Structures of oxidation products of 4,6-di-*tert*-butylpyrogallol

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Oxidation of 4,6-di-*tert*-butylpyrogallol gave two dimeric products instead of the expected 4,6-di-*tert*-butyl-3-hydroxy-1,2-benzoquinone (**2**). It was established by X-ray diffraction analysis that the first product has the structure of tetra-*tert*-butyl-6,10a-dihydroxy-1,2-dioxo-3,4a,7,9-1,2,4a,10a-tetrahydrodibenzo-1,4-dioxine. From this it follows that compound **2** undergoes regio- and stereospecific dimerization according to the [2π+4π]-cycloaddition mechanism, *viz.*, the hetero Diels—Alder reaction. The double intensities of the signals in the ^{1}H NMR spectrum are indicative of a symmetrical structure of the second product, 2,6,4′,6′-tetra-*tert*-butyl-4,4′-dihydroxy-3,5,3′,5′-tetraoxo-4,4′-bi(cyclohexene), which is a racemate of enantiomers formed upon recombination (*r*+*r* or *l*+*l*) of the intermediate of oxidation of pyrogallol, namely, of the *r,l*-stereogenic 3,5-di-*tert*-butyl-1-hydroxy-2,6-dioxocyclohex-3-enyl radical.

Key words: 4,6-di-*tert*-butylpyrogallol, 3,4a,7,9-tetra-*tert*-butyl-6,10a-dihydroxy-1,2-dioxo-1,2,4a,10a-tetrahydrodibenzo-1,4-dioxine, 4,6-di-*tert*-butyl-3-hydroxy-1,2-benzoquinone, 2,6,4′,6′-tetra-*tert*-butyl-4,4′-dihydroxy-3,5,3′,5′-tetraoxo-4,4′-bi(cyclohexene), Diels—Alder reaction; X-ray diffraction study, molecular structure.

Recently,[1,2] we have prepared 4,6-di-*tert*-butylpyrogallol (**1**), a poorly studied representative of sterically crowded phenols.[3—6] This compound opens up possibilities for the synthesis of 4,6-di-*tert*-butyl-3-hydroxy-1,2-benzoquinone (**2**), which is an oxidation product of pyrogallol **1** (Scheme 1), and 4,6-di-*tert*-butyl-3-hydroxy-1,2-quinoneimines (**5**), which are products of condensation of hydroquinone **2** with amines. Compounds **2** and **5** are of interest as three-center tautomeric systems and tridentate ligands in which intramolecular O,O′(O,N′)-migrations of the proton as well as of the atoms and atomic groups that replace the proton (**3a** ⇌ **3b**; **4a** ⇌ **4b**) are associated with the unusual topology[7] of [1,4]- or [1,8]-transalternations of the π-conjugation system in the ligands.

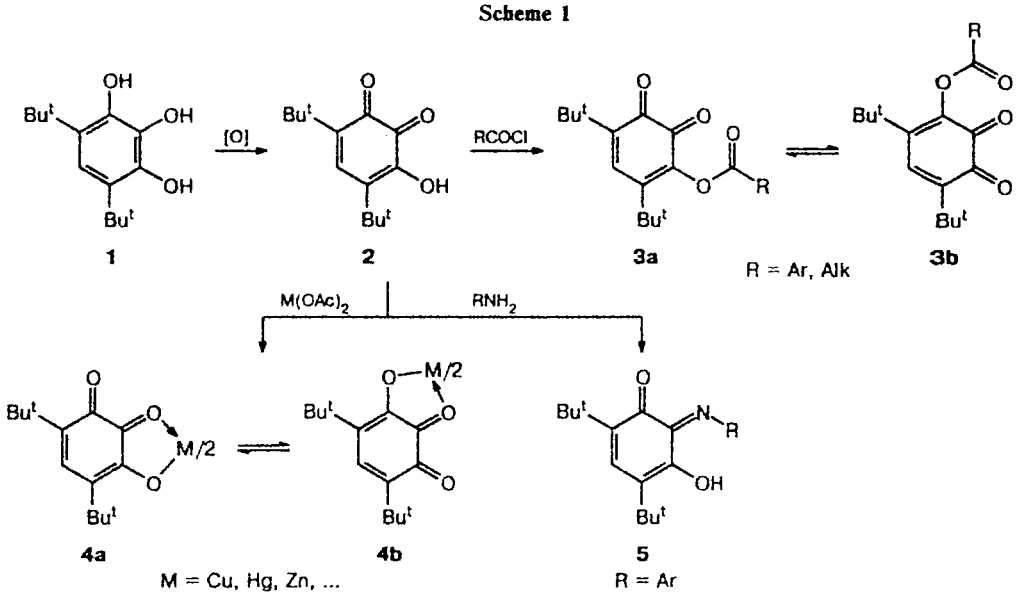
However, it appeared that treatment of pyrogallol **1** with various oxidizing agents afforded dimeric products instead of hydroxyquinone **2**. Thus, when nitrous acid ($NaNO_2$ in acetic acid), PbO_2, salts of variable-valence metals (Hg^{2+}), or "soft" organic oxidizing agents (*p*-quinone or 2,5-di-*tert*-butyl-*p*-quinone) were used, in all cases a dimeric product with the same structure was obtained in good yields (50—85%). The ^{1}H NMR spectrum (in $CDCl_3$) of this product has four nine-proton singlets of nonequivalent *tert*-butyl groups (at δ 1.13, 1.14, 1.15, and 1.38), two one-proton signals of the heterotopic hydrogen atoms of the six-membered rings (at δ 6.74 and 6.78), and two signals that correspond to the protons of the nonequivalent hydroxy groups (at δ 4.62 and 5.50). The spectrum has no peaks, which duplicate the above groups of the signals, which is indicative of the regiospecific formation of only one structure of a variety of possible dimeric forms.

Two singlet peaks at δ 6.74 and 6.78 in the ^{1}H NMR spectrum correspond to hydrogen atoms of six-membered aromatic or quinoid rings or rings possessing other π-conjugation systems. This means that dimerization of a particular intermediate *via* attack on the unsubstituted position 5 of the ring cannot occur upon oxidation of pyrogallol **1**. Based on the data ^{1}H NMR and IR spectroscopy and elemental analysis, it can be concluded that the dimer is formed from intermediate hydroxy-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 139—146, January, 1999.

1066-5285/99/4801-0139 $22.00

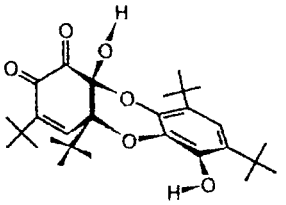
Scheme 1



quinone **2**. Monomeric units **2** in the dimer are bonded unsymmetrically. A wide range (about 20) of structural isomers satisfy these characteristics, which were estimated with the use of quantum-chemical calculations (PM3). The data obtained do not allow one to unambiguously choose between these isomers. The results of calculations only restrict the number of possible isomers to four-five isomers (**6**—**9**) with different structures. However, the calculated enthalpies of formation (ΔH_f) have similar values (see structures **6a**, **6b**, and **9** and structures **6c** and **7**).

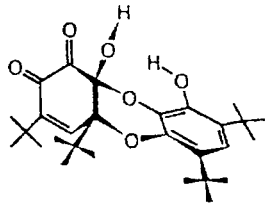
It was established by X-ray diffraction analysis that the dimer that formed under the above-mentioned conditions of oxidation of pyrogallol **1** has the structure of 3,4a,7,9-tetra-*tert*-butyl-6,10a-dihydroxy-1,2-dioxo-1,2,4a,10a-tetrahydrodibenzo-1,4-dioxine **6a** (Fig. 1; Tables 1—3). In the solid phase, compound **6a** exists as a 4 : 1 solvate with *n*-hexane. In the crystals of **6a**, there are two molecules (**A** and **B**) per asymmetric unit. The partially hydrogenated rings in these molecules have somewhat different conformations.

The cyclohexenedione fragment of molecule **6a** adopts a half-chair conformation. The C(7) and C(12) atoms deviate from the mean plane passing through the remaining atoms of the ring by −0.41 Å (**A**), 0.30 Å (**B**) and 0.27 Å (**A**), −0.42 Å (**B**), respectively. The presence of the bulky *tert*-butyl substituent at the endocyclic C(10)=C(11) double bond causes a substantial steric strain in this portion of the molecule. This is evidenced by the intramolecular shortened contacts O(6)...H(23a) (2.37 Å (**A**); the sum of the van der Waals radii[8] of the O and H atoms is 2.45 Å), O(6)...H(24d) (2.42 Å (**B**)),



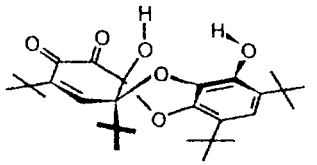
6a

(ΔH_f = −235.76 kcal mol^{-1})



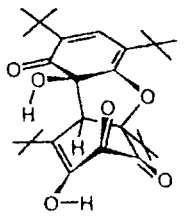
6b

(ΔH_f = −235.69 kcal mol^{-1})



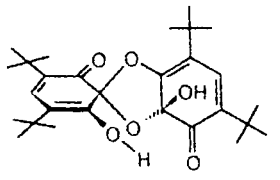
6c

(ΔH_f = −226.92 kcal mol^{-1})



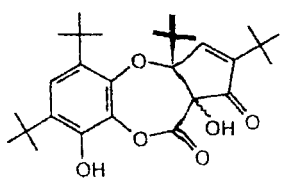
7

(ΔH_f = −226.17 kkcal mol^{-1})



8

(ΔH_f = −229.45 kcal mol^{-1})



9

(ΔH_f = −236.08 kcal mol^{-1})

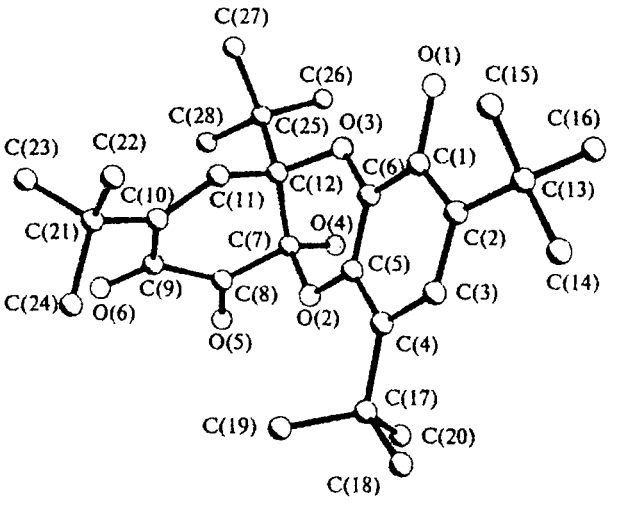


Fig. 1. Structure of compound **6a** (hydrogen atoms are omitted).

C(9)...H(23a) (2.80 Å (**A**); the sum of the van der Waals radii is 2.87 Å), C(9)...H(24c) (2.71 Å (**A**) and 2.72 Å (**B**)), C(11)...H(22b) (2.78 Å (**A**) and 2.81 Å (**B**)), C(11)...H(22a) (2.78 Å (**A** and **B**)), H(11)...C(22) (2.48 Å (**A**)), and H(11)...H(22f) (2.19 Å (**B**); the sum of the van der Waals radii is 2.32 Å). These unfavorable nonbonded interactions result in the elongation of the C(10)—C(21) bond (1.529(3) Å (**A**) and 1.525(3) Å (**B**)) compared to the average value[9] (1.501 Å). In addition, repulsions between the lone electron pairs of the oxygen atoms of the vicinal carbonyl groups lead to the noticeable elongation of the C(8)—C(9) bond length (1.533(3) Å (**A**) and 1.536 Å (**B**)), which becomes longer than that in the *o*-benzoquinone molecule.[10,11]

The dioxene ring adopts a sofa conformation. In molecule **A**, this conformation is slightly distorted. The C(12) atom deviates from the plane through the remaining atoms of the ring by 0.66 Å (**A**) and 0.67 Å (**B**).

Two partially hydrogenated rings are *cis*-fused (the O(4)—C(7)—C(12)—C(25) torsion angle is 51.8° (**A**) and 52.1° (**B**)). The substituents at the C(7) and C(12) atoms are in opposite orientations with respect to the

Table 1. Coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and equivalent isotropic thermal parameters of these atoms ($U_{eq} \times 10^3$) in the structure of **6a**

Atom	*x*	*y*	*z*	U_{eq}/Å^2
O(1)	683(1)	3224(1)	1934(1)	28(1)
O(2)	1235(1)	−85(1)	2179(1)	25(1)
O(3)	1070(1)	1733(1)	2593(1)	24(1)
O(4)	356(1)	−62(1)	2776(1)	32(1)
O(5)	1425(1)	−1509(1)	3105(1)	35(1)
O(6)	3084(1)	−1334(1)	3224(1)	42(1)
C(1)	796(1)	2369(1)	1696(1)	22(1)
C(2)	680(1)	2269(1)	1128(1)	22(1)
C(3)	831(1)	1368(2)	940(1)	24(1)
C(4)	1050(1)	567(1)	1269(1)	22(1)
C(5)	1098(1)	697(1)	1830(1)	21(1)
C(6)	1006(1)	1581(1)	2036(1)	21(1)
C(7)	1161(1)	43(2)	2735(1)	23(1)
C(8)	1716(1)	−771(2)	3004(1)	25(1)
C(9)	2651(1)	−642(2)	3082(1)	27(1)
C(10)	2948(1)	311(2)	2975(1)	26(1)
C(11)	2410(1)	1036(2)	2908(1)	24(1)
C(12)	1523(1)	1012(1)	2950(1)	23(1)
C(13)	355(1)	3082(1)	721(1)	25(1)
C(14)	367(2)	2820(2)	131(1)	45(1)
C(15)	861(2)	3986(2)	870(1)	50(1)
C(16)	−542(2)	3278(2)	735(1)	43(1)
C(17)	1245(1)	−393(2)	1038(1)	26(1)
C(18)	1184(2)	−345(2)	420(1)	34(1)
C(19)	2142(2)	−659(2)	1309(1)	32(1)
C(20)	647(2)	−1160(2)	1137(1)	35(1)
C(21)	3848(1)	419(2)	2943(1)	32(1)
C(22)	4041(2)	1433(2)	2813(1)	42(1)
C(23)	4426(2)	151(2)	3502(1)	46(1)
C(24)	4021(2)	−228(2)	2490(1)	42(1)
C(25)	1442(1)	1303(2)	3544(1)	29(1)
C(26)	560(2)	1593(3)	3543(1)	52(1)
C(27)	2017(2)	2141(2)	3745(1)	45(1)
C(28)	1710(2)	484(2)	3949(1)	40(1)

Atom	*x*	*y*	*z*	U_{eq}/Å^2
O(1′)	5159(1)	7628(1)	3160(1)	34(1)
O(2′)	4016(1)	4522(1)	3135(1)	26(1)
O(3′)	4029(1)	6354(1)	2699(1)	26(1)
O(4′)	3816(1)	4525(1)	2187(1)	32(1)
O(5′)	2649(1)	3374(1)	2461(1)	32(1)
O(6′)	1499(1)	4102(1)	2958(1)	29(1)
C(1′)	5181(1)	6752(2)	3412(1)	26(1)
C(2′)	5798(1)	6530(2)	3879(1)	26(1)
C(3′)	5752(1)	5625(2)	4098(1)	27(1)
C(4′)	5168(1)	4932(1)	3879(1)	25(1)
C(5′)	4591(1)	5190(1)	3399(1)	23(1)
C(6′)	4594(1)	6086(2)	3180(1)	23(1)
C(7′)	3473(1)	4776(2)	2618(1)	24(1)
C(8′)	2728(1)	4164(1)	2649(1)	23(1)
C(9′)	2120(1)	4563(2)	2966(1)	23(1)
C(10′)	2345(1)	5470(1)	3259(1)	22(1)
C(11′)	2861(1)	6034(2)	3073(1)	22(1)
C(12′)	3262(1)	5835(1)	2603(1)	23(1)
C(13′)	6491(1)	7225(2)	4129(1)	32(1)
C(14′)	7068(2)	6828(2)	4652(1)	42(1)
C(15′)	6132(2)	8152(2)	4288(1)	51(1)
C(16′)	7014(2)	7406(2)	3710(1)	44(1)
C(17′)	5196(1)	3940(2)	4130(1)	30(1)
C(18′)	5840(2)	3874(2)	4680(1)	46(1)
C(19′)	4360(2)	3669(2)	4244(1)	40(1)
C(20′)	5440(2)	3223(2)	3736(1)	38(1)
C(21′)	1941(1)	5733(2)	3725(1)	28(1)
C(22′)	2373(2)	6591(2)	4045(1)	35(1)
C(23′)	1033(2)	5982(2)	3482(1)	41(1)
C(24′)	2015(2)	4897(2)	4125(1)	47(1)
C(25′)	2722(1)	6225(2)	2042(1)	28(1)
C(26′)	3225(2)	6288(3)	1604(1)	47(1)
C(27′)	2416(2)	7214(2)	2141(1)	44(1)
C(28′)	1975(2)	5596(2)	1825(1)	40(1)

(to be continued)

Table 1. (*continued*)

Atom	x	y	z	U_{eq}/Å^2
C(1s)	4568(3)	5102(3)	13(2)	83(1)
C(2s)	4233(3)	6041(3)	−49(2)	111(2)
C(3s)	3339(3)	6171(3)	−13(2)	87(1)
H(O(1))	94(2)	320(2)	227(1)	58(9)
H(O(4))	27(2)	−65(2)	280(1)	66(10)
H(3)	78(1)	129(2)	55(1)	24(6)
H(11)	259(1)	166(2)	284(1)	19(5)
H(14c)	18(2)	334(2)	−10(1)	53(8)
H(14a)	95(2)	270(2)	11(1)	66(9)
H(14b)	−2(2)	225(2)	0(1)	62(9)
H(15c)	63(2)	447(2)	59(1)	57(8)
H(15b)	142(2)	390(2)	83(1)	72(11)
H(15a)	82(2)	428(2)	125(2)	90(11)
H(16c)	−71(2)	382(2)	49(1)	45(7)
H(16b)	−62(2)	346(2)	111(1)	53(8)
H(16a)	−89(2)	270(3)	60(1)	83(11)
H(18c)	63(2)	−24(2)	22(1)	38(7)
H(18b)	156(2)	16(2)	34(1)	34(6)
H(18a)	132(2)	−95(2)	29(1)	39(7)
H(19c)	255(2)	−17(2)	124(1)	35(6)
H(19b)	223(1)	−73(2)	170(1)	31(6)
H(19a)	229(1)	−128(2)	115(1)	36(6)
H(20c)	78(1)	−176(2)	99(1)	36(6)
H(20a)	7(2)	−101(2)	96(1)	43(7)
H(20a)	67(1)	−127(2)	153(1)	38(7)
H(22b)	395(2)	190(2)	310(1)	44(7)
H(22a)	370(2)	164(2)	247(1)	49(8)
H(22c)	462(2)	147(2)	278(1)	42(7)
H(23c)	430(2)	62(2)	376(1)	45(7)
H(23b)	502(2)	24(2)	347(1)	63(9)
H(23a)	434(2)	−52(2)	360(1)	64(9)
H(24c)	385(2)	−90(2)	253(1)	51(8)
H(24b)	370(2)	0(2)	213(1)	58(8)
H(24a)	461(2)	−21(2)	250(1)	38(7)
H(26c)	52(2)	176(2)	391(1)	52(8)
H(26b)	17(2)	105(2)	342(1)	72(10)
H(26a)	41(2)	213(2)	330(1)	69(10)
H(27a)	190(2)	237(2)	409(1)	51(8)
H(27b)	191(2)	268(2)	348(1)	71(9)
H(27c)	263(2)	194(2)	381(1)	68(10)
H(28c)	167(2)	73(2)	431(1)	55(8)
H(28b)	228(2)	29(2)	395(1)	49(8)
H(28a)	132(2)	−4(2)	387(1)	67(9)
H(O(1′))	470(2)	766(2)	294(1)	63(10)
H(O(4′))	379(2)	390(2)	217(1)	53(8)
H(3′)	616(1)	544(2)	441(1)	25(6)
H(11′)	298(1)	663(2)	323(1)	19(5)
H(14f)	749(2)	730(2)	478(1)	45(7)
H(14e)	736(2)	623(2)	459(1)	43(7)
H(14d)	676(2)	670(2)	493(1)	43(7)
H(15f)	580(2)	804(2)	457(1)	46(8)
H(15e)	658(2)	857(2)	444(1)	65(9)
H(15d)	579(2)	849(2)	398(1)	50(8)
H(16f)	731(2)	675(2)	363(1)	73(10)
H(16e)	745(2)	786(2)	386(1)	51(8)
H(16d)	667(2)	766(2)	336(1)	62(9)
H(18f)	643(2)	398(2)	464(1)	53(8)
H(18e)	582(2)	322(2)	482(1)	58(8)
H(18d)	569(2)	433(2)	494(1)	60(9)
H(19f)	441(2)	300(2)	442(1)	47(7)
H(19e)	422(2)	413(2)	450(1)	62(9)
H(19d)	390(2)	366(2)	390(1)	51(8)
H(20e)	544(2)	257(2)	390(1)	47(7)
H(20f)	602(2)	337(2)	367(1)	46(7)
H(20d)	506(2)	319(2)	339(1)	51(8)
H(22d)	213(2)	672(2)	437(1)	40(7)
H(22e)	296(2)	648(2)	418(1)	41(7)
H(22f)	230(2)	716(2)	382(1)	43(7)
H(23f)	75(2)	612(2)	377(1)	49(8)
H(23e)	99(2)	655(2)	322(1)	71(10)
H(23d)	72(2)	540(2)	330(1)	70(9)
H(24e)	179(2)	510(2)	444(1)	57(8)
H(24f)	261(2)	471(2)	428(1)	64(9)
H(24d)	169(2)	435(2)	394(1)	53(8)
H(26f)	290(2)	660(2)	128(1)	49(8)
H(26e)	372(2)	668(2)	172(1)	57(8)
H(26d)	339(2)	563(3)	149(1)	76(10)
H(27f)	210(2)	747(2)	177(1)	46(7)
H(27e)	204(2)	716(2)	242(1)	57(8)
H(27d)	289(2)	765(2)	228(1)	64(9)
H(28f)	166(2)	590(2)	149(1)	52(8)
H(28e)	213(2)	495(2)	172(1)	54(8)
H(28d)	159(2)	557(2)	206(1)	49(8)

cyclohexenedione and dioxene rings (the corresponding torsion angles are as follows: C(6)—O(3)—C(12)—C(25), −175.5(2)° (molecule **A**) and −179.0(2)° (**B**); C(10)—C(11)—C(12)—C(25), 94.7(3)° (**A**) and 91.6(3)° (**B**); C(5)—O(2)—C(7)—O(4), 86.0(2)° (**A**) and 90.8(2)° (**B**); and C(9)—C(8)—C(7)—O(4), 168.6(2)° (**A**) and −159.5(2)° (**B**)). This arrangement of the O(4)-hydroxy group is additionally stabilized by an attractive interaction with the nearest oxygen atom of the CO group (the H(O(4))...O(5) distance is 2.25 Å (**A**) and 2.31 Å (**B**)).

The *cis* fusion of the partially hydrogenated rings and the presence of the bulky *tert*-butyl group at the junction carbon atom lead to the appearance of substantial steric strains in the molecule. This is evidenced by the shortened intramolecular contacts O(3)...H(26a) (2.37 Å (**A**) and 2.42 Å (**B**)), O(4)...C(26) (2.99 Å (**A**) and 2.93 Å (**B**); the sum of the van der Waals radii is 3.00 Å), O(4)...H(26b) (2.32 Å (**A**) and 2.33 Å (**B**)), C(7)...H(28a) (2.80 Å (**A**) and 2.77 Å (**B**)), C(8)...C(28) (2.96 Å (**A**) and 2.94 Å (**B**)), C(8)...H(28b) (2.78 Å (**A**)), C(8)...H(28a) (2.64 Å (**A**) and 2.54 Å (**B**)), C(9)...C(28) (3.36 Å (**A**) and 3.16 Å (**B**); the sum of the van der Waals radii is 3.42 Å), and C(9)...H(28b) (2.74 Å (**A**) and 2.64 Å (**B**)). These unfavorable nonbonded interactions cause the elongation of the O(2)—C(7) (1.440(2) Å (**A**) and 1.437(3) Å (**B**); the average value is 1.416 Å), O(3)—C(12) (1.441(2) Å (**A**) and 1.442(2) Å (**B**)), and C(12)—C(25) bonds (1.579(3) Å (**A**) and 1.575(3) Å (**B**); the average value is 1.534 Å).

The presence of the bulky substituents leads also to noticeable steric strains in the aryl fragment as evidenced by the shortened intramolecular contacts O(2)...H(19b)

Table 2. Bond lengths (*d*) in the structure of **6a**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(1)	1.377(2)	C(13)—C(16)	1.528(3)	C(4′)—C(17′)	**1.531(3)**
O(2)—C(5)	1.389(2)	C(13)—C(14)	1.528(3)	C(5′)—C(6′)	1.378(3)
O(2)—C(7)	**1.440(2)***	C(17)—C(20)	1.528(3)	C(7′)—C(8′)	1.528(3)
O(3)—C(6)	1.389(2)	C(17)—C(18)	1.529(3)	C(7′)—C(12′)	1.533(3)
O(3)—C(12)	**1.441(2)**	C(17)—C(19)	1.533(3)	C(8′)—C(9′)	**1.536(3)**
O(4)—C(7)	1.376(3)	C(21)—C(22)	1.517(4)	C(9′)—C(10′)	1.476(3)
O(5)—C(8)	1.201(2)	C(21)—C(24)	1.534(4)	C(10′)—C(11′)	1.335(3)
O(6)—C(9)	1.214(3)	C(21)—C(23)	1.543(3)	C(10′)—C(21′)	**1.525(3)**
C(1)—C(6)	1.394(3)	C(25)—C(26)	1.525(4)	C(11′)—C(12′)	1.510(3)
C(1)—C(2)	1.394(3)	C(25)—C(27)	1.529(4)	C(12′)—C(25′)	**1.575(3)**
C(2)—C(3)	1.399(3)	C(25)—C(28)	1.531(3)	C(13′)—C(15′)	1.529(4)
C(2)—C(13)	**1.543(3)**	O(1′)—C(1′)	1.383(3)	C(13′)—C(14′)	1.532(3)
C(3)—C(4)	1.394(3)	O(2′)—C(7′)	**1.437(3)**	C(13′)—C(16′)	1.536(4)
C(4)—C(5)	1.399(3)	O(2′)—C(5′)	1.392(3)	C(17′)—C(18′)	1.532(3)
C(4)—C(17)	**1.537(3)**	O(3′)—C(6′)	1.390(3)	C(17′)—C(20′)	1.533(3)
C(5)—C(6)	1.372(3)	O(3′)—C(12′)	**1.442(2)**	C(17′)—C(19′)	1.535(4)
C(7)—C(8)	1.526(3)	O(4′)—C(7′)	1.382(3)	C(21′)—C(23′)	1.530(3)
C(7)—C(12)	1.537(3)	O(5′)—C(8′)	1.203(2)	C(21′)—C(24′)	1.532(3)
C(8)—C(9)	**1.533(3)**	O(6′)—C(9′)	1.219(2)	C(21′)—C(22′)	1.532(3)
C(9)—C(10)	1.479(3)	C(1′)—C(6′)	1.380(3)	C(25′)—C(28′)	1.519(3)
C(10)—C(11)	1.344(3)	C(1′)—C(2′)	1.395(3)	C(25′)—C(27′)	1.525(3)
C(10)—C(21)	**1.529(3)**	C(2′)—C(3′)	1.398(3)	C(25′)—C(26′)	1.533(4)
C(11)—C(12)	1.507(3)	C(2′)—C(13′)	**1.529(3)**	C(1s)—C(2s)	1.430(6)
C(12)—C(25)	**1.579(3)**	C(3′)—C(4′)	1.395(3)	C(1s)—C(1s)**	1.486(8)
C(13)—C(15)	1.525(3)	C(4′)—C(5′)	1.395(3)	C(2s)—C(3s)	1.525(6)

* Unusual (deviating from the average values) bond lengths are printed in bold type.
** Generated by a symmetry transformation $1-x, 1-y, -z$.

(2.43 Å (**A**) and 2.32 Å (**B**)), O(2)...C(20) (2.97 Å (**A**)), O(2)...H(20a) (2.37 Å (**A**)), and O(2)...C(19) (2.95 Å). As a result, the C(2)—C(13) (1.543(3) Å (**A**) and 1.529(3) Å (**B**)) and C(4)—C(17) (1.537(3) Å (**A**) and 1.531(3) Å (**B**)) bonds are elongated compared to the average C(Ar)—C(sp^3) bond length (1.511 Å).

The *n*-hexane molecule of solvation occupies a special position, namely, the center of symmetry.

Based on the X-ray diffraction data on the structure of the product, which corresponds to structure **6a** (see Fig. 1), it can be stated that dimerization of hydroxyquinone **2** proceeds according to the Diels—Alder cycloaddition mechanism.[12] One molecule **2** is involved in the reaction *via* its 4π-diene moiety (the dicarbonyl fragment), while the second molecule is involved in this reaction *via* the 2π-ethylene moiety (the C=C fragment of the six-membered ring, which carries the hydroxy and *tert*-butyl groups). According to the orbital symmetry and stereoselection rules,[13–15] electrocyclic [2π+4π]-cycloaddition reactions proceed simultaneously in the case of the *supra* orientations of the ethylene and diene moeties of the molecule that form the dioxine ring (Scheme 2).

However, under the above-mentioned conditions of oxidation of pyrogallol **1**, only one product was isolated. Therefore, this cyclodimerization gives the results only if the bulky *tert*-butyl groups at the C(4) and C(6) atoms of the ethylene and diketone participants of the reaction, respectively, are not brought into proximity as a result of mutual *syn—anti* twists of hydroxyquinone molecules **2** in the case of their *supra* orientations (see Scheme 2). The alternative *antara* orientation in the case of uncoordinated [2π+4π]-cycloaddition would afford dimer **6c** with the antiperiplanar arrangement of the *tert*-butyl groups at the adjacent stereogenic carbon centers along with other products. Dimers **6b** and **6c** were not detected among the oxidation products of pyrogallol **1**.

Scheme 2

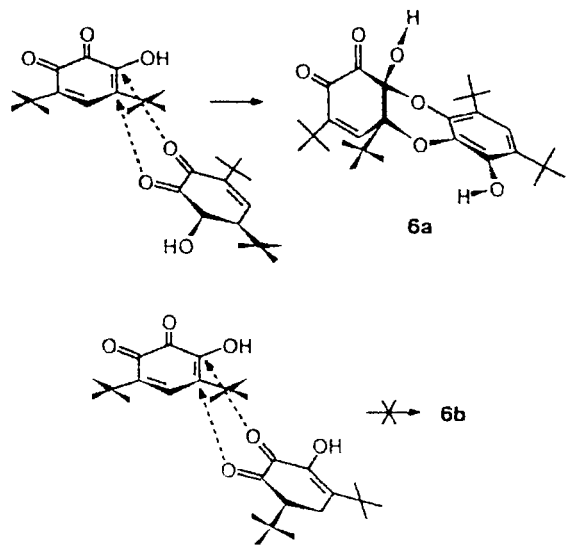


Table 3. Bond angles (ω) in the structure of **6a**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(5)—O(2)—C(7)	117.9(2)	C(14)—C(13)—C(2)	112.0(2)	O(5′)—C(8′)—C(7′)	121.2(2)
C(6)—O(3)—C(12)	114.5(2)	C(20)—C(17)—C(18)	107.8(2)	O(5′)—C(8′)—C(9′)	121.1(2)
O(1)—C(1)—C(6)	118.2(2)	C(20)—C(17)—C(19)	111.1(2)	C(7′)—C(8′)—C(9′)	117.6(2)
O(1)—C(1)—C(2)	122.0(2)	C(18)—C(17)—C(19)	106.2(2)	O(6′)—C(9′)—C(10′)	125.7(2)
C(6)—C(1)—C(2)	119.7(2)	C(20)—C(17)—C(4)	111.0(2)	O(6′)—C(9′)—C(8′)	117.3(2)
C(1)—C(2)—C(3)	116.3(2)	C(18)—C(17)—C(4)	111.9(2)	C(10′)—C(9′)—C(8′)	117.0(2)
C(1)—C(2)—C(13)	122.6(2)	C(19)—C(17)—C(4)	108.7(2)	C(11′)—C(10′)—C(9′)	116.8(2)
C(3)—C(2)—C(13)	121.0(2)	C(22)—C(21)—C(10)	111.5(2)	C(11′)—C(10′)—C(21′)	124.1(2)
C(4)—C(3)—C(2)	125.3(2)	C(22)—C(21)—C(24)	108.4(2)	C(9′)—C(10′)—C(21′)	119.0(2)
C(3)—C(4)—C(5)	115.6(2)	C(10)—C(21)—C(24)	109.8(2)	C(10′)—C(11′)—C(12′)	127.0(2)
C(3)—C(4)—C(17)	122.7(2)	C(22)—C(21)—C(23)	107.9(2)	O(3′)—C(12′)—C(11′)	108.4(2)
C(5)—C(4)—C(17)	121.7(2)	C(10)—C(21)—C(23)	109.6(2)	O(3′)—C(12′)—C(7′)	107.5(2)
C(6)—C(5)—O(2)	120.1(2)	C(24)—C(21)—C(23)	109.7(2)	C(11′)—C(12′)—C(7′)	107.7(2)
C(6)—C(5)—C(4)	120.7(2)	C(26)—C(25)—C(27)	108.7(2)	O(3′)—C(12′)—C(25′)	105.4(2)
O(2)—C(5)—C(4)	119.2(2)	C(26)—C(25)—C(28)	109.4(2)	C(11′)—C(12′)—C(25′)	111.4(2)
C(5)—C(6)—O(3)	121.9(2)	C(27)—C(25)—C(28)	107.8(2)	C(7′)—C(12′)—C(25′)	116.1(2)
C(5)—C(6)—C(1)	122.0(2)	C(26)—C(25)—C(12)	111.5(2)	C(15′)—C(13′)—C(2′)	110.5(2)
O(3)—C(6)—C(1)	116.0(2)	C(27)—C(25)—C(12)	108.9(2)	C(15′)—C(13′)—C(14′)	107.1(2)
O(4)—C(7)—O(2)	111.7(2)	C(28)—C(25)—C(12)	110.5(2)	C(2′)—C(13′)—C(14′)	111.9(2)
O(4)—C(7)—C(8)	112.7(2)	C(5′)—O(2′)—C(7′)	118.2(2)	C(15′)—C(13′)—C(16′)	110.9(2)
O(2)—C(7)—C(8)	98.5(2)	C(6′)—O(3′)—C(12′)	113.3(2)	C(2′)—C(13′)—C(16′)	108.9(2)
O(4)—C(7)—C(12)	112.2(2)	C(6′)—C(1′)—O(1′)	118.4(2)	C(14′)—C(13′)—C(16′)	107.5(2)
O(2)—C(7)—C(12)	109.4(2)	C(6′)—C(1′)—C(2′)	120.5(2)	C(4′)—C(17′)—C(18′)	111.7(2)
C(8)—C(7)—C(12)	111.6(2)	O(1′)—C(1′)—C(2′)	121.1(2)	C(4′)—C(17′)—C(20′)	108.9(2)
O(5)—C(8)—C(7)	120.8(2)	C(1′)—C(2′)—C(3′)	115.7(2)	C(18′)—C(17′)—C(20′)	107.5(2)
O(5)—C(8)—C(9)	121.6(2)	C(1′)—C(2′)—C(13′)	122.1(2)	C(4′)—C(17′)—C(19′)	111.3(2)
C(7)—C(8)—C(9)	117.3(2)	C(3′)—C(2′)—C(13′)	122.2(2)	C(18′)—C(17′)—C(19′)	106.9(2)
O(6)—C(9)—C(10)	125.6(2)	C(4′)—C(3′)—C(2′)	125.8(2)	C(20′)—C(17′)—C(19′)	110.3(2)
O(6)—C(9)—C(8)	117.2(2)	C(3′)—C(4′)—C(5′)	115.3(2)	C(10′)—C(21′)—C(23′)	109.0(2)
C(10)—C(9)—C(8)	117.2(2)	C(3′)—C(4′)—C(17′)	121.9(2)	C(10′)—C(21′)—C(24′)	109.4(2)
C(11)—C(10)—C(9)	118.2(2)	C(5′)—C(4′)—C(17′)	122.6(2)	C(23′)—C(21′)—C(24′)	110.8(2)
C(11)—C(10)—C(21)	123.5(2)	C(6′)—C(5′)—O(2′)	120.0(2)	C(10′)—C(21′)—C(22′)	110.7(2)
C(9)—C(10)—C(21)	118.4(2)	C(6′)—C(5′)—C(4′)	120.9(2)	C(23′)—C(21′)—C(22′)	108.8(2)
C(10)—C(11)—C(12)	127.6(2)	O(2′)—C(5′)—C(4′)	119.1(2)	C(24′)—C(21′)—C(22′)	108.1(2)
O(3)—C(12)—C(11)	108.6(2)	C(5′)—C(6′)—C(1′)	121.7(2)	C(28′)—C(25′)—C(27′)	108.4(2)
O(3)—C(12)—C(7)	107.9(2)	C(5′)—C(6′)—O(3′)	121.8(2)	C(28′)—C(25′)—C(26′)	108.6(2)
C(11)—C(12)—C(7)	107.8(2)	C(1′)—C(6′)—O(3′)	116.4(2)	C(27′)—C(25′)—C(26′)	109.0(2)
O(3)—C(12)—C(25)	104.5(2)	O(4′)—C(7′)—O(2′)	110.6(2)	C(28′)—C(25′)—C(12′)	111.0(2)
C(11)—C(12)—C(25)	111.4(2)	O(4′)—C(7′)—C(8′)	112.8(2)	C(27′)—C(25′)—C(12′)	108.4(2)
C(7)—C(12)—C(25)	116.4(2)	O(2′)—C(7′)—C(8′)	99.0(2)	C(26′)—C(25′)—C(12′)	111.3(2)
C(15)—C(13)—C(16)	109.3(2)	O(4′)—C(7′)—C(12′)	111.5(2)	C(2s)—C(1s)—C(1s)*	122.2(4)
C(15)—C(13)—C(14)	107.6(2)	O(2′)—C(7′)—C(12′)	110.8(2)	C(1s)—C(2s)—C(3s)	117.8(4)
C(16)—C(13)—C(14)	107.8(2)	C(8′)—C(7′)—C(12′)	111.5(2)		
C(16)—C(13)—C(2)	108.1(2)	C(15)—C(13)—C(2)	111.9(2)		

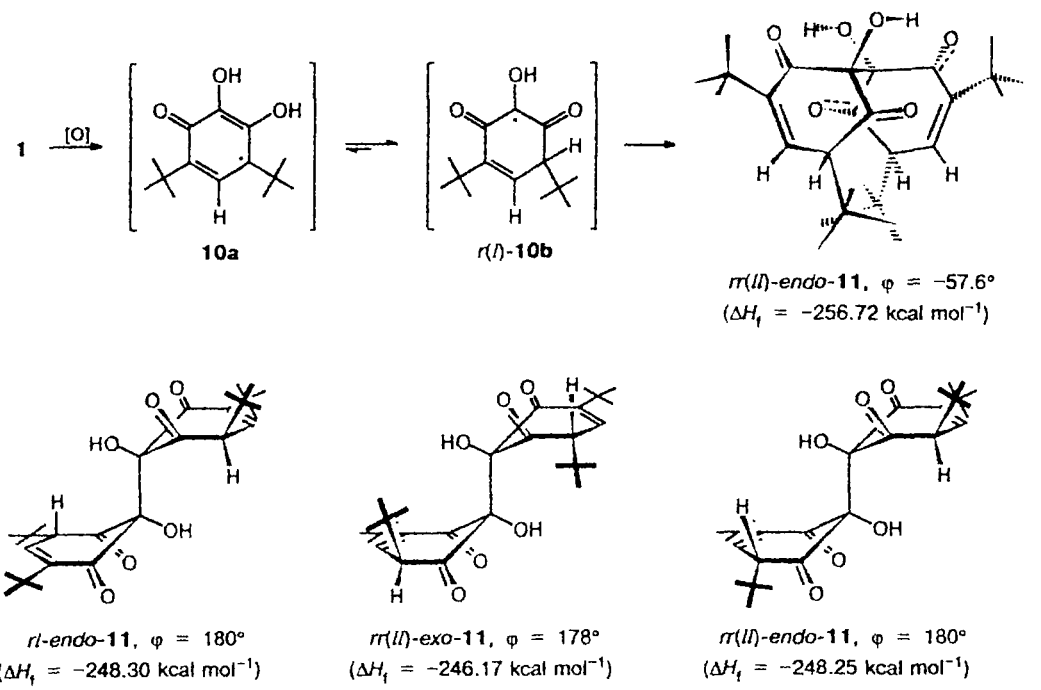
* Generated by a symmetry transformation $1-x, 1-y, -z$.

Oxidation of pyrogallol **1** in ether with an alkaline solution of potassium ferricyanide $K_3Fe(CN)_6$ afforded a dimer of the fundamentally different type in insignificant yield. The ^1H NMR spectrum (in $CDCl_3$) has two very characteristic signals: at δ 2.10 (which corresponds to the isochronous enantiotopic hydrogen atoms bonded to the *r,l*-stereogenic carbon atoms) and at δ 7.17 (which corresponds to the protons bonded to the vinyl fragments of the six-membered rings). Each signal is split into a doublet with the spin-spin coupling constant ^3J = 3.22 Hz. All peaks in the ^1H NMR spectrum of this product have double integrated intensities. Therefore, its structure corresponds to symmetrical 2,6,2′,6′-tetra-*tert*-butyl-4,4′-dihydroxy-3,5,3′,5′-tetraoxo-4,4′-bi(cyclohexene) (**11**) (Scheme 3).

Apparently, in this case the intermediate of oxidation of pyrogallol **1**, *viz.*, the 2,3-dihydroxy-1,4-quinomethide radical (**10a**), exists in the keto-enol equilibrium with the 1-hydroxy-2,6-dioxocyclohexene radical (**10b**), whose unpaired electron is localized at sterically unshielded position 1 (see Scheme 3). Diketone isomer **10b** recombines irreversibly to symmetrical product **11**.

Although the ^1H NMR spectrum and the data of elemental analysis allow one to judge with higher (compared to the above-considered case) assurance the structure of dimer **11**, the situation remains rather intricate.

Scheme 3



Radical **10b** contains the *r,l*-stereogenic carbon atom in the six-membered ring. Therefore, its recombination can afford three stereoisomers of dimer **11**, namely, the centrosymmetric (S_2) *r+l-meso* form and the axially symmetric (C_2) "left" (*l+l*) and "right" (*r+r*) enantiomers, which form a racemic mixture. In turn, the halves of each stereisomer can be either in the *exo* or in the *endo* orientation with the hydrogen atoms (or the *tert*-butyl groups) at the stereogenic carbon atom directed outward or inward, respectively. Furthermore, all rotations of the halves of the *meso* isomers of dimer **11** about the central C—C bond, except for φ = 0° (S_1) and φ = 180° (S_2), result in conformers, which have no symmetry elements and which cannot give isochronous (double intensity) signals in the ^{1}H NMR spectrum, while in the case of the analogous torsion dynamics of the enantiomers (*rr* and *ll*) all rotational isomers have the C_2 symmetry, which provides the homotopy of the identical atoms and atomic groups. Finally, in the case of any configuration and any rotational isomer of dimer **11**, there are alternatives to a nonplanar conformation (chair, boat, sofa, and twist form) of its cyclohexenedione fragments.

However, the selection can be unambiguously made among this variety by comparing the enthalpies of formation (ΔH_f) calculated by the semiempirical quantum-chemical PM3 method. The results of calculations demonstrate the following (see Scheme 3): (1) the *endo* orientation of the cyclohexenedione moieties of the dimer is 2—3 kcal mol^{-1} more favorable than the *exo* orientation; (2) the antiperiplanar (φ = 180°) conformers of the *meso* and enantiomeric forms of dimer **11** (with its halves in the *endo* orientations) have close values of the enthalpies of formation (varying from −247.4 to −248.3 kcal mol^{-1}) in the case of different conformations of the cyclohexenedione fragments, while the eclipsed (φ = 0°) rotational isomers do not exist due to steric repulsions between the closely-spaced *tert*-butyl substituents; (3) the synperiplanar orientation (φ ≈ −60°) of the halves of enantiomeric (*rr* and *ll*) dimer **11** with the cyclohexanedione fragments in the twist-boat conformation is substantially more favorable (by approximately 9 kcal mol^{-1}, see Scheme 3). The results of calculations agree with the experimental data. Thus, there is no evidence of duplication of the signals in the ^{1}H NMR spectrum of a solution (in $CDCl_3$) of dimer **11**, which is indicative of the preference of only one form among a variety of its conformational and rotational isomers.

So different structures of dimers **6a** (see Fig. 1) and **11** (see Scheme 3) can be related to the difference in the nature of the oxidizing agents (potassium ferricyanide is a one-electron oxidizer, while quinones, PbO_2, and HNO_2 are two-electron oxidizers). Evidently, in all cases 2,3-dihydroxy-1,4-quinonemethide radical **10a** is formed at the first stages of oxidation of pyrogallol **1** (see Scheme 3). However, in the case of a contact with a two-electron oxidizer (quinone), the lifetime of **10a** is small due to rapid subsequent oxidation to hydroxyquinone **2**, which undergoes dimerization to product **6a** (see Scheme 2). When a one-electron oxidizer ($K_3Fe(CN)_6$ in an alkali) is used, the lifetime of intermediate **10a** increases. In this case, the keto-enol rearrangement **10a** ⇌ **10b** occurs and radicals **10b** recombine to the enantiomers of dimer **11** (see Scheme 3).

Experimental

The ^{1}H NMR spectra were recorded on a Varian UNITY-300 spectrometer (300 MHz). The IR spectra were obtained on a Specord-75-IR instrument as thin films in Nujol mulls. The enthalpies of formation of different structural, configurational, and conformational isomers of dimers **6a** and **11** were calculated by the semiempirical quantum-chemical PM3 method using the HyperChem™ program (Release 4 for Windows Molecular Modeling System, Copyright ©1994 Hypercube, Inc.), which was kindly provided by Academician of RAS, Professor N. S. Zefirov and Professor Yu. A. Ustynyuk (Department of Chemistry, M. V. Lomonosov Moscow State University).

3,4a,7,9-Tetra-*tert*-butyl-6,10a-dihydroxy-1,2-dioxo-1,2,4a,10a-tetrahydrodibenzo-1,4-dioxine (6a). A solution of pyrogallol **1** (0.57 g, 2.39 mmol) and nonsubstituted *p*-quinone (0.26 g, 2.40 mmol) in hexane (10 mL) was refluxed for 2 h. The solvent was distilled off *in vacuo*. The solid residue was treated with hot water (40 mL) to remove the water-soluble hydroquinone, washed on a filter with water, dried, and crystallized from hexane. Dimer **6a** was obtained as yellow-orange crystals in a yield of 0.49 g, m.p. 153—154 °C. IR, ν/cm^{-1}: 3520 (OH); 3490 (OH); 3430 (OH); 1750 (C=O); 1680 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.13 (s, 9 H, Bu^t); 1.14 (s, 9 H, Bu^t); 1.15 (s, 9 H, Bu^t); 1.38 (s, 9 H, Bu^t at the tetrahedral C atom); 4.62 (s, 1 H, OH); 5.50 (s, 1 H, OH); 6.74 (s, 1 H, H arom.); 6.78 (s, 1 H, H arom.). Found (%): C, 71.64; H, 8.90. $C_{28}H_{40}O_6$. Calculated (%): C, 71.16; H, 8.53.

Reduction of dimer 6a. A Zn powder (0.5 g) was added to a solution of dimer **6a** (0.5 g, 1.06 mmol) in methanol (5 mL). The reaction mixture was heated to boiling, and concentrated HCl (0.5 mL) was added dropwise until the reaction mixture was decolorized (10—15 min). An excess of the zinc powder was separated by filtration, the solvent was removed *in vacuo*, and the residue was crystallized from hexane. Pyrogallol **1** was obtained as white needles in a yield of 0.2 g (40%), m.p. 121—122 °C (see Ref. 1: m.p. 122—123 °C). The spectral data (IR and ^{1}H NMR) correspond to those reported previously.[1]

4,4′-Dihydroxy-3,5,3′,5′-tetraoxo-2,6,4′,6′-tetra-*tert*-butyl-4,4′-bi(cyclohexene) (11). A mixture of a solution of pyrogallol **1** (2.3 g, 9.7 mmol) in diethyl ether (150 mL) and a solution of $K_3Fe(CN)_6$ (12 g, 36 mmol) and KOH (2.0 g, 36 mmol) in water (150 mL) was stirred using a magnetic stirrer at ~20 °C for 8 h. The ethereal layer was separated and washed several times with water to remove inorganic salts. The solvent was removed. The oil was ground with hexane. The resulting white precipitate (m.p. 233 °C) was crystallized from heptane. The yield of dimer **11** was 0.14 g. IR, ν/cm^{-1}: 3450 (OH); 1700 (C=O); 1630. ^{1}H NMR ($CDCl_3$), δ: 0.96 (s, 18 H, 2 Bu^t); 1.16 (s, 18 H, 2 Bu^t); 2.60 (d, 2 H, H at the tetrahedral C atom, ^3J = 3.22 Hz); 3.35 (s, 2 H, 2 OH); 7.17 (d, 2 H, H arom., ^3J = 3.22 Hz). Found (%): C, 71.13; H, 9.11. $C_{28}H_{42}O_6$. Calculated (%): C, 70.86; H, 8.92.

X-ray diffraction analysis of compound 6a. Crystals of $C_{28}H_{40}O_6 \cdot 0.25C_6H_{14}$ at 153(2) K are monoclinic, a = 16.659(6) Å, b = 14.101(5) Å, c = 25.026(9) Å, β = 103.83(3)°, V = 5708(4) Å^3, crystal dimensions 0.4×0.2×0.1 mm, space group $P2_1/c$, Z = 8, d_{calc} = 1.150 g cm^{-3}, $F(000)$ = 2148, μ = 0.079 mm^{-1}.

The intensities of 8280 reflections (of which 7911 reflections were independent, R_{int} = 0.035) were measured on an automated four-circle Siemens P3/PC diffractometer (graphite monochromator, Mo-Kα radiation, $\theta/2\theta$ scanning technique, $2\theta_{max}$ = 50°). The structure was solved by the direct method with the use of the SHELXTL PLUS program package.[16] The positions of the hydrogen atoms were located from the difference electron density synthesis. The structure was refined based on F^2 with anisotropic thermal parameters (with isotropic thermal parameters for hydrogen atoms, except for the H atoms of the *n*-hexane molecule of solvation; the latter were refined using the riding model with fixed $U_{iso} = nU_{eq}$ of the corresponding nonhydrogen atoms to which the hydrogen atoms are bonded, where n = 1.5 for the methyl group and n = 1.2 for the methylene group) by the full-matrix least-squares method (961 parameter) using 7358 reflections. The refinement converged to R_1 = 0.043 (based on 6352 reflections with $F > 4\sigma(F)$), wR_2 = 0.107, S = 1.05. The atomic coordinates are given in Table 1.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-33783a and 96-03-33902) and by the Russian Federation Government Program "Leading Scientific Schools" (Grant 96-15-97367).

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Received May 14, 1998