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The Quinones of Benzocyclobutadiene: A Computational Study

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The conventional (excluding non-Kekulé, singlet diradical structures) quinones of benzocyclobutadiene were studied computationally. Eight structures were examined, namely (based on the CA names for benzocyclobutenedione), benzocyclobutenedione or bicyclo[4.2.0]octa-1,3,5-triene-7,8-dione, bicyclo[4.2.0]octa-3,5,8-triene-2,7-dione, bicyclo[4.2.0]octa-1,4,6-triene-3,8-dione, bicyclo[4.2.0]octa-1(6),4,7-triene-2,3-dione, bicyclo[4.2.0]octa-1(8), 4,6-triene-2,3-dione, bicyclo[4.2.0]octa-1(6),3,7-triene-2,5-dione, bicyclo[4.2.0]octa-1(8),3,6-triene-2,5-dione, and bicyclo[4.2.0]octa-1,5,7-triene-3,4-dione (the question of resonance or tautomerism for the 2,3-dione pair and the 2,5-dione pair is considered). Using DFT (B3LYP/6-31G*) and ab initio (MP2/6-31G*) methods the geometries of the eight species were optimized, giving similar results for the two methods. The heats of formation of the quinones were calculated, placing them in low-energy (-17 kJ mol^{-1}, 7,8-dione), medium-energy (79$-$137 kJ mol^{-1}, 2,7-, 3,8-, and 3,4-diones), and high-energy (260$-$275 kJ mol^{-1}, 2,3- and 2,5-diones) groups. Diels$-$Alder reactivity as dienophiles with butadiene indicated the 2,7-, 3,8-, and particularly the 3,4-quinone may be relatively unreactive toward dimerization or polymerization and are attractive synthesis goals. Isodesmic ring-opening reactions and NICS calculations showed aromatic/nonaromatic properties to be essentially as expected from the presence of a benzene or cyclobutadiene ring. UV spectra, ionization energy electron affinity, and HOMO/LUMO energies were also calculated.

Introduction

The hydrocarbon benzocyclobutadiene, **1h**, gives rise conceptually to the quinones **1-6**; this paper reports a computational analysis of these eight (we address later **4a**/**4b** and **5a**/**5b**) quinones (Figure 1). Acyclic polyenes with alternating single and double bonds are conceptually the simplest examples of conjugated species known to the organic chemist. Cyclic polyenes or formal polyenes are conceptually formed from these by removing C$-$H bonds and connecting the resulting "special carbons" by C$-$C bonds. This process results in species that are generally recognized as aromatic or antiaromatic, as well as those compounds that are essentially nonaromatic as they lack the profound destabilization of cyclobutadiene and the glorious stabilization of the aromatic benzene, or even not much more than the glimmers of these phenomena. In turn, these polyenes are conceptually the parent of one or more quinones. In spawning a quinone, two hydrogens are replaced by two oxygens, wherein a $-(CH{=}CH)_n-$ moiety becomes $-CO-(CH{=}CH)_{n-1}-CO-$ for any $n \geq 1$, as in **7** → **7q** and **8** → **8q1,2** and **8q1,4** (Figure 2). In the current study we will not consider unconventional quinones like **8q1,3**; these are highly reactive diradicals which are not isolable by standard methods and require special techniques to address their energetics computationally or experimentally.[1,2]

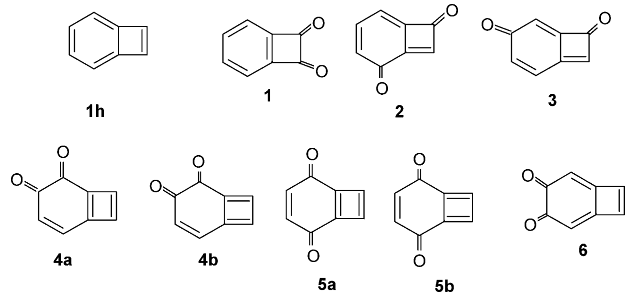

Figure 1. Benzocyclobutadiene and its structurally related quinones.

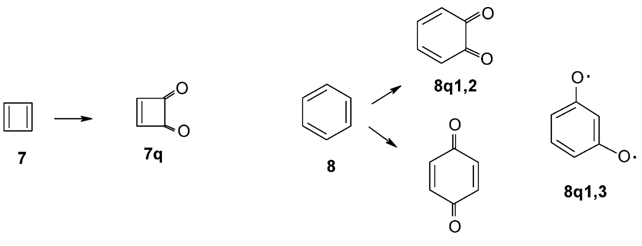

Figure 2. The relationship of polyenes to quinones.

Quinones have been studied for well over 100 years: 1,4-benzoquinone **8q1,4** was prepared in 1838[3] and the synthetically more challenging 1,2-benzoquinone **8q1,2** in 1898/1094.[4] The earlier era of quinone chemistry was confined to quinones of common aromatic compounds like benzene, naphthalene, and anthracene.[5,6] Their syntheses made use of the preformed carbon framework by such reactions as the oxidation/dehydrogenation of the corresponding arene diols. The study of quinones corresponding to less prosaic polyenes made its debut in 1971 with the synthesis of benzocyclobutenedione (**1**)[7] and cyclobutenedione (**7q**),[8] necessarily more arduous and creative, because the "obvious" hydrocarbon precursors, or suitable derivatives, evaded synthesis. Subsequently, quinones of other nonbenzenoid compounds have been examined: the azulenoquinones,[9] the cyclooctatetraenoquinones (**9q1,4** and **9q1,2**),[10−12] and the pentalene quinones (**10**, **11**, **12**, **13**)[13] (Figure 3). Again, indirect synthetic methodologies had to be used, as suitably

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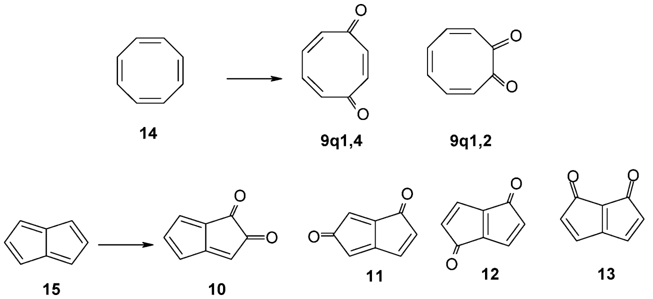


Figure 3. The quinones of cyclooctatetraene and pentalene.

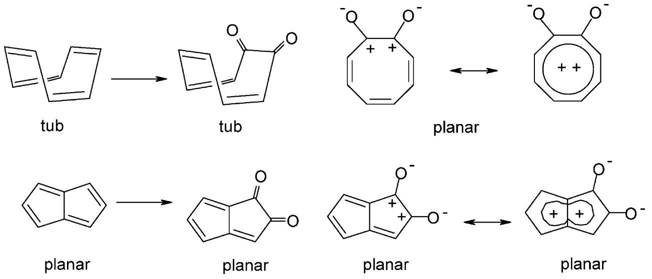


Figure 4. The grounds for aromaticity in a quinone related to a polyene with an even number of CC double bonds.

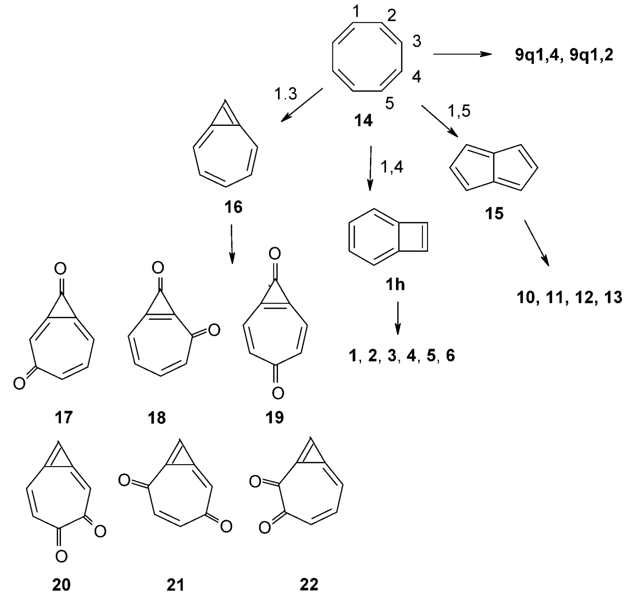


Figure 5. Cyclooctatetraene as the parent for a family of quinones.

functionalized derivatives of the parent hydrocarbons remain absent. Indeed, an important impetus for the study of the quinones of cyclooctatetraene and pentalene was their putative aromaticity, the theoretical basis for, and computational probing of which, has been discussed.[12,13] Briefly, a quinone formed from a polyene with an even number of CC double bonds is potentially aromatic if its carbonyl groups are sufficiently polarized to endow the molecule with significant dication character, so that it then has a Hückel aromatic $4n + 2$ number of π electrons, and if the energy to be gained by flattening, whenever necessary, is enough to allow atomic p−p overlap around the perimeter that the species can overcome incurred strain. A corollary of this is that a quinone from a cyclic polyene with an odd number of CC double bonds is potentially antiaromatic, although here there would seem to be no incentive for carbonyl polarization and ring flattening. The principle is outlined in Figure 4 for a quinone of cyclooctatetraene and one of pentalene. Cyclooctatetraene, **14**, has the nonplanar tub conformation, and calculations indicate both its 1,4- and 1,2-quinones to be nonplanar and nonaromatic, and NICS values[14−17] indicate that even the hypothetical planar conformations would be nonaromatic.[12] Pentalene, **15**, is planar and its quinones **10**−**13** are (almost perforce) planar, yet homodesmotic ring-opening reactions (a kind of isodesmic reaction[18−20]) showed **10** and **11** to be nonaromatic, while **12** and **13** were antiaromatic, evidently because their cyclopentadienone moieties usurp truly peripheral electron delocalization.[13]

Molecules **1**−**6** are members of a family of quinones derived conceptually from cyclooctatetraene and cross-linked cyclooctatetraenes (Figure 5). They are related to the quinones **9q1,4** and **9q1,2** of cyclooctatetraene (**14**), **17**−**22** of bicyclo[5.1.0]octa-1,3,5,7-tetraene (**16**), and **10**−**13** of pentalene (**15**). Some relevant comparisons of **1**−**6** with these structural siblings will be made.

Computational Procedures

Methods. Using the program Spartan[21] B3LYP/6-31G* and MP2/6-31G* (all MP2 calculations were frozen-core) structures were geometry-optimized, and where appropriate for reaction profiles, their normal-mode frequencies were calculated to determine if the stationary point was a relative minimum or a transition state on the potential energy surface.[22] Löwdin bond orders (which were calculated for transition states using HF/3-21G on B3LYP/6-31G* geometries)[23] and HOMO/LUMO energies were calculated with Spartan. NMR NICS calculations, TDDFT UV spectra, and G3MP2 energies for heats of formation were done with Gaussian 03, version 6.1.[24] Calculations were performed on a Pentium 4 machine running under XP and an Intel Core 2 Quad Q6600 running under Vista. "Raw" B3LYP/6-31G* and MP2/6-31G* (henceforth called DFT and MP2) energies were corrected by adding the zero-point energy (ZPE) calculated at that same level; for MP2 the ZPE was scaled by a factor of 0.9670 as recommended by Scott and Radom,[25] but for DFT the unscaled ZPE (recommended scaling factor 0.9806) was used as the error incurred here is considered trivial. Coordinates of computed geometries are given in the Supporting Information.

Reliability. Bond lengths should be accurate to within ca. 0.01 Å and bond angles to within ca. 1°;[26,27] relative energies should be accurate to within ca. 20 kJ mol^{-1},[28−30] except for the Diels−Alder reactions, where the B3LYP/6-31G* reaction activation energies are likely considerably more accurate than the MP2/6-31G* ones, as discussed in that section.

Results

1. Structures. The eight quinones of Figure 1 were optimized and their frequencies calculated at the DFT and MP2 levels. The geometries and symmetries are summarized in Figure 6, along with those of the reference molecules benzene, cyclobutadiene, benzocyclobutadiene, 1,4- and 1,2-benzoquinone, cyclobutadienoquinone, and dimethylenecyclobutene. All are "real" molecules at these computational levels (no imaginary frequencies). The DFT and MP2 geometries are quite similar, although MP2 predicts **4a** and **5a** to be slightly nonplanar: **4a** C_1, OCCO = 6.7° instead of 0°, and **5a** C_2, OCCO = 177.5° instead of 180°. The differences between the DFT and MP2 geometries are so small as to make a rationalization of them unnecessary.

Notable features of the geometry calculations are as follows:

(1) Structures **4a**/**4b** and **5a**/**5b** are not contributors to a resonance hybrid (at these computational levels!) but rather are

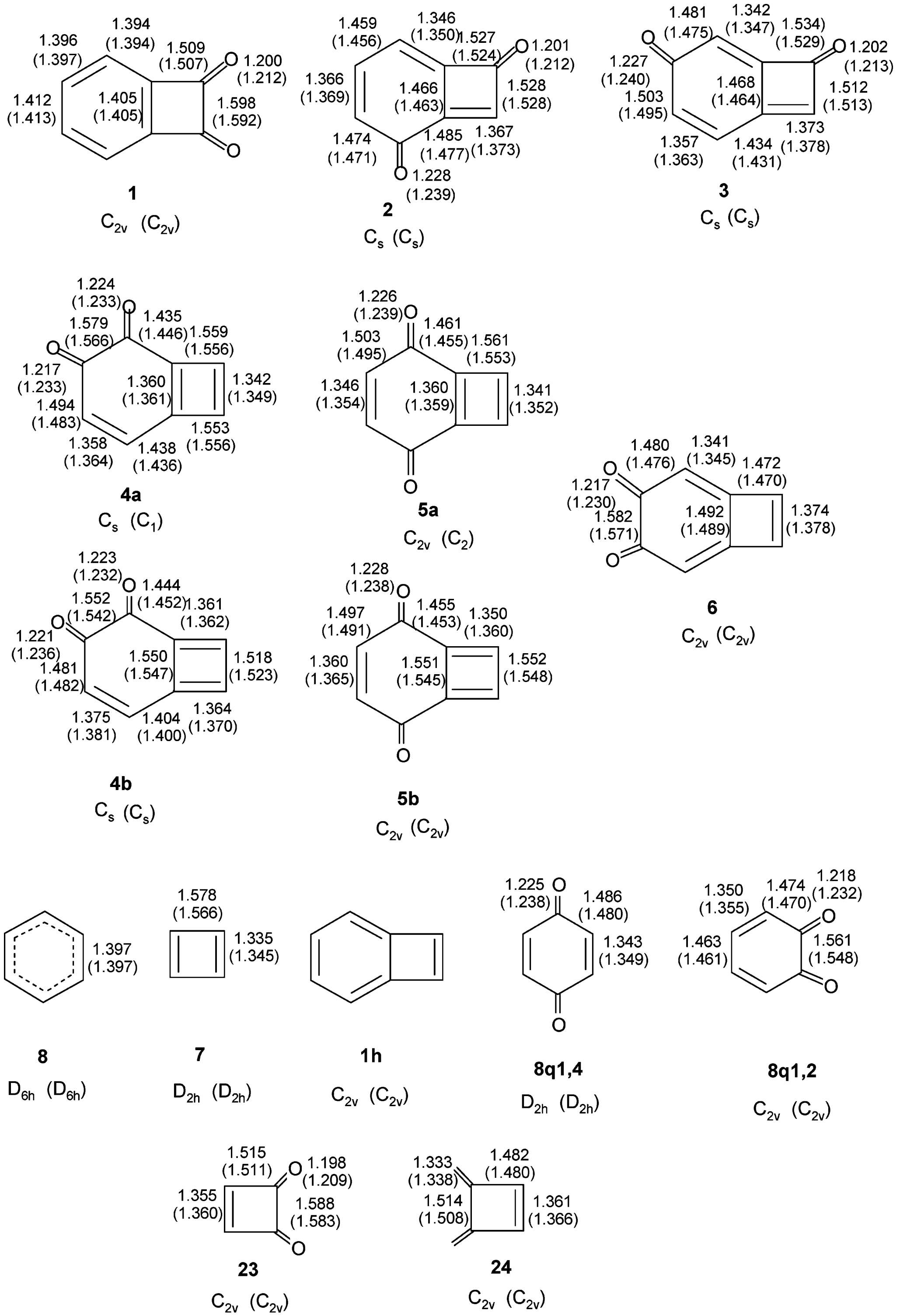


Figure 6. B3LYP/6-31G* and (in parentheses) MP2/6-31G* bond lengths, in angstroms, and symmetries, of quinones **1**−**6**.

distinct molecules, potentially in equilibrium. This finding arises from the fact that an input structure resembling **5a**, built with molecular mechanics, which recognizes bonds naively,[31] yields structure **5a** on DFT or MP2 optimization, with analogous behavior for **5b**. In contrast, an input structure for, say, 1,2-dimethylbenzene, or rather cyclohexatriene, with a CC double bond between the substituted ring carbons, yields on DFT or MP2 optimization the same structure as an input with a CC single bond between the substituted ring carbons. Thus the situation (at these computational levels) is not **4a** ↔ **4b** and **5a** ↔ **5b** (resonance), but rather **4a** ⇄ **4b** and **5a** ⇄ **5b** (valence tautomerism). For such structures this is a subtle distinction, although the well-established case of cyclobutadiene, which shows valence tautomerism with a shift of distinct single and double bonds with a barrier of ca. 36 kJ mol^{-1} (8.5 kcal mol^{-1}),[32] might suggest that tautomerism holds sway here. This is also analogous to the situation found for the isomeric, nearly isoenergetic, and slowly interconverting 1,2- and 1,8-dichloroperfluorocyclooctatetraenes.[33] The problem has been studied in detail by Maksić et al. for the 1,4-type quinone **5a**/**5b**.[34] Although **5a** was calculated to be the stabler by 21 kJ mol^{-1}, they found the barrier to be a mere 1 kJ mol^{-1} and "concluded with a high degree of confidence" that **5b** "does not exist" and that the situation is in fact resonance, not tautomerism. The related conundrum for benzocyclobutadiene was studied by Schulman et al., who similarly concluded that valence tautomerism is not operative here and **1h** best represents the molecule.[35] At our computational levels, the energetics of **4a**/**4b** and **5a**/**5b** were

Energy in hartrees (with ZPE):

$$\mathbf{4a}\ \text{DFT}, -457.44140 \quad \mathbf{5a}\ \text{DFT}, -457.44750$$
$$\mathbf{4b}\ \text{DFT}, -457.45048 \quad \mathbf{5b}\ \text{DFT}, -457.44722$$

DFT: **4b** stabler by 24 kJ mol^{-1}, **5a** stabler by 0.7 kJ mol^{-1}

$$\mathbf{4a}\ \text{MP2}, -456.09158 \quad \mathbf{5a}\ \text{MP2}, -456.10004$$
$$\mathbf{4b}\ \text{MP2}, -456.09846 \quad \mathbf{5b}\ \text{MP2}, -456.09643$$

MP2: **4b** stabler by 18 kJ mol^{-1}, **5a** stabler by 9.5 kJ mol^{-1} (hartrees were converted to kJ mol^{-1} by multiplying by 2626).

Like Maksić et al. we find **5a** to be stabler than **5b**, but only marginally so, well within the limits of error of our methods; **4b** is found to be more convincingly stable than **4a**, although not unambiguously so. We accept the conclusion that **5b** probably does not exist as a separate species but consider the case of **4a**/**4b** open, with the nonexistence of **4a** likelier than that of **4b**.

(2) Those quinones which may be considered on paper as composites of readily identifiable components, namely, **1** (viewed as a benzene and a cyclobutadienoquinone, **23**, moiety), **4a** (viewed as 1,2-benzoquinone and cyclobutadiene, **7**), **5a** (viewed as 1,4-benzoquinone and cyclobutadiene), and **6** (viewed as 1,2-benzoquinone and dimethylenecyclobutene, **24**) do in fact reveal themselves on computation to geometrically conform reasonably well to such structural dissection. This suggests the absence of any special cyclic electronic effects making the whole, the bicyclic species, particularly more than the parts, the monocyclic ring components.

2. Relative Energies and Heats of Formation. The relative energies of the quinones **1**−**6** are worth examining: although there is no obvious way they can interconvert, and thus an attempted synthesis of one should not lead to another (with the clear exception of the tricky cases **4a**/**4b** and **5a**/**5b**), a dramatic energy anomaly for any of them should alert one to some special underlying feature. The DFT and MP2 energies of **1**−**6** and their heats of formation (calculation discussed below) are shown in Table 1. We can place **1**−**6** in three energy classes: using heats of formation (the DFT and MP2 relative energies lead to the same kind of classification) we have low energy, **1** (−17 kJ mol^{-1}); medium energy, **3** (79 kJ mol^{-1}), **2** (105 kJ mol^{-1}), **6** (137 kJ mol^{-1}); high energy, **5a**/**5b** (ca. 260 kJ mol^{-1}), **4a**/**4b** (ca. 270 kJ mol^{-1}). This is easily explained: **1** is the only member with a benzene ring (canonically stable and no cyclobutadiene ring), while **5a**/**5b** and **4a**/**4b** are the only members with a high-energy[36] cyclobutadiene ring; this leaves **2**, **3**, and **6** as middle-energy species, rationalizing the order of which is not as obvious. A reviewer suggested, essentially, that the energy order **3** < **2** < **6** may be connected with the fact that **3** and **2** can be viewed as vinylogous 1,4-benzoquinones with **3** as a cross-conjugated cyclohexadienone being more similar to 1,4-benzoquinone than is **2**, while **6** in contrast is a substituted 1,2-benzoquinone; as shown below (Calculation of the Heats of Formation), 1,4-benzoquinone is indeed significantly lower energy than 1,2-benzoquinone, the heats of formation being ca. −120 and −87 kJ mol^{-1}. Compound **1** is known and stable,[7] and **4a**/**4b** and **5a**/**5b** should be highly reactive and probably unisolable at room temperature (the Diels−Alder reactivity of **1**−**6** is reported below), leaving **2**, **3**, and **6** as the most tempting targets for synthesis.

TABLE 1: Energies and 298 K Standard Heats of Formation of Quinones 1−6[a]

quinone	DFT energy	MP2 energy	relative energy DFT (MP2)	heat of formation G3 (MP2)
1	−457.559105	−456.214823	0 (0)	−17.36
2	−457.511160	−456.160898	126 (142)	105.2
3	−457.520804	−456.170976	101 (115)	78.79
4a	−457.441403	−456.091570	309 (324)	275.2
4b	−457.450484	−456.098462	285 (306)	260.2
5a	−457.447496	−456.100044	293 (301)	250.5
5b	−457.447222	−456.096429	294 (311)	264.0
6	−457.498577	−456.148313	159 (175)	136.9

[a] DFT (B3LYP/6-31G*) and MP2 (MP2/6-31G*) energies are in hartrees and include ZPEs (see Computational Methods). Relative energies are in kJ mol^{-1}. Hartrees were converted to kJ mol^{-1} by multiplying by 2626. The calculation of heats of formation (kJ mol^{-1}) is discussed in the text.

Calculation of the Heats of Formation (Standard Enthalpies at 298 K). This was obtained for **1** by the atomization method[37,38] using G3(MP2)[39] (rather than G2(MP2)) energies. The heats of formation of **2**−**6** were found from the value for **1** and the room-temperature G3(MP2) enthalpies of **2**−**6** as calculated by Gaussian 03 from their frequencies. The method follows from the procedure described in refs 37 and 38 and gives exactly the same result as the "full" procedure used for **1**; it is outlined below for **2**

$$\Delta H^\circ_{f298}(\text{quinone } \mathbf{1}) = -17.36 \text{ kJ mol}^{-1}$$

$$\text{G3(MP2) enthalpy of quinone } \mathbf{1} = -456.97931 \text{ hartrees}$$

$$\text{G3(MP2) enthalpy of quinone } \mathbf{2} = -456.93264 \text{ hartrees}$$

$$\begin{aligned}\Delta H^\circ_{f298}(\text{quinone } \mathbf{2}) &= \Delta H^\circ_{f298}(\text{quinone } \mathbf{1}) + [\text{enthalpy quinone } \mathbf{2} - \text{enthalpy quinone } \mathbf{1}] \\ &= -17.36 + [-456.93264 - (-456.97931)] \times 2625.5 \text{ kJ mol}^{-1} \\ &= -17.36 + [0.04667] \times 2625.5 \text{ kJ mol}^{-1} \\ &= -17.36 + 122.53 = \text{ kJ mol}^{-1} = 105.2 \text{ kJ mol}^{-1}\end{aligned}$$

These heats of formation are probably accurate to within 20 kJ mol^{-1}, as shown by our G3(MP2) calculated experimental values (kJ mol^{-1}):

methanol	calcd −210.9	exptl −205 ± 10 (ref 40)
cubane	calcd 604.5	exptl 622 ± 4 (ref 41)
1,4-benzoquinone	calcd −120.05	exptl −122.6 ± 3.8 (ref 42)
1,2-benzoquinone	calcd −86.6	exptl −87.9 ± 13 (ref 42)

3. Diels−Alder Reactivity. ***Calculations.*** The activation energy of **1**−**6** as dienophiles in the Diels−Alder (DA) reaction provides a palpable measure of their reactivity. A compound

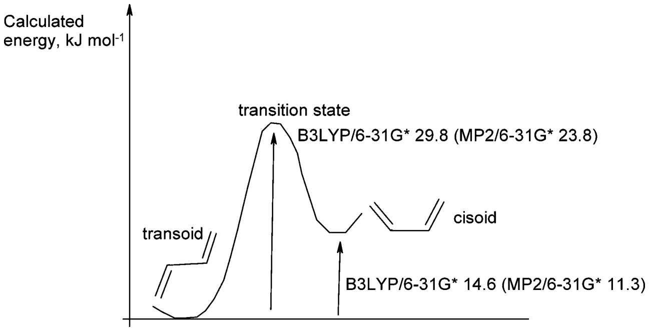


Figure 7. Calculated activation and reaction energies for 1,3-butadiene. ZPEs are included.

like cyclobutadiene, with very low calculated DA activation energy, is extremely reactive and cannot be isolated at room temperature[36] (unless sequestered in a some kind of cage[43]), while a compound like benzene, with a very high calculated DA activation energy, is not even usually considered to be a dienophile. We focused on B3LYP/6-31G* calculations rather than MP/6-31G* because the former give much better results for the ethene–butadiene reaction. We can compare the DFT activation energy of Houk and co-workers[44] with the MP2 energies of Carpenter and Sosa[45] (ZPEs are included); our results were virtually identical (we attribute the very small differences to slightly different algorithms and/or to different numerical "errors" in different computers):

B3LYP/6-31G*	103.8 kJ mol^{-1} (ref 44)	our work 104.1 kJ mol^{-1}
MP2/6-31G*	83.7 kJ mol^{-1} (ref 45)	our work 84.7 kJ mol^{-1}
experimental	115.1 ± 8 kJ mol^{-1} (ref 46)	

The B3LYP/6-31G* energy is formally only about 11 kJ mol^{-1} lower than the experimental and almost equal to the estimated lower value of 107 kJ mol^{-1}. The reaction energy is also better with DFT than with MP2

B3LYP/6-31G*	−153.1 kJ mol^{-1} (ref 44)	our work −153.4 kJ mol^{-1}
MP2/6-31G*	−192.0 kJ mol^{-1} (ref 47)	our work −190.6 kJ mol^{-1}
experimental	−160.7 kJ mol^{-1} (ref 48)	

In comparing calculated and experimental activation energies for DA reactions of 1,3-butadiene, it is standard to use the energy of the transoid, rather than the cisoid, diene in the calculation because although only the cisoid conformer is reactive in the DA addition, the rapid equilibrium between the two makes the transoid the *effective* diene reactant (Figure 7). However, for computational transparency we have chosen to present the activation and reaction energies relative to the *proximate* reactants (cisoid butadiene and the dienophile) taken as the zero of energy. This enables one to draw a simple reaction profile with the transition state and product energies relative to reactants set equal to zero. The reactions of **1**−**6** and some reference compounds, with 1,3-butadiene as the diene, and their activation and reaction energies, are shown in Figure 8. To obtain the standard calculated activation and reaction energies (e.g., those in ref 44), one adds to the values in Figure 8, 14.6 or 11.3 kJ mol^{-1}, for B3LYP or MP2, respectively; see Figure 7. Thus for the ethene–butadiene reaction the B3LYP/6-31G* standard activation and reaction energies in this work are 89.5 + 14.6 = 104.1 kJ mol^{-1} and −168.0 + 14.6 = −153.4 kJ mol^{-1}.

To limit to a reasonable number the Diels–Alder reactions studied, the CC double bond directly conjugated with a carbonyl group and lying in a four-membered ring (except for **6** where the conjugated CC bond is in the six-membered ring) was chosen as the relevant dienophilic CC bond, since this appears likely to be the most reactive bond in a DA reaction with a diene. The diene can approach the quinone in a "pseudoendo" or "pseudoexo" manner, as shown for **1** in Figure 8. Pseudoendo means that the diene moiety approaches under the reactive ring, pseudoexo means that it approaches from "outside" this ring. True endo and exo isomers, such as those that occur when the diene is cyclopentadiene, are not possible here. Apart from the illustrative **1** we depict in Figure 8 only the pseudoendo reactions (except for **6**, where the only transition state we could find was pseudoexo), because in those cases where the pseudoendo/pseudoexo activation energies are not similar (**4a**, **4b**, **5a**, **5b**, and cyclobutadiene) the pseudoendo reaction had the significantly lower activation energy. Table 2 gives the actual DFT energies on which the activation and reaction energies in Figure 8 are based (as well as the pseudoexo activation and reaction energies). Product structures resembled those of the corresponding transition states with the dienophile-diene connecting bonds shortened to ca. 1.55 Å. The reference dienophiles were ethene (the canonical, simplest dienophile), benzene (a very poor dienophile), cyclobutadiene (an extremely good dienophile), and 1,4- and 1,2-benzoquinone ("normal" dienophiles).

Discussion of the Diels–Alder Reactions. For all 13 compounds of Figure 8 (the eight **1**−**6** and the five reference compounds) the DA reaction energy is calculated to be negative (indicating exothermic reactions) except for benzene (39.0 kJ mol^{-1}); this is reasonable: the DA reaction is a widely applicable synthetic tool which usually proceeds "to completion",[49−51] but benzene is the canonical stable "polyene". The quinone with the least negative reaction energy is **1** (−67.1 kJ mol^{-1}), in which a benzene ring (strained and electronically activated by fusion to a cyclobutenedione moiety) is the dienophile; all the other quinones have reaction energies more negative than −100 kJ mol^{-1}.

The activation energies of the five reference compounds accord nicely with their known DA reactivity: benzene (calculated activation energy 180.7 kJ mol^{-1}) is scarcely a dienophile, requiring high pressure,[52] although an intermolecular reaction of a benzene moiety has been observed.[53,54] Cyclobutadiene (calculated activation energy 13.4 kJ mol^{-1}) is the direct opposite of benzene, being notoriously reactive toward dimerization,[36] and reacting as a normal dienophile with the hindered 3,6-di-*tert*-butyl-1,2-benzoquinone even at −10 °C.[55] Between those extremes we find ethene and the benzoquinones as more conventional dienophiles. Ethene (calculated activation energy 89.6 kJ mol^{-1}) is a poor dienophile with butadiene,[56−58] but the benzoquinones are reasonably good ones, with 1,2-benzoquinone (calculated activation energy 62.1 kJ mol^{-1}) known to be generally more reactive than 1,4-benzoquinone (calculated activation energy 70.3 kJ mol^{-1}). The reaction of 1,2-benzoquinone with butadiene does not seem to have been reported, but with cyclopentadiene the quinone acts as a dienophile (this initial product can rearrange to one formed formally by the quinone acting as the diene),[59] and 1,4-benzoquinone reacts fairly readily as a dienophile with butadiene.[60]

The transition state bond orders of the two dienophile–diene connecting bonds serves as a readily apprehended guide to the reactivity of the dienophile in these reactions (the use of bond orders as a guide to the progress of reactions has been presented by Lendvay[61]). Intuitively one expects a highly reactive dieno-

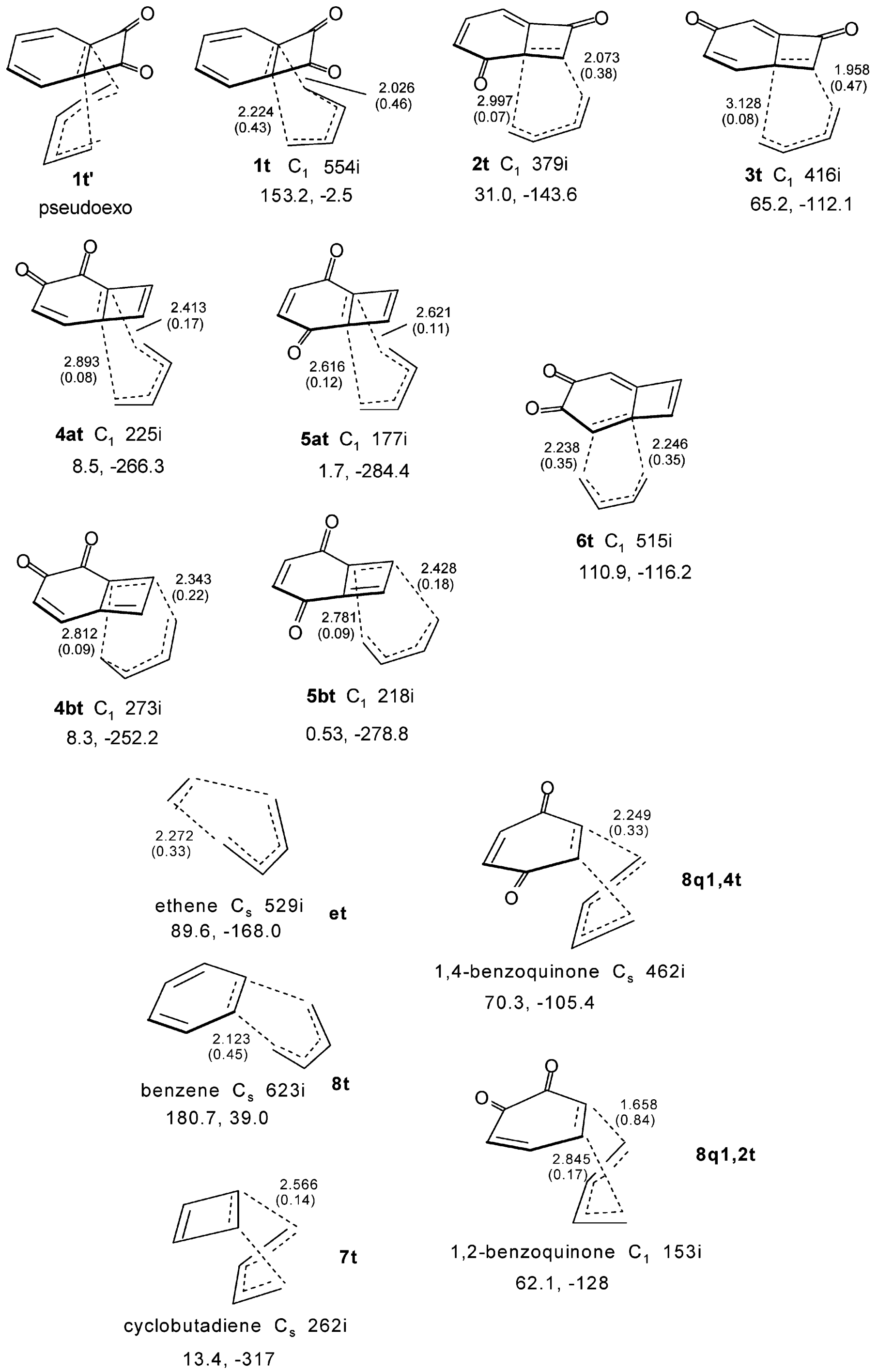


Figure 8. Transition states for Diels–Alder reactions with 1,3-butadiene of quinones **1**–**6** and five reference compounds. B3LYP/6-31G* calculations (except for bond orders, in parentheses: Löwdin bond orders,[23] HF/3-21G on B3LYP/6-31G* geometries). Bond lengths (Å) and orders of the dienophile–diene connecting bonds are shown, also symmetry (C_1) and imaginary frequency (e.g., 554i) and activation and reaction energies (e.g., 153.2, −2.5) in kJ mol^{-1}.

phile to bond to butadiene in an early transition state with low connecting bond orders, and an unreactive, reluctant dienophile to bond in a late transition state with high connecting bond orders. This expectation is nicely fulfilled: the relevant bond orders (Figure 8) for benzene and cyclobutadiene (**8t**, **7t**) are respectively 0.45 and 0.14; in between we find ethene (**et**, 0.33) and 1,4-benzoquinone (**8q1,4t**, 0.33), with 1,2-benzoquinone having, not surprisingly, because of the asymmetry of its CC bonds, a highly asynchronous transition state (**8q1,2t**, 0.17, 0.84). This latter species is approximately a diradical (for a discussion of diradicals and asynchronous transition states in the DA reaction see ref 44 and references therein) with the (approximately) unpaired ring electron allylic rather than α-carbonyl. B3LYP calculations on the two kinds of radical support this interpretation, giving these energies (without ZPE):

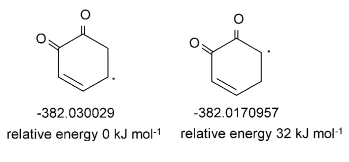


TABLE 2: B3LYP/6-31G* Energies and Relative Energies (kJ mol^{-1}) of Butadiene, Quinones 1−6, and Reference Compounds and Their Diels−Alder Transition States and Products[a]

reactants	TS	pdt	activation E, hartrees kJ mol^{-1}	reaction E, hartrees kJ mol^{-1}
cisoid				
butadiene				
(for all DA)				
−155.986456				
0.085251				
−155.901205				
quinone **1**	Q1 n TS	Q1 n pdt	Q1 n $E^{\ddagger}$	Q1 n ΔE
−457.656508	−613.586524	−613.649176	0.058344	−0.000964
0.097403	0.184558	0.187902	153.2	−2.5
−457.559105	−613.401966	−613.461274		
Q1 + but:				
−613.460310				
quinone **1**	Q1 x TS	Q1 x pdt	Q1 x $E^{\ddagger}$	Q1 x ΔE
−457.656508	−613.586706	−613.644661	0.058006	0.003459
0.097403	0.184402	0.187810	152.3	9.1
−457.559105	−613.402304	−613.456851		
Q1 + but:				
−613.460310				
quinone **2**	Q2 n TS	Q2 n pdt	Q2 n $E^{\ddagger}$	Q2 n ΔE
−457.607459	−613.584771	−613.656196	0.011821	−0.054688
0.096299	0.184227	0.189143	31.0	−143.6
−457.511160	−613.400544	−613.467053		
Q2 + but:				
−613.412365				
quinone **2**	Q2 x TS	Q2 x pdt	Q2 x $E^{\ddagger}$	Q2 x ΔE
−457.607459	−613.584042	−613.652869	0.012207	−0.051448
0.096299	0.183884	0.189056	32.1	−135.1
−457.511160	−613.400158	−613.463813		
Q2 + but:				
−613.412365				
quinone **3**	Q3 n TS	Q3 n pdt	Q3 n $E^{\ddagger}$	Q3 n ΔE
−457.617278	−613.580934	−613.653790	0.024830	−0.042684
0.096474	0.183755	0.189097	65.2	−112.1
−457.520804	−613.397179	−613.464693		
Q3 + but:				
−613.422009				
quinone 3	Q3 x TS	Q3 x pdt	Q3 x $E^{\ddagger}$	Q3 x ΔE
−457.617278	−613.583489	−613.652721	0.022320	−0.041554
0.096474	0.183800	0.189158	58.6	−109.1
−457.520804	−613.399689	−613.463563		
Q3 + but:				
−613.422009				
quinone **4a**	Q4a n TS	Q4a n pdt	Q4a n $E^{\ddagger}$	Q4a n ΔE
−457.535718	−613.520936	−613.631996	0.003222	−0.101395
0.094315	0.181550	0.187993	8.5	−266.3
−457.441403	−613.339386	−613.444003		
Q4a + but:				
−613.342608				
quinone **4a**	Q4a x TS	Q4a x pdt	Q4a x $E^{\ddagger}$	Q4a x ΔE
−457.535718	−613.517092	−613.629361	0.007310	−0.098375
0.094315	0.181794	0.188378	19.2	−258.3
−457.441403	−613.335298	−613.440983		
Q4a + but:				
−613.342608				
quinone **4b**	Q4b n TS	Q4b n pdt	Q4b n $E^{\ddagger}$	Q4b n ΔE
−457.545160	−613.531023	−613.636431	0.003156	−0.096044
0.094676	0.182490	0.188698	8.3	−252.2
−457.450484	−613.348533	−613.447733		
Q4b + but:				
−613.351689				
quinone **4b**	Q4b x TS	Q4b x pdt	Q4b x $E^{\ddagger}$	Q4b x ΔE
−457.545160	−613.523870	−613.632677	0.010210	−0.092226
0.094676	0.182391	0.188762	26.8	−242.2
−457.450484	−613.341479	−613.443915		
Q4b + but:				
−613.351689				
quinone **5a**	Q5a n TS	Q5a n pdt	Q5a n $E^{\ddagger}$	Q5a n ΔE
−457.542043	−613.529749	−613.645398	0.000650	−0.108319
0.094547	0.181698	0.188378	1.7	−284.4

TABLE 2: Continued

reactants	TS	pdt	activation E, hartrees kJ mol^{-1}	reaction E, hartrees kJ mol^{-1}
−457.447496	−613.348051	−613.457020		
Q5b+ but:				
−613.348701				
quinone **5a**	Q5a x TS	Q5a x pdt	Q5a x $E^{\ddagger}$	Q5a x ΔE
−457.542043	−613.525678	−613.643749	0.005182	−0.106278
0.094547	0.182159	0.188770	13.6	−279.1
−457.447496	−613.343519	−613.454979		
Q5a + but:				
−613.348701				
quinone **5b**	Q5b n TS	Q5b n pdt	Q5b n $E^{\ddagger}$	Q5b n ΔE
−457.541978	−613.530585	−613.643374	0.000203	−0.106185
0.094756	0.182361	0.188762	0.53	−278.8
−457.447222	−613.348224	−613.454612		
Q5a + but:				
−613.348427				
quinone **5b**	Q5b x TS	Q5b x pdt	Q5b x $E^{\ddagger}$	Q5b x ΔE
−457.541978	−613.522709	−613.639212	0.008030	−0.101733
0.094756	0.182312	0.189052	21.1	−267.2
−457.447222	−613.340397	−613.450160		
Q5b + but:				
−613.348427				
quinone **6**	Q6 n TS	Q6 n pdt	Q6 n $E^{\ddagger}$	Q6 n ΔE
−457.594540	−613.540989	−613.633000	0.042239	−0.044265
0.095963	0.183446	0.188953	110.9	−116.2
−457.498577	−613.357543	−613.444047		
Q6 + but:				
−613.399782				
quinone **6**	Q6 x TS	Q6 x pdt	Q6 x $E^{\ddagger}$	Q6 x ΔE
−457.594540	same as n	same as n	same as n	same as n
0.095963				
−457.498577				
Q6 + but:				
−613.399782				
reference reactions				
reactants	TS	pdt	activation E	reaction E
CBD	CB n TS	CB n pdt	CB n $\mathrm{E}^{\ddagger}$	CB n ΔE
−154.675474	−310.658956	−310.793261	0.005099	−0.120733
0.061245	0.148621	0.157094	13.4	−317.0
−154.614229	−310.510335	−310.636167		
CB + but:				
−310.515434				
CBD	CB x TS	CB x pdt	CB x $E^{\ddagger}$	CB x ΔE
−154.675474	−310.652025	−310.790653	0.012267	−0.117919
0.061245	0.148858	0.157300	32.2	−309.7
−154.614229	−310.503167	−310.633353		
CB + but:				
−310.515434				
benzene	benz n TS	benz n pdt	benz n $E^{\ddagger}$	benz n ΔE
−232.249579	−388.170041	−388.228308	0.068816	0.014852
0.100735	0.188808	0.193111	180.7	39.0
−232.148844	−387.981233	−388.035197		
benz + but:				
−388.050049				
benzene	benz x TS	benz x pdt	benz x $E^{\ddagger}$	benz x ΔE
−232.249579	−388.173637	−388.237003	0.065121	0.006024
0.100735	0.188709	0.192978	171.0	15.8
−232.148844	−387.984928	−388.044025		
benz + but:				
−388.050049				
o-benzoquin	*o*-benz n TS	*o*-benz n pdt	*o*-benz n $E^{\ddagger}$	*o*-benz n ΔE
−381.440487	−537.407303	−537.483953	0.023665	−0.048813
0.085187	0.174463	0.178635	62.1	−128.2
−381.355300	−537.232840	−537.305318		
o-benz + but:				
−537.256505				
o-benzoquin	*o*-benz x TS	*o*-benz x pdt	*o*-benz x $E^{\ddagger}$	*o*-benz x ΔE
−381.440487	−537.400879	−537.481772	0.028783	−0.046771
0.085187	0.173157	0.178496	75.6	−122.8
−381.355300	−537.227722	−537.303276		

TABLE 2: Continued

reactants	TS	pdt	activation *E*, hartrees kJ mol^{-1}	reaction *E*, hartrees kJ mol^{-1}
o-benz + but:				
−537.256505				
p-benzoquin	*p*-benz n TS	*p*-benz n pdt	*p*-benz n $E^‡$	*p*-benz n Δ*E*
−381.451735	−537.414570	−537.486884	0.026778	−0.040128
0.085339	0.173747	0.179155	70.3	−105.4
−381.366396	−537.240823	−537.307729		
p-benz + but:				
−537.267601				
p-benzoquin	*p*-benz x TS	*p*-benz x pdt	*p*-benz x $E^‡$	*p*-benz x Δ*E*
−381.451735	−537.412306	−537.496294	0.028894	−0.049573
0.085339	0.173599	0.179120	75.9	−130.2
−381.366396	−537.238707	−537.317174		
p-benz + but:				
−537.267601				
ethene	ethene TS	ethene pdt	ethene $E^‡$	ethene Δ*E*
−78.587448	−234.543906	−234.648315	0.034108	−0.063961
0.051203	0.140564	0.146904	89.6	−168.0
−78.536245	−234.403342	−234.501411		
ethene + but:				
−234.437450				

[a] The reactants column gives uncorrected energy, ZPE (uncorrected), and corrected energy (see text, Computational Methods). Here n and x are "pseudoendo and "pseudoexo"; they refer to different conformations, not different configurations; see text Diels-Alder Reactivity.

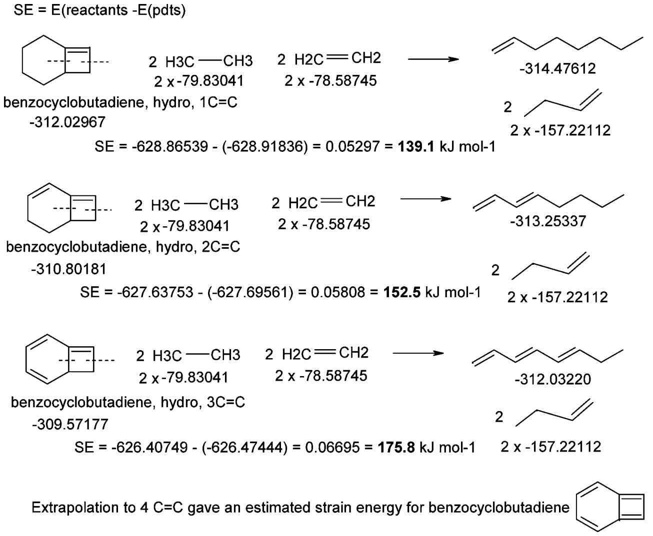


Figure 9. The homodesmotic reactions used to calculate by extrapolation (see Figure 10) the strain energy of benzocyclobutadiene, assumed to be the same as the C_8 array of quinones **1**−**6**.

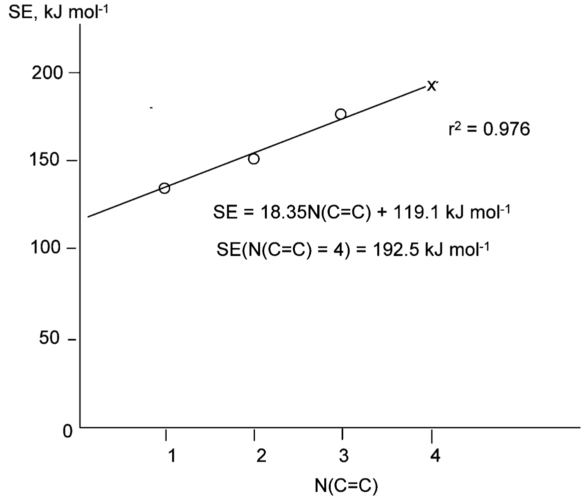


Figure 10. Extrapolation of strain energies to estimate the strain energy of benzocyclobutadiene, assumed to be similar to that of the common C_8 bicyclo[3.3.0] array of quinones **1**−**6** (allowance was made for CO/CO dipole/dipole repulsion-see text.

We may likewise note that the difference of the α-C−H bond dissociation energies for the alkenes 2-methylpropene and 2-methyl-1-butene are some 30 kJ mol^{-1} less than for the corresponding ketones, acetone and 2-butanone (C=O for C=CH$_2$), in agreement with the above finding.[62]

The B3LYP/6-31G* Diels−Alder calculations for the reference compounds assure us that the results for the quinones **1**−**6** are trustworthy. Focusing now on these quinones (Figure 8), we find, leaving aside for the moment the highly asynchronous **2t** and **3t**, and the interesting case of **6t**, that **1t**, from the only quinone that must perforce act as a benzene dienophile toward butadiene, has the highest bond orders (0.43, 0.46) and the cyclobutadiene dienophile transition states, **4at**, **4bt**, and **5bt**, have the lowest bond orders (ca. 0.1−0.2), corresponding to a late, high-energy and to early, low-energy transition states, respectively. We note that one expects **1t** and **5at** to have a symmetry plane (C_s symmetry), yet the B3LYP/6-31G* geometry optimizations gave C_1 symmetry with slightly different lengths and orders for the bonds under discussion. Optimization of a **1t**-like structure within C_s symmetry led to a second-order saddle point (564i, 32i) 0.06 kJ mol^{-1} higher than **1t**, with bond lengths/orders 2.120 Å/0.44. Attempted optimization of **5at** within C_s symmetry led to dissociation of the dienophile-diene components away from each other. We accept **1t** and **5at** as the de facto transition states at this computational level and attribute the slight distortions from C_s to numerical errors in the DFT algorithm. The activation energies are consonant with this (**6t** excepted), **1t** having as expected the highest (155.7 kJ mol^{-1}) and **4at**, **4bt**, **5at**, and **5bt** as expected the lowest (ca. 0.5−8 kJ mol^{-1}). Transition states **2t** and **3t** are, like the 1,2-benzoquinone transition state discussed above, readily interpreted as, approximately, diradicals, although the leading bond is not as well-formed in these cases as in the 1,2-benzoquinone

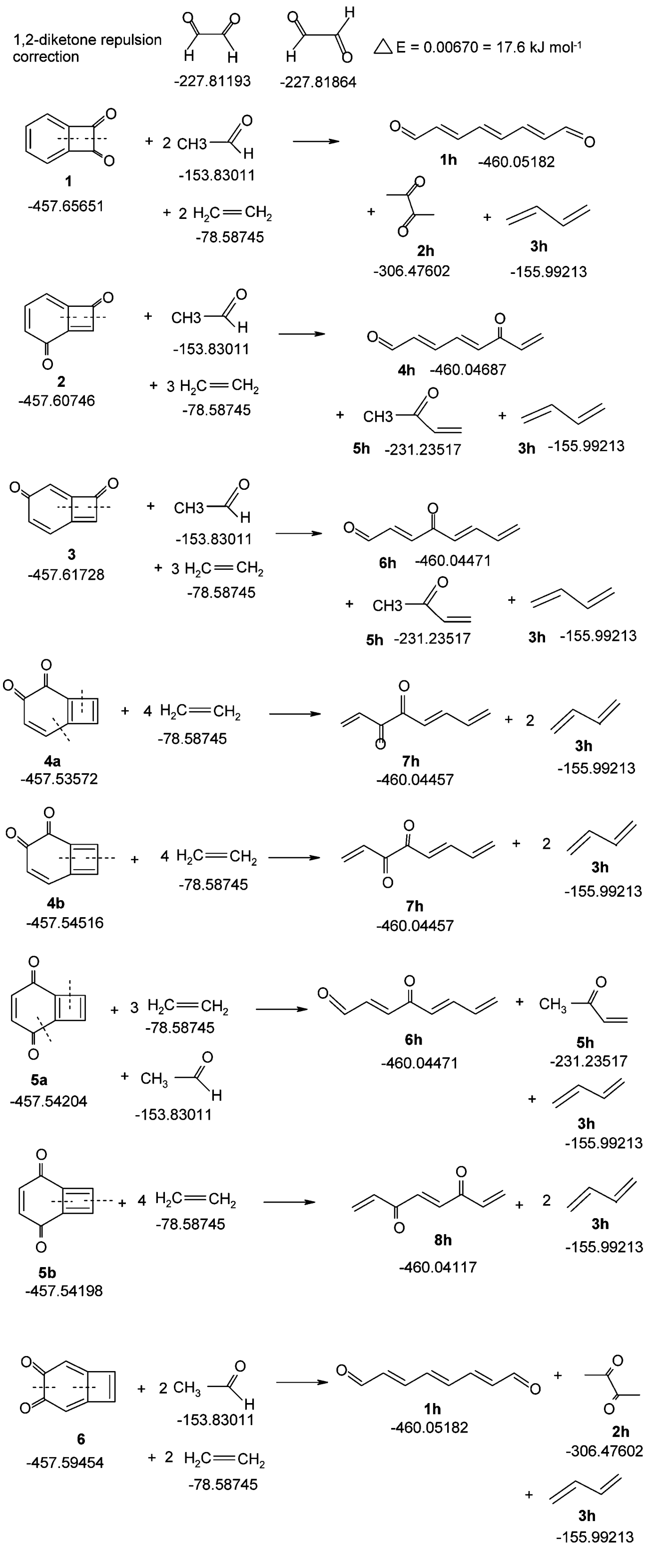


Figure 11. Homodesmotic reactions (and 1,2-diketone correction) used to probe aromaticity/antiaromaticity in quinones **1**−**6**.

transition state, and their activation energies lie between those of the benzene (**1t**) and cyclobutadiene (**4at**, **4bt**, **5at**, and **5bt**) cases.

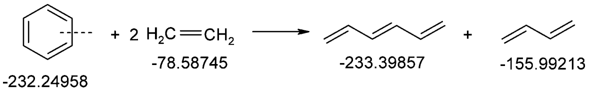
TABLE 3: NICS(1) Values for Quinones 1−6: GIAO, HF/6-31G* on B3LYP/6-31G* Geometries

compound	over the 6-ring	over the 4-ring
1	−12.4	−4.5
2	−2.3	−4.3
3	−2.7	−4.7
4a	0.16	14.7
4b	−4.2	13.2
5a	−0.52	15.4
5b	−3.8	16.8
6	−1.1	−4.2

TABLE 4: NICS(1) Values for Reference Compounds: GIAO, HF/6-31G* on B3LYP/6-31G* Geometries

compound	
benzene **8**	−12.8
cyclobutadiene **7**	17.6
1,4-benzoquinone **8q1,4**	0.08
1,2-benzoquinone **8qi,2**	1.3
cyclobutene	−2.65
cyclobutenedione **7q**	−5.1
dimethylenecyclobutanedione	−2.1
dimethylenecyclobutene	−3.45

4. Isodesmic-Type (Homodesmotic) Ring-Opening Reactions. As discussed in the Introduction, the quinones **1**−**6** offer at least a prospect of being aromatic. The most direct test for aromaticity (or its antithesis, antiaromaticity) in a cyclic molecule uses a homodesmotic ring-opening reaction[18−20] to calculate a reaction energy: with bond energy effects approximately canceling, a significant positive reaction energy is the aromatic stabilization energy (ASE), e.g.



ASE = [-233.39857 - 155.99213] - [-232.24958 - 78.58745]
= -398.39070 + 389.42448 = 0.03378 = 89 kJ mol^{-1}

Here B3LYP/6-31G* energies without ZPE, as recommended for strain energy calculations, which use exactly the same principle, are used.[63] We use the all-trans configurations and extended zigzag conformations of the open-chain molecules to calculate useful ASEs.[64,65] As has been pointed out, the precise value of the ASE depends on the calculational level;[64,65] the value of 89 kJ mol^{-1} found here for benzene is entirely reasonable, being within the range of several tens of kJ mol^{-1} that have been assigned, from ca. 90 kJ mol^{-1} (22.1 kcal mol^{-1})[65] to the traditional 151 kJ mol^{-1} (36 kcal mol^{-1}). The ASEs calculated here for **1**-**6** should be quantitatively meaningful, and more important, if significant differences are found, these should reflect some underlying electronic differences. In addition, we may test the accuracy of our predicted reaction endothermicity with quantities derived from the measured enthalpies of formation of benzene and ethane,[66] and that estimated for 2,4,6-octatriene (99 kJ mol^{-1}). This latter value may be obtained by a variety of methods (for (a) and (b) below, data for (*E*)-1,3,5-hexatriene;[67] for (c), enthalpy rule from Liebman[68]):

(a) Assume thermoneutrality for the transmethylation reaction

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 + 2CH_3{-}CH{=}CH{-}CH{=}CH_2 \rightarrow CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3 + 2CH_2{=}CH{-}CH{=}CH_2$$

$$168 + 2(76) = 100 + 2(110)$$

(b) Assume thermoneutrality for the disproportionation reaction

$$2CH_3{-}CH{=}CH{-}CH{=}CH_2 \rightarrow CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3 + CH_2{=}CH_2$$

$$2(76) = 100 + 52$$

(c) Assume "universal" olefin coupling is essentially isoenergetic for the reaction

$$CH_3{-}CH{=}CH{-}CH{=}CH_2 + CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3 + H_2$$

$$76 + 20 = 96$$

The above reaction is thus predicted to be endothermic by 101 kJ mol^{-1}, close to the above value of 107 kJ mol^{-1} calculated by direct opening with ethane without zero point energy or thermal corrections.

In the calculation above for an ASE of benzene, it was assumed, with reason, that the molecule is unstrained. For a strained molecule, to get the ASE, one must add the strain energy to the calculated reaction energy (because strain is always zero or positive, it will make a ring-opening reaction less endothermic than it otherwise would be). Finding the strain energies of **1**−**6** requires disentangling strain from any possible aromaticity (or anti aromaticity): if both effects are present, the homodesmotic ring opening gives a composite result. Since all eight quinones are bicyclo[4.2.0] arrays of sp^2 carbons, we assumed that the strain energy in all eight was about the same, the strain of benzocyclobutadiene, except for the 1,2-type quinones for which we add an extra strain term due to CO/CO dipole/dipole repulsion, estimated from the energy increment of cisoid over transoid 1,2-ethanedione. The strain of the common C_8 bicyclo[4.2.0] array was estimated from homodesmotic ring opening of bicyclo[4.2.0] species with one, two, and three double bonds and extrapolating to four double bonds, which is the point at which cyclic electron effects step in; this is shown in Figure 9. The strain energies for the molecules with one, two, and three CC double bonds obey a good linear relationship with the number of CC double bonds ($r^2 = 0.976$), giving confidence to the validity of the extrapolation (Figure 10). This strain estimation method and the homodesmotic reactions applied to **1**−**6** are entirely analogous to those that were used in probing, by ring opening, electronic effects in the quinones of pentalene.[13] In Figure 11 we show the homodesmotic ring cleavage reactions and the energies of their reactants and products for quinones **1**−**6**, and the energy changes in these reactions are presented and interpreted below.

$$\text{ASE} = E_{\text{products}} - E_{\text{reactants}} + \text{Strain } E$$

Quinone **1**

Without the α-diketone SE

TABLE 5: UV Spectra Calculated by TDDFT UV (B3P86/6-311++G on B3LYP/6-31G* Geometries) for 1−6 and Reference Compounds[a]**

compound	TDDFT UV, nm (oscillator strength) *experimental, nm* (*absorptivity*, ϵ)
1	233(0.0005), 259(0.0000), 260(0.0085), 268(0.0901), 352(0.0000), 472(0.0000) *271(2800), 277 (6800)* (ref 17)
2	288(0.0000), 299(0.0001), 302(0.0440), 389(0.0001), 432(0.0386), 489(0.0000)
3	272(0.0000), 282(0.0905), 310(0.0905), 335(0.0971), 367(0.0000), 472(0.0000)
4a	303(0.0694), 317(0.0000), 374(0.0060), 444(0.0000), 849(0.0000), 949(0.0078)
4b	328(0.0000), 387(0.0000), 400(0.0863), 481(0.0000), 639(0.0000), 642(0.0153)
5a	285(0.0001), 315(0.0967), 359(0.0037), 523(0.0000), 574(0.0000), 783(0.0049)
5b	382(0.0000), 388(0.0000), 400(0.0730), 481(0.0000), 497(0.0000), 621(0.0060)
6	276(0.0001), 308(0.0014), 314(0.0212), 332(0.0000), 399(0.0000), 507(0.0000)
benzene	174(0.0000), 175(0.0553), 189(0.0000), 189(0.0000), 203(0.0000), 229(0.0000) *184(60000), 204(7900), 256(200)* (ref 69)
cyclobutadiene	204(0.0000), 224(0.0000), 227(0.0090), 236(0.0154), 243(0.0000), 468(0.0000) *Above ca. 240, to 500 nm only a weak tail which rises suddenly at ca. 240* (ref 70)
1,4-benzoquinone	218(0.0000), 229(0.0005), 252(0.3241), 325(0.0000), 464(0.0000), 504(0.0000) *∼245 (∼13000), ∼290 (∼1100), ∼365 (∼280)* (ref 40)
1,2-benzoquinone	229(0.0000), 231(0.0545), 239(0.0001), 402(0.0473), 407(0.0000), 708(0.0000) *∼380 (∼4000), ∼620 (∼32)* (ref 40)
cyclobutenedione	185(0.0467), 195(0.0751), 227(0.0000), 234(0.0000), 356(0.0001), 395(0.0000) *214(3690), 340 (21)* (ref 8)
dimethylenecyclobutanedione	235(0.1038), 251(0.0002), 253(0.0000), 315(0.0000), 337(0.0872), 714(0.0000)
dimethylenecyclobutene	190(0.0329), 190(0.0000), 201(0.0027), 203(0.5290), 259(0.0699), 260(0.0000) *212(100000), 248(20000)* (ref 71)

[a] The transitions are for the first six excited singlets, i.e., absorptions of shorter wavelength than the shortest shown here were not calculated.

$$\mathrm{ASE} = -922.51997-[-922.49163] + 0.07331 = -0.02834 + 0.07331 = 0.04497 = 118.1\ \mathrm{kJ\ mol^{-1}}$$

With the α-diketone SE

$$118.1 + 17.6 = 135.7\ \text{strongly aromatic}$$

Quinone **2**

$$\mathrm{ASE} = -847.27417-[-847.19992] + 0.07331 = -0.07425 + 0.07331 = -0.00094 = -2.5\ \mathrm{kJ\ mol^{-1}}\ \text{nonaromatic}$$

Quinone **3**

$$\mathrm{ASE} = -847.27201-[-847.20974] + 0.07331 = -0.06227 + 0.07331 = 0.01104 = 29.0\ \mathrm{kJ\ mol^{-1}}\ \text{nonaromatic or marginally aromatic}$$

Quinone **4a**
Without the α-diketone SE

$$\mathrm{ASE} = -772.02883-[-771.88552] + 0.07331 = -0.14331 + 0.07331 = -0.07000 = -183.8\ \mathrm{kJ\ mol^{-1}}$$

With the α-diketone SE

$$-183.8 + 17.6 = -166.2\ \mathrm{kJ\ mol^{-1}}\ \text{strongly antiaromatic}$$

Quinone **4b**
Without the α-diketone SE

$$\mathrm{ASE} = -772.02883 - [-771.89496] + 0.07331 = -0.13387 + 0.07331 = -0.06056 = -159.0\ \mathrm{kJ\ mol^{-1}}$$

With the α-diketone SE

$$-159.0 + 17.6 = -141.4\ \mathrm{kJ\ mol^{-1}}\ \text{strongly antiaromatic}$$

Quinone **5a**

$$\mathrm{ASE} = -847.27201 - [-847.13450] + 0.07331 = -0.13751 + 0.07331 = -0.06420 = -168.6\ \mathrm{kJ\ mol^{-1}}\ \text{strongly antiaromatic}$$

Quinone **5b**

$$\mathrm{ASE} = -772.02543 - [-771.89178] + 0.07331 = -0.13365 + 0.07331 = -0.06034 = -158.5\ \mathrm{kJ\ mol^{-1}}\ \text{strongly antiaromatic}$$

Quinone **6**
Without the α-diketone SE

TABLE 6: Vertical IE and EA, and HOMO and LUMO energies for 1−6 and Some Reference Compounds[a]

compound	IE	EA	HOMO	LUMO
1	−457.44960 − (−457.78137) = 0.33177 = 9.03 eV experiment 9.23 eV (ref 40) exptl − calcd = 0.20	−457.78137 − (457.82498) = 0.04361 = 1.19 eV	−10.136	1.117
2	−457.39931 − (457.73247) = 0.33316 = 9.07 eV	−457.73247 − (457.80230) = 0.06983 = 1.90 eV	−8.966	0.312
3	−457.39175 − (457.74249) = 0.35074 = 9.54 eV	−457.74249 − (457.80614) = 0.06365 = 1.73 eV	−9.477	0.428
4a	−457.36030 − (457.66148) = 0.30118 = 8.20 eV	−457.66148 − (457.74959) = 0.08811 = 2.40 eV	−7.975	−0.249
4b	−457.36418 − (457.67070) = 0.30652 = 8.34 eV	−457.67070 − (457.74526) = 0.07456 = 2.03 eV	−7.919	0.289
5a	−457.34942 − (457.66902) = 0.31960 = 8.70 eV	−457.66902 − (457.75573) = 0.08671 = 2.36 eV	−8.490	−0.189
5b	−457.34801 − (457.66755) = 0.31954 = 8.70 eV	−457.66755 − (457.74232) = 0.07477 = 2.03 eV	−8.448	0.382
6	−457.39130 − (457.71928) = 0.32798 = 8.92 eV	−457.71928 − (457.76117) = 0.04249 = 1.16 eV	−9.695	1.252
benzene	−231.97022 − (−232.31125) = 0.34103 = 9.28 eV experiment 9.24 eV (ref 40) exptl − calcd = −0.08	−232.31125 − (−232.25824) = −0.05301 = −1.44 eV	−8.957	3.996
cyclobutadiene	−154.42910 − (−154.72110) = 0.20202 = 7.95 eV experiment 8.18 eV (ref 40) exptl − calcd = 0.23	−154.72112 − (−154.71190) = −0.00922 = −0.25 eV	−7.412	2.910
1,4-benzoquinone	−381.19461 − (−381.56168) = 0.36707 = 9.99 eV experiment 10.11 eV (ref 40) exptl − calcd = 0.12	−381.56168 − (−381.63288) = 0.07120 = 1.94 eV experiment 1.86 eV (ref 40) exptl − calcd = −0.08	−11.090	0.217
1,2-benzoquinone	−381.20103 − (−381.54966) = 0.34863 = 9.49 eV experiment 9.6 eV (ref 40) exptl − calcd = 0.11	−381.54966 − (−381.62399) = 0.07433 = 2.02 eV experiment 1.62 eV (ref 40) exptl − calcd = −0.40	−9.718	0.144

[a] IE and EA here are *E*(cation) − *E*(neutral) and *E*(neutral) − *E*(anion), B3LYP/6-311+G**//B3LYP/6-31G*. HOMO and LUMO are HF/6-31G*//B3LYP/6-31G*. IE and EA are given in hartrees and eV, HOMO and LUMO energies in eV.

$$\mathrm{ASE} = -922.51997 - [-922.42966] + 0.07331 = -0.09031 + 0.07331 = -0.01700 = -44.6\ \mathrm{kJ\ mol^{-1}}$$

With the α-diketone SE

$$-44.6 + 17.6 = -27.0\ \mathrm{kJ\ mol^{-1}}\ \text{essentially nonaromatic or very weakly antiaromatic}$$

Our interpretation of the energetics of the homodesmotic reactions (Figure 11) is largely in accord with their salient structural characteristics. Quinone **1**, with a benzene ring and no cyclobutadiene ring, is strongly aromatic, **2** is nonaromatic, and **3** is a borderline case (the carbonyl groups may be barely able to confer some 2-π-electron character on the bicyclic perimeter). Quinones **4a**−**5b**, with cyclobutadiene rings and no benzene rings, are strongly antiaromatic, and **6** is essentially nonaromatic, with a dubious indication of destabilization, although there is no reason to expect it to be antiaromatic. These conclusions, which agree with the calculated Diels−Alder activation energies, will be augmented in the next section, where we discuss NICS calculations on **1**−**6**.

5. NICS (Nucleus-Independent Chemical Shift) Calculations. In the NICS test for aromaticity or antiaromaticity, a probe nucleus with spin as its only property is placed (computationally) in the center (or along a line from the center point normal to the ring plane—see below) of the ring being probed. In the test as first developed by Schleyer et al.,[14] the probe nucleus was put at the center of the ring, but subsequent work indicated that placing it above the center, usually 0.5−1.0 Å, gives a better indication of the effect of the π electrons disentangled from that of the σ electrons.[15−17] In their study of the quinones of pentalene,[13] Lewars and co-workers used a "NICS curve"; cf. Morao and Cossio[17] and Schleyer et al.,[69] a plot of the chemical shift of the probe atom against a set of distances above the ring center. Here we use HF/6-31G* GIAO chemical shift calculations[70] on B3LYP/6-31G* geometries and report simply NICS(1) (the probe atom 1.0 Å above the center[69]) values; see Table 3 and the reference compounds in Table 4.

From Tables 3 and 4, the results of the NICS calculations are clear-cut. Quinone **1** has rings of aromatic (benzene) and nonaromatic (cyclobutenedione, or possibly dimethylenecyclobutanedione) nature. Quinones **2** and **3** are essentially nonaromatic. Quinones **4a**, **4b**, **5a**, and **5b** have rings of nonaromatic (benzoquinone) and antiaromatic (cyclobutadiene) nature. This accords with the results of both the homodesmotic and Diels−Alder activation energy calculations. Quinone **6** is simply nonaromatic.

6. UV Spectra. To help characterize these quinones and to see if any anomalies stand out, we calculated the UV spectra of **1**−**6** by the time-dependent DFT (TDDFT) method as implemented by Stratman et al., the most practical nonempirical approach for molecules of reasonable size,[71] using the recommended B3P86/6-311++G** method/basis of Wiberg et al.,[72] and requesting the UV bands for the first six excited singlets. The results are given in Table 5 for the quinones and some reference compounds. The oscillator strengths are a measure of relative intensities. First, we address the question of how good these calculated spectra are, with regard to the position and intensity of the bands, by comparing computed spectra with some experimental ones. Experimental spectra are available for **1** and for benzene, cyclobutadiene, the benzoquinones, cyclobutenedione, and dimethylenecyclobutene. We compare the salient features of the experimental and computed (Table 5) UV spectra for these compounds:

Quinone 1. The computed UV captures the strong experimental[7] bands at 271 and 277 nm (computed: 260, 268 nm). The other calculated bands are either outside the instrument range (233 nm) or possibly too weak to escape being obscured by the two strong absorptions. Bands with oscillator strength zero are formally forbidden by symmetry but can actually usually be seen because of vibrational distortions from perfect symmetry.

Benzene. The computed UV predicts formally zero-intensity absorptions at 189, 203, and 229 nm which may correspond to the experimental[73] ones at 184, 204, and 256 nm, although the intensities of the two shorter-wavelength one (ε 60000 and 7900) are much higher than the oscillator strengths might suggest.

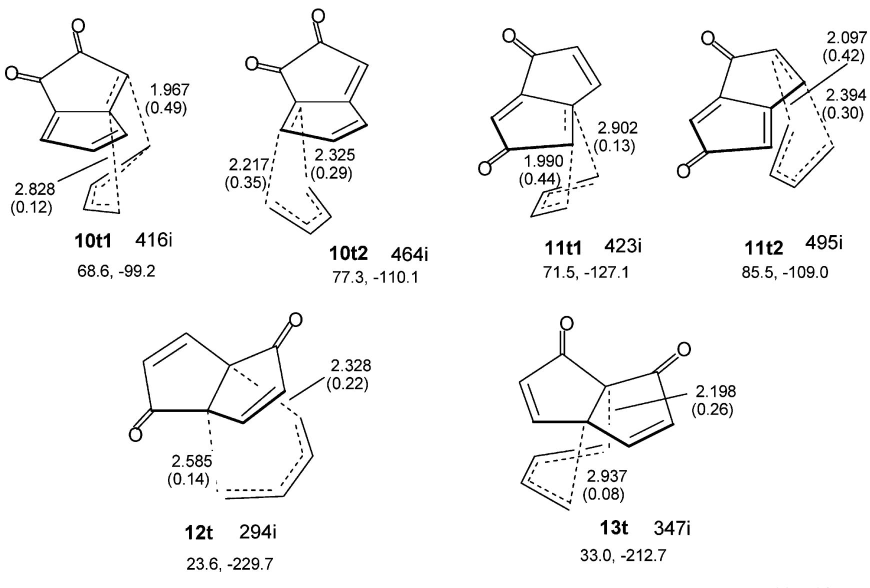


Figure 12. Transition states (all C_1 symmetry) for Diels−Alder reactions with 1,3-butadiene of quinones **10**−**13**. B3LYP/6-31G* calculations (except for bond orders, in parentheses: Löwdin bond orders,[23] HF/3-21G on B3LYP/6-31G* geometries). Bond lengths (Å) and orders of the dienophile-diene connecting bonds are shown, and the imaginary frequency (e.g., 416i) and activation and reaction energy (e.g., 68.6, −99.2) in kJ mol^{-1}. Data from Table 7.

TABLE 7: B3LYP/6-31G* Energies and Relative Energies (kJ mol^{-1}) of Butadiene, Quinones 10−13, and Their Diels−Alder Transition States and Products[a]

reactants	TS	pdt	activation E, kJ mol^{-1}	reaction E, hartrees kJ mol^{-1}
cisoid butadiene (for all DA) −155.986456 0.085251 −155.901205				
quinone **10** −457.632685 0.096736 −457.535949 Q10 + but: −613.437154	**10t1** −613.595398 0.184360 −613.411038	Q10t1 pdt −613.664621 0.189680 −613.474941	Q10t1 $E^{\ddagger}$ 0.026116 68.6	Q10t1 ΔE −0.037787 −99.2
quinone **10** −457.632685 0.096736 −457.535949 Q10 + but: −613.437154	**10t2** −613.592345 0.184631 −613.407714	Q10t2 pdt −613.668754 0.189684 −613.479070	Q10t2 $E^{\ddagger}$ 0.029440 77.3	Q10t2 ΔE −0.041916 −110.1
quinone **11** −457.633222 0.096672 −457.536550 Q11 + but: −613.437755	**11t1** −613.594712 0.184166 −613.410546	Q11t1 pdt −613.676007 0.189836 −613.486171	Q11t1 $E^{\ddagger}$ 0.027209 71.5	Q11t1 ΔE −0.048416 −127.1
quinone **11** −457.633222 0.096672 −457.536550 Q11 + but: −613.437755	**11t2** −613.589835 0.184634 −613.405201	Q11t2 pdt −613.669027 0.189749 −613.479278	Q11t2 $E^{\ddagger}$ 0.032554 85.5	Q11t2 ΔE −0.041523 −109.0
quinone **12** −457.607860 0.095746 −457.512114 Q12 + but: −613.413319	**12t** −613.588092 0.183770 −613.404322	Q12t pdt −613.690578 0.189775 −613.500803	Q12t $E^{\ddagger}$ 0.008997 23.6	Q12t ΔE −0.087484 −229.7
quinone **13** −457.610374 0.095906 −457.514468 Q12 + but: −613.415673	**13t** −613.586767 0.183656 −613.403111	Q13t pdt −613.686285 0.189608 −613.496677	Q13t $E^{\ddagger}$ 0.012562 33.0	Q13t ΔE −0.081004 −212.7

[a] Reactants column gives uncorrected energy, ZPE (uncorrected), and corrected energy (see text, Computational Methods). The transition state structures are shown in Figure 12.

Cyclobutadiene. The computed UV predicts bands the two strongest bands in the experimentally examined[74] range of 200−500 nm to be at 227 and 236 nm. These could correspond to bands at ca. 200 nm causing the observed tail and the sudden rise. Bands at longer wavelength might be observable at higher concentrations (the spectra were obtained in a cryogenic matrix).

1,4-Benzoquinone. Above 250 nm (in the normally observed region), the computed 252 and 325 nm bands likely mirror the experimental[40] ∼245 and ∼290 nm absorptions, with the predicted 464 nm band being poorly correlated with the weak ∼365 nm absorption.

1,2-Benzoquinone. The computed 402 (or possibly 407) and 708 nm bands presumably correspond to the experimental[40] ones at ∼380 and ∼620 nm, the longest-wavelength band being nicely separated from the one below in both calculation and experiment.

Cyclobutenedione. The computed 185 or 195 nm band may correspond to the experimental[8] 214 nm, and the computed 356 or 395 nm band presumably corresponds to the observed 340 nm absorption, with the predicted 227 and 234 nm bands being obscured by the relatively strong 214 nm absorption.

Dimethylenecyclobutene. The computed 203 nm band is presumably mirrored in the experimentally[75] very strong 212 nm absorption, and the 259 nm band in the strong 248 nm absorption, which would obscure a nearby weak (like the calculated 260 nm) band. As expected, **1**−**6** all appear to have weak long-wavelength bands at ca. 500−900 nm, presumably n → π^*, which should confer the yellow-red color characteristic of planar α-diketones.

It emerges clearly from the seven compounds above that the TDDFT UV spectra are, generally speaking, no better than semiquantitative; this may in part be due to two or more electronic transitions showing experimentally as one absorption.

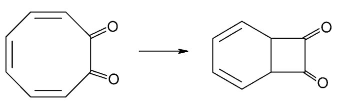
7. Ionization Energy (IE), Electron Affinity (EA), HOMO, and LUMO.

In another facet of the characterization of **1**−**6** and the search for anomalies, we calculated their (vertical) ionization energies and electron affinities. We also note their HOMO and LUMO energies, as these show some correlation with the orbital energies (more tenuous for EA). The data are given in Table 6. Comparison with experimental IEs (for benzene, cyclobutadiene, and the benzoquinones) showed that reasonably good IEs could be obtained by the fast method of

B3LYP/6-311+G** single-point energies on B3LYP/6-31G* geometries, taking the radical cation/neutral energy difference; the analogous (radical anion/neutral) method was used for EAs. Vertical, rather than adiabatic,[76] IEs and EAs were calculated because the former, eschewing geometry optimization of the ionized species, more closely represent an inherent electronic property of the molecule; in fact, the optimized ion is for certain molecules not even a stationary point on the potential energy surface. The IEs appear to be accurate to within 0.2 eV. The EAs, for which less experimental information is available, may be in error by ca. 0.4 eV. As expected, Koopmans's "theorem", which equates the negative of the HOMO energy with the IE, is only modestly accurate in predicting this quantity,[77] and the LUMO energy does not serve as an indication of the EA (better EAs for substituted benzoquinones can apparently be obtained with B3LYP/6-311G(3d,p) calculations[78]). As expected from the behavior of the benzoquinones, **1**−**6** have positive EAs; i.e., their anions are stable in the sense that they do not instantly eject an electron, like the anion of benzene or cyclobutadiene (negative EA). The first benzenoid hydrocarbon which forms a stable anion is anthracene.[79] Zhan et al. have studied the relationship between orbital energies and IE/EA in DFT.[80] Quinones **4a**/**4b**, and to a lesser extent **5a**/**5b**, are predicted to have somewhat lower IEs than the other benzocyclobutadiene quinones and the benzoquinones, and **1** and **6** lower EAs.

8. Comparison of 1−6 with the Quinones of Cyclooctatetraene and Its Cross-Linked Derivatives. We briefly compare **1**−**6** with the quinones of cyclooctatetraene (Figure 3), pentalene (Figure 3), and in passing bicyclo[5.1.0]octa-1,3,5,7-tetraene (Figure 5). As explained in the Introduction, all these quinones are based conceptually on cyclooctatetraene and its 1,3-, 1,4-, and 1,5-cross-linked structural relatives (Figure 5).

The cyclooctatetraeneoquinones, **9q1,4** and **9q1,2**, are known[10,11] and have been studied computationally.[12] They are nonplanar, nonaromatic, and very reactive, especially the 1,2-quinone, which at room temperature quickly isomerizes to the bicyclic valence isomer:



Computational studies indicate that they are nonplanar, and even the hypothetical planar structures, which are saddle points[12] wanting to distort from planarity, are not, as shown by NICS calculations, aromatic.[12]

The pentalenoquinones have been studied computationally.[13] Compounds **10** and **11** were found to be nonaromatic, and **12** and **13** (Figure 3) were antiaromatic, as might be expected from the bis(cyclopentadienone) character of the latter two; these two,[81,82] and the 3-phenyl derivative of **13**,[83] have been generated as reactive intermediates and trapped as both dienes and dienophiles. These four quinones were calculated[13] to have these barriers in Diels−Alder reactions as dienes with ethyne and with ethene, using the pBP/DN* DFT method:[84] **10** barrier with ethyne, 81 kJ mol^{-1} barrier with ethene, 77 kJ mol^{-1}; **11** barrier with ethyne, 73 kJ mol^{-1} barrier with ethene, 71 kJ mol^{-1}; **12** barrier with ethyne, 37 kJ mol^{-1} barrier with ethene, 29 kJ mol^{-1}; **13** barrier with ethyne, 41 kJ mol^{-1} barrier with ethene, 35 kJ mol^{-1}.

In Figure 12 and Table 7 we report, for direct comparison with the Diels−Alder reactivity of **1**−**6**, our B3LYP/6-31G* (rather than pBP/DN*) calculations for Diels−Alder addition of 1,3-butadiene to **10**, **11**, **12**, and **13** acting as dienophiles (rather than dienes). Quinones **10** and **11** are calculated to be comparable to the benzoquinones in reactivity as dienophiles, while **12** and **13**, which are cyclopentadienone derivatives, are more reactive but not as reactive as **4a**/**4b** and **5a**/**5b**, which are cyclobutadiene derivatives (Figure 8).

The calculated structures of the quinones of bicyclo[5.1.0]octa-1, 3, 5, 7-tetraene (Figure 5) show strong bond length alternation,[85] suggesting there is no cyclic electron delocalization.

Conclusions

Our calculations indicate that those quinones of benzocyclobutadiene which have a benzene (quinone **1**) or a cyclobutadiene (quinones **4a**/**4b** and **5a**/**5b**) ring will reflect in their properties the reactivity of these rings. The known **1** is indeed stable, while **4a**/**4b** and **5a**/**5b** should be highly reactive. We concur[34] that **5b** probably has no separate existence, **5a** being its essentially correct structural alter ego. We are agnostic on the case of **4a**/**4b**, with the nonexistence of **4a** seeming likelier than that of **4b**. Quinones **2**, **3**, and **6** are particularly interesting and are intriguing goals for synthesis. They lack cyclobutadiene and benzene rings, and so skirt the extremes of extravagant reactivity and prosaic stability. If the calculated Diels−Alder barriers with butadiene (Figure 8) are a guide to resistance toward dimerization or polymerization, then all three are much stabler in this respect than the other benzocyclobutadiene quinones, with **2** likely being the most reactive and **6** the least reactive of these three.

Supporting Information Available: The Cartesian coordinates of the relevant species and the data for the calculation of the heats of formation. This material is available free of charge via the Internet at http://pubs.acs.org.

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