

# Thermal cycloaddition reactions of azulene-1,5-quinones and azulene-1,7-quinones with cyclic dienes and cycloheptatriene

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[2+4]-[6+4] Cycloadducts were obtained from the thermal cycloaddition reactions of azulenequinones with cyclic  $4\pi$  systems such as 1,3-diphenylisobenzofuran and isobenzofuran while the reaction of cycloheptatriene and azulenequinones gave ene products as well as cage molecules. The first addition site of 1,3-diphenylisobenzofuran was different for 3-bromoazulene-1,5-quinone and azulene-1,5-quinone; the former reacted on the cyclopentenone part and the latter on the C-6–C-7 bond to avoid formation of an unstable cyclopentadienone structure.

A new non-benzenoid aromatic quinone, azulenequinone, is an isomer of naphthoquinone and has tropone and cyclopentenone moieties. According to the theoretical calculation on the stability of azulenequinones, only azulene-1,2-, 1,5-, and 1,7-quinones are stable.<sup>1</sup> The first characterization of azulenequinones was achieved by the trapping of azulene-1,4- and 1,6-quinones as Diels–Alder adducts<sup>2</sup> and by the isolation<sup>3</sup> of azulene-1,5-quinone and azulene-1,7-quinone as stable crystalline forms.

In 1984, Scott and Adams reported that azulene-1,5-quinone and azulene-1,7-quinone gave a single [2+4]-[6+4]<sup>4</sup> adduct from the thermal reaction with 1,3-diphenylisobenzofuran (Scheme 1).<sup>3</sup> Recently, we reported the high-pressure cycloaddition reactions of 3-bromoazulene-1,5-quinone and 3-bromoazulene-1,7-quinone<sup>5</sup> with several dienophiles,<sup>6,7</sup> which gave [2+4] cycloadducts on the seven-membered ring of azulenequinones to hinder formation of a reactive cyclopentadienone structure. In this paper, we report cycloaddition reactions with such cyclic  $4\pi$  and  $6\pi$  components as cyclopentadiene, 6,6-diphenylfulvene, 1,3-diphenylisobenzofuran, isobenzofuran, and cycloheptatriene.

## Bromoazulenequinones with cyclopentadiene

When a benzene solution of 3-bromoazulene-1,5-quinone and cyclopentadiene was heated at 80 °C in an ampoule for 5 h, a single product **1** was obtained in 55% yield (Scheme 2). The mass spectrum was consistent with a 1:1 adduct between 3-bromoazulene-1,5-quinone and cyclopentadiene and the <sup>1</sup>H NMR spectrum revealed six olefinic proton signals, three methine proton signals, and two methylene proton signals. These data supported that **1** was a [4+2] adduct between the tropone moiety of 3-bromoazulene-1,5-quinone and cyclopentadiene. The stereochemistry of the cyclopentene moiety was determined to be *endo* from the coupling constant ( $J_{8,9}$ , 0 Hz) of the bridgehead proton at C-8. The position of the double bond of the cyclopentene ring was speculatively assigned by the comparison of the <sup>1</sup>H NMR data with those of the adduct between 3-bromoazulene-1,7-quinone and cyclopentadiene as discussed below.

A benzene solution of 3-bromoazulene-1,7-quinone and cyclopentadiene was similarly heated to give the corresponding *endo*-[4+2] adduct **2** in 48% yield. When compared with the <sup>1</sup>H NMR data of the chemical shifts of the methylene and olefinic protons on the cyclopentene ring between adducts **1** and **2**, the chemical shifts of the methylene protons are almost identical [ $\delta$  2.06 (1H, ddm,  $J$  17.2 and 5.9 Hz) and 2.77 (1H, ddq,  $J$  17.2, 8.6 and 2.2 Hz) for **1** and 2.06 (1H, ddm,  $J$  17.7 and 5.8 Hz) and 2.76 (1H, ddq,  $J$  17.7, 9.9 and 2.2 Hz) for **2**] although the chemical shifts ( $\delta$  5.70 and 5.78 for **1** and 5.83 and 6.09 for **2**) of the olefinic proton at C-12 are different from each other. This indicated that the position of the double bond is near to the cyclopentenone moiety.

## Bromoazulenequinones with 6,6-diphenylfulvene

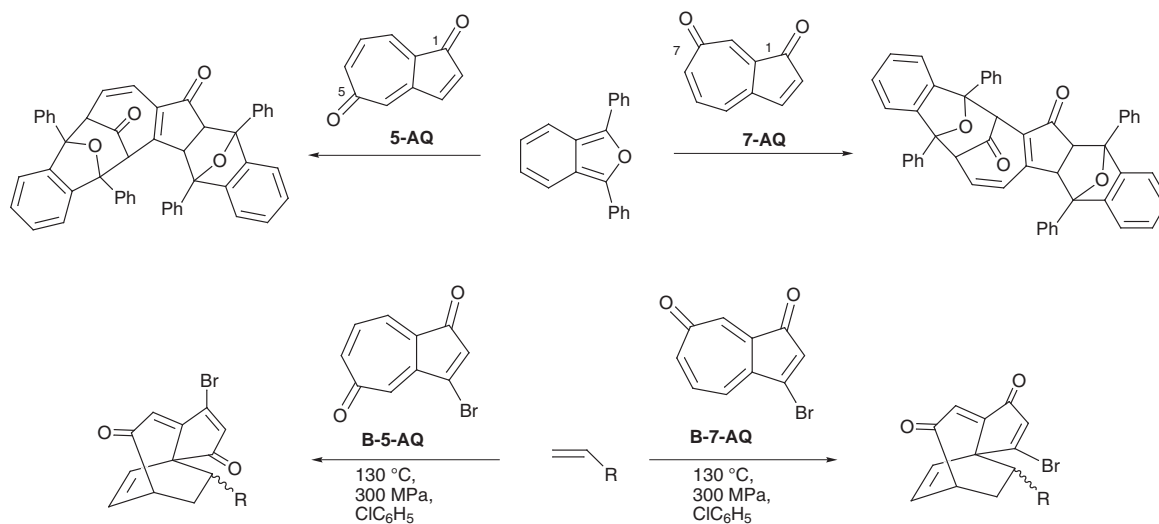
The reaction of 3-bromoazulene-1,5-quinone and 6,6-diphenylfulvene at 130 °C for 8 h gave two 1:1 adducts (**3** and **4**) in 25 and 8% yields, respectively. Both were a 1:1 adduct between 3-bromoazulene-1,5-quinone and 6,6-diphenylfulvene from the mass spectrum. The stereochemistry of the main adduct **3** was determined to be *endo* by the value ( $J_{8,9}$ , 1.5 Hz) of the coupling constant. The position of the diphenylmethylene group was established by the corresponding chemical shift ( $\delta$  3.42) of the bridgehead proton at C-8 which is observed upfield with respect to the bridgehead protons [ $\delta$  3.59 for **1** and 3.61 for **2**] of the related compounds. The structure of the minor adduct **4** was determined to be an *exo*-[4+2] adduct from the coupling constant ( $J_{8,9}$ , 6.6 Hz) of the bridgehead proton at  $\delta$  3.20.

On the other hand, the reaction of 3-bromoazulene-1,7-quinone and 6,6-diphenylfulvene gave a single product **5**, which was deduced to be an *endo*-[4+2] adduct from the <sup>1</sup>H NMR spectral data. The chemical shift of the olefinic proton at C-12 was observed at  $\delta$  6.54, which is further downfield than the corresponding olefinic proton at  $\delta$  6.15 of **3**. Then, the regiochemistry of the fulvene moiety was established as shown.

## Bromoazulenequinones with 1,3-diphenylisobenzofuran

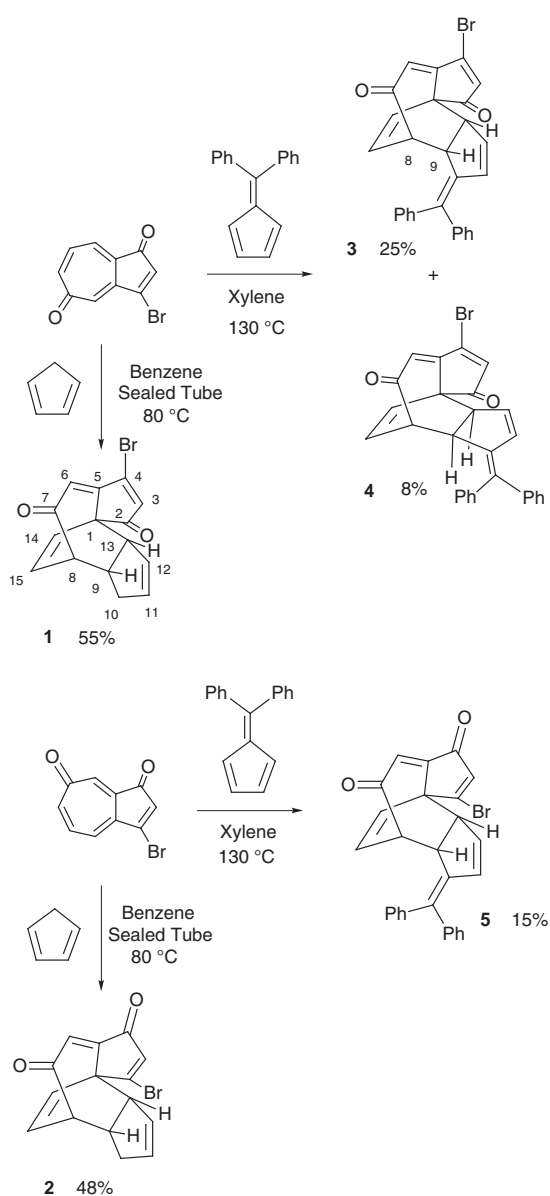
When 3-bromoazulene-1,5-quinone was refluxed with 1,3-diphenylisobenzofuran in chlorobenzene, a pair of 1:1 products (**6** and **7**) was formed in 38 and 16% yields at 50%

† Deceased on October 1, 1998.



5-AQ = azulene-1,5-quinone, 7-AQ = azulene-1,7-quinone,  
 B-5-AQ = 3-bromoazulene-1,5-quinone, B-7-AQ = 3-bromoazulene-1,7-quinone

Scheme 1



Scheme 2

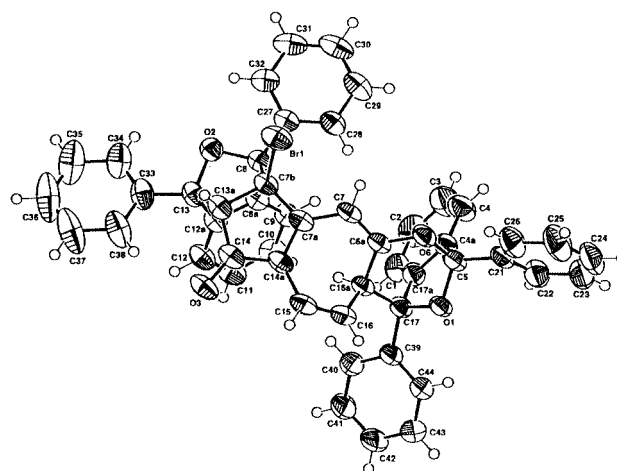
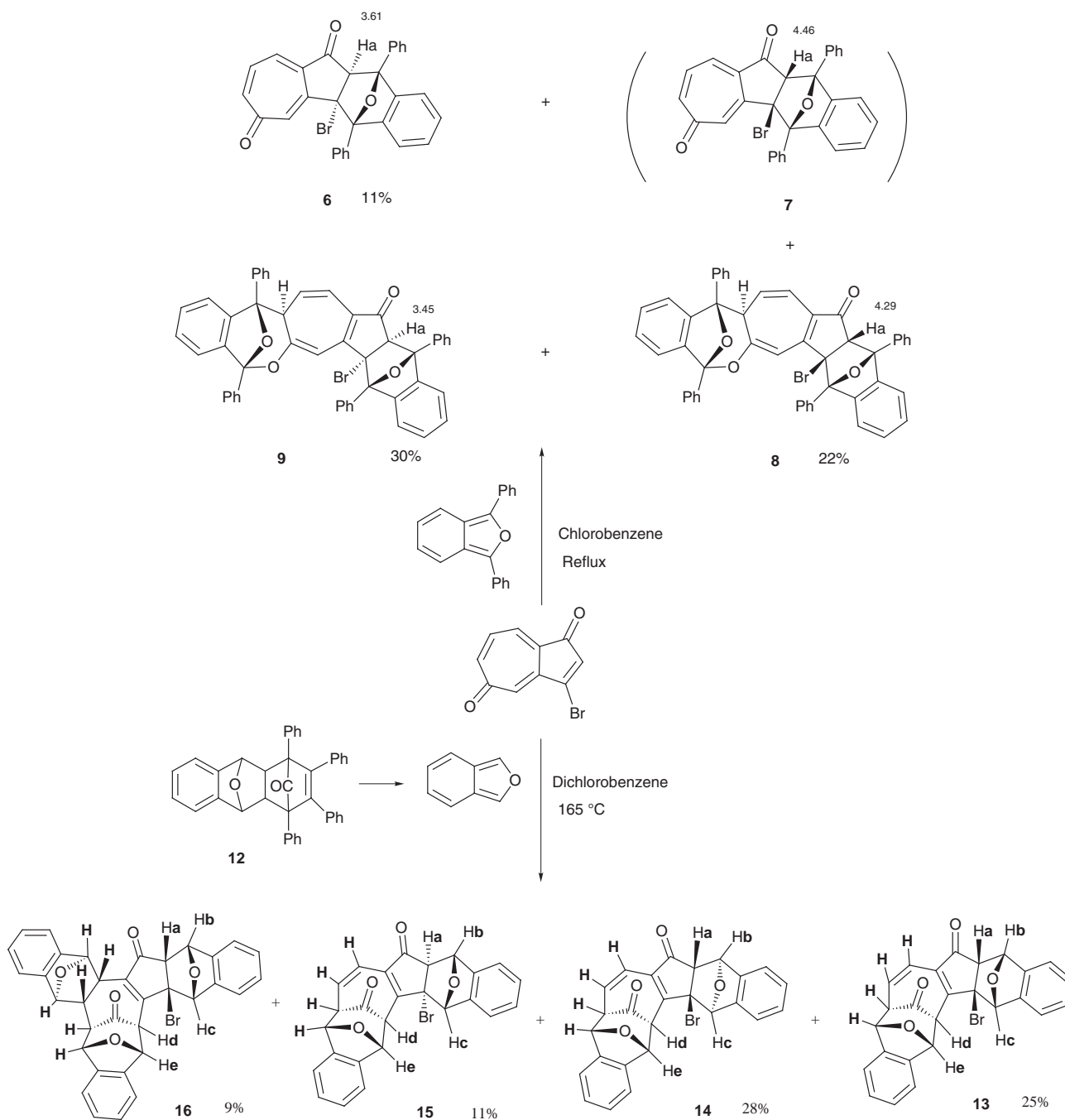


Fig. 1 ORTEP diagram of **8**.

conversion (Scheme 3).<sup>8</sup> At the later stages of the reaction, **7** disappeared, suggesting that **7** and **6** are kinetically and thermodynamically controlled *endo*- and *exo*-[2+4] adducts, respectively. After 4 h, the reaction was stopped to give three products, **6** (11%), **8** (22%), and **9** (30%). Similarly, when **6** and 1,3-diphenylisobenzofuran were refluxed in chlorobenzene, **8** and **9** were obtained in 40 and 42% yields, respectively. The above assignment for structures **6** and **7** was supported by the chemical shift comparison of the singlet proton signal (Ha) at  $\delta$  3.61 (**6**) and 4.46 (**7**); the large difference is probably due to the anisotropic effect from the aromatic ring. The mass spectra of **8** and **9** indicated that they were 1:2 adducts between bromoazulenequinones and 1,3-diphenylisobenzofuran. The <sup>13</sup>C NMR spectra of **8** and **9** revealed only one carbonyl carbon signal each at  $\delta$  198.1 and 197.6, respectively, suggesting that the tropone carbonyl group was involved in the cycloaddition reaction. The observed large <sup>1</sup>H NMR chemical shift difference ( $\Delta\delta$  0.84) for the Ha ( $\delta$  4.29 for **8** and 3.45 for **9**) suggested the different stereochemistry on the cyclopentenone moiety originated from 3-bromoazulene-1,5-quinone, *endolexo*.

To elucidate the stereochemistry, an X-ray crystallographic study of a single crystal of **8**, recrystallized from benzene, was performed. Its ORTEP diagram is shown in Fig. 1. The structure of **8** was established to be *syn-endo*-[2+4]-*exo*-[8+4]. The



Scheme 3

singlet olefinic proton of **9** appeared at  $\delta$  5.57, which is higher than that ( $\delta$  6.14) of **8**. Since this low field shift of **8** could be due to the effect of a bromine atom, isomer **9** should be assigned as a *syn-exo*-[2+4]-*exo*-[8+4] cycloadduct.

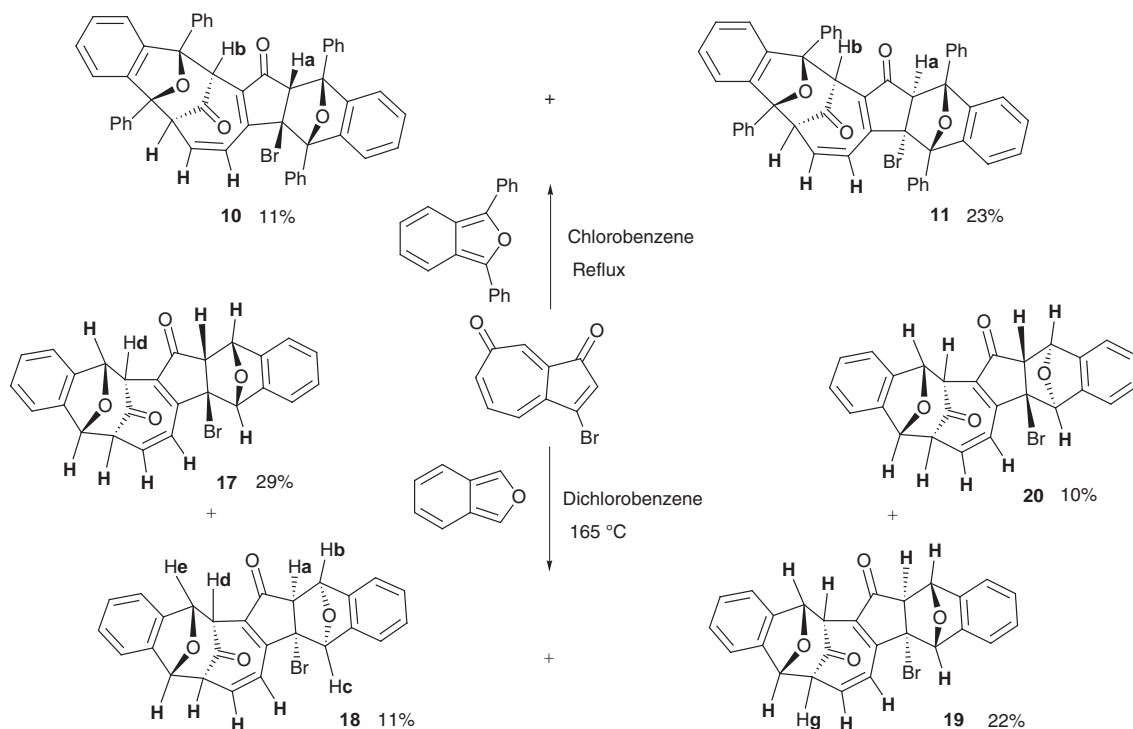
Similarly, when 3-bromoazulene-1,7-quinone was refluxed with 1,3-diphenylisobenzofuran in chlorobenzene for 4 h, two products, **10** (11%) and **11** (30%), were obtained. In these cases, since two carbonyl carbon signals were observed, the tropone carbonyl group is intact after the cycloaddition reaction. Their stereochemistry was assigned as follows; according to the  $^1\text{H}$  NMR spectral comparisons, the signals of olefinic protons ( $\delta$  5.29 and 5.56) of **11** appeared at considerably higher field than those ( $\delta$  6.08 and 6.58) of **10**. Assuming the preferred conformation of the phenyl groups on the bridgehead carbons is coplanar with the oxygen bridge, an *exo*-[2+4] configuration in **11** is consistent to this observed high-field shift of the olefinic protons. These facts led to the structure **11** as illustrated in Scheme 4.

The *syn-exo*-[2+4]-*exo*-[6+4] structure was confirmed by

X-ray crystallographic analysis of **11**; its ORTEP diagram is shown in Fig. 2. The other product **10** should be an *endo*-[2+4] derivative on the chemical shift criterion of Ha ( $\delta$  3.93). In addition, the chemical shift of the doublet signals ascribable to Hb ( $\delta$  3.78,  $J$  2.2 Hz) was considerably higher than that ( $\delta$  4.43,  $J$  1.8 Hz) of **11**. Then, the structure of **10** should be *syn-endo*-[2+4]-*exo*-[6+4] as depicted.

#### Bromoazulenequinones with isobenzofuran

When a mixture of 3-bromoazulene-1,5-quinone and isobenzofuran, generated *in situ* by thermolysis of the adduct (**12**) obtained from 1,4-epoxy-1,4-dihydronaphthalene and tetraphenylcyclopentadienone, was heated at 165 °C in chlorobenzene for 4 h, four products, **13** (25%), **14** (28%), **15** (11%), and **16** (9%), were formed.<sup>9</sup> The structures of **13**, **14**, and **15** were assigned to be 1:2 [2+4]-[6+4] cycloadducts, since there are two carbonyl carbon signals at  $\delta$  198.3, overlapped in **13**,  $\delta$  199.1 and 199.8 in **14**, and 199.2 and 199.5 in **15** in the  $^{13}\text{C}$



Scheme 4

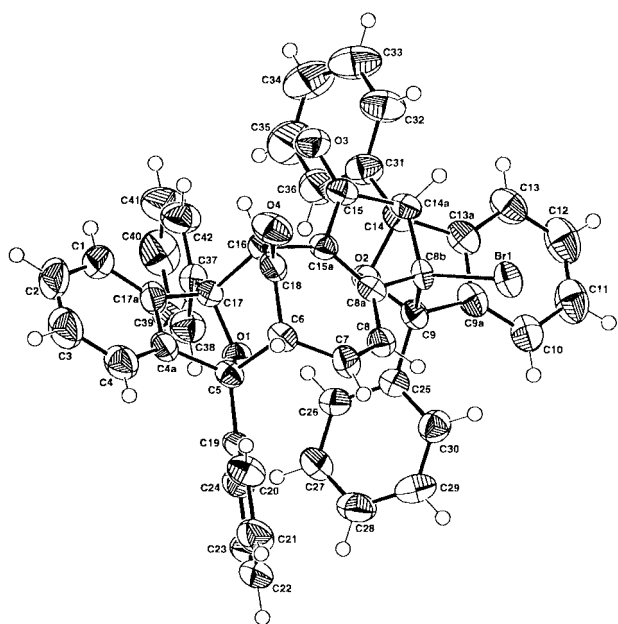


Fig. 2 ORTEP diagram of **11**.

NMR spectra. The  $^1\text{H}$  NMR spectrum of **13** revealed a relatively large vicinal coupling constant ( $J_{ab}$  5.9 Hz) for Ha and Hb which indicates *endo*-[4+2] mode while the coupling constants for Ha and Hb of **14** and **15** were nearly zero which indicates that they are *exo*-[2+4] products. The *exo*-[6+4] mode for **13** to **15** was also evident from the magnitude of the coupling constants (0–1.5 Hz)<sup>10</sup> of the bridgehead protons of the [6+4] juncture. Thus, **13** is an *endo-exo* product and **14** and **15** are *exo-exo* products. The fourth product **16** was a 1:3 cycloadduct as indicated by the mass spectrum. The  $^1\text{H}$  NMR features partially retained similarity to those of **13**.

In order to determine the *syn-anti*-relationship of these products, the X-ray crystallographic analysis was carried out with a single crystal of **13**. The ORTEP diagram is shown in Fig. 3. Clearly, **13** was a *syn-endo*-[2+4]-*exo*-[6+4] product. Since the Hd proton of **15** appeared at  $\delta$  4.15, which is lower

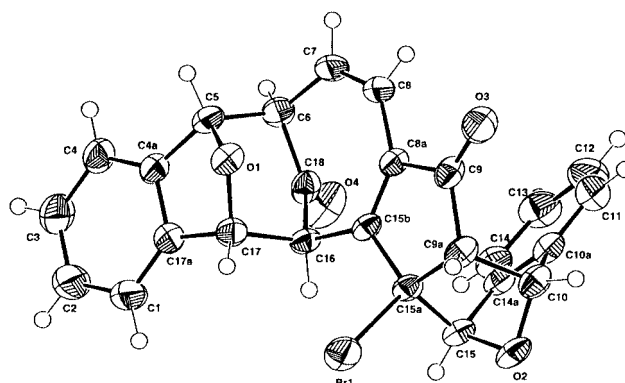
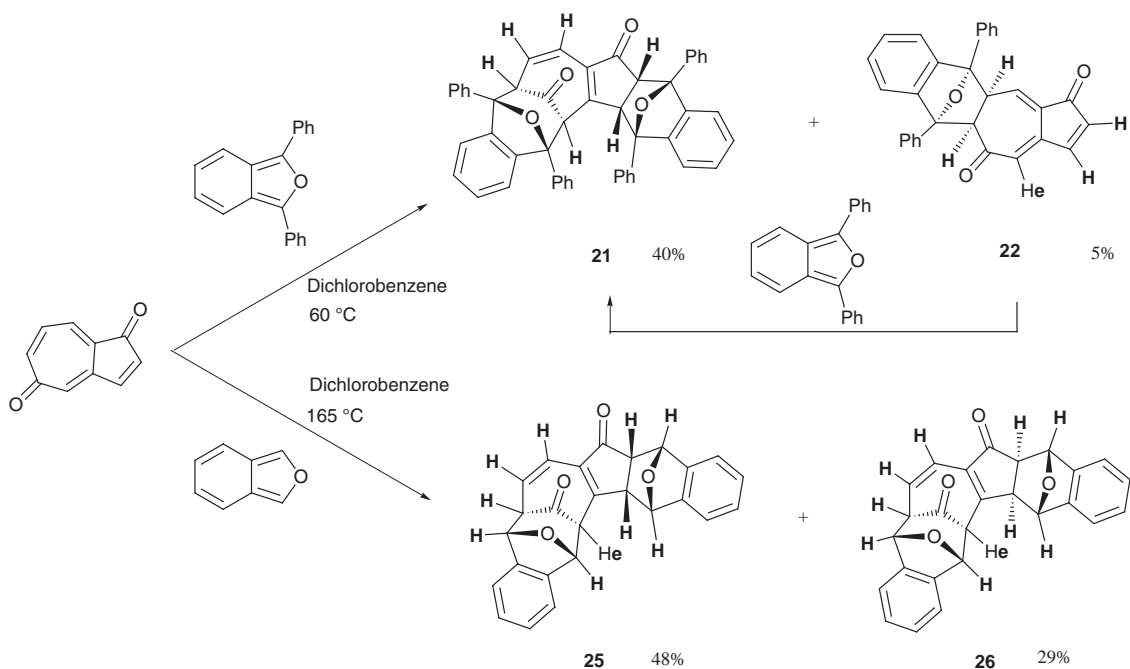


Fig. 3 ORTEP diagram of **13**.

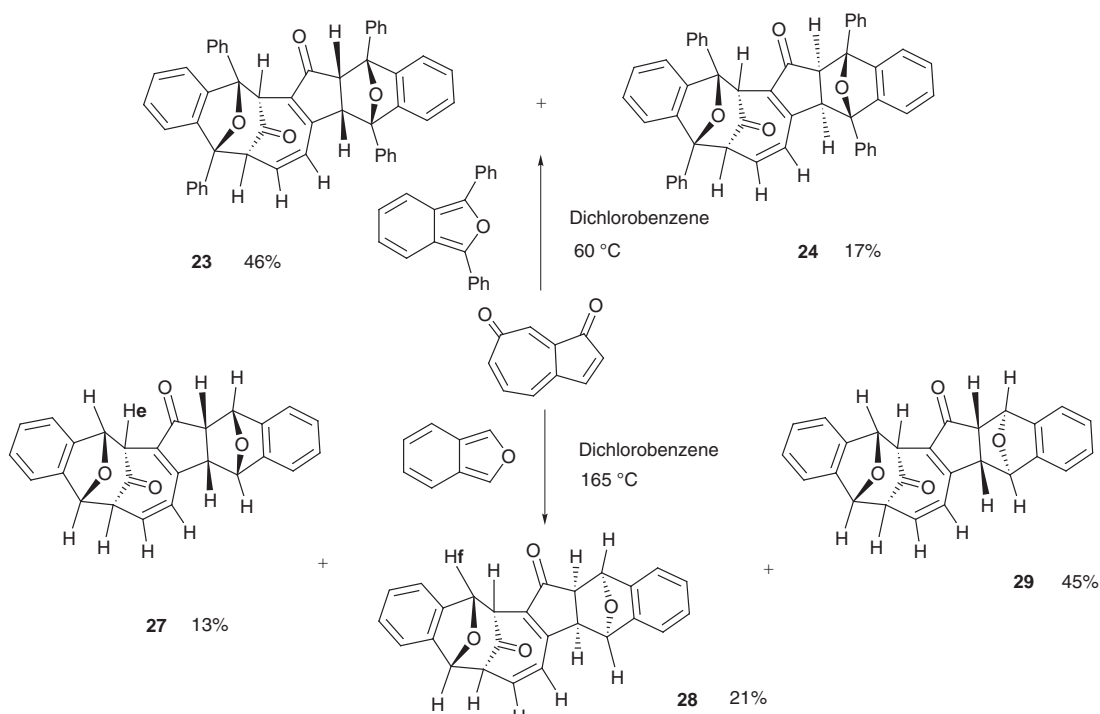
than the others ( $\delta$  3.45 for **13**,  $\delta$  3.71 for **14**, and  $\delta$  3.53 for **16**), the bromine atom of **15** was determined to be  $\alpha$ .

The unusually low-field shifted proton signal, ascribable to He at  $\delta$  6.32, in the  $^1\text{H}$  NMR spectrum of **13** was explained by the proposal that the distance between a bromine atom at C-3 and He is estimated to be 2.92 Å, and this close contact should be one of the reasons for the observed low-field shift.<sup>11</sup> This low-field shift of He is common to the cases of **14** and **16**; *i.e.*,  $\delta$  6.22 for **14** and 6.21 for **16**. The He signal of **15** appeared at  $\delta$  5.79, which is still considerably lower than the expected position.<sup>10</sup> Therefore, stereochemical relations of the bromine atom to He of **13**, **14**, and **16** are similar, but that of **15** might be different. Moreover, the clear NOE between Hc ( $\delta$  5.67 and 5.35) and Hd ( $\delta$  3.53 and 3.71) of **13** provided additional evidence for the stereochemistry.

Next, when a mixture of isobenzofuran and 3-bromoazulene-1,7-quinone was heated at 165 °C in a dichlorobenzene solution for 4 h, four products, **17** (29%), **18** (11%), **19** (22%), and **20** (10%) were formed. The structures of **17** and **18** were assigned as stereoisomeric 1:2 *endo*-[2+4]-*exo*-[6+4] cycloadducts on the basis of the appearance of two carbonyl carbon signals and very similar coupling constants for the methine protons on the ring junctures. The chemical shift of He ( $\delta$  4.09) of **18** was higher than those of the corresponding protons of the other



Scheme 5



Scheme 6

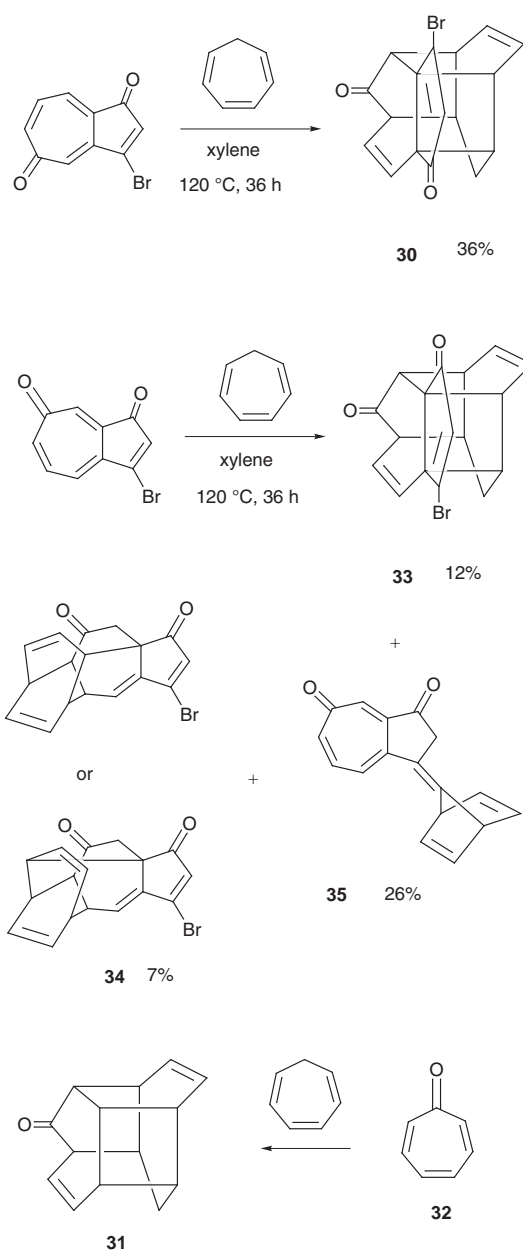
compounds. This is probably due to anisotropy of the benzene ring of the [2+4] cycloaddition part. Therefore, **17** is *syn* and **18** is *anti*. The NMR spectra of **19** and **20** are similar to each other. Since the *syn* isomer **11** was formed as a major adduct from the reaction of 3-bromoazulene-1,7-quinone and 1,3-diphenylisobenzofuran, **19** (22% yield) was assigned to be *syn* and **20** as *anti*.

#### Azulenequinones with 1,3-diphenylisobenzofuran

The cycloaddition of azulene-1,5-quinone with 1,3-diphenylisobenzofuran yielded a 1:2 adduct **21** and a 1:1 adduct **22** in 40 and 5% yields. The identity of **21** with Scott's product was confirmed by  $^1\text{H}$  NMR spectral comparison.<sup>3</sup> Its stereochemistry was deduced to be a *syn-endo*-[2+4]-*exo*-[6+4] structure by comparison with a series of cycloadducts obtained from

bromoazulenequinones and 1,3-diphenylisobenzofuran.<sup>9</sup> The olefinic protons on the seven-membered ring of **21** appeared at  $\delta$  5.42 and 5.86, which are characteristic of an *endo*-[2+4] adduct **13**. This indicated that **21** should be *endo*. In the case of an *anti-endo*-[2+4]-*exo*-[6+4] structure, however, two phenyl groups hinder each other as seen from the consideration of a stereomodel. Thus **21** was determined to be a *syn-endo*-[2+4]-*exo*-[6+4] structure. In the  $^1\text{H}$  NMR spectrum of **22**, two olefinic protons at  $\delta$  6.86 and 7.06 ( $J$  5.1 Hz) indicated that the cyclopentenone moiety is intact allowing the formation of a [2+4] adduct.

The reaction of azulene-1,7-quinone with 1,3-diphenylisobenzofuran gave two 1:2 adducts (**23** and **24**) in 46 and 17% yields, whose stereochemistry was established from the NMR chemical shift comparisons with the corresponding bromo derivatives. Under our conditions, **23** was the major adduct and



Scheme 7

the other product, **24** might be Scott's adduct.<sup>3</sup> The stereochemistry of **23** and **24** was determined to be *syn-endo* and *syn-exo* by comparison of their chemical shifts with those of **10** and **11** derived from the reaction between 3-bromoazulene-1,7-quinone and 1,3-diphenylisobenzofuran.

Similar treatment of isobenzofuran with azulene-1,5-quinone afforded two stereoisomeric [2+4]-[6+4] cycloadducts (**25** and **26**) in 48 and 29% yields while isobenzofuran and azulene-1,7-quinone gave three [2+4]-[6+4] adducts (**27–29**) in 13, 21, and 45% yields. The <sup>1</sup>H NMR spectra determined that **25**, **27**, and **28** are *endo*-[2+4] adducts and **26** and **29** are *exo*-[2+4] adducts. The higher chemical shift of the olefinic protons of **25** indicated that **25** should be *syn-endo*. Adduct **26** was speculated to be also *syn* because the chemical shifts of He ( $\delta$  3.38 for **25** and 3.70 for **26**) are different. A notable feature is that the Hf of **28** at  $\delta$  4.07 appeared at considerably higher field than the corresponding Hf protons of **27** and **29**. A high field shifted signal has been noticed for the He proton of an *anti-endo*-[2+4]-*exo*-[6+4] adduct from 3-bromoazulene-1,7-quinone.<sup>9</sup> Similarly, the He proton of **27** was higher than the other signals, which suggested that **27** was a *syn-endo*-[2+4]-*exo*-[6+4]. The structure of **29** was also established by detailed

NMR spectral analyses, including chemical shift comparisons with the corresponding bromo derivatives.

### Bromoazulenequinones with cycloheptatriene

When a xylene solution of 3-bromoazulene-1,5-quinone and cycloheptatriene was heated at 120 °C for 36 h, a product (**30**) was obtained in 36% yield. The structure was deduced from comparison with the <sup>1</sup>H NMR data of the 1:1 adduct (**31**) between tropone (**32**) and cycloheptatriene.<sup>12</sup> The <sup>1</sup>H NMR spectrum indicated the presence of four olefinic protons, six methine protons, and two methylene protons. The chemical shifts of the four olefinic protons, except for the singlet at  $\delta$  6.65 and the two methylene protons, were close to those of the corresponding protons of **31**. The <sup>13</sup>C NMR spectrum of **30** indicated the presence of two carbonyl groups, six olefinic carbon signals, and nine sp<sup>3</sup>-carbon signals. The IR spectrum showed the presence of a cyclopentanone ring.

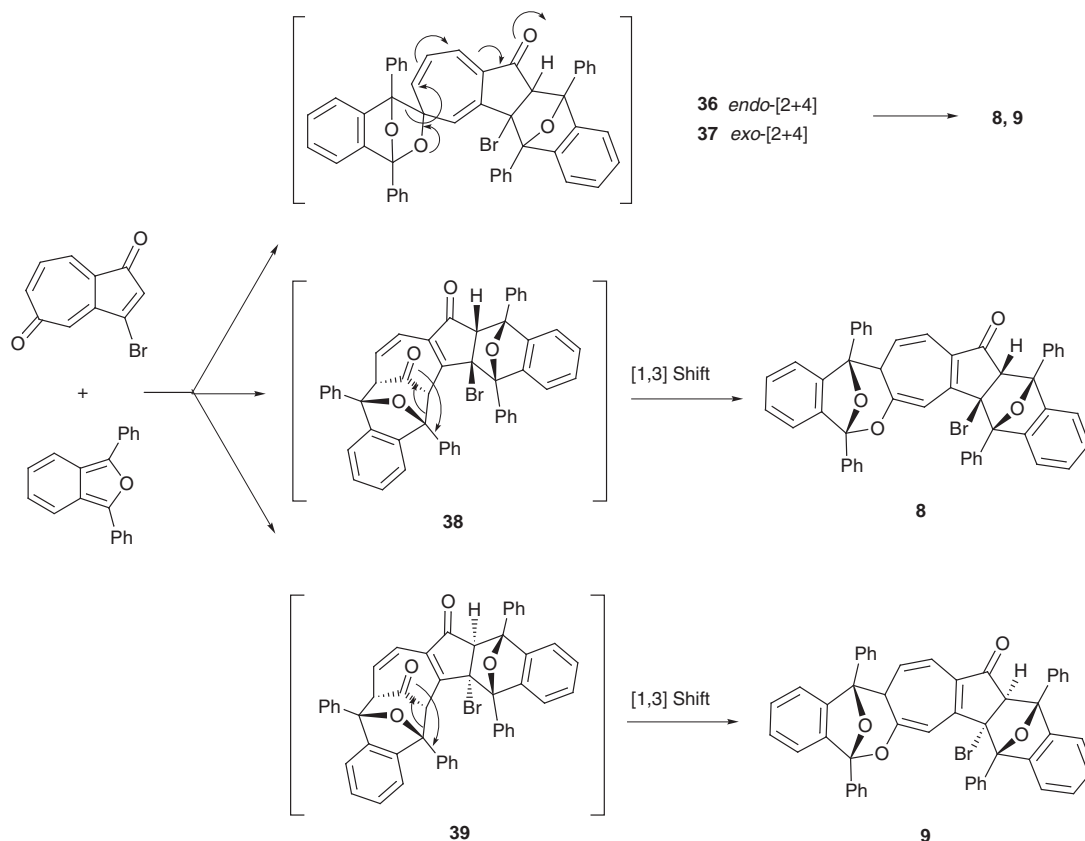
On the other hand, thermal reaction of 3-bromoazulene-1,7-quinone and cycloheptatriene in xylene at 120 °C gave three products (**33**, **34**, and **35**) in 12, 7, and 26% yields, respectively. The <sup>1</sup>H NMR spectrum of **33** was almost identical with that of product **30**. The second product **34** was a 1:1 adduct between 3-bromoazulene-1,7-quinone and cycloheptatriene. In the <sup>1</sup>H NMR spectrum, a singlet olefinic proton was observed at  $\delta$  6.44 to indicate that the cyclopentenone moiety is intact after the cycloaddition reaction. The methylene protons appeared at  $\delta$  2.32 (1H, d, *J* 16.9 Hz) and 3.01 (1H, d, *J* 16.9 Hz) as a pair of AB quartets to indicate the absence of adjacent protons. Four olefinic proton signals appeared as a doublet of doublets and the remaining olefinic proton appears as a doublet. From these data, the structure of **34** was proposed.

The major product **35** does not contain a bromine atom as indicated by the mass spectrum, which also indicated that the cyclopentenone part had reacted. Two methylene protons appeared at  $\delta$  1.71 as a singlet and the olefinic protons of the norbornadiene ring appeared at  $\delta$  5.84 (2H, *J* 7.7 and 6.6 Hz) and 6.17 (2H, *J* 7.7 and 6.6 Hz), which indicated a symmetrical structure as shown in Scheme 7.

### Discussion

Bromoazulenequinones reacted as a 4 $\pi$  component with both cyclopentadiene and 6,6-diphenylfulvene to give [4+2] adducts as observed in the reactions of dienophiles.<sup>5,6</sup> In the reaction of bromoazulenequinones and 1,3-diphenylisobenzofuran, 3-bromoazulene-1,5-quinone behaved differently from 3-bromoazulene-1,7-quinone; 3-bromoazulene-1,5-quinone gave two 1:1 products (**6** and **7**) and [2+4]-[8+4] cycloadducts (**8** and **9**) while the reaction of 3-bromoazulene-1,7-quinone and 1,3-diphenylisobenzofuran gave [2+4]-[6+4] adducts. Since the electronic effect of a bromine atom on the sp<sup>3</sup>-carbon should not be significant, the involvement of the tropone carbonyl of 3-bromoazulene-1,5-quinone in a cycloaddition could be attributed to a steric effect. According to the Woodward–Hoffmann rules,<sup>13</sup> **8** and **9** are thermally-disallowed [8+4] cycloadducts. The isolation of the 1:1 adduct **6** from 3-bromoazulene-1,5-quinone and 1,3-diphenylisobenzofuran is consistent with this 1:1 adduct being less reactive than the corresponding 1:1 adducts from 3-bromoazulene-1,7-quinone and 1,3-diphenylisobenzofuran, for steric reasons since the phenyl group and the bromine atom of **6** offer steric hindrance to the following [6+4] cycloaddition.

An [8+4] cycloaddition mechanism is of interest. One possibility is that the [8+4] adducts are formed *via* a ring-enlargement of the spirocyclic precursors, [2+4]-[2+4] cycloadducts (**36** and **37**), for which the tropone carbonyl group reacted as a 2 $\pi$  component. No [2+4] cycloadduct involving the tropone carbonyl group, however, has so far been recognized,<sup>14</sup> although that involving the C=S group of tropothione has been



Scheme 8

reported by Machiguchi.<sup>15</sup> The other possibility is a [1,3] shift, although thermally-disallowed, from a *syn-endo*-[2+4]-*exo*-[6+4] cycloadduct (**38**), which was not isolated due to high reactivity caused by steric hindrance between the bromine atom and the phenyl group at the [6+4] juncture. Similarly, the *syn-exo*-[2+4]-*exo*-[6+4] adduct (**39**), which was also not isolated, has a severe steric interaction between two inside phenyl groups to assist the isomerization to **9** via a non-concerted [1,3] shift.

The reaction of 3-bromoazulene-1,5-quinone and isobenzofuran gave 1:2 and 1:3 cycloadducts. Thus, bromoazulene-quinones were quite reactive with isobenzofuran to afford 1:2 and 1:3 cycloadducts. The formation of 1:2 cycloadducts is analogous to the results of reacting azulenequinones with 1,3-diphenylisobenzofuran reported by Scott,<sup>3</sup> but it is entirely different from the results with a typical diene, cyclopentadiene, from which only the 1:1 [4+2] products were obtained.

It is interesting that **21** and **22** were interconvertible; even during silica-gel column chromatography or standing in benzene solution **21** gave **22** and 1,3-diphenylisobenzofuran, and on standing, a mixture of **22** and 1,3-diphenylisobenzofuran in CDCl<sub>3</sub> at 60 °C gradually afforded **21**. No other compound could be detected during the reaction. In the conversion from **21** to **22**, removal of 1,3-diphenylisobenzofuran at the [2+4] juncture should be disfavored because of the generation of a highly reactive cyclopentadienone intermediate (**40**). An alternative path is the [1,5] shift of **21** to give a [4+2]-[2+4] adduct (**41**), from which elimination of 1,3-diphenylisobenzofuran afforded **22**. In monocyclic tropone derivatives, thermal [6+4]-to-[4+2] rearrangement was frequently observed,<sup>16</sup> but the [6+4]-to-[2+4] or [2+4]-to-[6+4] rearrangement has not been recorded.

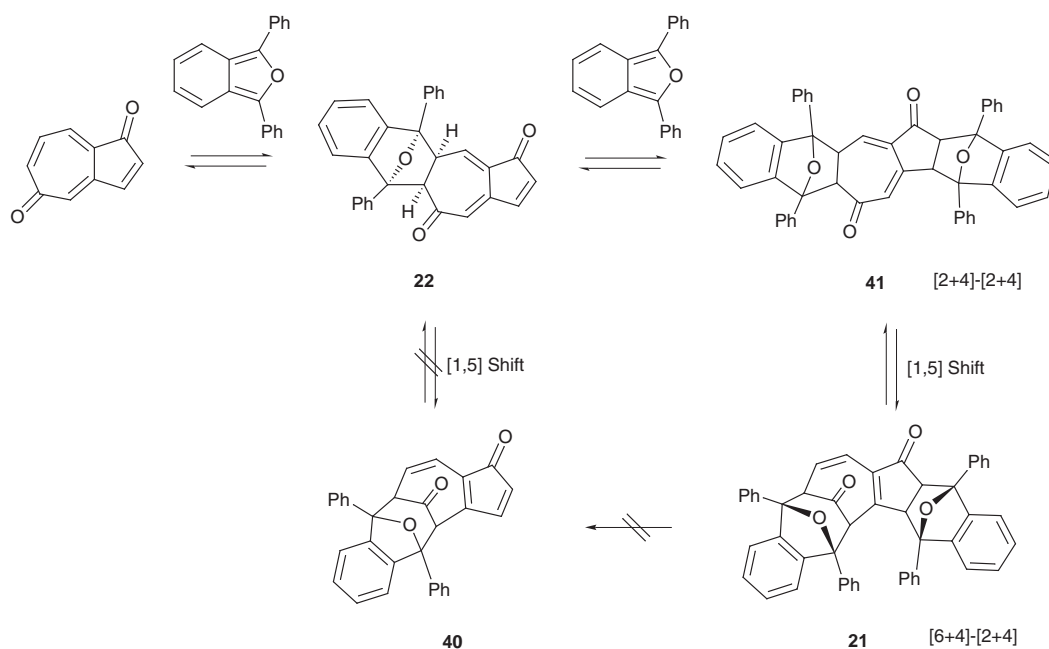
Thus, the first reaction site between 3-bromoazulene-1,5-quinone and 1,3-diphenylisobenzofuran was on the cyclopentenone part of 3-bromoazulene-1,5-quinone to give a 1:1 adduct which further reacted to afford [2+4]-[6+4] adducts. In

the case of the reaction of azulene-1,5-quinone and 1,3-diphenylisobenzofuran, the first addition took place on the C-6-C-7 bond of azulene-1,5-quinone and then, the 1,3-diphenylisobenzofuran part isomerized via a [1,5] shift to give the [2+4]-[6+4] adducts after the second 1,3-diphenylisobenzofuran attacked on the cyclopentenone part.

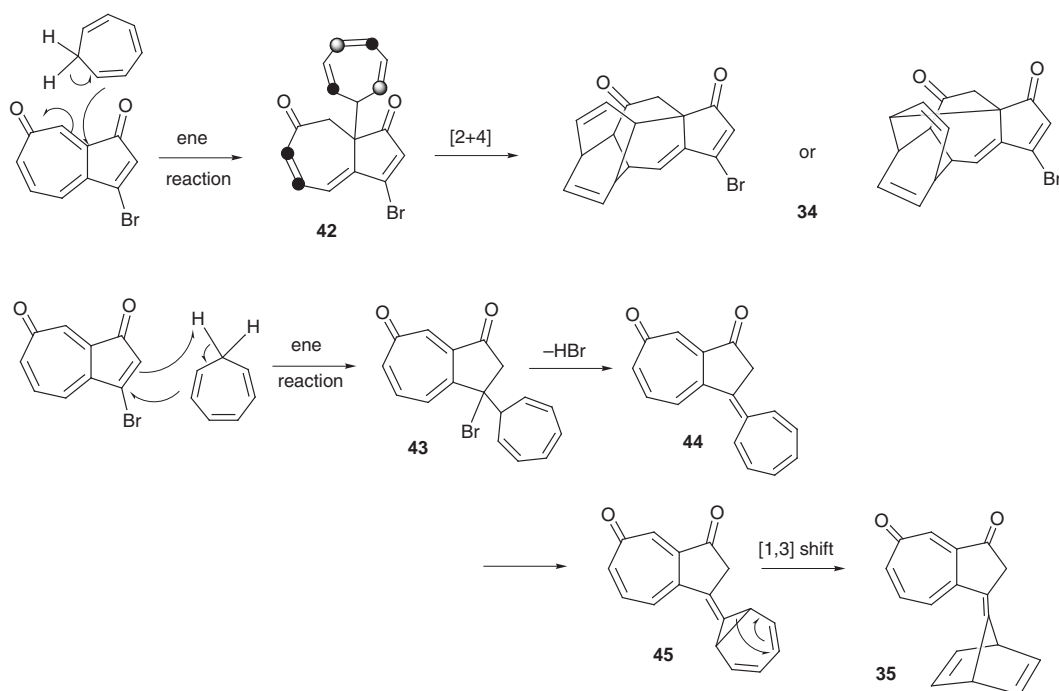
The reaction of cycloheptatriene and 3-bromoazulene-1,5-quinone and 3-bromoazulene-1,7-quinone showed not only cycloadditions but also ene reactions on the tropone and the cyclopentenone parts. The cage molecules **30** and **33** were derived from the intermolecular [4+6] cycloaddition reaction and the following intramolecular [2+4] cycloaddition reaction as observed in the reaction of tropone and cycloheptatriene.<sup>12</sup> The other products (**34** and **35**) were formed via an ene reaction on the tropone and the cyclopentenone rings. It is quite rare that an ene reaction takes place on the tropone ring. An ene reaction which occurred on the C-8-C-8a bond of 3-bromoazulene-1,7-quinone gave an intermediate (**42**), from which an intramolecular [4+2] cycloaddition afforded **34**. On the other hand, an ene reaction on the C-2-C-3 bond gave product **43**, from which a heptafulvene derivative (**44**) was formed by elimination of hydrobromic acid. Heptafulvene **44** isomerized to a norcaradiene derivative (**45**), which isomerized to **35** via a [ $\pi 2s + \sigma 2a$ ] process.<sup>17</sup>

In summary, azulenequinones reacted with 4 $\pi$  components to give [2+4]-[6+4] adducts while they afforded ene and cage products in the reaction with cycloheptatriene. The cycloaddition reactions of azulenequinones with 4 $\pi$  and 6 $\pi$  components took place to avoid formation of an unstable cyclopentadienone structure as observed in the reactions with monoolefines;<sup>6</sup> the C-2-C-3 bond of 3-bromoazulene-1,5-quinone and the C-6-C-7 bond of azulene-1,5-quinone in the reactions with 1,3-diphenylisobenzofuran.

We wish to thank Professor Klaus Hafner, Technische Hochschule Darmstadt, for his generous donation of the starting material, azulene.



Scheme 9



Scheme 10

## Experimental

The elemental analyses were performed at the elemental analysis laboratory of the Institute of Advanced Material Study, Kyushu University. The melting points were obtained on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in  $\text{CDCl}_3$ ; the chemical shifts are expressed in  $\delta$  units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks. UV spectra were measured on a Hitachi U-3200 spectrophotometer. Extinction coefficients are measured in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . The stationary phase for the column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane. The crystalline compounds were recrystallized from a mixture of hexane and chloroform.

## Thermal reaction of 3-bromoazulene-1,5-quinone with cyclopentadiene

A benzene solution ( $15 \text{ cm}^3$ ) of 3-bromoazulene-1,5-quinone (24 mg) in cyclopentadiene (10 mg) was heated in a shield tube at  $80^\circ\text{C}$  for 5 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **1** (17 mg, 55%).

Adduct **1**: yellow powder, mp  $84\text{--}86^\circ\text{C}$ ;  $\delta_{\text{H}}$  2.06 (1H, ddm,  $J = 17.2, 5.9 \text{ Hz}$ ), 2.77 (1H, ddq,  $J = 17.2, 8.6, 2.2 \text{ Hz}$ ), 3.05 (1H, br m), 3.37 (1H, br m), 3.59 (1H, dm,  $J = 7.7 \text{ Hz}$ ), 5.70 (1H, dq,  $J = 5.9, 2.2 \text{ Hz}$ ), 5.78 (1H, dq,  $J = 5.9, 2.2 \text{ Hz}$ ), 6.03 (1H, dd,  $J = 1.5, 0.7 \text{ Hz}$ ), 6.14 (1H, dt,  $J = 8.4, 1.1 \text{ Hz}$ ), 6.28 (1H, ddd,  $J = 8.4, 7.7, 0.7 \text{ Hz}$ ), and 6.79 (1H, d,  $J = 1.5, 0.7 \text{ Hz}$ );  $\delta_{\text{C}}$  38.4, 40.4, 56.6, 57.0, 59.2, 122.9, 128.4, 128.8, 132.0, 134.0, 139.2, 151.3, 159.4, 195.8, and 200.9; IR (KBr) 1711, 1660, 1540, 1450, and  $1271 \text{ cm}^{-1}$ ; MS  $m/z$  (%): 304 ( $\text{M}^+ + 1$  for  $^{81}\text{Br}$ , 34), 303 ( $\text{M}^+$



for  $^{81}\text{Br}$ , 51), 302 ( $M^+ + 1$  for  $^{79}\text{Br}$ , 44), 301 ( $M^+$  for  $^{79}\text{Br}$ , 14), 239 (82), 238 (99), 237 (89), 236 (64), 235 (30), 210 (22), 208 (26), 167 (29), 166 (35), 152 (27), 115 (16), and 66 (100); UV (MeOH) 231.8 nm ( $\epsilon$  6130, sh), and 284.5 (11750) [Found: C, 59.51; H, 3.79%. Calcd for  $\text{C}_{15}\text{H}_{11}\text{BrO}_2$ : C, 59.43; H, 3.66%].

#### Thermal reaction of 3-bromoazulene-1,5-quinone with 6,6-diphenylfulvene

A xylene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,5-quinone (24 mg) in 6,6-diphenylfulvene (48 mg) was heated at 130 °C for 8 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **3** (12 mg, 25%) and **4** (4 mg, 8%).

Adduct **3**: yellow crystals, mp 204–205 °C;  $\delta_{\text{H}}$  3.42 (1H, ddm,  $J = 7.7, 1.5$  Hz), 3.57 (1H, dd,  $J = 7.3, 1.5$  Hz), 3.98 (1H, d,  $J = 7.3$  Hz), 5.94 (1H, dd,  $J = 2.0, 0.6$  Hz), 6.08 (1H, dd,  $J = 8.4, 0.7$  Hz), 6.15 (1H, dd,  $J = 5.9, 2.4$  Hz), 6.19 (1H, dd,  $J = 8.4, 7.7$  Hz), 6.50 (1H, dd,  $J = 5.9, 2.4$  Hz), 6.79 (1H, d,  $J = 0.6$  Hz), and 7.11–7.38 (10H, m);  $\delta_{\text{C}}$  42.8, 54.7, 55.5, 56.7, 123.2, 127.0, 127.6, 128.0 (2C), 128.4, 128.8 (2C), 129.1 (2C), 129.9 (2C), 130.7, 135.2, 135.8, 137.7, 139.0, 141.2, 142.4, 144.8, 151.6, 158.4, 194.4, and 200.8; IR (KBr) 1709, 1667, 1614, 1538, 1492, 1442, 1318, 1263, 1229, 1129, 1072, 1021, 909, and 825  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 468 ( $M^+$  for  $^{81}\text{Br}$ , 3), 466 ( $M^+$  for  $^{79}\text{Br}$ , 3), 387 (2), 256 (2), 231 (17), 230 (100), 229 (52), 228 (19), 215 (24), 129 (10), and 101 (7); UV (MeOH) 233.0 nm ( $\epsilon$  15330) and 284.2 (25240) [Found: C, 71.84; H, 4.07%. Calcd for  $\text{C}_{28}\text{H}_{19}\text{BrO}_2$ : C, 71.96; H, 4.10%].

Adduct **4**: yellow crystals, mp 176–178 °C;  $\delta_{\text{H}}$  3.20 (1H, tm,  $J = 6.6$  Hz), 3.64 (1H, ddd,  $J = 8.2, 2.6, 1.5$  Hz), 3.95 (1H, dd,  $J = 8.2, 6.6$  Hz), 5.63 (1H, dd,  $J = 5.8, 2.6$  Hz), 6.09 (1H, dd,  $J = 8.2, 6.6$  Hz), 6.10 (1H, dd,  $J = 2.0, 0.5$  Hz), 6.21 (1H, dd,  $J = 8.2, 1.0$  Hz), 6.41 (1H, dd,  $J = 5.8, 2.6$  Hz), 6.81 (1H, d,  $J = 0.5$  Hz), and 6.99–7.39 (10H, m);  $\delta_{\text{C}}$  43.3, 53.4, 55.0, 58.5, 124.6, 127.1, 127.5, 128.0 (2C), 128.4 (2C), 129.7 (2C), 129.8 (2C), 130.9, 133.3, 133.4, 137.3, 139.1, 139.5, 141.8, 142.1, 142.3, 153.1, 156.4, 194.0, and 201.7; IR (KBr) 1714, 1665, 1624, 1537, 1491, 1442, 1265, 1125, 907, 887, and 809  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 468 ( $M^+$  for  $^{81}\text{Br}$ , 5), 466 ( $M^+$  for  $^{79}\text{Br}$ , 5), 279 (4), 238 (7), 236 (6), 231 (22), 230 (100), 229 (42), 228 (12), 215 (20), 182 (14), 149 (13), 105 (26), and 77 (12); UV (MeOH) 231.5 nm ( $\epsilon$  14680) and 281.3 (18580) [Found: C, 71.77; H, 4.32%. Calcd for  $\text{C}_{28}\text{H}_{19}\text{BrO}_2$ : C, 71.96; H, 4.10%].

#### Thermal reaction of 3-bromoazulene-1,7-quinone with cyclopentadiene

A benzene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,7-quinone (24 mg) in cyclopentadiene (10 mg) was heated in a sealed tube at 80 °C for 5 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **2** (15 mg, 48%).

Adduct **2**: yellow powder, mp 199–201 °C;  $\delta_{\text{H}}$  2.06 (1H, ddm,  $J = 17.7, 5.8$  Hz), 2.76 (1H, ddq,  $J = 17.7, 9.9, 2.2$  Hz), 3.12 (1H, ddm,  $J = 9.9, 8.4$  Hz), 3.43 (1H, dm,  $J = 8.4$  Hz), 3.61 (1H, dm,  $J = 7.4$  Hz), 5.83 (1H, dq,  $J = 5.9, 2.2$  Hz), 6.09 (1H, dq,  $J = 5.9, 2.2$  Hz), 6.21 (1H, d,  $J = 2.2$  Hz), 6.28 (1H, ddd,  $J = 8.4, 7.4, 1.1$  Hz), 6.35 (1H, ddd,  $J = 8.4, 1.1, 0.7$  Hz), and 6.84 (1H, s);  $\delta_{\text{C}}$  39.4, 40.1, 57.7, 59.3, 60.5, 121.8, 127.6, 128.9, 133.7, 134.6, 138.6, 154.5, 163.0, 190.5, and 196.3; IR (KBr) 1719, 1666, 1628, 1537, and 1270  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 304 ( $M^+ + 1$  for  $^{81}\text{Br}$ , 12), 303 ( $M^+$  for  $^{81}\text{Br}$ , 16), 302 ( $M^+ + 1$  for  $^{79}\text{Br}$ , 11), 301 ( $M^+$  for  $^{79}\text{Br}$ , 11), 239 (86), 238 (78), 237 (100), 236 (29), and 66 (92); UV (MeOH) 226.6 nm ( $\epsilon$  3280, sh), 262.6 (4055), and 281.3 (2940, sh) [Found: C, 59.58; H, 3.79%. Calcd for  $\text{C}_{15}\text{H}_{11}\text{BrO}_2$ : C, 59.43; H, 3.66%].

#### Thermal reaction of 3-bromoazulene-1,7-quinone with 6,6-diphenylfulvene

A xylene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,7-quinone (24

mg) in 6,6-diphenylfulvene (48 mg) was heated at 130 °C for 8 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **5** (7 mg, 15%).

Adduct **5**: yellow crystals, mp 220 °C (decomp.);  $\delta_{\text{H}}$  3.42 (1H, ddm,  $J = 7.3, 1.1$  Hz), 3.63 (1H, d,  $J = 7.3$  Hz), 4.01 (1H, d,  $J = 7.3$  Hz), 6.12 (1H, d,  $J = 2.2$  Hz), 6.19 (1H, dd,  $J = 8.8, 7.3$  Hz), 6.27 (1H, d,  $J = 8.8$  Hz), 6.50 (1H, dd,  $J = 5.9, 1.8$  Hz), 6.54 (1H, dd,  $J = 5.9, 1.8$  Hz), 6.80 (1H, s), and 7.10–7.40 (10H, m);  $\delta_{\text{C}}$  43.5, 55.7, 57.6, 58.5, 122.1, 127.1, 127.3, 127.7, 128.1 (2C), 128.9 (2C), 129.1 (2C), 129.9 (2C), 132.2, 135.3, 135.4, 138.2, 138.8, 141.0, 142.4, 144.2, 153.4, 162.6, 190.4, and 194.7; IR (KBr) 1707, 1675, 1563, 1510, 1492, 1442, 1256, 1103, and 867  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 468 ( $M^+$  for  $^{81}\text{Br}$ , 0.6), 466 ( $M^+$  for  $^{79}\text{Br}$ , 0.2), 253 (1), 239 (1), 231 (33), 230 (100), 229 (50), 228 (16), 215 (28), 202 (7), 165 (8), 105 (26), and 126 (8); UV (MeOH) 257.4 nm ( $\epsilon$  12050, sh) and 287.8 (9630, sh) [Found: C, 71.69; H, 4.24%. Calcd for  $\text{C}_{28}\text{H}_{19}\text{BrO}_2$ : C, 71.96; H, 4.10%].

#### Thermal reaction of 3-bromoazulene-1,5-quinone with 1,3-diphenylisobenzofuran

1) A chlorobenzene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,5-quinone (34 mg) and 1,3-diphenylisobenzofuran (71 mg) was refluxed for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give a mixture (5:1) of **6** and **7** (8 mg, 11%), **8** (24.6 mg, 22%), and **9** (33.6 mg, 30%).

Adduct **6**:  $\delta_{\text{H}}$  3.61 (1H, s), 6.69 (1H, dm,  $J = 2.6$  Hz), 7.02 (1H, ddd,  $J = 11.7, 2.6, 1.5$  Hz), 7.14 (1H, dd,  $J = 11.7, 8.1$  Hz), 7.2–7.8 (12H, m), 7.83 (1H, dd,  $J = 6.7, 1.5$  Hz), and 7.95 (2H, ddm,  $J = 8.4, 1.5$  Hz).

Adduct **8**: colorless crystals, mp 238–239 °C;  $\delta_{\text{H}}$  1.80 (1H, dd,  $J = 6.2, 1.5$  Hz), 4.29 (1H, s), 5.15 (1H, dd,  $J = 8.8, 6.2$  Hz), 6.30 (1H, d,  $J = 8.8$  Hz), 6.41 (1H, s), 6.57 (1H, dm,  $J = 7.0$  Hz), 6.86 (1H, dm,  $J = 7.0$  Hz), 7.11–7.23 (2H, m), 7.29–7.37 (8H, m), 7.40–7.57 (12H, m), 7.84–7.88 (2H, m), and 8.02 (2H, dm,  $J = 7.0$  Hz);  $\delta_{\text{C}}$  47.1, 68.9, 76.3, 87.1, 89.9, 93.5, 105.1, 109.1, 120.4, 120.5 (2C), 121.7, 121.9, 122.6, 125.3 (2C), 126.1 (2C), 126.5 (3C), 126.6, 127.4 (2C), 127.9 (2C), 128.1, 128.3 (4C), 128.5 (3C), 129.0 (2C), 129.5, 129.8, 135.3, 135.4, 136.7, 136.8, 137.1, 142.6, 143.1, 145.5, 146.5, 146.8, 159.1, and 198.1; IR (KBr) 1700, 1600, 1521, 1478, 1342, 1303, 1265, 1221, 1187, 997, 944, and 832  $\text{cm}^{-1}$ ; UV (MeOH) 254.2 nm ( $\epsilon$  6215) and 334.7 (3890), UV ( $\text{CHCl}_3$ ) 255.0 nm ( $\epsilon$  15520) and 337.0 (8930) [Found: C, 77.35; H, 4.16%. Calcd for  $\text{C}_{50}\text{H}_{33}\text{BrO}_4$ : C, 77.22; H, 4.28%].

Adduct **9**: colorless crystals, mp 172–174 °C;  $\delta_{\text{H}}$  2.27 (1H, d,  $J = 6.2$  Hz), 3.45 (1H, s), 5.05 (1H, dd,  $J = 9.2, 6.2$  Hz), 5.77 (1H, s), 6.43 (1H, dd,  $J = 9.2, 0.7$  Hz), 6.83 (1H, tt,  $J = 7.3, 1.5$  Hz), 6.93 (2H, t,  $J = 7.3$  Hz), 6.99–7.09 (3H, m), 7.20 (1H, dd,  $J = 7.3, 1.5$  Hz), 7.22–7.28 (2H, m), 7.36–7.54 (13H, m), and 7.62–7.72 (6H, m);  $\delta_{\text{C}}$  46.3, 65.9, 71.9, 87.1, 89.8, 91.2, 106.0, 108.2, 119.6, 120.4 (2C), 121.3, 121.9, 122.7, 125.1 (2C), 125.5 (2C), 126.4 (2C), 126.5 (3C), 126.8, 127.6 (2C), 128.0, 128.1 (3C), 128.4 (4C), 128.9 (2C), 129.3, 129.5, 133.8, 134.1, 135.7, 137.3, 138.0, 143.0, 144.6, 145.2, 146.7, 147.3, 159.1, and 197.6; IR (KBr) 1699, 1597, 1524, 1450, 1366, 1305, 1259, 1228, 1183, 1108, 1044, 994, 956, 923, and 863  $\text{cm}^{-1}$ ; UV ( $\text{CHCl}_3$ ) 257.1 nm ( $\epsilon$  21510) and 341.9 (10550) [Found (FAB MS): 777.1663 and 779.1591. Calcd for  $\text{C}_{50}\text{H}_{34}\text{BrO}_4$ : 777.1639 and 779.1619].

2) A chlorobenzene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,5-quinone (47.4 mg) and 1,3-diphenylisobenzofuran (54 mg) was refluxed for 1 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give a mixture (5:1) of **6** and **6** (28 mg, 54%), **8** (1 mg, 1%), **9** (1 mg, 1%), and unchanged 3-bromoazulene-1,5-quinone (23 mg).

**Table 1** Crystallographic data for **8**, **11** and **13**

	<b>8</b>	<b>11</b>	<b>13</b>
Formula	C <sub>50</sub> H <sub>33</sub> O <sub>4</sub> Br·2C <sub>6</sub> H <sub>6</sub>	C <sub>50</sub> H <sub>33</sub> O <sub>4</sub> Br·2C <sub>6</sub> H <sub>6</sub>	C <sub>26</sub> H <sub>17</sub> O <sub>4</sub> Br
Formula weight	933.94	933.94	473.32
Crystal color	Colorless	Colorless	Pale yellow
Crystal size/mm	0.55 × 0.45 × 0.20	0.40 × 0.23 × 0.05	0.50 × 0.30 × 0.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	P2 <sub>1</sub> /n
<i>a</i> /Å	26.276(4)	41.133(9)	12.699(2)
<i>b</i> /Å	16.196(3)	12.545(2)	16.985(2)
<i>c</i> /Å	24.731(2)	18.353(3)	9.715(2)
$\beta$ /deg	112.66(1)	99.29(2)	101.75(1)
<i>V</i> /Å <sup>3</sup>	9712(2)	9346(3)	2051.5(6)
<i>Z</i>	8	8	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.28	1.33	1.53
$\mu$ /mm <sup>-1</sup>	1.534	1.594	2.996
No. of reflections	8254	7951	3487
No. obs. refl. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6800	4697	3289
No. of refined parameters	605	604	280
Refinement	<i>F</i> <sup>2</sup> (SHELXL93)	<i>F</i> <sup>2</sup> (SHELXL93)	<i>F</i> <sup>2</sup> (SHELXL93)
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.049	0.061	0.038
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.138	0.182	0.103

**Thermal reaction of 6 with 1,3-diphenylisobenzofuran**

A chlorobenzene solution (5 cm<sup>3</sup>) of a mixture of **6** (8 mg) and 1,3-diphenylisobenzofuran (9 mg) was refluxed for 3 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **8** (4.8 mg, 40%) and **9** (5.1 mg, 42%).

**X-Ray crystallographic analysis of 8**

The monoclinic single crystals of **8** crystallized with two molecules of benzene. The measurement was made on an Enraf-Nonius FR590 diffractometer with graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å). The data were collected at a temperature 23 ± 2 °C using the  $\omega$ -2 $\theta$  scan technique to a maximum 2 $\theta$  value of 129.9°. The structure was solved by a direct method (SIR92<sup>18</sup>), and was refined using full-matrix least squares (SHELXL93<sup>19</sup>) based on *F*<sup>2</sup> of all independent measured reflections. All H atoms were located at ideal positions and were included in the refinement, but restrained to ride on the atom to which they are bonded. Isotropic thermal factors of H atoms were held fixed to 1.2 times or 1.5 times (for the phenolic proton) *U*<sub>eq</sub> of the riding atoms. The crystallographic data are listed in Table 1.†

**Thermal reaction of 3-bromoazulene-1,7-quinone with 1,3-diphenylisobenzofuran**

A chlorobenzene solution (15 cm<sup>3</sup>) of 3-bromoazulene-1,7-quinone (23.8 mg) and 1,3-diphenylisobenzofuran (54 mg) was refluxed for 24 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **10** (8.5 mg, 11%) and **11** (23 mg, 30%).

Adduct **10**: colorless crystals, mp 196–198 °C;  $\delta_{\text{H}}$  3.78 (1H, d, *J* = 2.2 Hz), 3.93 (1H, s), 4.05 (1H, dd, *J* = 7.3, 2.2 Hz), 6.08 (1H, dd, *J* = 11.4, 7.3 Hz), 6.58 (1H, d, *J* = 11.4 Hz), 6.70 (1H, dm, *J* = 1.8 Hz), 7.06 (1H, m), 7.15–7.23 (3H, br m), 7.3–7.53 (15H, m), 7.66 (2H, d, *J* = 7.3 Hz), 7.77 (1H, d, *J* = 7.3 Hz), and 7.79–7.85 (5H, m);  $\delta_{\text{C}}$  57.6, 62.7, 69.8, 76.1, 89.3, 89.9, 90.8, 93.0, 120.3, 121.3, 121.4, 121.5, 124.9 (2C), 125.4, 125.8 (2C), 127.0 (2C), 127.3 (2C), 127.9 (2C), 128.0 (3C), 128.1 (2C), 128.2, 128.3, 128.4 (3C), 129.0 (2C), 129.1 (2C), 132.8, 135.7, 136.4, 136.7, 137.4, 138.5, 140.8, 143.5, 143.8, 144.5, 163.1, 196.8, and 199.7; IR (KBr) 1701, 1592, 1523, 1499, 1459, 1449, 1336, 1303, 1259, 1227, 1181, 1081, 996, 956, 923, and 862

cm<sup>-1</sup>; UV (CHCl<sub>3</sub>) 255.8 nm ( $\epsilon$  14065), 287.7 (4630, sh), 299.5 (4020, sh), and 339.0 (6485) [Found (FAB MS): 777.1662 and 779.1605. Calcd for C<sub>50</sub>H<sub>34</sub>BrO<sub>4</sub>: 777.1639 and 779.1619].

Adduct **11**: colorless crystals, mp 167–168 °C;  $\delta_{\text{H}}$  3.26 (1H, s), 3.87 (1H, dd, *J* = 7.3, 1.8 Hz), 4.43 (1H, d, *J* = 1.8 Hz), 5.29 (1H, dd, *J* = 11.7, 7.3 Hz), 5.56 (1H, d, *J* = 11.7 Hz), 6.92 (1H, d, *J* = 7.0 Hz), 7.09 (1H, m), 7.12–7.24 (9H, m), 7.27–7.62 (12H, m), 7.71 (3H, m), and 7.90 (2H, d, *J* = 7.7 Hz);  $\delta_{\text{C}}$  56.9, 63.5, 64.9, 72.5, 89.5, 89.9, 91.1, 91.2, 120.1, 121.0, 121.7, 122.6, 125.0 (2C), 125.2 (2C), 126.2 (2C), 126.3, 126.4 (2C), 126.8, 127.4, 127.9, 128.0 (3C), 128.1 (2C), 128.3 (2C), 128.4 (2C), 128.5 (2C), 128.8, 129.1, 132.6, 133.5, 133.6, 135.2, 137.2, 138.4, 143.5, 144.3, 144.4, 146.8, 161.6, 195.7, and 201.0; IR (KBr) 1709, 1589, 1498, 1459, 1334, 1306, 1288, 1243, 1223, 1181, 1080, and 1012 cm<sup>-1</sup>; FAB MS *m/z* (%): 777.2 (10) and 779.2 (10); UV (MeOH) 255.4 nm ( $\epsilon$  1900), 270 (2510), 300 (2000, sh), and 325 nm (1470), UV (CHCl<sub>3</sub>) 252.0 nm ( $\epsilon$  8690, sh), 259.4 (8140, sh), 278.6 (7090), 287.7 (6880, sh), 299.7 (5765, sh), 327.5 (4125), and 339.4 (3850, sh) [Found: C, 77.14; H, 4.07%. Calcd for C<sub>50</sub>H<sub>33</sub>BrO<sub>4</sub>: C, 77.22; H, 4.28%].

**X-Ray crystallographic analysis of 11**

The monoclinic single crystals of **11** crystallized with two molecules of benzene, which was analyzed as is described for **8**. The crystallographic data are listed in Table 1.

**Thermal reaction of 3-bromoazulene-1,5-quinone with isobenzofuran**

To a dichlorobenzene solution (15 cm<sup>3</sup>) of 3-bromoazulene-1,5-quinone (24 mg) was added dropwise a dichlorobenzene solution of **12** (150 mg) at 165 °C under a N<sub>2</sub> stream and the reaction mixture was kept for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **13** (12 mg, 25%), **14** (13 mg, 28%), **15** (5 mg, 11%), and **16** (5 mg, 9%).

Adduct **13**: pale yellow crystals, mp 210 °C (decomp.);  $\delta_{\text{H}}$  3.27 (1H, ddd, *J* = 7.0, 2.2, 1.5 Hz), 3.53 (1H, dd, *J* = 2.2, 1.5 Hz), 3.93 (1H, d, *J* = 5.9 Hz), 5.33 (1H, d, *J* = 1.5 Hz), 5.67 (1H, s), 5.70 (1H, d, *J* = 5.9 Hz), 5.86 (1H, dd, *J* = 11.4, 7.0 Hz), 5.99 (1H, d, *J* = 11.4 Hz), 6.32 (1H, d, *J* = 1.5 Hz), and 7.00–7.50 (8H, m);  $\delta_{\text{C}}$  61.1, 63.1, 64.0, 71.7, 81.5, 84.4, 84.8, 89.5, 119.8, 121.1 (2C), 121.4, 122.1, 127.8, 128.3, 129.0, 129.3, 130.7, 139.6, 139.8 (2C), 141.4, 141.6, 155.3, and 198.3 (2C); IR (KBr) 1707, 1596, 1463, 1407, 1351, 1334, 1269, 1227, 1208, 1191, 1153, 1009, 977, 857, and 824 cm<sup>-1</sup>; MS *m/z* (%): 474 (M<sup>+</sup> for <sup>81</sup>Br, 5), 472 (M<sup>+</sup> for <sup>79</sup>Br, 6), 290 (7), 276 (37), 275 (46), 274 (20), 247

† CCDC reference number 207/338. See <http://www.rsc.org/suppdata/p1/1999/2129> for crystallographic files in .cif format.

(12), 219 (10), 191 (12), 189 (47), 165 (32), 139 (36), 132 (39), 131 (100), 120 (57), and 63 (20); UV (MeOH) 267.4 nm ( $\epsilon$  3955, sh), 275.0 (4235), 293.9 (3020), 323.2 (1850), and 331.2 (1720, sh) [Found: C, 66.19; H, 3.46%. Calcd for  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **14**: colorless crystals, mp 195 °C (decomp.);  $\delta_H$  2.89 (1H, s), 3.55 (1H, ddd,  $J = 7.3, 2.2, 1.5$ , Hz), 3.71 (1H, dd,  $J = 2.2, 1.5$  Hz), 5.35 (1H, s), 5.40 (1H, s), 5.47 (1H, d,  $J = 1.5$  Hz), 6.17 (1H, d,  $J = 11.4, 7.7$  Hz), 6.22 (1H, d,  $J = 1.5$  Hz), 6.60 (1H, d,  $J = 11.4$  Hz), and 7.25–7.50 (8H, m);  $\delta_C$  60.9, 61.6, 62.3, 67.2, 82.4, 83.5, 84.1, 84.8, 119.9, 120.6, 121.3 (2C), 123.7, 127.0, 128.2, 129.0, 129.3, 130.7, 141.3, 142.0, 142.4, 142.6, 143.1, 157.3, 199.1, and 199.8; IR (KBr) 1718, 1604, 1461, 1409, 1351, 1267, 1153, 1012, 936, 892, 856, 823, and 751  $cm^{-1}$ ; MS  $m/z$  (%): 475 ( $M^+ + 1$  for  $^{81}Br$ , 19), 474 ( $M^+$  for  $^{81}Br$ , 20), 473 ( $M^+ + 1$  for  $^{79}Br$ , 34), 472 ( $M^+$  for  $^{79}Br$ , 21), 275 (13), 247 (5), 219 (11), 190 (33), 189 (32), 165 (30), 152 (17), 139 (33), 138 (18), 132 (50), 131 (73), 120 (100), and 91 (34); UV (MeOH) 267.8 nm ( $\epsilon$  5460), 274.2 (5730), 293.1 (4680), and 321.3 (2640) [Found: C, 65.83; H, 3.67%.  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **15**: pale yellow crystals, mp 190 °C;  $\delta_H$  2.88 (1H, s), 3.51 (1H, dd,  $J = 7.3, 1.8$  Hz), 4.15 (1H, dd,  $J = 1.8, 1.5$  Hz), 5.47 (1H, d,  $J = 1.8$  Hz), 5.51 (1H, s), 5.56 (1H, s), 5.79 (1H, d,  $J = 1.5$  Hz), 6.18 (1H, dd,  $J = 11.4, 7.3$  Hz), 6.58 (1H, d,  $J = 11.4$  Hz), and 7.20–7.60 (8H, m);  $\delta_C$  61.0, 61.4, 62.6, 67.2, 82.2, 82.4, 83.4, 84.2, 119.6, 120.8, 121.4, 123.7, 127.1, 128.5, 129.1 (2C), 129.4, 130.8, 141.7, 141.9, 142.3, 143.0, 143.5, 158.8, 199.2, and 199.5; IR (KBr) 1717, 1603, 1459, 1408, 1335, 1262, 1151, 1016, 972, 956, 860, and 822  $cm^{-1}$ ; MS  $m/z$  (%): 474 ( $M^+$  for  $^{81}Br$ , 4), 472 ( $M^+$  for  $^{79}Br$ , 2), 354 (13), 276 (22), 275 (25), 247 (10), 219 (4), 189 (23), 165 (11), 152 (8), 145 (13), 139 (13), 131 (100), 120 (62), and 91 (29); UV (MeOH) 264.0 nm ( $\epsilon$  4655), 273.4 (4680), 293.0 (3280), and 320.6 (2100) [Found: C, 65.67; H, 3.82%. Calcd for  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **16**: colorless crystals, mp 240 °C;  $\delta_H$  2.34 (1H, d,  $J = 8.1$  Hz), 2.86 (1H, d,  $J = 8.1$  Hz), 3.06 (1H, s), 3.53 (1H, s), 3.56 (1H, s), 3.96 (1H, d,  $J = 6.2$  Hz), 4.96 (1H, s), 5.16 (1H, s), 5.67 (1H, s), 5.74 (1H, d,  $J = 6.2$  Hz), 6.21 (1H, d,  $J = 1.1$  Hz), and 7.10–7.26 (12H, m);  $\delta_C$  43.3, 47.0, 61.8, 62.1, 63.7, 72.0, 81.4, 82.5, 84.3, 85.0, 87.0, 89.5, 118.7, 119.7, 120.5, 121.2, 121.4, 122.5, 126.9, 127.2, 128.0, 128.7, 128.9, 129.0, 140.1, 140.2, 140.6, 141.7, 145.0, 145.1, 146.7, 156.6, 199.2, and 200.9; IR (KBr) 1706, 1627, 1460, 1365, 1260, 1226, 1199, 1154, 1096, 1030, 998, 973, 908, 860, and 845  $cm^{-1}$ ; UV (MeOH) 260.2 nm ( $\epsilon$  8060), 265.9 (8530), and 272.6 (8290) [Found (FAB MS): 591.0807 and 593.0793. Calcd for  $C_{34}H_{24}BrO_5$ : 591.0806 and 593.0786].

### X-Ray crystallographic analysis of 13

The single crystal of **13** was analyzed by a similar method to that mentioned above. The crystallographic data are listed in Table 1.

### Thermal reaction of 3-bromoazulene-1,7-quinone with isobenzofuran

To a dichlorobenzene solution (15  $cm^3$ ) of 3-bromoazulene-1,7-quinone (24 mg) was added dropwise a dichlorobenzene solution of **12** (150 mg) at 165 °C under an  $N_2$  stream and the reaction mixture was kept at that temperature for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **17** (14 mg, 29%), **18** (5.2 mg, 11%), **19** (10.5 mg, 22%), and **20** (5 mg, 10%).

Adduct **17**: colorless crystals, mp 97–98 °C;  $\delta_H$  3.03 (1H, dd,  $J = 1.8, 1.5$  Hz), 3.28 (1H, ddd,  $J = 7.3, 2.6, 1.8$  Hz), 3.93 (1H, d,  $J = 5.9$  Hz), 5.21 (1H, d,  $J = 1.8$  Hz), 5.38 (1H, d,  $J = 1.5$  Hz), 5.57 (1H, s), 5.70 (1H, d,  $J = 5.9$  Hz), 6.45 (1H, dd,  $J = 11.4, 7.3$  Hz), 6.54 (1H, d,  $J = 11.4$  Hz), and 7.20–7.60 (8H, m);  $\delta_C$  54.6, 61.1, 63.9, 69.5, 81.5, 82.7, 82.9, 88.7, 120.3, 120.9, 121.2, 121.4, 125.3, 128.2, 128.3, 128.9, 133.1, 137.5 (2C), 139.5, 140.3, 141.3,

141.6, 162.5, 198.0, and 198.3; IR (KBr) 1725, 1698, 1586, 1461, 1418, 1346, 1202, 1155, 1094, 1024, 980, 937, and 856  $cm^{-1}$ ; UV (MeOH) 253.4 nm (6670, sh), 283.4 (6570), 293.4 (6090, sh), and 318.4 ( $\epsilon$  4430) [Found: C, 65.91; H, 3.89%. Calcd for  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **18**: pale yellow crystals, mp 200 °C (decomp.);  $\delta_H$  3.29 (1H, dd,  $J = 2.2, 1.8$  Hz), 3.41 (1H, ddd,  $J = 7.3, 2.2, 1.8$  Hz), 3.91 (1H, d,  $J = 6.2$  Hz), 4.09 (1H, d,  $J = 1.8$  Hz), 5.23 (1H, d,  $J = 1.5$  Hz), 5.63 (1H, s), 5.73 (1H, d,  $J = 6.2$  Hz), 6.42 (1H, dd,  $J = 11.4, 7.3$  Hz), 6.50 (1H, d,  $J = 11.4$  Hz), and 7.12–7.27 (8H, m);  $\delta_C$  55.1, 61.6, 63.7, 70.2, 81.3, 82.6, 82.7, 88.6, 120.9 (2C), 121.0, 121.3, 121.8, 125.4, 127.6, 128.5, 128.8, 128.9, 133.9, 137.5, 140.1, 141.1, 142.1, 162.2, 198.2, and 199.3; IR (KBr) 1727, 1699, 1592, 1460, 1420, 1336, 1236, 1204, 1186, 1153, 1090, 1019, 986, 957, 934, 917, 880, and 857  $cm^{-1}$ ; UV (MeOH) 257.4 nm ( $\epsilon$  10815), 280.5 (10180), 295.0 (8870, sh), and 320.8 (5810) [Found: C, 65.70; H, 3.85%.  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **19**: pale yellow crystals, mp 205 °C (decomp.);  $\delta_H$  2.90 (1H, s), 3.54 (1H, ddd,  $J = 7.7, 2.2, 1.8$  Hz), 3.85 (1H, dd,  $J = 2.2, 1.5$  Hz), 5.23 (1H, s), 5.40 (1H, s), 5.44 (1H, d,  $J = 1.8$  Hz), 5.51 (1H, d,  $J = 1.5$  Hz), 6.60 (1H, dd,  $J = 11.3, 7.7$  Hz), 6.74 (1H, d,  $J = 11.3$  Hz), and 7.27–7.49 (8H, m);  $\delta_C$  56.2, 61.7, 61.9, 66.1, 82.3, 83.0, 83.1, 83.2, 119.7, 121.0, 121.5, 123.5, 125.6, 127.0, 128.2, 129.0, 129.1, 136.3, 137.4, 141.4, 142.0, 142.9, 143.0, 163.5, 199.6, and 199.8; IR (KBr) 1703, 1593, 1461, 1416, 1343, 1292, 1237, 1205, 1151, 1087, 1016, 974, 861, and 822  $cm^{-1}$ ; UV (MeOH) 257.4 nm ( $\epsilon$  5350), 277.3 (5100), 295.5 (4120, sh), and 320.3 (2860) [Found: C, 65.80; H, 6.83%. Calcd for  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

Adduct **20**: pale yellow crystals, mp 220 °C (decomp.);  $\delta_H$  2.86 (1H, s), 3.57 (1H, ddd,  $J = 7.7, 2.2, 1.8$  Hz), 3.81 (1H, dd,  $J = 2.2, 1.5$  Hz), 5.40 (1H, s), 5.45 (1H, d,  $J = 1.5$  Hz), 5.50 (1H, s), 5.51 (1H, d,  $J = 1.8$  Hz), 6.59 (1H, dd,  $J = 11.4, 7.7$  Hz), 6.71 (1H, d,  $J = 11.4$  Hz), and 7.25–7.49 (8H, m);  $\delta_C$  55.8, 61.5, 62.1, 65.8, 82.1, 82.9, 83.3, 83.5, 119.7, 121.0, 121.6, 123.5, 125.7, 127.0, 128.2, 129.0, 129.1, 136.3, 137.5, 141.7, 141.8, 142.8, 143.1, 163.6, 199.4, and 199.8; IR (KBr) 1724, 1701, 1591, 1460, 1420, 1346, 1228, 1203, 1169, 1154, 1090, 1022, 971, 882, and 859  $cm^{-1}$ ; UV (MeOH) 252.0 nm ( $\epsilon$  5020), 280.3 (4690), 293.6 (4130, sh), and 319.5 (2880) [Found: C, 65.90; H, 3.58%. Calcd for  $C_{26}H_{17}BrO_4$ : C, 65.98; H, 3.62%].

### Thermal reaction of azulene-1,5-quinone with 1,3-diphenylisobenzofuran

A dichloroethane solution (15  $cm^3$ ) of azulene-1,5-quinone (8 mg) and 1,3-diphenylisobenzofuran (25 mg) was heated at 60 °C for 2 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **21** (14 mg, 40%) and **22** (1 mg, 5%).

Adduct **21**: colorless crystals, mp 117–118 °C (lit.,<sup>3</sup> mp 139–140 °C);  $\delta_H$  3.07 (1H, d,  $J = 6.2$  Hz), 3.45 (1H, d,  $J = 6.2$  Hz), 3.83 (1H, dd,  $J = 7.3, 1.8$  Hz), 4.12 (1H, dd,  $J = 1.8$  Hz), 5.42 (1H, dd,  $J = 11.4, 7.3$  Hz), 5.86 (1H, d,  $J = 11.4$  Hz), 6.68 (1H, d,  $J = 7.0$  Hz), and 7.0–8.1 (27H, m); IR (KBr) 1703, 1659, 1605, 1498, 1459, 1307, 1277, 1157, 1021, 1000, 937, and 859  $cm^{-1}$ ; UV (MeOH) 215.2 nm ( $\epsilon$  48920, sh), 245.3 (19910, sh), 291.2 (6740, sh), and 324.2 (4650) [Found (FAB MS): 699.2539. Calcd for  $C_{50}H_{34}O_4$ : 699.2537].

Adduct **22**: colorless oil;  $\delta_H$  4.15 (1H, d,  $J = 8.4$  Hz), 4.83 (1H, dd,  $J = 8.4, 1.1$  Hz), 6.86 (1H, d,  $J = 6.2$  Hz), 7.01–7.11 (6H, m), 7.43–7.60 (7H, m), and 7.85–8.00 (4H, m);  $\delta_C$  52.0, 59.6, 91.2, 92.5, 120.8, 122.4, 127.3 (2C), 127.4, 127.6, 128.5 (4C), 128.6, 129.1 (2C), 129.6, 133.0, 134.5, 134.9, 136.7, 137.8, 141.7, 143.2, 145.7, 147.5, 151.5, 185.7, and 200.8.

### Thermal reaction of azulene-1,7-quinone with 1,3-diphenylisobenzofuran

A dichloroethane solution (15  $cm^3$ ) of azulene-1,7-quinone

(8 mg) and 1,3-diphenylisobenzofuran (25 mg) was heated at 60 °C for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **23** (16.2 mg, 46%) and **24** (6.2 mg, 17%).

Adduct **23**: colorless crystals, mp 173–175 °C;  $\delta_{\text{H}}$  3.58 (1H, d,  $J = 6.6$  Hz), 3.83 (1H, d,  $J = 2.2$  Hz), 3.88 (1H, dd,  $J = 7.0, 2.2$  Hz), 4.52 (1H, dd,  $J = 6.6$  Hz), 5.76 (1H, dd,  $J = 11.4, 7.0$  Hz), 6.08 (1H, d,  $J = 11.4$  Hz), and 6.08–7.85 (28H, m);  $\delta_{\text{C}}$  54.3, 57.1, 58.4, 62.7, 90.1, 90.2, 90.6, 91.1, 120.8, 120.9, 121.1, 121.5, 124.9 (2C), 125.7, 125.9 (2C), 127.4 (4C), 128.0 (2C), 128.1, 128.2, 128.3 (2C), 128.7 (2C), 128.8 (2C), 128.9 (2C), 129.0 (3C), 129.3, 133.1, 135.1, 135.6, 137.3, 137.6, 138.6, 142.1, 143.6, 143.9, 144.6, 164.2, 199.7, and 201.0; IR (KBr) 1726, 1695, 1589, 1459, 1448, 1352, 1334, 1288, 1246, 1204, 1157, 1090, 1024, 910, and 862  $\text{cm}^{-1}$ ; UV (MeOH) 216.3 nm ( $\epsilon$  14070, sh), 255.5 (2610), 298.6 (1820), and 323.2 (1455) [Found (FAB MS): 699.2517. Calcd for  $\text{C}_{50}\text{H}_{35}\text{O}_4$ : 699.2533].

Adduct **24**: colorless crystals, mp 228–229 °C (lit.,<sup>3</sup> mp 122–124 °C);  $\delta_{\text{H}}$  3.02 (1H, d,  $J = 5.5$  Hz), 3.39 (1H, d,  $J = 5.5$  Hz), 3.78 (1H, dd,  $J = 7.7, 1.8$  Hz), 4.35 (1H, d,  $J = 1.8$  Hz), 5.25 (1H, dd,  $J = 11.4, 7.7$  Hz), 5.60 (1H, d,  $J = 11.4$  Hz), and 6.99–7.72 (28H, m);  $\delta_{\text{C}}$  55.8, 58.0 (2C), 63.5, 88.8, 89.3, 89.6, 91.1, 119.0, 120.0, 120.9, 121.0, 121.7, 125.0 (2C), 125.6 (2C), 126.3 (2C), 126.5, 127.0, 127.2 (2C), 127.6, 127.8 (2C), 127.9 (2C), 128.1, 128.2 (2C), 128.3 (2C), 128.5 (2C), 128.7, 129.0, 132.2, 134.5, 135.2, 135.5, 137.6, 138.6, 143.4, 144.7, 146.5, 147.9, 162.1, 199.2, and 202.6; IR (KBr) 1689, 1657, 1589, 1450, 1333, 1267, 1216, 1084, 1020, 900, and 862  $\text{cm}^{-1}$  [Found (FAB MS): 699.2473. Calcd for  $\text{C}_{50}\text{H}_{35}\text{O}_4$ : 699.2533].

#### Thermal reaction of 3-bromoazulene-1,5-quinone with isobenzofuran

To a dichlorobenzene solution (15  $\text{cm}^3$ ) of 3-bromoazulene-1,5-quinone (14 mg) was added dropwise a dichlorobenzene solution of **12** (80 mg) at 165 °C under an  $\text{N}_2$  stream and the reaction mixture was kept for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **25** (16.8 mg, 48%) and **26** (10 mg, 29%).

Adduct **25**: colorless crystals, mp 165–168 °C;  $\delta_{\text{H}}$  3.20 (1H, dt,  $J = 7.3, 1.8$  Hz), 3.38 (1H, dd,  $J = 1.8, 1.5$  Hz), 3.61 (1H, t,  $J = 6.2$  Hz), 4.00 (1H, t,  $J = 6.2$  Hz), 5.35 (1H, d,  $J = 1.8$  Hz), 5.58 (2H, m), 5.61 (1H, s), 5.75 (1H, dd,  $J = 11.4, 7.3$  Hz), 5.97 (1H, d,  $J = 11.4$  Hz), and 7.03–7.44 (8H, m);  $\delta_{\text{C}}$  49.6, 53.6, 60.8, 63.5, 80.1, 80.9, 82.7, 84.5, 120.7, 120.8, 120.9, 121.1, 122.2, 127.4, 127.5, 127.7, 128.9, 129.2, 139.4, 140.3, 140.5, 141.2, 141.9, 159.8, 198.6, and 202.5; IR (KBr) 1702, 1611, 1461, 1408, 1350, 1310, 1279, 1255, 1211, 1155, 1133, 1012, 975, 854, and 820  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 395 ( $\text{M}^+ + 1, 4$ ), 394 ( $\text{M}^+, 7$ ), 209 (2), 185 (3), 153 (2), 149 (8), 132 (16), 131 (56), 119 (20), 118 (100), 105 (10), 97 (11), 85 (13), 83 (22), and 57 (19); UV (MeOH) 216.8 nm ( $\epsilon$  18790, sh), 267.2 (3940), 273.9 (3935), 289.4 (2380, sh), and 318.2 (1210, sh) [Found: C, 79.20; H, 4.54%. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4$ : C, 79.17; H, 4.60%].

Adduct **26**: colorless crystals, mp 276–278 °C;  $\delta_{\text{H}}$  2.78 (1H, d,  $J = 5.1$  Hz), 3.14 (1H, d,  $J = 5.1$  Hz), 3.46 (1H, dt,  $J = 7.7, 1.8$  Hz), 3.70 (1H, t,  $J = 1.8$  Hz), 5.29 (1H, s), 5.50 (2H, d,  $J = 1.8$  Hz), 5.58 (1H, d,  $J = 1.5$  Hz), 6.06 (1H, dd,  $J = 11.4, 7.7$  Hz), 6.56 (1H, d,  $J = 11.4$  Hz), and 7.22–7.50 (8H, m);  $\delta_{\text{C}}$  50.0, 52.8, 59.8, 62.1, 78.9, 80.2, 81.9, 83.5, 118.6, 118.9, 120.2, 120.3, 120.6, 126.1, 126.5, 127.0, 128.0, 128.2, 140.4, 140.9 (2C), 143.2, 144.2, 159.8, 198.8, and 202.6; IR (KBr) 1707, 1620, 1459, 1410, 1351, 1307, 1199, 1161, 1012, 971, 855, and 821  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 395 ( $\text{M}^+ + 1, 1$ ), 394 ( $\text{M}^+, 2$ ), 276 (2), 189 (4), 165 (3), 131 (9), 119 (24), 118 (100), 90 (10), and 63 (3); UV (MeOH) 216.3 nm ( $\epsilon$  26975, sh), 266.7 (660), 273.4 (6920), 288.3 (5290, sh), and 312.8 (3240, sh) [Found: C, 79.19; H, 4.46%. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4$ : C, 79.17; H, 4.60%].

#### Thermal reaction of 3-bromoazulene-1,7-quinone with isobenzofuran

To a dichlorobenzene solution (5  $\text{cm}^3$ ) of 3-bromoazulene-1,7-quinone (6 mg) was added dropwise a dichlorobenzene solution of **12** (40 mg) at 165 °C under a  $\text{N}_2$  stream and the reaction mixture was kept at that temperature for 4 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **27** (2 mg, 13%), **28** (3.1 mg, 21%), and **29** (6.6 mg, 45%).

Adduct **27**: colorless crystals, mp 242–244 °C;  $\delta_{\text{H}}$  2.98 (1H, t,  $J = 2.2$  Hz), 3.25 (1H, dm,  $J = 6.6$  Hz), 3.58 (1H, t,  $J = 6.2$  Hz), 3.96 (1H, dd,  $J = 6.2, 5.5$  Hz), 5.18 (1H, d,  $J = 1.5$  Hz), 5.34 (1H, d,  $J = 1.5$  Hz), 5.52 (1H, d,  $J = 5.5$  Hz), 5.58 (1H, d,  $J = 6.2$  Hz), 6.26 (1H, d,  $J = 11.4$  Hz), 6.32 (1H, dd,  $J = 11.4, 6.6$  Hz), and 6.86–7.24 (8H, m);  $\delta_{\text{C}}$  50.7, 53.1, 55.1, 61.4, 80.3, 80.8, 82.9, 83.2, 119.5, 120.7, 120.8, 121.4, 126.5, 127.4, 127.7, 128.7, 128.8, 133.2, 136.3, 140.3, 140.8, 141.2, 141.9, 163.4, 198.8, and 202.4; IR (KBr) 1721, 1694, 1597, 1461, 1419, 1345, 1314, 1277, 1238, 1209, 1195, 1152, 1118, 1087, 1020, 977, 930, 863, 853, and 820  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 395 ( $\text{M}^+ + 1, 4$ ), 394 ( $\text{M}^+, 8$ ), 277 (22), 276 (57), 248 (18), 247 (17), 219 (11), 202 (17), 191 (18), 190 (21), 189 (30), 165 (17), 117 (17), and 89 (59); UV (MeOH) 254.1 nm ( $\epsilon$  5890), 275.2 (5790), 296.5 (5460), and 319.2 (4480, sh) [Found: C, 78.92; H, 4.77%. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4$ : C, 79.17; H, 4.60%].

Adduct **28**: colorless crystals, mp 191–194 °C;  $\delta_{\text{H}}$  3.26 (1H, dd,  $J = 2.2, 1.5$  Hz), 3.33 (1H, ddm,  $J = 2.2, 1.5$  Hz), 3.55 (1H, t,  $J = 6.2$  Hz), 3.84 (1H, ddd,  $J = 6.6, 6.2, 1.5$  Hz), 4.07 (1H, d,  $J = 1.5$  Hz), 5.20 (1H, d,  $J = 1.5$  Hz), 5.58 (1H, d,  $J = 6.2$  Hz), 5.61 (1H, d,  $J = 6.2$  Hz), 6.28 (2H, m), and 6.86–7.24 (8H, m);  $\delta_{\text{C}}$  50.9, 52.8, 55.2, 61.6, 80.2, 80.8, 82.4, 82.7, 120.4, 120.9, 121.2, 121.3, 126.5, 126.8, 127.9, 128.6, 128.8, 133.8, 136.4, 140.9, 141.1, 141.3, 142.5, 163.2, 200.9, and 202.6; IR (KBr) 1727, 1687, 1588, 1464, 1417, 1347, 1310, 1281, 1253, 1206, 1155, 1116, 1085, 1017, 975, 930, 853, and 820  $\text{cm}^{-1}$ ; UV (MeOH) 256.2 nm ( $\epsilon$  2670), 275.5 (2850), 297.0 (2710), and 319.8 (2030, sh) [Found: C, 76.22; H, 4.40%. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4$ : C, 79.17; H, 4.60%].

Adduct **29**: colorless crystals, mp 245–247 °C;  $\delta_{\text{H}}$  2.69 (1H, d,  $J = 5.5$  Hz), 3.01 (1H, dd,  $J = 5.5, 1.5$  Hz), 3.51 (1H, ddd,  $J = 7.3, 2.2, 1.5$  Hz), 3.77 (1H, dd,  $J = 2.2, 1.5$  Hz), 5.33 (1H, s), 5.44 (1H, d,  $J = 1.5$  Hz), 5.48 (1H, d,  $J = 1.5$  Hz), 5.54 (1H, s), 6.47 (1H, dd,  $J = 11.4, 7.3$  Hz), 6.55 (1H, d,  $J = 11.4$  Hz), and 7.20–7.42 (8H, m);  $\delta_{\text{C}}$  52.5, 53.2, 56.2, 61.7, 80.0, 81.4, 83.1 (2C), 119.5, 120.0, 121.0, 121.6, 127.2, 127.4, 128.8, 129.0, 136.0, 136.4 (2C), 141.5, 142.3, 144.3, 145.4, 164.3, 200.9, and 202.6; IR (KBr) 1719, 1688, 1595, 1460, 1343, 1239, 1205, 1151, 1084, 1016, 977, 942, and 856  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 394 ( $\text{M}^+, 0.6$ ), 276 (7), 248 (8), 247 (9), 219 (11), 202 (22), 191 (29), 190 (32), 189 (46), 165 (36), 164 (13), 131 (15), 119 (66), 117 (70), 115 (27), 90 (100), and 63 (3); UV (MeOH) 256.5 nm ( $\epsilon$  5830, sh), 274.7 (5840), 295.2 (5160), and 319.8 (3820, sh) [Found: C, 68.87; H, 4.88%. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4$ : C, 79.17; H, 4.60%].

#### Thermal reaction of 3-bromoazulene-1,5-quinone with cycloheptatriene

A xylene solution of 3-bromoazulene-1,5-quinone (24 mg) cycloheptatriene (13 mg) was heated at 120 °C for 24 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **30** (12 mg, 36%).

Adduct **30**: colorless crystals, mp 132–134 °C;  $\delta_{\text{H}}$  2.08 (1H, ddd,  $J = 14.7, 4.4, 2.9$  Hz), 2.17 (1H, ddd,  $J = 14.7, 3.3, 2.9$  Hz), 2.43 (1H, dt,  $J = 7.0, 3.3$  Hz), 2.49 (1H, t,  $J = 7.0$  Hz), 2.73–2.77 (1H, br m), 2.9–3.1 (3H, m), 5.52 (1H, dd,  $J = 9.5, 0.7$  Hz), 6.03 (1H, dd,  $J = 9.2, 7.0$  Hz), 6.16 (1H, t,  $J = 9.5$  Hz), 6.27 (1H, dd,  $J = 9.2, 7.3$  Hz), and 6.65 (1H, s);  $\delta_{\text{C}}$  26.3, 32.9, 33.5, 40.8, 50.5, 51.4, 52.8, 64.2, 64.3, 128.5, 128.7, 129.0, 132.1, 136.4, 169.2, 205.1, and 211.2; IR (KBr) 1744, 1702, 1560, 1428, 1298, 1257,

1165, 1070, 974, 899, and 862  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 330 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 7), 328 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 13), 239 (6), 237 (7), 202 (12), 191 (16), 190 (24), 189 (35), 178 (44), 165 (21), 115 (32), 114 (20), 102 (81), 101 (60), 95 (29), 94 (16), 93 (50), 90 (100), 89 (31), and 75 (15); UV (MeOH) 254.1 nm ( $\epsilon$  2460, sh) and 319.8 (350, sh) [Found: C, 61.88, H, 4.06%. Calcd for  $\text{C}_{17}\text{H}_{13}\text{BrO}_2$ : C, 62.03, H, 3.98%].

### Thermal reaction of 3-bromoazulene-1,7-quinone with cycloheptatriene

A xylene solution of 3-bromoazulene-1,7-quinone (48 mg) cycloheptatriene (25 mg) was heated at 120 °C for 36 h. After the solution was evaporated under reduced pressure, the residue was chromatographed on a silica-gel column to give **33** (8 mg, 12%), **34** (5 mg, 7%) and **35** (13 mg, 26%).

Adduct **33**: colorless crystals, mp 137–138 °C;  $\delta_{\text{H}}$  2.12 (1H, ddm,  $J = 14.6$ , 2.9 Hz), 2.20 (1H, ddm,  $J = 14.6$ , 2.6 Hz), 2.44 (1H, dd,  $J = 7.0$ , 3.3 Hz), 2.74–2.79 (1H, br m), 2.90 (1H, t,  $J = 7.0$  Hz), 2.98 (1H, ddm,  $J = 7.3$ , 4.0 Hz), 3.07 (1H, ddm,  $J = 4.0$ , 1.5 Hz), 5.77 (1H, dd,  $J = 9.9$ , 0.7 Hz), 5.93 (1H, dd,  $J = 9.9$ , 7.3 Hz), 6.13 (1H, t,  $J = 9.5$  Hz), 6.29 (1H, dd,  $J = 9.5$ , 7.3 Hz), and 6.58 (1H, s);  $\delta_{\text{C}}$  26.4, 32.6, 35.5, 40.4, 42.5, 49.8, 50.4, 62.5, 64.5, 127.6, 127.7, 129.5, 129.8, 135.0, 163.4, 202.6, and 211.1; IR (KBr) 1738, 1697, 1576, 1425, 1391, 1357, 1270, 1258, 1159, 1095, 1032, 944, 899, and 847  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 330 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 9), 328 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 10), 239 (3), 237 (6), 222 (32), 221 (74), 205 (13), 203 (17), 193 (34), 192 (12), 179 (14), 178 (40), 165 (6), 115 (10), 105 (49), 104 (17), 95 (16), 92 (100), and 83 (6); UV (MeOH) 236 nm ( $\epsilon$  11100) [Found: C, 61.77; H, 4.23%. Calcd for  $\text{C}_{17}\text{H}_{13}\text{BrO}_2$ : C, 62.03; H, 3.98%].

Adduct **34**: colorless crystals, mp 115–117 °C;  $\delta_{\text{H}}$  2.32 (1H, d,  $J = 16.9$  Hz), 2.44 (1H, d,  $J = 9.2$  Hz), 2.94 (1H, d,  $J = 7.7$  Hz), 3.01 (1H, d,  $J = 16.9$  Hz), 3.12 (1H, t,  $J = 8.1$  Hz), 3.28 (1H, dd,  $J = 8.1$ , 1.5 Hz), 3.35 (1H, dd,  $J = 9.5$ , 1.8 Hz), 5.12 (1H, dd,  $J = 9.5$ , 7.0 Hz), 6.01 (1H, ddd,  $J = 8.4$ , 8.1, 0.7 Hz), 6.12 (1H, d,  $J = 7.0$  Hz), 6.25 (1H, dd,  $J = 9.5$ , 7.7 Hz), 6.44 (1H, s), and 6.64 (1H, dd,  $J = 8.4$ , 7.0 Hz);  $\delta_{\text{C}}$  36.9, 38.9, 39.8, 41.5, 45.0, 55.1, 56.6, 126.8, 130.3, 130.5, 133.2, 138.9, 141.8, 148.3, 152.7, 201.9, and 209.9; IR (KBr) 1703, 1575, 1528, 1412, 1362, 1335, 1280, 1260, 1146, 1030, 985, 887, and 861  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 330 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 10), 328 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 11), 328 (11), 221 (27), 190 (15), 189 (28), 179 (47), 178 (100), 177 (27), 165 (46), 164 (18), 152 (39), 151 (24), 150 (15), 149 (24), 129 (19), 115 (76), 114 (24), 102 (25), 101 (19), 92 (65), 90 (85), and 89 (23); UV (MeOH) 237.8 nm ( $\epsilon$  6310, sh) and 287.2 (4920) [Found: C, 62.31; H, 4.17%. Calcd for  $\text{C}_{17}\text{H}_{13}\text{BrO}_2$ : C, 62.03; H, 3.98%].

Adduct **35**: yellow crystals, mp 200 °C;  $\delta_{\text{H}}$  (benzene- $d_6$ ) 1.71 (2H, d,  $J = 3.3$  Hz), 2.71–2.77 (1H, m), 3.96 (1H, td,  $J = 6.6$ , 1.5 Hz), 5.44 (1H, d,  $J = 8.4$  Hz), 5.84 (2H, dd,  $J = 7.7$ , 6.6 Hz), 6.05 (1H, dd,  $J = 12.5$ , 8.4 Hz), 6.17 (2H, dd,  $J = 7.7$ , 6.6 Hz), 6.56 (1H, dd,  $J = 12.5$ , 2.9 Hz), and 7.36 (1H, d,  $J = 2.9$  Hz);

$\delta_{\text{C}}$  (benzene- $d_6$ ) 25.7, 31.8, 34.2, 119.3, 131.1, 132.7, 134.5, 136.0, 136.9, 138.7, 143.1, 145.7, 159.3, 187.4, and 190.4; IR (KBr) 1701, 1650, 1628, 1583, 1544, 1435, 1397, 1315, 1261, 1190, 1078, 922, and 850  $\text{cm}^{-1}$ ; MS  $m/z$  (%): 249 ( $\text{M}^+ + 1$ , 7), 248 ( $\text{M}^+$ , 15), 220 (100), 219 (60), 192 (56), 191 (84), 190 (32), 189 (32), 165 (37), 115 (19), 95 (28), 94 (14), 89 (11), 83 (19), and 82 (18); UV (MeOH) 234 nm ( $\epsilon$  13130), 288.2 (8740), 316.6 (6760, sh), 339.0 (5520, sh), 358.7 (4000, sh), and 400.5 (1990, sh) [Found: C, 81.88; H, 4.66%. Calcd for  $\text{C}_{17}\text{H}_{12}\text{O}_2$ : C, 82.24; H, 4.87%].

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