1,4-Addition of Lithium Organyls to *para*-Quinols / Structure Determination of 2,6-Di-*tert*-butyl-4-hydroxy-4,5-diphenylcyclohex-2-en-1-one

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Addition of lithium organyls to sterically hindered *para*-quinols leads to 1,2- or 1,4-adducts. The 1,4-addition prevails, if the 4-substituents in the quinol and the organic group in the lithium organyl are large. Four 1,4-addition products (2-cyclohex-2-en-1-ones) are synthesized and their structures investigated by NMR spectroscopy. The aryl groups at C-4 and C-5 acquire equatorial positions, the alkyl group at C-6 is bisectional. These results are confirmed by X-ray analysis of 2,6-di-*tert*-butyl-4-hydroxy-4,5-diphenylcyclohex-2-en-1-one, revealing a twist boat conformation of the cyclohexene ring.

Introduction

We have reported earlier that *para*-quinols 1 add lithium-organic compounds (2.0 - 2.5 equivalents, di-*n*-butyl-ether, 60 - 120 °C) to give mainly 1,2addition products 2 (6 - 92%), besides 1,4-addition products 3 (4-20%) and oxepins 4 (up to 20%) [1 - 6]. With 1.0 equivalent of lithium-organic compounds or potassium *tert*-butylate quinones 5 are obtained *via* base-catalyzed acyloin rearrangement of the quinolate anions (53 - 100%) [4].



The 1,2-addition products 2 can be transformed by acid either into the oxepins 4, the *ortho*-cyclohexadienones 6 or the phenols 7, depending on the amount of acid present and on the reaction

conditions [1 - 6]. The reaction sequence generally is in the order $2 \rightarrow 4 \rightarrow 6 \rightarrow 7$ or $2 \rightarrow 6 \rightarrow 7$. The step $4 \rightarrow 6$ can also be performed thermally without acid [3]. Meantime, similar observations have been reported by other authors [7 - 10].

In this paper, we wish to discuss the factors determining the ratio of 1,2:1,4-addition and to confirm the structure and configuration of the 1,4-addition products.

1,2- vs 1,4-Addition

Influence of the substituents R and R^1

It is expected that the 1,2-addition to the sterically hindered carbonyl group in $\mathbf{1}$ depends on the steric requirements of the group R^1 of the lithium organyl.

If we use the small MeLi, steric effects in the quinol **1** should not play a decisive role, *i. e.* 1,2-addition to the carbonyl group should not be at a disadvantage with respect to the 1,4-addition. Indeed, after alcaline hydrolysis of the reaction mixture, the 1,2-adducts **2** ($\mathbb{R}^1 = \mathbb{M}e$) are isolated in 84-92% yield [3, 6]. With larger groups in the lithium organyls (phenyl, 4-tolyl, 3-tolyl) the yields of 1,2-adducts **2** are smaller (generally 45-60%) [3 - 6], and the 1,4-adducts are formed as byproducts (8-13%) (see Table I); with 2-tolyl- or mesityllithium neither primary 1,2- nor 1,4-adducts could be obtained; the structure of the reaction products has not yet been determined.

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No	R	\mathbf{R}^1	m. p. [°C]	Yield [%]	1H NN tBu	MR Spe R	ectra (δ ppm) R ¹	=CH	H^{5}/H^{6} [J = 7-8 Hz]	ОН
a	Me	C ₆ H ₅	169	15	0.84^{a}	1.18	7.25 - 7.42	6.56	3.08/2.75	1.40
b	Me	$4-MeC_6H_4$	206	12	0.82^{b}	1.17	7.10 - 7.18 ^c	6.47	3.02/2.71	1.40(br)
c	<i>t</i> Bu	C_6H_5	118-119	20 ^d , 66 ^e	0.87^{b}	—7.	18 - 7.33 ^c —	6.28	3.49/2.65	1.24
d	C_6H_5	C_6H_5	148	$4^{\rm f}$	0.86 ^b 1.30	<u> </u>	97 - 7.26 ^g —	6.79	3.35/2.90	2.03

Table I. 2,6-Di-tert-butyl-4-hydroxy-4-R-5-R¹-cyclohex-2-en-1-ones 3

^a 60 MHz, CDCl₃; ^b 400 MHz, CDCl₃; ^c broad multiplet; ^d 0.16 molar C₆H₅-Li; in addition 46% **2c** (R = *t*Bu, R¹ = C₆H₅); ^e 0.56 molar C₆H₅-Li; in addition 9% **2c** (R = *t*Bu, R¹ = C₆H₅); ^f in addition 48% **2d** (R = R¹ = C₆H₅); ^g multiplet, partly broadened.

In addition, the size of the substituent R in 4position of the quinol is of influence. Large groups R, as phenyl or *tert*-butyl, shield the carbon atom 5 of the ring more than a methyl group. Thus, under comparable conditions, the yields of the 1,4-adducts are highest with R = Me (12-15%, see Table I). In the reaction of quinol **1a** (**1**: R = Me) with 4tolyllithium in addition to **3b** (**3**: R = Me, R¹ = 4-Tolyl) the exomethylene adduct **8** is formed in 8% yield, presumably by dehydration of the corresponding 1,2-adduct.

Influence of the concentration of $R^{1}Li$

The relative amount of 1,2:1,4-addition depends also on the *actual concentration* of the lithium organyl. Thus, the reaction of **1c** (1: $\mathbf{R} = t\mathbf{Bu}$) and **1d** (1: $\mathbf{R} = C_6\mathbf{H}_5$) with 0.16 M phenyllithium (2.5 equivalents) in di-*n*-butylether at 60°C produces after 4h 46% **2c** (2: $\mathbf{R} = t\mathbf{Bu}$, $\mathbf{R}^1 = C_6\mathbf{H}_5$)/20% **3c** (3: $\mathbf{R} = t\mathbf{Bu}$, $\mathbf{R}^1 = C_6\mathbf{H}_5$) and 48% **2d** (2: $\mathbf{R} = \mathbf{R}^1 = C_6\mathbf{H}_5$)/4% **3d** (3: $\mathbf{R} = \mathbf{R}^1 = C_6\mathbf{H}_5$), respectively. With a 0.56 M phenyllithium solution (again 2.5 equivalents), the yields starting with **1c** are 9% **2c**/66% **3c**.

The given molarities of phenyllithium refer to the situation at the beginning of the experiment, immediately after mixing the solution of **1** in di-*n*butylether with phenyllithium in diethylether. Due to evaporation of some of the diethylether and useup of the reagent, the concentration will vary with time. The results are probably due to steric effects, since phenyllithium is more strongly associated at higher concentrations, corresponding to a larger "size", favoring the 1,4-addition [11, 12]. If only 1.5 equivalents of phenyllithium are used to react with **1d** (**1**: $\mathbf{R} = C_6H_5$) at 37°C in diethylether for 12 h, the initially formed lithium salt of **1d** produces about 47% of the quinone **5** *via* acyloin rearrangement. In addition, 44% of 2,4-diphenyl-6-tertbutylphenol **7d** (**7**: $\mathbf{R} = \mathbf{R}^1 = C_6H_5$) are also obtained after acidic hydrolysis, due to acid-catalyzed rearrangement of the 1,2-adduct **2d** (**2**: $\mathbf{R} = \mathbf{R}^1 = C_6H_5$) [4]. In agreement with this assumption, the same compound **5** is formed, if **1d** ($\mathbf{R} = C_6H_5$) is treated with 1.5 equivalents of methyllithium under otherwise identical conditions. The quinone **5** can also be obtained by photolysis of **1d** (**1**: $\mathbf{R} = C_6H_5$) [5], where the mechanism, however, must be different.

Structure of the Reaction Products

The structure of the 1,2-adducts 2, the oxepins 4 and cyclohexadienones 6 has already been discussed [3]. The 1,4-adducts 3 are isomers of 2, as shown by elemental analysis and mass spectrometry. In the IR spectra, there is an OH-absorption between 3440 and 3550 cm^{-1} which is characteristic of a non-hindered OH-group. In addition, a carbonyl-absorption at 1654-1670 cm⁻¹ excludes a diol-structure. In the ¹H NMR spectra the absorption of *two tert*-butyl groups ($\delta = 0.82$ -0.87 and 1.24-1.30 ppm), of an olefinic proton ($\delta = 6.28-6.79$ ppm) and an OH-group ($\delta = 1.24-2.03$ ppm) is in agreement with structure 3. The tert-butyl signal at low field must be attributed to the tert-butyl group at the alkene carbon C-3, the one at higher field belongs to the group at C-6. In addition, AB type spectra of the two vicinal aliphatic protons H⁵ and H⁶ (*J* = 7-8 Hz) are also observed. For the related compound **9**, obtained by reduction of **1d** (**1**: R = C₆H₅) with NaBH₄ in methanol [13], $J_{\text{H}^6/\text{H}^5\text{e}} = 4.2$ Hz, $J_{\text{H}^6/\text{H}^5\text{a}} = 13.5$ Hz. As a consequence, both protons in **3** must be arranged axially.

The H⁵-signal is shifted to lower field (3.02 -3.49 ppm) by the paramagnetic anisotropy of the 5-aryl ring. The high-field shift of the signal of H^6 (2.65-2.90 ppm) may be explained by a diamagnetic anisotropic effect of the neighbouring carbonyl group which seems to overcompensate the inductive effect of that group. From 2D-NMR spectra it can be seen that the shifts of C-5 ($\delta = 46-54$ ppm) and C-6 (δ = 60-64 ppm) follow the opposite order. The assignment of H⁵/H⁶ is further supported by the fact that the doublet of H⁵ is somewhat broadened. Actually, one would expect an additional coupling of H^3 with H^5 . Such a coupling (J = 2.2 Hz) is observed in the compound 9, however, only with the equatorial H⁵e. This again supports the above assumption that in **3d** H⁵ is in axial position.

The total configuration of the 1,4-adducts **3** cannot definitely be determined by ¹H NMR. According to Dreiding models, there are at least twelve possible arrangements, eight of them can be excluded for steric reasons, two are ruled out due to the size of the dihedral angle. The two stereoisomers I and II remain from these considerations as the most probable ones.



For **3c** with a large group R (R = *t*Bu), the most probable configuration will be I: the 6-*tert*-butyl group as well as R and R¹ are arranged equatorially. Moreover, the 5-aryl ring is "perpendicular" with respect to the cyclohexene ring and thus arranged symmetrically between the adjacent *tert*butyl groups. Hence, the ¹H NMR signals of 4-*t*Bu and 6-*t*Bu practically coincide even at 400 MHz (in the ¹³C NMR spectra their signals are separated by 14 Hz at 100 MHz), which would not be expected for configuration II. With a configuration similar to I it is also possible to explain the characteristic trend of $\Delta \nu_{AB}$ of H⁵/H⁶ in **3a** - **d** (R is an aryl ring in each case). The largest difference is observed with **3c**, *i. e.* for a large R (= *t*Bu). With decreasing size of R,



Fig. 1. Plot of molecule **3d** along with the atomic numbering scheme. The ellipsoids represent 50% probability.

 $\Delta \nu_{AB}$ is diminished (from both sides) and is smallest for **3a** and **3b** (R = Me). Apparently, the large substituent 4-*t*Bu in **3c** not only causes the above mentioned twisting of the 5-aryl ring but also an intramolecular van-der-Waals interaction with proton H⁵, responsible for an additional low-field shift of the A signal. If 4-*t*Bu is replaced by the smaller Me group, the van-der-Waals repulsion is diminished and, simultaneously, the 5-aryl ring is less twisted with respect to the cyclohexene ring. Both effects cause a high-field shift of the H⁵-signal and a low-field shift of the signal of H⁶ (smaller diamagnetic anisotropy effect of 5-aryl), in agreement with the ¹H NMR spectra.

The rotation of the 5-aryl ring is hindered, as can be seen from dynamic NMR effects (line broadening, coalescene) at room temperature for the *ortho*and *meta*-protons and carbon atoms of the ring, depending on the frequency (60, 250, 400 MHz) used. The activation barriers were not determined quantitatively. Comparison of the spectra of 3c - d, however, reveals that the barrier is highest with 3c. This result agrees well with the above considerations.

In order to prove the structural conclusions definitely, the crystal structure of **3d** ($\mathbf{R} = \mathbf{R}^1 = \mathbf{C}_6\mathbf{H}_5$) was determined. The compound **3d** crystallizes in the monoclinic space group P2₁/c with 4 molecules in the unit cell. It is present as the racemic form due to the centrosymmetric space group.

The cyclohexenone ring exhibits the twist boat conformation ${}^{2}T_{4}$ [14] confirmed by the puckering parameters Q = 56.3 pm, $\Theta = 79.5^{\circ}$ and $\Phi = 199.6^{\circ}$ [15] and the endocyclic torsion angles (see Fig. 2). In the parent cyclohexene a twisted half-chair conformation [16] was observed.



Fig. 3. Intermolecular H-bridges.

The deviation of the conformation of 3d can be explained by steric effects, since the similar but less-hindered 2,4,5,6-tetramethyl-4,5,6-trinitro-cyclohex-2-en-1-one [17] still shows a slightly twisted half-chair arrangement. The aryl groups at C-4 and C-5 in 3d are in equatorial positions, the alkyl group at C-6 is bisectional [18]. An interesting aspect for the interpretation of the NMR spectra are the dihedral angles [19] H5-C5-C6-H6 with -150.6° and C17-C5-C6-H6 with -32.70°. From the dihedral angle of $ca. -151^{\circ}$ a coupling constant $J_{\rm H^5H^6}$ between 7 and 11 Hz can be derived from the Karplus curve, which agrees well with the value of 7-8 Hz found experimentally. Furthermore, intermolecular H-bonds O2-H2···O1' are observed with a distance $O2 \cdot \cdot \cdot O1'$ of 298 pm and an angle O2-H2...O1' of 152.8° (see Fig. 3).

Experimental Part

General:

IR spectra were obtained with a Perkin-Elmer 21 spectrometer. – NMR spectra were performed with Varian A-60 (60 MHz), Bruker AC 250 (250 MHz) and WM 400 (400 MHz) spectrometers using TMS as standard. Mass spectra were recorded with a MS9 of AEI, direct insert



Fig. 2. Conformation of the cyclohexene ring and scheme with endocyclic torsion angles.

(temperature 200 - 300°C), ionisation energy 70 eV. – TLC was performed on silica gel $HF_{254,346}$ (Merck) - For column chromatography silica gel Merck (0.05-0.20 mm) was used as adsorbent. The petroleum ether used had bp. 50 - 70°C.

Phenyllithium was prepared from bromobenzene and Li in ether [20]: 0.2 mol batches in 200 ml ether gave 0.9 -1.0 M solutions. 2-, 3-, 4-Tolyllithium were obtained from Li and the corresponding bromo-toluene in ether; 1 mol batches gave 0.6 - 0.7 M solutions.

General method for the preparation of 2,6-di-tert-butyl-1- R^{I} -4-R-cyclohexa-2,5-dien-1,4-diols (**2**) and 2,6-di-tertbutyl-4-hydroxy-4-R-5- R^{I} -cyclohex-2-en-1-ones (**3**)

2.5 Equivalents of the lithiumorganyl in ether were added, drop by drop, to 3.0 g of the 2,6-di-*tert*-butyl-4-R-4-hydroxy-cyclohexa-2,5-dien-1-one **1** (*para*-quinol) in 50 ml of di-*n*-butylether with stirring under N₂-atmosphere at 60°C. After 4 h of stirring at this temperature, the solvent was evaporated *in vacuo*. The residue was dissolved in a small amount of methanol, treated with saturated aqueous NH₄Cl solution until a pH of 8 was reached, and cooled to $0 - 5^{\circ}$ C. The reaction products were filtered off or extracted with ether and recrystallized from petroleum ether or methanol.

2,6-Di-tert-butyl-4-hydroxy-4-methyl-3-phenyl-cyclohex-5-en-1-one (**3a**)

3.0 g (13 mmol) of *para*-quinol **1a** (R = Me), treated with 2.5 equivalents of phenyllithium as described above, gave 0.4 g (13%) of **3a**, colorless needles, m. p. 169 - 170°C. – IR (KBr): 3550/3460 cm⁻¹ (OH), 2950 (*t*Bu), 1668 (C=O).

 $\begin{array}{c} C_{21}H_{30}O_2 \ (314.4) \\ Calcd \ C \ 80.21 \ H \ 9.62 \ \%, \\ Found \ C \ 80.07 \ H \ 9.82 \ \%. \end{array}$

2,6-Di-tert-butyl-4-hydroxy-4-methyl-3-(4-tolyl)cyclohex-5-en-1-one (**3b**) and 2,6-di-tert-butyl-1-(4-tolyl)-4-exomethylene-cyclohexa-2,5-diene (**8**)

2.0 g (8 mmol) of *para*-quinol 1a (R = Me), treated with 2.5 equivalents of 4-tolyllithium as described above,

gave an oil, which lead to 0.35 g (12%) of **3b** after recrystallization from petroleum ether, m. p. 206°C. – IR (KBr): 3550 cm⁻¹ (OH), 2960 (*t*Bu), 1667 (C=O). – MS (70 eV), *m/e* = 328 (M⁺). – ¹³C NMR (CDCl₃, 62.9 MHz): δ = 20.98 (Me), 29.07 (C-*t*Bu), 29.37 (Me), 29.91 (C– *t*Bu), 34.77 (C–*t*Bu), 35.63 (C–*t*Bu), 51.21 (C-5), 60.87 (C-6), 68.27 (C-4), 129.10 (C-Ar), 129.0 - 130.0 (br, C– Ar), 136.42 (C-Ar), 138.43 (C-Ar), 142.38 (C-3), 152.38 (C-2), 203.84 (C-1).

 $C_{22}H_{32}O_2$ (328.5)

Calcd C 80.44 H 9.82 %,

Found C 80.49 H 9.75 %.

From the mother liquor, a second fraction was obtained: 0.2 g (8%) **8**, m. p. 148–149 °C (from petroleum ether). – IR (KBr): 3450 cm⁻¹ (OH), 2950 (*t*Bu), 1650 (=CH₂). – MS (70 eV), m/e = 310 (M⁺).

C22H30O (310.5)

Calcd C 85.11 H 9.74 %, Found C 84.78 H 9.88 %.

2,4,6-Tri-tert-butyl-4-hydroxy-3-phenyl-cyclohex-5-en-1-one (**3c**)

a) 40.3 g (145 mmol) of *para*-quinol **1b** (R = *t*Bu) in 1.4 l of di-*n*-butylether were treated with 2.5 equivalents of phenyllithium in ether as described above (molarity of phenyllithium: 0.16). The reaction product was dissolved in methanol, whereupon 10.2 g (20%) of **3c** deposited as crystals, m. p. 118 - 119°C (from methanol). – IR (KBr): 3440 cm⁻¹ (OH), 2950 (*t*Bu), 1670 (C=O). – MS (70 eV), *m/e* = 356 (M⁺). – ¹³C NMR(CDCl₃, 100.6 MHz): δ = 25.57 (C-*t*Bu), 29.33 (C-*t*Bu), 29.47 (C-*t*Bu), 34.38 (C*t*Bu), 35.08 (C-*t*Bu), 41.34 (C-*t*Bu), 45.80 (C-5), 63.51 (C-6), 74.45 (C-4), 126.72 (C-Ar), 127.83 (br, C-Ar), 128.11 (br, C-Ar), 128.79 (br, C-Ar), 132.24 (br, C-Ar), 138.66 (C-3), 144.65 (C-Ar), 151.14 (C-6), 204.34 (C-1).

 $C_{24}H_{36}O_2$ (356.5)

Calcd C 80.85 H 10.18 %, Found C 80.90 H 10.11 %.

The mother liquor of **3c** was evaporated and the residue crystallized from petroleum ether to give 23.0 g (45%) of **2c** ($\mathbf{R} = \mathbf{R}^1 = t\mathbf{B}\mathbf{u}$); for the analytical data see ref. [3].

b) If the reaction was performed in 200 ml of di-*n*-butylether (molarity of phenyllithium: 0.56), but all other conditions identical as under a), the yields were: 34.0 g (66%) **3c** and 4.7 g (9%) **2c**.

2,6-Di-tert-butyl-4-hydroxy-4,5-diphenyl-cyclohex-5-en-1-one (**3d**)

3.0 g (10 mmol) of *para*-quinol 1c (R = Phenyl) in 50 ml of di-*n*-butylether were treated with 2.5 equivalents of

Table II. Crystal data and structure refinement for 3d.

Empirical formula	$C_{26}H_{32}O_2$
Formula weight	376.52
Temperature	293(2) K
Wavelength	71.073 pm
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 1147.0(1) \text{ pm}, \alpha = 90^{\circ}$
	b = 1826.0(1) pm,
	$\beta = 115.19(1)^{\circ}$
	$c = 1182.8(1) \text{ pm}, \gamma = 90^{\circ}$
Volume	$2.2417(3) \text{ nm}^{3}$
Z	4
Density (calculated)	1.116 g/cm^3
Absorption coefficient	0.069 mm^{-1}
F(000)	816
Crystal size	$0.25 \times 0.20 \times 0.07 \text{ mm}$
θ Range for data	
collection	$3 \text{ to } 23^{\circ}$
Index ranges	$0 \le h \le 12, 0 \le k \le 20.$
inden runges	-12 < l < 11
Reflections collected	3263
Independent reflections	$3092 (R_{int} = 0.0340)$
Reflections observed	1352
Refinement method	Full-matrix least-squares on F^2
Data, parameters	3091, 261
Goodness-of-fit	1.044
Final <i>R</i> indices	R1 = 0.0470, wR2 = 0.1046
$[F_0 > 4\sigma(F_0)]$	
R indices (all data)	R1 = 0.1967, wR2 = 0.1413
Extinction coefficient	0.006(2)
Largest diff. peak.	$187 e \times nm^{-3}$
hole	$-164 \text{ e} \times \text{nm}^{-3}$

phenyllithium in ether as described above to give 1.7 g (45 %) 2d, m. p. 166 °C (from petroleum ether); for analytical data see ref. [3]. The mother liquor of 2d was evaporated. The resulting light brown syrup was chromatographed (silica gel, petroleum ether). Elution (solvent in parenthesis) gave the following fractions: 1 + 2 (petroleum ether): biphenyl (yield ca. 5 % of the applied phenyllithium); 2-4 (petroleum ether:benzene = 10:1.5): 1.39 g (46%) 2-tert-butyl-4,6-diphenylphenol (7d); 5 (petroleum ether:benzene = 3:7): 151 mg (4 %) **3d**, m. p. 116 °C. – IR (KBr): 3500 cm⁻¹ (OH), 2950 (*t*Bu), 1654 (C=O). – MS (m/e): 376 (M^+) . – ¹³C NMR (CDCl₃, 100.6 MHz): $\delta = 28.94 (C-tBu), 29.93 (C-tBu), 35.07 (C-tBu), 35.88$ (C-tBu), 53.96 (C-5), 59.89 (C-6), 73.09 (C-4), 125.27 (C-Ar), 126.32 (C-Ar), 126.82 (C-Ar), 127.50 (C-Ar), 127.76 (C-Ar), 130.0 (br, C-Ar), 139.98 (C-Ar), 143.13 (C-3), 146.63 (C-Ar), 153.46 (C-2), 203.46 (C-1).

 $C_{26}H_{32}O_2$ (376.5)

Calcd C 82.94 H 8.57 %, Found C 82.65 H 8.69 %.

Table III. Atomic coordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[pm^2 \times 10^{-1}]$ for **3d**. U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

Atom	x/a	y/b	z/c	U(eq)
O(1)	4361(2)	4597(1)	776(2)	59(1)
O(2)	6787(2)	3917(1)	-569(2)	55(1)
C(1)	5275(4)	4171(2)	1116(3)	48(1)
C(2)	5056(4)	3385(2)	763(3)	47(1)
C(3)	5941(4)	3088(2)	459(3)	54(1)
C(4)	7121(3)	3476(2)	537(3)	43(1)
C(5)	7680(3)	3949(2)	1757(3)	44(1)
C(6)	6638(3)	4448(2)	1859(3)	46(1)
C(7)	3804(4)	2996(2)	546(4)	62(1)
C(8)	3213(4)	3282(3)	1408(4)	92(2)
C(9)	2832(4)	3131(2)	-819(4)	88(2)
C(10)	4006(5)	2174(2)	733(6)	127(2)
C(11)	8123(3)	2933(2)	532(3)	43(1)
C(12)	8482(4)	2352(2)	1376(3)	52(1)
C(13)	9433(4)	1869(2)	1434(4)	62(1)
C(14)	10047(4)	1964(2)	664(4)	64(1)
C(15)	9683(4)	2528(2)	-183(4)	61(1)
C(16)	8734(4)	3005(2)	-232(3)	49(1)
C(17)	8898(4)	4334(2)	1868(3)	47(1)
C(18)	10097(4)	4044(2)	2608(4)	59(1)
C(19)	11219(4)	4367(3)	2692(4)	70(1)
C(20)	11155(5)	4997(3)	2032(4)	74(1)
C(21)	9967(5)	5288(2)	1287(4)	71(1)
C(22)	8856(4)	4967(2)	1209(4)	57(1)
C(23)	6848(4)	4604(2)	3241(3)	55(1)
C(24)	8249(4)	4857(2)	4014(4)	78(1)
C(25)	5957(5)	5223(2)	3263(4)	92(2)
C(26)	6600(4)	3924(2)	3849(4)	74(1)

Crystal structure determination of 3d

All X-ray investigations were performed on an automated four-circle diffractometer CAD4-T (ENRAF-NONIUS, Delft) with graphite-monochromated MoK α radiation at room temperature. A colorless single crystal of approximate dimensions $0.25 \times 0.20 \times 0.07$ mm was mounted on a glass fibre. The lattice parameters were determined by refinement of the diffraction geometry of 100 precisely centered high-angle reflections. Intensity

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Table IV. Selected bond lengths [pm] and angles $[^{\circ}]$ for **3d**.

O(1) - C(1)	122.7(4)	O(2) - C(4)	144.2(4)
C(1) - C(2)	148.5(5)	C(1) - C(6)	151.7(5)
C(2) - C(3)	132.8(5)	C(2) - C(7)	152.4(5)
C(3) - C(4)	149.5(5)	C(4) - C(5)	156.6(4)
C(4) - C(11)	152.0(5)	C(5) - C(6)	154.8(4)
C(5)-C(17)	151.9(5)	C(6)-C(23)	157.3(5)
O(1)-C(1)-C(2)	120.1(4)	O(1)-C(1)-C(6)	120.3(3)
O(2)-C(4)-C(3)	108.9(3)	O(2)-C(4)-C(5)	111.9(3)
O(2)-C(4)-C(11)	105.6(3)	C(1)-C(2)-C(3)	114.4(4)
C(1)-C(2)-C(7)	122.2(4)	C(1)-C(6)-C(5)	113.5(3)
C(2)-C(1)-C(6)	119.6(3)	C(2)-C(3)-C(4)	124.5(4)
C(3)-C(2)-C(7)	122.5(4)	C(3)-C(4)-C(5)	108.9(3)
C(3)-C(4)-C(11)	110.9(3)	C(5)-C(4)-C(11)	110.5(3)
C(6)-C(5)-C(4)	111.7(3)		

data were collected with θ/ω scan. During the exposure time of 56 h no significant loss of intensity was observed.

The structure was solved by direct methods, which revealed the positions of all non-H atoms. The refinement with unique merged data, reflections with $F > 4 \sigma(F)$ and isotropic displacement factors led to an *R*-value of *R*1 = 0.122. The final least squares refinement (on F²) with anisotropic displacement parameters for all non-H atoms, positions of the H atoms as riding model with SHELXL-93 defaults, converged to *R* values of *R*1 = 0.047 and *wR*2 = 0.1046.

Calculations were performed with the programs CAD-SHEL [21], SIR92 [22], SHELXL-93 [23], SHELXTL-PLUS package [24] and PLATON-94 [15]. A summary of the crystal data, data-collection and structure-refinement parameters is given in Table II. Final atomic coordinates are listed in Table III, selected bond distances and angles in Table IV. A graphic representation of the molecule is given in Fig. 1, the shape of the six-membered cyclohexene ring in Fig. 2. In Fig. 3 the intermolecular H-bridges are shown [25].

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