Kinetic study of thermolysis of diarylhomonaphthoquinones. *Endo*/*exo* substituent and solvent effects

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The kinetics of thermal cyclopropane ring-opening of a series of *m*- and *p*-substituted *endo*/*exo* diphenylbromohomonaphthoquinones **1a**–**i** and the unsubstituted diphenylchlorohomonaphthoquinone **1j** have been investigated and compared with biphenyl-2,2′-diylhalogenohomonaphthoquinones **2a**,**b**. The first-order rate constants k/s^{-1} for **1a**–**i** at 100 °C in toluene increased with the electron-donating ability of the substituents. The kinetic substituent effects were much more pronounced for the *exo* family than for the *endo* one and revealed the crucial role of the resonance contribution of diaryl groups; $\log (k/k_o)_{exo} = -1.99\sigma^+ + 0.086$ and $\log (k/k_o)_{endo} = -0.784\sigma^+ + 0.002$, respectively. The compounds **2a**,**b** thermolyzed very quickly as compared with the corresponding diphenylhalogenohomonaphthoquinones **1e**,**j**. The kinetic solvent effects on the thermolysis of representative compound **1e** were so minute that the rates tended to slightly increase with the solvent polarity but decrease with the solvent basicity. These kinetic results were interpreted in terms of a concerted disrotatory ring opening of the incorporated cyclopropane ring.

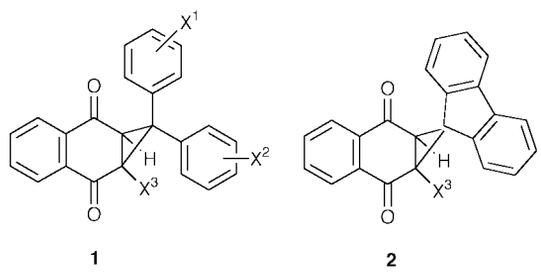
Introduction

Cyclopropane and its derivatives are fascinating compounds by virtue of their unusual structural, spectroscopic and chemical properties.[1] The cyclopropane ring closely resembles the C=C double bond and can interact with neighboring π-electron systems.[2] Therefore, the chemical consequence of the cyclopropane ring is highly dependent upon its conformational alignment associated with the conjugation with π- or p-orbitals.[3]

Thermal ring cleavage of cyclopropane rings with labile leaving groups like halogens,[4] tosyl group[5] and diazonium ion[6] has attracted theoretical attention in view of the stereospecific and disrotatory manner of ring-opening, as predicted by the orbital correlation diagram criteria.[7]

In our series of studies concerning the quinone-fused cyclopropanes, so-called homoquinones,[8] we have recently found that thermolysis of diarylbromohomonaphthoquinones **1e** and **2a** proceeds *via* ring cleavage of the incorporated cyclopropane ring to provide as primary products, 2-bromo-3-(diphenylmethylene)-2,3-dihydro-1,4-naphthoquinone **3e** and 2-(9-bromofluoren-9-yl)-1,4-naphthoquinone **4a**, depending on the structural features of the diaryl moieties (Scheme 1).[9] These homoquinones are intriguing compounds in that the incorporated cyclopropane rings are highly substituted with π-conjugative *endo* and *exo* aromatic nuclei as well as the two quinone carbonyl functions.

In this paper, we investigated the substituent and solvent effects on the thermolysis rates of a series of *m*- and *p*-substituted *endo*/*exo* diphenylhomonaphthoquinones **1a**–**k** as compared with biphenyl-2,2′-diyl-substituted analogues **2a**–**c** in order to gain an insight into the mechanistic pathways for thermolysis of homoquinones.



1 **2**

1a; X^1=X^2=*p*-OMe, X^3=Br
***endo*-1b**; X^1=*p*-OMe, X^2=H , X^3=Br
***exo*-1b**; X^1=H, X^2=*p*-OMe , X^3=Br
1c; X^1=X^2=*p*-Me , X^3=Br
***endo*-1d**; X^1=*p*-Me, X^2=H , X^3=Br
***exo*-1d**; X^1=H, X^2=*p*-Me , X^3=Br
1e; X^1=X^2=H , X^3=Br
1f; X^1=X^2=*p*-Cl , X^3=Br

***endo*-1g**; X^1=*p*-Cl, X^2=H , X^3=Br
***exo*-1g**; X^1=H, X^2=*p*-Cl , X^3=Br
1h; X^1=X^2=*m*-NO_2 , X^3=Br
***endo*-1i**; X^1=*p*-NO_2, X^2=H , X^3=Br
***exo*-1i**; X^1=H, X^2=*p*-NO_2 , X^3=Br
1j; X^1=X^2=H , X^3=Cl
1k; X^1=X^2=H , X^3=Me

2a; X^3=Br
2b; X^3=Cl
2c; X^3=Me

Results and discussion

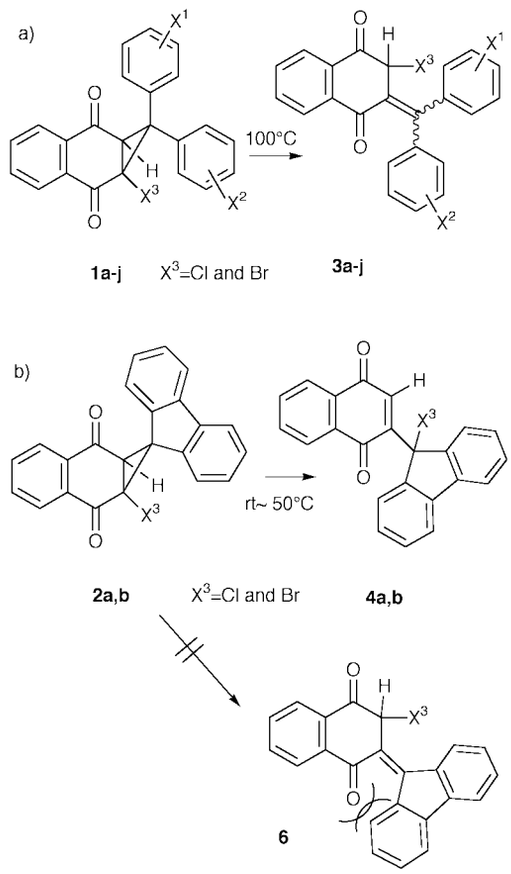
Synthesis

Homonaphthoquinones **1a**–**k** were prepared by 1,3-dipolar cycloaddition of *m*- and *p*-substituted diphenyldiazomethanes (DDMs) with 2-bromo-1,4-naphthoquinone as described previously.[10] The monosubstituted DDMs provided a mixture of *endo* and *exo* isomers. Each isomer was separated by column chromatography and purified by recrystallization. The stereochemistry was deduced on the basis of ^{1}H NMR measurements. The *endo* isomers are characterized by their higher field A_2B_2 quartet for the *p*-substituted phenyl ring due to the shielding effects of the facing naphthoquinone aromatic nucleus. For example, the methoxy-substituted *endo*-**1b** exhibited the A_2B_2 quartet at δ 6.44 and 7.06 ppm for the *p*-anisyl group, while *exo*-**1b** did so at δ 6.63 and 7.28 ppm, respectively. The *endo*/*exo* differentiating chemical shifts for other substituents

are also noticeably large: 0.39–0.46 ppm (**1d**: *p*-CH_3), 0.38–0.42 (**1g**: *p*-Cl) and 0.17–0.41 (**1i**: *p*-NO_2), respectively (see Experimental section). Biphenyl-2,2′-diylhomonaphthoquinones **2a**–**c** were synthesized by the reaction of 9-diazofluorene (9-DF) with the corresponding naphthoquinones as described elsewhere.[11] In the case of the reaction with 2-bromo-1,4-naphthoquinone, 2-(9-bromofluoren-9-yl)-1,4-naphthoquinone (**4a**) was obtained instead in almost quantitative yield (97%) due to a spontaneous thermolysis of the labile homonaphthoquinone **2a** (Scheme 1b).[9]

Product study

Unsubstituted diphenylbromohomonaphthoquinone **1e** thermolyzed at 100 °C in toluene for 24 h to give 2-bromo-3-(diphenylmethylene)-2,3-dihydro-1,4-naphthoquinone **3e** in an almost quantitative yield.[9] (Scheme 1a). The X-ray crystal structure of



Scheme 1

3e is shown in Fig. 1. It is worth noting that the naphthoquinone moiety adopts a non-planar conformation. The plane through the C(3)–C(2)–C(11) linkage significantly flips by 36.6° with respect to the best plane defined by the rest of the naphthoquinone moiety in such a way that the bulky diphenylmethylene function is effectively remote from the Br atom.

Further heating of some of the primary pyrolysates **3** resulted in the complication of product analysis owing to the occurrence of several consecutive reactions like radical dimerization, hydrogen abstraction and intramolecular cyclization.[9] Therefore, some of the products **3** were confirmed by trapping with methanol to afford S_N2' type adducts **5** (Scheme 2). Unfortunately, thermolysis of CH_3O-substituted **1a** and **1b** yielded complex reaction mixtures (by HPLC and NMR) and afforded no identified products in the methanol trapping experiment. The *m*-dinitro-substituted **1h** provided an intractable yellow powder (see Experimental section). In view of the clean first-order kinetics, these homoquinones **1a**, **1b** and **1h**

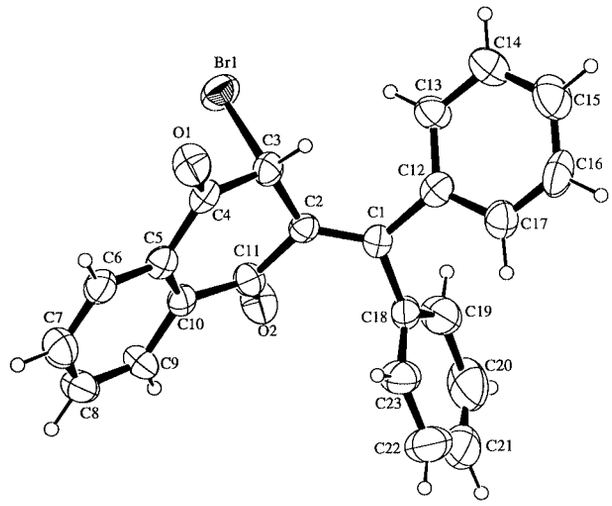
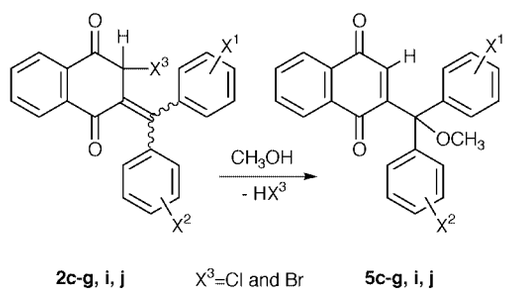


Fig. 1 Molecular structure of **3e**.



Scheme 2

appear to undergo primary cyclopropane ring cleavage as do others (*vide infra*).

Unlike bromohomonaphthoquinones **1a**–**i**, the chlorohomonaphthoquinone **1j** needed a high temperature (150 °C) to practically give the (diphenylmethylene)dihydro-1,4-naphthoquinone **3j** which was easily transformed to the methanol adduct **5j** (=**5e**) when treated with methanol. However, methylhomonaphthoquinone **1k** resisted thermolysis at 150 °C for over one week. By contrast, biphenyl-2,2′-diylchlorohomonaphthoquinone **2b** thermolyzed at relatively low temperature to yield a different type of product, 2-(9-chlorofluorenyl)-1,4-naphthoquinone **4b** in quantitative yield,[9] although the analogous methylhomonaphthoquinone **2c** remained intact even after being heated for 1 week at 150 °C (Scheme 1b).[9] For **2b**, the change of the reaction pathway may be due to the severe steric repulsion between the fluorene peri-hydrogen and the facing carbonyl group for the expected 2-halogeno-3-fluorenylidene-2,3-dihydro-1,4-naphthoquinones **6**.[9]

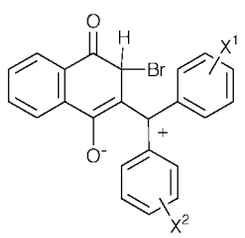
It is noted here that thermolysis of both the chloro-substituted *endo*-**1g** and *exo*-**1g** in toluene at 100 °C provided the identical isomer ratio (1 : 1.3) of *E*- and *Z*-**3g** (by NMR in $CDCl_3$ at 20 °C). Such a stereo-randomization apparently contradicts the well-known criterion of stereospecificity in the thermal ring-opening of halogenocyclopropanes.[7] However, this conflicting phenomenon can be rationalized by the observation that the isolated major isomer of **3g** easily isomerized to the minor one even at 50 °C in [$^2H_6$]benzene and came to equilibrium at the same isomer ratio of 1 : 1.3 as the above thermolysis. This ratio corresponds to the free energy difference (ΔG) of only 0.62 kJ mol^{-1} at 50 °C. The PM3 calculation predicted that the *E* structure is somewhat more stable than the *Z* one by only 0.6 kJ mol^{-1} in harmony with the experimental isomer ratio.[12] Thus, we tentatively assign the stable isomer as adopting the *E* form (see Experimental section). The isomerization of the *E* isomer was moderate in nonpolar [$^2H_6$]benzene ($k = 2.17 \times 10^{-4}$ s^{-1} and $t_{1/2} = 0.89$ h at 50 °C), but too fast to be followed by

Table 1 Rate constants for thermolysis of homonaphthoquinones **1a**–**k** and **2a**–**c** at 100 °C in toluene[a]

Entry	Homo-quinone	X^1	X^2	X^3	$10^6 k/s^{-1}$ [b]
1	**1a**	*p*-OCH_3	*p*-OCH_3	Br	6260 ± 94
2	***endo*-1b**	*p*-OCH_3	H	Br	171 ± 3.0
3	***exo*-1b**	H	*p*-OCH_3	Br	2360 ± 33
4	**1c**	*p*-CH_3	*p*-CH_3	Br	359 ± 4.7
5	***endo*-1d**	*p*-CH_3	H	Br	87.2 ± 1.1
6	***exo*-1d**	H	*p*-CH_3	Br	199 ± 2.6
7	**1e**	H	H	Br	46.2 ± 0.51
8	**1f**	*p*-Cl	*p*-Cl	Br	27.6 ± 0.39
9	***endo*-1g**	*p*-Cl	H	Br	40.3 ± 0.60
10	***exo*-1g**	H	*p*-Cl	Br	37.2 ± 0.57
11	**1h**	*m*-NO_2	*m*-NO_2	Br	0.805 ± 0.010
12	***endo*-1i**	*p*-NO_2	H	Br	10.3 ± 0.13
13	***exo*-1i**	H	*p*-NO_2	Br	1.64 ± 0.025
14	**1j**	H	H	Cl	0.946 ± 0.014[c]
15	**1k**	H	H	CH_3	NR[d]
16	**2a**	H	H	Br	very fast[e]
17	**2b**	H	H	Cl	1390 ± 19
18	**2c**	H	H	CH_3	NR[d]

[a] Carried out in sealed capillary tubes. [b] The k values are the average of at least two measurements. Error limit of k is ±2%. [c] Extrapolated value from the k values at higher temperature, $5.58(\pm 0.084) \times 10^{-5}$ s^{-1} (150 °C) and $1.99(\pm 0.035) \times 10^{-4}$ s^{-1} (170 °C), respectively. [d] No reaction over 1 week heating at 100 °C. [e] Spontaneously decomposed *in situ* on preparation of homoquinone **2a** at room temperature.

NMR in polar [$^2H_3$]acetonitrile. Hence, the thermal *E*–*Z* isomerization seems to occur *via* a resonance stabilized zwitterionic intermediate **I**.



I

Kinetic study

(a) Substituent effects. Thermolysis of homonaphthoquinones at 100 °C in toluene were monitored by HPLC using an internal standard procedure. During the thermolysis, no *endo*–*exo* isomerization of homoquinones was found by a careful HPLC analysis. The first-order rate constants for thermolysis of variously substituted **1** and **2** are collected in Table 1. These data contain typical electron-donating and -withdrawing groups, *p*-CH_3O and *p*-NO_2, as highly resonance sensitive substituents. A survey of the Table shows that the rates increase with increasing electron-donating ability of the aromatic substituents for each of the *endo* and *exo* family (entries 1–13). Thus, the *p*-CH_3O substituted *exo*-**1b** thermolyzed *ca*. 1440-fold faster than the *p*-NO_2 substituted *exo*-**1i**, although only a 17-fold increment was observed for the corresponding *endo*-**1b** compared with *endo*-**1i**.

The linear free energy treatment of log (k/k_o) for the respective mono-substituted *endo* and *exo* isomers gave a better fit *versus* Brown σ^+ [13] than Hammett σ,[14] where k_o is the rate constant for the unsubstituted **1e** (Fig. 2). The regression equations are $\log (k/k_0)_{exo} = -1.99\sigma^+ + 0.086$ ($r = 0.998$, $s = 0.090$, $n = 5$) for the *exo* series and $\log (k/k_0)_{endo} = -0.784\sigma^+ - 0.002$ ($r = 0.997$, $s = 0.043$, $n = 5$) for the *endo* one, respectively. For σ parameters, rather worse correlations are obtained for both series due to the noticeable upper deviation of the CH_3O substituent; $\log (k/k_o)_{exo} = -2.60\sigma + 0.455$ ($r = 0.942$, $s = 0.45$, $n = 5$)

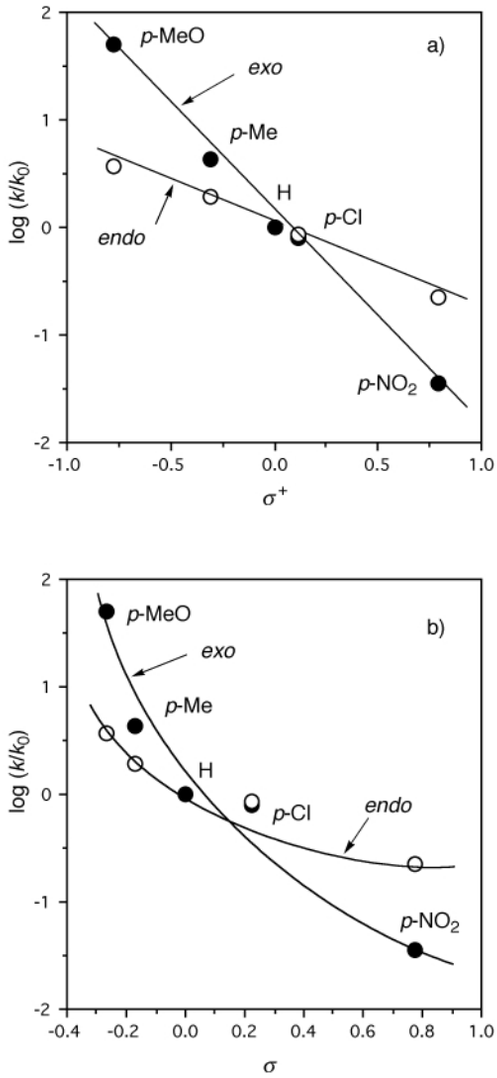


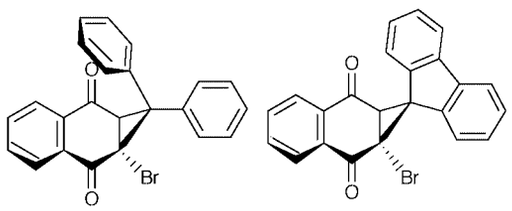
Fig. 2 The plots of log (k/k_0) for the thermolysis of diarylhomonaphthoquinones in toluene at 100 °C against the a) σ^+ and b) σ values; the lines were drawn for the *exo*-substituted (●) and the *endo*-substituted (○) series.

and $\log (k/k_o)_{endo} = -1.06\sigma + 0.147$ ($r = 0.972$, $s = 0.12$, $n = 5$), respectively. The excellent correlation against σ^+ with negative ρ values suggests that electron-donating resonance effects of the substituent play an important role in stabilizing the transition state, although a limited set of present data is not adequate for complete knowledge of the substituent effects. The absolute ρ value for *exo* isomers is about 2.5 times as large as that for *endo* isomers. This means a preferential effect of the *exo* aromatic substituents on the cyclopropane ring-cleavage of homonaphthoquinones. Also of interest is that the *endo*/*exo* disubstituted homonaphthoquinones with identical substituents ($X^1 = X^2$) gave an excellent correlation when plotted against the sum of the σ^+ values: $\log (k/k_0)_{disub} = -1.34\sigma^+ + 0.046$ ($r = 1.00$, $s = 0.029$, $n = 5$). The absolute ρ value is somewhat smaller than half of the sum (=−2.77) of the individual absolute ρ values for the *exo* and *endo* monosubstituted series. It is well known that the substituent effects of two aromatic rings are not additive and the discrepancy is most serious when the first substituent is strongly electron-donating or -withdrawing as in the present system.[15]

In order to obtain some steric features of these aromatic nuclei, we resorted to the X-ray crystal structure of the representative compound **1e**.[16] The obtained structure shows that there is a significant difference in the rotational freedom between the two phenyl rings. The *endo* phenyl ring lies in an almost castanets-like conformation with respect to the naph-

thoquinone plane to minimize the steric repulsion, therefore its rotation appears to be highly restricted. In contrast, the *exo* phenyl ring is located in the less hindered space. As such, the *exo* aromatic ring would enjoy a more favorable bisected conformation (II) which is essential for the ideal π-conjugation between the cyclopropane ring and the adjacent π-systems.[2,17]

As to the effect of the cyclopropane substituent, the less labile chlorine substituent markedly decreased the rate to about 1/50 times slower than the bromine substituent (entries 7 and 14). Of interest is that the replacement of the diphenyl group by planar biphenyl-2,2′-diyl brought about *ca.* 1500 times rate enhancement (entries 14 and 17). This is probably due to the inherent bisected structure (III) associated with the spiro-linkage of the planar fluorenylidene function to the rigid homoquinone skeleton for **2b**.



II III

(b) Solvent effects. The solvent dependencies of rate constants for the thermolysis of representative diphenylbromohomonaphthoquinone **1e** are so small that the total range amounts to only a factor of 3 over the wide range of solvent polarities investigated (Table 2). A careful survey, however, showed that rates tended to slightly increase with increasing solvent polarity except for acetic acid, and to decrease with increasing solvent basicity. Unfortunately, it is not at all clear why the most polar acetic acid exhibits an abnormal deviation (rate retardation). Therefore, the fit of log k with only one parameter for solvent polarity (E_T)[18] or solvent basicity (D_π)[19] was insufficient: $\log k = 0.0195E_T - 4.96$ ($r = 0.759$, $s = 0.11$, $n = 10$, except acetic acid) and $\log k = -0.249D_\pi - 4.20$ ($r = 0.863$, $s = 0.099$, $n = 8$), respectively. To gain more insight into the solvent effects, the two parameter procedure was used to greatly improve the correlation for the solvents for which both parameters are known: $\log k = 0.0196E_T - 0.146D_\pi - 4.97$ ($r = 0.947$, $s = 0.077$, $n = 8$). The weightings of the E_T and D_π parameters on the regression equation are approximately equal as estimated from their contributions, 54 and 46%, respectively. The small positive coefficient of E_T may be due to the rate-acceleration by solvation of a slightly polar transition state in which the fission of the polar C–Br bond will be facilitated in the polar medium. In contrast, the small negative coefficient of D_π suggests rate-retardation by solvation of the ground state naphthoquinone moiety, since the D_π parameter can be successfully used to reflect the π-acceptor properties of substrates.[20] Consequently, negligible solvent effects, consistent with the very poor polarization in the transition state, support a concertedness of the present thermolysis, indicating that the ring opening is synchronous with the departure of the leaving bromide.

Mechanistic considerations

It is generally accepted that thermolysis of cyclopropanes with labile leaving groups proceeds through a disrotatory mode of ring-opening to provide the propene derivatives.[7] This cyclopropyl–allyl cationic rearrangement is concerted and the stereochemistry can thus be predicted on the basis of the principle of orbital symmetry conservation.[7]

According to this mechanistic pathway, the present kinetic substituent effects, which exhibited a significant contribution of the *exo* substituents (Table 1), can be rationalized by considering that the electron-donating *exo* aryl group rotates inward in such a way that the lobes of the opening adjacent C_2–C_3 bond will facilitate the departure of the leaving bromide from the C_1 atom and stabilize the developing positive charge. The fact that the logarithmic rate constants correlate with σ^+, rather than σ, provides strong evidence for the resonance stabilization of the positive charge by the *exo* aromatic nucleus. Such a stereoelectronic interaction is at a maximum when the p-orbital axis of the aromatic ring is arranged parallel to the cyclopropane ring (bisected conformation). In fact, it has become apparent from the X-ray crystal structure of **1e**[16] that the less restricted *exo* aromatic ring is more easily capable of adopting a favorable bisected conformation so as to resonate with the breaking cyclopropane hybrid bond.[17] Such a preferable π-conjugation is less likely for the *endo* aromatic ring because of the highly congested circumstances. Moreover, as shown in Table 2, the poor kinetic solvent effects strongly support the concerted cyclopropane bond-opening linked with a simultaneous bromide migration. The small negative entropy of activation for the parent **1e** signifies a reactant-like transition state ($\Delta S^\ddagger = -2.5$ (0.5) J mol^{-1} K^{-1} and $\Delta H^\ddagger = 120.3(0.2)$ kJ mol^{-1} at 100 °C in acetonitrile, *cf.* Table 2).

Table 2 Rate constants for thermolysis of bromohomonaphthoquinones **1e** at 100 °C in various solvents[a]

Solvent	$10^5 k$/s^{-1} [b]	E_T [c]	D_π [d]
Nitromethane	12.3 ± 0.18	46.3	−0.724
1,2-Dichloroethane	10.2 ± 0.14	41.3	−1.22
Acetonitrile[e]	8.43 ± 0.16	45.6	−0.440
Butan-2-one	8.37 ± 0.11	41.3	0.177
Ethanol	8.30 ± 0.13	51.9	—
Benzene	5.27 ± 0.05	34.3	0
Triethylamine	5.26 ± 0.07	32.1	—
Toluene	4.62 ± 0.08	33.9	0.394
Ethyl acetate	4.56 ± 0.06	38.1	0.289
1,4-Dioxane	4.31 ± 0.08	36.0	0.590
Acetic acid	2.61 ± 0.05	51.7	—

[a] Carried out in sealed capillary tubes. [b] The k values are the average of at least two measurements. Error limit of k is ±2%. [c] E_T values; see ref. 18. [d] D_π values; see ref. 19. [e] The k values at 110 and 120 °C are $2.54(\pm0.03) \times$ and $6.74(\pm0.10) \times 10^{-4}$ s^{-1}, respectively. The activation parameters are $\Delta H^\ddagger = 120.3(\pm0.2)$ kJ mol^{-1} and $\Delta S^\ddagger = -2.5(\pm0.5)$ J mol^{-1} K^{-1} at 100 °C, respectively.

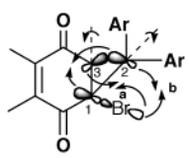


Fig. 3 $[{}_\sigma 2_s + {}_\sigma 2_a]$ orbital interaction.

The present kinetic results can also be interpreted by analyzing interactions of frontier orbitals. In this approach, the orbital interaction $[{}_\sigma 2_s + {}_\omega 0_s]$ can be envisaged,[21] in which the σ orbital (HO) of the C_2–C_3 bond interacts with the central vacant p orbital (LU), designated as ω. The electron donation from the aryl group will raise the HO energy and thereby enhance the overlapping with the LU orbital. An alternative orbital interaction $[{}_\sigma 2_s + {}_\sigma 2_a]$ can also satisfactorily explain our experimental results without postulating an intervention of cyclopropyl cation.[22] As illustrated in Fig. 3, the thermally allowed concerted process involves charge transmittance from the cyclopropane C_2–C_3 bond (HO) to the antibonding C_1–Br bond (LU). In the disrotatory motion, the electron donation from the bisected *exo*-aryl group will mostly raise the HO energy and facilitate the bromide migration to the C_3 atom (path a) for diphenyl-substituted series or the C_2 atom (path b) for biphenyl-2,2′-diyl-substituted ones, respectively. In contrast, the *endo* aryl group cannot satisfactorily participate in

the orbital interaction because of the insufficient bisected conformation. The rapid thermolysis for biphenyl-2,2′-diylhomonaphthoquinones is ascribed to the intrinsic bisected structure in which the planar fluorenylidene function can enjoy the ideal resonance interaction with the quasi π-orbital of cyclopropane ring. The path b migration is thought to be the result of a serious steric repulsion between the peri-hydrogen of the fluorenylidene function and the adjacent carbonyl group.[9] Whatever the mechanism, the present thermolysis of homoquinones proceeded through a concerted disrotatory ring-opening, undergoing the marked resonance effects of the *exo* aryl group.

Conclusion

It was found that thermolysis of a series of *m*- and *p*-substituted *endo*/*exo* diphenylbromohomonaphthoquinones **1a**–**i**, which undergo cyclopropane ring-cleavage to provide the corresponding 2-bromo-3-diphenyl-2,3-dihydro-1,4-naphthoquinones as primary pyrolysates, was much more accelerated by electron-donating substituents in the *exo* aromatic rings than in the *endo* ones, as indicated by the Hammett ρ values of −1.99 and −0.784 against σ^+, respectively. However, the solvent effect on thermolysis of the representative compound **1e** was so small that the rate constant increased by only a factor of several times in spite of the wide range of solvent polarity. It was also noticed that due to the intrinsic bisected conformation biphenyl-2,2′-diylhalogenohomonaphthoquinones **2a**,**b** thermolyzed more quickly to afford 2-(9-halogenofluoren-9-yl)-1,4-naphthoquinones **4a**,**b** instead of the predicted dihydro-1,4-naphthoquinones. These results were rationalized on the basis of a concerted disrotatory ring opening associated with the resonance interaction of the *endo* and *exo* aryl groups.

Experimental

Melting points were measured on a Yanagimoto microscopic apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 MHz spectrometer with Me_4Si as an internal standard and $CDCl_3$ as solvent unless otherwise noted. IR spectra were taken with a Perkin-Elmer 938G spectrophotometer. Mass spectra were obtained on a JEOL JMS DX303 spectrometer.

Kinetic measurements

The kinetic measurements were carried out on a Hitachi 655A-12 liquid chromatograph equipped with a Waters RCM 8 × 10 module, installing a Radial-Pak cartridge (8C_{18}, 5μ) in a similar manner to that previously described.[9] The reaction solutions for thermolysis of variously substituted **1a**–**k** and **2b,c** were prepared by mixing the homoquinone and naphthalene or biphenyl (as an internal standard) in toluene at ordinary temperature and sealed in 10–15 glass capillaries (φ = 1.8 mm). The reaction solutions for the kinetic solvent effects were similarly prepared by mixing unsubstituted **1e** and the internal standard in a given solvent and sealed in the capillary tubes. The reactions were initiated by fast immersion into a Haake EF thermostatted bath (±0.05 °C) at the given temperatures and after several minutes the reaction was followed at time intervals by monitoring the decreasing relative integral absorptions of homoquinone *versus* the internal standard at 280 nm up to the conversion of second-half lives. Clear first-order kinetics were observed for all reactions studied by plotting logarithmic values of the relative absorptions against time.

Materials

All solvents used were dried and purified in the usual manner.[23] All homoquinones **1a**–**k** and **2b**,**c** were prepared from the reactions of variously substituted diphenyldiazomethanes (DDMs) and 9-diazofluorene (9-DF) with 2-bromo-, 2-chloro-, and 2-methyl-1,4-naphthoquinones according to the previous procedure.[10] These homonaphthoquinones were isolated by column chromatography on silica gel and purified by recrystallization from a mixture of hexane and benzene. All new compounds **1a**–**d** and **1f**–**i** provided satisfactory analytical and spectroscopic data as shown below. The known compounds **1e**,[9] **1j**,[24] **1k**[25] and **2b**,[24] **2c**[25] were reported elsewhere. The compound **2a** was not obtained because of its thermal lability leading to ring-cleaved **4a**.[9]

1-Bromo-7,7-bis(*p*-anisyl)-3,4-benzobicyclo[4.1.0]heptane-2,5-dione 1a. Yield 55% (isolated); mp 126–128 °C; ν_{max}/cm^{-1} 1685, 1606, 1510, 1289, 1250, 1179, 1029 and 831; δ_H 3.55 (3H, s), 3.78 (3H, s), 3.88 (1H, s), 6.44 (2H, d, *J* 8.91 Hz), 6.87 (2H, d, *J* 8.58 Hz), 7.03 (2H, d, *J* 8.58 Hz), 7.40 (2H, d, *J* 8.91 Hz), 7.45–7.53 (2H, m), 7.80–7.87 (1H, m) and 7.87–7.94 (1H, m); *m*/*z* (EI) 383 (M^+ − Br). (Found: C, 65.02; H, 4.31. $C_{25}H_{19}O_4Br$ requires C, 64.80; H, 4.13%).

1-Bromo-7-*endo*-*p*-anisyl-7-*exo*-phenyl-3,4-benzobicyclo-[4.1.0]heptane-2,5-dione *endo*-1b. Yield 45% (by NMR); mp 157–158 °C; ν_{max}/cm^{-1} 1680, 1587, 1510, 1288, 1251, 1032, 828 and 698; δ_H 3.55 (3H, s), 3.77 (1H, s), 6.44 (2H, d, *J* 8.91 Hz), 7.06 (2H, d, *J* 8.91 Hz), 7.22–7.30 (1H, m), 7.32–7.40 (2H, m), 7.47–7.54 (4H, m), 7.81–7.86 (1H, m) and 7.90–7.95 (1H, m); *m*/*z* (EI) 353 (M^+ − Br). (Found: C, 66.75; H, 4.08. $C_{24}H_{17}O_3Br$ requires C, 66.52; H, 3.95%).

1-Bromo-7-*endo*-phenyl-7-*exo*-*p*-anisyl-3,4-benzobicyclo-[4.1.0]heptane-2,5-dione *exo*-1b. Yield 52% (by NMR); mp 116–117 °C; ν_{max}/cm^{-1} 1685, 1674, 1605, 1589, 1508, 1286, 1251 and 1031; δ_H 3.18 (3H, s), 3.78 (1H, m), 6.40–6.48 (1H, m), 6.53–6.62 (2H, m), 6.63 (2H, d, *J* 8.90 Hz), 6.70–6.76 (2H, m), 7.13–7.20 (2H, m), 7.28 (2H, d, *J* 8.90 Hz), 7.76–7.80 (1H, m) and 7.80–7.86 (1H, m); *m*/*z* (EI) 353 (M^+ − Br). (Found: C, 66.72; H, 4.04. $C_{24}H_{17}O_3Br$ requires C, 66.52; H, 3.95%).

1-Bromo-7,7-bis(*p*-tolyl)-3,4-benzobicyclo[4.1.0]heptane-2,5-dione 1c. Yield 68% (isolated); mp 134–135 °C; ν_{max}/cm^{-1} 1678, 1591, 1510, 1286, 812, 774, 718 and 685; δ_H 2.00 (3H, s), 2.30 (3H, s), 3.76 (1H, s), 6.70 (2H, d, *J* 7.92 Hz), 7.01 (2H, d, *J* 7.92 Hz), 7.15 (2H, d, *J* 7.92 Hz), 7.39 (2H, d, *J* 7.92 Hz), 7.43–7.51 (2H, m), 7.77–7.85 (1H, m) and 7.85–7.93 (1H, m); *m*/*z* (EI) 430 (M^+). (Found: C, 69.73; H, 4.60. $C_{25}H_{19}O_2Br$ requires C, 69.61; H, 4.44%).

1-Bromo-7-*endo*-*p*-tolyl-7-*exo*-phenyl-3,4-benzobicyclo-[4.1.0]heptane-2,5-dione *endo*-1d. Yield 47% (by NMR); mp 159–160 °C; ν_{max}/cm^{-1} 1676, 1592, 1445, 1286, 1217, 814, 759 and 697; δ_H 2.01 (3H, s), 3.77 (1H, s), 6.71 (2H, d, *J* 8.25 Hz), 7.02 (2H, d, *J* = 8.25 Hz), 7.25–7.40 (3H, m), 7.45–7.55 (4H, m), 7.78–7.85 (1H, m) and 7.86–7.92 (1H, m); *m*/*z* (EI) 416 (M^+). (Found: C, 69.12; H, 4.15. $C_{24}H_{17}O_2Br$ requires C, 69.07; H, 4.11%).

1-Bromo-7-*endo*-phenyl-7-*exo*-*p*-tolyl-3,4-benzobicyclo[4.1.0]-heptane-2,5-dione *exo*-1d. Yield 50% (by NMR); mp 159–160 °C; ν_{max}/cm^{-1} 1680, 1592, 1446, 1283, 753 and 700; δ_H 2.31 (3H, s), 3.78 (1H, s), 6.80–6.95 (3H, m), 7.10–7.20 (2H, m), 7.17 (2H, d, *J* 8.25 Hz), 7.38–7.50 (2H, m), 7.41 (2H, d, *J* 8.25 Hz), 7.78–7.84 (1H, m) and 7.85–7.91 (1H, m); *m*/*z* (EI) 416 (M^+). (Found: C, 69.07; H, 4.23. $C_{24}H_{17}O_2Br$ requires C, 69.07; H, 4.11%).

1-Bromo-7,7-bis(*p*-chlorophenyl)-3,4-benzobicyclo[4.1.0]-heptane-2,5-dione 1f. Yield 72% (isolated); mp 169–170 °C; ν_{max}/cm^{-1} 1685, 1671, 1588, 1489, 1290, 1092, 1013 and 799; δ_H 3.73 (1H, s), 6.92 (2H, d, *J* 8.58 Hz), 7.06 (2H,d, *J* 8.58 Hz), 7.34 (2H, d, *J* 8.58 Hz), 7.43 (2H, d, *J* 8.58 Hz), 7.50–7.60 (2H, m),

7.80–7.88 (1H, m) and 7.89–7.96 (1H, m); *m*/*z* (EI) 470 (M^+). (Found: C, 58.25; H, 2.97. $C_{23}H_{13}O_2BrCl_2$ requires C, 58.50; H, 2.78%).

1-Bromo-7-*endo*-*p*-chlorophenyl-7-*exo*-phenyl-3,4-benzobicyclo[4.1.0]heptane-2,5-dione *endo*-1g. Yield 46% (by NMR); mp 174–175 °C; ν_{max}/cm^{-1} 1677, 1590, 1487, 1287 and 761; δ_H 3.79 (1H, s), 6.91 (2H, d, *J* 8.58 Hz), 7.09 (2H, d, *J* 8.58 Hz), 7.27–7.41 (3H, m), 7.45–7.60 (4H, m), 7.80–7.88 (1H, m) and 7.88–7.96 (1H, m); *m*/*z* (EI) 436 (M^+). (Found: C, 62.93; H, 3.27. $C_{23}H_{14}O_2BrCl$ requires C, 63.11; H, 3.22%).

1-Bromo-7-*endo*-phenyl-7-*exo*-*p*-chlorophenyl-3,4-benzobicyclo[4.1.0]heptane-2,5-dione *exo*-1g. Yield 49% (by NMR); mp 182–183 °C; ν_{max}/cm^{-1} 1684, 1589, 1489, 1283, 1015, 793, 771 and 721; δ_H 3.73 (1H, s), 6.85–6.97 (3H, m), 7.10–7.15 (2H, m), 7.33 (2H, d, *J* 8.58 Hz), 7.44–7.52 (2H, m), 7.47 (2H, d, *J* 8.58 Hz), 7.78–7.85 (1H, m) and 7.85–7.92 (1H, m); *m*/*z* (EI) 436 (M^+). (Found: C, 63.06; H, 3.32. $C_{23}H_{14}O_2BrCl$ requires C, 63.11; H, 3.22%).

1-Bromo-7,7-bis(*m*-nitrophenyl)-3,4-benzobicyclo[4.1.0]-heptane-2,5-dione 1h. Yield 33% (isolated); mp 237–239 °C; ν_{max}/cm^{-1} 1686, 1589, 1527, 1349, 1285, 853, 742 and 690; δ_H 3.87 (1H, s), 7.22 (1H, t, *J* 7.92 Hz), 7.51–7.58 (3H, m), 7.62 (1H, t, *J* 7.92 Hz), 7.78–7.84 (1H, m), 7.84–7.97 (3H, m), 7.90–8.03 (1H, m), 8.17–8.23 (1H, m) and 8.38–8.42 (1H, m); *m*/*z* (EI) 492 (M^+). (Found: C, 56.08; H, 2.82: N, 5.75. $C_{23}H_{13}O_6N_2Br$ requires C, 56.00; H, 2.66; N, 5.68%).

1-Bromo-7-*endo*-*p*-nitrophenyl-7-*exo*-phenyl-3,4-benzobicyclo[4.1.0]heptane-2,5-dione *endo*-1i. Yield 39% (by NMR); mp 180–181 °C; ν_{max}/cm^{-1} 1685, 1601, 1589, 1516, 1352, 1286, 744 and 708; δ_H 3.85 (1H, s), 7.30–7.44 (5H, m), 7.48–7.58 (2H, m), 7.55 (2H, d, *J* 8.90 Hz), 7.78–7.88 (1H, m), 7.82 (2H, d, *J* 8.90 Hz) and 7.91–7.97 (1H, m); *m*/*z* (EI) 447 (M^+). (Found: C, 61.85; H, 3.32; N, 3.00. $C_{23}H_{14}O_4NBr$ requires C, 61.62; H, 3.15; N, 3.12%).

1-Bromo-7-*endo*-phenyl-7-*exo*-*p*-nitrophenyl-3,4-benzobicyclo[4.1.0]heptane-2,5-dione *exo*-1i. Yield 53% (by NMR); mp 205–206 °C; ν_{max}/cm^{-1} 1687, 1591, 1515, 1349, 1287, 852, 747 and 708; δ_H 3.78 (1H, s), 6.90–7.00 (3H, m), 7.12–7.18 (2H, m), 7.48–7.55 (2H, m), 7.72 (2H, d, *J* 8.91 Hz), 7.80–7.86 (1H, m), 7.89–7.95 (1H, m) and 8.23 (2H, d, *J* 8.91 Hz); *m*/*z* (EI) 447 (M^+). (Found: C, 61.79; H, 3.35; N, 3.03. $C_{23}H_{14}O_4NBr$ requires C, 61.62; H, 3.15; N, 3.12%).

Thermolysis of 1a–j

Preparative thermolysis was carried out at 100 °C in a sealed benzene solution according to the method employed previously for **1e**.[9] We succeeded in isolating the primary ring-opened products **3c**, **3f**, and **3g** (major isomer) by recrystallization from the reaction mixture. However, the thermolysis of **1a**, *endo*-, *exo*-**1b** and **1h** provided a complicated product mixture probably due to several subsequent reactions. So in confirming that the thermolysis primarily produces the allylic halides **3**, we carried out a similar thermolysis in the presence of the additive methanol (10% by volume) and obtained the corresponding methanol adducts **5c**,**d** and **5f**,**g**, and **5i** (Scheme 2). Unfortunately, this trapping experiment still failed to give the corresponding methanol adducts for the methoxy-substituted **1a**,**1b**, and the *m*-dinitro-substituted **1h**. The compounds **1a** and **1b** yielded dark intractable resinous products, while **1h** afforded an insoluble and inseparable yellow powder. Thermolysis of **1j** (50 mg) was performed at 150 °C for 7 h in a sealed toluene solution (0.5 ml) to yield an almost quantitative amount of **3j** (by NMR). When treated with methanol, **3j** was easily transformed to the methanol adduct **5j** (= **5e**). The spectral data of the isolated pyrolysates and the methanol adducts are as follows. The analytical data for **5e** and **4b** are given elsewhere.[9]

2-Bromo-3-[bis(*p*-tolyl)methylene]-2,3-dihydro-1,4-naphthoquinone 3c. Yield 84% (isolated); mp 161-162 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1696, 1672, 1590, 1572, 1288, 1246, 985, 815; δ_H 2.35 (3H, s), 2.41 (3H, s), 5.55 (1H, s), 6.91 (2H, d, *J* 8.25 Hz), 7.08 (2H, d, *J* 8.25 Hz), 7.20–7.30 (4H, m), 7.75–7.85 (2H, m), 8.05–8.15 (2H, m); *m*/*z* (EI) 351 (M^+ − Br). (Found: C, 69.71; H, 4.59. $C_{25}H_{19}O_2Br$ requires C, 69.61; H, 4.44%).

2-Bromo-3-[bis(*p*-chlorophenyl)methylene]-2,3-dihydro-1,4-naphthoquinone 3f. Yield 69% (isolated); mp 215–216 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1690, 1678, 1581, 1487, 1288, 1250, 1090, 987; δ_H 5.43 (1H, s), 6.95 (2H, d, *J* 8.58 Hz), 7.24–7.34 (4H, m), 7.44 (2H, d, *J* 8.58 Hz), 7.80–7.85 (2H, m), 8.08–8.14 (2H, m); *m*/*z* (EI) 471 (M^+ + H). (Found: C, 58.74; H, 2.97. $C_{23}H_{13}O_2BrCl_2$ requires C, 58.50; H, 2.78%).

2-Bromo-3-[(*p*-chlorophenyl)phenylmethylene]-2,3-dihydro-1,4-naphthoquinone *Z* or *E*-3g. Thermolysis of *endo*-**1g** (200 mg) was carried out at 100 °C for 12 h in toluene (5 ml) to provide a mixture of *Z*- and *E*-**3g** in almost quantitative yield (isomer ratio 1 : 1.3 by NMR). Similar thermolysis of *exo*-**1g** resulted in the identical isomer ratio of *Z*- and *E*-**3g**. The major isomer with the methine H resonating at δ 5.50 ppm was isolated from the mixture by a fractional crystallization (from benzene); mp 133–134 °C, yellow prisms, ν_{max}/cm^{-1} 1688, 1588, 1485, 1288, 1250, 984, 682; δ_H 5.50 (1H, s, methine), 6.97 (2H, d, *J* 8.25 Hz), 7.26 (2H, d, *J* 8.25 Hz), 7.30–7.40 (2H, m), 7.42–7.50 (3H, m), 7.78–7.86 (2H, m), 8.07–8.15 (2H, m); *m*/*z* (EI) 357 (M^+ − Br). (Found: C, 63.15; H, 3.39. $C_{23}H_{14}O_2BrCl$ requires C, 63.11; H, 3.22%). However, the corresponding minor isomer **3g** with the methine H at δ 5.46 ppm could not be isolated in pure form. Attempted NOE measurements unfortunately failed to give an unambiguous identification of *Z*–*E* configuration. However, the major isomer was predicted as *E*-form by PM3 calculations (*vide supra*).

2-Chloro-3-(diphenylmethylene)-2,3-dihydro-1,4-naphthoquinone 3j. Yield 100% (by NMR); mp 289–291 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1700, 1674, 1590, 1287, 1242, 985, 699; δ_H 5.35 (1H, s, methine), 7.01–7.45 (10H, m), 7.78–7.82 (2H, m), 8.07–8.11 (2H, m); δ_C 61.56, 127.3, 127.9, 128.2, 128.7, 129.0, 129.2, 129.7, 129.8, 130.2, 131.4, 134.4, 135.1, 135.8, 139.1, 140.6, 157.9, 186.9, 188.4. (Found: C, 76.80; H, 4.45. $C_{23}H_{15}O_2Cl$ requires C, 76.99; H, 4.21%).

2-[Methoxybis(*p*-tolyl)methyl]-1,4-naphthoquinone 5c. Yield 100% (by NMR); mp 184–185 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1668, 1660, 1597, 1305, 1250, 1069, 821, 769; δ_H 2.34 (6H, s), 2.94 (3H, s), 7.15 (4H, d, *J* 8.25 Hz), 7.41 (4H, d, *J* 8.25 Hz), 7.58–7.70 (3H, m), 7.86–7.91 (1H, m), 8.01–8.06 (1H, m); *m*/*z* (EI) 382 (M^+). (Found: C, 81.51; H, 5.90. $C_{26}H_{22}O_3$ requires C, 81.65; H, 5.80%).

2-[α-Methoxy-α-(*p*-tolyl)benzyl]-1,4-naphthoquinone 5d. Yield 100% (by NMR); mp 89–90 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1660, 1595, 1304, 1249, 1071, 900, 778, 700; δ_H 2.35 (3H, s), 2.95 (3H, s), 7.12–7.20 (2H, d, *J* 8.25 Hz), 7.28–7.38 (3H, m), 7.41 (2H, d, *J* 8.25 Hz), 7.52–7.57 (2H, m), 7.62–7.68 (3H, m), 7.86–7.92 (1H, s), 8.01–8.06 (1H, s); *m*/*z* (EI) 368 (M^+). (Found: C, 81.75; H, 5.65. $C_{25}H_{20}O_3$ requires C, 81.50; H, 5.47%).

2-[Bis(*p*-chlorophenyl)methoxymethyl]-1,4-naphthoquinone 5f. Yield 95% (by NMR); mp 161–162 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1666, 1489, 1251, 1095, 1071, 1015, 831, 779; δ_H 2.95 (3H, s), 7.33 (4H, d, *J* 8.58 Hz), 7.44 (4H, d, *J* 8.58

Hz), 7.63 (1H, s), 7.65–7.72 (2H, m), 7.88–7.91 (1H, m), 8.03–8.07 (1H, m); *m*/*z* (EI) 422 (M^+). (Found: C, 68.10; H, 3.97. $C_{24}H_{16}O_3Cl_2$ requires C, 68.10; H, 3.97%).

2-[α-(*p*-Chlorophenyl)-α-methoxybenzyl]-1,4-naphthoquinone 5g. Yield 100% (by NMR); mp 120–121 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1665, 1593, 1488, 1305, 1251, 1072, 777, 761; δ_H 2.95 (3H, s), 7.30–7.40 (5H, m), 7.44–7.54 (4H, m), 7.64–7.77 (3H, m), 7.86–7.92 (1H, m), 8.02–8.08 (1H, m); *m*/*z* (EI) 388 (M^+). (Found: C, 74.14; H, 4.55. $C_{24}H_{17}O_3Cl$ requires C, 74.13; H, 4.41%).

2-[α-Methoxy-α-(*p*-nitrophenyl)benzyl]-1,4-naphthoquinone 5i. Yield 100% (by NMR); mp 184–185 °C, yellow prisms (from benzene); ν_{max}/cm^{-1} 1668, 1660, 1597, 1305, 1250, 1069, 821, 769; δ_H 2.34 (6H, s), 2.94 (3H, s), 7.15 (4H, d, *J* 8.25 Hz), 7.41 (4H, d, *J* 8.25 Hz), 7.58–7.70 (3H, m), 7.86–7.91 (1H, m), 8.01–8.06 (1H, m); *m*/*z* (EI) 382 (M^+). (Found: C, 81.51; H, 5.90. $C_{26}H_{22}O_3$ requires C, 81.65; H, 5.80%).

Crystal structure determination of compound 3e †

Crystal data. $C_{23}H_{15}BrO_2$, $M = 403.27$, orthorhombic, space group *P*bca, $Z = 8$, $a = 18.062$ (4), $b = 19.795$ (9), $c = 9.931$ (2) Å, $V = 3550$ (1) Å^3, $F(000) = 1632$, μ(Mo-Kα) = 2.30 mm^{-1}, $R(F_0) = 0.063$ for 1712 observed reflections with $I > 2\sigma(I)$, $wR(F^2) = 0.170$ for all 5133 unique reflections. Intensity data in the θ range 3–30° were corrected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and corrected for Lorentz and polarization effects, and for absorption. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods anisotropically for non-hydrogen atoms. All hydrogen atoms fixed at magnitudes in excess of 1 e Å^{-3} were observed on the difference-Fourier maps.

† CCDC reference number 188/191. See http://www.rsc.org/suppdata/p2/a9/a905223b for crystallographic files in .cif format.

References

1 (*a*) *The Chemistry of the Cyclopropyl Group*, *part 1 and 2*, ed. Z. Rappoport, Wiley, New York, 1987; (*b*) *The Chemistry of the Cyclopropyl Group Volume 2*, ed. Z. Rappoport, Wiley, New York, 1995; (*c*) H. N. C. Wong, M. Y. Hon, C. W. Tse and Y. C. Yip, *Chem. Rev.*, 1989, **89**, 165.

2 (*a*) M. Charton, *The Chemistry of the Alkenes*, *vol. 2*, ed. J. Zabicky, Interscience, London, ch. 10, 1970; (*b*) A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 809.

3 (*a*) T. T. Tidwell, *The Chemistry of the Cyclopropyl Group, part 2*, ed. Z. Rappoport, ch. 10, pp. 565–632, Wiley, New York, 1987; (*b*) T. A. Crabb and A. V. Patel, *Rodd's Chemistry of Carbon Compounds*, 2nd Suppl. to the 2nd edn., ed. M. Sainsbury, Elsevier, Amsterdam, vol. IIA/B, ch. 1, pp. 1–80, 1992.

4 (*a*) D. C. Duffey, J. P. Minyard and R. H. Lane, *J. Org. Chem.*, 1966, **31**, 3865; (*b*) L. Ghosez, P. Laroche and G. Slinckx, *Tetrahedron Lett.*, 1967, 2767; (*c*) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 1967, 1379; (*d*) C. W. Jefford, E. H. Yen and R. Medary, *Tetrahedron Lett.*, 1966, 2069; (*e*) P. v. R. Schleyer, T. M. Su, M. Saunder and J. C. Rosenfeld, *J. Am. Chem. Soc.*, 1969, **91**, 5174; (*f*) M. S. Baird, D. G. Lindsay and C. B. Rees, *J. Chem. Soc.* (*C*), 1969, 1173; (*g*) D. C. Horwell and C. W. Rees, *J. Chem. Soc.*, *Chem. Commun.*, 1969, 1428; (*h*) C. B. Reese and A. Shaw, *J. Am. Chem. Soc.*, 1970, **92**, 2566; (*i*) M. S. Baird, B. S. Mahli and L. Sheppard, *J. Chem. Soc.*, *Perkin Trans. 1*, 1990, 1881.

5 (*a*) C. H. Depuy, L. G. Schnack, J. W. Hausser and W. Wiedemann, *J. Am. Chem. Soc.*, 1965, **87**, 4006; (*b*) C. H. Depuy, L. G. Schnack and J. W. Hausser, *J. Am. Chem. Soc.*, 1966, **88**, 3343; (*c*) P. v. R. Schleyer, G. W. Van Dine, U. Schöllkopfand and J. Paust, *J. Am. Chem. Soc.*, 1966, **88**, 2868.

6 W. Kirmse and H. Schütte, *J. Am. Chem. Soc.*, 1967, **89**, 1284.

7 (*a*) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395; (*b*) C. H. Depuy, *Acc. Chem. Res.*, 1968, **1**, 33; (*c*) L. Radom, P. C. Hariharan, J. A. Pople and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1973, **95**, 6531.

8 (*a*) T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1993, **34**, 649; (*b*) T. Oshima, Y. Nakajima and T. Nagai, *Chem. Lett.*, 1993, 1977; (*c*) H. Moriwaki, T. Oshima and T. Nagai, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 255; (*d*) H. Moriwaki, T. Oshima and T. Nagai, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1681; (*e*) H. Moriwaki, T. Oshima and T. Nagai, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 2517; (*f*) H. Moriwaki, K. Fukushima, T. Nagai and T. Oshima, *Chem. Commun.*, 1996, 495; (*g*) H. Moriwaki, T. Matsumoto, T. Nagai and T. Oshima, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 1461.

9 T. Oshima, K. Tamada and T. Nagai, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 3325.

10 T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2507.

11 T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2580.

12 The calculations by the PM3 method were performed with the MOPAC program (ver. 6) using a Cache Work-System.

13 (*a*) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 1957, **79**, 1913; (*b*) *ibid.*, 1958, **80**, 4979; (*c*) *ibid.*, 1959, **81**, 3323.

14 (*a*) H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191; (*b*) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

15 Y. Tsuno and M. Fujino, *Adv. Phys. Org. Chem.*, 1999, **32**, 267.

16 T. Oshima, K. Fukushima and T. Kawamoto, *Acta Crystallogr., Sect. C*, 1999, **55**, 608.

17 The C–C bond hybridization of the cyclopropane ring is popularly envisioned by the Walsh model (*cf.* A. D. Walsh, *Nature*, 1947, **165**, 712 and A. D. Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179); the lowest energy orbital (σ) by a linear combination of the three sp^2-hybrid atomic orbitals (AOs) and the two equal-energy orbitals (e_S and e_A, so-called *quasi* π) by linear combinations of three p-orbitals. Accordingly, the conjugation energy is a maximum when the neighboring p-orbital axis is arranged parallel to the plane of the cyclopropane ring (bisected conformation), while the magnitude of interaction is a minimum for the perpendicular arrangement.

18 (*a*) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 98; (*b*) C. Reichart and E. H. Görnert, *Liebigs Ann. Chem.*, 1983, 721; (*c*) C. Reichart, *Chem. Rev.*, 1994, **94**, 2319.

19 T. Oshima, S. Arikata and T. Nagai, *J. Chem. Res.*, 1981, (S) 204, (M) 2518.

20 (*a*) P. Brown and R. C. Cookson, *Tetrahedron*, 1965, **21**, 1977; (*b*) T. Oshima and T. Nagai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 555; (*c*) T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1985, **26**, 4785; (*d*) T. Oshima and T. Nagai, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2787.

21 E. L. Ansari, R. Qureshi and M. L. Qureshi, *Electrocyclic Reactions*, Wiley-VCH, Weinheim, 1999.

22 K. Fukui, *Acc. Chem. Res.*, 1971, **4**, 57.

23 J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, *Vol. II*, *Organic Solvents*, 3rd edn., ed A. Weissberger, John Wiley, New York, 1970.

24 Y. Nakano, M. Hamaguchi and T. Nagai, *J. Org. Chem.*, 1989, **54**, 1135.

25 F. M. Dean, P. G. Jones, R. B. Morton and P. S. Sidisunthorn, *J. Chem. Soc.*, 1963, 5336.

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