✾ Formation and structures of 2,5-di-*tert*-butylcyclopentadienone dimers

G. A. Abakumov, N. N. Vavilina, L. N. Zakharov, Yu. A. Kurskii, V. I. Nevodchikov, and A. S. Shavyrin*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 12 7497. E-mail: kursk@imoc.sinn.ru

The structures of dimers formed from 2,5-di-*tert*-butylcyclopentadienone in the reaction with alkaline metals and in the Diels—Alder reaction were studied. A photochemical rearrangement with ring contraction was found for the second dimer. Spectral features of the dimers related to steric hindrance were studied by 1D and 2D NMR procedures.

Key words: 2,5-di-*tert*-butylcyclopentadienone, Diels—Alder reaction, tricyclo[5.2.1.$0^{2,6}$]decane, tricyclo[5.3.0.$0^{2,6}$]decane, dynamic NMR, 2D NMR procedures, X-ray diffraction analysis.

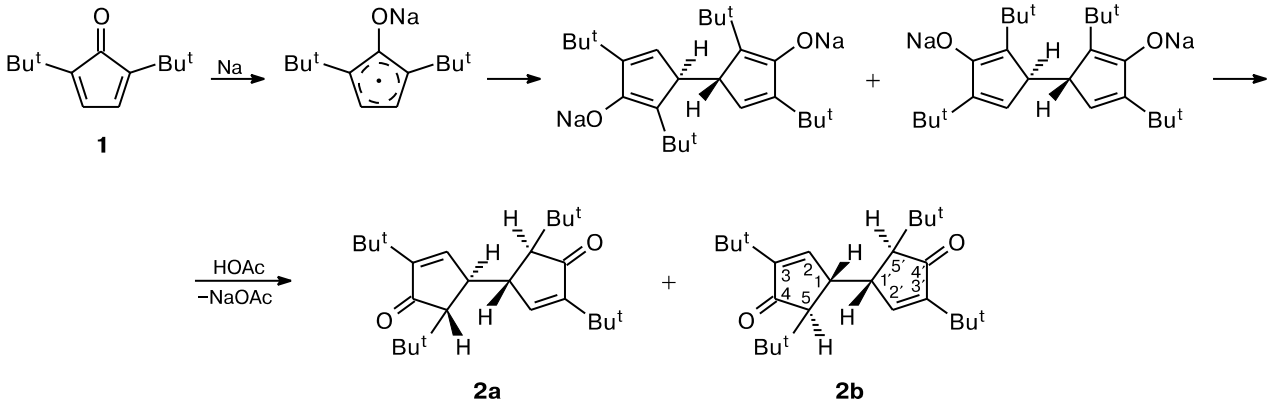
2,5-Di-*tert*-butylcyclopentadienone (**1**) is genetically related to 3,6-di-*tert*-butyl-*o*-benzoquinone and can be obtained photochemically from the latter.[1] An interest in cyclopentadiene derivatives is evoked by their wide use both as ligands for organometallic compounds and in reactions of fine organic synthesis. Therefore, the purpose of this work is to study the influence of steric shielding in compound **1** on the specific features of the structure of its dimers.

The reaction of compound **1** with alkaline metals can be considered as a model one for the synthesis of organometallic compounds of transition metals.[2] The products of the reaction of compound **1** with Na or K were studied after acidic hydrolysis of the reaction mixture. The reaction with alkaline metals affords radicals further recombining at positions 3 that are not occupied by bulky substituents (Scheme 1).

The product of radical dimerization is a mixture of *R*,*S*- and *R*,*R*- (or *S*,*S*-) diastereomers. Dienol formed after acidic hydrolysis isomerizes to 3,3′,5,5′-tetra-*tert*-butyl-1,1′-bi(cyclopent-2-en-1-yl)-4,4′-dione (**2**). The tautomeric transformation of the enol into ketone **2** is stereospecific due to the bulky substituents. The chiral sites in the 1,1′-positions specify the configuration of compound **2** formed.

The structure of compound **2** was established by NMR methods. The vicinal spin-spin coupling (SSC) constant between the HC(1)—HC(5) protons calculated by the Karplus[3] equation should be higher than 7.0 Hz for the synperiplanar position (dihedral angle $\theta = 0—20°$) and than 0.9—2.2 Hz for the anticlinal position ($\theta = 110—120°$). The experimental value of 0.9 Hz indicates the anticlinal arrangement of 1,5-protons and, hence, the *tert*-butyl groups in the 5,5′-positions toward the substituted five-membered rings in the 1,1′-positions. The ^{13}C NMR spectrum exhibits doubling of signals from C(2,2′) and C(5,5′) related to the presence of diastereomers **2a** and **2b**. The content of one of the diastereomers

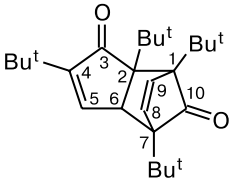
Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2179—2183, October, 2004.

(and its enantiomer) is 55%, and the content of another diastereomer is 45%.

In solution at room temperature, compound **1** dimerizes slowly in the Diels—Alder reaction to form 1,2,4,7-tetra-*tert*-butylcyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione (**3**). Owing to the shielding effect of the *tert*-butyl groups, compound **1** is much more stable than unsubstituted cyclopentadienone dimerizing to tricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3,10-dione already at the moment of its synthesis.[4]



3

The NMR spectra of compound **3** are of special interest. Signals of the *tert*-butyl groups in this compound are more complicated than it was expected. The ^{1}H NMR spectrum contained two singlets with an intensity of 9 H each (δ 1.13 and 1.15), three singlets (δ 0.75, 1.07, and 1.38) with an intensity of 3 H each, and a strongly broadened signal (width at least 40 Hz) at 0.7—1.5 ppm. Evidently, steric hindrance in compound **3** decreases the rotation rate of one of the *tert*-butyl groups to such an extent that the methyl groups become nonequivalent. This effect is well known in dynamic NMR spectroscopy but is very rare for a *tert*-butyl group at room temperature. In the case of the hindered chemical or positional exchange in NMR spectra, several steps can be distinguished depending on the rate of the exchange process.[5] For a slow exchange, exchanging nuclei (in our case, methyl protons of the *tert*-butyl groups) appear as particular peaks. A coalescence point, in which exchanging signals coalesce to form one broadened peak, appears in the region of an intermediate exchange rate. For a fast exchange, the width of a single peak decreases.

The spatial structure of compound **3** was studied by 2D NOESY NMR spectroscopy (Fig. 1). The nuclear polarization transfer observed in the NOESY spectrum can occur due to both the nuclear Overhauser effect (NOE) between nuclei closely arranged in the space and exchange processes (exchange EXSY spectroscopy). These two directions can easily be distinguished, because NOE cross peaks are in the counter phase toward diagonal peaks and exchange cross peaks.[6] For the C(6)H proton (δ 3.25), the NOE cross peaks with the *tert*-butyl group C(7)CMe_3 (δ 1.15) and three methyl groups C(2)CMe_3 (δ 0.75, 1.07, and 1.38) are observed. Therefore, compound **3** has an *endo*-configuration.

Exchange cross peaks are observed between three methyl groups C(2)CMe_3 (see Fig. 1). The intensity of the exchange cross peaks in the EXSY or NOESY spectrum depends on an exchange rate constant k and a mixing time τ_m, during which the polarization transfer occurs. A series of EXSY experiments with different τ_m makes it possible to determine the exchange rate constant.[6] Under

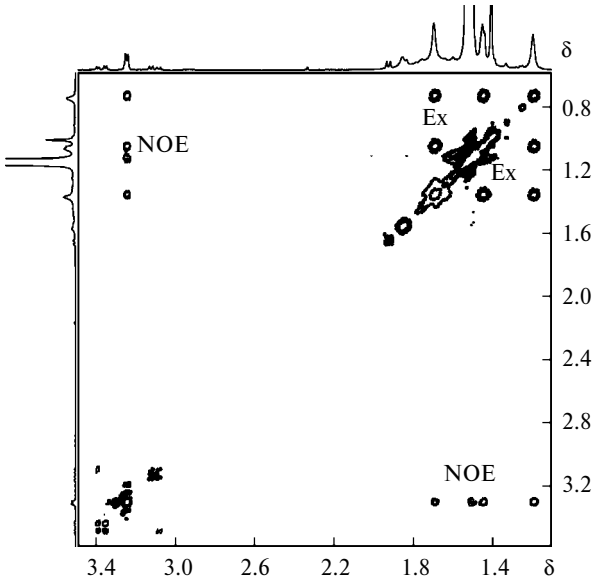


Fig. 1. Fragment of the correlation ^{1}H-^{1}H 2D (NOESY) NMR spectrum of compound **3**. NOE and exchange cross peaks are marked on the spectrum.

the condition that the exchange rate exceeds considerably the rate of intramolecular dipole-dipole relaxation, the ratio of intensities of the nondiagonal exchange peak a_{ij} in the EXSY spectrum to the diagonal peak a_{ii} can be expressed as follows[7]:

$$a_{ij}/a_{ii} = (1 - \exp(-k\tau_m))/(1 + \exp(-k\tau_m)), \quad (1)$$

An analysis of the experimental data (Table 1) by Eq. (1) gives for the exchange rate constant at room temperature $k = 7.6\ s^{-1}$.

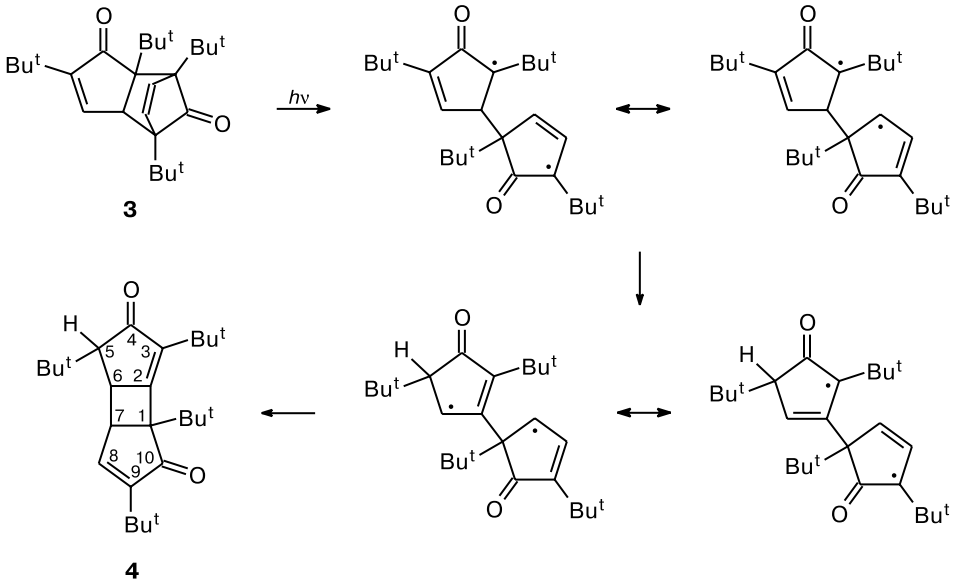
An alternative estimation of the rate constants of three-position exchange from the line widths of the methyl groups using the WinDNMR program gives for C(1)Bu^t $k \approx 100\ s^{-1}$, and for C(2)Bu^t $k = 6—8\ s^{-1}$.

In compound **3**, the C(2)Bu^t group rotates slowly in the NMR scale, C(1)Bu^t rotates with an intermediate

Table 1. Dependence of the ratio of intensities of the nondiagonal EXSY peaks (a) to the diagonal peak a_{ii} (0.75 ppm) on the time of mixing (τ_m)

$\tau_m \cdot 10^3$/s	$a(i; \delta') \cdot 100/a_{ii}$	
	$\delta' = 1.07$	$\delta' = 1.38$
10	2.8	3.0
20	6.6	6.3
35	11.7	11.5
75	26.4	26.1
125	44.6	44.5
150	52.8	52.6

Scheme 2



rate, and C(4)Bu^t and C(7)Bu^t rotate rapidly. It should be mentioned that in isostructural compound **3**, 1,2,4,7-*tetra*-(trimethylsilyl)tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione, according to the ^{1}H and ^{13}C NMR data, all trimethylsilyl groups rotate rapidly.[8] Therefore, steric strain is created by the added methyl groups rather than by the C or Si atoms in the 1,2-positions of the substituents. Since silicon atoms are larger than carbon atoms, the methyl groups are remote from the tricyclic framework, and the rotation of the trimethylsilyl groups becomes free.

Dimer **3** in solution is stable only in the dark, whereas in the light it undergoes photochemical isomerization. For example, more than 15% of compound **3** isomerize in a $CDCl_3$ solution in sunlight for 3 h. Due to a strong steric strain appeared for the fixed *gauche* arrangement of the *tert*-butyl groups in positions 1 and 2 of compound **3**, the C(1)—C(2) bond cleaves easily to form a primary biradical in which only one of the unpaired electrons is delocalized in the five-membered ring. The second unpaired electron is stabilized due to the delocalization over the second ring only after the prototropic rearrangement (Scheme 2). The recombination of the secondary biradical produces 1,3,5,9-tetra-*tert*-butyltricyclo[5.3.0.0^{2,6}]deca-2,8-diene-4,10-dione (**4**), which has no steric strain due to the absence of closely arranged *tert*-butyl groups.

For unsubstituted and perchlorosubstituted dimers of cyclopentadienone with the tricyclo[5.3.0.0^{2,6}]decane framework, photochemically induced transformations passing through biradical states of four-membered into six-membered rings for the unsubstituted[9] isomers and into eight-membered rings for the chlorosubstituted[10] isomers are described. In our case, steric strain inverts completely the direction of the photochemical reaction: the four-membered ring in compound **4** is more stable than the sterically hindered six-membered ring in compound **3**. Compound **4** is stable to both the visible light and UV irradiation ($\lambda < 380$ nm).

The structure of compound **4** was proved by NMR spectroscopy and X-ray diffraction analysis. According to the X-ray data (Fig. 2, Table 2), compound **4** has a *syn*-configuration. The ^{13}C and ^{1}H NMR spectra contained signals of four *tert*-butyl groups and a chain of mutually interacting protons HC(5)—HC(6)—HC(7)—HC(8). The high vicinal SSC constant (9.9 Hz) between the HC(6)—HC(7) protons indicates their synperiplanar arrangement.

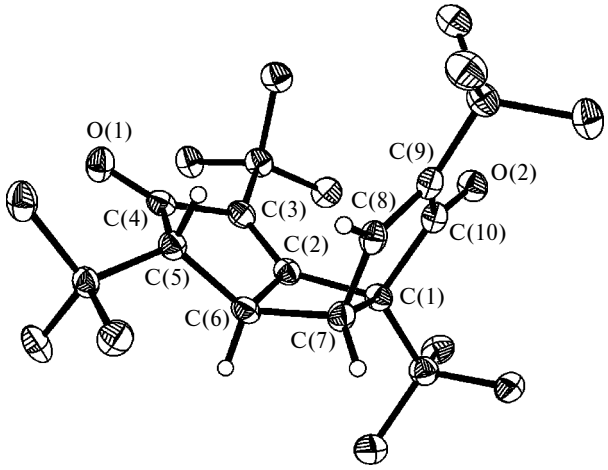


Fig. 2. General view of molecule **4**. Hydrogen atoms are shown only at cyclic moieties.

Table 2. Main bond lengths (*d*) and bond angles (ω) in compound **4**

Bond	*d*/Å	Angle	ω/deg
C(1)—C(10)	1.536(4)	C(2)—C(1)—C(10)	110.3(2)
C(1)—C(2)	1.557(4)	C(2)—C(1)—C(7)	85.7(2)
C(1)—C(7)	1.568(4)	C(7)—C(1)—C(10)	103.1(2)
C(2)—C(3)	1.344(4)	C(1)—C(2)—C(3)	145.3(3)
C(2)—C(6)	1.495(4)	C(1)—C(2)—C(6)	93.2(2)
C(3)—C(4)	1.517(4)	C(6)—C(2)—C(3)	114.2(2)
C(4)—O(1)	1.209(3)	C(2)—C(3)—C(4)	105.6(2)
C(4)—C(5)	1.546(4)	C(3)—C(4)—C(5)	107.9(2)
C(5)—C(6)	1.518(4)	C(4)—C(5)—C(6)	101.2(2)
C(6)—C(7)	1.569(4)	C(2)—C(6)—C(7)	87.8(2)
C(7)—C(8)	1.486(4)	C(5)—C(6)—C(7)	126.1(2)
C(8)—C(9)	1.345(4)	C(6)—C(7)—C(8)	116.8(2)
C(9)—C(10)	1.478(4)	C(1)—C(7)—C(8)	104.7(2)
C(10)—O(2)	1.215(3)	C(7)—C(8)—C(9)	113.9(3)
		C(8)—C(9)—C(10)	109.0(2)
		C(9)—C(10)—C(1)	108.9(2)

Thus, the *tert*-butyl substituents in compound **1** determine both the direction of radical dimerization of the sodium derivative and the properties of its Diels—Alder dimer **3**. Compound **3** is photochemically unstable due to the repulsion of the closely arranged bulky substituents.

Experimental

1D and 2D NMR spectra were recorded on a Bruker Avance DPX-200 instrument with working frequencies of 200 and 50 MHz for ^{1}H and ^{13}C, respectively. The following 2D NMR experiments were carried out: COSY (COSY45) — proton-proton correlation due to the spin-spin coupling; NOESY and EXSY — proton-proton correlation due to the dipole-dipole and exchange interactions; XHCORR carbon-proton correlation due to the spin-spin coupling between adjacent nuclei. The XwinNMR 2.1 program was used for processing. The time of mixing in NOESY experiments was 250 ms when stereochemistry of the products was studied and 10—150 ms for studying exchange processes (EXSY). An X-ray diffraction experiment was carried out on a Bruker Smart 1000 diffractometer at 110 K (graphite monochromator, λMo-Kα radiation). IR spectra were recorded on a Perkin Elmer 577 instrument in Nujol.

2,5-Di-*tert*-butylcyclopentadienone (1) was synthesized by a known procedure.[1] ^{1}H NMR ($CDCl_3$), δ: 1.13 (s, 18 H, CMe_3); 6.40 (s, 2 H, CpH). ^{13}C NMR ($CDCl_3$), δ: 29.1 ($C\underline{Me}_3$); 31.6 ($\underline{C}Me_3$); 135.5 (C(3)H and C(4)H); 140.3 (C(2) and C(5)); 202.6 (C=O).

3,3′,5,5′-Tetra-*tert*-butyl-1,1′-bis(cyclopent-2-en-1-yl)-4,4′-dione (2). ***A.*** Metallic Na (0.5 g) was added to a solution of compound **1** (0.38 g, 2 mmol) in 95% EtOH (60 mL) until the solution became colorless, then AcOH (10 mL) was added, and the solution was stirred and diluted with a large volume of water (~150 mL). A white precipitate that formed was filtered off, washed with water, and dried. After recrystallization from hexane, dimer **2** (0.27 g, 73%) was obtained.

B. Compound **1** (0.19 g, 1 mmol) in THF (30 mL) and metallic K (0.4 g) were placed in an evacuated ampule. The ampule was shaken until the yellow color of the solution disappeared. After K was separated, AcOH (5 mL) was added, and the mixture was poured into water. A white precipitate that formed was separated and washed. After recrystallization from hexane, product **2** was obtained in 75% yield (0.14 g), m.p. 215—216 °C. Found (%): C, 80.96; H, 10.72. $C_{26}H_{42}O_2$. Calculated (%): C, 80.77; H, 10.95. IR (Nujol), ν/cm^{-1}: 1670 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.98 (s, 18 H, C(5)—CMe_3); 1.11 (s, 18 H, C(3)CMe_3); 1.87 (d, 2 H, C(5)H, J = 0.9 Hz); 2.84 (m, 2 H, C(1)H); 6.87 (d, 2 H, C(2)H, J = 2.13 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.6 (C(5)—C($\underline{C}H_3)_3$); 28.2 (C(3)C$\underline{Me}_3$); 32.0, 34.2 (both $\underline{C}Me_3$); 44.6 (C(1)H); 59.7 (C(5)H); 153.8 (C(2)H); 155.6 (C(3)); 208.8 (C(4)=O). For the signals at 59.7 and 153.8 ppm in the ^{13}C NMR spectrum, doubling is observed, and the difference in chemical shifts is 0.043 and 0.036 ppm, respectively. The ratio of intensities for the doubled signals is approximately 45 : 55. The assignment was performed using the CHCORR and COSY spectra.

1,2,4,7-Tetra-*tert*-butyltricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3,10-dione (3). Compound **1** (0.29 g, 1.5 mmol) was dissolved in hexane (50 mL), and the solution was left for 3 days in the dark at room temperature (~20 °C). The solution turned its color from yellow to colorless. On cooling to −10 °C, white crystals of dimer **3** precipitated, m.p. 88—92 °C (with decomp.). The product was obtained in 53% yield (0.31 g). Found (%): C, 81.30; H, 10.10. $C_{26}H_{40}O_2$. Calculated (%): C, 81.20; H, 10.48. IR (Nujol), ν/cm^{-1}: 1660, 1750 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.75, 1.07, and 1.38 (all s, 3 H each, C(2)$\underline{Me}CMe_2$); 1.13 (s, 9 H, C(4)CMe_3); 1.10 (br.s, C(1)CMe_3); 1.15 (s, 9 H, C(7)CMe_3); 3.25 (d, 1 H, C(6)H, J = 3.0 Hz); 5.86 (d, 1 H, C(8)H, J = 7.0 Hz); 6.14 (d, 1 H, C(9)H, J = 7.0 Hz); 6.88 (d, 1 H, C(5)H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 26.7 (C(2)$\underline{Me}CMe_2$); 27.1 (C(7)C$\underline{Me}_3$); 28.3 (C(4)C$\underline{Me}_3$); 31.0, 32.5, 33.3, and 35.7 (all $\underline{C}Me_3$); 34.4 (C(2)—($C\underline{H}_3$)CMe_2); 48.1 (C(6)H); 62.7, 66.6, 66.9 (C(1),C(7),C(2)); 129.5 (C(8)H); 135.9 (C(9)H); 151.3 (C(5)H); 160.7 (C(4)); 206.0, 206.4 (C(3)=O, C(10)=O). The lines in the proton and carbon spectra were assigned using the DEPT, CHCORR, COSY, and NOESY procedures.

1,3,5,9-Tetra-*tert*-butyltricyclo[5.3.0.0^{2,6}]deca-2,8-diene-4,10-dione (4). Compound **3** (0.77 g, 2 mmol) was dissolved in hexane (50 mL), and the mixture was left at ~20 °C in the light for 10 days. Then the mixture was cooled to −15 °C. Large colorless crystals of compound **4** with m.p. 140—142 °C crystallized gradually in cold. The yield was 0.15 g (25%). Found (%): C, 81.24; H, 10.43. $C_{26}H_{40}O_2$. Calculated (%): C, 81.20; H, 10.48. IR (Nujol), ν/cm^{-1}: 1670 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.02, 1.15 (both s, 9 H each, CMe_3); 1.18 (both s, 18 H, CMe_3); 1.66 (d, 1 H, C(5)H, J = 4.3 Hz); 3.14 (dd, 1 H, C(6)H, J = 9.9 Hz, J = 4.3 Hz); 3.47 (dd, 1 H, C(7)H, J = 9.9 Hz, J = 3.0 Hz); 6.89 (d, 1 H, C(8)H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.3, 27.8, 28.5, and 29.1 ($C\underline{Me}_3$); 31.9, 32.6, 32.9, and 34.6 (all $\underline{C}Me_3$); 43.9 (C(7)H); 46.6 (C(6)H); 65.4 (C(5)H); 146.7 (C(8)H); 151.9, 159.8 (C(3), C(9)); 168.6 (C(2)); 203.9 (C(4)=O); 208.1 (C(10)=O).

X-ray study of compound 4. The crystals are orthorhombic, a = 19.438(4) Å, b = 43.749(10) Å, c = 11.232(3) Å, α = β = γ = 90°, V = 9551(4) Å^3, Z = 16, D_c = 1.070 mg m^{-3}, μ = 0.065 mm^{-1}, space group of symmetry *Fdd*2. The total number of measured reflections was 14301, of which 5083 (R_{int} = 0.0546) were independent reflections, R_1 = 0.0582, wR_2 = 0.1136 for $I > 2\sigma(I)$. Absorption was applied by the SADABS program.[11]

The structure of compound **4** was solved by the direct methods and calculation of subsequent electron density syntheses and refined by the full-matrix least-squares method. All nonhydrogen atoms were refined with anisotropic thermal parameters. Positions of H atoms were found by the difference electron density synthesis and refined in the isotropic approximation. Calculations on the determination and refinement of the crystal structure were performed using the SHELXTL program package.[12]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-33065) and the Foundation of the President of the Russian Federation (Program "Leading Scientific Schools of Russia," Grant NSh-1649.2003.3).

References

1. V. B. Vol´eva, V. V. Ershov, I. S. Belostotskaya, and N. L. Komissarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 739 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23** (Engl. Transl.)].
2. I. L. Fedyushkin, V. I. Nevodchikov, M. N. Bochkarev, S. Dechert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 145 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 154].
3. M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870.
4. *Comprehensive Organic Chemistry*, Ed. D. Barton and W. D. Ollis, Vol. **1**, *Oxygen Compounds*, Ed. J. F. Stoddart, Pergamon Press, Oxford, 1979.
5. H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, **21**, 1688.
6. S. Braun, H. Kalinovski, and S. Berger, *100 and More NMR Experiments*, Weinheim, VCH, 1996, 210 pp.
7. J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
8. F. Hong, J. Wu, Y. Huang, H. Gau, and C. Lin, *J. Organomet. Chem.*, 1999, **580**, 98.
9. P. E. Eaton and T. W. Cole, *J. Chem. Soc., Chem. Commun.*, 1970, 1493; P. E. Eaton and S. A. Cerefice, *J. Chem. Soc., Chem. Commun.*, 1970, 1494.
10. A. Padwa, J. Masaracchia, and V. Mark, *Tetrahedron Lett.*, 1971, 3161; P. E. Eaton, D. Tang, and R. Gilardi, *Tetrahedron Lett.*, 2002, 3.
11. G. M. Sheldrick, *SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS*, Madison, Wisconsin, USA, 1998.
12. G. Sheldrick, *Bruker XRD*, Madison, WI.

Received January 19, 2004;
in revised form June 15, 2004