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Structure and electronic properties of quinone dimers connected with acetylene and diacetylene linkages

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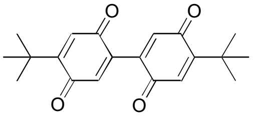
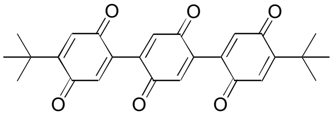
A B S T R A C T

Quinone dimers connected with acetylene (**QAQ**) and diacetylene linkages (**QAAQ**) have been synthesized and their structure and electronic properties studied. X-ray analysis, DFT calculations, and UV–vis measurements showed that, unlike directly connected quinone dimers (**QQ**), they had planar and thus efficiently extended π conjugation systems. The respective reduction potentials of **QAQ** and **QAAQ** were considerably raised, and **QAQ** thereby behaved as a mild oxidizing agent.

1. Introduction

Quinones have been widely employed in various fields of chemistry, including reaction chemistry, medicinal chemistry, biochemistry, and material chemistry.[1] As the usefulness of quinones is based on their strong electron acceptor characters, a significant number of studies have been conducted with the aim of modulating or enhancing these characters. It is well known that such characters can be enhanced by the extension of the π system[2] or by the substitution of electron-withdrawing groups. In addition, we recently reported that a covalent linkage between quinone moieties significantly enhances their electron acceptor characters; covalently connected quinone dimers (**QQ**) and trimers (**QQQ**) were observed to have considerably higher reduction potentials as compared to quinone monomers.[3] The enhanced electron acceptor characters of **QQ** and **QQQ** are likely to be largely attributable to the 'substituent effect' of the quinone moiety; the contribution of the extension of the π system appeared to be small since the X-ray structure and the electronic absorption spectra of **QQ** and **QQQ** indicated that quinone moieties were highly twisted owing to the steric repulsion between the hydrogen and the oxygen atoms, and as a result the π systems were not fully conjugated.


QQ


QQQ

These findings prompted us to investigate quinone dimers connected with acetylene and diacetylene linkages, denoted as **QAQ** and **QAAQ**, respectively. It was expected that the π systems in those compounds would be more efficiently conjugated since the linkages would reduce the steric repulsion in order to enhance the planarity of the π system,[4] as well as that two (**QAQ**) or four (**QAAQ**) additional p atomic orbitals would contribute to the extension of the π systems. In fact, there are several compounds in which TTF,[5] porphyrin,[6,7] anthraquinone,[8] and dendrimeric moieties[9] are connected by acetylene and/or diacetylene linkages, exhibiting remarkable photochemical and electrochemical properties due to their extended π systems. Acetylene and diacetylene linkages are also advantageous in view of the rigidity of the molecular structure and the facileness of the synthesis, which determines their common use in material chemistry.[10] Quinones connected with diacetylene linkages were previously prepared as partial structures of *p*-quinone-fused hexadehydro[18]annulenes,[11] although the effects of the diacetylene linkages could not be examined due to the lack of analogues, which are connected either directly or with acetylene linkages.[12] Herein, **QAQ** and **QAAQ** were synthesized, their electronic and structural properties were investigated by means of X-ray diffraction, Raman and UV–vis spectra, DFT calculations, and cyclic voltammetry (CV), and the results were compared with those for **QQ**. Additionally, the capabilities of **QAQ** and **QAAQ** as oxidizing agents were studied.

2. Results and discussion

QAQ and **QAAQ** were synthesized as shown in Scheme 1. Similarly to **QQ**, *tert*-butyl groups were substituted into **QAQ** and **QAAQ** in order to increase their solubility and stability. 2-*tert*-Butyl-5-iododimethoxybenzene (**1**) was subjected to Sonogashira coupling[13]

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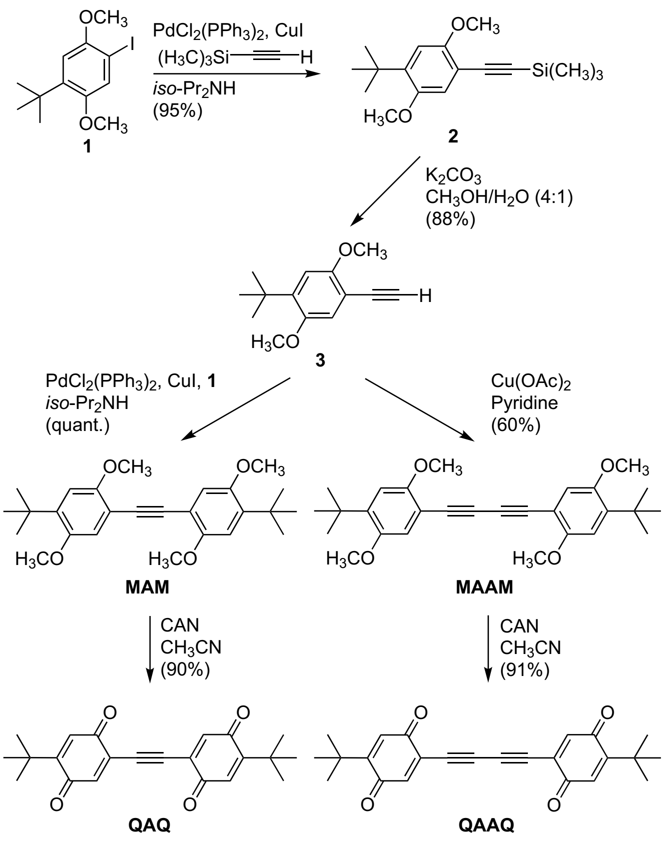
with trimethylsilylacetylene to give **2**, followed by the removal of the TMS protections under basic conditions to give **3**, which was in turn subjected to Sonogashira coupling with **1** to afford **MAM**, while the Eglinton coupling[14] of **3** gave **MAAM**. By oxidation using cerium(IV) ammonium nitrite (CAN), **MAM** and **MAAM** yielded **QAQ** and **QAAQ** as thermally stable, deep red powders, respectively.



Scheme 1. Synthesis of **QAQ** and **QAAQ**.

An X-ray analysis of **QAQ** was performed using a good crystal prepared by slow evaporation from a 1,2-dimethoxyethane solution. The X-ray structure of **QAQ** was revealed to be a centrosymmetrical molecule (Fig. 1, left). While the two quinone moieties of **QQ** were considerably twisted in its X-ray structure, the π system of **QAQ** was found to be almost planar owing to the acetylene linkage. An X-ray analysis was also conducted for a crystal of **QAAQ** obtained from a dichloromethane solution. As shown in Figure 2 (left), the molecule was centrosymmetric, situated on the inversion center of the crystal, with a nearly planar conformation. As seen in the X-ray structures of several other oligoyne compounds,[15] the diacetylene moiety was found to bear a slight deviation from linearity. It is noteworthy that while the quinone ring of **QQ** was in the boat form due to the steric repulsion between the oxygen atoms in the crystalline,[3] no structural distortion of the quinone moieties was found in **QAQ** and **QAAQ**. The values of the structural parameters of **QAQ** and **QAAQ** (bond lengths, bond angles, and dihedral angles) were virtually identical to the standard values of these parameters for quinone and acetylene moieties within errors, indicating that there is no influence from the acetylene moiety on the structural parameters of the quinone moieties, and vice versa. On the other hand, $\nu_{\mathrm{C\equiv C}}$ of **QAQ** (2203 $\mathrm{cm^{-1}}$) was observed to shift bathochromically as compared to those of diphenylacetylene (2226 $\mathrm{cm^{-1}}$)[16] and **MAM** (2220 $\mathrm{cm^{-1}}$), while $\nu_{\mathrm{C\equiv C}}$ of **QAAQ** was found to be 2215 $\mathrm{cm^{-1}}$, which is comparable to that of **MAAM** (2217 $\mathrm{cm^{-1}}$).

The potential energy curves for the –C≡C– and ≡C–C≡ bond rotations were calculated by means of the B3LYP/6-311+G(d,p) method for model compounds bearing no *tert*-butyl groups, denoted as **QAQ′** and **QAAQ′**. It was revealed that **QAQ′** and **QAAQ′** had three and four potential minima, respectively, among which the *anti* conformers ($\phi \sim 180°$) represented the global minima and the *syn* conformers ($\phi \sim 0°$) represented one of the next energy levels (Fig. 3). The potential energies of the *anti* and *syn* conformers of **QAQ′** and **QAAQ′**, together with those of **MAM′** and **MAAM′**, are compared as shown in Table 1. **QAQ′**, **QAAQ′**, and **MAM′** prefer *anti* to *syn* conformations, while those two conformations are energetically comparable for **MAAM′**. It should be noted that the energetic difference between the *anti* and *syn* conformers is 1.5 $\mathrm{kcal\,mol^{-1}}$ for **QAQ′**, which is more significant than that for **MAM′**. This cannot be explained in terms of different magnitudes of the steric repulsion between the oxygen atoms since those atoms are well separated even in the *syn* conformers: the oxygen–oxygen distance is 4.26 Å in the *syn* conformer of **QAQ′**, which is considerably larger than the sum of van der Waals radii (3.18 Å).[17] The larger disadvantage of the *syn* conformer of **QAQ′** probably arises from the more significant electrostatic repulsion between the oxygen atoms in **QAQ′**, since the C=O bond of **QAQ′** is more polarized than the aryl–O bond of **MAM′**, which magnifies the δ- character of the oxygen atom. On the other hand, the *syn* conformers are also disfavored in **QAAQ′**, albeit more weakly than in **QAQ′**. This indicates that the disadvantage of the *syn* conformers originates from long-distance interactions, i.e., from Coulombic forces. Although **QAQ′** and **QAAQ′** prefer *anti* conformations, the energy difference between the *syn* and *anti* conformers appear to be relatively small.

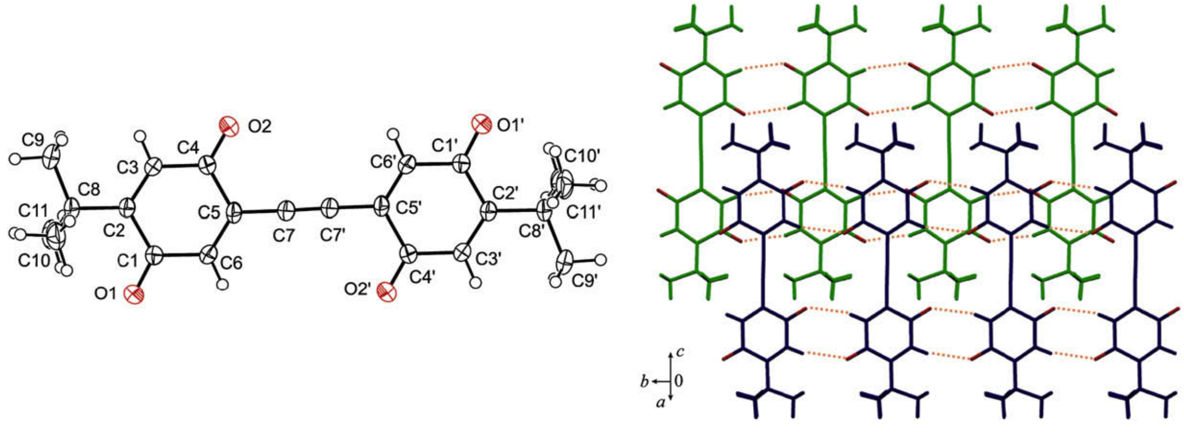


Figure 1. X-ray structure of **QAQ**. (left) ORTEP drawing (50% probability). (right) A top view of ribbon motif formed by CH/O interactions (represented by orange broken lines).

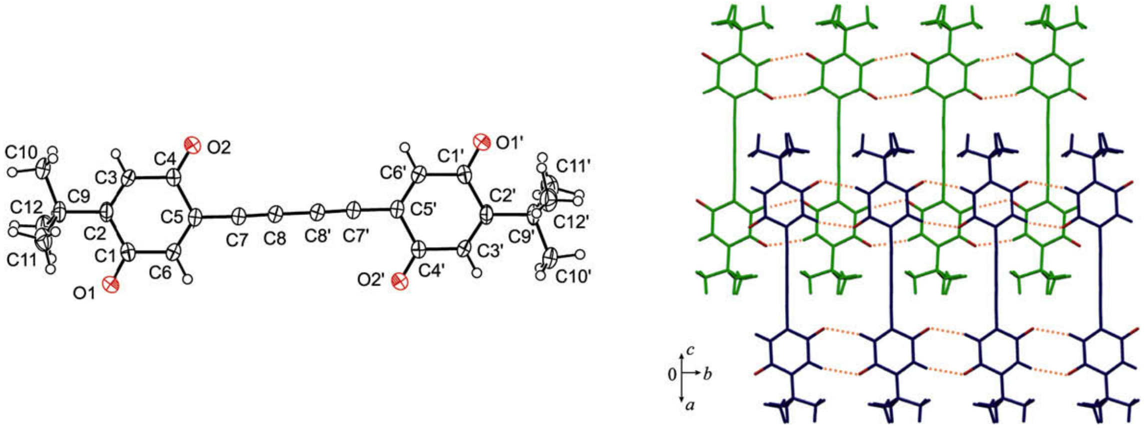


Figure 2. X-ray structure of **QAAQ**. (left) ORTEP drawing (50% probability). (right) A top view of ribbon motif formed by CH/O interactions (represented by orange broken lines).

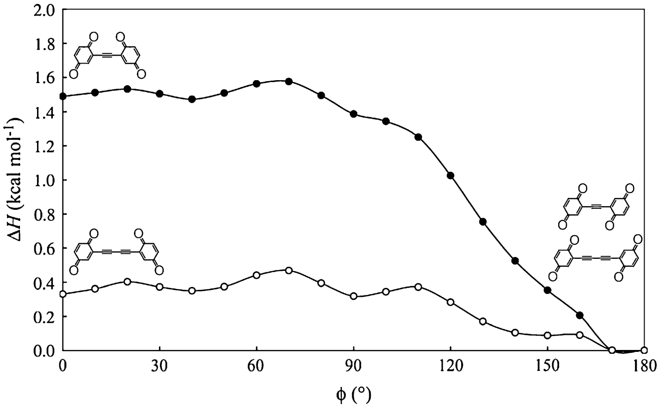


Figure 3. Potential energy curves for the –C≡C– (**QAQ′**, filled circles) and ≡C–C≡ (**QAAQ′**, open circles) bond rotation relative to the energy of the conformers (ϕ=180°) calculated by B3LYP/6-311+G(d,p) methods.

Thus, planar conformations observed in the X-ray structure of **QAQ** and **QAAQ** are due not only to intramolecular factors but also to intermolecular interactions probably. In fact, Figures 1 (right) and 2 (right) show the presence of four-fold CH/O interactions[18] between the adjacent molecules in crystalline ($d_{C\cdots O}$=3.367 and 3.387 Å for **QAQ** and 3.367 and 3.371 Å for **QAAQ**), which may assist the conformations of **QAQ** and **QAAQ** to be planar. The stacking of the ribbon motifs formed with the aid of CH/O interactions is also shown in Figures 1 and 2, describing no significant overlapping of the π moieties between the layers (blue and green). Also, the acetylene (**QAQ**) and diacetylene (**QAAQ**) moieties are far apart so that neither photo-dimerization nor polymerization is likely to take place in crystalline.

The electronic absorption spectra (1,4-dioxane) of 4,4′-di-*tert*-butyl-2,2′,5,5′-tetramethoxybiphenyl (**MM**), **MAM**, **MAAM**, **QQ**, **QAQ**, and **QAAQ** are shown in Figure 4. Compared to **QQ**, substantial bathochromic shifts of the absorption edge were observed in the spectra of **QAQ** and **QAAQ** (570 nm, vs 390 nm in **QQ**). Additionally, new absorption peaks appeared around 320, 380, and 470 nm. These indicate the efficient extension of the π conjugation system in **QAQ** and **QAAQ** owing to the acetylene and diacetylene linkages. It is noteworthy that the bathochromic shifts of the absorption peaks were more significant for **QQ**, **QAQ**, and **QAAQ** than for **MM**, **MAM**, and **MAAM**. On the other hand, although the bathochromic shift of the absorption edge between **MAM** and **MAAM** was found to be 20 nm, no notable shift was observed between **QAQ** and **QAAQ**.

Table 1
Potential energies (kcal mol^{-1}) and dihedral angles (°, in parentheses) of the *syn* and *anti* conformers of **QAQ′**, **QAAQ′**, **MAM′**, and **MAAM′** geometrically optimized using the B3LYP/6-311+G(d,p) method

Compound	ΔE[a] (dihedral angle)	
	anti	*syn*
QAQ′	0.00 (179.7)	1.49 (0.0)
QAAQ′	0.00 (179.5)	0.33 (0.2)
MAM′	0.00 (179.6)	0.77 (0.2)
MAAM′	0.00 (177.7)	−0.10 (12.9)

[a] Relative to the energy of the *anti* conformer.

The redox behavior of 2,5-di-*tert*-butyl-1,4-benzoquinone (**Q**), **QQ**, **QAQ**, and **QAAQ** was measured by means of CV (Table 2). In a dichloromethane solution, **QQ**, **QAQ**, and **QAAQ** commonly exhibited two reversible reduction waves ($E_1^{1/2}$ and $E_2^{1/2}$) corresponding to the formation of radical anions and dianions, respectively. The respective third waves (E_3) were irreversible, and were followed by the decay of the resultant species since the E_3 waves appeared to be accompanied by small shoulder-like

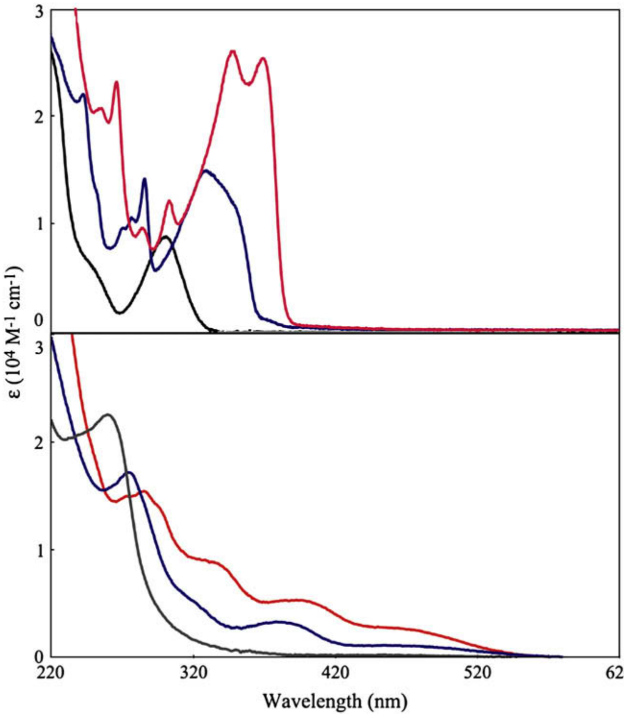


Figure 4. Electronic absorption spectra of **MM** (upper black), **MAM** (upper blue), **MAAM** (upper red), **QQ** (lower black), **QAQ** (lower blue), and **QAAQ** (lower red) in 1,4-dioxane.

Table 2
Reduction potentials for compounds **Q**, **QQ**, **QAQ**, and **QAAQ**[a]

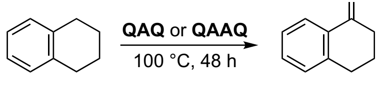
Compound	$E_1^{1/2}$	$E_2^{1/2}$	E_3^{pc}
Q	−1.06 (1e)	−1.78 (1e)	
QQ	−0.73 (1e)	−1.07 (1e)	−1.54[b]
QAQ	−0.63 (1e)	−0.80 (1e)	−1.58[b]
QAAQ	−0.60 (1e)	−0.73 (1e)	−1.61[b]

[a] Electrode; Pt (working), Pt (counter), and Ag/Ag$^+$ (reference). Supporting electrolyte n-Bu$_4$NClO$_4$. Solvent; CH$_2$Cl$_2$. Scan rate; 100 mV s^{-1}.

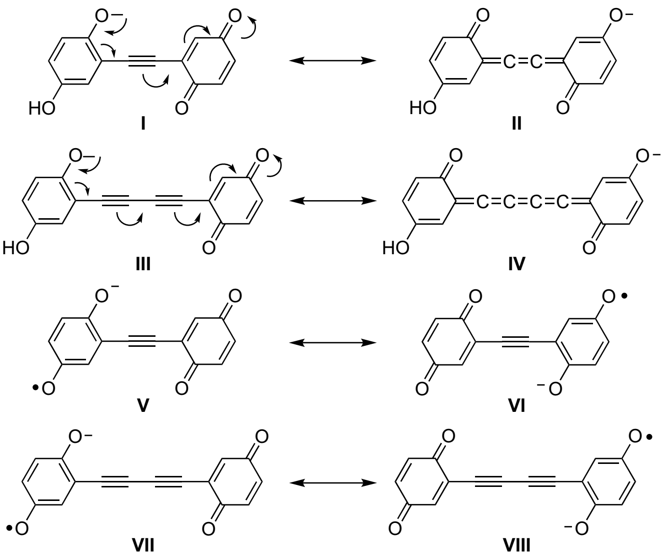
[b] Irreversible.

extensions, as shown in Figure S1. The rise of the $E_1^{1/2}$s of **QAQ** and **QAAQ** as compared to **QQ** is indicative of the efficient extension of the π conjugation system by the acetylene and diacetylene linkages, although it was smaller than expected from the comparison with the $E_1^{1/2}$ of **Q**. This indicates that $E_1^{1/2}$ can be significantly lowered by any linkage of quinone moieties, as well as that the contribution of the planarization of the π system to the lowering of $E_1^{1/2}$ is relatively small. On the other hand, $E_2^{1/2}$s were considerably raised in the order of **QQ**, **QAQ**, and **QAAQ**, which is explainable in terms of the reduction of the on-site Coulombic repulsion in the extended π systems of **QAQ** and **QAAQ**.

As **QAQ** and **QAAQ** were found to have strong electron acceptor characters, their capabilities as oxidizing agents were examined. When a tetralin (1,2,3,4-tetrahydronaphthalene) solution of **QAQ** was heated at 100 °C for 48 h, **QAQ** disappeared completely, and nearly double the molar quantity of α-tetralon based on **QAQ** was obtained. When **QAAQ** was used instead of **QAQ** under the same conditions, the α-oxidation of tetralin proceeded, albeit rather slowly: 32% of unreacted **QAAQ** was recovered, and ca. 1.8 times the molar quantity of α-tetralon based on the consumed **QAAQ** was obtained (Scheme 2). The different behavior of **QAQ** and **QAAQ** should be attributable to the different reaction rates of hydride ion transfer from the 1-position of tetralin to the carbonyl oxygen of **QAQ** and **QAAQ**, respectively, which is known to be the rate-determining step in the general mechanism of benzylic oxidation by quinones.[19] The hydride ion transfer is likely to occur faster in **QAQ** because of the higher stability of the phenoxide **I** compared to **III** (Scheme 3). In the phenoxide compounds, the negative charges may be regarded as being localized considerably as depicted in **I** and **III** because of the intrinsically asymmetrical molecular structure. Moreover, the contribution of the resonance formulae **II** and **IV** is not important due to the lack of aromaticity. This indicates that the quinone moieties in **I** and **III** should affect the phenoxide moieties mainly in an inductive manner. Generally, the inductive effect is greater when the substituent locates closely. Therefore, the stabilization effects by the quinone moiety should be greater in **I** than in **III** in order that the hydride transfer to **QAQ** occurred faster than that to **QAAQ**. Note that the situation is thoroughly different in the radical anions **V** and **VII**, the latter being more stabilized than the former. This is due to highly delocalized characters of the radical spins and negative charges as described by the resonance formulae **VI** and **VIII**. As the stabilization effects would be generally larger in the more extended π compounds, **VII** would be more stabilized than **V**. This is supported by the fact that the $E_1^{1/2}$ of **QAAQ** was observed to be lower than that of **QAQ** (Table 2). In contrast, heating a tetralin solution of **QQ** yielded a complex mixture containing 18% of 3,7-di-*tert*-butyl-8-hydroxydibenzofuran-1,4-dione[20] and a trace amount of α-tetralon. On the other hand, products were not observed in hot *o*-xylene solutions of any of the three dimers **QQ**, **QAQ**, and **QAAQ**. This can be explained in terms of relative stability of the intermediate carbocations;[21] benzylic cation generated from *o*-xylene by hydride abstract is less stabilized than that from tetralon because the former is a primary cation while the latter is a secondary one. Next, as quinone is an electron-accepting moiety, **QAQ** was expected to behave as a dienophile, similarly to acetylenedicarboxylic acid diesters, and was thus subjected to Diels–Alder reactions with tetraphenylcyclopentadienone, cyclopentadine, furan, and Danishefsky's diene (1-methoxyl-3-trimethylsiloxybutadiene).[22] However, all attempts resulted in yielding inseparable complex mixtures.



Scheme 2.



Scheme 3.

3. Conclusions

We have described the synthesis and the properties of **QAQ** and **QAAQ**, in which two quinone moieties are connected by acetylene and diacetylene linkages, respectively. DFT calculations showed that **QAQ** and **QAAQ** prefer the planar conformations, although their planar structure observed in the X-ray structure should be due not only to the intramolecular factors but also to intermolecular CH/O interactions. The intrinsically planer character of the π conjugation system of **QAQ** and **QAAQ** gives rise to the bathochromic shift in their UV–vis spectra and the notable rise of the reduction potentials as compared to **QQ**. It was also observed that both **QAQ** and **QAAQ** behaved as mild oxidizing agents, while **QQ** decayed by itself in the same conditions due to its thermal instability. Studies of quinone trimers and higher oligomers linked directly or connected with acetylene or diacetylene linkages are currently underway as further exploration of co-oligomers consisting of quinone and acetylene moieties.

4. Experimental section

4.1. General

All commercially available chemicals were used without further purification except pyridine, which was dried over KOH. All reactions were performed in standard glassware under an inert argon atmosphere, unless otherwise stated. Melting points were determined on microscopic thermometer without correction. ^{1}H (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a JEOL JNM-ECP600 in CDCl$_3$ with tetramethylsilane as internal reference. Mass spectra were conducted on a JEOL MStation JMS-

700 (EI) and a JEOL JMS-SX102A (HRMS/EI). Raman spectra were measured on a JASCO RFT-200. Electronic absorption spectra were recorded on a SHIMADZU UV-2400PC. Cyclic voltammetry (CV) was performed on an ALS model 600A in 1.0 mM of substrate. All oxidation CV measurements were carried out in anhydrous dichloromethane containing 0.1 M tetrabutylammonium perchlorate (n-Bu_4NClO_4) as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode and a platinum wire as a counter electrode. All potentials were recorded versus Ag/Ag^+ electrode (in acetonitrile) as a reference electrode. The redox processes were analyzed by using semiderivative technique.

4.2. Synthesis of 2-*tert*-butyl-5-trimethylsilylethynyl-1,4-dimethoxybenzene (2)

A solution of 2-*tert*-butyl-5-iodo-1,4-dimethoxybenzene (**1**) (3.73 g, 12 mmol) and CuI (56 mg, 0.29 mmol) in diisopropylamine (40 mL) was degassed with argon. After dichlorobis-(triphenylphosphine)palladium (0.41 g, 0.58 mmol) and trimethylsilylacetylene (2.5 mL, 17 mmol) was added, the reaction mixture was stirred at ambient temperature for 4 h. After addition of water, the reaction mixture was extracted with ethyl acetate. Combined organic phase was washed with 3 mol L^{-1} HCl, brine, dried over Na_2SO_4, and evaporated to dryness. From the crude product, **2** (3.20 g, 95%) was isolated by preparative chromatography (SiO_2, n-hexane/EtOAc 9:1) as a brown powder. Mp 118–120 °C. ^{1}H NMR: δ=6.90 (1H, s, Ar), 6.81 (1H, s, Ar), 3.85 (3H, s, $-OCH_3$), 3.79 (3H, s, $-OCH_3$), 1.35 (9H, s, *t*-Bu), 0.26 (9H, s, $-SiMe_3$). ^{13}C NMR: δ=154.50, 152.30, 141.00, 116.65, 111.40, 109.91, 101.45, 97.79, 56.86, 55.62, 35.29, 29.53, 0.12. MS (EI): m/z=290 (M^+). HRMS (m/z): 290.1698 (M^+, calcd 290.1702 for $C_{17}H_{26}SiO_2$).

4.3. Synthesis of 2-*tert*-butyl-5-ethynyl-1,4-dimethoxybenzene (3)

A solution of **2** (3.20 g, 11 mmol) in methanol/hexane (4:1 v/v) (200 mL) was degassed with argon. After K_2CO_3 (0.76 g, 5.5 mmol) was added, the reaction mixture was stirred at ambient temperature for 3 h. After addition of water, organic layer was separated, and aqueous layer was extracted with ethyl acetate. Combined organic phase was washed with brine, dried over Na_2SO_4, and evaporated to dryness to give **3** (2.11 g, 88%) as a brown solid. Mp 58–60 °C. ^{1}H NMR: δ=6.94 (1H, s, Ar), 6.85 (1H, s, Ar), 3.88 (3H, s, $-OCH_3$), 3.79 (3H, s, $-OCH_3$), 3.28 (1H, s, $-C{\equiv}CH$), 1.37 (9H, s, *t*-Bu). ^{13}C NMR: δ=154.71, 152.26, 141.31, 116.75, 110.84, 108.60, 80.47, 80.26, 56.59, 55.64, 35.34, 29.52. MS (EI): m/z=218 (M^+). IR (Nujol, cm^{-1}): 3278 (ν_{C-H}), 2098 ($\nu_{C\equiv C}$). HRMS (m/z): 218.1305 (M^+, calcd 218.1307 for $C_{14}H_{18}O_2$).

4.4. Synthesis of bis(4-*tert*-butyl-2,5-dimethoxyphenyl)-acetylene (MAM)

A solution of **1** (2.35 g, 7.4 mmol) and CuI (35 mg, 0.18 mmol) in diisopropylamine (40 mL) was degassed with argon. After dichlorobis(triphenylphosphine)palladium (0.26 g, 0.36 mmol) and **3** (2.41 g, 11 mmol) was added, the reaction mixture was stirred at ambient temperature for 4 h. After addition of water, the reaction mixture was extracted with ethyl acetate. Combined organic phase was washed with 3 mol L^{-1} HCl, brine, dried over Na_2SO_4, and evaporated to dryness. From the crude product, **MAM** (3.09 g, quant) was isolated by preparative chromatography (SiO_2, n-hexane/EtOAc 9:1) as a white powder. Mp 231–233 °C. ^{1}H NMR: δ=7.00 (2H, s, Ar), 6.86 (2H, s, Ar), 3.91 (6H, s, $-OCH_3$), 3.82 (6H, s, $-OCH_3$), 1.37 (18H, s, *t*-Bu). ^{13}C NMR: δ=154.02, 152.40, 140.36, 116.22, 111.47, 110.54, 89.38, 56.97, 55.68, 35.27, 29.58. Raman (cm^{-1}): 2218 ($\nu_{C\equiv C}$). MS (EI): m/z=410 (M^+). HRMS (m/z): 410.2455 (M^+, calcd 410.2457 for $C_{26}H_{34}O_4$).

4.5. Synthesis of bis(5-*tert*-butyl-1,4-benzoquinon-2-yl)-acetylene (QAQ)

To a solution of **MAM** (0.12 g, 0.3 mmol) in acetonitrile (5 mL) was added cerium ammonium nitrite (CAN, 0.79 g, 1.5 mmol) at ambient temperature in dark. After stirring for 4 h, the reaction mixture was quenched with water, then subjected to supersonic treatment until the solid was precipitated. The precipitate was separated by suction filtration, washed with acetone/water (1:1 v/v), dried, and recrystallized from 1,2-dimethoxyethane to give **QAQ** as a deep red powder (0.09 g, 90%). Mp 200–203 °C. ^{1}H NMR: δ=6.96 (2H, s, CH), 6.66 (2H, s, CH), 1.29 (18H, s, *t*-Bu). ^{13}C NMR: δ=186.24, 183.34, 157.05, 140.50, 131.44, 129.60, 93.35, 35.45, 29.04. IR (cm^{-1}): 1665, 1445 ($\nu_{C=O}$). Raman (cm^{-1}): 2203 ($\nu_{C\equiv C}$). MS (EI): m/z=350 (M^+). HRMS (m/z): 350.1520 (M^+, calcd 350.1518 for $C_{22}H_{22}O_4$).

4.6. Synthesis of bis(4-*tert*-butyl-2,5-dimethoxyphenyl)buta-1,3-diyne (MAAM)

A solution of **3** (0.50 g, 2.3 mmol) and $Cu(OAc)_2$ (0.83 mg, 4.6 mmol) in pyridine (50 mL) was stirred at 40 °C for 3 h. After addition of water, the reaction mixture was extracted with chloroform for three times. Combined organic phase was washed with 3 mol L^{-1} HCl, satd $NaHCO_3$, brine, dried over Na_2SO_4, and evaporated to dryness. From the crude product, **MAAM** (0.30 g, 60%) was isolated by preparative chromatography (SiO_2, n-hexane/EtOAc 9:1) as a light brown powder. Mp 200–203 °C. ^{1}H NMR: δ=6.95 (2H, s, Ar), 6.84 (2H, s, Ar), 3.88 (6H, s, $-OCH_3$), 3.79 (6H, s, $-OCH_3$), 1.37 (18H, s, *t*-Bu). ^{13}C NMR: δ=155.51, 152.24, 141.71, 116.64, 110.86, 108.66, 78.79, 77.59, 56.61, 55.60, 35.44, 29.48. Raman (cm^{-1}): 2217 ($\nu_{C\equiv C}$). MS (EI): m/z=435 ($[M+1]^+$). HRMS (m/z): 434.2459 (M^+, calcd 434.2457 for $C_{28}H_{34}O_4$).

4.7. Synthesis of bis(5-*tert*-butyl-1,4-benzoquinon-2-yl)buta-1,3-diyne (QAAQ)

To a solution of **MAAM** (0.51 g, 1.2 mmol) in acetonitrile (30 mL) was added cerium ammonium nitrite (3.24 g, 5.9 mmol) at ambient temperature in dark. After stirring for 4 h, the reaction mixture was quenched with water, then subjected to supersonic treatment until the solid was precipitated. The precipitate was separated by suction filtration, washed with acetone/water (1:1 v/v), dried, and recrystallized from dichloromethane to give **QAAQ** as a deep red powder (0.40 g, 91%). Mp >300 °C. ^{1}H NMR: δ=6.92 (2H, s, CH), 6.65 (2H, s, CH), 1.28 (18H, s, *t*-Bu). ^{13}C NMR: δ=186.01, 183.14, 157.24, 141.39, 131.50, 129.45, 85.18, 77.79, 35.50, 29.02. IR (cm^{-1}): 1658, 1447 ($\nu_{C=O}$). Raman (cm^{-1}): 2215 ($\nu_{C\equiv C}$). MS (EI): m/z=374 (M^+). HRMS (m/z): 374.1521 (M^+, calcd 374.1518 for $C_{24}H_{22}O_4$).

4.8. Oxidation of tetralin and *o*-xylene by QQ, QAQ, and QAAQ

Typical procedure. A solution of **QAQ** (35 mg, 0.10 mmol) in tetralin (2 mL) was heated at 100 °C for 48 h. After cooling, the reaction mixture was subjected to column chromatography (SiO_2, n-hexane/EtOAc 9:1) to give α-tetralon (28 mg, 0.19 mmol).

4.9. X-ray analysis

X-ray diffraction data were collected on a four-circle diffractometer. Crystal parameters were determined by means of peaksearch method, and all intensities were converted to structure factors in a conventional manner. The crystal structure was solved by direct methods and Fourier technique (SHELXL-97[23] on PC-Linux). All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were found on a differential Fourier map and refined isotropically. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 718053 and 718054. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

QAQ. $C_{22}H_{22}O_4$, MW=350.40, monoclinic, $P2_1/c$ (no. 14), a=9.381(2), b=6.775(3), c=14.9256(18) Å, β=93.443(15)°, Z=2, T=200 K, D_{calcd}=1.229 g cm^{-3}, $R1$=0.046 ($I>2\sigma(I)$), $wR2$=0.136 (all data).

QAAQ. $C_{24}H_{22}O_4$, MW=374.42, monoclinic, $C2/c$ (no. 15), a=22.685(4), b=6.724(4), c=17.703(5) Å, β=131.021(10)°, Z=4, T=200(2) K, D_{calcd}=1.221 g cm^{-3}, $R1$=0.083 ($I>2\sigma(I)$), $wR2$=0.275 (all data).

4.10. Molecular orbital (MO) calculations

Molecular orbital (MO) calculations were performed using Spartan '04 Windows (Wavefunction, Inc.) on Microsoft Windows XP. All calculations were performed using B3LYP/6-311+G(d,p) methods. Computational analysis was performed for the compounds bearing no *tert*-butyl substituents, bis(1,4-benzoquinon-2-yl)acetylene (**QAQ′**), bis(1,4-benzoquinon-2-yl)buta-1,3-diyne (**QAAQ′**), bis(2,5-dimethoxyphenyl)acetylene (**MAM′**), and bis(2,5-dimethoxyphenyl)buta-1,3-diyne (**MAAM′**) as a model compound. Fully geometrical optimization was performed for their *anti* and *syn* conformers. As to **QAQ′** and **QAAQ′**, fully relaxed triple-bond (**QAQ′**) or (central) single-bond (**QAAQ′**) torsional potentials were also calculated; i.e., for each fixed torsional angle (ϕ) around the triple (**QAQ′**) or single-bond (**QAAQ′**), all remaining internal degrees of freedom were optimized. A 10° grid of points was applied. During calculations, C_2 molecular symmetry was postulated for all cases except **QAAQ′** at ϕ=170° and 0°, geometrical optimization process of which did not converge by any means. Thus, geometrical optimization of C_1 symmetrical structure was conducted for **QAAQ′** at ϕ=170°, while for **QAAQ′** at ϕ=0° the forementioned *syn* conformer of **QAAQ′** substituted, because its ϕ was nearly equal to zero. The obtained total energies appear in Table S1.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.001.

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