The Carbene/Bridgehead-Olefin Rearrangement: DFT Calculations on 1-Bicyclo[2.1.1]hexylcarbene and 1-Bicyclo[3.1.1]heptylcarbene; Rearrangement of (5-Bromobicyclo[3.1.1]heptyl)bromocarbene

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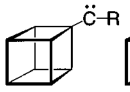
Keywords: Small ring systems / Strained molecules / [3.1.1]Propellane / Alkene dimerization

B3LYP/6-31G(d) calculations on bicyclo[2.1.1]hexylcarbene **7a** showed a preferred propensity for enlargement of the four-membered ring to give 1-norbornene **8**. Only at high temperature does a rearrangement of bridgehead olefin **8** to 2-norbornylidene **11** seem to be possible; the competing rearrangement to afford 2-bicyclo[3.1.1]heptylidene **10** has a higher activation barrier by 20.2 kcal/mol. For 1-bicyclo[3.1.1]heptylcarbene **12**, the preferred stabilization is again enlargement of the four-membered ring to give bicyclo[3.2.1]oct-1(7)-ene **13**. The further rearrangement of this alkene to 7-bicyclo[3.2.1]octylidene **16** is endothermic by 32.2 kcal/mol and should not take place under moderate conditions. (5-Bromobicyclo[3.1.1]heptyl)bromocarbene **32**, a derivative of **12** generated from the tetrabromide **23** with MeLi, rearranged by enlargement of the four-membered ring to give alkene **31**, which reacted to give the head-to-head 2π+2π dimer **26**, whose structure was established by X-ray crystallography.

The fascinating carbene-bridgehead olefin−carbene rearrangement has been observed with cubylcarbenes **1**[1] and 1-bicyclo[1.1.1]pentylcarbenes **4**.[2][3] The second rearrangement, **2** → **3** and **5** → **6**, will only take place if the bridgehead olefin is highly distorted, as in **2** or **5**. The results of DFT calculations concerning the interconversion of **4** → **5** → **6** compared well with experimental observations, and so it seemed interesting to extend these calculations to the higher homologue carbenes **7** and **12** to determine whether these rearrangements are feasible experimentally.



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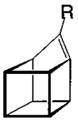

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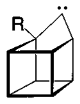

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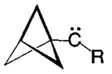

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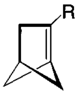

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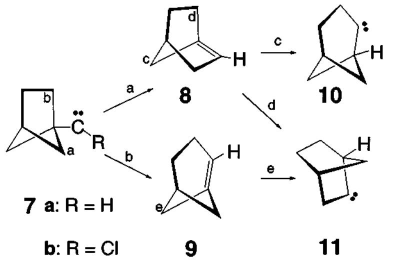
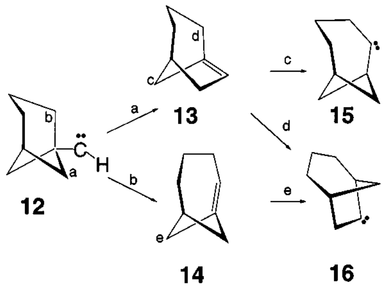
6

Carbenes **7** and **12** differ from **1** and **4** in that for the former the rearrangement can take place in two ways: the migrating atom can either be part of the four-membered or five-membered ring or, alternatively, the six-membered ring, as depicted in Schemes 1 and 2. It seemed interesting to find out by theoretical and experimental methods which of these alternatives was energetically more favorable.



Scheme 1



Scheme 2

DFT Calculations on the Rearrangement of 7 and 12

The DFT calculations were carried out with Becke's three parameter hybrid functional and the LYP correlation functional[4][5] using the Gaussian 94 and Gaussian 98 program packages.[6] Optimized structures were obtained at the B3LYP/6-31G(d) level of theory and frequency calculations

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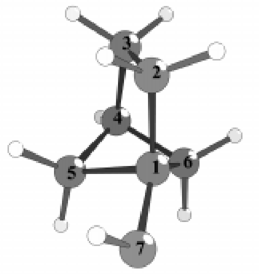
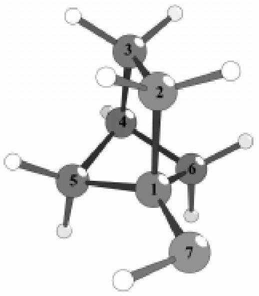
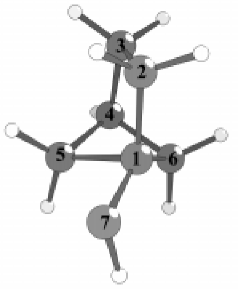
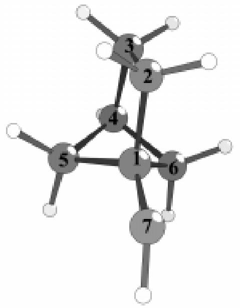
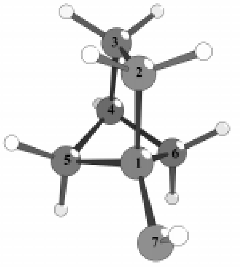
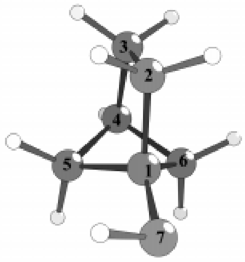
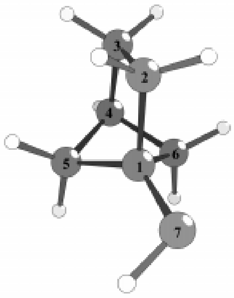
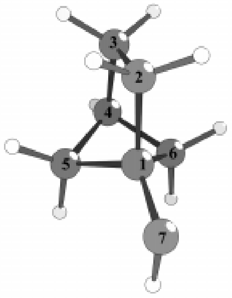
Table 1. Computer-generated B3LYP/6-31G(d) structures of **7a−m1** to **7a−m3**, **7a−triplet**, and **7a−b1** to **7a−b4**, their corresponding B3LYP/6-31G(d,)//B3LYP/6-31G(d) energies, B3LYP/6-31G(d) Zero-point energies (corrected with the factor 0.9804[a]), {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)}$_c$ energies (Zero-point energy corrected) and selected structural data

7a-m1	**7a-m2**	**7a-m3**	**7a-triplet**
			
E(B3LYP/6-31G*) = –272.5815721 a.u.	E(B3LYP/6-31G*) = –272.579728 a.u.	E(B3LYP/6-31G*) = –272.5829266 a.u.	E(B3LYP/6-31G*) = –272.5883059 a.u.
ZPE = 0.146687(0) a.u.	ZPE = 0.146142(0) a.u.	ZPE = 0.147011(0) a.u.	ZPE = 0.145891(0) a.u.
E(B3LYP/6-311G**)$_c$ = –272.505517 a.u.	E(B3LYP/6-311G**)$_c$ = –272.504543 a.u.	E(B3LYP/6-311G**)$_c$ = –272.506779 a.u.	E(B3LYP/6-311G**)$_c$ = –272.511649 a.u.
E(rel.) = 0.79 kcal/mol	E(rel.) = 1.40 kcal/mol	E(rel.) ≡ 0.00 kcal/mol	E(rel.) = –3.06 kcal/mol
Structural Data:	Structural Data:	Structural Data:	Structural Data:
H712 19.86°	H712 87.38°	H712 172.28°	H712 179.90°
5-1 1.6622 Å	5-1 1.5724 Å	5-1 1.6761 Å	5-1 1.5844 Å
6-1 1.5578 Å	6-1 1.5618 Å	6-1 1.5677 Å	6-1 1.5844 Å
2-1 1.5481 Å	2-1 1.6062 Å	2-1 1.5391 Å	2-1 1.5558 Å
7-1 1.4261 Å	7-1 1.4346 Å	7-1 1.4162 Å	7-1 1.4449 Å
H71 104.97°	H71 106.28°	H71 107.25°	H71 133.66°
7a-b1	**7a-b2**	**7a-b3**	**7a-b4**
			
E(B3LYP/6-31G*) = –272.5740355 a.u.	E(B3LYP/6-31G*) = –272.5776618 a.u.	E(B3LYP/6-31G*) = –272.5772071 a.u.	E(B3LYP/6-31G*) = –272.5741894 a.u.
ZPE = 0.145392(1) a.u.	ZPE = 0.145377(1) a.u.	ZPE = 0.145397(1) a.u.	ZPE = 0.145425(1) a.u.
E(B3LYP/6-311G**)$_c$ = –272.499075 a.u.	E(B3LYP/6-311G**)$_c$ = –272.503378 a.u.	E(B3LYP/6-311G**)$_c$ = –272.502656 a.u.	E(B3LYP/6-311G**)$_c$ = –272.499623 a.u.
E(rel.) = 4.83 kcal/mol	E(rel.) = 2.13 kcal/mol	E(rel.) = 2.59 kcal/mol	E(rel.) = 4.49 kcal/mol
Structural Data:	Structural Data:	Structural Data:	Structural Data:
H 712 0.00°	H712 61.42°	H712 121.73°	H712 179.94°
5-1 1.5937 Å	5-1 1.5920 Å	5-1 1.5752 Å	5-1 1.5894 Å
6-1 1.5939 Å	6-1 1.5648 Å	6-1 1.5890 Å	6-1 1.5894 Å
2-1 1.5552 Å	2-1 1.5716 Å	2-1 1.5714 Å	2-1 1.5511 Å
7-1 1.4579 Å	7-1 1.4494 Å	7-1 1.4486 Å	7-1 1.4542 Å
H71 107.87°	H71 104.38°	H71 108.60°	H71 113.76°

[a] See Ref.[8]

indicated whether the structures were local energy minima or first order saddle points. Finally, the energies were recalculated at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) level of theory. The restricted formalism was used with the exception of compounds **8**, **9**, **13**, and **14**, where the unrestricted mode was also applied. In these cases the $<S^2>$ values were 0.00, indicating that pure singlet states of the bridgehead olefins were obtained.

Carbenes 7

Our B3LYP calculations show that carbene **7a** in its singlet electronic state exists as a collection of rotamers **7a−m1** to **7a−m3** and their mirror images, which are all local energy minima. These rotamers are separated by the transition structures **7a−b1** to **7a−b4** and the mirror images of **7a−b2** and **7a−b3** (see Table 1). Structure **7a−m3** is the rotamer of lowest energy and the rotational barrier to its mirror image is 4.5 kcal/mol and that to **7a−m2** is 2.6 kcal/mol. Rotamer **7a−m1** is separated from its mirror image by a barrier of 4.0 kcal/mol, and from **7a−m2** by a barrier of 0.7 kcal/mol.

The structures of the local minima **7a−m1** to **7a**−**m3** are the result of an interaction of the empty orbital at the carbenic carbon C7 with appropriate orbitals of the CC framework of the bicyclo[2.1.1]hexane skeleton. This interaction leads to a shortening of the C1−C7 bond and, depending on the dihedral angle H−C7−C1−C2, to a lengthening of the corresponding framework C−C bond (C1−C5 for **7a−m1** and **7a−m3**, C1−C2 for **7a−m2**, see Table 1).

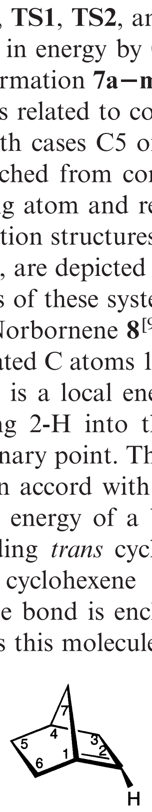
No systematic efforts were undertaken to find all stationary points of the triplet of **7a** (**7a−triplet**) with respect to the variation of the dihedral angle H−C7−C1−C2. Calculations with starting values for the dihedral angle H−C7−C1−C2 of 0°, 45°, 90°, 135°, and 180° afforded **7a-triplet** as the structure of minimum energy, and this is 3.1 kcal/mol below **7a−m3**. The bond lengths of **7a−triplet** are close to those of the transition structure **7a−b4**; the main differences in these structures is the angle at the carbenic carbon (133.7° versus 113.8°).

Substitution of the hydrogen by chlorine at the carbenic center stabilizes the singlet state considerably.[7] The singlet state of 1-bicyclo[1.1.1]pentyl-chlorocarbene has been computed to be more stable by 6.8 kcal/mol than the triplet state.[3] This also holds for 1-bicyclo[2.1.1]hexylchlorocarbene **7b**: the singlet of **7b** was lower in energy than the triplet by 8.1 kcal/mol (**7b−singlet**: E_S {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)} = −732.3015897 a.u.; corrected Zero-point energy{B3LYP/6-31G(d)} = 0.138577 a.u.; $E(ZPE_{cor})$ = −732.163020 a.u.; **7b−triplet**: E_T {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)} = −732.2889628 a.u.; corrected Zero-point energy {B3LYP/6-31G(d)} = 0.138853 a.u.; $E(ZPE_{cor})$ = −732.150110 a.u; $E_T - E_S$ = 8.1 kcal/mol).

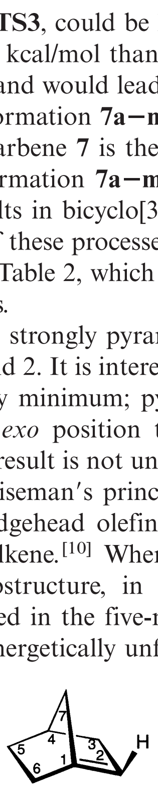
Rearrangement of Carbene 7a

Depending on the conformation of **7a**, three transition states, **TS1**, **TS2**, and **TS3**, could be located: **TS1**, which is lower in energy by 0.5 kcal/mol than **TS2**, is reached from conformation **7a−m3** and would lead to 1-norbonene **8exo**. **TS2** is related to conformation **7a−m1** and leads to **8endo**. In both cases C5 of carbene **7** is the migrating atom. **TS3** is reached from conformation **7a−m2** with C2 as the migrating atom and results in bicyclo[3.1.1]hept-1-ene **9**. The transition structures of these processes, together with **8endo** and **9**, are depicted in Table 2, which also shows the energy values of these systems.

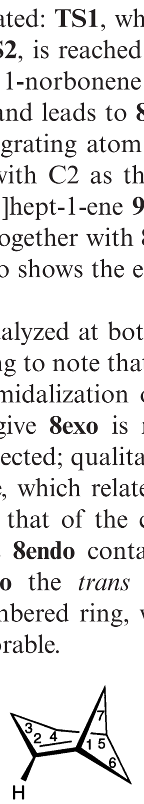
1-Norbornene **8**[9] is strongly pyramidalyzed at both unsaturated C atoms 1 and 2. It is interesting to note that only **8endo** is a local energy minimum; pyramidalization of C2 placing 2-H into the *exo* position to give **8exo** is not a stationary point. This result is not unexpected; qualitatively it is in accord with Wiseman's principle, which relates the strain energy of a bridgehead olefin to that of the corresponding *trans* cycloalkene.[10] Whereas **8endo** contains a *trans* cyclohexene substructure, in **8exo** the *trans* C−C double bond is enclosed in the five-membered ring, which makes this molecule energetically unfavorable.



8endo



8exo



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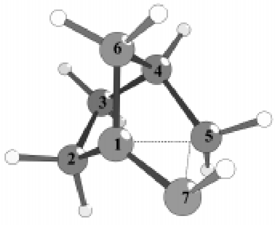
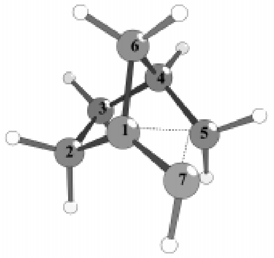
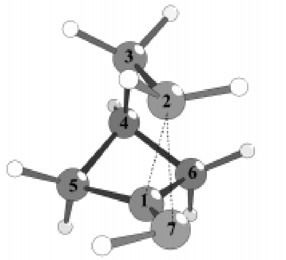
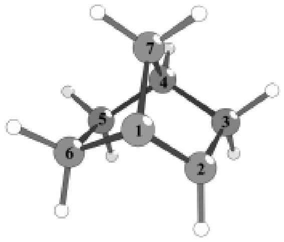
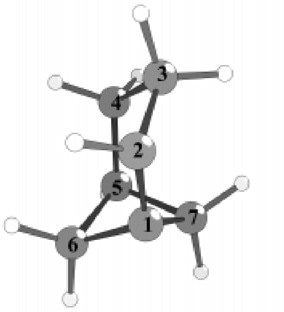
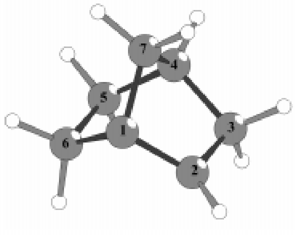
The twisting of the C−C double bond in **8** could favor the triplet state. Our calculation showed that the triplet energy was 14.85 kcal/mol above that of the singlet state. An interesting feature of the structure of the triplet is, besides the long C1−C2 bond of 1.485 Å, the position of 2-H, which is located in the *exo* hemisphere of **8**.

The data in Table 2 show that in carbene **7a** the propensity for migration is considerably higher for C5 than for C2 (atom a versus atom b, see Scheme 1). The transition structure **TS2** is lower in energy by 5.0 kcal/mol compared to **TS3**. The low activation barrier of only 2.3 kcal/mol for the formation of 1-norbornene **8endo** will leave little chance for the external trapping of carbene **7a**.

At −39.3 kcal/mol and −34.2 kcal/mol, both reactions of carbene **7a** to **8endo** and **9** are strongly exothermic. This result lends weight to the assumption that the bridgehead olefins **8endo** and **9** are not sufficiently strained to undergo a second rearrangement, as observed in the case of the lower homologue where the carbene/bridgehead-olefin conversion was only slightly exothermic.[3] Alkene **8endo** could lead either to carbene **10** or to carbene **11** depending on whether atom c or d migrates. In contrast, the carbon skeleton of olefin **9** can only rearrange to carbene **11** (see Scheme 1).

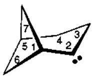
The transition states **TS4** (**8endo** → **11**), **TS5** (**8endo** → **10**) and **TS6** (**9** → **11**) of these rearrangements could be located. The results are shown in Table 3.

Table 2. Computer-generated B3LYP/6-31G(d) structures of **TS1**, **TS2**, **TS3**, **8endo**, **9**, and **8-triplet**, their corresponding B3LYP/6-31G(d,)//B3LYP/6-31G(d) energies, B3LYP/6-31G(d) Zero-point energies (corrected with the factor 0.9804[a]), {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)}$_c$ energies (Zero-point energy corrected) and selected structural data

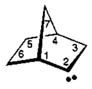
TS1	**TS2**	**TS3**
		
$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.5796108 a.u. ZPE = 0.146941(1) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272.503790 a.u. E(rel.)[b] = 1.88 kcal/mol	$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.5784499 a.u. ZPE = 0.146651(1) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272.503063 a.u. E(rel.)[b] = 2.33 kcal/mol	$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.5708546 a.u. ZPE = 0.146381(1) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272. 495089 a.u. E(rel.)[b] = 7.34 kcal/mol
Structural Data: 5-1 1.8627 Å 7-1 1.3912 Å 7-5 1.7493 Å	Structural Data: 5-1 1.8396 Å 7-1 1.3948 Å 7-5 1.9611 Å	Structural Data: 2-1 1.8689 Å 7-1 1.3820 Å 7-2 1.9119 Å
8endo	**9**	**8-triplet**
		
$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.6488844 a.u. ZPE = 0.149214(0) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272. 569396 a.u. E(rel.)[b] = –39.29 kcal/mol	$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.64062234 a.u. ZPE = 0.149071(0) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272.561212 a.u. E(rel.)[b]= –34.16 kcal/mol	$E(\mathrm{B3LYP/6\text{-}31G^{*}})$ = –272.6202127 a.u. ZPE = 0.146929(0) a.u. $E(\mathrm{B3LYP/6\text{-}311G^{**}})_c$ = –272.545732 a.u. E(rel.)[b]= –24.44 kcal/mol
Structural Data: 2-1 1.3584 Å H234 126.17° H216 49.97° H217 164.81°	Structural Data: 2-1 1.3570 Å H216 49.77° H217 153.74°	Structural Data: 2-1 1.4849 Å H234 198.13° H216 234.52° H217 124.42°

[a] See ref.[a] – [b] With respect to the energy of **7a–m3** (see Table 1).

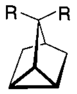
In Figure 1 the energetic diagram of the rearrangement of 1-norbornene **8endo** is depicted. The rearrangements of **8endo** to carbenes **10** and **11** are energetically unfavorable as they not only demand high energy barriers, but also show considerable endothermicity. This result could lead to the assumption that the reversible reaction, **11** → **8endo** (barrier 13.0 kcal/mol) or, less probably, **11** → **9** (barrier 22.6 kcal/mol), could take place under reasonably mild conditions. However, this assumption does not hold: The reaction **11** → **8** and competing routes of stabilization of 2-norbor-



10



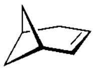
11



17a: R = H

17b: R = Me

18



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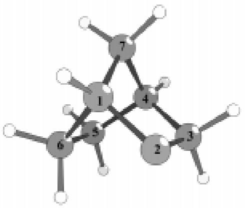
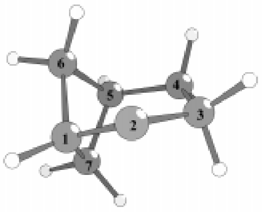
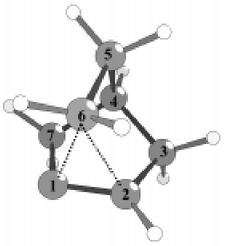
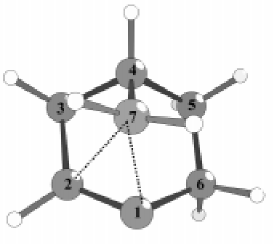
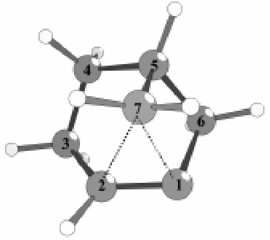
nylidene **11** have been thoroughly studied theoretically by Platz and Schaefer et al.[11] These authors found that insertion of the carbenic center C2 into the C6−H(*endo*) bond to give nortricyclane **17a** is the fastest process, a situation that is completely in accord with experimental results.[12][13]

An impressive experimental report concerning the behavior of **8** came from the laboratory of Barton, who found that 7,7-dimethyl-1-norbornene, generated at about 600°C in the gas phase, was converted into nortricyclane **17b** as the final product, probably via 3,3-dimethylbicyclo[2.2.1]hept-2-ylidene (3,3-Me$_2$-**11**).[14] For carbene **10**, the preferred modes of stabilization were found to be CH insertion into one of the methylene groups of the four-membered ring to give **18**, and hydrogen migration to produce alkene **19**.[15]

Rearrangement of bridgehead alkene **9**, which is less stable by 5.1 kcal/mol than **8endo**, will lead to carbene **11**. At 26.8 kcal/mol, the barrier to give carbene **11** is higher by 4.5 kcal/mol than the barrier of **8endo** → **11**. As seen

Table 3. Computer-generated B3LYP/6-31G(d) structures of **10**, **11**, **TS4**, **TS5**, and **TS3**, their corresponding B3LYP/6-31G(d,)//B3LYP/6-31G(d) energies, B3LYP/6-31G(d) Zero-point energies (corrected with the factor 0.9804[a]), {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)}$_c$ energies (Zero-point energy corrected)

11	**10**	**TS4**
		
E(B3LYP/6-31G*) = –272.6317708 a.u. ZPE = 0.148079(0) a.u. E(B3LYP/6-311G**)$_c$ = –272.554583 a.u. E(rel.)[b] = 9.30 kcal/mol	E(B3LYP/6-31G*) = –272.6065584 a.u. ZPE = 0.147458(0) a.u. E(B3LYP/6-311G**)$_c$ = –272.529782 a.u. E(rel.)[b] = 24.85 kcal/mol	E(B3LYP/6-31G*) = –272.6093881 a.u. ZPE = 0.147148(1) a.u. E(B3LYP/6-311G**)$_c$ = –272.533918 a.u. E(rel.)[b] = 22.26 kcal/mol
TS5	**TS6**	
		
E(B3LYP/6-31G*) = –272.576177 a.u. ZPE = 0.145926(1) a.u. E(B3LYP/6-311G**)$_c$ = –272.501608 a.u. E(rel.)[b] = 42.53 kcal/mol	E(B3LYP/6-31G*) = –272.594258 a.u. ZPE = 0.146918(1) a.u. E(B3LYP/6-311G**)$_c$ = –272.518561 a.u. E(rel.)[b] = 31.90 kcal/mol	

[a] See ref.[8] – [b] E(rel.) with respect to **8endo** (see Table 2).

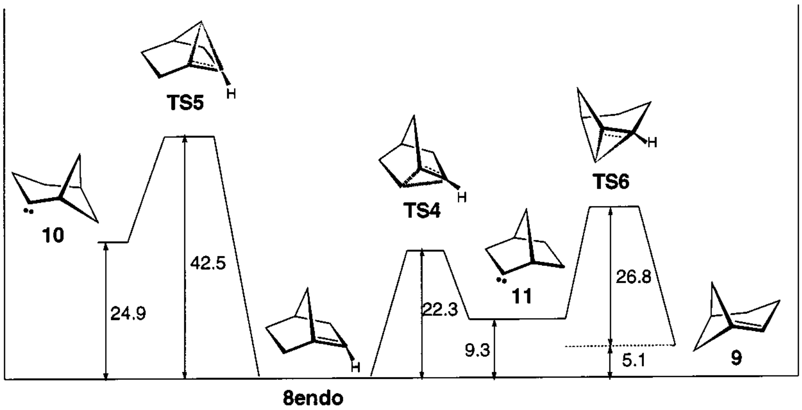


Figure 1. Energies (kcal/mol) for **8endo**, **9**, **10**, **11** and transition barriers **TS4**, **TS5**, and **TS6**, which separate these molecules

for **8endo**, a high temperature rearrangement of **9** to afford carbene **11** seems possible, which again could lead to nortricyclane **17**.

Rearrangement of Carbene 12

A search for all stationary points of carbene **12** with respect to the dihedral angle H−C8−C1−C2 was not undertaken. Calculations starting with dihedral angles of 0°, 45°, 90°, 135°, 180°, 225°, 270°, and 315° showed that the minimum energy conformation was **12m**, whose structure is given in Table 4. This structure is strongly related to the minimum energy structure of the lower homologue **7a−m3**, the empty carbene orbital interacting with the bond C1−C6, which is markedly elongated (1.687 Å).

The rearrangement of **12** can lead to bridgehead alkenes **13** and **14** (see Scheme 2), whose energies and structures are also shown in Table 4. The transition structures **TS7** (**12m** → **13**) and **TS8** (**12m** → **14**) could be located. The relative energies of **12m**, **13**, **14**, and the barriers (**TS7−12m**) and (**TS8−12m**) are also given in Table 4. The $E_{(\mathrm{rel})}$ values reveal that both rearrangements are strongly exothermic. Whereas the bond shift of **12m** to give **13** hardly needs any activation, the rearrangement of **12m** to form **14** must pass over a barrier of 7.9 kcal/mol and should not compete favorably with the conversion of **12m** into **13**.

A consecutive carbon skeletal rearrangement of bridgehead olefins **13** and **14** to afford carbenes **15** and **16** seems rather unlikely for energetic reasons. The calculated energy difference, corrected for ZPE, that was obtained from a B3LYP/6-31G(d) calculation amounted for *E*(**16**) − *E*(**13**) to 32.2 kcal/mol [*E*(**16**): B3LYP/6-31G(d)//B3LYP/6-31G(d) = −311.9515576 a.u.; ZPE/corr. = 0.177062(0) a.u.; B3LYP/6-311G(d,p)//B3LYP/6-31G(d) corrected for ZPE = −311.855383 a. u.], for *E*(**15**) − *E*(**13**) to 53.5 kcal/mol [*E*(**15**): B3LYP/6-31G(d)//B3LYP/6-31G(d) = −311.9166982 a.u.; ZPE/corr. = 0.176029(0) a.u.; B3LYP/6-311G(d,p)//B3LYP/6-31G(d) corrected for ZPE = −311.821445 a.u.], and for *E*(**16**) − *E*(**14**) to 17.3 kcal/mol. These strongly varying energy differences reflect the increase in strain energy in the reaction of **13** → **15**, and the decrease in strain energy in going from **14** → **16** (see Scheme 2).

Summing up the results of our calculations, carbenes **7a** as well as **12** will rearrange to the corresponding bridgehead olefins **8endo** and **13** over small energy barriers with a preferred migration of the methylene group from the four-membered ring. At high temperatures **8endo** could be converted into 2-norbornylidene **11**; a related rearrangement of **13** to **16** is unlikely.

Generation of 1-(5-Bromobicyclo[3.1.1]heptyl)bromocarbene

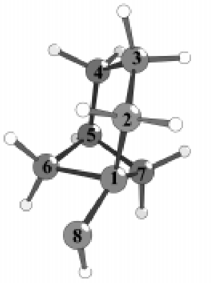
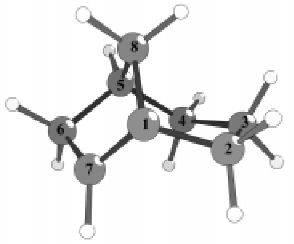
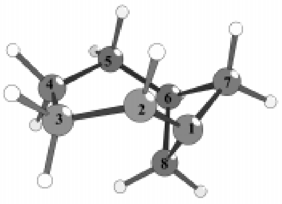
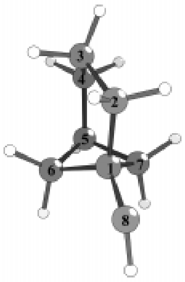
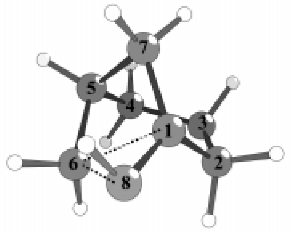
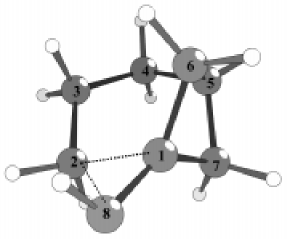
In this section the formation of the title compound, a dibromo derivative of carbene **12**, and aspects of its chemistry under mild reaction conditions is reported.

[3.1.1]Propellane **20** has become accessible with moderate effort from tetrahalide **21** with MeLi.[16] This hydrocarbon shares with **22**, the parent hydrocarbon of the [*n*.1.1]propellane family, the facile radical chain addition of halomethanes across the central C−C bond. The addition of carbon tetrabromide to **20** afforded adduct **23** in 45% yield. Compound **23** was treated with MeLi/LiBr under different experimental conditions. On using cyclohexene as a solvent and as a trap for carbenic intermediates, a 4% yield of adduct **24** was isolated. In addition, **25** and **26** were obtained in yields of 3% and 32%, respectively. Furthermore, a fourth compound was isolated in 5% yield, whose structure is presumably **27**.

The structure of **24** is based on the NMR spectroscopic data of the adduct; the configuration at C-7 of the norcarane subunit has not been established. Compound **25** was identical with the product obtained by the addition of bromoform to **20**.[17] Compounds **26** and **27** are (2π + 2π) cyclodimers of bridgehead olefin **31**.

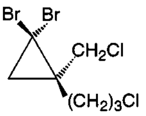
The structure of **26** was determined by X-ray crystallography (see Figure 2) and **26** was found to have a C_2 axis of symmetry, which was in accord with the NMR spectra.

Table 4. Computer-generated B3LYP/6-31G(d) structures of **12m**, **13**, **14**, **12-triplet**, **TS7**, and **TS8**, their corresponding B3LYP/6-31G(d,)//B3LYP/6-31G(d) energies, B3LYP/6-31G(d) Zero-point energies (corrected with the factor 0.9804[a]), {B3LYP/6-311G(d, p)//B3LYP/6-31G(d)}$_c$ energies (Zero-point energy corrected) and selected structural data

12m	**13**	**14**
		
E(B3LYP/6-31G*) = –311.9084771 a.u. ZPE = 0.176273(0) a.u. E(B3LYP/6-311G**)$_c$ = –311.813364 a.u. E(rel.) ≡ 0.00 kcal/mol	E(B3LYP/6-31G*) = –312.005808 a.u. ZPE = 0.178830(0) a.u. E(B3LYP/6-311G**)$_c$ = –311.906666 a.u. E(rel.) = –58.55 kcal/mol	E(B3LYP/6-31G*) = –311.9818362 a.u. ZPE = 0.178278(0) a.u. E(B3LYP/6-311G**)$_c$ = –311.883166 a.u. E(rel.) = –43.80 kcal/mol
Structural Data: H812 168.35° 6-1 1.6871 Å 7-1 1.5596 Å 2-1 1.5314 Å 8-1 1.4156 Å H81 107.82°	Structural Data: 7-1 1.3466 Å H712 35.57° H765 –136.65° H718 171.08°	Structural Data: 2-1 1.3403 Å H217 –39.66° H218 –155.13° 3217 115.16° 3218 –0.31°
12-triplet	**TS7**	**TS8**
		
E(B3LYP/6-31G*) = –311.9094975 a.u. ZPE = 0.174863(0) a.u. E(B3LYP/6-311G**)$_c$ = –311.814513 a.u. E(rel.) =–0.72 kcal/mol	E(B3LYP/6-31G*) = –311.9066021 a.u. ZPE = 0.175747(1) a.u. E(B3LYP/6-311G**)$_c$ = –311.812323 a.u. E(rel.) = 0.65 kcal/mol	E(B3LYP/6-31G*) = –311.8951291 a.u. ZPE = 0.175196(1) a.u. E(B3LYP/6-311G**)$_c$ = –311.800799 a.u. E(rel.) = 7.88 kcal/mol
Structural Data: 6-1 1.5840 7-1 1.5768 2-1 1.5539 8-1 1.4562 H81 132.58° d H 812 186.14°	Structural Data: 6-1 1.8632 Å 8-6 1.7100 Å 8-1 1.3972 Å 681 72.90° H817 –29.53°	Structural Data: 2-1 1.8461 Å 8-2 1.8712 Å 8-1 1.3832 Å 821 43.68° H817 177.55°

[a] See ref.[8]

20



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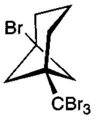
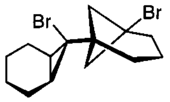
22



23



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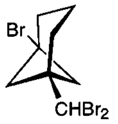

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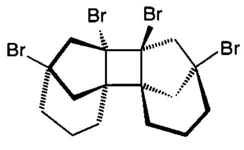
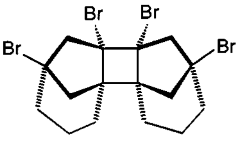


26



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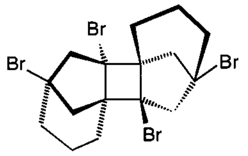

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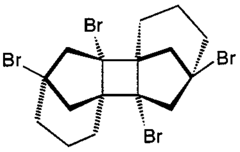


29

The NMR spectra and analytical data of the last compound indicated that it was a stereoisomer of **26**; the probable structure is **27**, but the head-to-tail structures **28** and **29** cannot be excluded from the available data.

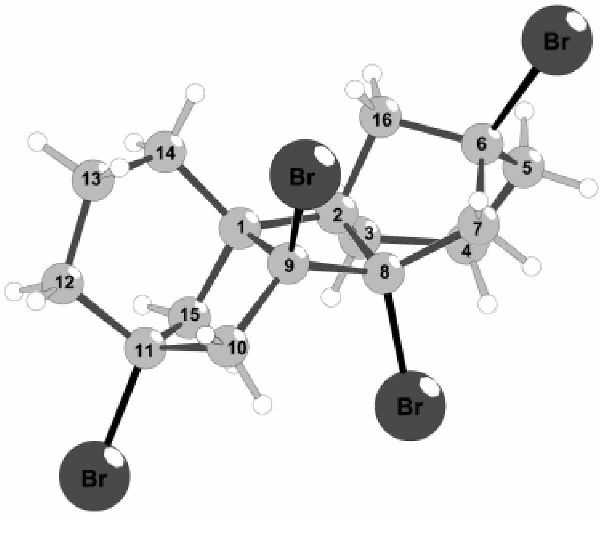
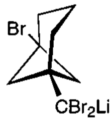
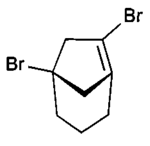


Figure 2. X-ray structure of **26**; selected structural parameters: bond lengths [Å]: C1−C2 1.532(10), C1−C9 1.536(7), C2−C3 1.525(8), C3−C4 1.524(11), C4−C5 1.537(10), C5−C6 1.519(9), C6−C7 1.530(9), C7−C8 1.552(10), C8−C9 1.586(9), C2−C16 1.539(9), C6−C16 1.500(10), C6−Br 1.969(6), C8−Br 1.967(6); bond angles [°]: C2−C1−C9 90.06, C1−C9−C8 88.11; dihedral angles (°): C1−C2−C8−C9 −14.41, Br−C8−C9−Br 135.13

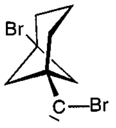
Formation of **24** and **25** are due to carbenoid **30**, which can give the cycloadduct **24** with cyclohexene; **25** is the product of protonation of carbenoid **30** by a proton source present in the reaction mixture. Bridgehead olefin **31** would be the logical precursor of dimer **26**. Under this premise, this result implies that carbene **32**, formed by α-elimination of LiBr from carbenoid **30**, rearranges by enlargement of the four-membered ring to give **31**. Evidence for the alternative formation of alkene **33** by enlargement of the six-membered ring was not obtained. This is in full agreement with our calculations discussed previously and with the experiments described by Wolf and Jones, who also found the preferred migration of the small-ring methylene group to an exocyclic carbenic center.[18]



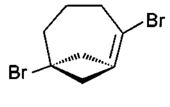
30



31



32



33

Experimental Section

Materials: Methyllithium (MeLi) was synthesized according to standard procedures from bromomethane and lithium in ether. The content was determined by Gilman's double titration.[19] Tricyclo[3.1.1.0^{1,5}]heptane (**20**, [3.1.1]propellane) was obtained as reported earlier[16] by reaction of tetrahalide **21** with MeLi.

1-Bromo-5-tribromomethylbicyclo[3.1.1]heptane (23): A solution of **21** (1.13 g, 3.48 mmol) was mixed with MeLi (6.96 mmol) in ether (20 mL) at −78 °C and allowed to warm up to room temperature under nitrogen. After 24 h, all volatile components were condensed into a trap cooled with liquid nitrogen. To this distillate was added tetrabromomethane (3.46 g, 10.4 mmol) and the mixture kept for 20 h at room temp. The solvent was removed in vacuo and the oily residue purified by flash column chromatography with silica gel and petroleum ether as eluent. This process afforded **23** (660 mg, 45%, with respect to **21**) as a white solid, which melted at 83−85 °C after crystallization from petroleum ether. IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 2953, 2867, 1447, 1332, 1319, 1233, 1154, 936, 883, 840, 707, 698, 522. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.02 (m, 2 H, 3-H$_2$), 2.20 (m, 2 H, 4-H$_2$), 2.29 (m, 2 H, 6-H$_{endo}$, 7-H$_{endo}$), 2.36 (m, 2 H, 2-H$_2$), 2.98 (m, 2 H, 6-H$_{exo}$, 7-H$_{exo}$). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.4 (t, C-3), 30.6 (t, C-4), 39.4 (t, C-2), 47.3 (t, C-6, C-7), 50.4 (s, C-5), 55.43 (s, C-1), 59.1 (s, CBr$_3$). − MS (70 eV, EI); *m/z* (%): 349, 347, 345, 343 (5, 15, 17, 6) [M$^+$− Br], 267 (47), 265 (92), 263 (45), 186 (30), 185 (100), 184 (28), 183 (77), 105 (91), 82 (48), 80 (51), 79 (33), 77 (49). − $C_8H_{10}Br_4$ (425.78): calcd. C 22.57, H 2.37, Br 75.06; found C 22.76, H 2.43, Br 75.34.

1-Bromo-5-dibromomethylbicyclo[3.1.1]heptane (25):[17] A solution of [3.1.1]propellane **20** in ether, obtained from **21** (1.46 g, 4.49 mmol) and MeLi (9.98 mmol) in ether (30 mL) as described above, was charged with bromoform (3.41 g, 13.5 mmol) and ether (70 mL) and the solution irradiated in a quartz apparatus with a 150 watt mercury high-pressure lamp. The solvent of the dark-brown solution was evaporated under vacuum. Flash column chromatography of the residue with silica gel and petroleum ether as eluents afforded **25** (980 mg, 63%) as colorless crystals, which melted, after purification from petroleum ether, at 79−81°C. IR (KBr): ṽ = 3006 cm^{-1}, 2981, 2952, 2864, 1449, 1321, 1283, 1195, 1149, 947, 885, 836, 692, 505. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (m, 4 H, 3-, 4-H_2), 2.30 (m, 2 H, 6-H_{endo}, 7-H_{endo}), 2.33−2.41 (m, 4 H, 2-H_2, 6-H_{exo}, 7-H_{exo}), 5.70 (s, $CHBr_2$). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (t, C-3), 27.3 (t, C-4), 39.3 (t, C-2), 48.8 (t, C-6, C-7), 49.8 (s, C-5), 51.4 (s, C-1), 55.1 (d, $CHBr_2$). − MS (70 eV, EI); *m/z* (%): 269, 267, 265 (35, 71, 36) [M^+− Br], 187 (98), 185 (100), 106 (39), 105 (89), 91 (27), 79 (29). − $C_8H_{11}Br_3$ (346.88): calcd. C 27.70, H 3.20, Br 69.10; found C 27.93, H 3.22, Br 69.11.

Reaction of 23 with MeLi: A solution of MeLi (3.45 mmol) in ether was added dropwise to a solution of **23** (1.32 g, 3.10 mmol) in cyclohexene (30 mL) with stirring at room temp. After aqueous workup, 0.91 g of a solid product was isolated by removing all volatile components of the organic phase in vacuo. Recrystallization of the solid from chloroform afforded 6,(*E*-8,9),11-tetrabromopentacyclo[9.3.1.1^{2,6}.0^{1,9}.0^{2,9}]hexadecane (**26**) (535 mg, 32%), m.p. 233−235°C (dec.). The chloroform was removed from the mother liquor and the residue crystallized from petroleum ether, which led to the isolation of an isomer of **26** for which the structure 6,(*Z*-8,9),11-tetrabromopentacyclo[9.3.1.1^{2,6}.0^{1,9}.0^{2,9}]hexadecane (**27**) has been assumed [90 mg, 5%, colorless crystals of m.p. 225−226°C (dec.)]. The remaining material from the mother liquor was subjected to a preparative HPLC separation (Eurospher 100, petroleum ether), which led to the isolation of 1-bromo-5-(7-bromobicyclo[4.1.0]hept-7-yl)bicyclo[3.1.1]heptane (**24**) (41 mg, 4%) as colorless crystals of m.p. 87°C, and **25** (30 mg, 3%) as crystals of m.p. 77−79°C, i.e. identical to the product described above.

26: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40−1.53 (m, 2 H), 1.61−1.66 (m, 2 H), 1.77−1.84 (m, 2 H), 1.89−1.94 (m, 2 H), 2.13−2.20 (m, 2 H), 2.20−2.27 (m, 2 H), 2.46−2.50 (m, 2 H), 2.97 (dd, 2 H, *J* = 15.4 Hz, *J* = 3.7 Hz), 3.30 (td, 2 H, *J* = 11.8 Hz, *J* = 2.9 Hz), 3.94 (dd, 2 H, *J* = 15.4 Hz, *J* = 1.5 Hz). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (t), 29.6 (t), 44.1 (t), 50.1 (t), 57.2 (s), 61.3 (t), 64.0 (s), 77.5 (s). − MS (70 eV, EI); *m/z* (%): 455, 453, 451, 449 (5, 14, 14, 5) [M^+− Br], 169 (23), 155 (22), 141 (38), 129 (35), 128 (42), 115 (40), 100 (54), 83 (32), 81 (40), 79 (36), 41 (100). − $C_{16}H_{20}Br_4$ (531.95): calcd. C 36.13, H 3.79, Br 60.08; found C 36.63, H 3.87, Br 58.93.

27: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76−1.94 (m, 6 H), 2.61 (m, 2 H), 2.84−2.94 (m, 4 H), 2.15, 2.31 (2 × dd, 2 H each, *J* = 11.1 Hz, *J* = 2.6 Hz), 2.93, 3.01 (2 × dd, 2 H each, *J* = 13.4 Hz, *J* = 3.0 Hz). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7 (t), 30.6 (t), 39.2 (t), 47.9 (t), 56.6 (s), 61.3 (t), 61.3 (t), 61.9 (s), 82.2 (s). − MS (70 eV, EI); *m/z* (%): 456, 454, 452, 450 (5, 13, 16, 9) [M^+ − Br + H], 455, 453, 451, 449 (21, 59, 60, 20) [M^+ − Br], 209 (41), 141 (54), 131 (41), 129 (56), 128 (55), 115 (56), 91 (100), 79 (68), 77 (69). − $C_{16}H_{20}Br_4$ (531.95): calcd. C 36.13, H 3.79, Br 60.08; found C 36.06, H 3.64, Br 59.59.

24: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03, 1.20, 1.45 (3 × m, 6 H), 1.84−2.06 (m, 6 H), 2.08 (m, 2 H), 2.22 (m, 2 H), 2.31 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.4 (d, 2 C), 19.0 (t), 20.7 (t, 2 C), 20.8 (t, 2 C), 31.0 (t), 39.9 (t), 47.2 (t, 2 C), 49.4 (s), 55.3 (s), 60.8 (s). − MS (70 eV, EI); *m/z* (%): 269, 267 (2, 2) [M^+ − Br], 187 (71), 145 (39), 131 (62), 119 (52), 105 (44), 93 (38), 91 (100), 81 (32), 79 (69), 77 (51). − $C_{14}H_{20}Br_2$ (348.12): calcd. C 48.30, H 5.79, Br 45.91; found C 48.02, H 5.73, Br 46.78.

Crystal Structure Analysis for Compound 26: Empirical formula $C_{16}H_{20}Br_4$; formula weight 531.96; temperature 293(2) K; wavelength 0.71073 Å; crystal system monoclinic; space group *C*2/c; unit cell dimensions a = 12.356(2) Å, b = 10.525(2)Å, β = 114.580(2)°, c = 14.133(3) Å; volume 1671.4(5) Å^3; Z = 4; density (calculated) 2.114 Mg/m^3; absorption coefficient 9.620 mm^{-1}; $F(000)$ 1024; crystal size 0.50 × 0.40 × 0.20 mm; theta range for data collection 2.65 to 22.95°; index ranges $-13 \le h \le 12$, $0 \le k \le 11$, $-13 \le l \le 15$; reflections collected 1712; independent reflections 1158 [R(int) = 0.0424]; absorption correction semi-empirical from ψ-scans; max. and min. transmission 0.9947 and 0.6771; refinement method full-matrix least-squares on F^2; data/restraints/parameters 1158/0/91; goodness-of-fit on F^2 1.188; final R indices [$I > 2\sigma(I)$] $R1$ = 0.0339, w$R2$ = 0.0862; R indices (all data) $R1$ = 0.0428, w$R2$ = 0.0888; largest diff. peak and hole 0.413 and −0.593 e·Å^{-3}.[20]

The structure of **26** was solved using the programs SHELXS-86[21] and SHELXL-93.[22]

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