Novel pentafulvalene derivatives: synthesis, crystal structures, ^{1}H and ^{13}C NMR chemical shift assignments of *trans*- and *cis*-isomers of bis-2,2′-(4,5,6,7-tetrachloro-8,8-dimethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan-1,3a-dienylidene)

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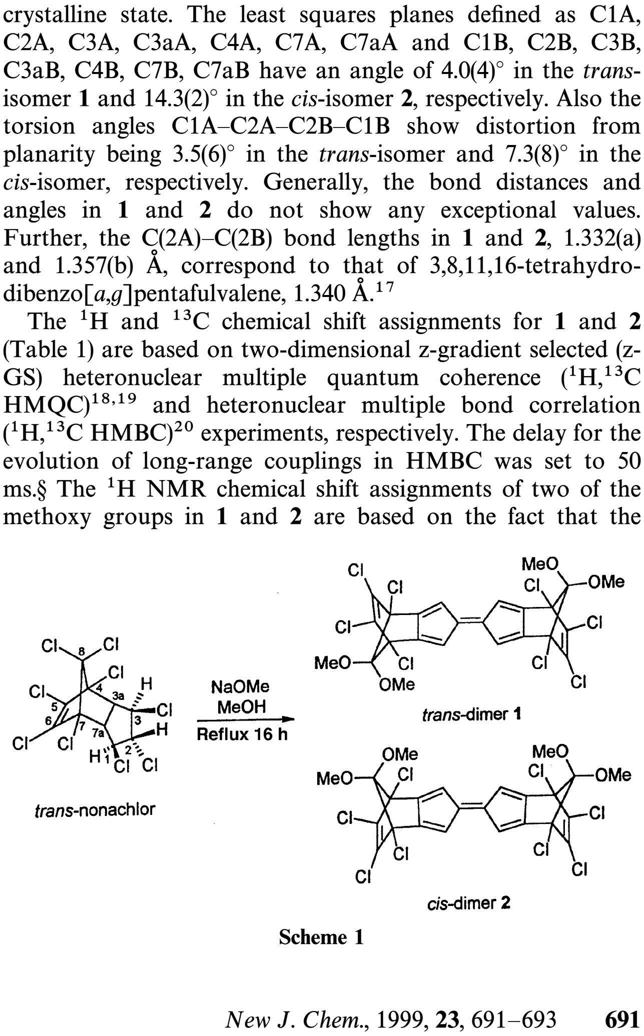
Synthesis, single crystal structures, ^{1}H and ^{13}C NMR chemical shift assignments based on z-gradient selected (z-GS) heteronuclear multiple quantum coherence (^{1}H,^{13}C HMQC) and heteronuclear multiple bond correlation (^{1}H,^{13}C HMBC) experiments are given for novel pentafulvalene derivatives, *trans*- and *cis*-isomers of bis-2,2′-(4,5,6,7-tetrachloro-8,8-dimethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan-1,3a-dienylidene), 1 and 2, derived from 1-*exo*-2-*endo*-3-*exo*-4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (*trans*-nonachlor) by treatment with sodium methoxide.

Joint with our ongoing project to prepare model compounds such as 1-*exo*-2-dichlorochlordene[1] suitable for environmental analysis of persistent organic pollutants we were able to prepare and purify novel pentafulvalene derivatives, *trans*- and *cis*-isomers of bis-2,2′-(4,5,6,7-tetrachloro-8,8-dimethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan-1,3a-dienylidene) **1** and **2**. Pentafulvalene itself is a challenging compound especially with respect to aromaticity, π-electron delocalization and charge density distribution in cross-conjugated molecules.[2] Synthetic routes leading to pentafulvalene formation are (i) dimerization of cyclopentadienylidene (carbene) generated by UV-photolysis from 1-diazocyclopenta-2,4-diene in various matrices at low temperatures,[3–5] (ii) oxidative coupling of cyclopentadienide with copper(II) chloride,[6] (iii) reaction of cyclopentadienide with iodine, converting the resulting unstable dihydrofulvalene to the dilithium salt with butyllithium, and finally treating the salt with oxygen[7] and (iv) oxidation of dicyclopentadiene in alkaline methanol by exposure to air.[8] From a theoretical point of view, fulvalene systems show interesting electronic excitation properties.[9] Keeping in mind that electronic excitation energy is also included in the paramagnetic term of the NMR shielding tensor,[10] the ^{13}C NMR chemical shifts of pentafulvalene derivatives are especially interesting. In this work we wish to report a simple synthetic route to novel isomeric pentafulvalene derivatives **1** and **2** (Scheme 1) starting from the commercially available chlorinated hydrocarbon *trans*-nonachlor (1-*exo*-2-*endo*-3-*exo*-4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetra-hydro-4,7-methanoindane).

In Scheme 1 the structures of *trans*-nonachlor and its dimeric reaction products **1** and **2** are described. The numbering of the methanoindano moieties in **1** and **2** is the same as in *trans*-nonachlor, the halves of the dimer denoted by suffixes A and B (see Fig. 1). The formation of the pentafulvalene derivatives **1** and **2** from *trans*-nonachlor involves three steps, (i) dehydrohalogenation of the partially chlorinated five membered ring with carbene formation,[11] (ii) dimerization of the formed carbene[12] and (iii) an anchimeric assistance to nucleophilic displacement at the dichloromethano-bridge by methoxide ion giving the ketal.[13] A possible rationalization of the mechanism for the last step is as follows. A simple S_N1/S_N2 substitution of the bridge-methylene chlorine atoms in polychlorinated norbornanes is unlikely.[14–16] Therefore, it is obvious that in this special case a neighbouring group effect operates involving the 10π pentafulvalene moiety (as in the corresponding benzene derivative[13]) followed by displacement of a chlorine at C-8 (*anti* to pentafulvalene). After that the newly formed chloro-ether undergoes a conventional S_N1 displacement with stabilization of the new cationic center at C-8 by the OMe-substitent and the proximate π-system.†

Fig. 1 shows the ORTEP-III plots and some selected bond lengths and angles for **1** and **2**.‡ Their crystal structures show that the pentafulvalene moieties are not fully planar in the crystalline state. The least squares planes defined as C1A, C2A, C3A, C3aA, C4A, C7A, C7aA and C1B, C2B, C3B, C3aB, C4B, C7B, C7aB have an angle of 4.0(4)° in the *trans*-isomer **1** and 14.3(2)° in the *cis*-isomer **2**, respectively. Also the torsion angles C1A–C2A–C2B–C1B show distortion from planarity being 3.5(6)° in the *trans*-isomer and 7.3(8)° in the *cis*-isomer, respectively. Generally, the bond distances and angles in **1** and **2** do not show any exceptional values. Further, the C(2A)–C(2B) bond lengths in **1** and **2**, 1.332(a) and 1.357(b) Å, correspond to that of 3,8,11,16-tetrahydrodibenzo[*a*,*g*]pentafulvalene, 1.340 Å.[17]

The ^{1}H and ^{13}C chemical shift assignments for **1** and **2** (Table 1) are based on two-dimensional z-gradient selected (z-GS) heteronuclear multiple quantum coherence (^{1}H,^{13}C HMQC)[18,19] and heteronuclear multiple bond correlation (^{1}H,^{13}C HMBC)[20] experiments, respectively. The delay for the evolution of long-range couplings in HMBC was set to 50 ms.§ The ^{1}H NMR chemical shift assignments of two of the methoxy groups in **1** and **2** are based on the fact that the



Scheme 1

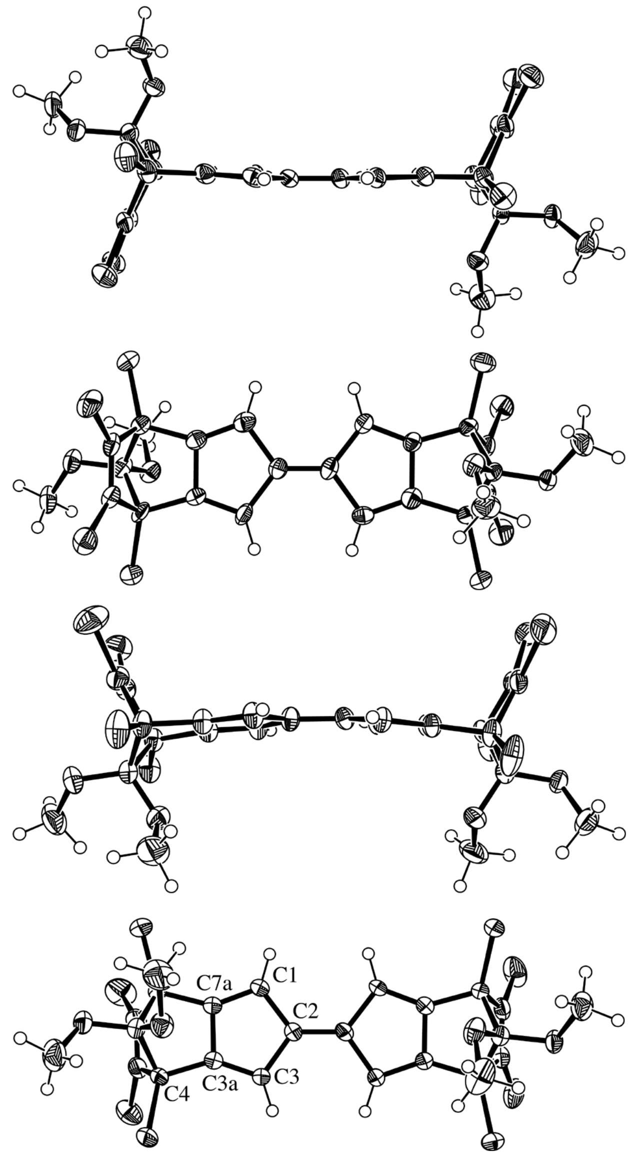


Fig. 1 ORTEP-III[22] plots of **1** and **2**. Selected bond lengths (Å) and angles (°) in **1** (top two structures): C(1A)–C(2A) 1.487(9), C(1A)–C(7aA) 1.337(8), C(3aA)–C(7aA) 1.477(9), C(2A)–C(2B) 1.332(9), C(1A)–C(2A)–C(3A) 107.6(5), C(2A)–C(3A)–C(3aA) 105.5(6), C(3A)–C(3aA)–C(7aA), 110.6(6) and C(1B)–C(2B)–C(2A) 127.6(6). The corresponding parameters in **2** (bottom two structures) are: 1.479(6), 1.347(6), 1.473(6), 1.357(6), 107.9(3), 106.4(4), 110.0(4) and 127.0(4).

Table 1 ^{1}H and ^{13}C NMR chemical shifts (δ in ppm) for **1** and **2** measured in CDCl$_3$ at 30 °C

	δ	
Nucleus	1	2
H-1/3	6.323	6.323
OCH_3[a]	3.654	3.649
OCH_3	3.558	3.539
C-1/3	111.00	110.98
C-2	152.69	152.65
C-3a/7a	150.62	150.65
C-4/7	75.64	75.67
C-5/6	132.87	132.87
C-8	118.92	118.95
OCH$_3$[a]	53.00	52.98
OCH$_3$	52.68	52.65

[a] *syn* to pentafulvalene.

methoxy located above the C5=C6 double bond experiences a shielding effect in comparison with the methoxy *syn* to the pentafulvalene moiety. Symmetry distortions found in the crystalline state are not manifested by NMR in solution. The ^{13}C NMR chemical shifts of the pentafulvalene moiety of **1** and **2** differ markedly from those of substituted pentafulvenes,[21] C-3a/7a and C-2 being remarkably deshielded and C-1/3 shielded when compared with the shifts of pentafulvenes. These findings can be useful in estimating the reliability of the theoretical calculations performed for pentafulvalene and related compounds.[9]

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Notes and references

† 2.39 g (0.104 mol) of Na was dissolved in 45 ml (1.111 mol) of methanol. To this solution was added 2.67 g (6.01 mmol) of *trans*-nonachlor in 40 ml of dry methanol and the mixture was refluxed for 16 h.[1] The methanol was evaporated under reduced pressure. 400 ml of water was added to the residue and then the water solution was extracted three times with 300 ml of light petroleum (bp 40–60 °C). The organic phase was washed twice with 200 ml of water, dried with Na$_2$SO$_4$ and evaporated to dryness. This residue was further refluxed in 140 ml of light petroleum for 3 h and the solution was concentrated to 5 ml volume. The brownish precipitate was 95% *trans*-isomer **1**. The yield was 257 mg. The final purification was done by column chromatography (Silica gel, CHCl$_3$). The clean product crystallized from CHCl$_3$ forming orange crystals suitable for single crystal X-ray analysis. The *cis*-isomer **2** was separated from the brownish crude product by repeated column chromatography: (i) silica gel, light petroleum, (ii) silica gel, light petroleum–acetone 20 : 1, (iii) silica gel, CHCl$_3$ and finally the orange fraction from the previous separation was column chromatographed by (iv) silica gel, *n*-hexane–toluene 1 : 3 giving **2** as a clean product forming crystals suitable for X-ray structure analysis.

‡ Crystal data: **1**: $C_{24}H_{16}O_4Cl_8 \cdot CHCl_3$, $M = 771.34$, triclinic, space group $P1$ (no. 2), $a = 13.281(1)$, $b = 13.328(1)$, $c = 19.818(1)$ Å, $\alpha = 105.40(1)$, $\beta = 92.78(1)$, $\gamma = 113.24(1)°$, $V = 3060.7(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 1.031 mm^{-1}, $T = 173.0 \pm 0.1$ K, $F(000) = 1544$. 14140 independent reflections collected in the range $3 < \theta < 28°$, 6512 data with $I > 2\sigma(I)$ were used for refinement. Final R values were $R = 0.092$ and $R_w = 0.206$ for 729 parameters. **2**: $C_{24}H_{16}O_4Cl_8$, $M = 651.97$, monoclinic, space group $P2_1/n$ (no. 14), $a = 15.134(1)$, $b = 13.357(1)$, $c = 15.331(1)$ Å, $\beta = 118.89(1)°$, $V = 2713.4(3)$ Å^3, $Z = 4$, μ(Mo-Kα) = 0.861 mm^{-1}, $T = 173.0 \pm 0.1$ K, $F(000) = 1312$. 6352 independent reflections collected $3 < \theta < 28°$, 4416 data with $I > 2\sigma(I)$ were used for refinement. Final R-values were $R = 0.067$ and $R_w = 0134$ for 329 parameters. CCDC reference number 440/115. See http://www.rsc.org/suppdata/nj/1999/691/ for crystallographic files in .cif format.

§ All NMR experiments were run on a Bruker Avance DRX 500 spectrometer equipped with a z-gradient acessory and an inverse detection 5 mm diameter probehead working at 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C, respectively. The detailed list of acquisition and processing parameters are available from E.K. on request.

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