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Low and high temperature bromination of 2,3-dicarbomethoxy and 2,3-dicyano benzobarrelene: unexpected substituent effect on bromination†

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The bromination of 2,3-dicarbomethoxy benzobarrelene yielded the dibromide regio- and stereospecifically arising from the aryl shift where the bromine exclusively attacks the double bond from the *exo* face of the double bond. High temperature bromination of this compound yielded aryl-shift products. From the low temperature bromination of 2,3-dicyano benzobarrelene, non-rearranged products were obtained along with the rearranged products. Surprisingly, we observed that the yield of non-rearranged products decreased on increasing the temperature. A possible role of the substituent was discussed using DFT calculations on model compounds.

Introduction

Electrophilic bromination of simple olefins has been extensively studied within the last two decades. In general, the reaction is stereoselective and leads to *trans*-1,2-dibromides *via* a three-membered bromonium intermediate.[1] The bromination of unsaturated bicyclic systems with molecular bromine leads to rearrangements of the molecular skeleton.[2] For example, bromination of benzobarrelene (**1**) at 10 °C gives only rearranged products.[2b] No trace of non-rearranged products was observed from this reaction. While studying the bromination reaction, it was noticed that the reaction temperature has a dramatic influence on the product distribution. The bromination reaction of benzobarrelene (**1**) at 77 °C results in the formation of non-rearranged products in 15% yield, whereas increasing temperature to 150 °C allowed formation of non-rearranged products up to 50% yield *via* radical intermediates.[2a] An electronegative bromine atom substituted on the olefin also directs the reaction. For example, bromination of tribromobenzobarrelene (**3**) gives only non-rearranged products, even at room temperature,[3] whereas bromination of 2,3-dibromobenzoberelene (**2**) requires higher temperatures to obtain non-rearranged products.[2d,e] Reaction of **2** with bromine at 77 °C mainly gives non-rearranged products up to 78% yield.[2d,e] Similar to related compounds,[2,4] these results show that attachment of an additional bromine atom to the double bond leads to an increase in the amount of the non-rearranged products from 0% (in the case of **1**) up to 100% (in the case of **3**). The temperature employed to prevent skeletal rearrangement during bromination depends on the substituent condensed to benzobarrelene. In this paper, we report on the bromination reaction of benzobarrelene derivatives (**4** and **5**) which have substituents which are highly electron-withdrawing *via* inductive and mesomeric effects (Fig. 1).

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Results and discussion

Synthesis of starting materials 4 and 5

Firstly, the starting materials **4** and **5** were prepared according to the published method. The Diels–Alder cycloaddition reaction of naphthalene (**6**) with dimethyl acetylene dicarboxylate (**7**) at 160 °C gave 2,3-dicarbomethoxy benzobarrelene (**4**).[5] The second target compound, **5**,[6] was synthesized by successive replacement of bromine atoms in 2,3-dibromobenzobarrelene (**2**) with nitrile groups by reaction of **2** with cuprous cyanide in dimethylformamide (Scheme 1).

Bromination of 4 and 5 at 25 °C

The electrophilic addition of bromine to 2,3-dicarbomethoxy benzobarrelene (**4**) was performed in chloroform solution at 25 °C. Contrary to the parent molecule **1** and dibromide derivative **2**, which produce complex rearranged product mixtures, the bromination of 2,3-dicarbomethoxy benzobarrelene (**4**) yielded the dibromide regio- and stereospecifically, arising from the aryl shift where the bromine exclusively attacks the double bond from the *exo* face of the double bond, in quantitative yield (Scheme 2).

The bromination reaction of 2,3-dicyanobenzobarrelene (**5**) at the same temperature resulted in the formation of the

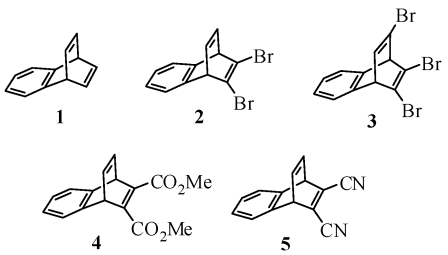
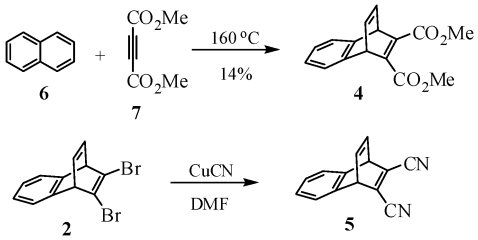
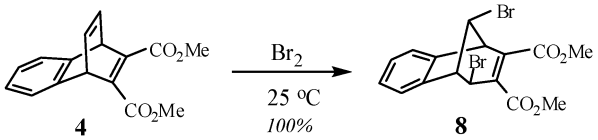


Fig. 1 Structures of benzobarrelene derivatives.



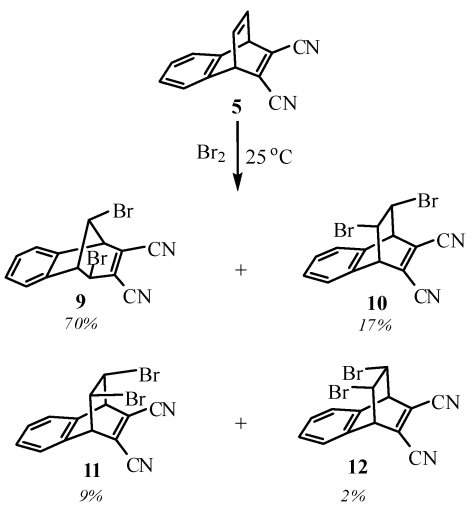
Scheme 1 Synthesis of starting materials.



Scheme 2 Bromination of **4** at 25 °C.

rearranged product **9** and non-rearranged products, *trans*-dibromide **10**, *exo-cis*-dibromide **11** and *endo-cis*-dibromide **12**, in 70, 17, 9 and 2% yields, respectively (Scheme 3).

To rationalize the formation of the isomeric bromides **8–12** formed at 25 °C, we propose the following mechanism by comparing the bromination of **5** with brominations of the parent molecule benzobarrelene (**1**)[2b] and 2,3-dibromobenzobarrelene (**2**)[2d,e] (Scheme 4). Electrophilic bromine can attack the double bond in **1**/**2**/**4**/**5** from both the *exo* and *endo* faces of the double bond to form the cyclic bromonium ions **13–16** and **17–20**, respectively. The ions **13–20** can be trapped by the bromide anion to give the *trans* addition products **10**/**34–36**. The bromide anion can attack the carbon atom C1 in **21–24** to form the rearranged dibromides **8**/**9**/**25–30** and the carbon atom C2 from the *exo* side to form *exo-cis* products **11**/**31–33**. The *endo*-bromonium ions **17–20** follow a similar course to generate the non-classical carbocations **37–40**. The bromide anion can attack the carbon atom C1 in **37–40** to form the rearranged dibromides **41–48**, the carbon atom C4 to form the cyclopropanoid dibromides **49–56** and the carbon atom C2 from *endo* side to form *endo-cis* products (**12**/**57–59**).



Scheme 3 Bromination of **5** at 25 °C.

In the bromination of benzobarrelene (**1**), it was observed that the ratio of products obtained *via* the *exo*-bromonium ion **13** to products obtained *via* the *endo*-bromonium ion **17** is approximately 4 : 1. This is evidently due to the higher rate of the formation of ion **13**, which is stabilized by the π participation of the aromatic ring (ion **21**). Such participation is significantly more effective than the participation of the double bond, as in ion **37**. In the case of 2,3-dibromobenzobarrelene (**2**), we found that the ratio of the products formed from the *exo* ion **14** and the products formed from the *endo* ion **18** amounts to ~6 : 1.[2d,e] In the present work, we observed that during the bromination of **4**, only the *exo* bromonium ion **15** is formed and the reaction results in the formation of only dibromide **8** in quantitative yield. These differences result from the fact that the intermediate **19** (and ion **39**) is less favourable because of the strongly electron-withdrawing ester group at the double bond in molecule **4**. Similarly, the bromination reaction of nitrile derivative **5** mainly gives product **9***via* the *exo*-bromonium ion **16**. No trace of alkyl migration products **45–48** and cyclopropanoid compounds such as **53–56** is observed in these reactions. Unlike benzobarrelene derivatives **1**, **2** and **4**, the reaction of **5** with bromine at 25 °C results in the formation of non-rearranged products **10–12** in a total yield of 28%. The formation of *cis* products **11** and **12** is also straightforward. It is likely that these compounds were formed by the opening of the intermediates such as **24** and **40** (Scheme 4).

The structures and relative stabilities of possible cation intermediates of the addition reactions of bromine with 2,3-dicarbomethoxy benzobarrelene (**4**) at low temperatures have been determined by carrying out geometrical optimizations using DFT/B3LYP (density functional theory with B3LYP—the hybrid Becke's three parameter functional and Lee–Yang–Parr exchange–correlation potential)[8] method with the 6-311 + G(d,p)[9] basis set and the total energies (E_{tot}) have been calculated. Solvent effects were calculated on the basis of the same theory as the optimizations were performed by single-point calculations on the optimized structures using the CPCM (conducting polarized continuum model)[10] method (with UAKS cavities[11]) in chloroform (ε = 4.90). All calculations were performed with the GAUSSIAN 03 software on an IBM PC Pentium IV computer.

According to the results of the calculations, the most stable cation of cationic intermediates derived from **15** is the non-classical, delocalized bromocarbonium ion **23** (Scheme 4 and Fig. 2). The non-classical bromocarbonium cation has a stability of 7.691 kcal mol^{-1} (B3LYP/6-311 + G(d,p)) and 7.868 kcal mol^{-1} (CPCM-B3LYP/6-311 + G(d,p)//B3LYP/6-311 + G(d,p)) and is more stable than the *exo*-bridged-bromonium cation **15**. The skeletal isomerization of the *exo*-bromonium cation **15** into the non-classical bromocarbonium cation **23** is thermodynamically feasible. In the non-classical bromocarbonium ion **23**, the positive charge is partially transferred to the benzene ring and the ion becomes more stable due to the overlapping of the π orbitals of the aromatic ring. The lengths of the C1–C2, C1–C3 and C2–C3 bonds of the non-classical bromocarbonium ion **23** (Fig. 2) optimized by the B3LYP/6-311 + G(d,p) method are 1.441, 1.664 and 1.642 Å, respectively. For the non-classical cation **23**, the C1–C3 bond tends to break, while the C2–C3 bond tends to

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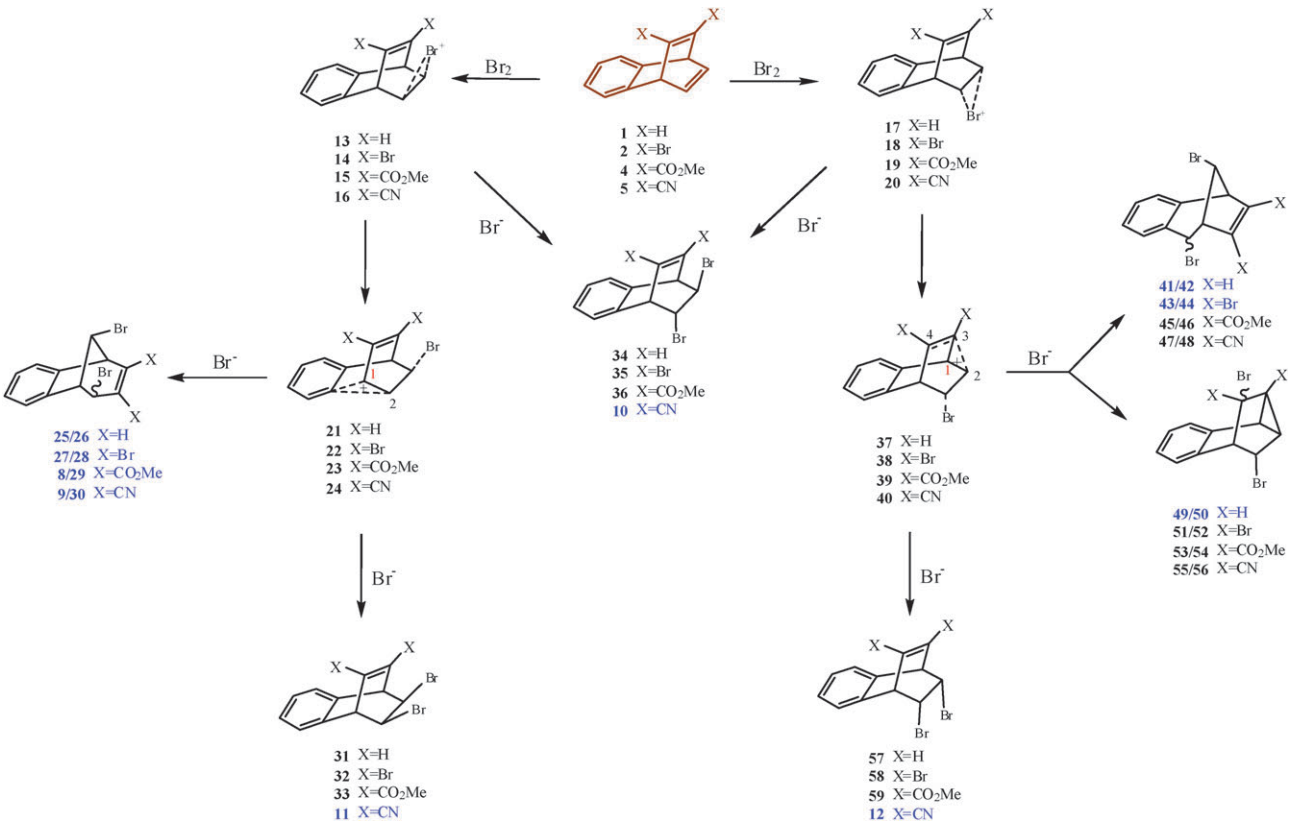

Scheme 4 Mechanism for low temperature bromination of benzobarrelene derivatives.

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form and the C1–C2 bond has a double bond character. In the non-classical ion, both the C1 cation center and carbomethoxy group are located in the same plane (Fig. 2). Interaction between the C1 cation center and the electron cloud of the double bond positively affects the stability of cation **23**. The ionic addition of bromine to 2,3-dicarbomethoxy benzobarrelene (**4**) is predicted to proceed *via* the non-classical bromocarbonium ion **23**. The C1 atom of the non-classical delocalized cation **23** has the maximum positive charge (+0.144 *e*); in other words, because of the aryl shift, the cationic centre is shifted to the C1 atom. Because of the interaction between the C1 cationic centre and the π-electron clouds of the benzene ring, the nucleophilic attack of the initially formed bromide ion (Br^-) at the cationic center occurs from the opposite side of the benzene ring, and only one rearrangement product, *exo*,*anti*-4,8-dibromo-2,3-dicarbomethoxy-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**8**), is formed. In the ionic addition of Br_2 to 2,3-dicarbomethoxy benzobarrelene (**4**), the formation of *endo*,*anti*-4,8-dibromo-2,3-dicarbomethoxy-6,7-benzobicyclo-[3.2.1]octa-2,6-diene (**29**) is not possible due to the electronic interaction (Fig. 2, cation **23**).

The structures and stabilities of cationic intermediates formed in the addition reaction of bromine to 2,3-dicyano-benzobarrelene (**5**) at low temperature have been investigated by the B3LYP/6-311+G(d,p) method. By using the optimized geometries of cations at the B3LYP/6-311+G(d,p) level, their single-point energies have been computed by the CPCM-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) method. The results show that the difference between the total energies of the non-classical (**24**) and *exo*-bromonium (**16**) cations is small. The non-classical cation **24** is more stable than the *exo*-bromonium cation **16**. The lengths of the C1–C2, C1–C3 and C2–C3 bonds (Fig. 2) are 1.450, 1.618 and 1.665 Å, respectively, optimized by the B3LYP/6-311+G(d,p) method in non-classical bromocarbonium cation **24**. For non-classical cation **24**, the C1–C3 bond distance is extended and the C2–C3 distance is shortened. In non-classical cation **24**, the double bond electrons and cyano group electrons are conjugated (Fig. 2). The non-classical cation **24** possesses two effective cationic centers, which are C1(+0.110 *e*) and C2 (+0.090 *e*). As a result of the attack of the bromide (Br^-) ion at the C1 center of the non-classical cation **24**, the weak C1–C3 bond is broken and the C2–C3 bond is formed; thus, *exo*,*anti*-4,8-dibromo-2,3-dicyano-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**9**) is formed as a Wagner–Meerwein rearrangement product. Furthermore, between the C2 cationic center and the π-electron clouds of the benzene ring, nucleophilic attack of the bromide ion at this center occurs on the opposite side of the benzene ring and, thus, *exo-cis* product **11** (Scheme 4) is formed. According to the theoretical results, there is a small difference between the stabilities of the *exo*-bromonium (**16**) and *endo*-bromonium (**20**) cations. The non-rearranged *trans*-adduct **10** is formed *via* the *exo*-bromonium (**16**) and *endo*-bromonium (**20**) ions. The difference between the total energies of the *endo*-bromonium (**20**) and classical bromo-carbonium (**40**) cations is small. The bromide anion can attack the carbon atom C2 in **40** on the *endo* side to form *endo-cis* product **12** (Scheme 4).

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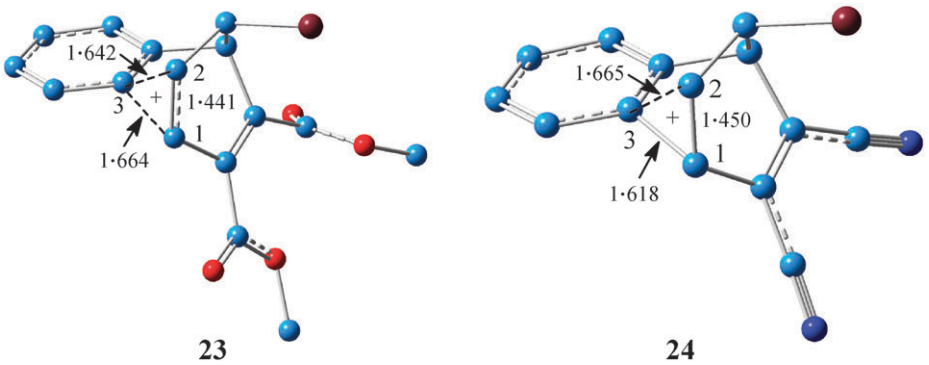


Fig. 2 The optimized geometries of cations (B3LYP/6-311 + G(d,p)) (bond lengths are in Å).

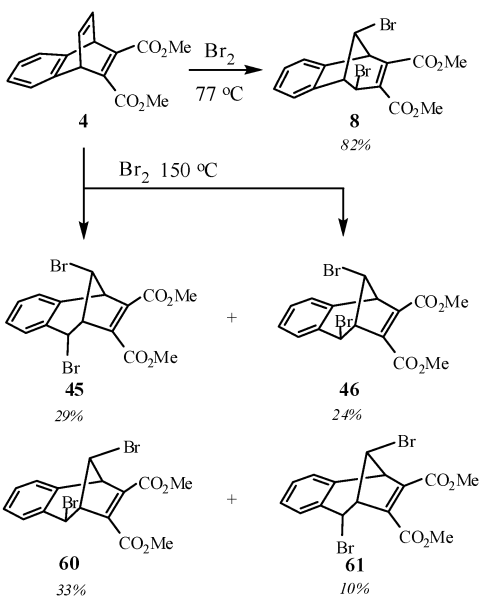
High temperature bromination of 4 and 5

In the following experiments, we aimed to minimize the formation of rearranged products and obtain non-rearranged products in high yield. The reaction of **4** with bromine at 77 °C was investigated. Unlike bromine analogue **2**, from the bromination reaction of **4**, rearranged product **8** was obtained in high yield. This is an unexpected situation because our previous studies and the literature have demonstrated that it is possible to prevent skeletal rearrangement by using high temperature bromination methods. When we tried the reaction at a higher temperature, 150 °C, we unexpectedly observed the formation of vinyl migration products **45**, **46**, **60** and **61**. No trace of non-rearranged products such as **33**/**36**/**59** and aryl-shift products such as **8**/**29** were detected from this reaction (Scheme 5).

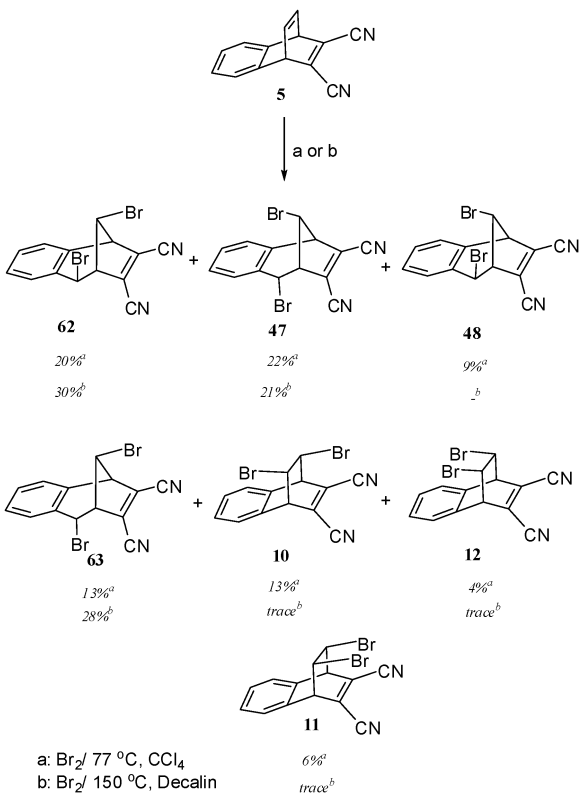
Seeing that bromination of **5** at 25 °C gave non-rearranged products **10–12** in moderate yield, we expected that these would be the major products of the high temperature bromination. Contrary to our expectations, we found that the rate of non-rearranged products **10–12** was decreased on increasing the temperature. From the reaction at 25 °C, dibromides **10–12** are formed in 28% yield, whereas in bromination reactions at 77 and 150 °C, this was determined to be 23% and trace yields, respectively. At a higher temperature of 150 °C, mainly alkyl-shift products **47**, **48**, **62** and **63** were observed (Scheme 6).

To rationalize the formation of the isomeric dibromides formed at a high temperature, we propose the following mechanism by comparing the bromination of **4** and **5** with the bromination of the parent molecule benzobarrelene (**1**)[2b] and 2,3-dibromobenzobarrelene (**2**)[2d,e] (Scheme 7).

The mechanism of bromine addition at higher temperatures is different from the mechanism at low temperatures. We have already demonstrated that at high temperatures, bromine radicals are also involved as well as ionic reactions.[2a,b,4] As is known, the radicals have a very low tendency for rearrangement; however, as we previously demonstrated, rearranged products are also formed *via* radical intermediates in benzobarrelene systems.[2a,b,d,e,7] Yet, bromination of 2,3-dibromobenzobarrelene



Scheme 5 Bromination of **4** at 77 and 150 °C.



Scheme 6 Bromination of **5** at 77 and 150 °C.

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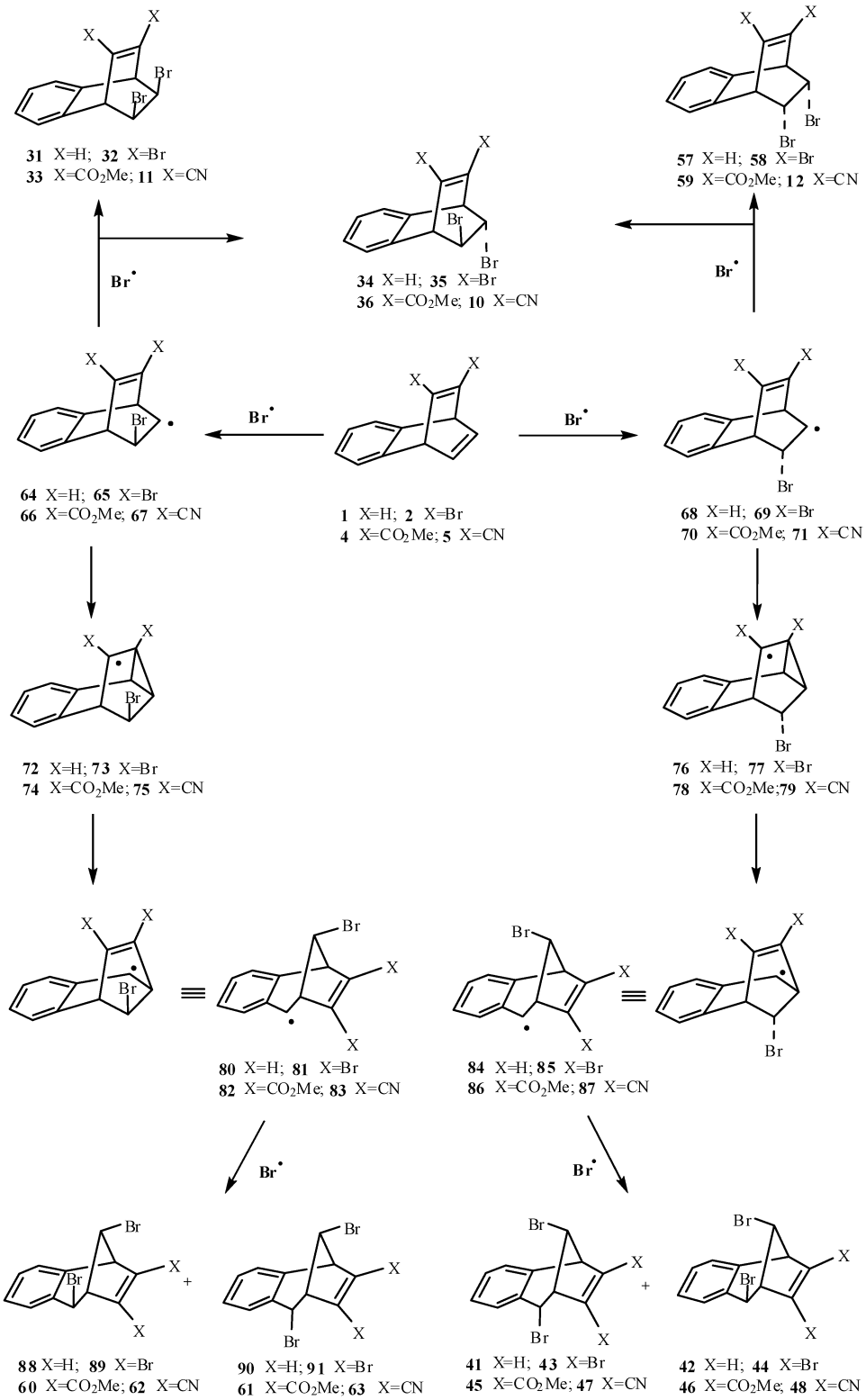

Scheme 7 Reaction mechanism for radical brominations.

(**2**) at 77 °C gives non-rearranged products up to 88% yield.[2d,e] The following question is raised as a result of the present study: why do cyanide and ester derivatives of benzobarrelene behave differently to dibromide derivative **2**? Bromine, cyano and ester groups act as inductively-electron-withdrawing groups. In addition, the bromine atom also acts as a mesomeric electron-donating group. But this cannot account for the different behaviour of the dibromides **4** and **5**. Bordwell and Lynch[12] have calculated the relative radical stabilizing effects of the ester and cyano groups and have shown that the

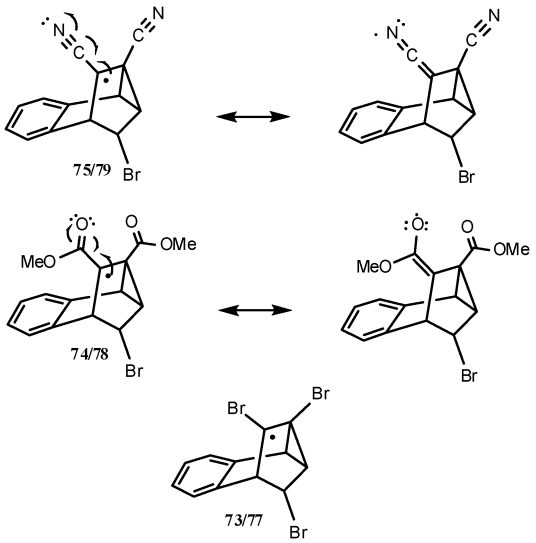

Fig. 3 Stabilization of radicals by the resonance effect.

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resonance stabilization energies are of a size comparable with the methyl group. Balci's studies[6,13] also comply with Bordwell and Lynch's results. We assumed that the differences arise from the stabilization of radicals **74**, **75**, **78** and **79**, which are responsible for the formation of radicals **82**, **83**, **86** and **87**. Since radicals **74**, **75**, **78** and **79** are stabilized by the resonance effect (Fig. 3), the lifetimes of radicals **66**, **67**, **70** and **71** are very short and they rapidly change to more stable radicals (Fig. 3). Radicals **72**/**73** and **76**/**77** are not as stable as radicals **74**, **75**, **78** and **79**; therefore, conversion of radicals **65** and **69** to **81** and **85** is not so fast and radicals **65** and **69** have adequate lifetime to react with a bromine atom to give normal addition products **32**, **35** and **58**.

To find support for this postulate, we carried out some DFT calculations on both possible radical intermediates. The structure and the stability of the predicted radical intermediates (**65**, **69**, **73**, **77**, **81** and **85**, Scheme 7) of bromination reaction of 2,3-dibromo benzobarrelene (**2**) at high temperatures have been determined by carrying out geometrical optimizations using UB3LYP/6-311 + G(d,p) method, which was followed by the calculation of the total energies. According to the results, there is a very small difference between the stabilities of the radicals **65** and **69**. The results obtained by the UB3LYP/6-311 + G(d,p) method indicate that radicals **65** and **69** are more stable than radicals **73** and **77**, respectively. The differences between the total energies of radicals **73** and **65** and of radicals **77** and **69** are 4.558 and 4.913 kcal mol^{-1}, respectively. Therefore, radicals **65** and **69** cannot be converted into the more stable radicals **81** and **85***via* radicals **73** and **77**, respectively. For this reason, radicals **65** and **69** are the essential intermediates in the radicalic addition of bromine to 2,3-dibenzobarrelene (**2**) and the reaction products are predicted to be formed *via* these radicals.

The radical intermediates (**66**, **70**, **74**, **78**, **82** and **86**, Scheme 7) formed in the addition reaction of bromine to 2,3-dicarbomethoxy benzobarrelene (**4**) at high temperatures have been investigated by the UB3LYP/6-311 + G(d,p) method with full geometry optimization and their total energies have been calculated. The results show that the stabilities of radicals **66** and **70** are close to each other. Radicals **74** and **78** have stabilities of 4.747 and 4.641 kcal mol^{-1} and are more stable than radicals **66** and **70**, respectively. Overlapping of p orbitals of the radical centers of **74** and **78** radicals with carbomethoxy group orbitals leads to uncoupled electron delocalization and this increases the stability of the radical (Fig. 4, radical **74**). The radicals **82** and **86** have stabilities of 9.973 and 9.543 kcal mol^{-1} and are more stable than the radicals **66** and **70**, respectively. Therefore, radicals **66** and **70** can be converted to radicals **82** and **86***via* radicals **74** and **78**, respectively. The most stable radicals of the radical intermediates are radicals **82** and **86**. For this reason, radicals **82** and **86** are the essential intermediates in the radicalic addition of bromine to 2,3-dicarbomethoxy benzobarrelene (**4**) and the reaction products are predicted to form *via* these radicals.

The geometrical optimization of radical intermediates (**67**, **71**, **75**, **79**, **83** and **87**, Scheme 7) of bromination reaction of 2,3-dicyano benzobarrelene (**5**) at high temperatures have been determined by the UB3LYP/6-311 + G(d,p) method and their total energies have also been calculated. The results show that radical **67** and radical **71** have almost equal stability. Radicals **75** and **79** have stabilities of 4.986 and 4.922 kcal mol^{-1} and are more stable than radicals **67** and **71**, respectively. Overlapping of p orbitals of radical centers of **75** and **79** radicals with the cyano group π orbitals leads to uncoupled electron delocalization and this increases the stability of the radical (Fig. 4, radical **75**). Moreover, radicals **83** and **87** have stabilities of 10.864 and 10.090 kcal mol^{-1} and are more stable than the radicals **67** and **71**, respectively. Therefore, it is thermodynamically possible that radicals **67** and **71** are converted to radicals **83** and **87***via* radicals **75** and **79**, respectively.

NMR spectral studies and configurational assignments. The structures of these compounds have been elucidated on the basis of ^{1}H and ^{13}C NMR data and extensive double resonance experiments and by comparison with some spectral data of related systems reported in the literature.[2b,d,e,7,14] Below is a summary of the proton coupling constants exhibited by these closely-related [3.2.1]octadienes (structures A and B in Fig. 5).

The coupling patterns that are important for stereochemical characterization of this duo are $J_{8,10syn}$, $J_{8,10anti}$, $J_{8,9exo}$ and $J_{8,9endo}$ in A, and $J_{9,10syn}$, $J_{9,10anti}$, $J_{8exo,9}$ and $J_{8endo,9}$ in B. As a consequence of the rigid geometries and reliability of the Karplus rule[15] in [3.2.1]octane systems,[2b,d,e,7,14] the dihedral relationship of the H8 proton to $H10_{anti}$ in A and the H9 proton to $H10_{syn}$ in B (~40°), and to $H10_{syn}$ in A and to $H10_{anti}$ in B (~80°) is sufficiently distinctive to be revealed by the magnitude of the spin–spin interaction. Thus, the high value of $J_{H10anti}$ in A and J_{H10syn} in B (J = 4.4–4.7) is uniquely accommodated by the *syn*-orientation of the bromine atom in A (*anti*-orientation of bromine in B) bonded to the bridge atom. $H10_{syn}$ in A and $H10_{anti}$ in B give a singlet with line broadening ($J \leq 1$ Hz). The configuration of bromine at the C9 atom in A and at the C8 atom in B were determined from the coupling constants $J_{8,9}$ (in A and in B). Inspection of Dreiding's models indicates that the dihedral angle between protons H8 (H9 in B) and $H9_{exo}$ ($H8_{exo}$ in B) is approximately 40°,

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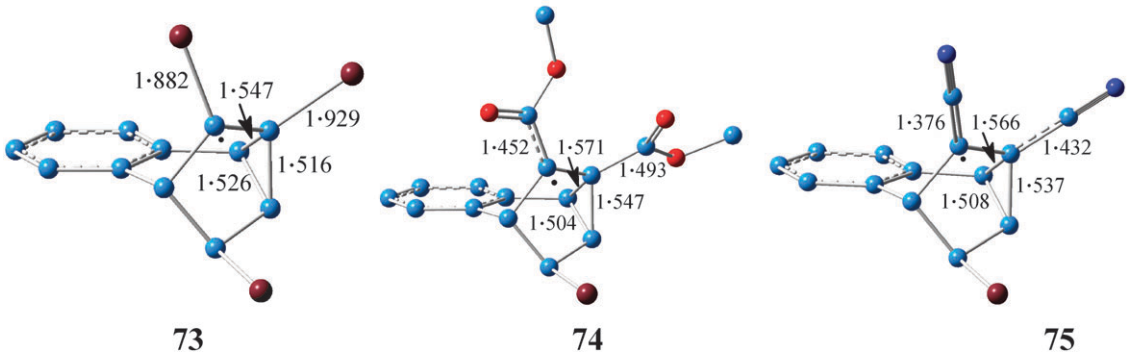

Fig. 4 The optimized geometries of the radicals (UB3LYP/6-311+G(d,p)) (bond lengths are in Å).

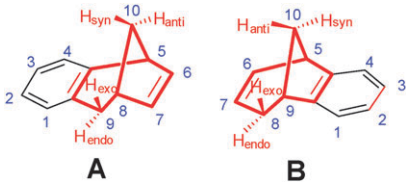

Fig. 5 Representation of numbering of carbons.

whereas the dihedral angle between H8 (H9 in B) and $H9_{endo}$ ($H8_{endo}$ in B) is 60°. Large coupling constants of J = 5.1–5.4 Hz are observed in the case of the *endo*-orientation of bromine (*exo*-proton) and J = 1.0–2.2 Hz in the case of the *exo*-orientation of bromine (*endo*-proton). Aryl-shift products type B and alkyl-shift products type A can also be easily distinguished in the typical pattern of aromatic resonances.[3b] The dibromide **61** formed initially could not be isolated in a pure state because of its instability on the column. The spectral data for the isomer **61** were extracted from the NMR spectra of the mixture. The coupling constant (J = 5.4 Hz) between the protons H8 and H9 shows that the bromine atom attached to carbon C9 is *endo* and that there is no measurable coupling constant between the protons H10 and H5/H8 shows that the bromine atom at carbon C10 is *anti*.

Conclusion

The results of the present work demonstrate that bromination of 2,3-dicarbometohoxy benzaberrelene (**4**) at room temperature resulted in the formation of aryl-shift product **8** in quantitative yield. Increasing the reaction temperature to 150 °C generated alkyl-shift products **45**, **46**, **60** and **61**, instead of the expected non-rearrangement products. Reaction of 2,3-dicyanobenzo-barrelene (**5**) at room temperature mainly yielded aryl-shift product **9**, along with non-rearranged products **10–12**. For the reaction of this compound at higher temperatures, we mainly expected the formation of non-rearrangement products **10–12**. However, we observed that the rate of non-rearrangement products was decreased, while the ratio of aryl-shift products was increased with increasing temperature. In the light of our present and previous results, we conclude that the high-temperature bromination method is a useful synthetic method for generating non-rearranged bromine addition products in norbornene **92** (Fig. 6), benzonorbornadiene **93** and related systems, which have a great tendency to undergo Wagner–Meerwein rearrangement because the bromination reaction is radicalic at high temperatures and the radicals have a very low tendency towards rearrangement. However, in benzobarrelene (**1**) and norbornadiene (**94**) systems, rearrangements occur *via* vinyl–vinyl bridging intermediates under radicalic conditions and benzo-vinyl bridging is not favorable. So, bromination of norbornene and benzonorbornadiene derivatives in radicalic conditions results in the conservation of skeletal rearrangement, while bromination of benzobarrelene and norbornadiene systems in the same conditions also gives rearranged products *via* vinyl–vinyl bridging intermediates. Substituents connected to molecules also direct the reaction. The experimental results were supported by theoretical calculations.

Experimental

General. Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 400 (100)-MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). All substances reported in this paper are in their racemic form.

Caution: it has been reported[16] that of three laboratory workers who have used dibromides and bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders that contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromide derived from benzonorbornadiene there are no toxicological reports in the literature. However, we recommend that the compounds must be handled only with extreme caution.

Bromination of dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (4) at 25 °C. 400 mg (1.48 mmol) 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarboxylate (**4**) was dissolved in 10 mL of dry chlorofom in a 50 mL flask. A

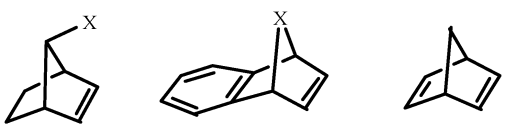

Fig. 6 Norbornene derivatives.

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solution of bromine (249 mg, 1.55 mmol) in 2 mL chlorofom was added dropwise over 1 min at 25 °C. The bromine colour disappeared immediately. The solvent was evaporated and crude product recrystallised from dichloromethane–*n*-hexane (1 : 2) to give dibromide **8** as the sole product (632 mg, 100%). Dimethyl-(5*R*(*S*),8*S*(*R*),9*R*(*S*),10*S*(*R*))-8,10-dibromo-8,9-dihydro-5*H*-5,9-methanobenzo[*a*][7]annulene-6,7-dicarboxylate (**8**). mp: 145–146 °C, yellow crystals [Found: C, 44.21; H, 3.39; requires $C_{16}H_{14}Br_2O_4$: C, 44.68; H, 3.28%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.13 (m, 4H, H_{aryl}), 4.86 (bd, $J_{8,9}$ = 1.5 Hz, 1H, H8), 4.80 (t, $J_{5,10}$ = $J_{9,10}$ = 4.1 Hz, 1H, H10), 4.19 (d, $J_{5,10}$ = 4.1 Hz, 1H, H5), 3.88 (bd, $J_{9,10}$ = 4.1 Hz, 1H, H9), 3.83 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 166.64, 165.65, 146.01, 140.05, 136.99, 134.53, 128.84, 128.75, 124.68, 122.56, 53.05, 52.74, 50.29, 47.66, 45.79, 42.21 ppm. IR (KBr, cm^{-1}): 2947, 2840, 1724, 1460, 1435, 1343, 1272, 1253, 1236, 1152, 1080, 1043, 937, 881, 726.

Bromination of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarbonitrile (5) at 25 °C. 250 mg (1.22 mmol) 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarbonitrile (**5**) was dissolved in 10 ml of dry chloroform in a 50 mL flask. A solution of bromine (205 mg, 1.28 mmol) in 2 ml chloroform was added dropwise over 1 min at 25 °C. The bromine colour disappeared immediately. The solvent was evaporated and crude product was chromatographed on silica gel (30 g) eluting with ethylacetate–*n*-hexane (1 : 9).

Four compounds were isolated:

The first fraction. (1*S*(*R*),4*R*(*S*),9*R*(*S*),10*R*(*S*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**10**). (75 mg, 17%) mp: 147–148 °C, white crystals from dichloromethane–*n*-hexane (1 : 1). [Found : C, 46.34; H, 2.31; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.38 (m, 4H, H_{aryl}), 4.61 (d, $J_{1,10}$ = 2.9 Hz, 1H, H1), 4.43 (d, $J_{4,9}$ = 2.9 Hz, 1H, H4), 4.36 (t, $J_{4,9}$ = $J_{9,10}$ = 2.9 Hz, 1H, H9), 4.03 (t, $J_{1,10}$ = $J_{9,10}$ = 2.9 Hz, 1H, H10) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 134.65, 133.80, 132.75, 130.84, 129.16, 129.02, 127.55, 125.16, 113.55, 112.91, 52.55, 51.55, 50.67, 50.33. IR (KBr, cm^{-1}): 3003, 2964, 2919, 2851, 2224, 1474, 1463, 1259, 1222, 1161, 1022, 856, 772, 735, 596 ppm. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 2), 285/283(M^+, −Br, 8), 203(M^+, −2Br, 16), 178(100), 151(7), 102(3), 88(5).

The second fraction. (1*S*(*R*),4*R*(*S*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**12**). (9 mg, 2%) mp: >300 °C, white crystals from dichloromethane– *n*-hexane (2 : 3). [Found : C, 46.37; H, 2.19; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.36 (AA′BB′ system, 4H, H_{aryl}), 4.57 (AA′ part of AA′BB′ system, 2H, H1 and H4), 4.50 (BB′ part of AA′BB′ system, 2H, H9 and H10) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 133.56, 132.51, 128.65, 127.38, 112.74, 52.14, 47.17 ppm. IR (KBr, cm^{-1}): 2923, 2846, 2218, 1457, 1373, 1206, 1152, 1110, 1068, 913, 748.

The third fraction. (5*R*(*S*),8*S*(*R*),9*R*(*S*),10*S*(*R*))-8,10-dibromo-8,9-dihydro-5*H*-5,9-methanobenzo[*a*][7]annulene-6,7-dicarbonitrile (**9**). (310 mg, 70%) mp: 203–204 °C, white crystals from dichloromethane–*n*-hexane (1 : 2). [Found : C, 46.55; H, 2.38; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.43–7.31 (m, 4H, H_{aryl}), 4.81 (t, $J_{5,10}$ = $J_{9,10}$ = 4.2 Hz, 1H, H10), 4.61 (d, $J_{8,9}$ = 1.6 Hz, 1H, H8), 4.00 (d, $J_{5,10}$ = 4.2 Hz, 1H, H5), 3.90 (bd, $J_{9,10}$ = 4.2 Hz, 1H, H9) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 144.44, 139.19, 130.59, 130.15, 129.62, 125.04, 124.38, 123.09, 114.56, 113.99, 50.29, 48.70, 43.53, 39.15 ppm. IR (KBr, cm^{-1}): 2963, 2857, 1465, 1262, 2224, 1586, 1410, 1261, 1236, 1197, 1088, 1024, 845, 800, 732, 585. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 13), 285/283(M^+, −Br, 77), 204(M^+, −2Br, 100), 177(34), 151(15), 128(9), 102(18), 75(16), 62(8).

The fourth fraction. (1*S*(*R*),4*R*(*S*),9*R*(*S*),10*S*(*R*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**11**). (40 mg, 9%) mp: 260–261 °C, pale yellow crystals from dichloromethane–*n*-hexane (1 : 2). [Found: C, 46.38; H, 2.34; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.32 (AA′BB′ system, 4H, 4H, H_{aryl}), 4.76 (AA′ part of AA′XX′ system, 2H, H1 and H4), 4.27 (XX′ part of AA′XX′ system, 2H, H9 and H10) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 135.94, 131.50, 129.34, 125.22, 113.77, 53.17, 47.67 ppm. IR (KBr, cm^{-1}): 2919, 2851, 2218, 1474, 1460, 1267, 1236, 764, 737, 702. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 1), 285/283(M^+, −Br, 7), 204(M^+, −2Br, 26), 178(100), 151(14), 102(12), 75(10).

Bromination of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarboxylate (4) at 77 °C. 700 mg (2.60 mmol) of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarboxylate (**4**) was dissolved in 10 mL of carbon tetrachloride in a 50 mL flask which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution, a hot solution of bromine (497 mg, 3.11 mmol) in 2 mL of carbon tetrachloride was added dropwise over 2 min. The resulting reaction mixture was heated for 5 min at reflux temperature. After being cooled to room temperature, the solvent was evaporated and the crude product recrystallised from dichloromethane–*n*-hexane (1 : 2) to give dibromide **8** as the sole product (908 mg, 82%).

Bromination of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarboxylate (4) at 150 °C. 600 mg (2.22 mmol) of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarboxylate (**4**) was dissolved in 10 mL of decalin in a 50 mL two-necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 2 mL round-bottom flask that contained 426 mg (2.66 mmol) of bromine. Bromine vapors, obtained by heating of the flask to 100 °C, were transferred directly to a decalin solution having a temperature of 150 °C, in 5 min while stirring magnetically. The color of the bromine disappeared immediately. The solvent was removed under reduced pressure. The residue was chromatographed on silica gel (50 g) eluting with ethylacetate–*n*-hexane (1 : 9). Three compounds were isolated:

The first fraction. Dimethyl (5*S*(*R*),8*S*(*R*),9*R*(*S*),10*S*(*R*))-9,10-dibromo-8,9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulene-6,7-dicarboxylate (**60**), (313 mg, 33%) mp: 168–169 °C, white crystals from dichloromethane–*n*-hexane (1 : 2). [Found: C,

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45.01; H, 3.51; requires $C_{16}H_{14}Br_2O_4$: C, 44.68; H, 3.28%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.37–7.05 (m, 4H, H_{aryl}), 5.54 (d, $J_{8,9}$ = 2.1 Hz, 1H, H9) 5.13 (s, 1H, H10), 4.04 (m, 1H, H5), 3.91 (m, 1H, H8), 3.82 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 164.43, 163.54, 149.10, 137.84, 135.74, 133.40, 133.30, 129.46, 128.67, 127.28, 61.34, 56.90, 55.40, 52.78, 52.67, 46.73 ppm. IR (KBr, cm^{-1}): 2952, 2851, 1722, 1636, 1480, 1435, 1348, 1262, 1220, 1196, 1092, 1078, 950, 892, 833,796, 758. MS (EI, 70 eV) *m*/*z*: 432/430/428(M^+, 1), 351/349(M^+,-Br, 100), 318(22), 289(24), 269(M^+,-2Br, 36), 210(60), 179(18), 152(35), 128(19), 76(10).

The second fraction. Dimethyl (5*S*(*R*),8*S*(*R*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-8,9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulene-6,7-dicarboxylate (**45**). (275 mg, 29%) mp: 94–95 °C, white crystals from dichloromethane–*n*-hexane (1 : 1). [Found: C, 45.00; H, 3.43; requires $C_{16}H_{14}Br_2O_4$: C, 44.68; H, 3.28%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57–7.09 (m, 4H, H_{aryl}), 5.74 (d, $J_{8,9}$ = 5.2 Hz, 1H, H9), 4.82 (t, $J_{5,10}$ = $J_{8,10}$ = 4.7 Hz, 1H, H10), 3.86 (ddd, $J_{8,9}$ = 5.2 Hz, $J_{8,10}$ = 4.7 Hz, $J_{5,8}$ = 1.0 Hz, 1H, H8), 3.82 (dd, $J_{5,10}$ = 4.7 Hz, $J_{5,8}$ = 1.0 Hz, 1H, H5), 3.80 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 164.07, 163.29, 147.04, 139.27, 135.87, 133.17, 132.19, 129.26, 128.63, 128.15, 53.30, 52.83, 52.65, 52.62, 52.61, 45.85 ppm. IR (KBr, cm^{-1}): 2997, 2953, 2846, 1720, 1644, 1480, 1435, 1337, 1270, 1205, 1154, 1120, 1085, 1025, 952, 782. MS (EI, 70 eV) *m*/*z*: 432/430/428(M^+, 5), 398(18), 351/349(M^+, −Br, 36), 317(47), 269(M^+, −2Br, 35), 210(100), 183(32), 152(58), 128(21), 76(12).

The third fraction. Dimethyl (5*S*(*R*),8*S*(*R*),9*R*(*S*),10*R*(*S*))-9,10-dibromo-8,9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulene-6,7-dicarboxylate (**46**). (228 mg, 24%) mp: 123–124 °C, yellow crystals from dichloromethane–*n*-hexane (1 : 1). [Found: C, 44.85; H, 3.38; requires $C_{16}H_{14}Br_2O_4$: C, 44.68; H, 3.28%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57–7.07 (m, 4H, H_{aryl}), 5.47 (s, 1H, H9), 4.91 (t, $J_{5,10}$ = $J_{8,10}$ = 4.5 Hz, 1H, H10), 3.92 (bd, $J_{5,10}$ = 4.5 Hz, 1H, H5), 3.82 (s, 3H, OCH_3), 3.76 (dt, $J_{8,10}$ = 4.5 Hz, $J_{5,8}$ = $J_{8,9}$ = 1.0 Hz, 1H, H8), 3.74 (s, 3H, OCH_3) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 163.75, 163.05, 148.17, 138.83, 135.01, 133.58, 133.22, 129.33, 128.57, 128.35, 52.95, 52.79, 52.57, 52.41, 46.39, 41.39 ppm. IR (KBr, cm^{-1}): 2952, 2846, 1722, 1636, 1452, 1435, 1320, 1270, 1217, 1152, 1082, 1015, 948, 878, 839, 760. MS (EI, 70 eV) *m*/*z*: 432/430/428(M^+, 8), 398(17), 351/349(M^+, −Br, 86), 317(35), 289(33), 269(M^+, −2Br, 36), 210(100), 183(29), 152(60), 128(32), 76(12).

Bromination of 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarbonitrile (5) at 77 °C. 700 mg (3.43 mmol) of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarbonitrile (**5**) was dissolved in 10 mL of carbon tetrachloride in a 50 mL flask which was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution, a hot solution of bromine (659 mg, 4.12 mmol) in 2 mL of carbon tetrachloride was added dropwise over 2 min. The resulting reaction mixture was heated for 1 h at reflux temperature. After being cooled to room temperature the solvent was evaporated and crude product was chromatographed on silica gel (30 g) eluting with ethylacetate–*n*-hexane (1 : 9). Seven compounds were isolated:

The first fraction. (1*S*(*R*),4*R*(*S*),9*R*(*S*),10*R*(*S*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**10**) (161 mg, 13%).

The second fraction. ((1*S*(*R*),4*R*(*S*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**12**) (49 mg, 4%).

The third fraction. (5*S*(*R*),8*S*(*R*),9*R*(*S*),10*R*(*S*))-9,10-dibromo-8-9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**48**). (115 mg, 9%) mp: 192–193 °C, white crystals from dichloromethane–*n*-hexane (1 : 2). [Found: C, 46.26; H, 2.29; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.12 (m, 4H, H_{aryl}), 5.25 (m, 1H, H9), 4.87 (t, $J_{5,10}$ = $J_{8,10}$ = 4.4 Hz, 1H, H10), 3.90 (d, $J_{5,10}$ = 4.4 Hz, 1H, H5), 3.77 (dt, $J_{8,10}$ = 4.4 Hz, $J_{5,8}$ = $J_{8,9}$ = 1.0 Hz, 1H, H8) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 137.70, 133.63, 132.54, 131.75, 130.86, 129.67, 128.47, 126.35, 111.27, 111.23, 53.55, 52.32, 44.40, 38.48 ppm. IR (KBr, cm^{-1}): 2964, 2919, 2851, 2224, 1600, 1476, 1454, 1259, 1203, 1172, 1138, 1085, 1038, 881, 772, 744. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 1), 285/283(M^+, −Br, 74), 204(M^+, −2Br, 100), 178(64), 149(25), 102(39), 175(32).

The fourth fraction. (5*S*(*R*),8*S*(*R*),9*R*(*S*),10*S*(*R*))-9,10-dibromo-8-9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**62**). (248 mg, 20%) mp: 153–154 °C white crystals from dichloromethane–*n*-hexane (1 : 2). [Found: C, 46.09; H, 2.32; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.08 (m, 4H, H_{aryl}), 5.34 (d, $J_{8,9}$ = 2.2 Hz, 1H, H9), 5.19 (s, 1H, H10), 4.02 (m, 1H, H5), 3.90 (m, 1H, H8) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 138.91, 134.61, 133.68, 132.27, 131.04, 129.87, 127.27, 123.67, 112.15, 111.82, 61.44, 58.10, 53.08, 43.55 ppm. IR (KBr, cm^{-1}): 3070, 2997, 2919, 2851, 2224, 1600, 1477, 1454, 1315, 1264, 1236, 1150, 892, 772, 741, 716, 654. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 1), 285/283(M^+, −Br, 74), 204(M^+, −2Br, 100), 177(34), 151(13), 140(4), 128(20), 102(22), 89(23), 75(21), 74(11).

The fifth fraction. (5*S*(*R*),8*S*(*R*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-8-9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**47**). (260 mg, 21%) mp: 149–150 °C, white crystals from dichloromethane–*n*-hexane (1 : 2). [Found: C, 46.60; H, 2.59; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.09 (m, 4H, H_{aryl}), 5.69 (d, $J_{8,9}$ = 5.1 Hz, 1H, H9), 4.76 (t, $J_{5,10}$ = $J_{8,10}$ = 4.6 Hz, 1H, H10), 3.82 (bd, $J_{5,10}$ = 4.6 Hz, 1H, H5), 3.72 (ddd, $J_{8,9}$ = 5.1 Hz, $J_{8,10}$ = 4.6 Hz, $J_{5,8}$ = 0.9 Hz, 1H, H8) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 136.42, 132.62, 132.57, 131.97, 130.67, 129.61, 127.79, 127.34, 112.29, 111.24, 53.48, 52.88, 50.50, 43.04 ppm. IR (KBr,cm^{-1}): 3070, 2958, 2919, 2851, 2224, 1594, 1480, 1454, 1328, 1292, 1266, 1245, 1197, 1166, 920, 895, 875, 827, 765. MS (EI, 70 eV) *m*/*z*: 366/364/362(M^+, 1), 285/283(M^+, −Br, 70), 204(M^+, −2Br, 100), 177 (39), 151 (13), 140 (3), 128 (17), 102 (18), 89 (13), 75 (20), 74 (9).

The sixth fraction. (5*S*(*R*),8*S*(*R*),9*S*(*R*),10*S*(*R*))-9,10-dibromo-8,9-dyhidro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**63**). (161 mg, 13%) mp: 175–176 °C, yellow crystals from

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dichloromethane–*n*-hexane (1 : 2). [Found: C, 46.48; H, 2.39; requires $C_{14}H_8Br_2N_2$: C, 46.19; H, 2.22%]; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.61–7.09 (m, 4H, H_{aryl}), 5.57 (d, $J_{8,9}$ = 5.2 Hz, 1H, H9), 4.55 (s, 1H, H_{10}) 3.99 (bd, $J_{8,9}$ = 5.2 Hz, 1H, H8), 3.98 (m, 1H, H5) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): 135.72, 134.05, 133.10, 131.90, 130.92, 129.93, 126.75, 126.42, 113.10, 111.89, 59.90, 57.92, 54.26, 42.94 ppm. IR (KBr, cm^{-1}): 2924, 2857, 2224, 1706, 1597, 1476, 1451, 1379, 1270, 909, 749.

The seventh fraction. (1*S*(*R*),4*R*(*S*),9*R*(*S*),10*S*(*R*))-9,10-dibromo-1,4-dihydro-1,4-ethanonaphthalene-2,3-dicarbonitrile (**11**) (74 mg, 6%).

Bromination of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarbonitrile (5) at 150 °C. 720 mg (3.53 mmol) of dimethyl 1,4-dihydro-1,4-ethanonaphtalene-2,3-dicarbonitrile (**5**) was dissolved in 10 mL of decalin in 50 mL two-necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to 2 mL of round-bottom flask that contains 678 mg (4.24 mmol) of bromine. Bromine vapours, obtained by heating of the flask to 100 °C, were transferred directly to the decalin solution having a temperature of 150 °C, in 5 min while stirring magnetically. The color of the bromine disappeared immediately. The solvent was removed under reduced pressure. The crude product was chromatographed on silica gel (30 g) eluting with ethylacetate–*n*-hexane (1 : 9). Three compounds were isolated:

The first fraction. (5*S*(*R*),8*S*(*R*),9*R*(*S*),10*S*(*R*))-9,10-dibromo-8-9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**62**) (384 mg, 30%).

The second fraction. (5*S*(*R*),8*S*(*R*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-8-9-dihydro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**47**) (269 mg, 21%).

The third fraction. (5*S*(*R*),8*S*(*R*),9*S*(*R*),10*S*(*R*))-9,10-dibromo-8,9-dyhidro-5*H*-5,8-methanobenzo[*a*][7]annulen-6,7-dicarbonitrile (**63**) (358 mg, 28%).

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