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Ken-Ichi Sugiura [a] , Takanori Tanaka [a] , Masam1 Sawada [a] & Yoshiteru Sakata [a]

[a] The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka, 567, Japan

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CRYSTAL STRUCTURE OF 2,5-DIAZIDE-3,6-DICHLORO-*p*-BENZOQUINONE (DADCQ)

This paper is dedicated to Professor Fumio Ogura and Professor Yusei Maruyama on the occasion of their retirements from Hiroshima University and from Institute for Molecular Science, respectively.

KEN-ICHI SUGIURA, TAKANORI TANAKA, MASAMI SAWADA,
and YOSHITERU SAKATA*
The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka 8-1, Ibaraki, Osaka 567, Japan

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Abstract The crystal structure of 2,5-diazide-3,6-dichloro-*p*-benzoquinone has been revealed. $C_6Cl_2N_6O_2$, P_{bca} (#61), a = 11.763(5), b = 14.893(2), c = 5.163(1) at 25 °C, Z = 4, D_c = 1.902 g cm^{-3}, λ(Mo-Kα) = 7.10 cm^{-1}. Merocyanine resonance structure was observed for the title compound.

Keywords: Crystal structure, quinone, azide, d-π interaction, merocyanine

Introduction

Recently, new materials with strong electronic couplings between d-and π-electrons have attracted much attention from the view points of conductivity and magnetism. Such materials are constructed by the complexation of transition metals and π-organic donor and/or acceptor molecules with substituents which can coordinate to metals. For example, the complexes of Cu-dicyanoquinodiimine (DCNQI)[1] and Vtetracyanoethylene[2] show metallic conductivity and room-temperature bulk ferromagnetism, respectively. However, only nitrile groups are used for the ligands in these complexes. For the further development of new materials, π-systems with substituents different from nitrile groups are requested.

For such coordinated π-systems, 2,5-diazide-3,6-dichloro-*p*-benzoquinone (DADCQ) seems to be a good candidate, where two azide groups can coordinate to metals. DCDAQ was reported for the first time by Ochwat in 1923[3] and later, its strong electron accepting ability was estimated by Matsunaga on the basis of charge transfer absorption bands with several organic donor molecules in solution.[4] However, structural information is lacking for this interesting acceptor molecule.[5,6] In this report, we wish to describe the crystal structure of DADCQ.

Results and Discussion

DADCQ was prepared according to the reported method.[4,7] A red prismatic crystal suitable for the crystallographic experiment was obtained by recrystallization from ethyl acetate. The experimental details and atomic coordinate were summarized in Tables 1 and 2, respectively. The ORTEP drawing of the crystal structure of DADCQ was shown in Fig. 1 together with the numbering atoms, bond lengths, and bond angles. All of the ring atoms lie in a least squares plane within 0.001 Å mean deviation. Introduced substituents, two azide groups and chlorine atoms, deviate from this plane; 0.003 Å for N(1), 0.108 Å for N(2), 0.214 Å for N(3) and 0.017 Å for Cl(1) (Fig 1). Bond lengths and geometry of the azide groups are qualitatively in good agreement with reported azide compounds indicating the canonical structure **1a** for DADCQ.[8]

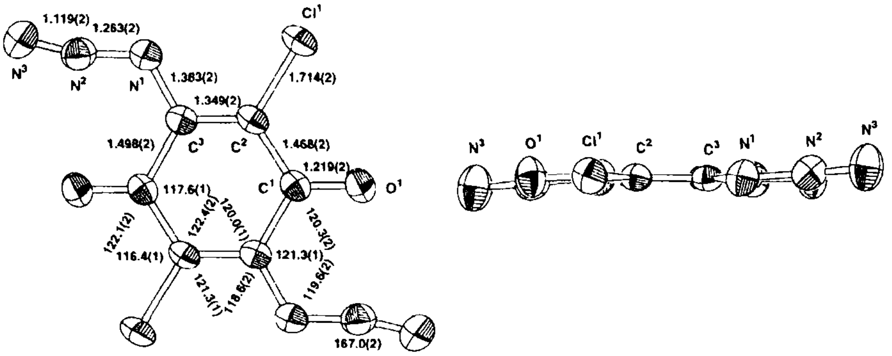


FIGURE 1. ORTEP drawing, atom-numbering, bond lengths and bond angles for DADCQ. Thermal ellipsoids are at the 30% probability level. The crystallographically unique atoms are labeled.

TABLE 1. Experimental Details

A. Crystal Data

Empirical Formula	$C_6Cl_2N_6O_2$
Formula Weight	259.01
Crystal Color, Habit	red, prismatic
Crystal Dimensions	0.25 X 0.50 X 0.13 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (43.6-44.9°)
Omega Scan Peak Width at Half-height	0.28°
Lattice Parameters	a = 11.763(5) Å b = 14.893(2) Å c = 5.163(1) Å V = 904.5(5) $Å^3$
Space Group	P_{bca} (#61)
Z value	4
D_{calc}	1.902 g/cm^3
F_{000}	512.00
μ(MoKα)	7.10 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 3.40, 11.34, 38.03)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	258 mm
Temperature	20.0 °C
Scan Type	ω-2θ
Scan Rate	12.0 °/min (in ω)-up to 10 scans
Scan Width	$(1.00 + 0.35 \tan\theta)^\circ$
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 1256
Corrections	Lorentz-polarization Absorption (trans. factors: 0.9235 - 0.9983) Decay (0.47 % increase) Secondary Extinction (coefficient: 4.44190e-07)

C. Structure Solution and Refinement

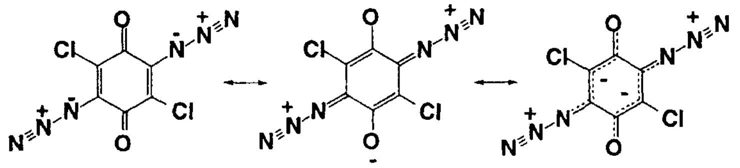
Structure Solution	Direct Methods (SAPI91)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/(\sigma^2 Fo) = (4Fo^2)/(\sigma^2 Fo^2)$
p-factor	0.0200
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	874
No. Variables	74
Reflection/Parameter Ratio	11.81
Residuals: R; Rw	0.029 ; 0.039
Goodness of Fit Indicator	1.40
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.23 $e^-/Å^3$
Minimum peak in Final Diff. Map	0.24 $e^-/Å^3$

TABLE 2. Atomic Coordinates in Positional Crystal Coordinates and Thermal Parameters B(eq) for DADCQ.[a)]

atom	x	y	z	B(eq)[b)]
Cl(1)	0.98779(4)	0.16556(3)	0.62423(9)	3.38(1)
O(1)	0.8439(1)	0.00569(8)	0.6270(3)	3.74(3)
N(1)	1.1529(1)	0.14588(10)	1.0407(3)	3.27(3)
N(2)	1.2224(1)	0.1487(1)	1.2268(3)	3.37(3)
N(3)	1.2886(2)	0.1666(1)	1.3736(4)	4.67(5)
C(1)	0.9155(1)	0.0038(1)	0.7977(3)	2.56(3)
C(2)	0.9983(1)	0.0765(1)	0.8332(3)	2.53(3)
C(3)	1.0782(1)	0.07450(10)	1.0206(3)	2.46(3)

a) Standard deviations in units of the last decimal place are given in parentheses.

b) $B_{eq} = \frac{8}{3}\pi(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}\,aa^*bb^*\cos\gamma + 2U_{13}\,aa^*cc^*\cos\beta + 2U_{23}\,bb^*cc^*\cos\alpha)$



1a 1b 1c

FIGURE 2. Possibilities of **1a** and **1b** for the canonical resonance structures of DADCQ. 'Merocyanine' resonance structure **1c** as an admixture of **1a** and **1b**.

Behavior of bond alternation in the ring agrees with that of *para*-quinoid structure **1a** (Fig. 2).[9] Namely, DADCQ contains one set of two double bonds, C(2)-C(3), and two sets of four single bonds, C(1)-C(2) and C(3)-C(1*). However, the actual bond lengths of DADCQ are significantly different from the reported *p*-benzoquinone (BQ) and the corresponding derivatives. The bond lengths of C(1)-C(2) and C(3)-C(1*) are 1.468(2) and 1.498(2) Å, respectively, and these are assigned to single bond. The former bond, C(1)-C(2), is not negligibly shorter and the latter one, C(3)-C(1*), is longer than that of BQ (1.474 Å) (Fig. 3). On the other hand, C(2)-C(3) is 1.349(2) Å and is longer than that of BQ (1.334 Å). The distance of C(1)-O(1) (1.219(2) Å) shows a typical bond length for quinone derivatives (1.222 Å for BQ).

The results strongly support the contribution of the resonance structure **1b** for DADCQ (Fig. 2). The *para*-quinodiimine resonance structure is achieved by two azide groups having lone pair electrons. Although the bond length of C(3)-N(1) (1.383(2) Å)

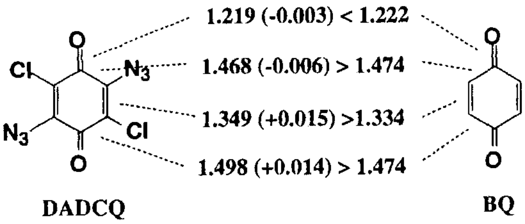


FIGURE 3. Comparison of bond lengths for DADCQ with BQ (Å).

is shorter than the corresponding value of aryl azides (1.417 Å for *p*-nitrophenyl azide (NPA))[8] and alkyl azide (1.47 Å for methyl azide),[10] it is considerably longer than DCNQI.[11] To achieve the resonance structure **1b** in the molecule, bond angle C(3)-N(1)-N(2) becomes much larger (119.6(2)°) than that of NPA (115.0°). The value of C(2)-Cl(1) (1.714(2) Å) shows the typical bond length for chlorinated bonzoquinones (1.701 Å for chloranil,[12] 1.717 Å for 2,5-dichloro-*p*-benzoquinone (2,5-DCQ) and 1.715 Å for 2,3-dichloro-*p*-benzoquinone[13]). This indicates that two chlorine atoms do not take part in any resonance contributions for DADCQ. Such an admixture of resonance structures **1c** (merocyanine structure)[14] was also reported for *p*-benzoquinone derivatives with substitutents having lone pair electrons at 2 and 5 positions, *i.e.*, 2,5-DCQ,[13] 2,5-diamino-3,6-dichloro-*p*-benzoquinone,[15] fluoranic acid.[16]

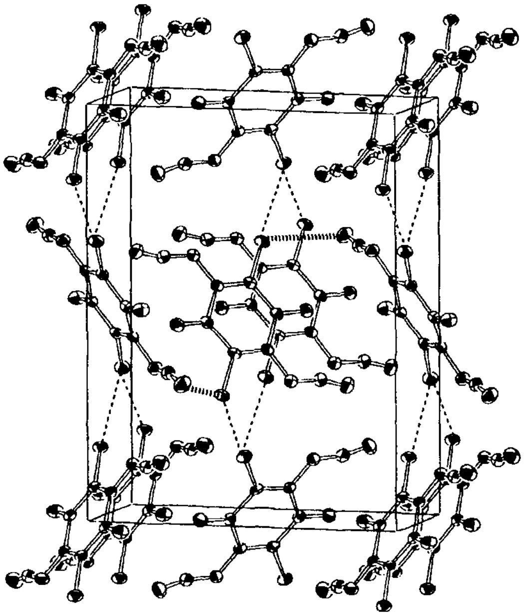


FIGURE 4. Packing arrangement of DADCQ seen perpendicular to *ab* plane. Solid and dotted lines indicate intermolecular Cl(1)-Cl(1) (3.6043(6) Å) and Cl(1)-N(3) (3.425(2) Å) contacts, respectively.

The molecular packing is shown in Fig.4. The crystal is constructed by usual van der Waals (vdW) interactions and even the closest intermolecular contacts are much longer than the sum of vdW radii, *i.e.*, Cl(1)-Cl(1) contact for 3.6043(6) Å and Cl-N(3) for 3.425(2) Å. Molecular complexes and coordination chemistry of DCDAQ will be published elsewhere.

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