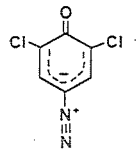
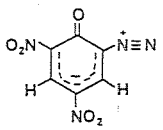
09.2-8 THE CRYSTAL STRUCTURES OF TWO DIAZO OXIDES AND A PROPOSED BONDING DESCRIPTION. C. K. Lowe-Ma and W. S. Wilson, Chemistry Division, Research Department, Naval Weapons Center, China Lake, CA 93555, USA.

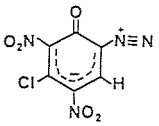
Although diazo oxides (or diazophenols) have been known for some time, their bonding description has been ambiguous, with quinonoid, zwitterionic, and resonance hybrid structures having been proposed. X-Ray crystal structures of the only examples determined, namely 3,6-bisdiazocyclohexanetetraone (G. B. Ansell, J. Chem. Soc., 1969, (B), 729) and 2,6-dichloro-4-diazo oxide, I (C. T. Presley and R. L. Sass, Acta Cryst., 1970, B26, 1195) have been considered to be atypical. Crystal structure determinations were, therefore, carried out for 2-diazo-4,6-dinitrophenol, II, and 5-chloro-2-diazo-4,6-dinitrophenol, III. From the observed molecular geometries of II and III, a bonding description is proposed, which is similar to that obtained from the MO calculations of Kazitsyna, et al.



I



II



III

The crystal data for II and III are listed below.

	II	III
Formula	$C_6H_2N_4O_5$	$C_6HN_4O_5Cl$
Space group	$P2_12_12_1$	$P2_1$
Z	4	2
a	6.184(2)A	4.964(2)A
b	8.625(3)	10.287(4)
c	15.222(4)	8.644(3)
β	...	101.21(3)°
D_x	1.719 g/cm^3	1.876 g/cm^3
Obs Refl	1488	870
R, wR	0.061, 0.070	0.039, 0.049

09.2-9 STRUCTURES OF MACROCYCLES CONTAINING THE 1,3,4-THIADIAZOLE SUBUNIT. Frank R. Fronczek and Steven F. Watkins, Department of Chemistry, Louisiana State University, Baton Rouge, LA, 70803, USA, and Sebastiano Pappalardo, Instituto Dipartimentale di Chimica e Chimica Industriale, Universita di Catania, Catania, Italy.

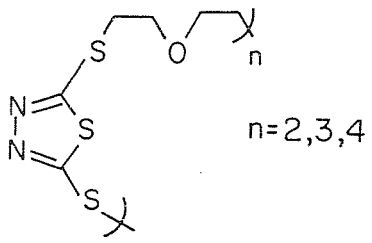
Macrocycles in which the 1,3,4-thiadiazole heterocycle has been incorporated via thiacrown or dithiabutyl linkages have been prepared, and their crystal structures determined, using CAD4's.

I (n=2) is monoclinic, C2/c, a=15.747(3), b=7.400(2), c=16.432(3)Å, β=104.88(2)°, Z=4, R=0.034 for 1103 observations. The centrosymmetric molecule forms no cavity. We have previously reported the structure of the complex with $Cu(NO_3)_2$ (ACA McMaster, poster PB24, 1986).

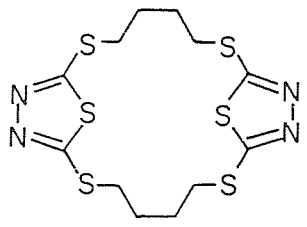
I (n=3) xH_2O is trigonal, $R\bar{3}$, a=23.107(4), c=11.206(2)Å, Z=6, R=0.085 at present stage of refinement for 1527 data. Macrocycles lie on threefold axes, forming central cavities which contain disordered water molecules, probably x=2.

I (n=4) is monoclinic, $P2_1/c$, a=9.417(2), b=38.371(5), c=10.198(2)Å, β=149.45(2)°, Z=2, R=0.047 for 3736 data. The centrosymmetric tetramer forms no cavity, but is elongated into a cigar shape, with S and O heteroatoms generally facing inward, N outward.

II is triclinic, $P\bar{1}$, a=5.7314(8), b=8.2460(9), c=9.9133(11)Å, α=100.228(9), β=103.768(12), γ=101.330(10)°, Z=1, R=0.049 for 1585 observations. The molecule is centrosymmetric, with an overall rectangular shape. The heterocyclic rings are joined by parallel paraffinic chains in fully extended conformations.



I



II