NMR study of products of thermal transformation of substituted *N*-aryl-*o*-quinoneimines*

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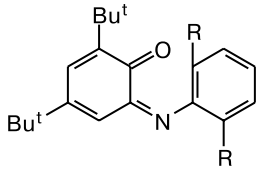
Products of thermal transformation of substituted *N*-aryl-*o*-quinoneimines were studied using NMR spectroscopy. The formation of 4a*H*-phenoxazine, which was further dimerized by the Diels—Alder reaction, was established.

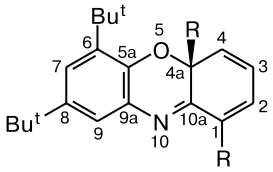
Key words: substituted *N*-aryl-*o*-quinoneimines, hexaphene, 4a*H*-phenoxazine, NMR, 2D NMR, structure.

Aryl-substituted *o*-benzoquinoneimines are quinone derivatives bearing several reaction centers capable of entering into various chemical reactions.[1] The area of their application covers chelating systems, dyes, and starting compounds for syntheses of metal-coordinating ligands.

The purpose of our work is to study the products formed both on heating of individual *N*-(2,6-dialkylphenyl)-3,5-di-*tert*-butyl-*o*-benzoquinoneimines **1** and during the synthesis of these compounds.



1a,b



2a,b

R = Me (**a**), Pr^i (**b**)

The synthesis of **1** from 3,5-di-*tert*-butyl-*o*-benzoquinone and 2,6-disubstituted anilines affords, along with the main product, a new compound being, probably, a dimer, because the total number of protons and nonequivalent carbon atoms in the NMR spectra doubles compared to that expected for compound **1**. The resulting compound has a distinct melting point. According to the IR spectroscopic data, it contains no carbonyl groups and is asymmetric, because the most part of protons and almost all carbon atoms, except for those of the methyl groups in the *tert*-butyl substituents, are nonequivalent in the NMR spectra. The methyl groups in the isopropyl substituents are also nonequivalent, indicating the presence of chiral centers or steric hindrance. Similar products were isolated upon heating of individual compounds **1a** and **1b**. It was found that heating of **1a,b** in heptane for 12 h resulted in decoloration of the solution. Since the initial compounds **1a** and **1b** are intensely dark red, we can suggest their complete transformation. Compounds **1a,b** are not completely consumed in methanol under the same conditions.

It is known that quinoneimines with the aryl substituent at the nitrogen atom can form cyclic products[1,2] due to the electrocyclic reaction of ring closure.[3] For example, the oxidation of 2-amino-4,6-di-*tert*-butylphenol with 3,5-di-*tert*-butylbenzoquinone affords 2,4,6,8-tetra-*tert*-butyl-1*H*-phenoxazin-1-one in high yields and quinoneimine as an intermediate.[2] It should be mentioned that compounds **1** can exhibit *Z*/*E*-isomerism similar to that observed for other quinoneimines.[4,5] Ring closure is possible only for the *Z*-isomer relatively to the C=N bond. Probably, this rearrangement can be initiated by the *Z*/*E*-transition *via* the torsion twisting mechanism.[4] The aromatic and quinoneimine rings are situated in different planes, and rotation of the rings relatively to each other is sterically hindered. Due to this, the NMR spectra exhibit the nonequivalent methyl groups of the isopropyl substituents in compound **1b**.

Prevalence of ring closure reactions for the quinoneimine systems suggests the formation of the cyclic product of the phenoxazine type at the first step of thermal transformation of compound **1**. The *Z*-isomer of **1** should produce 4a*H*-phenoxazine derivative **2** when the aromatic ring turns to the same plane with the quinoneimine ring. Molecule **2** has a chiral center in position 4a, *i.e.*, a mixture of *R*- and *S*-enantiomers forms. This phenoxazine isomer has not previously been prepared, and its formation was assumed only as an intermediate.[3] We succeeded to detect the formation of compound **2b** by NMR on

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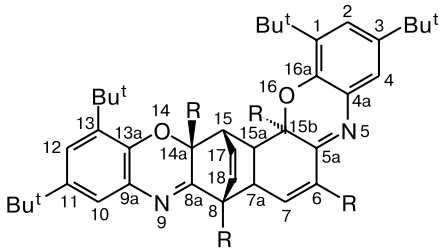
heating in methanol-d_4. The presence of the ABM system of protons in the diene region, AB system in the aromatic region, and signals from the *tert*-butyl groups in the ^{1}H NMR spectrum of intermediate **2b** proves the structure of **2b**. The individual compound was not isolated, because the product was unstable and readily entered into subsequent transformations.

Considering possible routes for the preparation of the dimer, we concluded that dimerization by the Diels—Alder reaction was most probable. An attempt to grow crystals appropriate for X-ray diffraction analysis was unsuccessful. The modern two-dimensional NMR methods make it possible to obtain (in the liquid phase) data, whose informative content is comparable with that of X-ray diffraction analysis.[6] The structure of the product was determined using the one- and two-dimensional procedures[6,7]



3a,b

R = Me (**a**), Pr^i (**b**)

Table 1. Correlations in the 2D NMR spectra of compound **3a**

Atom, group	Cross-peaks		
	COLOC	COSY	NOESY
C(1)	C(1)C(C$\underline{H}_3$)$_3$		
C(3), C(11)	C(3)C(C$\underline{H}_3$)$_3$, C(11)—C(C$\underline{H}_3$)$_3$		
C(1)—C(C$\underline{H}_3$)$_3$	C(1)$\underline{C}$(CH$_3$)$_3$	H$_{arom}$ w	C(15)H, H$_{arom}$
C(1)—$\underline{C}$(CH$_3$)$_3$	C(1)C(C$\underline{H}_3$)$_3$		
C(3)—C(C$\underline{H}_3$)$_3$, C(11)—C(C$\underline{H}_3$)$_3$	C(3)$\underline{C}$(CH$_3$)$_3$, C(11)—$\underline{C}$(CH$_3$)$_3$	H$_{arom}$ w	H$_{arom}$
C(3)—$\underline{C}$(CH$_3$)$_3$, C(11)—$\underline{C}$(CH$_3$)$_3$	C(3)C(C$\underline{H}_3$)$_3$, C(11)—C(C$\underline{H}_3$)$_3$		
C(5a)	C(6)C$\underline{H}_3$, C(15b)C$\underline{H}_3$, C(7)H		
C(6)	C(6)C$\underline{H}_3$		
C(6)$\underline{C}$H$_3$	C(7a)H, C(7)H, C(6), C(15a)H	C(7)H w, C(7a)H w	C(7)H
C(7)H	C(6)C$\underline{H}_3$	C(6)CH$_3$ w, C(7a)H w, C(15a)H	C(8)C$\underline{H}_3$, C(6)CH$_3$, C(7a)H
C(7a)H		C(6)CH$_3$ w, C(15a)H, C(7)H	C(8)CH$_3$, C(15b)CH$_3$, C(6)CH$_3$, C(15a)H, C(7)H
C(8)	C(8)C$\underline{H}_3$		
C(8)$\underline{C}$H$_3$	C(8), C(8a)	C(18)H w	C(18)H, C(7)H
C(8a)	C(15)H w, C(8)CH$_3$, C(14a)C$\underline{H}_3$ w		
C(13)	C(13)C(C$\underline{H}_3$)$_3$		
C(13)—C(C$\underline{H}_3$)$_3$	C(13)$\underline{C}$(CH$_3$)$_3$	H$_{arom}$ w	C(14a)CH$_3$, H$_{arom}$
C(13)—$\underline{C}$(CH$_3$)$_3$	C(13)C(C$\underline{H}_3$)$_3$		
C(14a)	C(14a)C$\underline{H}_3$		
C(14a)$\underline{C}$H$_3$	C(14a), C(15)H, C(8a)	C(15)H w, C(17)H w	C(15)H, C(15a)H, C(13)—C(CH$_3$)$_3$
C(15)H	C(14a)C$\underline{H}_3$	C(14a)CH$_3$ w, C(15a)H, C(18)H, C(17)H	C(14a)CH$_3$, C(15a)H, C(18)H w, C(17)H, C(1)C(CH$_3$)$_3$
C(15a)H	C(15b)C$\underline{H}_3$	C(7a)H, C(15)H, C(7)H w, C(17)H w, C(15b)CH$_3$ w	C(15b)CH$_3$, C(7a)H, C(15)H, C(1)C(CH$_3$)$_3$, C(14a)CH$_3$ w
C(15b)	C(15b)C$\underline{H}_3$		
C(15b)$\underline{C}$H$_3$	C(15b), C(15a)H		C(15a)H
C(17)H	C(15b)CH$_3$	C(14a)CH$_3$ w, C(8)CH$_3$, C(15)H, C(18)H, C(15a)H w	C(15)H, C(18)H, C(14a)CH$_3$
C(18)H		C(15)H, C(17)H, C(8)CH$_3$ w	C(8)CH$_3$, C(15)H w, C(17)H
H$_{arom}$	H$_{arom}$, C($\underline{C}$H$_3$)$_3$	H$_{arom}$, C(CH$_3$)$_3$ w	H$_{arom}$, C(C$\underline{H}_3$)$_3$
C$_{arom}$	H$_{arom}$, C(C$\underline{H}_3$)$_3$		

Table 2. Correlations in the 2D NMR spectra of compound **3b**

Atom, group	Cross-peaks		
	COLOC	COSY	NOESY
C(1)	C(1)C(C$\underline{H}_3$)$_3$ w		
C(1)C(C$\underline{H}_3$)$_3$	C(1) w		H_{arom}, C(15a)H w
$\underline{C}$(1)C(CH$_3$)$_3$	C(1)C(C$\underline{H}_3$)$_3$ w		
C(3),C(11)	C(3)C(C$\underline{H}_3$)$_3$ w, C(11)C(C$\underline{H}_3$)$_3$ w		
$\underline{C}$(3)C(CH$_3$)$_3$, $\underline{C}$(11)C(CH$_3$)$_3$	C(3)C(C$\underline{H}_3$)$_3$ w, C(11)C(C$\underline{H}_3$)$_3$ w		
C(3)C(C$\underline{H}_3$)$_3$, C(11)C(C$\underline{H}_3$)$_3$	C(3) w, C(11) w		H_{arom}
C(4a)	C(6)CH(C$\underline{H}_3$)$_2$ w		
C(5a)	C(7)H		
C(6)	C(6)CH(C$\underline{H}_3$)$_2$ w		
C(6)C$\underline{H}$(CH$_3$)$_2$	C(6)CH(C$\underline{H}_3$)$_2$ w	C(6)CH(C$\underline{H}_3$)$_2$	C(7)H, C(6)CH(C$\underline{H}_3$)$_2$
C(6)CH(C$\underline{H}_3$)$_2$	C(6), C(4a)H w	C(6)C$\underline{H}$(CH$_3$)$_2$	C(6)C$\underline{H}$(CH$_3$)$_2$
C(6)CH(C$\underline{H}_3$)$_2$	C(6), C(4a)H w	C(6)C$\underline{H}$(CH$_3$)$_2$	C(7)H, C(6)C$\underline{H}$(CH$_3$)$_2$
C(7)H	C(5a)	C(7a)H	C(8)CH(C$\underline{H}_3$)$_2$, C(7a)H, C(6)CH(C$\underline{H}_3$)$_2$
C(7a)H	C(15a)H	C(7)H	C(7)H, C(8)CH(C$\underline{H}_3$)$_2$ w
C(8)	C(8)CH(C$\underline{H}_3$)$_2$ w		
C(8)C$\underline{H}$(CH$_3$)$_2$	C(8)CH(C$\underline{H}_3$)$_2$ w	C(8)CH(C$\underline{H}_3$)$_2$	C(8)CH(C$\underline{H}_3$)$_2$
C(8)CH(C$\underline{H}_3$)$_2$	C(8) w	C(8)C$\underline{H}$(CH$_3$)$_2$	C(8)C$\underline{H}$(CH$_3$)$_2$, C(7)H, C(7a)H w, C(18)H w
C(8)CH(C$\underline{H}_3$)$_2$	C(8) w	C(8)C$\underline{H}$(CH$_3$)$_2$	C(8)C$\underline{H}$(CH$_3$)$_2$, C(7)H, C(7a)H w, C(18)H w
C(8a)	C(15)H w		
C(13)	C(13)C(C$\underline{H}_3$)$_3$ w		
C(13)C(C$\underline{H}_3$)$_3$	C(13) w		H_{arom}, C(15)H w
$\underline{C}$(13)C(CH$_3$)$_3$	C(13)C(C$\underline{H}_3$)$_3$ w		
C(14a)	C(14a)CH(C$\underline{H}_3$)$_2$ w		
C(14a)C$\underline{H}$(CH$_3$)$_2$	C(14a)CH(C$\underline{H}_3$)$_2$	C(14a)CH(C$\underline{H}_3$)$_2$	
C(14a)CH(C$\underline{H}_3$)$_2$	C(14a) w	C(14a)C$\underline{H}$(CH$_3$)$_2$	C(14a)C$\underline{H}$(CH$_3$)$_2$
C(14a)CH(C$\underline{H}_3$)$_2$	C(14a) w	C(14a)C$\underline{H}$(CH$_3$)$_2$	C(14a)C$\underline{H}$(CH$_3$)$_2$
C(15)H	C(8a)	C(15a)H, C(18)H, C(17)H	C(13)C(C$\underline{H}_3$)$_3$, C(18)H w, C(17)H
C(15a)H	C(7a)H	C(7a)H, C(15)H	C(15b)CH(C$\underline{H}_3$)$_2$, C(7a)H, C(1)C(C$\underline{H}_3$)$_3$
C(15b)	C(15b)CH(C$\underline{H}_3$)$_2$ w		
C(15b)C$\underline{H}$(CH$_3$)$_2$	C(15b)CH(C$\underline{H}_3$)$_2$	C(15b)CH(C$\underline{H}_3$)$_2$	C(15b)CH(C$\underline{H}_3$)$_2$
C(15b)CH(C$\underline{H}_3$)$_2$	C(15b) w	C(15b)C$\underline{H}$(CH$_3$)$_2$	C(15b)C$\underline{H}$(CH$_3$)$_2$
C(15b)CH(C$\underline{H}_3$)$_2$	C(15b) w	C(15b)C$\underline{H}$(CH$_3$)$_2$	C(15b)C$\underline{H}$(CH$_3$)$_2$, C(15a)H
C(17)H	C(18)H	C(18)H, C(15)H	C(15)H, C(18)H
C(18)H	C(17)H	C(17)H, C(15)H	C(17)H, C(15)H w, C(8)CH(C$\underline{H}_3$)$_2$ w
H_{arom}	H_{arom}, C(C$\underline{H}_3$)$_3$		all C(C$\underline{H}_3$)$_3$
C_{arom}	H_{arom}, C(C$\underline{H}_3$)$_3$		

of ^{1}H and ^{13}C NMR, DEPT, COSY, NOESY, XHCORR (carbon-proton correlation), and COLOC (carbon-proton long-range correlation) (Tables 1 and 2). These procedures allow one to observe hyperfine interactions, including those invisible in the 1D ^{1}H and ^{13}C NMR spectra. We succeeded to establish that the thermal transformation of compounds **1a** and **1b** produced products **3a** and **3b**, respectively.

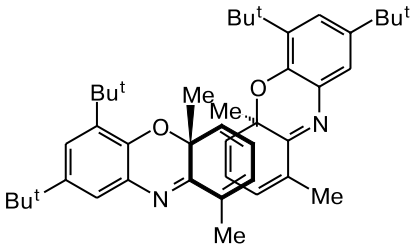
Let us consider how NMR data can be applied for revealing the structure of the product using the C(15)H group and its nearest environment. It is impossible to determine the position of the signal belonging to C(15)H using the ^{1}H NMR spectra only. Based on the chemical shifts and multiplicities of the ^{1}H NMR signals, we find the pair of adjacent protons at the double bond of C(17)H and C(18)H at 6.26 and 5.77 ppm. It is seen from the

COSY spectrum that this pair is characterized by the scalar spin-spin coupling, and the proton at 6.26 ppm has the scalar coupling with the protons at 1.11, 1.68, and 3.64 ppm. The signals at 1.11 and 1.68 ppm (C(14a)CH_3 and C(8)CH_3) belong to protons of the methyl groups (^{1}H NMR, DEPT). Therefore, the signal at 3.64 ppm belongs to C(15)H, which is confirmed by the ^{13}C NMR, XHCORR, and DEPT data. This proton is characterized by spin-spin couplings (in the COSY spectrum) with the methyl group at δ 1.11 and with the protons at δ 3.31, 6.26, and 5.77 (C(15a)H, C(17)H, and C(18)H, respectively). The two-dimensional NOESY spectrum manifests the interaction of C(15)H with the protons at δ 1.11, 3.31, and 5.77 (C(14a)CH_3, C(15a)H, and C(17)H, respectively), indicating their close arrangement in the space. The COLOC spectrum exhibits the long-range spin-spin ^{13}C—H coupling of $\underline{C}$(15) with C(14a)C$\underline{H}_3$.

All observed interactions coincide with those expected for the C(15)H fragment in structure **3a**. The data of the COSY and NOESY spectra make it possible to monitor the chain of correlations C(7)H—C(7a)H—C(15a)H—C(15)H—C(17)H—C(18)H and others characteristic of structures **3a** and **3b**. The XHCORR and COLOC spectra allowed us to assign all lines in the ^{13}C NMR spectra and confirmed the connectivities revealed in the homonuclear correlation experiments. Thus, based on the data of the one- and two-dimensional spectra, we obtained a consistent pattern for interactions in the molecule. This pattern was expected for the proposed structure. All lines observed in the proton and carbon spectra were assigned to the fragments of the structure.

Note that four isomers of the carbon framework could be generated by the dimerization reaction due to the involvement of different double bonds in the reaction. Each isomer could have several diastereomers due to different relative orientations of the molecules during the interaction. In the case of several isomers or several diastereomers in the reaction product, we would observe an increase in the number of the ^{1}H and ^{13}C NMR spectral lines, which could not be assigned to one molecule because necessary 2D-correlation cross-peaks would be absent from the spectra. In fact, the reaction produces predominantly one isomer with a certain relative configuration of chiral centers, because we assigned all signals in the ^{1}H and ^{13}C NMR spectra using the two-dimensional procedures and found no signal of any additional isomers. Therefore, only one certain double bond reacts as a dienophile of two bonds present in molecule **2**, and only one variant is realized during [2+4]-cycloaddition among several variants of relative orientation of asymmetric molecules **2**: one diastereomer and its enantiomer are formed. Such a high stereoselectivity confirms that dimerization occurs due to the Diels—Alder reaction.

The fine analysis of the NOESY spectrum and three-dimensional model of the molecule allowed the relative configuration of all six chiral centers of **3a** to be determined. For example, a weak intensity of the cross-peaks of C(15a)H and C(7a)H with the protons of the C(17)H=C(18)H bridge in the NOESY spectrum of **3a** suggests that the distance between these pairs of protons is greater than 4Å.[6] According to the three-dimensional model of the molecule optimized in the HyperChem program, this is possible only if the C(15a)H and C(7a)H protons are in the *endo*-position relatively to the bridge in the C(7a)—C(8)—C(8a)—C(14a)—C(15)—C(15a) ring and, *vice versa*, the methyl protons of C(14a)CH_3 are arranged in the *exo*-position relatively to the C(17)H=C(18)H bridge, because the NOESY spectrum contains cross-peaks between the protons of the C(14a)C$\underline{H}_3$ and C(17)H groups. The methyl group of the C(15b)CH_3 fragment is situated at one side of the C(5a)—C(6)—C(7)—C(7a)—C(15a)—C(15b) ring with the protons at the C(7a) and C(15a) atoms, because the NOESY spectrum exhibits the dipole-dipole interaction between the protons of the C(15b)CH_3, C(15a)H, and C(7a)H fragments. The resulting configuration corresponds to the *exo*-product of the Diels—Alder reaction, and the reacting molecules during the reaction should fit each other as it is shown below.



This variant of the approach is more sterically favorable because the substituents in position 4a of the reacting molecules are directed to opposite sides relatively to the plane in which the diene rings localized. The reaction involves *R*+*R*- or *S*+*S*-**2**. The predominant formation of the *exo*-product can be explained by the fact that this provides better conditions during the reaction for the dienophile π-orbitals, which are not involved in the reaction, to overlap. The [2+4]-cycloaddition reaction involves the π-C(6)—C(7) bonds of one molecule and C(6)—C(7) and C(8)—C(9) bonds of another molecule. The C(8)—C(9) bond does not act as a dienophile, probably, due to steric hindrance.

Thus, the intermediate and final products of the thermal transformation of *N*-aryl-*o*-benzoquinoneimines **1** in hexane and methanol were established. Based on the structures of the intermediate and final products, we con-

cluded that the reaction mechanism should include the ring closure of quinoneimine **1** to form 4a*H*-phenoxazine **2** followed by the dimerization of **2** through [2+4]-cycloaddition to form compound **3**. Product **3** forms with a high stereospecificity.

Experimental

One-dimensional and two-dimensional NMR spectra were obtained on a Bruker Avance DPX-200 instrument (200 MHz for ^{1}H, 50 MHz for ^{13}C). The following two-dimensional experiments were carried out: COSY, proton-proton correlation due to spin-spin coupling (including COSY45 (short-range interactions) and COSY90 (longer-range interactions)); NOESY, proton-proton correlation due to the dipole-dipole interaction; XHCORR, carbon-proton correlation due to the spin-spin interaction between the adjacent nuclei; and COLOC, carbon-proton correlation due to the long-range spin-spin interaction between nuclei. Two-dimensional COLOC experiments were carried out with optimization for constants of 3 and 10 Hz. In NOESY experiments, mixing time of 250 ms was used. IR spectra were recorded on a Perkin Elmer 577 instrument.

3,5-Di-*tert*-butylquinone was synthesized using a known procedure.[8] 2,6-Dimethylaniline was a commercial product available from Fluka, and commercial 2,6-diisopropylaniline (Aldrich) was used.

***N*-(2,6-Dimethylphenyl)-3,5-di-*tert*-butyl-*o*-benzoquinoneimine (1a).** 3,5-Di-*tert*-butylquinone (2.2 g, 10 mmol) and 2,6-dimethylaniline (1.5 mL, 12 mmol) were dissolved in MeOH (20 mL), and 1—2 drops of 88% HCOOH were added. The mixture was stirred using a magnetic stirrer at ~20 °C for 6 h until the starting quinone disappeared. Compound **1a** was isolated from the reaction mixture in 82% yield (3.83 g) as dark cherry-colored crystals, m.p. 102—103 °C. Found (%): C, 82.22; H, 9.00. Calculated (%): C, 81.73; H, 8.97. IR (Nujol, ν/cm^{-1}): 1670 (C=O); 1630 (C=N). ^{1}H NMR ($CDCl_3$), δ: 1.09, 1.34 (both s, 9 H each, Bu^t); 1.94 (s, 6 H, CH_3); 5.84 (d, 1 H, C=CH, J = 2.3 Hz); 6.90—7.00 (m, 3 H, PhH); 7.02 (d, 1 H, C=CH, J = 2.3 Hz).

***N*-(2,6-Diisopropylphenyl)-3,5-di-*tert*-butyl-*o*-benzoquinoneimine (1b).** Compound **1b** was synthesized similarly from 3,5-di-*tert*-butylquinone (2.2 g, 10 mmol) and 2,6-diisopropylaniline (1.8 mL, 11 mmol) in 68% yield (2.58 g) as dark red crystals, m.p. 145—147 °C. Found (%): C, 83.00; H, 10.24. Calculated (%): C, 82.30; H, 9.76. IR (Nujol), ν/cm^{-1}: 1670 (C=O); 1635 (C=N). ^{1}H NMR: ($CDCl_3$), δ: 1.10 (s, 9 H, Bu^t); 1.39 (s, 9 H, Bu^t); 1.08 (d, 6 H, 2 $CH_3CHC\underline{H}_3$, J = 6.8 Hz); 1.18 (d, 6 H, 2 $C\underline{H}_3CHCH_3$, J = 6.8 Hz); 2.68 (sept, 2 H, 2 $CHMe_2$, J = 6.8 Hz); 5.90 (d, 1 H, C=CH, J = 2.3 Hz); 7.04 (d, 1 H, C=CH, J = 2.3 Hz); 7.16 (m, 3 H, PhH).

6,8-Di-*tert*-butyl-1,4a-diisopropyl-4a*H*-phenoxazine (2b). Quinoneimine **1b** (3.2 g, 10 mmol) was dissolved in MeOH (70 mL) in an evacuated system and heated on a boiling water bath for 3 h. The formation of compound **2b** in the resulting mixture was detected by NMR. ^{1}H NMR (CD_3OD), δ: 1.33, 1.45 (both s, 9 H each, Bu^t); 2.12 (br.sept, 1 H, C(1)C$\underline{H}$Me$_2$); 2.28 (sept, 1 H, C(4a)C$\underline{H}$Me$_2$); 6.11 (dd, 1 H, C(4)H, $J_{4,2}$ = 1.3 Hz, $J_{4,3}$ = 9.5 Hz); 6.29 (dt, 1 H, C(2)H, $J_{2,3}$ = 6.0 Hz, $J_{2,4}$ = 1.3 Hz, $J_{H(2),C(1)C\underline{H}Me_2}$ = 1.4 Hz); 6.38 (dd, 1 H, C(3)H, $J_{3,2}$ = 6.0 Hz, $J_{3,4}$ = 9.5 Hz); 7.27 (d, 1 H, C(9)H, $J_{9,7}$ = 2.4 Hz); 7.30 (d, 1 H, C(7)H, $J_{7,9}$ = 2.4 Hz).

Constants and refined chemical shifts of protons in the region of 6.0—7.3 ppm were obtained by iteration fitting of the simulated spectra of the AB and ABM systems.

1,3,11,13-Tetra-*tert*-butyl-6,8,14a,15b-tetramethyl-7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene (3a). Quinoneimine **1a** (3.2 g, 10 mmol) was dissolved in heptane (70 mL) in an evacuated system and heated on a boiling water bath for 12 h until the solution became colorless. Compound **3a** was isolated from the reaction mixture at ~20 °C in 72% yield (2.3 g) as colorless crystals. Found (%): C, 81.20; H, 9.00. $C_{44}H_{58}N_2O_2$. Calculated (%): C, 81.69; H, 9.04; O, 4.95. IR (Nujol), ν/cm^{-1}: 1645 (C=N); 1235 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 1.10 (s, 3 H, C(14a)CH_3); 1.27 (s, 3 H, C(15b)CH_3); 1.33 (s, 18 H, C(3)C$(CH_3)_3$ and C(11)C$(CH_3)_3$); 1.44 (s, 9 H, C(13)C$(CH_3)_3$); 1.47 (s, 9 H, C(1)C$(CH_3)_3$); 1.68 (s, 3 H, C(8)CH_3); 2.00 (br.s, 3 H, C(6)CH_3); 2.80 (m, 1 H, C(7a)H); 3.34 (d, 1 H, C(15a)H, J = 8.0 Hz); 3.64 (d, 1 H, C(15)H, J = 6.8 Hz); 5.77 (dd, 1 H, C(18)H, J = 8.1 Hz, J = 1.1 Hz); 6.00 (m, 1 H, C(7)H); 6.26 (dd, 1 H, C(17)H, J = 6.8 Hz, J = 8.1 Hz); 7.18, 7.19, 7.22, 7.31 (all m, 1 H each, C(2)H, C(4)H, C(10)H, C(12)H). ^{13}C NMR ($CDCl_3$), δ: 16.9 (C(8)$\underline{C}H_3$); 18.1 (C(6)$\underline{C}H_3$); 18.3 (C(14a)$\underline{C}H_3$); 25.8 (C(15b)$\underline{C}H_3$); 30.0 (C(1)C$(\underline{C}H_3)_3$); 30.3 (C(13)C$(\underline{C}H_3)_3$); 31.56, 31.61 (C(3)C$(\underline{C}H_3)_3$, C(11)C$(\underline{C}H_3)_3$); 34.39, 34.46 (C(3)$\underline{C}(CH_3)_3$, C(11)$\underline{C}(CH_3)_3$); 35.0 (C(13)$\underline{C}(CH_3)_3$); 35.2 C(1)$\underline{C}(CH_3)_3$); 43.7 (C(15a)H); 44.3 (C(15)H); 48.0 (C(7a)H); 48.6 (C(8)); 73.8 (C(15b)); 74.3 (C(14a)); 121.5, 122.4, 123.0, 123.2 (C(2)H, C(4)H, C(10)H, C(12)H); 130.9 (C(17)H); 132.6 (C(7)H); 132.4 (C(6)); 135.0, 136.1, 141.5, 141.4 (C(4a), C(9a), C(13a), C(16a)); 136.0 (C(18)H); 136.5 (C(1)); 137.4 (C(13)); 143.3, 143.4 (C(3), C(11)); 161.1 (C(5a)); 170.5 (C(8a)).

1,3,11,13-Tetra-*tert*-butyl-6,8,14a,15b-tetraisopropyl-7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene (3b) was synthesized similarly from quinoneimine **1a** (3.8 g, 10 mmol). Compound **3b** was isolated in 65% yield (2.47 g) as colorless crystals. Found (%): C, 82.31; H, 9.58. $C_{52}H_{74}N_2O_2$. Calculated (%): C, 82.27; H, 9.83. IR (Nujol), ν/cm^{-1}: 1645 (C=N); 1235 (C—O—C). ^{1}H NMR ($CDCl_3$), δ: 0.69 (d, 3 H, C(14a)(C$\underline{H}_3$)CHCH_3, J = 7.1 Hz); 0.75 (d, 3 H, C(14a)(CH_3)CHC$\underline{H}_3$, J = 7.1 Hz); 0.82 (d, 3 H, C(15b)(C$\underline{H}_3$)CHCH_3, J = 7.1 Hz); 0.94 (d, 3 H, C(15b)(CH_3)CHC$\underline{H}_3$, J = 7.1 Hz); 1.04 (d, 3 H, C(6)(C$\underline{H}_3$)CHCH_3, J = 7.1 Hz); 1.11 (d, 3 H, C(6)(CH_3)CHC$\underline{H}_3$, J = 7.1 Hz); 1.29 (d, 3 H, C(8)(C$\underline{H}_3$)CHCH_3, J = 7.1 Hz); 1.32, 1.33 (both s, 9 H each, C(3)C(C$\underline{H}_3)_3$, C(11)C(C$\underline{H}_3)_3$); 1.44 (s, 9 H, C(1)C(C$\underline{H}_3)_3$); 1.51 (s, 9 H, C(13)C(C$\underline{H}_3)_3$); 1.58 (d, 3 H, C(8)(CH_3)CHC$\underline{H}_3$, J = 7.1 Hz); 1.96 (m, 1 H, C(15b)C$\underline{H}$(C$H_3)_2$); 2.10 (m, 1 H, C(14a)C$\underline{H}$(C$H_3)_2$); 2.11 (m, 1 H, C(8)C$\underline{H}$(C$H_3)_2$); 3.17 (m, 1 H, C(7a)H); 3.22 (m, 1 H, C(6)C$\underline{H}$(C$H_3)_2$); 3.37 (d, 1 H, C(15a)H, J = 7.8 Hz); 3.63 (d, 1 H, C(15)H, J = 6.8 Hz); 5.70 (d, 1 H, C(18)H, J = 8.0 Hz); 5.83 (d, 1 H, C(7)H, J = 3.6 Hz); 6.16 (dd, 1 H, C(17)H, J = 6.8 Hz, J = 8.0 Hz); 7.10, 7.13, 7.08, 7.13 (all m, 1 H each, C(2)H, C(4)H, C(10)H, C(12)H). ^{13}C NMR ($CDCl_3$), δ: 16.1 (C(15b)(C$\underline{H}_3$)CHCH_3); 17.3 (C(15b)(CH_3)CHC$\underline{H}_3$); 17.7 (C(8)(C$\underline{H}_3$)CHCH_3); 18.35 (C(6)(C$\underline{H}_3$)CHCH_3); 18.36 (C(8)(CH_3)CHC$\underline{H}_3$); 19.9 (C(14a)(C$\underline{H}_3$)CHCH_3); 22.1 (C(6)(CH_3)CHC$\underline{H}_3$); 22.8 (C(14a)(CH_3)CHC$\underline{H}_3$); 27.8 (C(6)C$\underline{H}$(C$H_3)_2$); 30.2

(C(1)C($\underline{C}H_3)_3$); 30.6 (C(13)C($\underline{C}H_3)_3$); 31.3 (C(14a)$\underline{C}H(CH_3)_2$); 31.5, 31.6 (C(3)C($\underline{C}H_3)_3$, C(11)C($\underline{C}H_3)_3$); 32.4 (C(8)$\underline{C}H(CH_3)_2$); 34.2, 34.3 (C(3)$\underline{C}(CH_3)_3$, C(11)$\underline{C}(CH_3)_3$); 34.93 (C(13)$\underline{C}(CH_3)_3$); 35.00 (C(1)$\underline{C}(CH_3)_3$); 37.5 (C(15b)$\underline{C}H(CH_3)_2$); 41.2 (C(15a)H); 41.5 (C(15)H); 45.6 (C(7a)H); 54.7 (C(8)); 80.3 (C(14a)); 81.0 (C(15b)); 121.6, 122.2, 123.7, 123.8, (C(2)H, C(4)H, C(10)H, C(12)H); 127.6 (C(7)H); 129.0 (C(17)H); 130.4 (C(6)); 133.9 (C(13)); 136.4 (C(1)); 139.0 (C(18)H); 142.0, 134.5, 143.2 (C(9a), C(13a), C(16a)); 142.07, 142.7 (C(3), C(11)); 147.3 (C(4a)); 159.7 (C(5a)); 167.9 (C(8a)).

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