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Synthesis and Dynamic NMR Studies of Heptachloro-7-(dihalomethyl)naphthalenes

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Abstract: Photochlorinations of nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (**1**) and nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (**2**) give nonachloro-3-(dichloromethyl)-1,4-dihydronaphthalene (**3**) and nonachloro-7-(dichloromethyl)-1,4-dihydronaphthalene (**4**), respectively. Dechlorination of both **3** and **4** by means of $SnCl_2.2H_2O$ affords heptachloro-7-(dichloromethyl)naphthalene (**5**). Photobromination of heptachloro-7-methylnaphthalene (**6**) with Br_2 results in 2-(bromomethyl)heptachloronaphthalene (**8**) or heptachloro-7-(dibromomethyl)naphthalene (**7**), depending on the reaction time. Intermediate **8** can be prepared in high yield by bromination of **6** with NBS in the presence of AIBN. Theoretical calculations in **7** indicate the existence of two energetically favoured conformers and that one of them seems to be slightly more stable than the other one. Accordingly, the ^1H NMR spectra of **5**, **7**, and 2-(bromochloromethyl)heptachloronaphthalene (**9**) are temperature dependent, displaying two singlets that collapse in a sharp singlet about 100 °C. Although the two conformers of **5**, **7**, and **9** can be detected in solution, only the most stable of each pair, at least in the case of **7**, is present in solid form (X-ray analysis). A dynamic ^1H NMR study shows that the barriers to rotation of $CHCl_2$, CHBrCl, and $CHBr_2$ groups in **5**, **9**, and **7** are as high as 16.8, 18.2, and 19.3 kcal mol^{-1}, respectively. The X-ray structure of **7** is commented, and spectral data of the synthesized compounds are reported.

The essence of conformational analysis is the study of how molecules accommodate strain. A lot of research has gone into the conformational analysis of those substituted naphthalenes with substituents at the 1 and 8 positions (peri positions).[1] Relief of steric strain in these naphthalenes tends to favour out-of-plane distortions because of a buttressing effect exerted by the 2,7 hydrogens.

In the context of our investigations on highly chlorinated compounds, we have reported the synthesis of many polychloronaphthalenes and their properties.[2] In this paper, principally we report the synthesis of (dichloromethyl)naphthalene **5** and (dibromomethyl)naphthalene **7** which offer a good opportunity to study in solution the conformational analysis by dynamic nuclear magnetic resonance (DNMR) of perchloroaromatic

naphthalenes with a substituent in the 2 position. By analogy with the conformational analysis in benzenes, it has been indicated that a low-strain conformation of dichloromethyl group in pentachloro(dichloromethyl)benzene is obtained when the two α-chlorines are located above and below the ring and the hydrogen lies on it.[3] It has also been reported that the barriers to rotation of dihalomethyl group in 1,3,5-trichloro-2-(dichloromethyl)benzene and 1,3,5-trichloro-2-(dibromomethyl)benzene are as high as 14.9 and 18.2 kcal mol^{-1}, respectively.[4]

From the above information, two low strain conformations were conceived for the dihalomethyl substituent in naphthalenes **5** and **7**: one of them with the aliphatic halogens above and below of the plane C_6-C_7-C_8 (see Figure 1), with the hydrogen near the neighboring aromatic α-chlorine, and the other one with the aliphatic halogens also in different side of the plane C_6-C_7-C_8, but with the hydrogen near the β-chlorine. These arrangements prompted us to initiate a study about the hindered rotation of dihalomethyl group in these new naphthalenes **5** and **7**, and, for comparison reasons, in (bromochloromethyl)naphthalene **9**.[2]

We also report theoretical calculations (semiempirical MNDO-PM3 model) for naphthalene **7** and, because of the importance of knowing just what conformations are favored for molecules of this type in the solid state, we have determined the structure of **7** by X-ray diffraction.

RESULTS AND DISCUSSION

Synthesis of the New Products

Heptachloro-7-(dichloromethyl)naphthalene (**5**) was obtained in three ways (see scheme 1): (i) photochlorination with Cl_2 of dihydronaphthalene **1**[2] to nonachloro-3-(dichloromethyl)-1,4-dihydronaphthalene (**3**) and subsequent dechlorination of this compound with $SnCl_2.2H_2O$; (ii) following the preceding method, but starting from dihydronaphthalene **2**,[2] and through nonachloro-7-(dichloromethyl)-1,4-dihydronaphthalene (**4**); and (iii) chlorination of 2-methylnaphthalene with Silberrad's Reagent,[2] purification of the crude material until a mixture containing only **1** and **2** is obtained, photochlorination with Cl_2 of this mixture to a material rich in **3** and **4** and, finally, treatment of this material with the inorganic dihalide. Since the separation of **1** from **2** is a difficult task, we recommend way (iii).

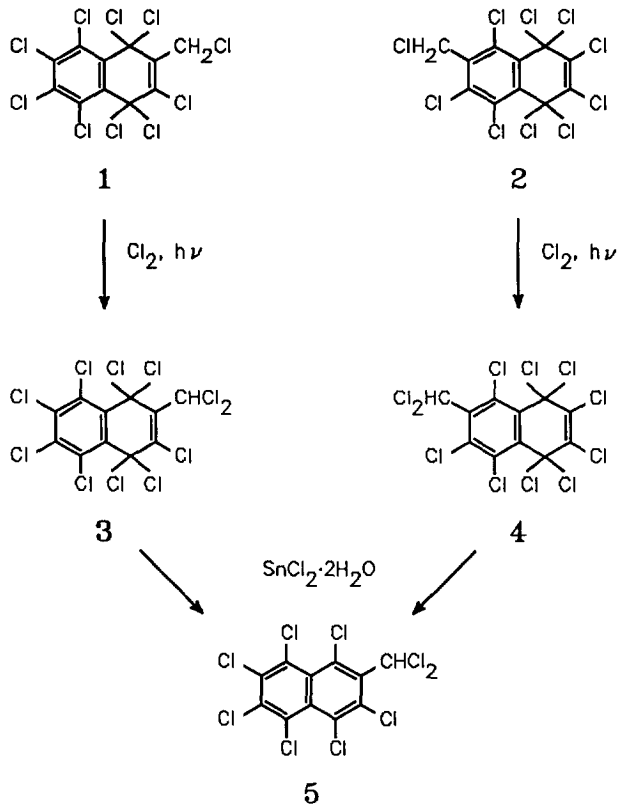
Heptachloro-7-(dibromomethyl)naphthalene (**7**) was synthesized (see scheme 2) by photobromination with Br_2 of methylnaphthalene **6**,[2] and in this connection it is mentioned that shorter reaction times permitted the preparation of 2-(bromomethyl)heptachloronaphthalene (**8**), which can also be prepared by bromination of **6** with *N*-bromosuccinimide (NBS) in the presence of small proportions of AIBN.

Structural Assignments

Structures of isomeric dihydronaphthalenes **3** and **4** were assigned by UV, IR, ^1H and ^{13}C NMR

spectroscopy. Their UV spectra are very similar in shape to those of perchloro-1,4-dihydronaphthalene,[5] nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene,[2] and nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene,[2] indicating that both **3** and **4** are dihydronaphthalenes. From the migration moment of Cl (+14)[6] and constellations 1,3,2-$Cl_2(CHCl_2)$ (-31.2),[6] *o*-$CCl_2CCl{=}CClCCl_2$ (-16.6),[2] and *o*-$CCl_2C(CHCl_2){=}CClCCl_2$ (-16.6),[7]

SCHEME 1

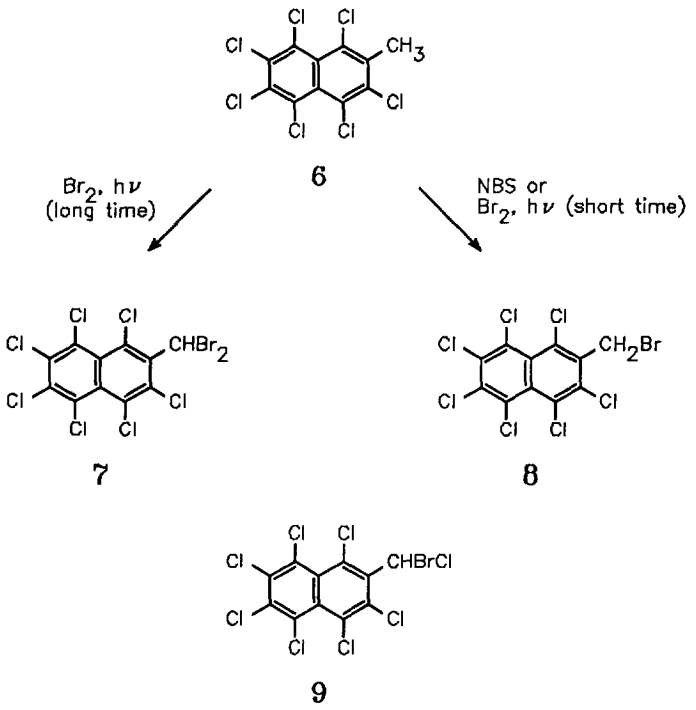


the smoothed maximum absorptivities (ε) for the secondary band of **3** and **4** were calculated.[6] The values obtained (974 for **3** and 1890 for **4**) agree reasonably with the experimental ones (1020 and 1970) supporting the structures given for these compounds. The structures of **3** and **4** were confirmed by IR and ^1H NMR spectroscopy: the position of the vinylene stretching peak of isomer **4** (1650 cm^{-1}), unlike that of **3** (1665 cm^{-1}), is almost coincident with that of perchloro-1,4-dihydronaphthalene (1645 cm^{-1});[5] the chemical shift of the singlet due to the $CHCl_2$ group is higher for **4** (δ 7.89) than for **3** (δ 6.95).

Molecular Structure of Naphthalene 7

In a single crystal of **7**, two molecules (**7a** and **7b**) with slightly different conformation were observed, probably due to the molecular packing in the crystal. A diagrammatic representation of these molecules with atom numbering and identification of the rings is shown in Figure 1. The distances between *peri* chlorines range from 2.980 to 2.999 Å, and are similar to those found for perchloronaphthalene (2.998 and 3.006 Å).[8] The other distances between neighboring chlorines range from 3.011 to 3.086 Å, all them shorter than the

SCHEME 2



sum of the van der Waals radii of two chlorine atoms (3.5 Å).[9]

In **7a**, the aromatic carbon atoms more distant from the mean plane of the bicyclic system (C_1-C_{10}) are C_1(0.242) and C_8(-0.201 Å), the atoms of ring A more distant from the mean plane of this ring are C_9 (0.103) and C_{10} (-0.108 Å), and the atoms of ring B more remote from the mean plane of this ring are also C_9 (-0.072) and C_{10} (0.098 Å). The bicyclic system, ring A and ring B are planar to within 0.443, 0.211, and 0.170 Å, respectively.

In **7b**, as in **7a** but with opposite bending, the aromatic carbon atoms more distant from the mean plane of the bicyclic system are C_1(-0.225), C_5(-0.225), and C_8(0.194 Å), the atoms of ring A more distant from the mean plane of this ring are C_9 (0.107) and C_{10} (-0.097 Å), and the atoms of ring B more remote from the

mean plane of this ring are C_{10} (0.098) and C_9 (-0.085 Å). The bicyclic system, ring A and ring B are planar to within 0.419, 0.204 and 0.183 Å, respectively. The dihedral angle between the mean planes of the rings in both molecules is ~16°.

As found for perchloronaphthalene,[8] the overcrowding of α-chlorines in **7a** and **7b** is relieved by out of plane displacements in different directions within a pair. These displacements cause the α-chlorines in both molecules to be the most remote from the corresponding bicycle mean plane (mean distance 0.72 Å). The fact that the inner naphthalene angle centered at C_7 is significantly lower than 120° in the two molecules (~116.6°)

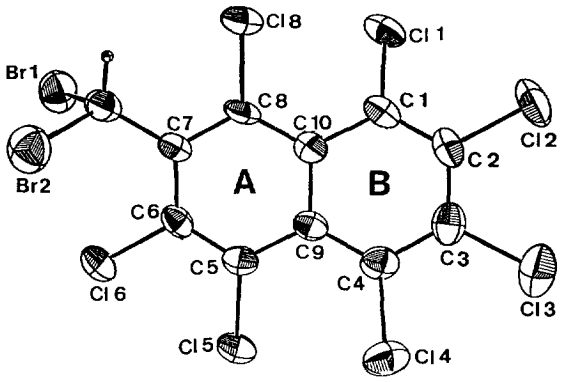


Fig. 1 Diagrammatic representation of **7a** and **7b** with atom numbering and identification of the rings

may be due to steric repulsion between the dibromomethyl group and the neighboring chlorines.

From torsion angles in the region of the dibromomethyl group (C_8-C_7-C_{11}-H, C_6-C_7-C_{11}-H, C_8-C_7-C_{11}-B_1, C_6-C_7-C_{11}-B_1, C_8-C_7-C_{11}-B_2,C_6-C_7-C_{11}-B_2) it was concluded that the dibromethyl group in both molecules is arranged in such a way that the hydrogen atom is located near Cl_8, and the two bromines are placed above and below the plane C_6-C_7-C_8. Accordingly, the intramolecular non-bonded distances shown in Table 1 were observed.

Theoretical Calculations

Among the several theoretical models, we chose semiempirical ones because of their computational economy and good agreement with experimental results. After a preliminary comparative evaluation of MINDO/3, MNDO, AM1, and MNDO-PM3, it was decided to use the last one because it proved to be the most reliable method for crowded aromatic systems, especially if several halogen atoms interact strongly.[10]

We have made an extensive study of (dibromomethyl)naphthalene 7. The most important results are summarized as follows:

a) As expected, the calculations indicate the existence of two energetically favored conformers, one

of them with the hydrogen near the neighboring α-chlorine (conformer A), and the other one with the hydrogen near the neighboring β-chlorine (conformer B). The molecular geometries of these two conformers

Table 1. Selected intramolecular non-bonded distances (Å).

Distance (Å)	7a	7b
$H...Cl_8$	2.468	2.451
$Br_1...Cl_8$	4.146	4.327
$Br_2...Cl_8$	4.423	4.245
$H...Cl_6$	4.034	3.946
$Br_1...Cl_6$	3.435	3.319
$Br_2...Cl_6$	3.312	3.427

were minimized without restrictions. The geometry calculated for the conformer A and that observed for **7** (species **7a**, see X-ray analysis of **7**) can be superimposed with a good correlation (average deviation: 0.8 Å). This result support the goodness of the model used.

b) Conformer A is slightly more stable than conformer B. Due to the low ΔG (experimental: 0.39 kcal mol^{-1} at 293 K), the results obtained in the determination of the equilibrium between these two conformers are near the methodology error limits. However, when we compared the relative stability of the two conformers, it was found that calculated ΔG (actually $\Delta\Delta G_f$, relative difference of formation free energy) is 0.2 kcal mol^{-1} favoring conformer A, which is the species present in solid **7** (X-ray analysis).

c) In the transition state between conformers A and B, the hydrogen appears located on one side and the pair of bromines on the other side of the plane C_6-C_7-C_8. Supporting this structure, the calculated value of $\Delta G^{\ddagger}$ (16.5 kcal mol^{-1} at 353 K) is in good agreement with the experimental value (19.3 kcal mol^{-1}, Table 2).

d) The obtained values of $\Delta H^{\ddagger}$ (4.8 kcal mol^{-1} at 353 K) and $\Delta S^{\ddagger}$ (2.4 cal K^{-1} mol^{-1} at 353 K) differ markedly from experimental data (Table 2). These differences are attributed, at least partially, to the different physical state of the sample (vacuum in front of solution), one inconvenient that constitutes a general problem for the explanation of chemical processes from theory.

Table 2. Dynamic NMR data.

Compound	T_c[a]	$\Delta G^{\ddagger}$[b,e]	$\Delta G^{\ddagger}$[c,e]	$\Delta G^{\ddagger}$[d,e]	$\Delta H^{\ddagger}$[e]	$\Delta S^{\ddagger}$[f]
5	301	15.1	16.4	16.8	25.6±0.4	29.2±1.5
7	353	17.8	19.4	19.3	33.5±0.5	40.2±2.0
9	325	16.3	17.8	18.2	29.8±0.5	35.6±2.4

(a) Coalescence temperature (K). Calculated by: (b) simple coalescence,[12] (c) coalescence method modified for different populations,[12] (d) complete band shape analysis as implemented in DNMR5 program.[14] (e) kcal mol^{-1}. (f) cal K^{-1} mol^{-1}.

Dynamic NMR (DNMR)

At ambient temperature, the ^1H NMR spectrum of the (dibromomethyl)naphthalene **7** displays two singlets at 7.78 and 7.90 ppm, the spectrum of (dichloromethyl)naphthalene **5** presents a broad singlet at 7.85 ppm and the spectrum of (bromochloromethyl)naphthalene **9** shows a very broad singlet (with a shoulder) at 7.91 ppm. In all these spectra, the signal is converted into a sharp singlet at around 100 °C and it splits into two singlets lowering the temperature (see for instance Figure 2).

In order to assign these singlets, calculations based in the effect of the ring currents were performed.[11] The results indicate that the chemical shift of the signal corresponding to the conformer with the hydrogen near the neighboring aromatic α-chlorine is about 30 Hertz higher (at 7.0 T of magnetic field) than the signal corresponding to the conformer with the hydrogen near the neighboring β-chlorine. (Supporting these results, the difference of the chemical shifts between the two singlets in the spectra of **5**, **7**, and **9** is also around 30 Hertz). Therefore, the singlet with higher chemical shift in the spectra of **5**, **7**, and **9** is attributed to the first mentioned conformer that, incidentally, would be the most abundant in solution (the ratios between the areas of the two singlets in the spectra of **5**, **7**, and **9** are 74/26 ,66/34 , and 68/32 (in $(Cl_2CH)_2$, at 273 K), respectively. In this connection it is emphasized that this preferred conformation in solution is adopted at least by **7** in solid form (X-ray analysis).

DNMR can be performed with relative facility if the signals of exchanging protons are singlets.[12] However, in our case the problem was the exchange between two conformers with non-equivalent populations which imply that the simple coalescence method is not applicable to obtain the interconversion rate constant. On the other hand, DNMR analysis would yield data about temperature independent activation parameters,

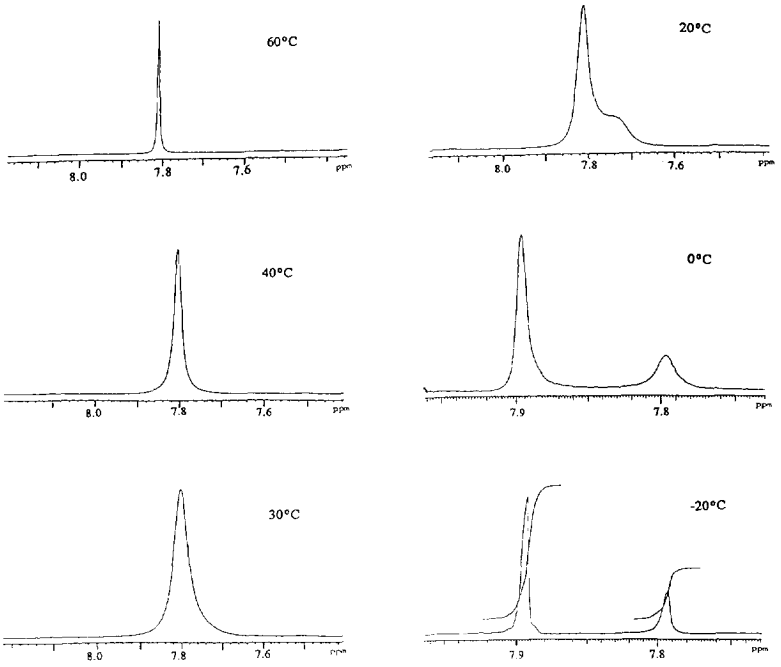


Fig. 2 ^{1}H NMR spectra of (dichloromethyl)naphthalene **5** at selected temperatures

but it is well known that in similar cases the propagated error in these calculations reduce the confidence in $\Delta H^{\ddagger}$ and specially in $\Delta S^{\ddagger}$.[13]

With the aim of a comparative study, the analysis of obtained data was performed using three alternatives: simple coalescence,[12] coalescence method modified for non equal populations[12] and complete band shape analysis as implemented in DNMR5 program.[14] The results are given in Table 2. The good agreement between results obtained from the coalescence methods and band shape analysis indicates that simplified methods are good enough in our case. It is pointed out that the values of $\Delta G^{\ddagger}$ for compounds **5**, **7**, and **9** are similar to those previously reported for 1,3,5-trichloro-2-(dichloromethyl)benzene (14.9 kcal mol^{-1}) and 1,3,5-trichloro-2-(dibromomethyl)benzene (18.2 kcal mol^{-1}).[4] This coincidence supports that the two singlets in the NMR spectra of **5**, **7**, and **9** are due to the hindered rotation of dihalomethyl group.

^{13}C NMR Spectra

The aromatic carbon signals of **3**, **4**, **8**, **5**, **7**, **9**,[15] and heptachloro-7-(chloromethyl)naphthalene[16] appear in the range 125-140 ppm and they are usually resolved in separated lines. The spectra of the compounds with a dihalomethyl group flanked by two chlorines (**4**, **5**, **7**, and **9**) display more lines than the number of carbons,

and this is attributed, at least in the case of **5**, **7**, and **9** to the presence of the two above-mentioned rotational isomers of these compounds.

CONCLUSIONS

Heptachloro-7-(dibromomethyl)naphthalene (**7**) -and by extension its dichloromethyl (**5**) and bromochloromethyl (**9**) analogs- presents two energetically favored conformational isomers attributed to the preferred rotational positions of the dihalomethyl group, one of them with the hydrogen near the neighboring aromatic α-chlorine, and the other one with the hydrogen near the neighboring β-chlorine. Probably, the conformer with the hydrogen facing the neighboring aromatic α-chlorine is slightly more stable than the other one. The obtained barriers to rotation of $CHBr_2$ and $CHCl_2$ groups in **7** and **5** (19.3 and 16.8 kcal mol^{-1}, respectively) are close to those reported for these groups (18.2 and 14.9 kcal mol^{-1}, respectively) in 1,3,5-trichloro-2-(dibromomethyl)benzene and 1,3,5-trichloro-2-(dichloromethyl)benzene. This coincidence supports the conviction that the two singlets in the NMR spectra of **5**, **7**, and **9** are due to the hindered rotation of the dihalomethyl group. In view of the above conformational results, it is considered that compounds containing a dihalomethyl group bonded to an aromatic system and flanked by two chlorines could be interesting in conformational analysis research.

EXPERIMENTAL SECTION

General

Melting points are uncorrected. TLC analyses were performed on plastic sheets precoated with Merck silica gel 60 F_{254}. Flash chromatography separations were carried out on SDS silica gel of 40-60 μm. Heptachloro-7-methylnaphthalene (**6**) and 2-(bromochloromethyl)heptachloronaphthalene (**9**) were prepared by reduction and photobromination of heptachloro-7-(chlorome-thyl)naphthalene, respectively.[2] Since the locations of the IR peaks of highly chlorinated compounds differ markedly from those of their nonchlorinated counterparts, they are included in this section, although weak peaks in the region 400-1300 cm^{-1} are not given. NMR spectra were recorded with a Varian Unity 300, working at 300 MHz for ^1H and 75 MHz for ^{13}C.

Nonachloro-3-(dichloromethyl)-1,4-dihydronaphthalene 3. A solution of nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (**1**)[2] (0.579 g) in CCl_4 (25 mL) was placed in a round-bottomed, Pyrex-brand flask equipped with a reflux condenser and an inlet tube. Dry Cl_2 was passed through the refluxing solution while illuminating with a 500 W incandescent lamp situated underneath the Pyrex container, thus providing the heat. When TLC analysis (hexane) indicated that no more starting material was present (30 min), the resulting solution was evaporated to dryness to leave a residue, which was purified by successive recrystallizations (hexane) giving pure **3** (0.365 g, 68%) as prisms mp 220-2 °C. IR (KBr) 3020 (w), 1665 (m), 1525 (m), 1360

(s), 1345 (m), 1320 (m), 1245 (s), 1225 (s), 1215 (s), 1140 (s), 1120 (m), 1030 (m), 980 (m), 940 (m), 840 (m), 805 (s), 775 (s), 760 (s), 750 (m), 730 (s), 710 (m), 690 (m), 625 (s), 610 (s), 555 (s), 500 (m), 470 (s) cm^{-1}. UV (C_6H_{12}) λ_{max} 221 nm, 229 (sh), 291 (sh), 301, 312 (ε 39 940, 34 160, 590, 970, 1070). ^1H NMR ($CDCl_3$) δ 6.95 (s, $CHCl_2$). ^{13}C NMR ($CDCl_3$) δ 139.1, 138.9, 136.9, 134.0, 133.6, 131.6, 131.0, 129.7, 79.9, 79.7, 66.5 (d). Anal. Calcd for $C_{11}HCl_{11}$: C, 25.3; H, 0.2; Cl, 74.5. Found: C, 25.4; H, 0.3; Cl, 74.5. The mother liquors were combined and evaporated to dryness to give a residue (0.152 g) consisting of slightly impurified **3** (IR and ^1H NMR).

Nonachloro-7-(dichloromethyl)-1,4-dihydronaphthalene **4.** Nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (**2**)[2] (0.502 g) was chlorinated as described in the preceding reaction until the disappearance (TLC) of **2** (20 min). The resulting solution was evaporated to dryness to leave a residue (0.558 g) which was subjected to flash chromatography (silica gel, hexane) yielding: (i) slightly impurified **4** (0.027 g), identified by IR and TLC; (ii) a solid (0.465 g) which was purified by recrystallization (hexane) to give **4** (0.334 g, 62%) as needless mp 238-42 °C. IR (KBr) 3040 (w), 1650 (w), 1535 (w), 1520 (w), 1400 (w), 1370 (m), 1150 (s), 1020 (m), 940 (m), 775 (s), 740 (s), 615 (m) cm^{-1}. UV (C_6H_{12}) λ_{max} 222 nm, 296 (sh), 306, 316 (ε 36 700, 1110, 1870, 2070). ^1H NMR ($CDCl_3$) δ 7.89 (s, $CHCl_2$). ^{13}C NMR ($CDCl_3$) δ 140.4, 139.1, 138.8, 137.2, 137.0, 136.1, 133.4, 132.4, 132.3, 132.2, 130.0, 79.5, 79.3, 66.7 (d), 66.0 (d). Anal. Calcd for $C_{11}HCl_{11}$: C, 25.3; H, 0.2; Cl, 74.5. Found: C, 25.6; H, 0.2; Cl, 74.9; and (iii) a fraction (0.030 g) of slightly impurified **4**, identified by IR and TLC.

Heptachloro-7-(dichloromethyl)naphthalene (5). (a) From dihydronaphthalene **3.** A solution of **3** (0.237 g, 0.4 mmol) and $SnCl_2.2H_2O$ (0.110 g, 0.5 mmol) in dioxane (16 mL) was refluxed under N_2 for 4 h. The solvent was then evaporated at vacuum, the residue was digested in refluxing hexane, the insoluble part was filtered off, and the filtrate was passed through silica gel. Concentration of the resulting solution afforded **5** (0.150 g, 73%) as needles mp 102-3 °C. IR (KBr) 3025 (w), 1540 (m), 1520 (s), 1415 (m), 1360 (m), 1325 (m), 1295 (m), 1280 (s), 1245 (s), 1225 (m), 1080 (s), 995 (s), 870 (s), 840 (s), 790 (m), 775 (s), 750 (s), 705 (m), 675 (s), 660 (s), 610 (m), 560 (s), 495 (s) cm^{-1}. UV (C_6H_{12}) λ_{max} 252 (sh) nm, 276, 330, 341 (sh), 379 (sh) (ε 22 900, 54 400, 6680, 6290, 1960). ^1H NMR ($CDCl_3$) δ 7.85 (broad s, $CHCl_2$). ^{13}C NMR ($CDCl_3$) δ 136.4, 135.4, 135.0, 134.9, 131.3, 130.9, 129.9, 128,9, 128.7, 127.6, 66.8 (d), 66.3 (d). Anal. Calcd for $C_{11}HCl_9$: C, 29.2; H, 0.2; Cl, 70.6. Found: C, 29.5; H, 0.3; Cl, 70.6.

(b) From dihydronaphthalene **4.** A solution of **4** (0.102 g, 0.2 mmol) and $SnCl_2.2H_2O$ (0.052g, 0.2 mmol) in dioxane (10 mL) was refluxed as described in the preceding reaction. The resulting mass was poured over 6M aqueous HCl (10 mL), the resulting mixture was extracted with $CHCl_3$, and the extract was washed with water, dried and evaporated. The residue obtained was then passed through silica gel (hexane) and recrystallized (same solvent) to give **5** (0.069 g, 78%), mp 101.5-3 °C, identified by its mp and IR spectrum.

(c) From 2-methylnaphthalene. This compound was chlorinated by means of Silberrad's reagent according to the general procedure described elsewhere to obtain a mixture of dihydronaphthalenes **1** and **2** (3.096 g, molar ratio **1/2**: 28/72).[2] This mixture was then dissolved in CCl_4 (50 mL) and photochlorinated in a fashion analogous to that described in the preceding photochlorinations until the disappearance of the ^1H NMR signals of **1** and **2** (2.5 h). The resulting solution was then evaporated to dryness, and the residue (3.551 g) was treated with $SnCl_2.2H_2O$ (1.698 g) in refluxing dioxane (100 mL) for 4 h under an argon atmosphere. The solution obtained was poured over 6M aqueous HCl, the resulting mixture was extracted with $CHCl_3$, and the extract was washed with water, dried and evaporated to dryness. The residue (2.984 g) was then flash chromatographed (silica gel, hexane) giving: (i) perchloronaphthalene (0.082 g, 1%) identified by its IR spectrum; (ii) an oil (2.196 g) which by successive recrystallizations afforded **5** (1.964 g, 25 %), mp 101.5-3 °C, identified by its mp and IR spectrum; and (iii) slightly impure **5** (0.347 g), identified by IR and ^1H NMR.

2-(Bromomethyl)heptachloronaphthalene 8. (a) A solution of heptachloro-7-methylnaphthalene (**6**)[2] (0.305 g, 0.8 mmol) and B_2 (0.5 mL, 9.8 mmol) in CCl_4 (30 mL) was illuminated and refluxed in a round-bottomed Pyrex-Brand flask, in a fashion analogous to that described for the synthesis of dihydronaphthalene **3.** The reaction was allowed to proceed until TLC analysis indicated that no more starting material was present (3 h). The resulting solution was then evaporated to dryness and the residue was purified by flash chromatography (silica gel, hexane), followed by crystallization (hexane) giving **8** (0.211 g, 57%) as needles mp 99-101 °C. IR (KBr) 3025 (w), 1545 (w), 1530 (s), 1435 (m), 1415 (m), 1365 (m), 1340 (w), 1330 (w), 1290 (s), 1245 (s), 1220 (m), 1085 (m), 995 (m), 885 (m), 835 (m), 760 (m), 665 (s), 610 (s), 575 (m), 545 (s), 460 (s) cm^{-1}. UV (C_6H_{12}) λ_{max} 253 (sh) nm, 276, 332, 342 (sh), 279 (sh) (ε 24 500, 54 500, 7020, 6470, 1670). ^1H NMR ($CDCl_3$) δ 5.00 (s, CH_2Br). ^{13}C NMR ($CDCl_3$) δ 136.1, 136.0, 135.7, 135.1, 131.0, 131.0, 129.6, 129.5, 128.9, 29.1 (t). Anal. Calcd for $C_{11}H_2BrCl_7$: C, 28.6; H, 0.4; B, 17.3; Cl, 57.7. Found: C, 28.8; H, 0.3; B, 18.0; Cl, 57.3.

(b) *N*-Bromosuccinimide (0.689 g, 3.9 mmol) and AIBN (0.072 g) were added to a solution of methylnaphthalene **6** (0.496 g, 1.3 mmol) in CCl_4 (30 mL), and the resulting mixture was refluxed with stirring for 4 h under argon. Evaporation of the solvent gave a residue which was digested with boiling hexane (30 mL). The insoluble part was filtered off, and the filtrate was flash chromatographed (silica gel, hexane) giving **8** (0.540 g, 90%), mp 96-9 °C, identified by its mp and IR spectrum.

Heptachloro-7-(dibromomethyl)naphthalene 7. A solution of methylnaphthalene **6** (0.277 g, 0.7 mmol) and B_2 (0.5 mL, 9.8 mmol) in CCl_4 (30 mL) was illuminated and refluxed in a fashion analogous to that described for the synthesis of dihydronaphthalene **3.** When TLC analysis showed consumption of intermediate **8** (91 h), the resulting solution was evaporated to dryness. The residue was then flash chromatographed (silica gel, hexane) affording **7** (0.225 g, 65%), prisms mp 126-8 °C. IR (KBr) 3030 (w), 1540 (m), 1525 (m), 1500 (m), 1415 (m), 1365 (m), 1330 (w), 1285 (s), 1280 (m), 1245 (s), 1235 (m), 1165 (m), 1155 (m), 1075 (s),

995 (s), 835 (s), 760 (s), 730 (m), 715 (s), 660 (m), 650 (m), 600 (m), 545 (m), 535 (m), 480 (s) cm^{-1}. UV (C_6H_{12}) λ_{max} 252 (sh) nm, 280, 319 (sh), 331, 342 (sh), 365 (sh), 381 (sh) (ε 22 300, 57 800, 5420, 6710, 6140, 2640, 2090). ^1H NMR ($CDCl_3$) δ 7.78 (s, $CHBr_2$), 7.90 (s, $CHBr_2$). ^{13}C NMR ($CDCl_3$) δ 136.4, 136.3, 135.6, 135.4, 134.7, 132.0, 131.2, 130.8, 130.5, 130.0, 129.8, 128.7, 128.1, 126.3, 32.3 (d), 32.2 (d). Anal. Calcd for $C_{11}HBr_2Cl_7$: C, 24.4; H, 0.2; B, 29.5; Cl, 45.9. Found: C, 24.4; H, 0.2; B, 29.7; Cl, 45.9. Elution with more hexane gave impure **7** (0.081 g) identified by TLC and IR spectrum.

X-ray Analysis.[17] Prismatic colorless crystal 0.70 x 0.22 x 0.20 mm, triclinic, space group: P-1 (#2); a = 9.374 (2), b = 9.769 (2), c = 18.492 (5) Å; α = 75.10 (2)°, β = 79.77 (2)°, γ = 73.66 (2)°; V = 1560 (9) $Å^3$; Z = 2; D_{calcd} = 1.126 g/cm^3; μ(Mo Kα) = 31.7 cm^{-1}; R = 5.4% (over 4228 reflections with $F > 3\sigma(F)$). Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation.

The structure was solved by direct methods using MULTAN 11/84,[18] the refinement was carried out with anisotropic full-matrix least-squares methods[19] and scattering factors were taken from ref 20.

Theoretical calculations. All calculations were performed in a Hewlett-Packard HP-9000 (835S) minicomputer with a recompiled version of MOPAC 5.0[21] using the MNDO-PM3 model. Geometries of the ground states were fully optimized with a gradient norm below 0.2. The exploration of the possible transition states was made by a systematic rotation of dibromomethyl group and full optimization of each geometry. Final optimization of the transition state was performed by application of non linear least squares method to gradient norm and test the presence of only one negative force constant. Thermochemical data for each state were obtained by using the THERMO option in MOPAC 5.0.

^1H DNMR. Variable temperature unit was calibrated and tested using known NMR thermometers (CH_3OH and $HOCH_2CH_2OH$ using general accepted calibration data).[22] The sample used was prepared by dissolving the compound under study (10 mg) in 0.8 mL of 1,1,2,2-tetrachloroethane-D_2 and adding a little amount of dimethylsulfoxide (0.5 mg). In all cases we previously determined the coalescence temperature in a rough way and performed an acquisition set of 40 °C around that temperature separated by 5 °C to have enough number of rate constants. After setting the desired temperature and waited for equilibrium (~30 min) we performed a previous acquisition to test the goodness of shimming, using the signal of dimethylsulfoxide as reference, to obtain a consistent set of data containing only variations in linewidth due to chemical exchange. The Fourier transformed data (without weighting functions) of the dihalomethyl region (0.3 ppm, 1440 points centered in the signals under study) were processed using DNMR5[14] program with 360 smoothed points. We used usually two independent acquired spectra and used the average value of the calculated rate constant.

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16 ^{13}C NMR ($CDCl_3$) δ 136.3, 135.8, 135.8, 135.1, 131.4, 131.1, 129.6, 129.5, 128.9, 42.6 (t).

17 The authors have deposited positional parameters for this structure to the Cambridge Crystallographic Data Centre. The parameters can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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