. The phenyl ring is completely out of the plane of the molecule (122°).



***N*-(4-Phenyl)-2-isobutylnaphtho[2,3-*d*]oxazole-4,9-dione 4-Imine (9c−c′).** The X-ray single-crystal structure determination was performed on the racemic mixture of the two isomers. The structures were obtained by modeling the ring N and O by a hybrid NO atom constructed as being 50% N occupied and 50% O occupied. As expected no distortions of the *N*-phenyl ring were observed and the oxazole ring also conforms to the reported structure.[12] The isobutyl group is bending over to the *N*-phenyl ring, with the hydrogen atom pointing to the ring. This unexpected structure is due to efficient molecular packing along the *a*-axis of the crystal. In this conformation the distances between the phenyl rings along the *a*-axis of the crystal are smaller than those with the opposite conformation. As a result a high degree of molecular packing is accomplished along the *a*- and *b*-axes, as shown in Figure 4.

The single-crystal X-ray structure of **9c−c′** is depicted in Figure 5. The phenyl ring is twisted 96.7 ± 0.06° compared to the main body of the molecule. The main body of the molecule is basically planar, but there are indications that the N of the oxazole ring is not in the same plane.

***N*,*N*′-Diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione Diimine (11).** The crystal structure for this diimine is shown in Figure 6. In the crystal form, both phenyl groups on N are found adjacent to the sulfur in the thiophene ring, indicating less steric hindrance on that side than over the CH. The main body of the molecule is planar, with the quinone ring and the two

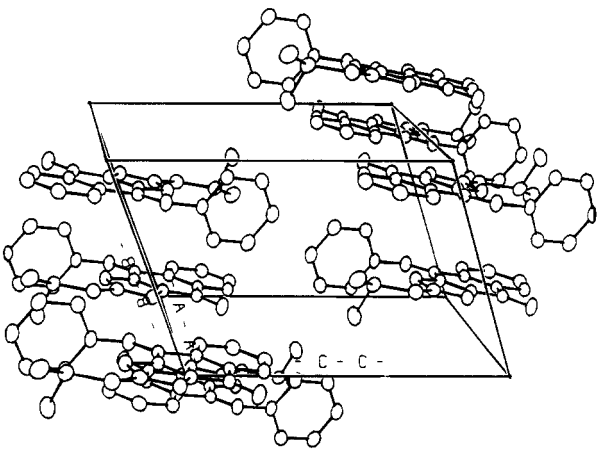


Figure 4. Molecular packing in the crystals of *N*-phenyl-2-isobutylnaphth[2,3-*d*]oxazole-4,9-dione 4-imine (**9c**).

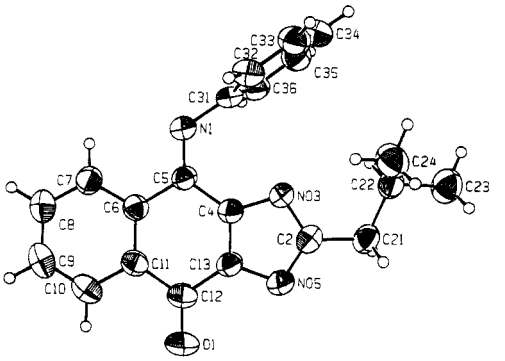


Figure 5. X-ray crystal structure of *N*-phenyl-2-isobutylnaphth[2,3-*d*]oxazole-4,9-dione 4-imine (**9c**).

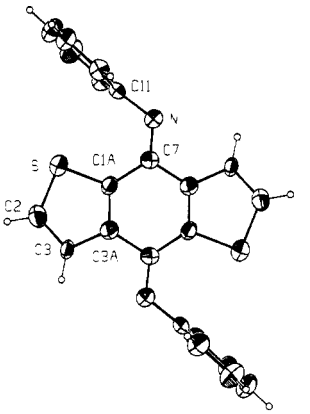


Figure 6. X-ray crystal structure of *N*,*N*′-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione diimine (**11**).

thiophene rings completely coplanar. The *N*-phenyl rings, on the other hand, are twisted out of the plane of the benzoquinone by 90.2°.

Comparison of the X-ray Structures. All the bond lengths and bond angles in the quinone imine derivatives are in good agreement with those reported for similar compounds.[12] The small discrepancies that we could identify can be attributed to the fluoro-substituent on the phenyl ring. In Table 1, the dihedral angles for the atoms around the imine bond are reported. The exocyclic angle **a** at the C=N bond is large, as is the C=N—C angle **b**; however, the endocyclic angle **c** at the C=N bond is small. This indicates that the bulkiness of the *N*-phenyl ring distorts these bonds due to steric hindrance.

On the other hand, replacing the anthraquinone moiety by heterocyclic quinone or by naphthoquinone,

Table 1. Dihedral and Planar Angles for the Quinone (Di)imines

angle	DAQ	6a	9a	9a′	9b	9c−c′	11
a	130/126	125	127	127	128	127	128
b	124/124	122	120	120	122	122	122
c	112/114	117	113	113	113	114	114
α	54/59	71	79	110	114	97	90
β	38	0	4.25	2.36	7.56	0	0

the steric hindrance in the molecule is reduced. Indeed the main body of the molecules in the present study proved to be planar, as, for example, for the bisthiophenoquinone diimine **11**, or close to planar (within 5°), in sharp contrast to the butterfly conformation adopted by the anthraquinone system in its diimine DAQ.[4] The same behavior was observed in the structure of substituted *N,N′*-dicyanoquinone diimines.[12]

The *N*-arylimino group is located on the side of the less hindered oxazole or thiophene ring. Further, this *N*-aryl group is always twisted out of the plane of the main body of the molecule, regardless of the nature of the quinone units. Even with naphthoquinone, the *N*-phenyl substituent upon imine formation is twisted completely out of the plane of the quinone. These data are also included in Table 1. The same phenomenon has been reported in the literature for *N,N′*-diphenylbenzoquinone diimine itself.[3] The *N*-phenyl substituents are not even in the same plane as the central ring in the cases of *N*-(diphenylmethylene)aniline[13] and salicylideneaniline[14] in which the C=N bond is not exocyclic, 63° and 44°, respectively. This clearly indicates that the *N*-phenyl substituent is in conjugation with the lone pair on the nitrogen and not with the C=N π-bond, even if the latter is linked with an extended conjugated system.

The color of the crystals of the heterocyclic benzoquinone mono- and diimines was orange to red, in contrast to the yellow anthraquinone diimine crystals. The UV data also indicate higher λ_{max} values for the heterocyclic benzoquinone diimines. The λ_{max} values for the model compounds are summarized in Table 2 along with data for other quinone diimines described in the previous paper.[2] The more planar heterocyclic quinone diimines show consistently higher λ_{max} values than the buckled anthraquinone derivatives, indicating increased conjugation in these planar systems. The lowest value is recorded for the 1,5-dichloroanthraquinone diimine, which could be due to increased steric hindrance and buckling of the central ring system. The electron-donating substituent in the para-position of the *N*-phenyl group increases the λ_{max} value as expected.

Heterocyclic quinone imines in this study tended to crystallize in thin sheets or needles. This observation intuitively indicates that the heterocyclic quinone imines have better molecular packing than anthraquinone diimines. In other words, heterocyclic quinone imines have a higher level of $\pi-\pi$ overlapping between the molecules in the solid state. Indeed the quinone imines in this study showed two-dimensional stacking, which might be the cause of the crystallization in thin plates or needles. The main bodies stack along the *x*-axis, while the *N*-arylimino groups stack along the *y*-axis. Only van der Waals forces exist along the *z*-axis, resulting in thin plates or needles. In the case of naphthoquinone diimines the van der Waals forces are stronger due to the symmetric nature of this molecule and the size of the cavities formed by the *N*-phenyl rings.

The substituents on the oxazole ring also affect the stacking. The bulky *tert*-butyl group inhibits efficient stacking, while with the smaller isobutyl group more efficient stacking was observed by rotating the latter.

Theoretical Calculations

From the X-ray structure analysis, we can conclude that the planarity of the central ring system in quinone diimines depends strongly on the steric effects. In the anthraquinone imine derivatives the central ring system is always buckled to reduce the interference with the substituent on N. Eliminating these effects by switching to the naphthoquinone system, or by introducing the smaller oxazole and thiophene rings instead of the phenyl ring, relieves the buckling of these structures. However, removal of this steric hindrance has no effect on the twist angle of the *N*-phenyl substituent compared to the main ring system. Moreover, as mentioned above, in imines in which the C=N is not exocyclic we still observe large twist angles for the *N*-phenyl group compared to the C=N−C plane. Therefore, the stereochemistry has to be dominated by conjugative effects for this family of compounds. Conformational analysis and MOPAC (MNDO, AM1, and PM3) calculations were used to better understand and to quantify the interactions responsible for the distorted structures.

First, the calculated MOPAC geometries of *N,N′*-diphenylanthraquinone diimine (DAQ) and **9a** and **9a′** were compared to the single-crystal X-ray structures. MOPAC calculations were also performed on *N,N′*-diphenylbenzoquinone diimine for comparison; this structure has been reported in the literature.[3] Relevant structural features are reported in Table 3, including the length of the imine bond b and the angle α between the planes respectively defined by the main body of the molecule and by the phenyl ring.

It has been suggested that the MNDO method overestimates nonbonded atom core repulsion energies,[15] and indeed the values of α are significantly higher than those predicted by the other methods. Otherwise, the agreement between the X-ray structure determinations and MOPAC calculations is good.

MNDO and AM1 calculations on *N,N′*-diphenylbenzoquinone diimine have already been reported.[3] Our PM3 calculations are in good agreement. It is important to point out that even in this compound, and indeed in polyaniline itself, the *N*-phenyl substituent twists completely out of the plane of the quinone.

Calculations were also performed on altered geometries of these molecules. The main body of each molecule was defined as planar, while the remaining moieties of the molecules were fully optimized. According to these calculations, little energy (between 1 and 3 kcal·mol^{-1}) is associated with the bending of the heterocyclic naphthoquinonoid system.

A second approach was to compute the change in heat of formation (AM1) (kcal/mol) as a function of the torsional angle α between the central ring plane and the *N*-phenyl substituent. In order to simplify the calculations, they were performed while maintaining the main body of the molecules planar. The rotational energy barriers are depicted in Figure 7. Indeed, the smallest heats of formation were found for torsional angles larger than 60°. This is consistent with all our structural data in which the angle α is pretty consistently larger than 60°.

Conclusions and Implications for Polymer Structure

We successfully synthesized a wide variety of tricyclic quinone diimines as model compounds for the poly-

Table 2. Ultraviolet Data for Model Compounds and Polymers in Tetrahydrofuran

quinone	substituent on N in diimine	λ_{max} for quinone diimine (nm)	diamine used in polymn	λ_{max} for poly(quinoneimine) (nm)
anthraquinone	phenyl	398	methylenedianiline	410
	p-fluorophenyl	398	thiodianiline	424
	p-methoxyphenyl	422	oxydianiline	432
	p-nitrophenyl	390	phenylenediamine	468
1,5-dichloroanthraquinone	phenyl	372		
naphthoquinone	phenyl	433		
	p-fluorophenyl	436		
	p-bromophenyl	468		
	p-iodophenyl	448		
2-*tert*-butyloxazolonaphthoquinone	phenyl	440		
	p-fluorophenyl	440		
	p-bromophenyl	442		
	p-iodophenyl	444		
bis(oxazolo)benzoquinone	phenyl	456		
	p-bromophenyl	462		
	p-iodophenyl	468		
bis(imidazolo)benzoquinone	phenyl	436	methylenedianiline	448
			thiodianiline	470
bisthiophenobenzoquinone	phenyl	424	methylenedianiline	450

Table 3. Relevant Structural Features of the MOPAC and X-ray Geometries of Heterocyclic Naphthoquinone Monoimines

compound	method	C=N	C−N	b	α
9a	MNDO	1.292	1.417	126	97
	AM1	1.292	1.409	125	116
	PM3	1.294	1.425	128	103
	X-ray	1.26	1.44	120	79
9a′	MNDO	1.293	1.415	127	95
	AM1	1.292	1.405	126	48
	PM3	1.295	1.427	127	97
	X-ray	1.28	1.41	120	110
benzoquinonediimine	MNDO	1.296	1.417	125	72
	AM1	1.299	1.409	123	48
	PM3	1.300	1.427	125	59
	X-ray	1.32	1.42	121	53
DAQ	MNDO	1.296	1.408	131	70
	AM1	1.294	1.403	129	67
	PM3	1.294	1.428	126	95
	X-ray	1.27	1.416	124	59

(quinone imine) polymers. For the polymerizations, only fully substituted derivatives of benzoquinone can be used to avoid Michael additions in the quinone ring system. Anthraquinone has been the most successful quinone to date in the polycondensations. As known from our previous study, the anthraquinone ring system is not planar but adopts a "butterfly" conformation.[4]

In this study the diimine model compounds of bisthiopheno and bis(oxazolo) derivatives of benzoquinone have been synthesized, and their structure has been determined. The central ring systems remain planar in the diimine. Therefore, we can conclude that some of the steric hindrance has been relieved by using five-membered rings and by using heteroatoms in the side rings. It is interesting to note that the *N*-phenyl rings are always on the side of the heteroatom. This can be due to either steric hindrance or to electronic reasons. Sterically the lone pairs on the heteroatoms could cause less steric hindrance than a C−H group, or the *N*-phenyl substituent is electron-poor due to its conjugation with the imine bond and prefers the $\pi-\pi$ stacking with the electron-rich heteroatom.

Similarly, in the naphthoquinone imine derivatives investigated in this study, the *N*-phenyl ring is on the side away from the C−H groups. This is true for either the naphthoquinone imine itself or for the heterocyclic substituted naphthoquinone imines.

The *N*-phenyl ring is always twisted out of the plane of the central ring system, independent of the starting

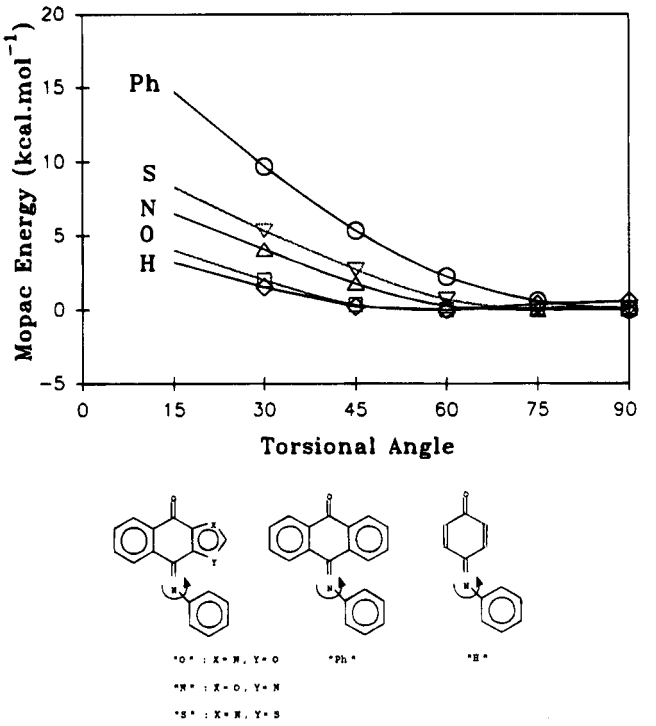


Figure 7. Rotational barrier for the rotation of the *N*-phenyl group around the C−N bond.

quinone structure. This angle α varies depending on the nature of the quinones. This must indicate that the phenyl group is in conjugation with the lone pair on the imine nitrogen and not with the imine bond. The reason for this must be electronic. Even in the parent quinone diimine analyzed by Baughman the phenyl ring is twisted out of the plane.[3] However, Baughman also reports that in the doped form, the salt form, the structure flattens out and the torsion angle is within 15°, which can be considered as planar as far as physical properties are concerned.

These structure determinations have given us valuable information about the structure of the polyaromatic quinone diimine polymers. First of all, even the formally fully conjugated polymers of anthraquinone and *tert*-butylanthraquinone with phenylenediamine are not fully conjugated, because the *N*-aryl substituent is always twisted out of the plane of the C=N bond. Second, the polymers derived from anthraquinone have buckled anthracene ring systems, while the polymers

derived from heterocyclic benzoquinones have planar central ring systems. This has two effects: (1) the conjugation length in the anthraquinone polymers is shorter, as shown by the λ_{max} values in the UV, and (2) the anthraquinone polymers are more soluble than the heterocyclic benzoquinone polymers. The latter has an effect on the ease of polycondensation: with the heterocyclic systems higher boiling solvents are needed to obtain higher reaction temperatures to keep the polymers in solution as they form, and the yields and molecular weights are generally lower. Higher molecular weight polymers will be synthesized for the heterocyclic benzoquinones using diamines with solubilizing long-chain alkyl substituents and by varying the structure of the quinone monomers.

The quinone imine structures determined by X-ray single-crystal structure analysis only refer to the structure in crystalline form. These quinone imines might have a different conformation in solution. In particular, the syn–anti equilibrium, which can be studied by variable-temperature NMR spectroscopy, should be of great interest. These studies are currently in progress. The syn–anti equilibria in the polymers will also be investigated.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-250 nuclear magnetic resonance spectrometer. Infrared spectra were recorded on a Perkin-Elmer 903 spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are corrected. GC–MS measurements were performed by the MS facility of the University of Arizona, Tucson, AZ. X-ray analyses were performed by the Molecular Structure Laboratory of the University of Arizona.

Sources of Chemicals. 2,3-Dichloro-1,4-naphthoquinone, chloranil, and pivalic anhydride were obtained from Aldrich and used without further purification. Triphenylarsine oxide was obtained from Lancaster Synthesis and recrystallized from benzene.

Representative Syntheses of Quinones. 2-Methylnaphth[2,3-*d*]oxazole-4,9-dione (2a). 2-(*N*-Acetylamino)-3-hydroxy-1,4-naphthoquinone (**1a**) (0.5 g) and 10 mL of acetic anhydride were placed in a 25-mL round-bottomed flask and heated up to reflux for 24 h. The yellow precipitate was filtered off and washed with water and acetone. Yield: 90%. Mp: 316 °C (dec). IR (KBr): 3100 (C=C), 1680 (C=O), 1600 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{12}H_7NO_3$: C, 67.60; H, 3.31; N, 6.57. Found: C, 67.66; H, 3.24; N, 6.67.

2-Isobutylnaphth[2,3-*d*]oxazole-4,9-dione (2c). 2-(*N*-Isovalerylamino)-3-hydroxy-1,4-naphthoquinone (**1c**) (3 g), 40 mL of dry benzene, and a magnetic stirrer were placed in a 100-mL round-bottomed flask equipped with a condenser and a drying tube. A suspension of P_2O_5 in Et_3N (10 g/30 mL) was added. The reaction mixture was heated to reflux for 24 h. The dark red solution was decanted from the residue, and the benzene, removed under reduced pressure. The product was recrystallized from isopropyl alcohol to give creamy white needles. Yield: 66%. Mp: 195–196 °C. IR (KBr): 3068, 2900, 1672 (C=O), 1600 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.28; H, 4.94; N, 5.43.

Benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (5).[7] *N,N*-Diethyl-3-thiophenecarboxamide (2.28 g, 12.5 mmol) is dissolved in 190 mL of dry tetrahydrofuran in an argon atmosphere and chilled to −90 °C. TMEDA (1.45 g, 12.5 mmol) was added, and then 13.8 mL (13.8 mmol) of *sec*-butyllithium (0.93 M) was added dropwise. After 1 h 1.40 g (12.5 mmol) of 3-thiophenecarboxaldehyde dissolved in 5 mL of THF was also added, followed by 15.6 mL (15.6 mmol) of *sec*-butyllithium. The mixture was allowed to warm to room temperature overnight. The flask was opened to air, and the reaction mixture was acidified with excess ammonium hydrochloride. THF is evaporated, and the product is extracted from the solids with dichloromethane. The product is purified by preparative column chromatography on silicagel with chloroform as eluent, followed by sublimation at 180° at 1 mmHg. Yield: 77%. Mp: 253–256 °C (lit.[16] mp 258–260 °C).

Physical Data for Other Quinones. 2-*tert*-Butylnaphth[2,3-*d*]oxazole-4,9-dione (2b). Yield: 78%. Mp: 152–153 °C. ^{1}H NMR ($CDCl_3$): δ 1.53 (s, 9H), 7.75–7.82 (m, 2H), 8.18–8.27 (m, 2H). IR (KBr): 3068, 2960, 1680 (C=O), 1600 (C=) cm^{-1}. Elem. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.54; H, 5.06; N, 5.48.

Representative Syntheses of Diimines. *N,N'*-Diphenyl-2-*tert*-butylnaphth[2,3-*d*]oxazole-1,4-dione Diimine (8a). Quinone **3** (1 g, 3.92 mmol) and 1.26 g (3.91 mmol) of triphenylarsine oxide were dissolved in 3 mL of 1,2-dichloroethane. The mixture was heated to reflux. A solution of phenyl isocyanate (1.02 g, 8.60 mmol) in 7.0 mL of 1,2-dichloroethane was added dropwise over 1 h. The reaction was continued for an additional 1 h and filtered. The filtered solid was washed with ether, and the solution was added to the filtrate. The crude product was obtained by concentrating the filtrate and was recrystallized from isopropyl alcohol. Yield: 65%. Mp: 155–156 °C. ^{1}H-NMR ($CDCl_3$): δ 8.61 (m, 2H), 7.67 (m, 2H), 7.33 (m, 4H), 7.12 (m, 2H), 6.93 (m, 4H), 0.89 (s, 9H). IR (KBr): 3050, 2950, 1620 (C=N), 1590 (C=C) cm^{-1}. UV (CH_3CN): λ_{max} 440 nm. Elem. Anal. Calcd for $C_{27}H_{23}N_3O$: C, 79.97; H, 5.72; N, 10.36. Found: C, 79.90; H, 5.68; N, 9.48.

***N,N'*-Diphenylbenzo[1,2-*b*:4,5-*b*']Dithiophene-4,8-dione Diimine (11).** Bisthiophenoquinone (0.52 g, 2.37 mmol) is dissolved in 30 mL of toluene, while heating to 90 °C. Triethylamine (1.4 mL, 14.2 mmol) and aniline (0.56 mL, 5.93 mmol) were added. $TiCl_4$ (0.8 mL, 3.56 mmol) was mixed with 5 mL of toluene and added dropwise to the reaction mixture over a period of 20 min. The reaction mixture is stirred for 24 h at 90 °C, after which the precipitate is filtered off. The solids are washed with hot toluene. The solvent was removed on a rotaevaporator. The crude product was recrystallized from methyl ethyl ketone to obtain orange thin needle crystals. Yield: 100%. Mp: 296–8 °C. UV–vis: λ_{max} 424 nm, ϵ 3280 M^{-1} cm^{-1}. For additional data see the preceding paper.[2]

Physical Data for Other Diimines. *N,N'*-Bis(4-fluorophenyl)naphthoquinone 1,4-Diimine (6a). This was recrystallized from isopropyl alcohol. Yield: 6%. Mp: 203–204 °C. ^{1}H-NMR ($CDCl_3$): δ 8.48 (m, 2H), 7.66 (m, 2H), 7.07 (m, 4H), 6.85 (m, 6H). IR (KBr): 3066, 1606 (C=N), 1581 (C=C) cm^{-1}. UV (THF): λ_{max} 436 nm. Elem. Anal. Calcd for $C_{22}H_{14}N_2F_2$: C, 76.73; H, 4.10; N, 8.14. Found: C, 76.67; H, 4.06; N, 8.23.

***N,N*-Bis(4-bromophenyl)naphthoquinone 1,4-Diimine (6b).** This was recrystallized from isopropyl alcohol. Yield: 29%. Mp: 234–5 °C. ^{1}H-NMR ($CDCl_3$): δ 8.48 (m, 2H), 7.67 (m, 2H), 7.48 (m, 4H), 6.77 (m, 6H). IR (KBr): 3049, 1606 (C=N), 1588 (C=C) cm^{-1}. UV (THF): λ_{max} 468 nm. Elem. Anal. Calcd for $C_{22}H_{14}N_2Br_2$: C, 56.68; H, 3.03; N, 6.01. Found: C, 56.80; H, 2.85; N, 5.93.

***N,N'*-Bis(4-iodophenyl)naphthoquinone 1,4-Diimine (6c).** This was recrystallized from isopropyl alcohol. Yield: 36%. Mp: 213–4 °C. ^{1}H-NMR ($CDCl_3$): δ 8.47 (m, 2H), 7.67 (m, 6H), 6.83 (m, 4H), 6.65 (m, 4H). IR (KBr): 3037, 1608 (C=N), 1579 (C=C) cm^{-1}. UV (THF): λ_{max} 448 nm. Elem. Anal. Calcd for $C_{22}H_{14}N_2I_2$: C, 47.17; H, 2.52; N, 5.00. Found: C, 47.11; H, 2.44; N, 4.84.

***N,N'*-Bis(4-fluorophenyl)-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione Diimine (8b).** This was recrystallized from isopropyl alcohol. Yield: 15%. Mp: 176–7 °C. ^{1}H-NMR ($CDCl_3$): δ 8.56 (m, 2H), 7.65 (m, 2H), 6.6–7.2 (m, 8H), 0.96 (s, 9H). IR (KBr): 3050, 1619 (C=N), 1588 (C=C) cm^{-1}. UV (THF): λ_{max} 440 nm. Elem. Anal. Calcd for $C_{27}H_{21}N_3OF_2$: C, 73.46; H, 4.79; N, 9.52. Found: C, 73.26; H, 4.99; N, 8.98.

***N,N'*-Bis(4-bromophenyl)-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione Diimine (8c).** This was recrystallized from isopropyl alcohol. Yield: 5%. Mp: 135–6 °C. ^{1}H-NMR ($CDCl_3$): δ 8.56 (m, 2H), 7.67 (m, 2H), 6.6–7.5 (m, 8H), 0.96 (s, 9H). IR (KBr): 3050, 2923, 2913, 1619 (C=N), 1589 (C=C)

cm^{-1}. UV (THF): λ_{max} 442 nm. Elem. Anal. Calcd for $C_{27}H_{21}N_3OBr_2$: C, 57.57; H, 3.76; N, 7.46. Found: C, 59.64; H, 4.21; N, 7.07.

***N,N'*-Bis(4-iodophenyl)-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione Diimine (8d).** Recrystallized from isopropyl alcohol. Yield: 21%. Mp: 231–2 °C. ^{1}H-NMR ($CDCl_3$): δ 8.58 (m, 2H), 7.66 (m, 6H), 6.90 (m, 4H), 0.96 (s, 9H). IR (KBr): 3050, 1619 (C=N), 1591 (C=C) cm^{-1}. UV (THF): λ_{max} 444 nm. Elem. Anal. Calcd for $C_{27}H_{21}N_3OI_2$: C, 49.34; H, 3.22; N, 6.39. Found: C, 49.15; H, 3.11; N, 5.96.

***N,N'-Bis*(4-iodophenyl)-2-methylnaphth[2,3-*d*]oxazole-4,9-dione Diimine (8e).** This was recrystallized fron isopropyl alcohol. Yield: 9%. Mp: 278 °C (dec). IR (KBr): 3050, 1619 (C=N), 1590 (C=C) cm^{-1}. UV (THF): λ_{max} 450 nm. Elem. Anal. Calcd for $C_{24}H_{15}N_3OI_2$: C, 46.86; H, 2.46; N, 6.83. Found: C, 47.54; H, 2.39; N, 6.71.

***N,N'*-Diphenyl-2-isobutylnaphth[2,3-*d*]oxazole-4,9-dione Diimine (8f).** This was recrystallized from isopropyl alcohol. Yield: 50%. Mp: 163–4 °C. IR (KBr): 3050, 1619 (C=N), 1588 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{27}H_{23}N_3O$: C, 80.00; H, 5.73; N, 10.40. Found: C, 76.13; H, 5.53; N, 8.41.

***N,N'*-Diphenyl-2,2'-dimethylbenzo[1,2-*d*:5,4-*d'*]dioxazole-4,8-dione Diimine (10a).** This was recrystallized from toluene. Yield: 60%. Mp: sublimes. IR (KBr): 3055, 1610 (C=N), 1586 (C=C) cm^{-1}. Elem. Anal. Calcd for $C_{22}H_6N_4O_2$: C, 71.73; H, 4.34; N, 15.21. Found: C, 71.81; H, 4.32; N, 15.10.

***N,N'*-Bis(4-bromophenyl)-2,2'-dimethylbenzo[1,2-*d*:5,4-*d'*]dioxazole-4,8-dione Diimine (10b).** This was recrystallized from toluene. Yield: 53%. Mp: 283 °C (dec). IR (KBr): 3055, 1620 (C=N), 1572 (C=C) cm^{-1}. UV (THF): λ_{max} 462 nm. Elem. Anal. Calcd for $C_{22}H_6N_4O_2Br_2$: C, 50.22; H, 2.68; N, 10.06. Found: C, 49.94; H, 2.50; N, 10.21.

***N,N*-Bis(4-iodophenyl)-2,2'-dimethylbenzo[1,2-*d*:5,4-*d'*]dioxazole-4,8-dione Diimine (10c).** This was recrystallized from toluene. Yield: 55%. Mp: 285 °C (dec). IR (KBr): 3055, 1620 (C=N), 1571 (C=C) cm^{-1}. UV (THF): λ_{max} 468 nm. Elem. Anal. Calcd for $C_{22}H_6N_4O_2I_2$: C, 42.61; H, 2.28; N, 9.03. Found: C, 42.70; H, 2.22; N, 8.70.

Representative Synthesis of Monoimines. *N*-Phenyl-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione 4-Imine (9a) and 9-Imine (9a'). Quinone **2b** (1 g, 3.95 mmol) and 0.63 g (1.96 mmol) of triphenylarsine oxide were dissolved in 3 mL of 1,2-dichloroethane and placed in a 50-mL round-bottomed flask equipped with a condenser and an addition funnel. The mixture was heated to reflux, and a solution of phenyl isocyanate (0.48 g, 3.95 mmol) in 7.0 mL of 1,2-dichloroethane was added dropwise over 1 h. The reaction was continued for an additional 1 h after the addition was complete. The solution was filtrated, and the residual precipitate, washed with ether. The crude mixture of isomers was obtained by concentrating the solution to dryness. They were separated from each other by flash chromatography, using a 10:1 mixture of cyclohexane/ether as the solvent.

Fraction 1: isomer **9a'**; orange needles. Yield: 0.13 g (10%). Mp: 138 °C. ^{1}H NMR ($CDCl_3$): δ 8.58 (dd, 1H), 8.28 (dd, 1H), 7.71 (m, 2H), 7.35 (t, 2H), 7.18 (t, 1H), 6.95 (d, 2H), 1.26 (s, 9H). Elem. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.08; H, 5.49; N, 8.38.

Fraction 2: isomer **9a**; red chunky crystals. Yield: 0.56 g (43%). Mp: 150 °C. ^{1}H-NMR ($CDCl_3$): δ 8.54 (dd, 1H), 8.34 (dd, 1H), 7.73 (m, 2H), 7.42 (t, 2H), 7.23 (t, 1H), 6.96 (d, 2H), 1.17 (s, 9H). Elem. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.23; H, 5.47; N, 8.31.

Physical Data for Other Monoimines. *N*-(4-Fluorophenyl)-2-*tert*-butylnaphth[2,3-*d*]oxazole-4,9-dione 4-Imine and 9-Imine (9b/b'). This was recrystallized from isopropyl alcohol. Mp: 183–4 °C. Elem. Anal. Calcd for $C_{21}H_{18}N_2O_2F_2$: C, 72.40; H, 4.92; N, 8.04. Found: C, 72.27; H, 4.86; N, 8.11.

N-Phenyl-2-isobutylnaphth[2,3-*d*]oxazole-4,9-dione 4-Imine and 9-Imine (9c/c'). This was recrystallized from isopropyl alcohol. Mp: 175 °C. Elem. Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 75.40; H, 5.43; N, 8.41.

N-Phenylnaphthoquinone Monoimine (7a). Synthesized from naphthoquinone and *N*-phenyltriphenylphosphinimine in benzene at reflux. Yield: 90%. Mp: 238 °C. IR (KBr): 1645 (C=O), 1610 (C=N). Elem. Anal. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.57; N, 6.00. Found: C, 82.74; H, 4.45; N, 5.73.

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Supplementary Material Available: Structures of **6a**, **9a**, **9a'**, **9b**, **9c/9c'**, and **11** and tables of experimental details, positional parameters, general displacement parameter expressions, bond distances and angles, least-squares planes, dihedral angles between planes, and torsional angles for these compounds (65 pages). Ordering information is given on any current masthead page.

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