NOVEL ASSOCIATIONS OF *ORTHO* QUINONE MONOOXIMES: HYDROGEN BONDED DIMERS OF 4,6-DI-*TERT*-BUTYL-1,2-BENZOQUINONE-2-MONOOXIME

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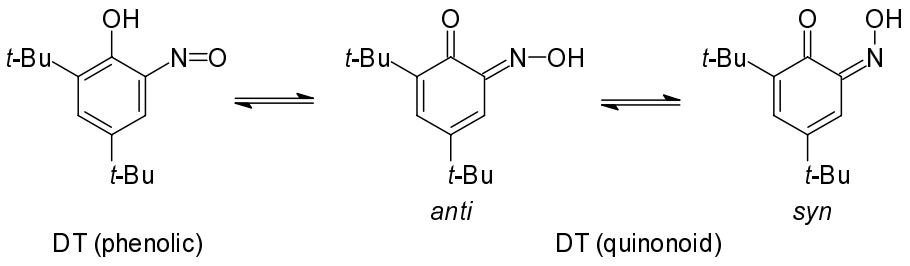
Abstract

Unlike previously reported X-ray structures of *ortho* quinone monooximes, which exhibit either intramolecular hydrogen bonding or chain-like structures in the solid state, the sterically demanding 4,6-di-*tert*-butyl-1,2-benzoquinone-2-monooxime (DT) crystallizes as dimers. In crystals from toluene DT forms dimers held together by two hydrogen bonds in a six-membered ring commonly found for simple oximes, but not for *ortho* quinone monooximes. Crystals from methanol contain DT dimers held together by two bridging methanol molecules, each of which participate in three hydrogen bonds. Although phenolic and quinonoid tautomeric forms of DT coexist in solution, with nonpolar solvents favoring the aromatic phenolic tautomer, both crystals exist in the quinonoid form, independent of the solvent from which they were crystallized. These quinonoid forms are stabilized by intermolecular multi center hydrogen bonds and dipole-dipole interactions countering the effect of the loss of aromatic stabilization. With copper (II) perchlorate, DT yielded crystals of Cu(II)(HL)(L)ClO_4, where HL = DT. HL and L ligands are coordinated to Cu(II) in a *cis* relationship.

Introduction

The chemistry of quinone monooximes is marked by the existence of a tautomeric equilibrium with nitrosophenols, shown below for 4,6-di-*tert*-butyl-1,2-benzoquinone-2-monooxime (DT).



Spectroscopic methods[1-8] have revealed various structural effects on this equilibrium, and shown that, in general, quinonoid forms are favored in polar solvents, while phenolic forms are favored in nonpolar solvents.

Despite the existence of the phenolic form in solution for certain cases, X-ray crystallography has shown that all nitrosophenols reported thus far are quinonoid in the solid state[9-14] with the oximo (=N-OH) group oriented either *syn* or *anti* to the keto (-C=O) group. The *syn* orientation resulted in an intramolecular hydrogen bond between oximo and keto groups,[13] while the *anti* form favored a chain-like arrangement of quinone monooxime molecules connected through intermolecular hydrogen bonds.[9]

o-Quinone monooximes are known to form stable complexes with d-metal ions in which the metal ion is bound to the keto oxygen and oximo nitrogen. Numerous analytical[15] and synthetic[16] uses were reported for these complexes. Tarnopol'skii[17] also studied the effectiveness of DT for metal ion extractions. By analysis of bond length data it was shown that a complexed metal ion causes a mesomeric shift toward the *o*-nitrosophenoxide form of the ligand.[18, 19]

The purpose of this work was to determine the effect of sterically demanding substituents on crystal structures obtained from polar and nonpolar solvents and on a crystalline metal complex. DT was chosen for this investigation because of strong solvent effects [20,21] on its tautomeric equilibrium. However, DT differs from previously examined *o*-quinone monooximes by the presence of bulky *tert*-butyl groups. The work was also an attempt to obtain an uncomplexed *o*-nitrosophenol crystal in the phenolic form.

Experimental

Instrumentation

IR data was collected on a Mattson GL 2020 IR spectrometer. A modified Nicolet NT 270 spectrometer operating at 270 MHz was used to collect NMR spectra, and samples were analyzed with a Fisons GC 8000 gas chromatograph connected to a Fisons MD 800 mass spectrometer. The GC was equipped with a methyl silicone capillary column (G&W Scientific DB-5MS) and the MS with an EI source at 70 eV.

Synthesis

4,6-di-*tert*-Butyl-1,2-benzoquinone 2-monooxime was prepared from 3,5-di-*tert*-butyl-1,2-quinone and hydroxylamine.[20] Recrystallization from MeOH gave shiny orange crystals which upon drying became an amorphous-like orange solid; m.p. 85-87 ^{o}C; IR (KBr) Λ_{max} /cm^{-1} 3222, 2963, 1661, 1622, 1370, 1301, 1265, 1053, 1013, 943, 889, 797; NMR δ_H (270 MHz, solvent $CDCl_3$; standard $SiMe_4$) 1.33 (9H, s, *t*-Bu), 1.38 (9H, s, *t*-Bu), 7.5 (1H, br, ArH), 7.8 (1H, br, ArH); MS m/z 235, 220, 190, 162, 147, 134, 91, 57, 41.

Crystals for X-ray analyses were prepared by slow solvent evaporation from a solution exposed to the atmosphere at room temperature. Orange DT crystals, obtained from methanol, changed appearance after drying and over ca. 30 days the dry solid degraded regardless of refrigeration or storage in an inert atmosphere at ambient temperature. For this reason, as soon as crystals were removed from the mother liquor, they were immediately mounted on the sample holder at liquid nitrogen temperature for X-ray analysis. Orange crystals obtained from toluene showed no such signs of change, even over a longer period at room temperature and exposure to the atmosphere.

The Cu(II) DT complex was prepared by mixing 2 equivalents of DT with 1 equivalent of $Cu(ClO_4)_2 \cdot 6H_2O$ in toluene. However, crystallization from toluene did not result in useful monocrystals. Recrystalization of this product from cyclohexane gave dark violet crystals of $Cu(II)(HL)(L) \cdot ClO_4$ (where HL = 4,6-di-*tert*-butyl-1,2-benzoquinone-2-monooxime), suitable for X-ray data collection.

X-Ray structure analysis

For DT from toluene or methanol, crystals were mounted on glass fibers and data taken at 203(2) K on a Siemens P4/R4 four-circle diffractometer equipped with a rotating Mo anode. Unit cell parameters and crystal orientation were obtained by means of least-squares refinement on at least 25 reflections. Periodic measurements of three standard reflections revealed no appreciable decay. Both structures were solved by direct methods through Siemens XSCANS and SHELXTL programs.[22]

For the Cu complex, data were collected on a Siemens SMART CCD single-crystal diffractometer with a Mo anode and graphite monochromator. Crystals were mounted on a glass fiber and placed in a nitrogen stream at 173(2) K. A sphere of data was collected to an effective 2θ value of 55 degrees, using omega scans. Routine Lorentz and polarization corrections were applied. An empirical correction was used[23] for absorption and other systematic errors, based on measured intensities of equivalent reflections at different phi and omega values. The structure was solved by direct methods using Siemens SMART, SAINT, and SHELXTL programs.[22,24] For all structures, refinements were full-matrix least-squares on F^2 using all data, and the weighting scheme was $w = 1 / [\sigma^2 (Fo^2) + (A P)^2 + (B P)]$ where $P = (Fo^2 + 2 Fc^2) / 3$.

Results and discussion

DT crystals from toluene (DT_{Tol})

Crystal data for all crystals [25] as well as information about data collection and refinement are given in Table 1. Selected bond lengths of all three structures are given in Table 2. Considerable double bond localization in benzene-ring bond distances indicates a quinonoid structure, as confirmed by short exo C-N (1.292(2) Å) and C-O (1.221(2) Å) bond lengths appropriate for oximo and keto groups, respectively. All atoms of the dimer in Figure 1 lie nearly in plane except for *tert*-butyl groups. The oximo group is in an *anti* configuration with its oxygen directed away from the keto function, thus preventing formation of an intramolecular hydrogen bond. The molecules are connected through two hydrogen bonds and a weak interaction to carbonyl oxygens as indicated in Figure 1. Interatomic distances and angles of hydrogen bonds are given in Table 3.

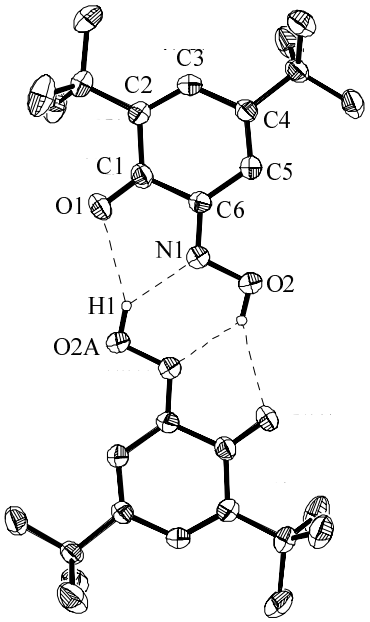


Figure 1 Hydrogen bonding between molecules of 4,6-di-tert-butyl-1,2-benzoquinone 2-monooxime derived from toluene solution. Labeled are non-hydrogen atoms of the molecule from the asymmetric unit. O2A and H1 atoms are from the symmetry related molecule. H atoms on the ring and t-butyl groups are not shown.

Table 1. Crystal data and structure refinement information.

Compound / solvent	DT / toluene	DT / methanol	Cu(II)DT / toluene and cyclohexane
Empirical formula	$C_{14}H_{21}NO_2$	$C_{15}H_{25}NO_3$	$C_{28}H_{41}N_2O_8ClCu \cdot C_{3.5}H_{3.5}$
Relative formula weight	235.32	267.36	678.18
Temperature	203(2) K	203(2) K	173(2) K
Wavelength	0.71073 Δ	0.71073 Δ	0.71073 Δ
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 2_1/n, No. 14	P-1, No. 2	P-1, No. 2
Unit cell parameters	a = 12.447(1) Δ α = 90°	a = 9.258(3) Δ α = 75.55(2)°	a = 10.513(1) Δ α = 111.054(1)°
	b = 8.419(1) Δ β = 91.18(1)°	b = 9.370(3) Δ β =69.33(3)°	b = 18.454(1) Δ β = 90.302(1)°
	c = 13.431(1) Δ γ = 90°	c = 9.812(3) Δ γ = 82.51(4)°	c = 18.708(1) Δ γ = 95.774(1)°
Volume, Z	1407.2(2) $Δ^3$, 4	770.3(4) $Δ^3$, 2	3366.7(3) $Δ^3$, 4
Density (calculated)	1.111 Mg/m^3	1.153 Mg/m^3	1.338 Mg/m^3
Absorption coefficient	0.074 mm^{-1}	0.079 mm^{-1}	0.778 mm^{-1}
F(000)	512	292	1430
Crystal size	0.5 x 0.3 x 0.3 mm	0.6 x 0.6 x 0.6 mm	0.3 x 0.3 x 0.4 mm
Theta range for data collection	2.25 to 25.00°	2.25 to 27.51°	1.19 to 28°
Limiting indices	-1<=h<=14, -1<=k<=10	-1<=h<=11, -11<=k<=11	-14<=h<=13, -23<=k<=24
	-15<=l<=15	-12<=l<=12	-24<=l<=24
No. of reflections collected	3229	4108	36209
No. of independent reflections	2461 [R(int) = 0.0297]	3456 [R(int) = 0.0964]	15538 [R(int) = 0.0254]
Goodness-of-fit on F^2	1.060	1.029	1.073
Final R indices [I>2σ(I)]	R1 = 0.0397, wR2 = 0.1100	R1 = 0.0530, wR2 = 0.1400	R1 = 0.0559, wR2 = 0.1385
R indices (all data)	R1 = 0.0491, wR2 = 0.1134	R1 = 0.0710, wR2 = 0.1562	R1 = 0.0705, wR2 = 0.1511
Largest diff. peak and hole	0.169 and -0.146 e$Δ^{-3}$	0.324 and -0.254 e$Δ^{-3}$	2.464 and -2.016 e$Δ^{-3}$

DT crystals from methanol (DT_{MeOH})

DT_{MeOH} also is a dimeric structure with the two DT held together by hydrogen bonding to two bridging methanol molecules as shown in Figure 2. Bond lengths in the benzene ring and exo bonds, C-N (1.297(2) Å) and C-O (1.221(2) Å) indicate each DT to be in the quinonoid form as found for DT_{Tol}. Both DT molecules are nearly planar and all four molecules (2 DT + 2 MeOH) are nearly coplanar. The oximo group is in an *anti* configuration preventing intramolecular hydrogen bonding. The methanol OH group is a donor of two weak hydrogen bonds in which the keto oxygen and oximo nitrogen act as acceptors. The hydrogen bond connecting the oximo group (donor) and methanol oxygen (acceptor), on the other hand, is shorter indicating significant stabilization. Hydrogen bond parameters are given in Table 3.

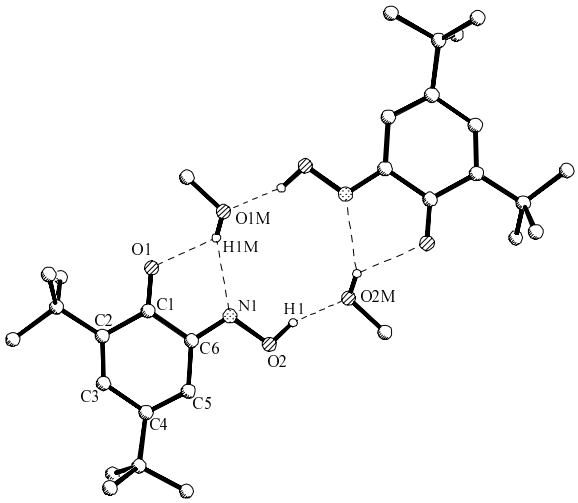


Figure 2 Hydrogen bonding between molecules of 4,6-di-tert-butyl-1,2-benzoquinone 2-monooxime and methanol molecules. Labeled are non-hydrogen atoms of the molecule from the asymmetric unit. O2M atom is from the symmetry related methanol molecule. H atoms on the ring and t-butyl groups are not shown.

In the solvents which were used the position of the tautomeric equilibrium should differ substantially, since the phenolic: quinonoid ratio is 38:62 in ethanol and 79:21 in benzene.[19] The strong preference for the quinonoid form in the solid phase, even when recrystallized from toluene, must be due to strong intermolecular attractions not present in dilute solution.

In regard to hydrogen bonding the DT molecule has the potential alternative of forming an intramolecular hydrogen bond.[9,13,26] This bond, although strong, would involve only two heteroatoms, leaving the third one nonbonded or perhaps weakly bonded whereas in the above discussed structures intermolecular hydrogen bonding involves all three heteroatoms in stabilizing contacts. The DT_{MeOH} structure includes additional (stronger) intermolecular hydrogen bonds involving the methanol oxygen.

The balance of energy contributions that govern methanol inclusion is very delicate, as shown by ease of methanol removal when crystals are exposed to ambient atmosphere at room temperature. The crystal is then in a disordered state that leads to decomposition, a phenomenon not observed in toluene-derived crystals even over longer periods. However, the fact that the interaction is sufficient to exist in the solid state indicates that intramolecular bonding is not likely in a solution with abundant solvent molecules that readily form hydrogen bonds.

Table 2. Selected bond lengths in 4,6-di-*tert*-butyl-1,2-benzoquinone 2-monooxime (DT) and Cu(II)(HL)(L)·ClO_4 (where HL=DT) crystals.

			Length Å			
Compound	DT_{Tol}	DT_{MeOH}	Cu(II)DT			
			Complex 1		Complex 2	
Bond			Ligand 1[a]	Ligand 2[a]	Ligand 1[a]	Ligand 2[a]
O(1)-C(1)	1.221(2)	1.221(2)	1.257(3)	1.272(3)	1.250(3)	1.267(3)
O(2)-N(1)	1.3723(14)	1.367(2)	1.335(3)	1.289(3)	1.343(3)	1.288(3)
N(1)-C(6)	1.292(2)	1.297(2)	1.303(4)	1.327(3)	1.306(4)	1.327(4)
C(1)-C(2)	1.472(2)	1.472(2)	1.454(4)	1.450(4)	1.454(4)	1.454(4)
C(1)-C(6)	1.501(2)	1.499(2)	1.484(4)	1.462(4)	1.487(4)	1.454(4)
C(2)-C(3)	1.351(2)	1.341(2)	1.363(4)	1.367(4)	1.359(4)	1.366(4)
C(2)-C(0A)	1.527(2)	1.531(2)	1.534(4)	1.530(4)	1.527(4)	1.529(4)
C(3)-C(4)	1.460(2)	1.460(2)	1.469(4)	1.456(4)	1.466(4)	1.456(4)
C(4)-C(5)	1.340(2)	1.342(2)	1.357(4)	1.351(4)	1.350(4)	1.359(4)
C(4)-C(0B)	1.527(2)	1.525(2)	1.528(4)	1.534(4)	1.529(4)	1.529(4)
C(5)-C(6)	1.440(2)	1.434(2)	1.439(4)	1.426(4)	1.427(4)	1.430(4)
O(1M)-C(1M)	-	1.414(2)	-	-	-	-
Cu(1)-N(1)	-	-	1.980(2)	1.962(2)	1.973(2)	1.958(2)
Cu(1)-O(1)	-	-	2.004(2)	1.990(2)	1.998(2)	1.956(2)
Cu(1)-O(1Cl)	-	-	2.149(2)	-	2.129(3)	-

[a] Ligands 1 and 2 are the oximo (HL) and oximato (L^-) ligand in the copper (II) DT complexes.

DT-copper(II) perchlorate complex

As shown in Figure 3, Cu(II) is bonded to two DT (both bidentate) with a fifth coordination site occupied by perchlorate. One DT is in anion form giving the overall formula Cu(II)(HL)(L)·ClO_4 where DT is represented as a ligand HL. The geometries of the two DT ligands differ slightly as shown by values for bond lengths in Table 2. The

asymmetric unit of this compound contains two different Cu(II)(HL)(L)ClO_4 complex molecules and one solvent (toluene) molecule, originating from preparative work, which is disordered. Tables 2 and 3 show that bond lengths are similar in both complexes. In both cases the oximo and oximato groups of DT ligands are in a *cis* relationship and hydrogen bonded to each other. There is no indication of the trapped solvent affecting much the DT ligands.

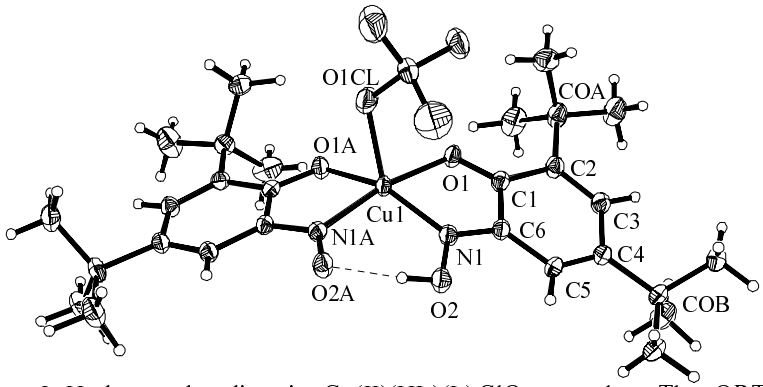


Figure 3 Hydrogen bonding in Cu(II)(HL)(L)ClO_4 complex. The ORTEP picture shows only one of the two complex molecules from the asymmetric unit.

The Cu(II)-DT complex resembles similar structures reported in the literature,[27, 28] thus indicating little influence of bulky substituents. The 2:1 complex with square pyramidal geometry in which the metal is bound to the keto oxygen and oximo nitrogen of quinonoid ligands is the most commonly encountered arrangement among five-coordinated Cu (II) complexes.[29] However, the *cis* geometry of oximo groups in the present case, with a pseudo mirror plane, is unusual, since reported examples have these groups *trans*. The cis geometry may result from the complex having a HL and L ligands whereas reported structures have only L ligands. HL acts as a hydrogen bond donor but the hydrogen bond can form only in the cis and not in a trans geometry. It is not clear whether this *cis/trans* effect is in any way due to *tert*-butyl groups. Slight differences in geometries within ligands bound to the same metal ion were also reported in a number of similar structures.[18]

Benzene ring bond lengths in complexed ligands show less variation than in DT_{Tol} or DT_{MeOH}. This shift toward the quinolic form is further confirmed by bond lengths of keto and oximo groups. These results are in agreement with the reported

effect of bound metal ions causing a mesomeric shift toward the phenolic limiting structure.[18]

Table 3. Parameters of hydrogen bonds in crystals of 4,6-di-*tert*-butyl-1,2-benzoquinone-2-monooxime.

Crystal	X-H···Y[a]	X-H, Å	Y···H, Å	X-Y, Å	∠X-H···Y,°
DT / Toluene	O2A-H1···O1	0.90(2)	2.42(2)	3.245(1)	152(2)
	O2A-H1···N1	0.90(2)	2.06(2)	2.792(2)	138(2)
DT / Methanol	O1M-H1M···O1	0.82(1)	2.239(8)	2.882(2)	136(1)
	O1M-H1M···N1	0.82(1)	2.33(1)	3.091(2)	154.2(9)
	O2-H1···O1M	0.91(3)	1.75(3)	2.621(1)	159(3)
Cu(II)(HL)(L)ClO_4	O2-H1···O2A[b]	0.88(5)	1.71(5)	2.556(3)	162(4)
	O2-H1···O2A[c]	0.87(5)	1.71(6)	2.571(4)	168(5)

[a] Atoms marked according to notations in figures

[b] Hydrogen bond in complex 1

[c] Hydrogen bond in complex 2

Conclusions

Although the quinonoid form of DT is favored in protic and polar ethanol and the phenolic in nonpolar benzene, the present results show that in the solid state DT exists in the quinonoid form whether crystals are obtained from toluene or methanol. In dilute benzene solution, stabilizing factors for the phenolic form are aromaticity and intramolecular OH---NO hydrogen bonding. Loss of aromaticity in quinonoid forms found in the solid state must be compensated for by other forces such as hydrogen bonds and increased dipole-dipole interactions in the more polar quinonoid forms.

The structure of DT_{MeOH} is especially interesting in that it is fundamentally the same as DT_{Tol} except that two bridging methanol molecules add two more H bonds to the dimeric structure. To our knowledge this is the first report of dimeric *o*-quinone monooxime structures. None of the compounds previously reported possess large bulky groups that could affect packing. Side groups in these molecules were chain-like, and several possessed strongly polar groups such as $-SO_3^-$ that could affect packing through additional strong hydrogen bonds. In the structures described in this paper the *tert*-butyl

group *vicinal* to the keto group hinders formation of a chain-like structure. The observed intermolecular hydrogen bonding to methanol molecules in the solid state suggests that the often postulated intramolecular hydrogen bonding of *o*-quinone monoximes is not likely in protic solvents due to the abundance of solvent sites for hydrogen bonding.

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Povzetek

Za razliko od objavljenih rentgenskih struktur *orto* kinon monooksimov, ki v trdni fazi vsebujejo intramolekularno vodikovo vez ali imajo verigasto strukturo, sterično ovirani 4,6-di-*tert*-butil-1,2-benzokinon-2-monooksim (DT) kristalizira kot dimer. V kristalih pridobljenih iz toluena so DT molekule povezane v dimere z dvema vodikovima vezema v šestčlenskem obroču, ki je običajen za enostavne oksime a ne za kinon monooksime. V kristalih pridobljenih iz metanola so DT dimeri povezani z dvema povezovalnima molekulama metanola od katerih vsaka sodeluje v treh vodikovih vezeh. Čeprav sta v raztopini prisotni fenolna in kinonska tautomerna oblika, s tem, da nepolarna topila stabilizirajo aromatično fenolno obliko, sta obe kristalni strukturi, neodvisno od topil v katerih sta nastali, v kinonski obliki. Kinonski obliki sta stabilizirani z močnimi intermolekularnimi, večcentričnimi vodikovimi vezmi in dipol-dipol interakcijami, ki nasprotujejo vplivu izgube aromatične stabilizacije. DT je z bakrovim (II) perkloratom tvoril kristale tipa $Cu(II)(HL)(L)ClO_4$, kjer je HL = DT. HL in L sta koordinirana na Cu(II) atom v *cis* obliki.