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# Perchloro-2-methylnaphthalene, a Novel Chlorocarbon with a Highly Strained Structure

J. Carilla,*[1a] Ll. Fajarí,[1a] R. García,[1a] L. Juliá,*[1a] C. Marcos,[1a] J. Riera,*[†,1a] C. R. Whitaker,[1b]
J. Rius,[1b] and C. Alemán[1c]

*Departament de Materials Orgànics Halogenats, Centre d'Investigació i Desenvolupament (CSIC), Jordi Girona, 18-26, 08034 Barcelona, Spain, Institut de Ciència de Materials (CSIC), Campus de la UAB, Bellaterra, 08193 Barcelona, Spain, and Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya (UPC), Diagonal 647, 08028 Barcelona, Spain*

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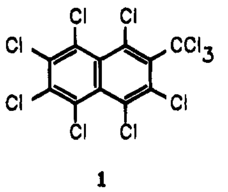
Perchloro-2-methylnaphthalene (**1**) is prepared in a two-step reaction: treatment of 2*H*-heptachloronaphthalene (**3**) with CCl$_3$F in the presence of AlCl$_3$ yields heptachloro-7-(trifluoromethyl)naphthalene (**4**), which in CS$_2$ and with an excess of AlCl$_3$ affords **1**. The spectra and X-ray crystal structure of chlorocarbon **1** are reported, as well as that of the much less strained heptachloro-7-(dichloromethyl)naphthalene (**10**). The unusual UV spectrum, due to the distortion of the aromatic rings, is also discussed. The reduction of **1** with copper wire to give perchloro(2-naphthyl)methyl radical (**11**) has been studied by means of electron spin resonance. Steric inhibition to resonance of the free electron within the aromatic ring in **11** has been estimated by a semiempirical AM1 method.

## Introduction

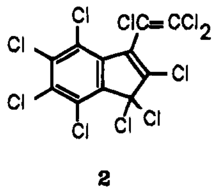
Distortion of the benzene ring from its planar and hexagonal configuration has long interested both theoretical and experimental chemists. The molecules of perchlorinated alkylbenzenes with the alkyl substituent flanked by two *o*-chlorines, such as perchlorotoluene,[2] perchloroethylbenzene, perchloro-*p*-xylene,[3] perchlorobi-*p*-tolyl,[4] and perchloro-*m*-xylene[5a] are highly strained, and as a consequence, the aromatic rings are out-of-plane distorted. These distortions manifest themselves in large bathochromic band shifts in the electronic spectra. When the remaining (*o*- or α) hydrogen in heptachlorotoluene is replaced by chlorine to form perchlorotoluene, a large molecular distortion occurs, and consequently, a bathochromic shift and the disappearance of the hyperfine structure in the secondary band of its electronic spectrum results.[6]

In addition, large deviations from planarity occur in perchloronaphthalene because the strain between the α-chlorines cannot be relieved by in-plane splaying apart due to the buttressing effect of the β-chlorines.[7] This out-of-plane distortion is also displayed in its electronic spectrum. The three characteristic bands of perchloronaphthalene are bathochromically shifted with respect to those of 1,4,5,8-tetrachloronaphthalene.[8]

Recently, we have been able to introduce the trifluoromethyl group in very hindered aromatic positions flanked by two *o*-chlorines using a new and effective trifluoromethylating reagent of polychlorobenzenes consisting of the binary system AlCl$_3$–CCl$_3$F.[5] These (trifluoromethyl)benzenes can subsequently be converted to their more crowded trichloromethyl counterparts using AlCl$_3$ in CS$_2$. By use of both reactions, perchlorotoluene[5b,9] has been prepared from pentachlorobenzene, and other previously unknown (trichloromethyl)polychlorobenzenes have been synthesized.[5b] In this paper we present the synthesis of perchloro-2-methylnaphthalene (**1**), applying the strategy mentioned above. This highly crowded naphthalene **1** is interesting because it presents both situations described above: an alkyl group flanked by two *o*-chlorines and the presence of α-chlorines whose strain cannot be reduced via in-plane bending due to the presence of bulky β-substituents. Accordingly, a considerable deformation of the bicyclic system is expected.



**1**



**2**

It is worth mentioning that all attempts to synthesize such a molecule by conventional chlorination methods of the parent hydrocarbon[12,13] were unsuccessful. The

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[†] Deceased.

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(1) (a) Centre d'Investigació i Desenvolupament (CSIC). (b) Institut de Ciència de Materials (CSIC). (c) Universitat Politècnica de Catalunya (UPC).

(2) Rius, J.; Miravitlles, C.; Castañer, J.; Riera, J. *Acta Crystallogr.* **1991**, *C47*, 627.

(3) Solans, X.; Galí, S.; Miravitlles, C.; Font-Altaba, M. *Acta Crystallogr.* **1978**, *B34*, 3790.

(4) Castañer, J,: Riera, J.; Molins, E.; Más, M. *Anal. Quim.*, in press.

(5) (a) Castañer, J.; Riera, J.; Carilla, J.; Robert, A.; Molins, E.; Miravitlles, C. *J. Org. Chem.* **1991**, *56*, 103. (b) Riera, J.; Castañer, J.; Carilla, J.; Robert, A. *Tetrahedron Lett.* **1989**, *30*, 3825.

(6) Ballester, M.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4259. Ballester, M.; Castañer, J.; Riera, J. *Anal. Quim.* **1977**, *73*, 546.

(7) Gafner, G.; Herbstein, F. H. *Nature* **1963**, *200*, 130.

(8) Mosby, W. L. *J. Am. Chem. Soc.* **1955**, *77*, 1955. Ballester, M.; Castañer, J.; Riera, J.; Parés, J. *Anal. Quim.* **1980**, *C76*, 157.

(9) The only way to synthesize perchlorotoluene was accomplished many years ago, by chlorination of 2,3,4,5-tetrachloro-1-(trichloromethyl)benzene by means of the powerful and selective BMC reagent.[10] The initial composition of BMC is similar to that of the reagent described by Silberrad.[11] It consists of a solution of AlCl$_3$ and S$_2$Cl$_2$ in SO$_2$Cl$_2$. Some differences in concentration of the chemical species makes BMC a more powerful yet selective perchlorinating agent for aromatic rings; the actual chlorinating species is assumed to be a chlorine-releasing electrophilic complex.

(10) Ballester, M.; Molinet, C.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4254.

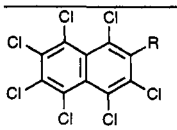
(11) Silberrad, O. *J. Chem. Soc.* **1921**, *119*, 2029; **1922**, *121*, 1015; **1925**, *127*, 2677.

(12) García, R.; Riera, J.; Carilla, J.; Juliá, L.; Molins, E.; Miravitlles, C. *J. Org. Chem.* **1992**, *57*, 5712.

(13) Sun, J.; Grutzmacher, H.-F.; Lifshitz, C. *J. Am. Chem. Soc.* **1993**, *115*, 8382.

0022-3263/95/1960-2721$09.00/0

**Table 1. UV Spectral Data of Some (Halomethyl)heptachloronaphthalenes**

|  | $^1B_b$ band | | $^1L_a$ band | | $^1L_b$ band | |
|---|---|---|---|---|---|---|
| R = | $\lambda_{max}$ (nm) | $\epsilon$ | $\lambda_{max}$ (nm) | $\epsilon$ | $\lambda_{max}$ (nm) | $\epsilon$ |
| $CH_3$, **8** | 272 | 44 900 | 330 | 7540 | 374 | 1040 |
| $CH_2Cl$, **9** | 274 | 51 900 | 331 | 7100 | 375 | 1650 |
| $CHCl_2$, **10** | 276 | 54 400 | 330 | 6680 | 380 | 1960 |
| $CCl_3$, **1** | 277 | 38 700 | 330 | 5950 | 396 | 3080 |

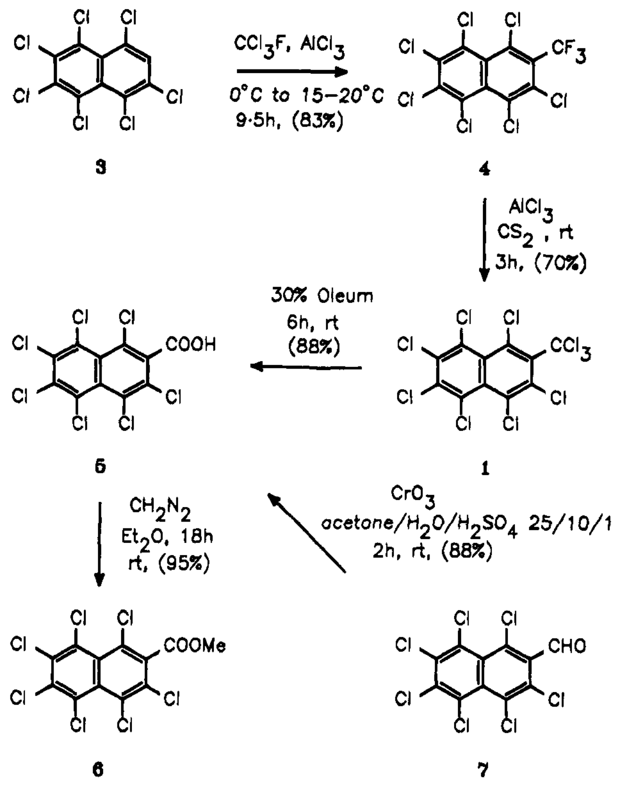
chlorination of 2-methylnaphthalene by Silberrad's reagent[11] gives a complex mixture from which nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene and nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene were isolated.[12] Longer reaction times permitted the isolation of perchloro-3-vinylindene (**2**).[12] In the course of the preparation of this paper, Grützmacher *et al.*[13] have claimed to have synthesized **1** by chlorination of 2-methylnaphthalene with $Cl_2$ and Fe powder in $SO_2Cl_2$ at 64 °C. However, the $^{13}C$ NMR spectrum reported for this compound is quite different from that reported here (see Experimental Section) and is identical to the spectrum of the isomeric perchloro-3-vinylindene (**2**),[12,14] the structure of which was unequivocally ascertained by us by X-ray diffraction analysis.

Naphthalene **1** has been now fully characterized by elemental analysis, $^{13}C$ NMR, and infrared spectra, and its molecular structure has been determined via its electronic spectrum and by X-ray analysis. X-ray analysis of heptachloro-7-(dichloromethyl)naphthalene (**10**), recently synthesized by some of us,[15] is also included for comparison.

## Results and Discussion

**Synthesis.** The treatment of 2*H*-heptachloronaphthalene (**3**)[12] with $CCl_3F$ in the presence of $AlCl_3$[16] at room temperature afforded (trifluoromethyl)naphthalene **4** in high yield. Compound **4** reacts further with $AlCl_3$ in $CS_2$ giving perchloro-2-methylnaphthalene (**1**) in a good yield. For identification purposes the following reactions have been performed: (i) hydrolysis of **1** to heptachloro-2-naphthoic acid (**5**); (ii) esterification of this acid to methyl ester **6**; and (iii) oxidation of aldehyde **7**[12] to acid **5**.

**Ultraviolet Spectra.** Brinkman *et al.* have reported UV spectra of polychloronaphthalenes and studied the influence of the chlorine substituents on the shifts of the three aromatic bands, $^1B_b$, $^1L_a$, and $^1L_b$.[17] Table 1 shows the spectral data of some previously synthesized highly chlorinated 2-methylnaphthalenes[12,15] and that of chlorocarbon **1**. The introduction of a methyl group in 2*H*-heptachloronaphthalene (**3**) causes a bathochromic shift in $^1B_b$ and $^1L_b$ bands with respect to those of **3** but does not significantly affect the position of $^1L_a$ band. The introduction of two chlorine atoms in the methyl group of naphthalene **8** does not affect significantly the position of $^1L_a$ band, but causes a slight bathochromic shift in the $^1B_b$ and $^1L_b$ bands. Replacement of the last hydrogen atom with chlorine in the methyl group does not affect the position of $^1B_b$ and $^1L_a$ bands, but it causes a large bathochromic shift (16 nm) with a hyperchromic effect in the $^1L_b$ band as a consequence of the molecular out-of-plane distortion, as also observed for perchloro-*p*-xylene.[10] For this reason, this band appears in the visible region and perchlorocompound **1** is a bright yellow color.



**Electron Spin Resonance (ESR) Spectrum of Perchloro(2-naphthyl)methyl Radical (11).** The ESR spectrum of a $CCl_4$ solution of chlorocarbon **1**, which had been sealed under argon in a quartz tube and kept in contact with copper wire during a prolonged period at room temperature, showed a strong signal corresponding to the perchloro(2-naphthyl)methyl radical (**11**). Less stable solutions of this radical were obtained when **11** was generated by reduction of **1** with stannous chloride in dioxane at 60 °C or by photolysis of a toluene solution of **1** in the presence of tributyltin hydride and di-*tert*-butyl peroxide at −40 °C.

The ESR spectrum of the radical **11** displayed in Figure 1 presents seven broad, equally spaced, and overlapping lines with a coupling constant of 2.85 G (in $CCl_4$), due to the interaction of the free electron with the two chlorine nuclei directly attached to the trivalent carbon atom. This coupling constant is similar to that observed for perchlorobenzyl radical when generated from perchlorotoluene under similar conditions.[18]

The high value of the α $^{13}C$ coupling constant of radical **11** (58.1 G), as in the perchlorobenzyl radical (59.1 G),[18] indicates that the odd-electron localization on that carbon is high, which is due to the steric inhibition to resonance within the aromatic ring. In this context, calculations using an unrestricted Hartree–Fock (UHF) wavefunction with the AM1 semiempirical method[19] have demon-

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[14] $^{13}C$ NMR ($CDCl_3$) $\delta$ 144.82, 139.00, 136.58, 133.95, 132.66, 130.61, 130.32, 125.47, 119.05, 81.53.

[15] García, R.; Sánchez-Baeza, F. J.; Riera, J.; Carilla, J.; Juliá, L.; Molins, E. *Tetrahedron*, in press.

[16] The excess of $AlCl_3$ is necessary since it has been observed that it reacts with $CCl_3F$, losing the catalytic activity.

[17] Brinkman, U. A. Th.; De Kok, A.; Reymer, H. G. M.; De Vries, G. *J. Chromatogr.* **1976**, *129*, 193.

[18] Olivella, S.; Ballester, M.; Castañer, J. *Tetrahedron Lett.* **1974**, 587.

[19] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, 4107, 3902.

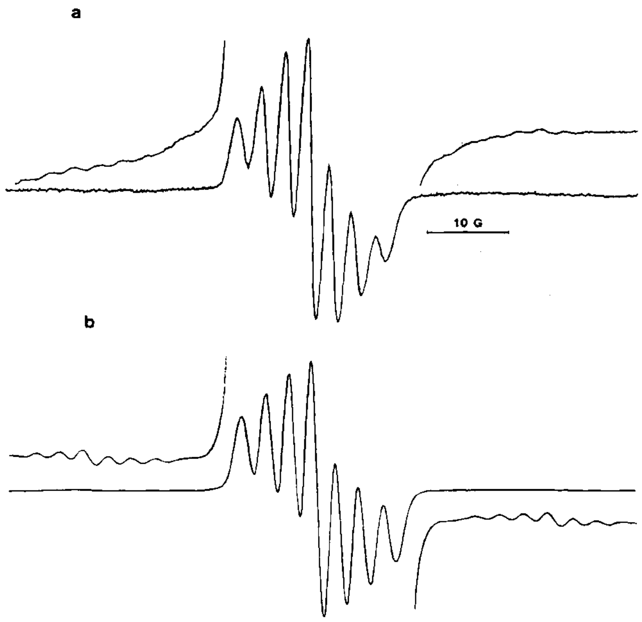
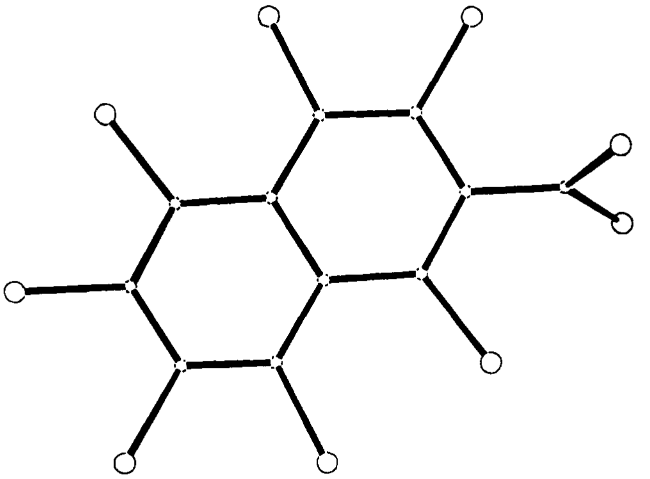


**Figure 1.** ESR spectrum of perchloro(2-naphthyl)methyl radical (**11**) in $CCl_4$ with α-$^{13}C$ splitting: (a) experimental, (b) simulated (for a Gaussian line shape).

strated that the conformation of **11** is affected significantly by steric factors between *o*- and α-chlorines. For these calculations, the naphthalene ring was fixed in the plane and the dichloromethylene group was rotated between 0° and 180°. In Figure 2, the variation of energy with torsion angle is shown. The full-minimized conformation is that which corresponds to a torsion angle of 75°. The optimized structure for **11** is shown below.



It has been reported that the ESR spectrum of the α,α,2,3,5,6-hexachlorobenzyl radical shows no splitting of the free electron with the aromatic proton, which indicates that the spin density at the *para* carbon atom is nearly zero. As in **11**, this is accounted for by steric inhibition to resonance between the free electron in the dichloromethylene group and the aromatic ring.[18] Lande's *g* value for radical **11** (2.0076) is high and rather different from that of the free electron (2.0023) which indicates an important spin-orbit coupling with the α-chlorines. The line widths of the ESR lines ($\Delta H_{pp}$: 1.5 G) is traced to unresolved interaction with the aromatic chlorine atoms, as in other perchlorinated radicals.[20]

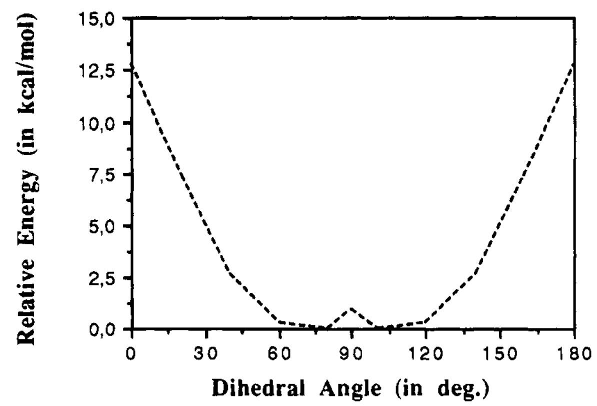


**Figure 2.** Torsion angle potential curve for perchloro(2-naphthyl)methyl radical (**11**).

**Molecular Structure of Perchloro-2-methylnaphthalene (1) and Heptachloro-7-(dichloromethyl)-naphthalene (10).** A representation of these molecules with the atom numbering and ring identification is shown in Figure 3. The deviations of the aromatic carbon atoms from the mean planes of rings A and B are significantly high and establish the conformation of the bicyclic system in both molecules. In naphthalene **1** the least-squares mean plane calculation shows that ring A presents higher $\chi^2$ (17483.9) than ring B (1089.7) and that the rings are planar to within 0.267 and 0.070 Å, respectively. The dihedral angle between the mean planes of the rings is 9.6 (3)°. In naphthalene **10**, rings A and B, which are planar to within 0.177 and 0.173 Å, present similar $\chi^2$ values (2974.2 and 2804.1, respectively), and the dihedral angle between the mean planes of the rings is 14.0(2)°. The exceptionally high value of $\chi^2$ of ring A (17483.9) in naphthalene **1** is mainly attributed to the presence of the trichloromethyl group attached to C2 and, particularly, to steric repulsions between the pairs Cl1−Cl9, and Cl3−Cl11. This ring adopts a twisted-boat conformation in which the prow C2 and the stern C4a present similar deviations from the mean plane, 0.144(2) and 0.120(2) Å, respectively. The carbon atom of the trichloromethyl substituent (C9) in naphthalene **1** is displaced (0.490(2) Å) from the mean plane of ring A, and this group rotates in such a way to avoid unfavourable steric interactions with neighboring Cl1 or Cl3 atoms. Cl1 and Cl3 deviate significantly from the mean plane by −0.817 and −0.437 Å, respectively. In compounds **1** and **10** the mean aromatic C−C distance is 1.40 Å, identical to the average for perchloronaphthalene;[21] the mean aromatic and aliphatic C−Cl distances are 1.72 and 1.78 Å, respectively, identical to those found in other perchloroalkylaromatic compounds.[2-4,5a] The differences between the individual distance values and the appropiate mean value are not statistically significant. The bond lengths for C2−C9 are 1.525(3) Å for naphthalene **1** and 1.509(4) Å for naphthalene **10**.

Two conformers of naphthalene **10** can be detected in solution, with a barrier to rotation as high as 16.8 kcal $mol^{-1}$ (dynamic $^1H$ NMR),[15] but only the most stable is present in solid form. In the crystal, the dichloromethyl substituent in naphthalene **10** lies with the H atom bond approximately parallel to the distorted plane of ring A

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(20) Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380.

(21) Gafner, G.; Herbstein, F. H. *Acta Crystallogr.* **1960**, *13*, 702; *Nature* **1963**, *200*, 130.

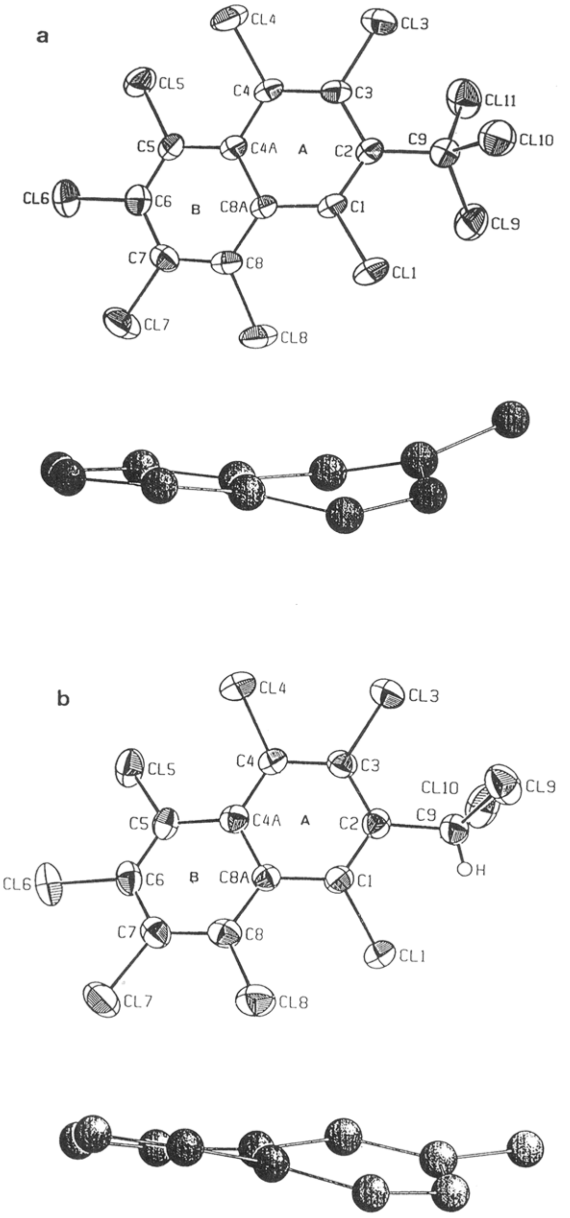

**Figure 3.** Diagrammatic representation of (a) naphthalene **1** and (b) naphthalene **10** with atom numbering and ring identification.

**Table 2. Selected Torsion Angles for 1 and 10**

| torsion angle (**1**) | deg | torsion angle (**10**) | deg |
|---|---|---|---|
| C1–C2–C9–Cl9 | 28.1(3) | C1–C2–C9–Cl9 | −113.8(3) |
| C1–C2–C9–Cl10 | −94.8(2) | C1–C2–C9–Cl10 | 120.6(3) |
| C1–C2–C9–Cl11 | 143.6(2) | C1–C2–C9–H | 7(2) |
| C3–C2–C9–C19 | −157.2(2) | C3–C2–C9–Cl9 | 65.6(3) |
| C3–C2–C9–C110 | 79.9(2) | C3–C2–C9–Cl10 | −60.0(4) |
| C3–C2–C9–Cl11 | −41.6(2) | C3–C2–C9–H | −174(2) |

with the hydrogen facing toward Cl1 (Cl1 ··· H = 2.41 (4) Å), and the two chlorines placed above and below the plane of ring A. A similar low-strain arrangement occurs as for the dichloromethyl group in 2,6-dichloro-1-(dichloromethyl)benzene[10] and for the dibromomethyl group in heptachloro-7-(dibromomethyl)naphthalene.[15] Relevant torsion angles in the region of the trichloromethyl group in **1** and dichloromethyl group in **10** are given in Table 2.

In naphthalenes **1** and **10**, distances between *peri* chlorines (Cl1 ··· Cl8, 2.9578(9) Å and Cl4 ··· Cl5, 2.9964(8) Å for **1**, and Cl1 ··· Cl8, 2.978(1) Å and Cl4 ··· Cl5, 2.984(1) Å for **10**) are smaller than twice the van der Waal's radius for chlorine (1.80 Å) and similar to those reported for perchloronaphthalene,[21] indicating that the presence of bulky substituents on C2 does not significantly affect those distances. A side-on view for both structures **1** and **10**, showing the strain-induced twist-boat conformation for naphthalene **1**, is also given in Figure 3. The intermolecular packing distance is approximately 3.82 Å for both compounds **1** and **10**. Intermolecular chlorine–chlorine distances less than 3.5 Å (twice van der Waal's radius for chlorine) are as follows: for **1**, Cl5 ··· Cl10 = 3.36 Å ($x$, $y$ − 1, $z$) and Cl8 ··· Cl9 = 3.40 Å (1 − $x$, 1 − $y$, $z$), and for **10**, Cl1 ··· Cl9 = 3.33 Å ($x$ − 1/2, 1 − $y$, $z$), Cl3 ··· Cl10 = 3.45 Å ($x$ + 1/2, −$y$, $z$), and Cl4 ··· Cl5 = 3.35 Å ($x$ + 1/2, −$y$, $z$). In **1**, the molecules lie parallel to the *b*-axis in the plane of the *ac* diagonal, while in **10**, the molecules lie in puckered layers running parallel to the bc plane.

## Experimental Section

**General.** Melting points are uncorrected. Naphthalenes **3**, **7**, **8**, **9**, and **10** were prepared as previously reported.[12,15] The UV spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrometer coupled with a Perkin-Elmer 7300 computer, and the IR spectra were recorded with a Perkin-Elmer Model 683 spectrometer. 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 $^1$H and 75 MHz for $^{13}$C. ESR spectra were recorded with a Varian E-109 spectrometer working in the X band. For ESR analysis, solutions in the ESR tubes were carefully degassed by a freeze–pump–thaw technique (four cycles) and kept under an argon atmosphere. The quartz tube with the $CCl_4$ solution of **1** and copper was flame-sealed. Photolysis were carried out directly in the cavity of the ESR spectrometer with an ORIEL 500 W high-pressure mercury lamp.

**Heptachloro-7-(trifluoromethyl)naphthalene (4).** Powdered anhydrous $AlCl_3$ (6.017 g) was added to a solution of heptachloronaphthalene **3** (1.061 g) in $CCl_3F$ (100 mL) at 0 °C, and the resulting mixture was stirred at 15–20 °C until the disappearance (HPLC) of **3** (9.5 h). The reaction mixture was filtered and the solid washed with $CCl_4$. The organic solution was evaporated to dryness giving **4** (1.046 g, 83%) as pale yellow needles, mp 94–6 °C (from ethanol): IR (KBr) 1540 (m), 1515 (m), 1405 (m), 1360 (m), 1320 (m), 1295 (m), 1280 (m), 1245 (s), 1210 (s), 1170 (m), 1145 (s), 1135 (s), 950 (m), 710 (m), 685 (m), 655 (s), 545 (m) cm$^{-1}$; UV ($C_6H_{12}$) $\lambda_{max}$ 247 (sh) nm, 273, 314 (sh), 329, 339 (sh), 376 (sh) ($\epsilon$ 20 400, 44 400, 4940, 6890, 6540, 2540); $^{19}$F NMR ($CDCl_3$) $\delta$ 21,18 (s, $CF_3$). Anal. Calcd for $C_{11}Cl_7F_3$: C, 30.2; Cl, 56.8; F, 13.0. Found: C, 30.1; Cl, 56.8; F, 13.0.

**Perchloro-2-methylnaphthalene (1).** Powdered anhydrous $AlCl_3$ (0.654 g) was added to a solution of (trifluoromethyl)naphthalene **4** (0.398 g) in $CS_2$ (12 mL). The resulting dark red mixture was stirred at room temperature for 3 h. The reaction mixture was poured over cracked ice and extracted with ether. The ethereal layer was washed with water, dried, and evaporated. The residue obtained was passed through silica gel (hexane) and crystallized (same solvent) to yield **1** as yellow prisms (0.311 g, 70%), mp 119–20 °C: IR (KBr) 1530 (m), 1510 (s), 1400 (m), 1270 (s), 1260 (s), 1240 (s), 1070 (s), 990 (s), 870 (m), 830 (m), 800 (m), 770 (s), 750 (m), 690 (m), 670 (m), 650 (s), 640 (m), 520 (s) cm$^{-1}$; UV ($C_6H_{12}$) $\lambda_{max}$ 213 nm, 255 (sh), 277, 314, 330, 338 (sh), 396 ($\epsilon$ 20 800, 24 000, 38 700, 5090, 6950, 5380, 3080); $^{13}$C NMR ($CDCl_3$) $\delta$ 140.24, 137.15, 136.26, 134.37, 133.65, 130.24, 129.91, 129.68, 129.44, 129.30, 92.95. Anal. Calcd for $C_{11}Cl_{10}$: C, 27.2; Cl, 72.8. Found: C, 27.3; Cl, 72.5.

**Heptachloro-2-naphthoic Acid (5).** A solution of $CrO_3$ (0.500 g) in water (30 mL) was added slowly (0.5 h) to a stirred solution of naphthaldehyde **7** (0.496 g) in acetone (75 mL)–concd $H_2SO_4$ (3 mL) at room temperature. The reaction mixture was stirred for 2 h. The resulting mixture was poured into water (100 mL), and the precipitate was separated by filtration. The solid obtained was dissolved in ether. The ethereal layer was extracted with aqueous $NaHCO_3$, and the aqueous solution obtained was acidified with concd HCl and extracted with ether. The resulting ethereal solution was dried and evaporated to give acid **5** (0.454 g, 88%) as white needles, mp 219–21 °C [from ether–hexane or sublimed (150–60 °C, 0.01 mmHg)]: IR (KBr) 3680–2000 (broad), 1725 (s), 1630 (m), 1560 (m), 1530 (m), 1410 (m), 1380 (m), 1350 (w), 1330 (w), 1250 (s), 975 (m), 820 (m), 640 (m), 560 (m), 545 (m), cm$^{-1}$; UV ($CH_3CN$) $\lambda_{max}$ 239 nm (sh), 267, 330, 369 (sh) ($\epsilon$ 23 300, 39 300, 7270, 1300); $^1H$ NMR ($CDCl_3$) $\delta$ 7.70 (broad, COOH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 163.80, 136.06, 133.41, 132.55, 131.42, 129.33, 128.74, 128.40, 127.91, 127.27, 99.81. Anal. Calcd for $C_{11}HCl_7O_2$: C, 32.0; H, 0.2; Cl, 60.1. Found: C, 32.0; H, 0.3; Cl, 60.1.

**Methyl Heptachloro-2-naphthoate (6).** An excess of diazomethane in ether was added to a solution of the acid **5** (0.840 g) in the same solvent (20 mL) and the resulting mixture was left undisturbed for 18 h. The solvent was evaporated and the residue obtained was filtered through silica gel (hexane:$CCl_4$ = 3:2) to afford **6** (0.882 g, 95%) as a white powder which crystallized from hexane as a mixture of prisms, mp 96–7 °C, and needles, mp 116.5–7.5 °C: IR (KBr) 3480 (w), 3020 (w), 2960 (w), 2840 (w), 1750 (s), 1560 (s), 1540 (s), 1430 (s), 1420 (m), 1370 (s), 1340 (m), 1280 (s), 1240 (s), 1225 (s), 1160 (m), 1060 (s), 990 (s), 930 (s), 860 (m), 830 (s), 800 (m), 770 (m), 760 (s), 730 (m), 660 (m), 650 (s), 565 (m), 490 (s) cm$^{-1}$; UV ($C_6H_{12}$) $\lambda_{max}$ 242 nm (sh), 269, 330, 372 (sh) ($\epsilon$ 24 700, 46 700, 7800, 1550); $^1H$ NMR ($CDCl_3$) $\delta$ 4.05 (s, $CH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 164.01, 136.28, 136.22, 135.31, 131.81, 131.09, 129.73, 129.10, 128.98, 128.67, 126.97, 53.37. Anal. Calcd for $C_{12}H_3Cl_7O_2$: C, 33.7; H, 0.7; Cl, 58.1. Found: C, 33.7; H, 0.7; Cl, 58.4.

**Hydrolysis of Perchloro-2-methylnaphthalene (1).** A mixture of naphthalene **1** (0.102 g) and 30% oleum (2 mL) was stirred for 6 h. The resulting solution was poured over cracked ice and extracted with ether. The ethereal layer was extracted with aqueous $NaHCO_3$ and then dried and evaporated to leave some starting material (0.010 g) (IR spectrum and TLC). The basic aqueous solution obtained was acidified with concd HCl and extracted with ether. The resulting ethereal solution was dried and evaporated to give acid **5** (0.077 g, 88%), identified by its mp and IR spectrum.

**X-ray Analysis.**[28] **Perchloro-2-methylnaphthalene (1).** Molecular formula: $C_{11}Cl_{10}$, molecular weight 486.653, monoclinic, space group $P2_1/n$, $a = 11.162(4)$ Å, $b = 10.1813(4)$ Å, $c = 14.532(5)$ Å, $\beta = 107.84(2)°$, $V = 1572.2(8)$ Å$^3$, $Z = 4$, $F(000) = 944$, $D_c = 2.056$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 17.7 cm$^{-1}$. Good crystals were obtained by crystallization from $n$-hexane. Crystal specimen: irregular tablet, 0.21 × 0.56 × 0.65 mm, bright yellow. 4917 reflections with $1.00 \le \theta \le 30.44°$, $h$ −15/15, $k$ 0/14, $l$ 0/20, were measured on an Enraf-Nonius CAD4 diffractometer in $3\omega/5\theta$ mode at 293 K, with graphite-monochromated Mo K$\alpha$ radiation, $\lambda = 0.710\,73$, scan width ($0.80 \pm 0.34 \tan\theta$) ± 25% to determine the background, and maximum measurement time of 60 s. Cell parameters were determined from refinement of 25 reflections with $10.0 \le \theta \le 25.1°$ using the CELDIM procedure.[22] Three standard reflections were measured every 3600 s to check for intensity variation, and three standards were measured every 50 reflections to check the crystal orientation. Overall variation in intensity was −1.851% and was not corrected. Absorption effects were corrected using $\psi$-scans, $T_{max}$ 99.97%, $T_{min}$ 80.43%. The structure was solved using the tangent formula[23] and refined using 3498 observed reflections with $I \ge 3\sigma(I)$, full matrix, all atoms with anisotropic thermal parameters, total number of parameters refined 190.[24] Final $R$-factors: $R = 0.032$, $R_w = 0.046$, goodness of fit = 1.60. Final shifts/errors were less than 0.01 in the last cycle, maximum and minimum residual electron density peaks in the final difference Fourier were 0.501 and −0.116 eÅ$^{-3}$. Scattering factors were taken from ref 25.

**X-ray Analysis.**[28] **Heptachloro-7-(dichloromethyl)-naphthalene (10).** Molecular formula: $C_{11}HCl_9$, molecular weight, 452.208, orthorhombic, space group $Pca2_1$, $a = 7.657(1)$ Å, $b = 10.026(1)$ Å, $c = 19.540(1)$ Å, $V = 1500.0(2)$ Å$^3$, $Z = 4$, $F(000) = 880$, $D_c = 2.005$ g cm$^{-3}$, $\mu = 16.8$ cm$^{-1}$. Good crystals were obtained by crystallization from $n$-hexane. Crystal specimen: irregular plate, 0.48 × 0.50 × 0.09 mm, very pale yellow. 2604 Reflections of $1.00 \le \theta \le 30.44°$, $h$ 0/10, $k$ −14/0, $l$ 0/27, were measured on an Enraf-Nonius CAD4 diffractometer in $\omega$-scan mode at 293 K, with graphite-monochromated Mo K$\alpha$ radiation, $\lambda = 0.710\,73$, variable scan width, and maximum measurement time of 60 s. Cell parameters were determined from refinement of 25 reflections with $20.79 \le \theta \le 24.38°$ using the SET4 procedure.[22] Three standard reflections were measured every 3600 s to check for intensity variation, and three standards were measured every 50 reflections to check the crystal orientation. Overall variation in intensity was −0.802% and was not corrected. Absorption effects were corrected using $\psi$-scans, $T_{max}$ 99.99%, $T_{min}$ 69.93%. The structure was solved using MULTAN11/84[26] and refined using 1856 observed reflections with $I \ge 3\sigma(I)$, full matrix, all non-hydrogen atoms with anisotropic thermal parameters. The hydrogen atom position was found from the difference density Fourier; its position and isotropic thermal parameters were refined. Total number of parameters refined was 184.[24] Final $R$-factors: $R = 0.027$, $R_w = 0.035$, goodness of fit = 1.23. Final shifts/errors were less than 0.01 in the last cycle, maximum and minimum residual electron density peaks in the final difference Fourier were 0.299 and −0.201 eÅ$^{-3}$. Scattering factors were taken from ref 25, and plots were made with ORTEP-II and PLUTO programs.[27]

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