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Structure of the organometallic radical, di-t-butylbenzoquinonetricarbonyltriphenylphosphinerhenium, $DTBQ^{\cdot}$-$Re(CO)_3PPh_3$

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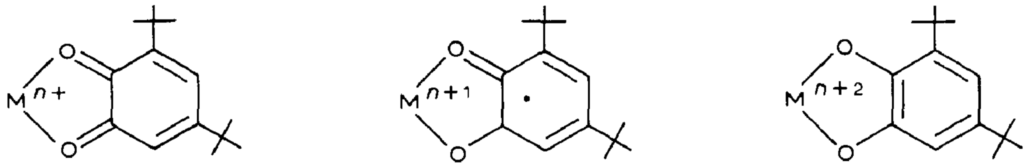
Abstract

The compound $DTBQ^{\cdot}$-$Re(CO)_3PPh_3$, was prepared by photochemical reaction of DTBQ with $Re_2(CO)_{10}$, followed by triphenylphosphine substitution. The structure of the deep-blue crystal has been established by X-ray diffraction studies at room temperature (monoclinic, space group $P2_1/n$, $Z = 4$, a 13.191(4) Å, b 17.856(3) Å, c 14.082(5) Å, β 98.55(3)°, $R = 0.032$ for 4680 independent reflections, $2\theta \leq 50°$). Judging from the DTBQ C–O bond length of 1.297 Å, the X-ray data indicate that DTBQ coordinates to Re as a semiquinone, with electron transfer from rhenium to the $\pi^{\star}$ orbital of DTBQ.

Introduction

In general, organometallic radical species are very reactive and their presence in chemical reactions can then only be inferred from kinetic data [1–5]. However, spin trapping by nitroso compounds or nitrones is also a well-known and useful technique in identifying the nature of organometallic radicals involved in chemical transformations. Recently, α,β-diketones have also proved to be potent spin trapping reagents, especially *o*-benzoquinone and its derivatives [6–10].

o-Benzoquinones are non-innocent ligands. They can coordinate to transition metal ions as quinone, semiquinone, or catechol [11]. When 3,5-di-t-butyl-*o*-benzoquinone (DTBQ) is taken as an example, three types of bonding (including possible resonance hybrids) can be assigned to the complex. EPR spectroscopy, if appli-



cable, may furnish information on which bonding mode is the most favorable, but only an X-ray structure determination guarantees unambiguous assignment for the species in the solid state.

The photochemical reaction between $Re_2(CO)_{10}$ and DTBQ resulted in a spin-trapped radical DTBQ$^{\cdot}$-$Re(CO)_4$. Its EPR spectra both in solution and frozen solution seem to indicate that the unpaired electron is largely localized on the organic part. As with other organometallic radical species [9,10], the carbonyl substitution reaction of DTBQ$^{\cdot}$-$Re(CO)_4$ is also facile. To shed light on the nature of the α-β-diketone-trapped radical, we report here on the structure of DTBQ$^{\cdot}$-$Re(CO)_3PPh_3$ and will add to the short list [12–15] of structurally known organometallic radicals.

Experimental

Dirhenium decacarbonyl was purchased from Strem Chemical Co. and was used without further purification. Di-t-butylbenzoquinone (DTBQ) and triphenylphosphine were purchased from Aldrich Chemical Co. and were used directly. Solvent dichloromethane and n-hexane were dried by standard procedures.

Table 1

Summary of crystal data and intensity collection

Empirical formula	$C_{35}H_{35}O_5PRe$
Color; habit	deep blue chunk
Size	$0.40 \times 0.33 \times 0.28$ mm
Space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a 13.191(4) Å
	b 17.856(3) Å
	c 14.082(5) Å
	β 98.55(3)°
Volume	3280(2) $Å^3$
Molecules/cell	4
Molecular weight	752.87 AMU
Density (calc.)	1.52 g/cm^3
Radiation	Mo-K_α (λ 0.71073 Å)
Diffractometer used	Nicolet R3/V
Temperature	23° C
Monochromator	Highly oriented graphite crystal
2θ range	2.5 to 50.0°
Scan type	$\theta/2\theta$
Scan speed	Variable; 2.09 to 14.95°/min
Standard reflections	3 measured every 50 reflections
Reflections collected	6712 (5807 of which had $I > 3\sigma(I)$)
No. of independent reflections	4680
Absorption coefficient	38.39 cm^{-1}
Min./max. transmission	0.745
Final residuals	R 3.20%
	R_w 2.56%
Goodness-of-fit	1.32
Largest Δ/σ	0.042
Data-to-parameter ratio	11.3/1
Largest difference peak	0.72 $e^-/Å^3$

Preparation of crystals: DTBQ (20 mg, 9.0×10^{-2} mM) and 29 mg $Re_2(CO)_{10}$ (4.5×10^{-2} mM) were dissolved in 10 ml CH_2Cl_2. The solution was thoroughly degassed and was irradiated with an 180 W medium pressure mercury lamp for 1.5 h, then 24 mg of PPh_3 (9.0×10^{-2} mM) was added to the dark-red solution, and the solution rapidly turned blue. It was left to stand for 30 min to allow the reaction to go to completion. Separation was by flash chromatography on Merck 60H silica with the mixed solvent CH_2Cl_2/n-C_6H_{14} (1/1) as eluent. The blue, pure DTBQ$^{\cdot}$-$Re(CO)_3PPh_3$ was obtained in 75% yield. IR (ν(C≡O): 2009(s), 1938(s), 1908(s). EPR (x-band): a_P 25.15 G; a_{Re} 39.00 G; $g = 1.995$. Single crystals were obtained by slow evaporation of the mixed solvent.

X-ray diffraction study. A crystal and molecular structure determination of the title compound was carried out. Crystal data and details of the intensity collection are summarized in Table 1. Unit cell dimensions were determined by least-squares refinement of the angular positions of fourteen independent reflections (2θ ranging from 7.52° to 21.04°). The intensities were corrected for Lorentz and polarization effects. Seven reflections with 2θ angles ranging from 7.50° to 41.0° and their χ angles near 90° were scanned in 10° steps of ϕ, and the crystal showed transmission factors varying from 0.651 to 0.874, thus, empirical corrections were made for absorption.

The space group $P2_1/n$ was determined from the systematic absences: $0k0$, $k = 2n + 1$; $h0l = 2n + 1$. The heavy atom position was determined by direct methods. The non-hydrogen atoms were subsequently located from a Fourier map and then anisotropically refined by full matrix least squares. The positions of all hydrogen atoms were calculated and refined isotropically. A final difference map showed no other features with electron densities of less than 0.72 e$^-$/Å^3 near the Re atom position. All calculations were performed on a MicroVAX II based on the Nicolet SHELXTL PLUS systems.

Results and discussion

The photochemical reaction between $Re_2(CO)_{10}$ and di-t-butyl-*o*-benzoquinone in benzene resulted in a red solution which contains the organometallic radical:

$$Re_2(CO)_{10} + DTBQ \xrightarrow[\text{benzene}]{h\nu} DTBQ^{\cdot}\text{-}Re(CO)_4$$

When PPh_3 is added to the red solution, a substitution reaction occurs rapidly and the solution turns blue:

$$DTBQ^{\cdot}\text{-}Re(CO)_4 + PPh_3 \rightarrow DBTQ^{\cdot}\text{-}Re(CO)_3(PPh_3) + CO$$

When separated by flash chromatography, a pure solution of the radical is obtained. A blue crystal of DTBQ$^{\cdot}$-$Re(CO)_3PPh_3$ was obtained by slow evaporation of a CH_2Cl_2/hexane (1/1) solution.

The molecular structure and atomic labeling of DTBQ$^{\cdot}$-$Re(CO)_3PPh_3$ is depicted in Fig. 1. It is clear from the ORTEP drawings that Re is octahedrally coordinated by three carbonyls, one PPh_3, and DTBQ which binds to Re with the two carbonyl oxygens. The three carbonyls are at facial positions. The bond lengths and bond angles are listed in Tables 2 and 3, respectively.

The Re–P distance of 2.496 Å is significantly longer than those reported, for example: 2.40(1) Å in $H_3Re_3(CO)_9(PPh_3)_3$ [16]; 2.42(1) Å in $H_3Re_3(CO)_{11}(PPh_3)$

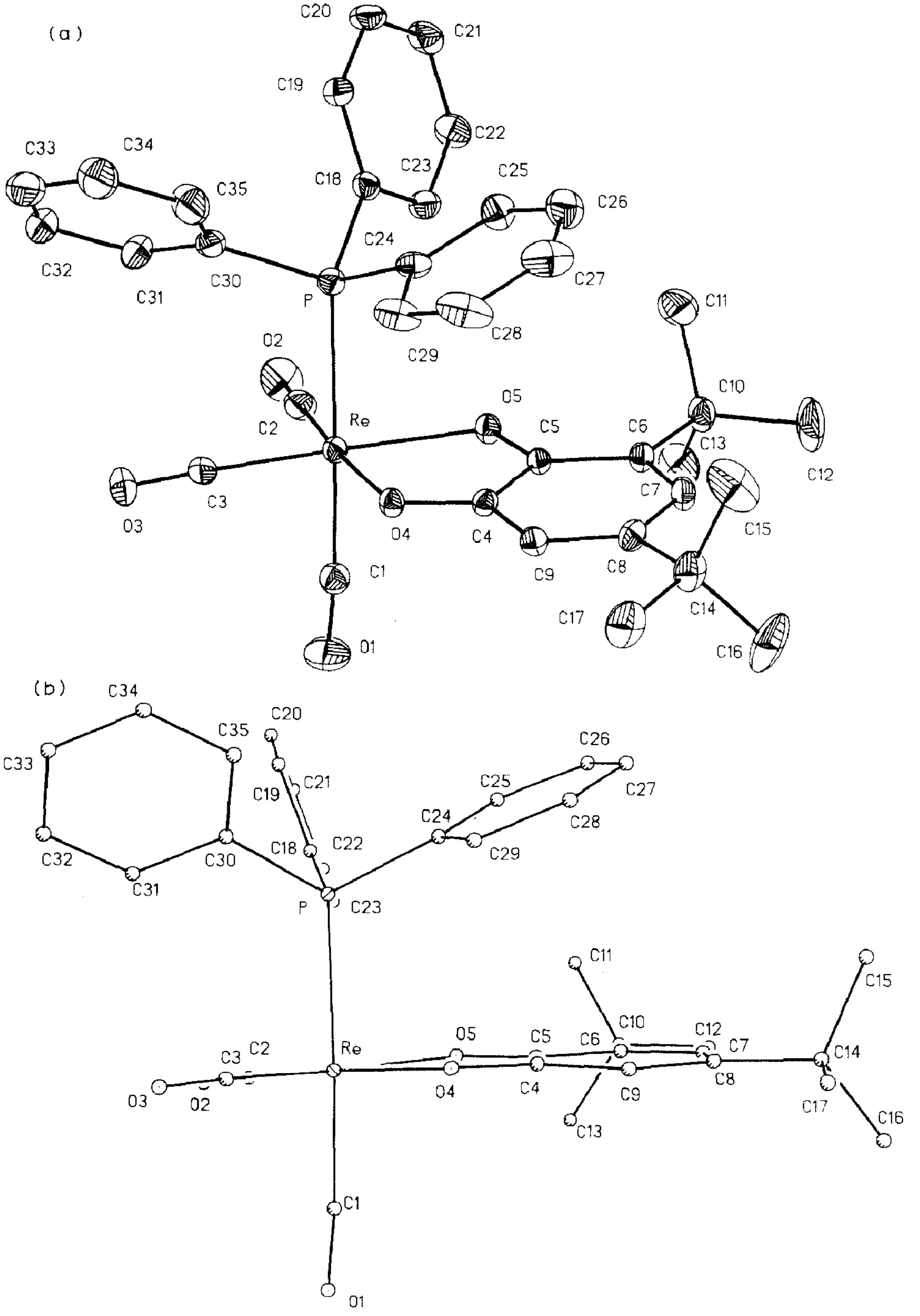


Fig. 1. DTBQ-Re(CO)$_3$PPh$_3$ ORTEP drawing viewed from two different angles.

[17]; 2.457 Å and 2.449 Å in Re$_2$(CO)$_6$(μ-H)$_2$(μ-dppm) [18]. This lengthening of Re–P distance by 0.1 Å can be attributed to the weak back-donation because of the *trans*-CO. There is much evidence to support this. For example, Re–C(ax) and Re–C(eq) difference in H$_3$Re$_3$(CO)$_9$(PPh$_3$)$_3$ is 0.08 Å. ReCl(dppe)$_2$ [19], which

Table 2

Bond lengths (Å)

Re–P	2.495(1)	Re–O(4)	2.129(3)
Re–O(5)	2.135(3)	Re–C(1)	1.937(6)
Re–C(2)	1.906(5)	Re–C(3)	1.899(5)
P–C(18)	1.826(5)	P–C(24)	1.819(5)
P–C(30)	1.834(5)	O(1)–C(1)	1.149(6)
O(2)–C(2)	1.149(6)	O(3)–C(3)	1.151(6)
O(4)–C(4)	1.293(5)	O(5)–C(5)	1.301(5)
C(4)–C(5)	1.453(6)	C(4)–C(9)	1.417(6)
C(5)–C(6)	1.418(6)	C(6)–C(7)	1.377(6)
C(6)–C(10)	1.530(7)	C(7)–C(8)	1.409(7)
C(8)–C(9)	1.365(6)	C(8)–C(14)	1.531(6)
C(10)–C(11)	1.523(8)	C(10)–C(12)	1.538(8)
C(10)–C(13)	1.521(8)	C(14)–C(15)	1.510(9)
C(14)–C(16)	1.549(9)	C(14)–C(17)	1.525(8)
C(18)–C(19)	1.393(7)	C(18)–C(23)	1.391(7)
C(19)–C(20)	1.389(7)	C(20)–C(21)	1.387(8)
C(21)–C(22)	1.379(8)	C(22)–C(23)	1.378(7)
C(24)–C(25)	1.385(7)	C(24)–C(29)	1.388(7)
C(25)–C(26)	1.383(7)	C(26)–C(27)	1.381(9)
C(27)–C(28)	1.360(10)	C(28)–C(29)	1.382(8)
C(30)–C(31)	1.384(8)	C(30)–C(35)	1.370(8)
C(31)–C(32)	1.398(8)	C(32)–C(33)	1.397(12)
C(33)–C(34)	1.353(12)	C(34)–C(35)	1.371(9)

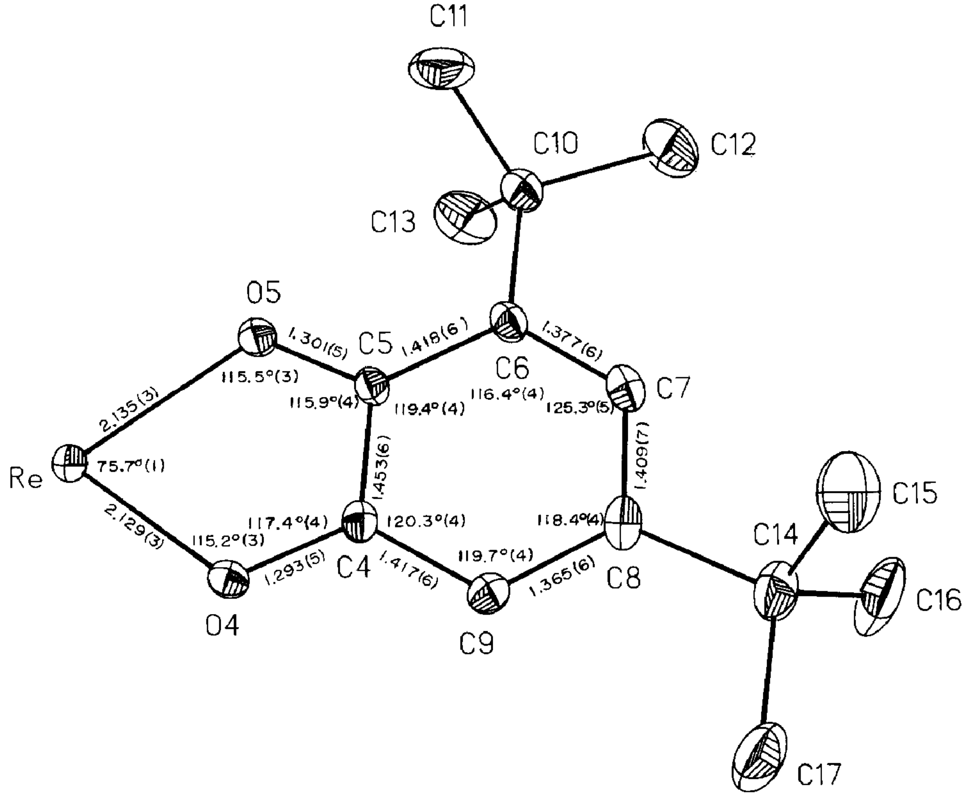


Fig. 2. Bond angles and lengths of atoms in the plane of DTBQ and Re metal atom.

Table 3

Bond angles (°)

O(4)–Re–P	91.4(1)	O(5)–Re–P	85.4(1)
O(5)–Re–O(4)	75.7(1)	C(1)–Re–P	178.3(1)
C(1)–Re–O(4)	90.1(2)	C(1)–Re–O(5)	95.8(2)
C(2)–Re–P	90.8(2)	C(2)–Re–O(4)	173.0(2)
C(2)–Re–O(5)	97.8(2)	C(2)–Re–C(1)	87.8(2)
C(3)–Re–P	92.5(2)	C(3)–Re–O(4)	95.7(2)
C(3)–Re–O(5)	171.1(2)	C(3)–Re–C(1)	86.5(2)
C(3)–Re–C(2)	90.9(2)	C(18)–P–Re	116.9(2)
C(24)–P–Re	112.5(2)	C(24)–P–C(18)	103.3(2)
C(30)–P–Re	113.3(2)	C(30)–P–C(18)	102.6(2)
C(30)–P–C(24)	107.2(3)	C(4)–O(4)–Re	115.2(3)
C(5)–O(5)–Re	115.5(3)	O(1)–C(1)–Re	174.7(5)
O(2)–C(2)–Re	177.5(5)	O(3)–C(3)–Re	177.3(4)
C(5)–C(4)–O(4)	117.4(4)	C(9)–C(4)–O(4)	122.3(4)
C(9)–C(4)–C(5)	120.3(4)	C(4)–C(5)–O(5)	115.9(4)
C(6)–C(5)–O(5)	124.7(4)	C(6)–C(5)–C(4)	119.4(4)
C(7)–C(6)–C(5)	116.4(4)	C(10)–C(6)–C(5)	121.0(4)
C(10)–C(6)–C(7)	122.6(4)	C(8)–C(7)–C(6)	125.3(5)
C(9)–C(8)–C(7)	118.8(4)	C(14)–C(8)–C(7)	118.7(5)
C(14)–C(8)–C(9)	122.5(5)	C(8)–C(9)–C(4)	119.7(4)
C(11)–C(10)–C(6)	109.9(5)	C(12)–C(10)–C(6)	111.5(5)
C(12)–C(10)–C(11)	108.6(6)	C(13)–C(10)–C(6)	110.3(5)
C(13)–C(10)–C(11)	109.2(6)	C(13)–C(10)–C(12)	107.3(6)
C(15)–C(14)–C(8)	108.1(5)	C(16)–C(14)–C(8)	109.5(5)
C(16)–C(14)–C(15)	111.4(7)	C(17)–C(14)–C(8)	111.7(5)
C(17)–C(14)–C(15)	108.3(6)	C(17)–C(14)–C(16)	107.9(6)
C(19)–C(18)–P	120.2(4)	C(23)–C(18)–P	120.9(4)
C(23)–C(18)–C(19)	118.9(5)	C(20)–C(19)–C(18)	120.8(5)
C(21)–C(20)–C(19)	119.7(5)	C(22)–C(21)–C(20)	119.4(5)
C(23)–C(22)–C(21)	121.3(6)	C(22)–C(23)–C(18)	119.9(5)
C(25)–C(24)–P	121.8(4)	C(29)–C(24)–P	119.3(5)
C(29)–C(24)–C(25)	118.4(5)	C(26)–C(25)–C(24)	121.0(6)
C(27)–C(26)–C(25)	119.9(7)	C(28)–C(27)–C(26)	119.3(6)
C(29)–C(28)–C(27)	121.5(6)	C(28)–C(29)–C(24)	119.9(7)
C(31)–C(30)–P	115.6(5)	C(35)–C(30)–P	124.6(5)
C(35)–C(30)–C(31)	119.7(6)	C(32)–C(31)–C(30)	119.8(8)
C(33)–C(32)–C(31)	117.8(8)	C(34)–C(33)–C(32)	122.4(9)
C(35)–C(34)–C(33)	118.7(10)	C(34)–C(35)–C(30)	121.6(9)

lacks a strong π ligand, has Re–P distances that range from 2.26 Å to 2.38 Å and are thus considerably shorter than the common 2.40 Å.

The rhenium-to-carbonyl carbon bond length is in the expected range [20,21]. Re–C(1) is longer (by ±0.03 Å) than both Re–C(2) and Re–C(3). It indicates that DTBQ is a poor π-acceptor on the basis of d_π–p_π back-donation. The C–O distances of carbonyl groups are essentially the same.

As depicted in Fig. 2, the rhenium atom is coordinated by benzoquinone through its two carbonyl oxygen atoms. Rhenium and DTBQ form a plane, the relevant data of which are collected in Table 2. The Re–O(4) and Re–O(5) distances are 2.132 Å, which is much longer than the Re–O double bond length of 1.697 Å in ReOI(MeC≡CMe) [22]. The C(4)–O(4) and C(5)–O(5) average distance of 1.297 Å

Table 4

Deviations of atoms from the least squares plane of DTBQ and the coordinated rhenium atom

	least-squares plane equation (x_0 = orthogonal, x = crystal coordinates)			
	$0.2738x_0 - 0.1439y_0 + 0.9510z_0 = 12.4462$			
	$1.706x - 2.569y + 13.391z = 12.4462$			
Re	O(4)	O(5)	C(4)	C(5)
0.0443	−0.0481	−0.0145	−0.0116	−0.0070
C(6)	C(7)	C(8)	C(5)	
0.0004	0.0002	0.0071	0.0292	

is close to that observed in $Cr(DTSQ)_3$ [23]; 1.285(7) Å and $Co_4(DTSQ)_8$ [24]: 1.285(7) Å. When other *o*-quinones, such as tetrachloro-*o*-benzoquinone and 9,10-phenanthroquinone, coordinate to metal as semiquinones, the C–O bond lengths are in the range of 1.28–1.31 Å [11]. This bond length is characteristic of *o*-semiquinone, because in the catecholate complex, the C–O bond length is $\approx$ 1.33 Å [11]. The bond distances between carbons in DTBQ coordinates to Re as a semiquinone.

From the above discussion, it is suggested that in $DTBQ^{\cdot}$-$Re(CO)_3PPh_3$, there is an electron transfer from metal to DTBQ. Rhenium is in the +1 oxidation state and DTBQ is in the semiquinone state. The solution EPR parameters [10,11] of $DTBQ^{\cdot}$-$Re(CO)_{4-n}(PPh_3)_n$ ($n = 0, 1, 2$) $g \approx 2.00$ and $a_{H(C(7))} \approx 3$ G ($n = 0, 1$) are consistent with one unpaired electron being localized mainly on DTBQ. Furthermore, from the pattern of the coupling constants with proton, in which $a_{H(C(9))}$ is unobservable, it can be concluded that the unpaired electron resides mainly on the $\pi^{\star}$ orbital of DTBQ. Analysis of the EPR parameters of a series of radicals: X–$PQ^{\cdot}$-$Re(CO)_{4-n}(PPh_3)_n$ [25] and X–$PQ^{\cdot}$-$Mn(CO)_{4-n}(PPh_3)_n$ [26] (X–PQ represents substituted 9,10-phenanthroquinone), the variation in a_{Re}, a_P, a_{Mn} and a_H's can also be satisfactorily explained in terms of the interaction between the $\pi^{\star}$ orbital of X–PQ and the appropriate π orbital of the metal fragment.

Supplementary material available. Tables of atomic positions, anisotropic thermal parameters, hydrogen atom positions, and observed and calculated structure factors for the title compound (20 pages) are available from the authors.

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