Monatshefte für Chemie 134, 1229–1240 (2003)
DOI 10.1007/s00706-003-0028-y

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Synthesis and Comparative Analysis of Molecular and Supramolecular Structures of 4,8-Disubstituted 1,5-Dichloro-2,6-dioxotricyclo[5.1.0.0^{3,5}]octanes

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Received November 7, 2002; accepted (revised) December 16, 2002
Published online June 23, 2003

Summary. A series of 4,8-disubstituted 1,5-dichloro-2,6-dioxotricyclo-[5.1.0.0^{3,5}]octanes, synthesized by various methods, were studied by X-ray single crystal diffraction. The conformation (*syn*/*anti*) of the molecules does not depend on the method of preparation and nature of substituents. All the compounds crystallize in centrosymmetric space groups with half of the molecules in the asymmetric part of the unit cell. The main influence which the substituents render is on the packing of molecules in crystals and on the types of intermolecular interactions and supramolecular structures.

Keywords. *Michael* addition; *Darzens* condensation; Homo-*p*-quinones; Supramolecular chemistry; X-Ray structure determination.

Introduction

The full structural analysis of symmetrically substituted tricyclo-[5.1.0.0^{3,5}]octane-2,6-diones (bis-homo-*p*-quinones), carried out by the two known and principally different methods, has been made by means of NMR-studies. The methods of synthesis of the title compounds include debrominative as well as dehydrobrominative cyclopropane formations of 2,4,6,8-tetrabromocyclooctane-1,5-diones (method I) [1] and double addition of one-carbon units to *p*-quinone derivatives (method II), which has been achieved: a) by the action of diazomethane or diazoethane [2] on duroquinone followed by nitrogen elimination, b) by the action of dimethylsulfoxonium methylide (*Corey-Chaykovsky* reagent [3]) on *p*-quinonemonoacetal [4, 5],

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and c) by the addition of dihalocarbenes to duroquinone [6]. In these investigations it has been shown that depending on the synthetic method the configuration of bis-homo-*p*-quinones is *syn* (method I minor, II a, b) or *anti* (method II major, II c).

Results and Discussion

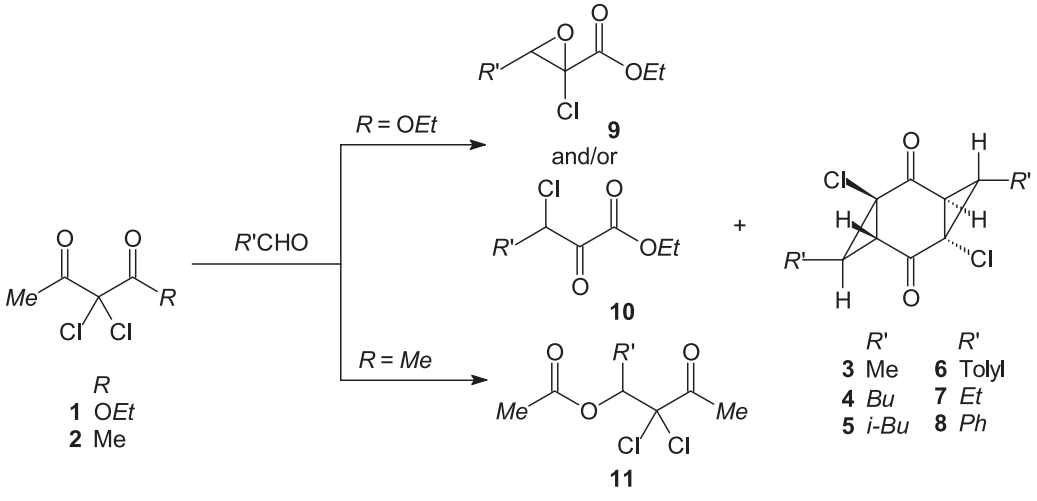
Synthesis of Homoquinones

The formation of bis-homo-*p*-quinones (**3**–**8**) as by-products with 8–12% yields has been observed by us in the reactions of ethyl 2,2-dichloroacetoacetate (**1**) [7] and 3,3-dichloropentane-2,4-dione (**2**) [8] with aldehydes under the conditions of the *Darzens* condensation along with main *Darzens* products; chloroepoxides **9** and/or chloroketones **10** in the first case and products **11** of insertion of aldehydes to the σ C–C bond in the second case (Scheme 1).

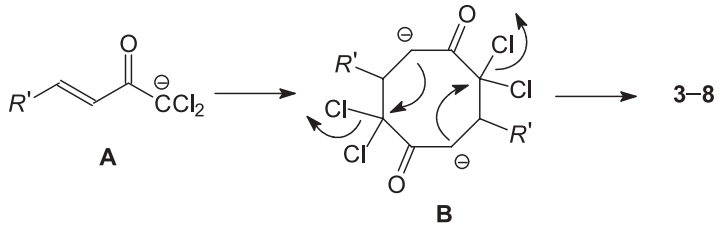
The mechanism of the formation of bis-homo-*p*-quinones (Scheme 2), which includes intramolecular double *Michael* addition of the *Knoevenagel* product **A** with the intermediate formation of 3,3,7,7-tetrachlorocyclooctane-2,6-dion-1,5-dianione (**B**), allowed to develop a new convenient method to obtain these attractive compounds. It consists of the cycloaddition of dichloroacetylalkenes **13**, which was achieved by *Friedel-Crafts* alkylation of an appropriate hydrocarbon with the vinylogue of dichloroacetylchloride **12** [9] obtained by addition of dichloroacetylchloride to acetylene under the conditions of the *Kondakov* reaction [10] (Scheme 3).

A second method provides **13** by the reaction of α, β-unsaturated esters with lithiodihalomethanes [11] (Scheme 4).

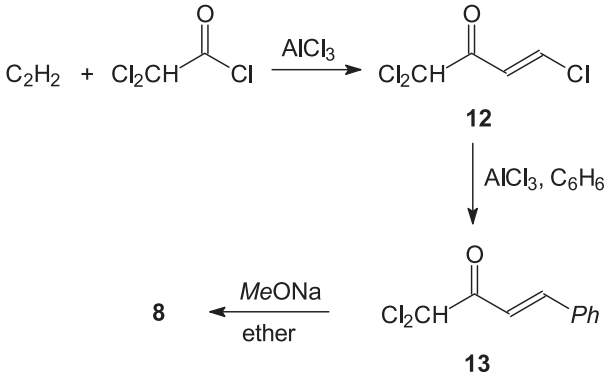
The structure of bis-homo-*p*-quinones obtained by these two latter methods is established not only by spectroscopic (IR, NMR) data [12], but also by X-Ray investigations for representatives of these compounds, for example, those received from the reactions of ethyl 2,2-dichloroacetoacetate with propionic aldehyde [7]



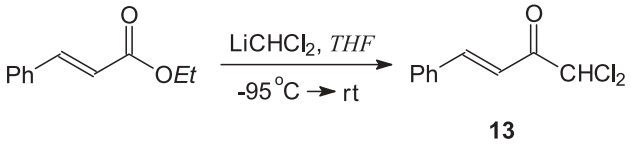
Scheme 1



Scheme 2



Scheme 3



Scheme 4

and 3,3-dichloropentan-2,4-dione with benzaldehyde [8a], which have shown formation of the *anti*-configured diastereomers.

Because the methods for the preparation of bis-homo-*p*-quinones involve different intermediates one might assume the formation of various isomeric bis-homo-*p*-quinones. Therefore we have compared the X-Ray data of six bis-homo-*p*-quinones obtained by various methods. The Cambridge crystallographic database [13] contains no data of further compounds of this class.

Crystal Structure

First, it should be noted that in the X-ray investigation we used crystals of the compounds prepared by different synthetic methods. Thus, **3**, **4**, **5**, and **7** were obtained *via* synthesis Schemes 1 and 4 and **6** and **8** *via* Schemes 1, 3, and 4. Judged by cell parameters, the crystals obtained *via* these methods appeared to be identical.

The X-Ray single crystal diffraction study of **3**–**6** revealed that bis-homo-*p*-quinones exist in a symmetric chair conformation (Fig. 1). The conformation of the

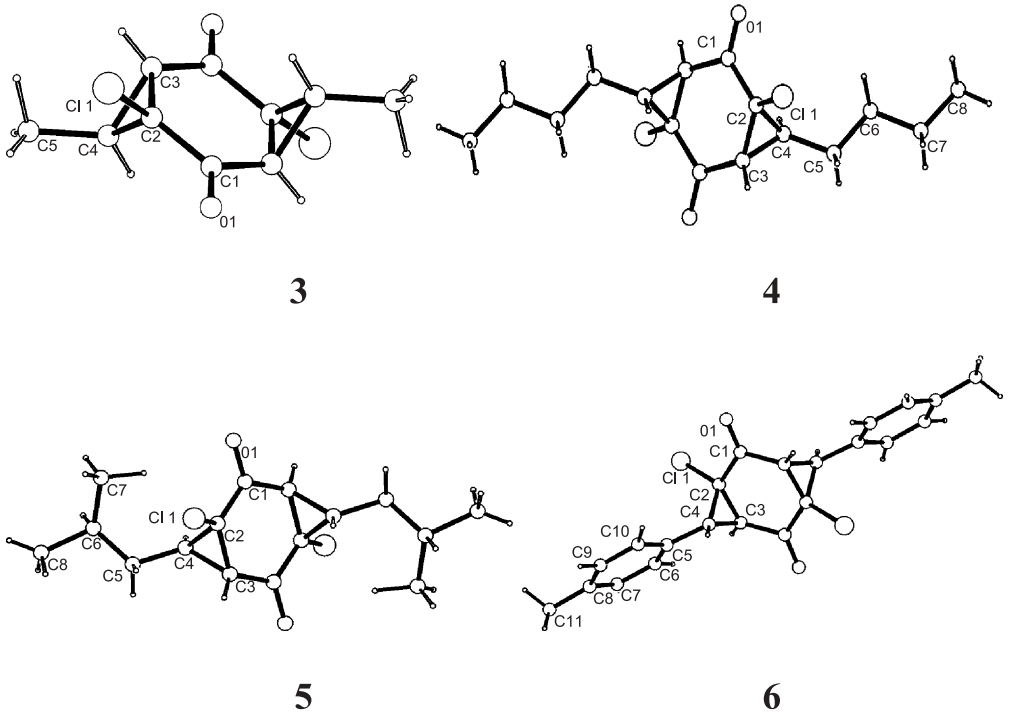


Fig. 1. PLUTO drawing of bis-homo-*p*-quinones **3**–**6** and the atom labelling scheme

central six-membered ring is planar. The dihedral angle between the plane of this ring and the cyclopropane ring is in the range of 74–78°. The substituents at the C(4) and C(4′) atoms occupy equatorial positions. The distances C(2)–Cl(1) are close to standard C–Cl distances in Cl-substituted cyclopropanes (1.755 Å) [14], that is the hybridisation of the C(2) atom is close to sp^3. It should be noted that all investigated compounds including **7** and **8** crystallize in centrosymmetric space groups with half of the molecules in the asymmetric part of the unit cells.

Molecules of all compounds are located in the centres of symmetry and have their own symmetry -1. Selected geometric parameters of **3**–**6** and the data of the earlier published structures **7** and **8** are presented in Table 1. Because of the low accuracy of the geometrical parameters in the reference compound **8**, a more detailed comparison with these data was impossible. For the correct analysis a new, more accurate X-ray single-crystal experiment with **8** was performed, and in Table 2 the data of this experiment are presented.

As shown in Table 1, the type of substituents practically does not affect both carbocycle conformations and angles in molecules. Thus, no systematic changes of the geometric parameters from molecules with small substituents to more bulky ones were observed. All compounds crystallize without inclusion of solvent molecules. The conformation of the tricycle appears to be very stable, so even the presence of bulky substituents does not change its geometric parameters essentially.

Table 1. Selected geometrical parameters of the compounds **3–8**

	3	**4**	**5**	**6**	**7**	**8**
Dihedral angle/°	76.7(2)	74.8(3)	75.9(3)	78.0(6)	76.1(1)	77.6(2)
d(C1-O1)/Å	1.203(2)	1.201(6)	1.237(4)	1.190(9)	1.202(1)	1.213(1)
d(C2-Cl1)/Å	1.749(2)	1.751(3)	1.759(4)	1.756(7)	1.753(1)	1.744(2)
d(C3-H3)/Å	0.89(2)	0.95(3)	0.96(4)	0.971(8)	1.14(2rt)	0.95(2)
d(C1-C2)/Å	1.496(2)	1.489(5)	1.459(5)	1.51(1)	1.477(2)	1.492(2)
d(C2-C3)/Å	1.523(2)	1.495(6)	1.523(5)	1.47(1)	1.527(2)	1.510(2)
d(C3-C4)/Å	1.522(2)	1.478(6)	1.517(4)	1.50(1)	1.533(2)	1.517(2)
d(C2-C4)/Å	1.520(2)	1.494(4)	1.519(5)	1.48(1)	1.507(2)	1.528(2)
d(C4-H4)/Å	1.10(2)	0.91(3)	0.92(4)	0.977(8)	1.08(1)	0.95(2)
d(C4-C5)/Å	1.518(2)	1.514(5)	1.503(6)	1.50(1)	1.506(1)	1.491(2)
∠(C1-C2-C3)/°	121.9(1)	120.9(3)	121.7(3)	122.3(6)	121.7(2)	121.8(1)
∠(C2-C3-C4)/°	59.90(9)	60.3(2)	60.0(2)	59.6(5)	59.0(1)	60.66(9)
∠(C3-C2-C4)/°	60.04(9)	59.3(3)	59.8(2)	61.3(5)	60.7(1)	59.89(9)
∠(C3-C4-C2)/°	60.1(1)	60.4(3)	60.2(2)	59.2(5)	60.3(1)	59.44(9)

Hydrogen Bonding

The analysis of data gives evidence, that the main influence which the substituents render is the type of molecular packing in crystals and the type of intermolecular interactions. In Fig. 2 the fragments of the hydrogen bonding system (a) and packing of molecules in crystals (b) of compounds **3–6** are shown, and in Fig. 3 similar data of **7** and **8**, for which such analysis was not carried out earlier, are presented. It is necessary to remark, that in these compounds there are no classic hydrogen bonds. However, the presence of a significant number of weaker interactions (C–H···O, C–H···Cl) renders an essential influence on the packing of molecules. Taking into account that all of the investigated molecules are centrosymmetric, a rather ramified system of hydrogen bonding should be observed.

Different types of intermolecular contacts appear in the crystals. The molecules of **3** form an infinite two-dimensional network in the 0xy plane *via* the bifurcate hydrogen bonds of O(1) atoms with protons H(4′) (x, y − 1, z) (O···H 2.64(1) Å, ∠(O···H–C) 149.6(4)°) and (H3″) (−1 + x, −1 + y, z) (O···H 2.62(2) Å, ∠(O···H–C) 123.8(5)°) (Fig. 2. **3**(**a**)). Among other short contacts the interaction Cl(1)···H(4‴) (1 + x, y, z) (Cl···H 2.91(1) Å, ∠(Cl···H–C) 113.8(4)°) was found. The mutual packing of molecules in the crystal is such that a bilayered structure is formed in the crystal (Fig. 2. **3**(**b**)). The layers containing chlorine atoms alternate with layers containing tricycles parallel to crystallographic plane 0xy. Such a localization of chlorine atoms in the crystal can be considered as the pseudochanel and indicates the existence of a selected direction and probably an anisotropy of the crystalline properties.

In **7**, as investigated earlier [7], the participation of O(1) in two short contacts with protons H(3′), H(4′) of the nearest molecule (x, −1/2 + y, 3/2 − z) is observed. The parameters of interactions are identical: (O···H 2.58(3) Å, ∠(O···H–C) 117.6(3)°). As each molecule of **7** takes part in two similar contacts as an acceptor and in four contacts as a donor, an infinite two-dimensional network of hydrogen-bonded

Table 2. Crystallographic data for compounds **3**–**6**

Crystal data	**3**	**4**	**5**	**6**
Chemical formula	$C_{10}H_{10}Cl_2O_2$	$C_{16}H_{22}Cl_2O_2$	$C_{16}H_{22}Cl_2O_2$	$C_{22}H_{18}Cl_2O_2$
Chemical formula weight	233.10	317.26	317.26	385.29
Cell setting	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$	P-1	$P2_1/a$
a/Å	5.604(3)	5.460(4)	5.712(4)	9.337(9)
b/Å	6.1169(8)	11.408(5)	6.038(2)	8.875(8)
c/Å	7.840(3)	13.387(9)	13.935(6)	11.123(7)
α/°	92.97(2)	90.00	86.37(3)	90.00
β/°	91.55(4)	92.12(6)	78.52(2)	91.27(7)
γ/°	109.32(3)	90.00	68.97(2)	90.00
V/Å^3	253(2)	833(1)	439(1)	921(1)
Z	1	2	1	2
D_x/mg m^{-3}	1.53	1.26	1.20	1.39
Crystal form	Prismatic	Prismatic	Plate	Plate
Crystal size/mm	$0.05 \times 0.2 \times 0.2$	$0.08 \times 0.2 \times 0.3$	$0.05 \times 0.1 \times 0.2$	$0.03 \times 0.3 \times 0.3$
Crystal colour	Colorless	Colorless	Colorless	Colorless
F(000)	120	336	168	400
Temperature/K	294	294	294	294
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Recording range θ_{max}/°	74.24	49.80	74.14	26.31
Absorption correction	Empirical	None	Empirical	None
μ/cm^{-1}	56.49	35.53	33.68	3.64
No. of recorded reflections	1131	1749	1001	5039
No. of independent reflections with $F^2 \geq 3\sigma(F^2)$	850	1169	700	730
R/%	5.0	5.3	5.0	5.2
wR/%	6.1	6.0	6.2	4.8
S	2.8	1.9	2.4	1.2
H-refinement	Isotropically	Isotropically	Not refined	Not refined
No. of refined parameters	84	135	103	118

molecules in the plane 0yz is formed (Fig. 3. **7**). A mutual disposition of molecules in the unit cell and longer substituents, than in **3**, prevent the localization of the chlorine atoms in one layer. However, they do not eliminate formations of layered superstructures.

In **4** with *n*-butyl substituents in a zigzag conformation, the interaction of O(1) with the methyne proton H(71′) of the molecules, related by the symmetry operation $(x-1/2,\ 1/2-y,\ 1/2+z)$ is observed (O···H 2.59(5) Å, ∠(O···H–C) 176(3)°) (Fig. 2. **4**(**a**)) form a three-dimensional system of hydrogen bonds due to this crystallographic special position of the molecule in the crystal.

In *i*-butyl-substituted compound **5** the formation of sloping stacks of molecules is also observed and the molecules of neighboring stacks take part in intermolecular interactions *via* O(1)···H(3′) $(x-1,\ 1+y,\ z)$ (O···H 2.49(3) Å, ∠(O···H–C) 122.1(5)°) and Cl(1)···H(52″) $(x,\ 1+y,\ z)$ (Cl···H 2.67(3) Å, ∠(Cl···H–C) 116.8(3)°) contacts (Fig. 2. **5**(**a**)). Thus an infinite two-dimensional

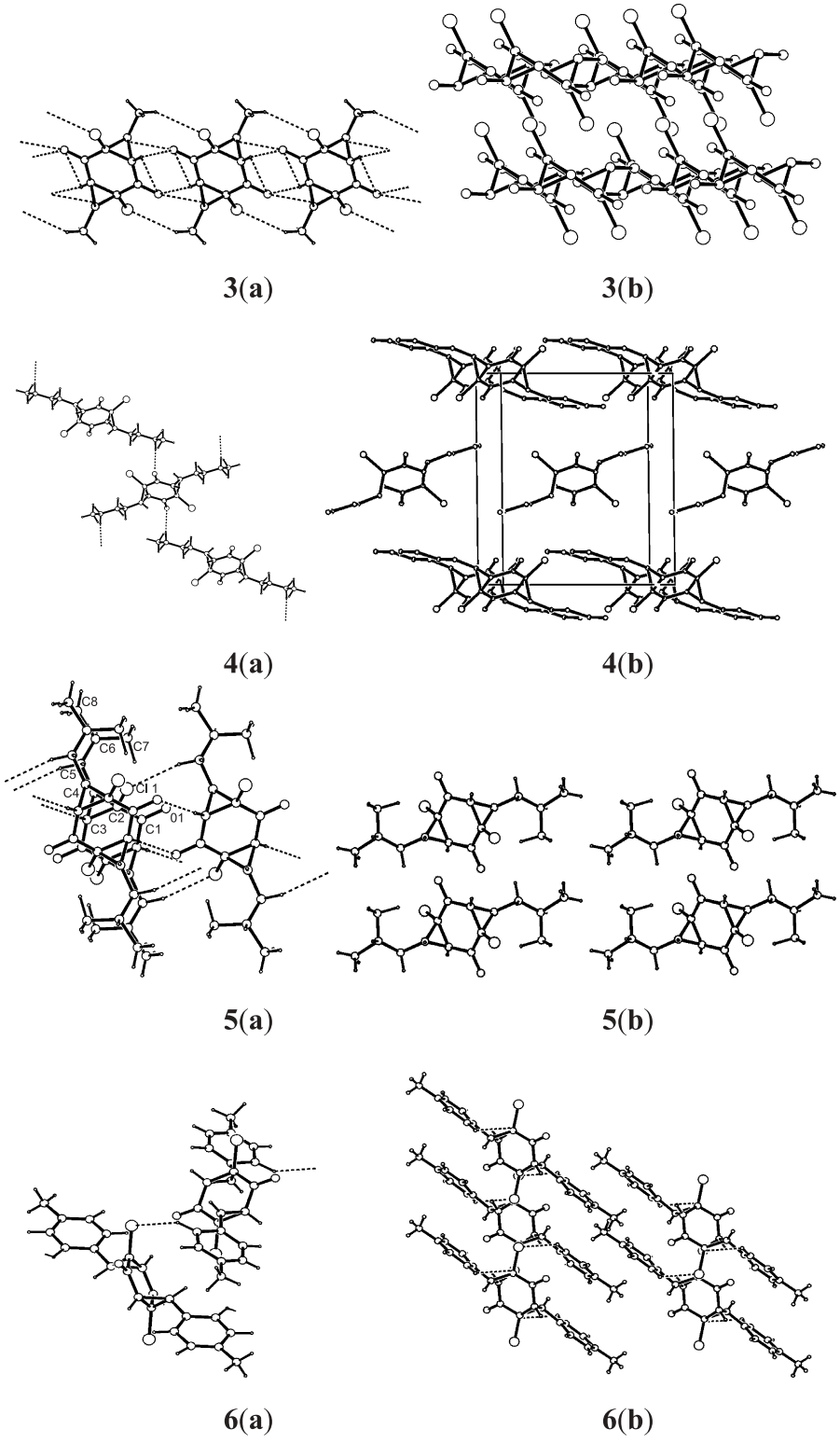
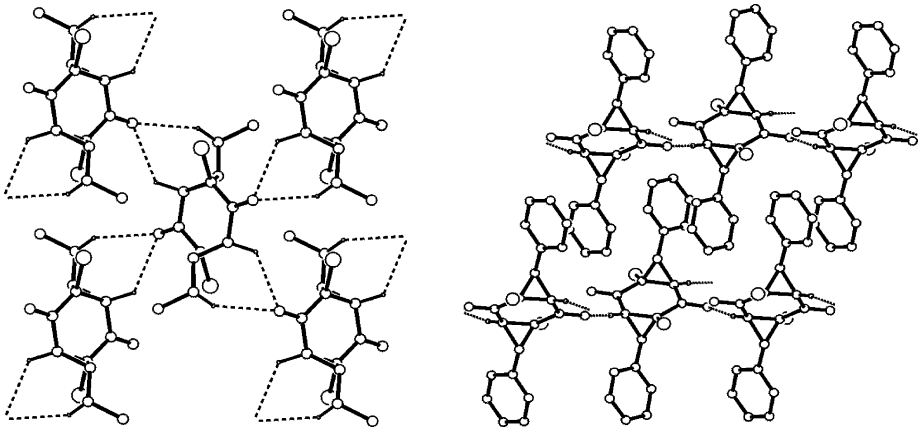


Fig. 2. The fragments of the **3**–**6** compounds' unit cells showing intermolecular hydrogen bonding (**a**) and the crystal packing (**b**)



7 **8**

Fig. 3. The fragments of the unit cells showing intermolecular hydrogen bonding in **7** (view along 0*x*, only H atoms participating in hydrogen bonds are shown) and crystals packing in **8** (view along 0*y*, hydrogen atoms not shown)

network of hydrogen-bonded molecules in the plane 0xy is formed. Layers containing *i*-butyl groups alternate with those consisting of cyclic fragments of molecules.

For the bis-homo-*p*-quinones with aromatic substituents **6** and **8** π–π and π–H interactions in the crystal are observed. Among other short contacts in **6** the interaction C–H···Cl between the chlorine atom Cl(1) and the phenyl proton H(10′) $(1/2-x, -1/2+y, -z)$ (Cl···H 2.75(6) Å, ∠(Cl···H–C) 139.2(2)°) (Fig. 2. **6(a)**) should be noted. This leads also to an infinite two-dimensional network of hydrogen-bonded molecules. No participation of H(3) and H(4) in hydrogen bonding is observed. The oxygen atom O(1) takes part in contacts with phenyl and methyl protons. For **8** an interaction between O(1) and the phenyl proton H(7′) (x − 1, y, z) only was observed. This interaction leads to an infinite layer of molecules.

Crystal Packing

Despite the different types of hydrogen bonding the crystal packing of the majority of the investigated compounds can be presented as bilayered structures. It should be noted that for the choice of molecular fragments as a supramolecular unit of the structure we were guided by principles, included in *Lehn's* supramolecular concept, namely "... Supramolecular chemistry may be defined as "chemistry beyond the molecule," bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces" [15]. Thus, layers in bilayered structures represent the complete element of hydrogen bonding of molecules in the crystal. Depending on whether the atoms participating in hydrogen bonding are inside these layers or on a surface, we can speak about hydrophilic or hydrophobic shells in between them.

The formation of bilayered structures with a hydrophobic part is characteristic for compounds with methyl and ethyl substituents. However, in **3** involvement of the oxygen atom in a bifurcate hydrogen bonding leads to the formation of layers, in which the bis-homo-*p*-quinone molecules have their six-membered cycles perpendicular to the plane of layers (supramolecular blocks). Therefore, methyl groups can be localized more precisely in layers. In the ethyl-substituted compound the six-membered cycles are practically parallel to the layers. As a result the ethyl groups are inclined towards the layer direction (Fig. 3. **7**). In bis-homo-*p*-quinone **3** the localization of areas with chlorine atoms representing layers along the unit cell diagonal can be observed (Fig. 2. **3**(**b**)).

The extension of the substituents (in the case of the bis-homo-*p*-quinone **4** with butyl groups) leads to formation of a three-dimensional supramolecular system instead of layered structures. Nevertheless, as a result of supramolecular isomorphism the fragments of a bilayered structure can be observed. Interestingly enough, the disposition of the alkyl-substituents with respect to bilayers appears to be even more ''slanting'' (Fig. 2. **4**(**b**)).

Crystal packing of the *i*-butyl substituted compound **5** appears to be similar to the one of methyl-substituted bis-homo-*p*-quinone. The molecules of **5** are packed into similar stacks, bound to each other by hydrogen bonds. Thus, the structure can be designated as supramolecularely bilayered, in which molecules are located again perpendicularly to the layer direction. Butyl groups rather precisely appear between these layers (Fig. 2. **5**(**b**)).

In the compounds with aromatic substituents the packing of molecules and the supramolecular structure is also bilayered with a sloping orientation of the hydrogen-bonded cyclic fragments with respect to the layer, probably closer to their perpendicular disposition (Fig. 2. **6**(**b**) and Fig. 3. **8**). The mutual disposition of the aromatic fragments is favorable for $\pi-\pi$ and $\pi-$H interactions between electronic systems of cycles. However, no formation of layers from chlorine atoms in other structures is observed.

Conclusions

Despite of various modes of synthesis, for each of the compounds the same crystals are obtained. All compounds crystallize in centrosymmetric space groups without involvement of solvate molecules in a unit cell. The conformations of all bis-homo-*p*-quinone molecules are identical, geometric parameters also vary unessentially.

In spite of the absence of classical hydrogen bonds the system of intermolecular interactions existing in the crystals leads to the formation of various supramolecular structures. For all compounds excluding the bis-homo-*p*-quinone with butyl groups the formation of layered supramolecular structures due to weak intermolecular interactions is characteristic, though the character of mutual disposition of molecules in layers and their hydrogen bonding differs significantly. On exterior surfaces of the layers there are enough hydrophobic fragments, alkyl and aromatic substituents or for some compounds areas containing chlorine, leading to the formation of pseudo channels in the crystals. The extension of alkyl substituents leads apparently to steric obstacles for their mutual packing.

Experimental

Melting points were determined with a Kofler hot plate apparatus and are uncorrected. Infrared spectra were obtained on a Infra-Red Spectrophotometer Model "UR-20" (KBr). The NMR spectra were measured with a Bruker MSL-400 spectrometer at 400.13 MHz for ^{1}H and 100.6 MHz for ^{13}C using *TMS* as internal standard. Microanalyses were performed with a elemental analyzer (CHN-3-analisator, USSR). Their results agreed favourably with the calculated values.

General Methods

The general methods for the preparation of 1,5-dichloro-4,8-disubstituted[5.1.0.$0^{3,5}$]octane-2,6-diones based on the reaction of ethyl 2,2-dichloroacetoacetate (**1**) and 3,3-dichloropentane-2,4-dione (**2**) with aldehydes and the reaction of α,β-unsaturated esters with lithiodihalomethanes have been already reported [7, 8, 11]. The preparation and characterization will be described only for **3** and **6** which are hitherto unpublished. We also demonstrate a new effective method for the preparation of the title compounds taking as an example the synthesis of **8**.

1,5-Dichloro-4,8-dimethyltricyclo[5.1.0.$0^{3,5}$]octane-2,6-dione (**3**, $C_{10}H_{10}Cl_2O_2$)

To a solution of 12.4 cm^3 of 1.61 *M* *n*-BuLi (20 mmol) in *n*-hexane in 50 cm^3 of THF was added slowly 2.13 g of CH_2Cl_2 (25 mmol) at $-95\,^{\circ}C$. The mixture was stirred for 30 min at this temperature. Then 3.24 g of ethyl crotonate (28 mmol) were added. The solution was stirred for 10 min and then 10 cm^3 of H_2O were added. The cooling bath was removed and after the mixture was warmed up to room temperature, 10% HCl was added to acidify the solution. The solvent was removed *in vacuo* and the solid was washed with ether to obtain 0.944 g (41%) of **3** as a white solid, mp 228 °C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.46$ (d, $J = 6.0$ Hz, 6H), 2.00 (dq, $J = 6.0$, 6.3 Hz, 2H), 2.21 (d, $J = 6.3$ Hz, 2H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.4$, 27.7, 40.6, 50.4, 192.8 ppm; IR (KBr): $\bar{\nu} = 3385$, 3018, 2950, 2910, 2825, 1685, 1565 cm^{-1}.

1,5-Dichloro-4,8-di(p-tolyl)tricyclo[5.1.0.$0^{3,5}$]octane-2,6-dione (**6**, $C_{22}H_{18}Cl_2O_2$)

In the same manner as for **3**, using ethyl (E)-4-methylcinnamate **6** was prepared in 42% yield. Mp 192 °C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.37$ (s, 6H), 3.05 (d, $J = 6.8$ Hz, 2H), 3.28 (d, $J = 6.9$ Hz, 2H), 7.15–7.26 (m, 8H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.19$, 36.05, 38.51, 50.41, 127.01, 129.10, 129.42, 138.82, 191.62 ppm; IR (KBr): $\bar{\nu} = 3400$, 3052, 1709, 1515, 1445, 1243, 1098, 812, 517 cm^{-1}.

1,1,4-Trichlorobut-3-en-2-on (*Dichloromethyl-β-chlorovinylketone*, **12**)

To a mixture of 20 g of freshly distilled dichloroacetylchloride (12.5 mmol) in 100 cm^3 of CCl_4 under vigorous stirring and cooling with ice was added 30 g of $AlCl_3$ (22.5 mmol) during 1 h in small portions. After addition of the first portion of $AlCl_3$ at first a weak and then more intensive current of dry acetylene was passed through the solution. After 6 h of acetylene passage the reaction mixture was quenched with crushed ice for 10 min. After separation of the organic layer, the aqueous layer was extracted with 2×50 cm^3 of $CHCl_3$ and 2×50 cm^3 of ether and then the organic extracts were combined. After evaporation the crude product was purified by distillation *in vacuo* (72–73°C/1333 Pa) affording 17.5 g (78%) of **12** as a colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$:CCl_4 (1:1)): $\delta = 5.83$ (s, 1H), 6.93 (d, $J = 14.5$ Hz, 1H), 7.43 (d, $J = 14.5$ Hz, 1H) ppm.

1,1-Dichloro-4-phenylbut-3-en-2-on (*Dichloromethyl-β-phenylvinylketone*, **13**)

Through a solution of 11 g of **12** (63.44 mmol) in 50 cm^3 of benzene, cooled with ice, a fierce current of moist HCl gas was passed during 10 min. Then 9.49 g of $AlCl_3$ (63.74 mmol) were added in small portions with intensive mixing and an still intensive current of HCl was passed through. After addition of all $AlCl_3$ cooling was stopped and the reaction mixture was stirred passing HCl through the solution for further 8 h. A dark-red complex precipitated. After 40 min at room temperature the reaction mixture was treated with ice and conc. HCl and extracted with 3×100 cm^3 of ether. The organic extracts were combined and washed with 2×200 cm^3 of H_2O, dried ($CaCl_2$), and evaporated. The resulting residue was purified by distillation *in vacuo* (124–126 °C/133 Pa) affording 11 g (81%) of **13** as a colorless oil. ^{1}H-NMR (250 MHz, $CDCl_3$:CCl_4 (1:1)): $\delta = 5.94$ (s, 1H), 7.26 (d, $J = 16.5$ Hz, 1H), 7.89 (d, $J = 16.5$ Hz, 1H) (compare with Ref. [1]); IR (KBr): $\bar{\nu} = 1695$ (CH=CH), 1710 (C=O) cm^{-1}.

*Reaction of **13** with MeONa*

To a solution of 4.3 g of **13** (20 mmol) in 50 cm^3 of dry ether at −80 °C small portions of 1.1 g MeONa (20 mmol) were added under Ar. At the same temperature stirring was continued for 4 h. Then the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. The precipitated product was filtered off, washed with H_2O, and dried. Recrystallization from *DMSO* gave 2.6 g of an analytically pure (compare Ref. [2]) sample of **8** (73%).

X-Ray Structure Determination

The X-Ray diffraction data for crystals of **3**–**6** were collected on a CAD4 Enraf-Nonius automatic diffractometer using graphite monochromated Cu K_α (1.54184 Å) radiation for **3**–**5** and Mo K_α (0.71073 Å) radiation for **6**. The details of crystal data, data collection, and refinement are given in Table 2. The stability of crystals and of experimental conditions were checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. Corrections for *Lorentz* and polarization effects were applied. The structures were solved by direct methods and difference *Fourier* syntheses using the SIR program [16] and MolEN package [17]. All non-hydrogen atoms were refined anisotropically, H-atoms were located in ΔF maps. All figures were drawn using the program PLATON [18].

Crystallographic data (excluding structure factors) for the structures **3**–**6** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 181762–181765. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors thank the Russian Fund for Basic Research (Grants No. 02-03-32280, 03-03-32865) and the Japan Society for the Promotion of Science (Grant No. RC 39626110) for financial support.

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