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Cinzia Chiappe · Christian Silvio Pomelli
Dieter Lenoir · Carsten Wattenbach

The first intermediates in the bromination of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane, combination of experiments and theoretical results

Abstract Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**1**) and adamantylideneadamantane (Ad = Ad) are two caged olefins with closely related structures at the double bond. Both compounds react instantaneously with Br_2 in chlorinated hydrocarbon solvents to give mixtures of olefin–Br_2 aggregates identified as the 1:1 π-complex and bromonium tribromide, bromonium pentabromide ion pairs. The stoichiometry, formation constants and the electronic spectra of all the species present at equilibrium (π-complex and bromonium ions), obtained by addition of bromine to alkene **1**, have been determined in 1,2-dichloroethane at 25° C and compared with the values that characterize the corresponding aggregates arising from Ad = Ad. The absence of the two bridging CH_2 groups in **1** significantly affects all the formation constants. Moreover, at variance with Ad = Ad, olefin **1** reacts with bromine to give, depending on reagent concentration, a substitution product. DFT (B3LYP) and ONIOM computations of 1:1 Br_2–olefin complexes for **1** and Ad = Ad confirm that the association energy is larger for the complex **1**–Br_2. The higher stability of this species seems to be correlated to the greater IP of **1** with respect to Ad = Ad which is able to compensate the reduced polarizability. The experimental value of the formation constant found for the complex **1**–Br_2, 643 vs 289 M^{-1} further supports the primary role exerted by dispersion interactions in alkene-Br_2 π-complexes.
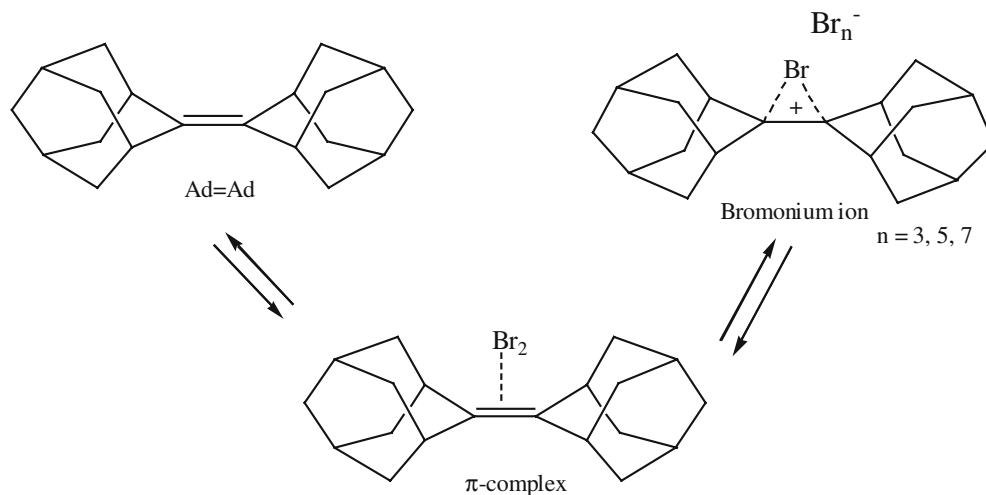
Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday.

C. Chiappe (✉)
Dipartimento di Chimica Bioorganica e Biofarmacia,
Università di Pisa, 56126 Pisa, Italy
E-mail: cinziac@farm.unipi.it

C. S. Pomelli
Dipartimento di Chimica e Chimica Industriale,
Università di Pisa, 56126 Pisa, Italy

D. Lenoir · C. Wattenbach
Institut für Ökologische Chemie, GSF Forschungszentrum,
Postfach 1129, 85758 Neuherberg, Germany

Introduction

Electrophilic bromine addition to olefins is a classical widely- investigated reaction in organic chemistry [1–6]. Much information about the mechanistic features of this seemingly simple reaction has been obtained using crowded olefins, in which the rapid formation of the ionic intermediate and its subsequent trapping are retarded by the substituents on the double bond [5, 7–14]. A significant contribution to these studies has been made by adamantylideneadamantane (Ad = Ad), an allylically bridgehead tetrasubstituted olefin that shows unique behavior among all the alkenes investigated [15]. Its highly congested structure absolutely prevents the progress of Br_2 addition beyond the stage of bromonium ion formation and, in halogenated solvents, an equilibrium between free Ad = Ad, free Br_2, Ad = Ad–Br_2 π-complex, and bromonium tribromide, pentabromide, and heptabromide ion pairs is established instantaneously, see Scheme 1 [16, 17]. The unusual stability of the bromonium ion of Ad = Ad is kinetically controlled; as a consequence of the rehybridation of double bond carbon atoms, the two adamantylidene moieties in the bromonium ion are oriented in a such way as to prevent the rear attack of the counteranion (Br^- or Br_3^-).

Surprisingly, despite the large number of studies performed on this topic, no other olefin has been found to give a bromonium ion of comparable stability. For example, d,l-d_3-trishomocubylidene-d_3-trishomocubane, is an allylically bridged tetrasubstituted olefin with a structure very similar to Ad = Ad. The reduced dimension of the two cages with respect to Ad = Ad, however, drastically changes the reactivity of the system. d,l-d_3-trishomocubylidene-d_3-trishomocubane reacts with Br_2 to give the normal addition product; the ionic intermediate can neither be isolated nor detected [18]. On the other hand, even the simple introduction of two methyl

Sch. 1 Reaction of
adamantylideneadamantane
with Br_2 in chlorinated solvents

groups on the allylic carbons of $Ad=Ad$ gives an olefin that reacts with bromine; in this case a substitution product has been isolated [19]. Analogously, the introduction of substituents on the homoallylic carbon of $Ad=Ad$ generally reduces the stability of the corresponding bromonium ions; it has been been shown that several $Ad=Ad$ derivatives react with Br_2 to give substitution products [20].

Herein, we report the results of a theoretical and experimental investigation of the reaction of bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**1**) with bromine (Scheme 2). This olefin, which has a closely related structure to $Ad=Ad$, gives, with Br_2, a stable π-complex (**2**) and a quite stable bromonium ion (**3**, **4**).

The stability constants of all the species present at equilibrium (π-complex, and bromonium ions) have been determined in this work and compared with those characterizing $Ad=Ad$. At variance with $Ad=Ad$, olefin **1** reacts slowly with bromine to give a substitution product. We report the structure of the substitution product. Finally, we give details of a theoretical description of the bonding in the π-complex, in the halonium ion and an interpretation for the formation of the substitution product.

Results and discussion

Spectral data

Preliminarily, to verify the ability of **1** to give a sufficiently stable bromonium ion, equal volumes of 1,2-dichloroethane (DCE) solutions of olefin **1** (ca 1.5×10^{-3} M) and Br_2 (3×10^{-3} M) were mixed at 25° C.[1] In analogy with $Ad=Ad$, many of the colored mixtures obtained from **1** were stable for at least 20 min and

therefore they could be investigated by conventional spectrophotometric techniques. Spectral data were collected in the 250–500 nm wavelength range working at 2.0×10^{-4} to 1.0×10^{-2} M Br_2 and 4×10^{-4} to 7×10^{-3} M olefin. All spectra exhibited a maximum around 270 nm, near the λ_{max} values found previously, both for the Br_3^- ion and for many 1:1 olefin–Br_2 complexes (including that of $Ad=Ad$), and the observed dependence of the 270-nm absorption on reagent concentrations, when these solutions were progressively diluted, pointed to the presence of two species of different stoichiometry, probably the π-complex **2** and the bromonium tribromide ion pair **3**. Furthermore, an examination of the entire UV spectrum revealed that an increasing excess of Br_2 produced a shoulder around 320 nm, attributable to the formation of a bromonium pentabromide salt (**4**). In analogy with $Ad=Ad$, all these data showed that several species of different stoichiometry are present at equilibrium in DCE solutions of **1** and Br_2.

It is worth mentioning that the stability of mixtures obtained by mixing **1** and bromine, depended on reagent concentration; diluted solutions containing a large excess of Br_2 ([**1**] = 5×10^{-4}, 1.5×10^{-3} [Br_2] < 2×10^{-2}) or a moderate excess of olefin ([Br_2] = 5×10^{-4}, 2×10^{-3} < [**1**] < 6×10^{-3}) were sufficiently stable to be investigated using a conventional UV–vis spectrophotometer. More concentrated solutions containing an excess of **1** ([Br_2] = 6×10^{-4}, 1×10^{-2} < [**1**] < 0.6) showed a disappearance of the coloration. All the spectrophotometric measurements related to solutions of **1** and Br_2 that did not show any detectable disappearance of the absorbances were fitted using the NLLSQ computational procedure [16] previously used for $Ad=Ad$. Fitting parameters were the formation constants $K_{m,n}$ of the A_mB_n complexes, defined from olefin and bromine (A stands for olefin, B for Br_2, the (m,n) pair having the value 1:1, 1:2, and 1:3), and the extinction coefficients of the 1:1 π-complex, the spectra of salts **3** and **4** being fixed at the values reported for $Bu_4N^+Br_3^-$ and $Bu_4N^+Br_5^-$, respectively.

The presence of more species (**2**, **3**, and **4**) in equilibrium must be considered to obtain good fits (rms

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[1] It has been reported that olefin **1** gives a iodonium triflate sufficiently stable to be investigated by NMR, whereas the corresponding bromonium triflate had to be maintained at −60° C to prevent decomposition (see Ref. [5])

Sch. 2 Structure of adamantylidenadamantane (Ad = Ad) and bicyclo[3.3.1]non-ylidenbicyclo[3.3.1]nonane (**1**)

Ad=Ad   **1**
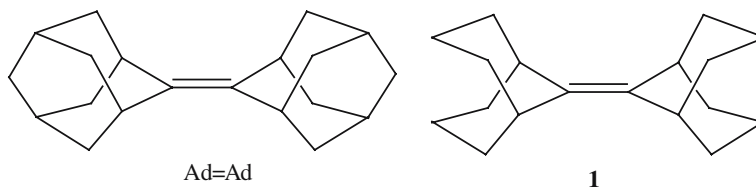
deviations < 0.03 absorbance units) of the spectro-photometric data (Scheme 3). In Table 1 the equilibrium constants of species **2**, **3**, and **4** and the extinction coefficient the complex **2** at the absorption maximum are reported. Furthermore, the values of the corresponding species for Ad = Ad–Br_2 system have been reported [16] for comparison. In analogy with Ad = Ad, the formation of **3** from **1** was too fast to be followed even with a stopped-flow apparatus. Therefore, it was impossible to check experimentally if **3** was formed directly from **1** and Br_2, or through the complex **2**. For this reason, the formation constant of **3** was defined in the computational procedure, as in the case of Ad = Ad, from **1** and Br_2, with $m = 1$ and $n = 2$. Although the formation constant of bromonium pentabromide salt **4** was again defined in the computational procedure from **1** and Br_2, with $m = 1$ and $n = 3$, there is, however, no doubt that **4** arises from **3** and Br_2. The pertinent formation constant is $K'_{13} = K_{13}/K_{12}$ and the value of this constant (18.9 M^{-1}) is, as expected, not too different from that found for the bromonium pentabromide of Ad = Ad, formed from the corresponding bromonium

tribromide [16], and with the value characterizing the formation of $Bu_4N^+Br_5^-$ from $Bu_4N^+Br_3^-$ and Br_2, 14.3 M^{-1} [21].

The comparison of the values of the formation constants computed in the present work for complexes olefin **1**–Br_2, with those previously evaluated for Ad = Ad–Br_2, shows that the stability of all the intermediates is considerably affected by the lack of the two bridging CH_2 groups. The formation constant for the π-complex is significantly higher in the case of **1** than for Ad = Ad, whereas that of the bromonium ion tribromide is lower of one order of magnitude.

Reaction products

In analogy with Ad = Ad, olefin **1** reacts with an excess of Br_2 to give an ionic intermediate sufficiently stable to allow the UV investigation. However, when an equimolar amount of bromine at 0° C, in DCE or dichloromethane-d_2, was added to a solution of **1** of concentration lower than 10^{-3} M, after the disappearance of the color,

Sch. 3 Reaction of olefin **1** with Br_2 in 1,2-dichloroethane under controlled reagent concentrations
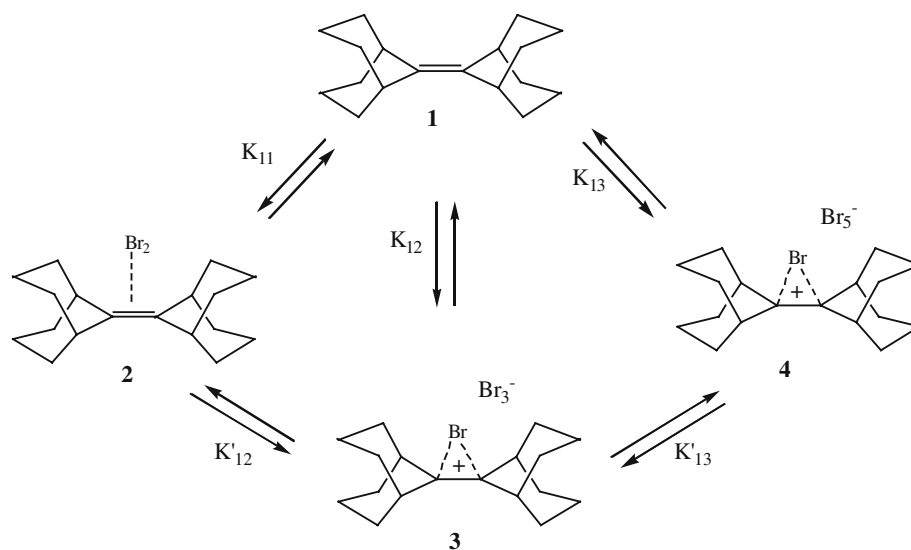

Table 1 Formation constants and molar extinction coefficients at 270 nm and 25° C for the Br_2–**1** complexes obtained from the NLLSQ fitting of UV–vis spectral data

Alkene	K_{11} (M^{-1})	ε_{270} (M^{-1} cm^{-1})	K_{12} (M^{-2})	K_{13} (M^{-3})	K'_{13} (M^{-1})
1	643 (43)	2,934 (64)	2.96 (0.1)×10^4	5.51 (0.5)×10^5	18.9
Ad = Ad	289	17,780	3.23×10^5	7.2×10^6	22.2

a non-ionic reaction product was recovered. On the basis of its mass spectrum ($C_{18}H_{27}Br$) and NMR spectra, we propose structure 5. The ^{13}C NMR–DEPT analysis shows the presence of a tetrasubstituted double bond and of a CH carbon at 50.16 ppm, attributable to a CH carbon bearing a bromine atom. The spectrum is, moreover, characterized by other two signals due to CH carbons, at 33.05 and 33.3 ppm, and by six signals due to CH_2 carbons at 17.08, 22.69, 34.42, 34.72, 35.83, and 40.27 ppm. The total number of signals in the ^{13}C NMR spectrum suggests the formation of a bromo adduct characterized by a structure having a symmetry plane. Therefore, between the two adducts bearing a bromine atom on a secondary carbon (CHBr), reported in Scheme 4, we suggest structure 5.

Although Ad = Ad and derivatives give, with suitable electrophiles which combine an electrophilic and a sufficient basic moiety, homoallylic substitution products of the type of 6 [22–25], compound 1 seems to yield, at least under the reaction conditions, the substitution product at the more distant CH_2 carbon.[2]

Theoretical investigation of complexes and bromonium ions

To obtain more detailed information about the factors that determine the different stability and reactivity of the intermediates formed by bromine addition to olefin 1 and Ad = Ad, we have performed a theoretical investigation on olefin 1, the corresponding olefin–Br_2 π-complex, 2, and the bromonium ion, 3. The results have been compared with those previously obtained for Ad = Ad and its derivatives [20]. To find a level of calculation that gave an appropriate description of these systems with a reasonable computational cost, especially for π-complexes, the following strategy was chosen: the geometries of olefin, π-complex, and bromonium ions were refined at a B3LYP/CEP-121G level with supplementary basis functions on all atoms as previously reported [20] for Ad = Ad derivatives. On the final geometries a frequency calculation was performed. For the π-complex alone, an ONIOM calculation, on the model system constituted by the bromine atoms and the quaternary (sp_2) carbons described at the MP2 level, was performed in order to compare the data with those previously reported for the π-complex Ad = Ad–Br_2. All the calculations were performed using the Gaussian Package [26]. Geometries of complex 2, of the corresponding bromonium ions and of the bromonium tribromide ion pair 3, are reported in Figs. 1, 3, 4, 5, and 6, whereas Tables 2 and 3 summarize the energies of the investigated species. The calculated intermolecular distances are given in Table 4.

Figure 1 shows that the complex 2 and the analogous complex of Ad = Ad have the angular geometry (T-shape) generally reported [27] for these systems. The two structures are characterized, however, by different distances between the axial protons at homoallylic positions. The distance between the homoallylic protons directed toward Br_2 is 4.647 Å in the complex 2 and 5.082 Å in the Ad = Ad complex; at the same time the distances between the homoallylic protons opposite to Br_2 in the same complexes are 2.240 and 2.343 Å, respectively. These distances are moreover, in both cases, significantly different from those characterizing the same H-atoms in the starting olefins (3.342 Å in 1 and 3.699 Å in Ad = Ad). At variance with ethylene, for which practically no rehybridization has been calculated [20] on going from olefin to the complex, in 1 as well as in Ad = Ad, a significant rehybridization at the carbons already occurs in the π-complex, suggesting that an "inner" character being more important than that in complexes of linear non-congested alkenes.

In Table 2 are reported the energetic results for the 1–Br_2 π-complex (2) and the more significant parameters have been compared with those previously calculated [20] for the Ad = Ad–Br_2 system. The meaningful energetic values are those at the ONIOM level. At this level of calculation, the π-complex 2 is slightly more stable than the corresponding Ad = Ad–Br_2 complex, in agreement with the experimental results obtained in solution, see Table 1.

To shed further light on the prominent factors that affect the stability of these complexes, we have calculated[3] the ionization potential (IP) and polarizability (α) for olefin 1 (IP 7.44 eV; α 202.9 a.u.) and for Ad = Ad (IP 7.37 eV; α 214.0 a.u). Recently, we have shown that for alkyl-tetrasubstituted olefins a good linear relation may be found [28] by plotting the constant of formations of the π-complex olefin–Br_2 (log K_f) against the calculated induced dipole-induced dipole dispersion interactions (d_6, atomic units) defined as reported in Eq. 1:

$$d_6 = \frac{3}{2}\alpha_1\alpha_2 \frac{IP_1 IP_2}{IP_1 + IP_2} \tag{1}$$

where indexes 1 and 2 are for bromine (α_1 30.35 a.u., IP_1 0.387 eV) and olefin, respectively.

On the basis of the calculated values of IP and α for olefins 1 and Ad = Ad values of d_6 of 1628.5 and 1554.8 a.u. can be evaluated, respectively. The correlation between the formation constants of several olefin–Br_2 π-complexes and the respective d_6 values [28], including also the complex of olefin 1, is reported in Fig. 2. The increased formation constant (K_f) of 2, with respect to the analogous complex of Ad = Ad, may therefore be attributed to the higher IP value of 1, which is able to overcompensate the reduced polarizability of this olefin with respect Ad = Ad.

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[2] It has been reported (see Ref. [24]) that 1 does not react with NBS whereas with NCS gives the 4(e)-chlorobicyclo[3.3.l]nonylidenebicyclo[3.3.l]nonane, characterized by 16 signals in the ^{13}C NMR spectrum

[3] Both values are calculated at the B3LYP/CEP-121G(d,p) level of calculation

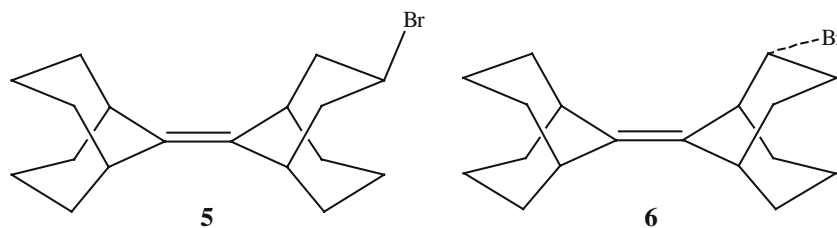**Sch. 4** Possible substitution products obtained from alkene **1**

5   **6**

Table 2 Numerical results on the π-complex **2**

System	E(B3LYP)		E(ONIOM)		ZPE(B3LYP)
1	−118.620541		−117.759099		0.423799
Br$_2$	−26.764366		−26.607046		0.000722
π-complex, **2**	−145.387113		−144.386469		0.426185
ΔG_{form}	−1.38	(2.95)[a]	−12.76	(−9.66)[a]	1.04
Deformed[b] **1**	−118.613626		−117.7533588		
ΔE_{def} C=C	4.34	(3.87)[a]	3.60	(3.48)[a]	

Absolute energies (a.u.), relative energies (kcal mol^{-1})
[a]Values in parenthesis are refereed to the corresponding complex of Ad=Ad
[b]Energy of olefin **1** in the "deformed" structure of the complex **2**, for definition see Ref. [20]

Table 3 Numerical results of the bromonium ion systems

System	E(B3LYP)	ZPE(B3LYP)	$\Delta(E+ZPE)$
Chair bromonium ion	−131.755154	0.426402	–
Boat bromonium ion	−131.748709	0.426258	–
Br$_3^-$	−40.285980	0.001167	–
Chair bromonium ion + Br$_3^-$	−172.041134	0.427569	0.00
Boat bromonium ion + Br$_3^-$	−172.034689	0.426425	3.70
Chair T-shaped complex	−172.151946	0.427090	
Boat bromonium ion– Br$_3^-$ complex	−172.122648	0.427408	−18.19

Finally, to obtain information about the possible pathway through which olefin **1** reacts with Br$_2$ to give a substitution product, we have performed geometrical optimization of the corresponding bromonium ion and of the bromonium ion of Ad=Ad and we have compared the relative stabilities and geometrical features of these species.

Two different conformations have to be considered for the bromonium ion of olefin **1**. Since in vacuo calculations have been performed by us, we cannot directly compare charged and non-charged systems [20]. π-Complexes and bromonium ions are very different from the physical point of view: the absence of significant dispersion interactions in bromonium ions allow us to perform B3LYP calculations and avoid the more expensive ONIOM calculations.

Reported in Table 3 are the absolute energies of the bromonium ion of **1** in different conformations and the energies of the complexes between the bromonium ion and Br$_3^-$; all these species are represented in Figs. 3, 4, and 5. Note that the comparison between neutral complexes (ion pairs) instead of bromonium ions reduces the error introduced by disregarding the solvent effect into the calculations.

Figure 3 represents the "classical" bromonium ion with the olefin skeleton in its more stable conformation.

In the second structure (Fig. 4) one of the side-chain rings is passed from the chair to the boat conformation. In the third one (Fig. 5) we consider the bromonium tribromide ion pair, i.e., the complex between the structure of Fig. 4 and a Br$_3^-$ ion. Finally, represented in Fig. 6 is a chair bromonium tribromide complex with an aspecific interaction of Br$_3^-$ with Br$^+$ that represents the reactive pathway leading back to the π-complex.

The most stable form of the bromonium ion arising from **1** is that reported in Fig. 3 (chair conformation of bromonium ion), but its preference over the other conformation (boat conformation reported in Fig. 4) is small.

It is, however, worth mentioning that the formation of the complex between the boat conformation of the bromonium ion and the Br$_3^-$ anion, tends to a structural situation (Fig. 5) characterized by a quasi-collinear position of Br1, H1, H2, and Br2. The approach of the Br atom of tribromide, reported as 2 in Fig. 5, toward the proton 2, shift the bromine atom of bromonium nearer to C1, giving an ionic intermediate with higher bromocarbenium character. We have previously shown [20] that the ionic intermediates arising from bromine addition to the double bond of tetrasubstituted olefins (including Ad=Ad derivatives), which are characterized by a more β-bromocarbenium character, are generally
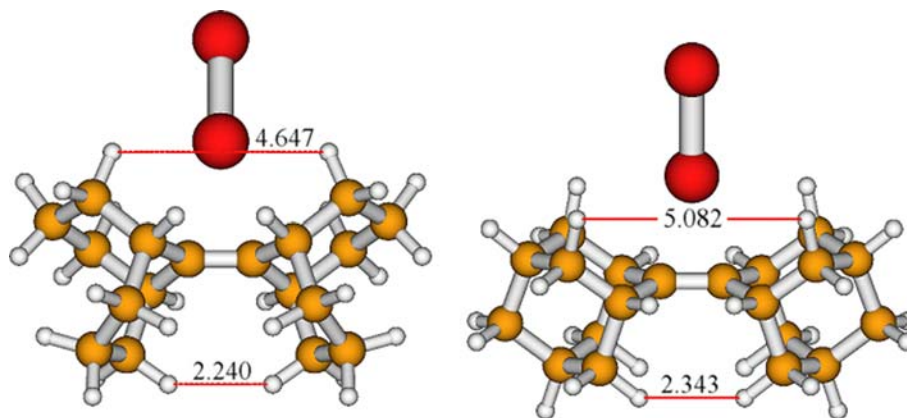
more prone to evolve toward substitution products. In agreement with this statement, the boat bromonium ion arising from **1** has significantly different Br1–C distances (Table 4 and Figs. 4, 5) and therefore a significantly different charge development on the two carbons. This structure can be compared with the isomeric T-shaped 2:1 bromine–**1** complex reported in Fig. 6. The C1, C2–Br1 distances for this latter T-shaped complex shows that this species has a nature very similar to the π-complex and this arrangement of bromine atoms and **1** may be considered a regression from the bromonium ion toward the π-complex. The structure in Fig. 5 is 18.19 kcal mol^{-1} is more stable than the T-shaped complex of Fig. 6 as reported in Table 3, and this value is in agreement with the tendency of this olefin to react with bromine to give a substitution product.

Considering the structure reported in Fig. 5, it is indeed possible to hypothesize that the abstraction of the proton labeled as H2 by the base (Br$_3^-$ or Br) and the shift of Br1 from the C1 carbon to the γ position may be responsible of the formation the substitution product **5**. The two processes, which are represented in Scheme 5 through a synchronous mechanism, can really occur at different times. Proton abstraction might precede Br$^+$ shift or, alternatively, the initial expulsion of Br$^+$ as
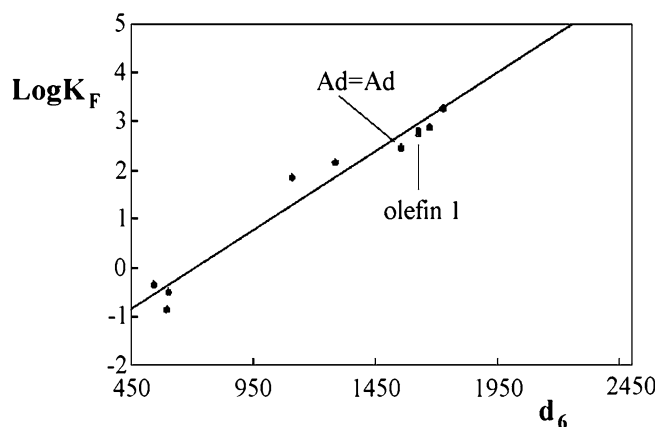
HBr could give a μ-hydridobridged carbocation, stabilized by the interaction with the double bond through the σ-bonds, able to give the product **5** by subsequent reaction with Br$_3^-$ (Scheme 6).

Calculations are in due course to verify these latter hypotheses. However, the reduced tendency of **1** to give the substitution product on increasing bromine concentration (i.e., under conditions which shift all the equilibria of Scheme 3 toward the bromonium pentabromide ion pair) suggests that the basicity of the counteranion plays a role in the mechanism of product formation. This feature is more in agreement with the mechanistic pathway of Scheme 5.

Conclusion

The comparison of the results reported here for the bromination of **1** with the previous ones for Ad = Ad
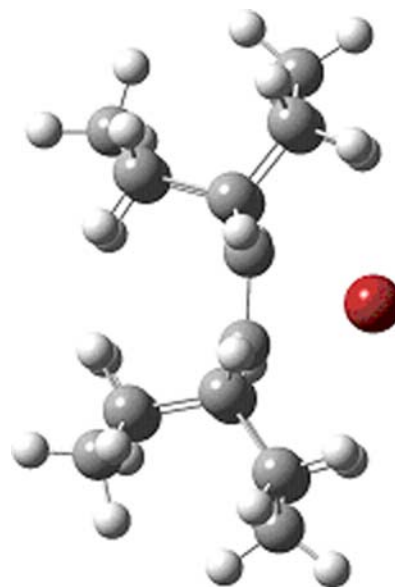

Fig. 2 Correlation between π-complex formation constant (log K_f) and induced dipole-induced dipole dispersion interactions (d_6)

Fig. 3 Bromonium ion of **1** with both the side chains in their standard chair conformations

Table 4 Comparative bond distances (Å)

Distances	π-Complex **2**[a]	Chair conform. brom. ion	Boat conform. brom. ion	Boat complex
Br1–C1	2.87	2.19	2.15	2.09
Br1–C2	2.87	2.19	2.23	2.41
Br1–H1	4.31	4.36	2.78	2.80
Br2–H2	–	–	–	2.82

The atom labels are defined in Fig. 5
[a]The distance Br1–π (middle point of the C1–C2 bond) is 2.78 Å (for Ad=Ad–Br$_2$ is 2.41 Å)

shows a marked effect due to the absence of the two bridging CH_2 groups on the reactivity of the double bond. It modifies the stability of all intermediates involved on the reaction coordinate.
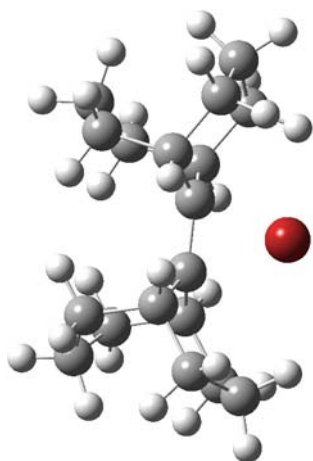

Fig. 4 Bromonium ion of **1** with one of the cyclic side chains in a boat conformation
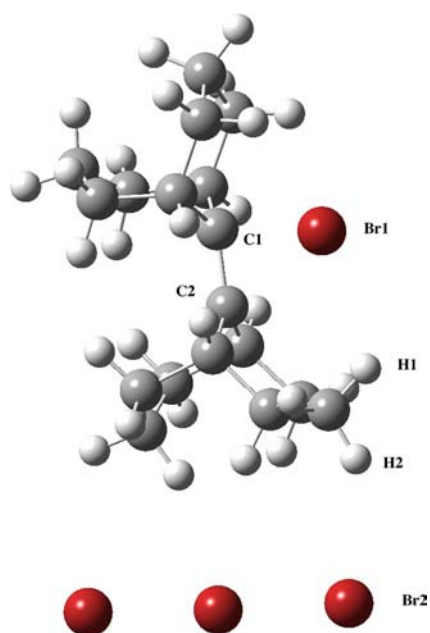

Fig. 5 Complex of the boat conformation bromonium ion with Br$_3^-$

Analogously to Ad=Ad, olefin **1** reacts with bromine instantaneously to form a 1:1 π-complex (**2**) which further rapidly evolves to the ionic intermediate. The formation constant of the π-complex **2** (643 M^{-1} at 25° C) is two times higher than that reported for the analogous complex of Ad=Ad. This increase is consistent with the different polarizability and the donor ionization potential of **1**. The previously proposed equation [28], which takes into account both effects, is also able in this case to describe this complex better than the Mulliken analysis.

The bromonium tribromide ion pair arising from olefin **1** is characterized by a lower stability constant with respect to the same species formed from Ad=Ad and Br$_2$, in agreement with the higher tendency of **1** to give a substitution product with bromine. This peculiar behavior of **1**, which distinguish this olefin from Ad=Ad, may be considered a consequence of the lack of the bridging CH_2 groups which, allowing the fused cyclohexanes to perform other conformations, permits proton abstraction and Br$^+$ shift. Generally, ionic intermediates having a greater β-bromocarbenium character are more prone to evolve to products. DFT calculations show that the boat conformation of **3** is characterized by a significantly high difference of charge on the two carbons of the bromonium ring; a situation which does not occur in the bromonium ion arising from Ad=Ad.

Experimental section

Bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (**1**) was prepared as previously reported [29]. 1,2-Dichloroethane (DCE, Fluka, puriss. pa ACS) was used as supplied without further purification. Bromine was drawn from 1-ml vials (C. Erba, RPE grade >99.5%) opened immediately before use.
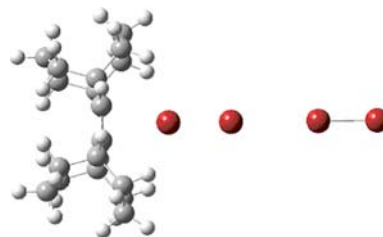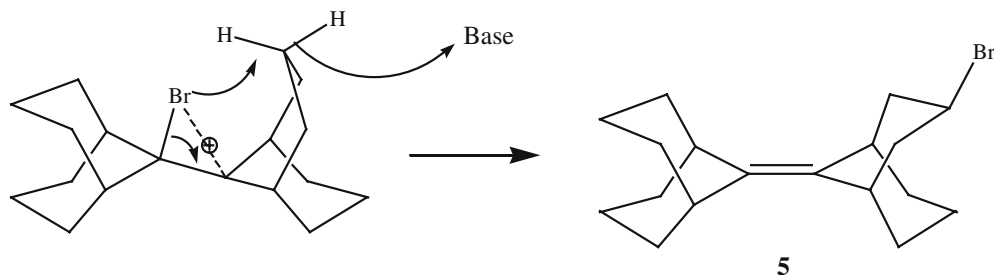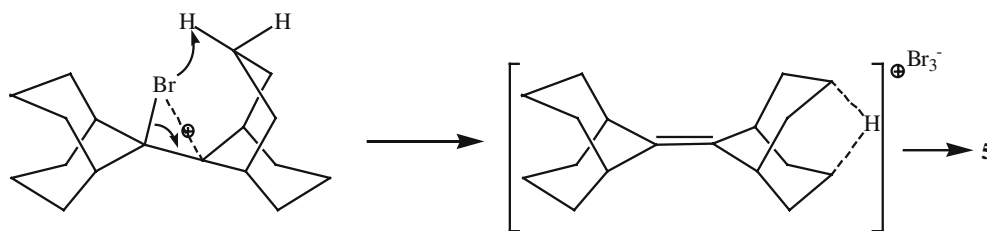

Fig. 6 T-shaped complex of chair bromonium ion

Sch. 5 Suggested mechanistic transformation of the bromonium ion intermediate into the substitution product **5**

Sch. 6 Formation of **5** through a μ-hydridobridged carbocation

Spectrophotometric measurements

1,2-Dichloroethane solutions of **1** and Br_2 were prepared by weighing the reagents in accurately calibrated volumetric flasks. The Br_2 solutions were stored in the dark and checked spectrophotometrically for their concentrations. They were discarded when the absorptions around the Br_2 UV minimum (280–350 nm) were found to be higher than expected.

Working-strength solutions were prepared by mixing solvent and aliquots of the reagent stock solutions withdrawn with precision microburets. The analytical concentrations of Br_2 and olefin are reported in the text. The UV spectra were registered at 25° C in 1 or 0.1 cm cells in the 250–420 nm range. An already described, a nonlinear least-squares procedure was applied to fit the spectrophotometric data. The root-squares deviation was 0.032 absorbance units.

Product study

To precooled DCE (or dichloromethane-d_2) solutions (0.5–2 ml) of **1** (ca 30 mg), an equimolar amount of Br_2 was added at 0° C in the dark. After the complete disappearance of color, the samples were directly analyzed by NMR, when the reactions were carried out in the deuterated solvent, or after removal of the volatile components by means of a rotary evaporator when the reactions were carried out in DCE. ^1H NMR (CD_2Cl_2, δ) 3.95 (tt, 1H, C*H*Br), 3.10 (br, 2H); 2.85 (br s, 2H), 2.5–1.2 (br, 22H); ^{13}C NMR- DEPT (CD_2Cl_2, δ) 138.0 (>C<), 126.1 (>C<), 50.16 (*C*HBr), 40.27 (CH_2), 35.83 (CH_2), 34.72 (CH_2), 34.42 (CH_2), 22.69 (CH_2), 17.08 (CH_2), 33.35 (CH) and 33.3 (CH). 21.7. Mass spectrum, m/e 322:324 (1:1).

Computational methodology

All calculations were performed with the Gaussian 03 suite of programs [26]. All the geometries were optimized at the B3LYP/CEP-121G level with supplementary basis functions on all atoms as previously reported [20]. A frequency calculation was performed on the final geometries. Only for the π-complexes was an ONIOM calculation with the bromines and the sp^2 carbons described at the MP2 level performed. All the calculations were performed on an APPRO 1124 workstation with two Athlon MP1800+ processor, 1 Gb RAM and 18 Gb SCSI Hard Disk with Suse 9.1 O.S. The Gaussian Package was compiled with MP support with a Portland pgf 77 5.1 fortran compiler.

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