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Diazophenols—Their Structure and Explosive Properties

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FOREWORD

Diazophenols constitute a class of potential primary explosives or detonants, whose structures have not been unequivocally characterized until now. This report documents their elucidation by X-ray crystal structure determination and by ^{13}C nuclear magnetic resonance (NMR) spectroscopy, supported by molecular orbital calculations. The report also collates thermochemical data and explosive sensitivity data for representative diazophenols.

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(U) The bonding structure of diazophenols has been examined by X-ray crystal structure determination and by ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Results of these experiments indicate that these molecules contain both a carbonyl function and a cationic diazonium grouping, with the negative counter charge being distributed over the carbocyclic ring. These conclusions appear to be in agreement with physical and chemical data previously obtained. Explosive sensitivity and stability data have also been collected for selected diazophenols. These compounds show properties typical of primary explosives or detonants.

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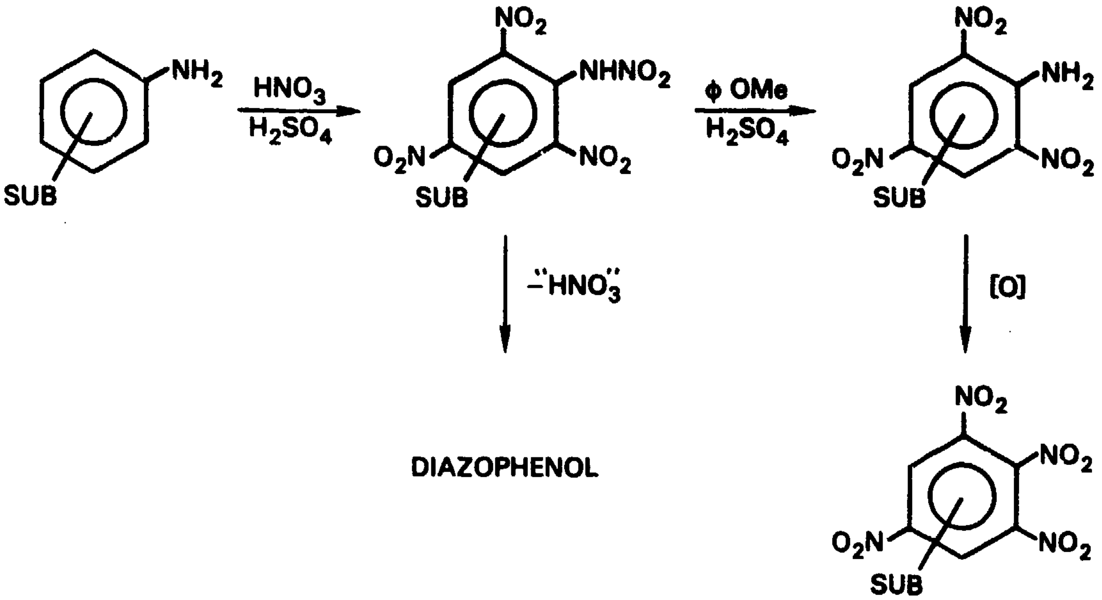
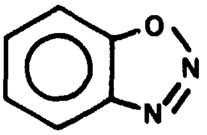
INTRODUCTION

The principal objectives of the Energetic Materials Branch of the Chemistry Division over the last decade or so have been the synthesis of new dense explosives which exhibit increased performance and/or reduced sensitivity to inadvertent initiation by such stimuli as shock, impact, and "thermal excursion." Prominent achievements have been the preparation of highly nitrated aromatics such as hexanitrobenzene (Reference 1), pentanitrotoluene (Reference 2), and decanitrobiphenyl (Reference 3). The general stratagem adopted to prepare this class of compounds is illustrated in Scheme 1, and involves nitration of a suitably substituted aniline to afford a polynitroaromatic nitramine, conversion to a polynitroaniline by treatment with anisole in sulfuric acid, and finally oxidation of the amine functionality to give the polynitroaromatic.



Polynitroaromatic nitramines are, however, also subject to rearrangement with the elimination of the elements of nitric acid to produce compounds which have been identified as diazophenols (Reference 4). Examples of this class of compound, which have also been described variously as diazo oxides, diazonium phenolates, diazoquinones or quinone diazides, have found application both in the dye industry (Reference 5) and as explosives (Reference 6). They have been known since 1858 (Reference 7), but have been prepared more usually by treatment of 2- or 4-hydroxyphenyldiazonium salts with base or by solvolysis of other 2- or 4-substituted phenyldiazonium salts. Yet, there has been no concensus regarding the structure of these compounds. This paper seeks to address this problem and provides details of explosive properties of representative examples of diazophenols.

Both *o*- and *p*-diazophenols have been prepared, but no *m*-diazophenol has been reported. (The term diazophenol will be used throughout as a generic descriptor, without any structural inference being intended.) Diazophenols are highly colored crystalline solids (usually lustrous yellow, bronze, or red), are soluble in polar solvents, and melt with decomposition of varying vigor in the temperature range of about 130 to 180°C. They show N-N and C-O stretching vibration bands at about 2100 to 2250 and 1580 to 1640 cm^{-1}, respectively, in the infrared (IR) spectra. Various structures have been proposed for these materials, including principally **1a-c** and **2a-c** below. Variants of these structures found in the literature are perhaps best attributed to differing perceptions of organic bonding theory.



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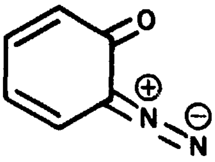

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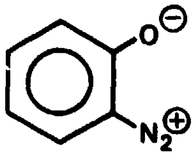

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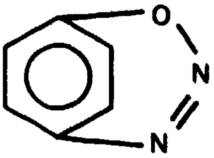

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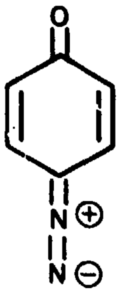

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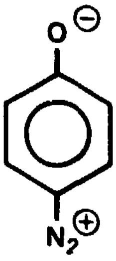

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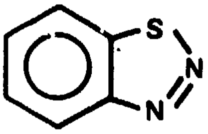

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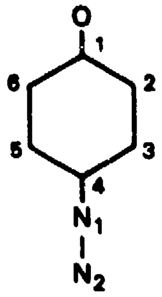
o- and *p*-Diazophenols show remarkably similar properties (chemical, physical, and spectral), indicating that the structures should also be similar. However, while at first glance **1a** might appear to be a reasonable structure, **2a** clearly is not. Further, the related benzothiadiazole, **3**, has been prepared, but it exhibits properties vastly different from those of diazophenols, being a low-melting colorless solid soluble in nonpolar solvents and volatile in steam (Reference 8). The structures **1a** and **2a** can thus be ruled out for diazophenols. (Indeed **1a** has now been prepared and has been found to be unstable, isomerizing with a half-life of 6.2 min to a product identified with the structure **1b** during the recording of an IR spectrum in a matrix of argon at 15.5 K (Reference 9).

Diazophenols might then be represented either by the quinonoid structures **1b** and **2b**, by the zwitterionic diazonium phenolate forms **1c** and **2c**, or by some resonance hybrid between these extremes. This question has been addressed in a recent monograph by Sorriso (Reference 10).

Sidgwick appears to have been the first to consider a resonance hybrid structure for diazophenols (Reference 11). Anderson and Roedel proposed the quinonoid structures **1b** and **2b** on the basis of the visible and ultraviolet (UV) spectra and their similarity to those of the corresponding quinones (Reference 12). Le Fèvre concluded, however, on the basis of dipole moments and IR and UV spectra that diazophenols are resonance hybrids in which the quinonoid structures are clearly favored (Reference 13). Dipole moments of 3-5 debye units (D) were measured for diazophenols in benzene solution and were compared with calculated values of 1.6 to 4.0 D for the quinonoid structures and 13.7 and 27.4 D for the *o*- and *p*-zwitterionic forms. Infrared measurements were cited in support of this conclusion. In particular the N-N stretching vibration is lower than the value of 2296 cm^{-1} found for phenyldiazonium tetrafluoroborate, while the C-O stretching vibration is also somewhat lower than that for the parent quinone (ca 1670 cm^{-1}), but far from that for a phenoxide (ca 1250 cm^{-1}) (Reference 13). However, such conclusions seem somewhat equivocal. The estimated dipole moments for the zwitterionic structures seem rather high, and the N-N stretching vibrations could equally well be due to the triple bond of the diazonium function in the zwitterionic form or to the cumulated double bond of the diazide moiety in the quinonoid form.

Mention should be made of the Hückel molecular orbital calculations of Kazitsyna and co-workers, who concluded that *o*- and *p*-diazophenols, indeed, each show elements of both quinonoid and zwitterionic structures (Reference 14). In the molecule **4** for example, it was found that the C-C bond order was slightly lower than double, that the negative charge on oxygen was slightly higher than is usual for a carbonyl oxygen, and that the bond order for C(1)-C(2) and C(1)-C(6) is very close to that for a quinone. However, the bond order for C(3)-C(4) and C(4)-C(5) is significantly higher, and the C(4)-N(1) and N(1)-N(2) bonds are almost entirely single and triple, respectively. Further, the positive charge is localized on the nitrogen atoms, while the negative charge is distributed between the oxygen atom and the ring carbons C(2), C(4), and C(6) as represented by **5**. The precise charge distribution is of course affected by ring substituents, if any, but a structure such as **5** appears to account best for the properties of diazophenols.



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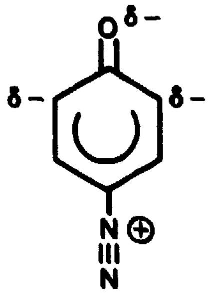

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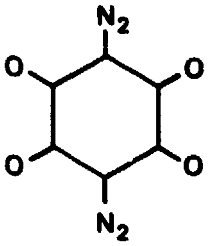
In light of the uncertain structure of diazophenols, it is surprising that so little has been done in the way of X-ray crystal structure determination. Indeed, only two studies have been reported to date, namely those on 6 and 7 (Reference 15 and 16). Each showed evidence of a carbonyl C-O bond, a C-N single bond and a N-N triple bond, but interestingly these materials have been described as "not representative of this class of compound" and "cannot give insight on the electronic structure of these molecules" (Reference 10). (Our own studies suggest that this could not be further from the case.) We, therefore, determined to examine both the X-ray crystal structures and the ^{13}C nuclear magnetic resonance (NMR) spectra of selected diazophenols in order to shed some light on this subject. The results of that study are presented in this paper, together with pertinent explosive data compiled for these compounds.



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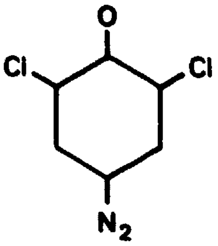

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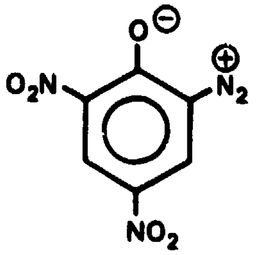
MATERIALS

The compounds selected for this study were those previously designated 2-diazo-4,6-dinitrophenol (DDNP or DINOL), 2-diazo-5-chloro-4,6-dinitrophenol (5-Cl-DDNP), and 2-diazo-3-methyl-4,5,6-trinitrophenol (3-Me-5-NO_2-DDNP), and to which had been attributed the structures 8, 9 and 10. These materials were prepared by the method developed in this laboratory, namely, nitration of an appropriate polynitroaniline and rearrangement of the resultant nitramine (Reference 4). This procedure is illustrated in Scheme 1 and pertinent spectral data are listed in Table 1.


DDNP

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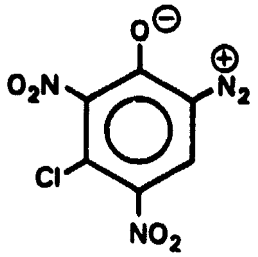
5-Cl-DDNP

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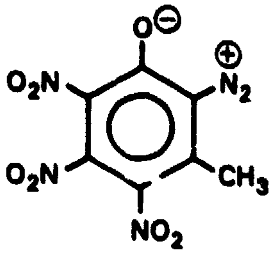
3-Me-5-NO$_2$-DDNP

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TABLE 1. Spectral Data For Diazophenols.

Compound	Spectral data
DDNP	IR (cm^{-1}) 2200 (N$_2$), 1640 (CO). 1560, 1525, 1350, 1325 (NO$_2$) ^{1}H NMR (acetone-d$_6$) (δ) 9.24 (d, 1 H, J = 3.1 Hz), 8.86 (d, 1 H, J = 3.1 Hz) Parent ion m/z 210
5-Cl-DDNP	IR (cm^{-1}) 2210 (N$_2$), 1630, 1610 (CO), 1560, 1530, 1340, 1310 (NO$_2$) ^{1}H NMR (acetone-d$_6$) (δ) 9.18 Parent ion m/z 244, 246
3-Me-5-NO$_2$-DDNP	IR (cm^{-1}) 2200 (N$_2$), 1640 (C)), 1570, 1550, 1395, 1370, 1345, 1330 (NO$_2$) ^{1}H NMR (acetone-d$_6$) (δ) 2.87 Parent ion m/z 269

CRYSTAL STRUCTURE DETERMINATION

EXPERIMENTAL SECTION

2-Diazo-4,6-dinitrophenol was crystallized as yellow-orange square plates by slow evaporation of a dichloromethane/chloroform solution. The edges of the plates were {100} and {001}. 2-Diazo-5-chloro-4,6-dinitrophenol crystallized as triangular platelets by evaporation of dichloroethane. 2-Diazo-3-methyl-4,5,6-trinitrophenol proved to be very difficult to crystallize in a form suitable for structure determination, forming twinned crystals and heavily striated aggregates. No satisfactory crystals have been obtained at this time. Unit cell parameters for DDNP and 5-Cl-DDNP (Table 2) were obtained by a symmetry-constrained least-squares fit of 25 reflections with 2θ values ranging from 9 to 28 degrees (Mo K_α). Intensity data were collected on a Nicolet R3 with graphite monochromated Mo K_α radiation using $2\theta/\theta$ scans. Other experimental details are given in Table 2. Two check reflections ((341) and (112)) were monitored every 94 reflections for DDNP; three check reflections (($\bar{1}40$), (032), and (310)) were monitored every 45 reflections for 5-Cl-DDNP. The check reflections were constant. The intensity data were corrected for Lorentz and polarization effects, but not for the absorption (μ = 1.43 cm^{-1} for DDNP, μ = 4.51 cm^{-1} for 5-Cl-DDNP).

Preliminary precession photographs for DDNP indicated orthorhombic symmetry. Systematic absences (h00, h = 2n+1; 0k0, k = 2n+1; 00ℓ, ℓ = 2n+1) indicated space group $P2_12_12_1$. A phase solution for DDNP was obtained from the multisolution direct methods of SHELXTL (Reference 17) only after three reflections frequently forming negative quartets and three reflections that were weak links in the convergence procedure were included in the starting set. For 5-Cl-DDNP, preliminary alignment precession photographs suggested 2/m Laue symmetry. Systematic absences in the diffractometer intensity data (0k0, k = 2n+1) and the calculated density suggested space group $P2_1$. With default parameters for the multisolution methods in SHELXTL, all of the carbon, nitrogen, oxygen, and chlorine atoms of 5-Cl-DDNP were observed on the first E-map.

Refinement for each compound was by SHELXTL's blocked-cascade least-squares minimization of $[\Sigma w(|F_o|-k|F_c|)^2]$ for 93 parameters of DDNP and 103 parameters of 5-Cl-DDNP. Weights were $w = 1/[\sigma_F^2 + gF^2]$, with g = 0.0007 for DDNP and g = 0.0006 for 5-Cl-DDNP. For 5-Cl-DDNP the y-coordinate of Cl(1) was held constant during refinement to fix the origin. In DDNP N(1), N(2) and the oxygen atoms of the nitro groups (O(2), O(3), O(4), and O(5)) were refined anisotropically. The hydrogen atoms were observed on the first difference Fourier map after a solution was obtained and were subsequently constrained to "ride" on their adjacent carbon atoms with fixed geometry during refinement, but without constraints on their thermal paramenters. The maximum shift to estimated standard deviation (esd) ratio for the final cycle for DDNP was less than 0.02. The final Fourier map had peaks and troughs ranging from +0.82 to −0.57 $e^-/Å^3$. All but one of the six strongest difference peaks (+0.82 to +0.41 e^-) were associated with the midpoints of the C-C bonds of the ring, suggesting that the carbon atoms might have been better modelled with anisotropic thermal parameters. For 5-Cl-DDNP, the terminal nitrogen of the diazonium group (N(2)), all of the oxygen atoms, and the chlorine atom were refined anisotropically. All other atoms were refined isotropically, including the one hydrogen atom H(1), which was refined without constraints. The final least-squares cycle had shift/esd ratios of less than 0.02. The final difference Fourier map for 5-Cl-DDNP had peaks and troughs of +0.27 to −0.27 $e^-/Å^3$.

TABLE 2. Crystallographic Data and Experimental Conditions.

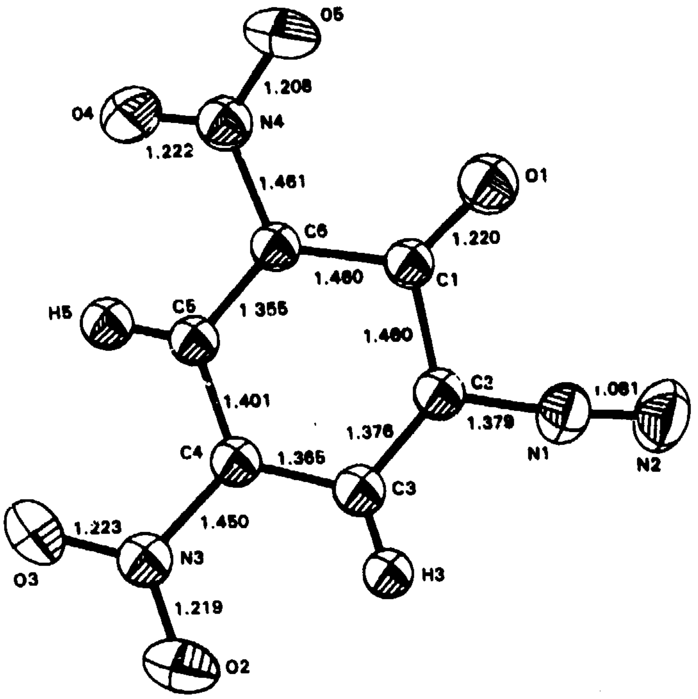
Parameter	DDNP	5-Cl-DDNP
Formula and weight	$C_6H_2N_4O_5$ 210.11 g/mol	$C_6HN_4O_5Cl$ 244.55 g/mol
Unit cell	a = 6.184(2), b = 8.625(3), c = 15.222(4)Å, Vol. = 811.96(41)Å^3	a = 4.964(2), b = 10.287(4), c = 8.644(3)Å, β = 101.21(3) deg, Vol. = 432.98(28)Å^3
	Orthorhombic, $P2_12_12_1$, Z = 4	Monoclinic, $P2_1$, Z = 2
Density	D_x = 1.719 g/cm^3	D_x = 1.876 g/cm^3
Crystal size	~ 0.10 x 0.34 x 0.40 mm	~ 0.04 x 0.34 x 0.26 mm
Data collection		
Scan	$2\theta/\theta$	$2\theta/\theta$
Range	1 deg<$K\alpha_1(2\theta_{hkl})$ to 1 deg>$K\alpha_2(2\theta_{hkl})$	1 deg<$K\alpha_1(2\theta_{hkl})$ to 1.03 deg<$K\alpha_2(2\theta_{hkl})$
Speed	Fixed, 4 deg/min	Variable, 2 to 6 deg/min
Background/scan time	1.0	1.0
Data range	4 to 60 deg (2θ), [λ = 0.71069Å (monochr)]	4 to 53 deg (2θ), [λ = 0.71069Å (monochr)]
Octants/hkl	$\bar{h}k\ell$, $hk\ell$, [h, -9 to +9/k, 0 to 13/ℓ, 0 to 22]	$\bar{h}k\bar{\ell}$, $\overline{hk}\ell$, $hk\bar{\ell}$ (partial, complete to 50 deg), $hk\ell$ (partial, complete to 50 deg) [h, -7 to +7/k, 0 to 13/ℓ, -11 to +11]
Number of measured reflections	2762	2305
Refinement		
Number of unique reflections	2375	952
R(int) [R(merge)]	0.0067	0.0172
Number observed	1488 with $\lvert F_o \rvert > 5\sigma_F$ (in refinement)	870 with $\lvert F_o \rvert > 4\sigma_F$ (in refinement)
Number of parameters	93	103
R, wR, S	0.061, 0.070, 1.58	0.039, 0.049, 1.39

DISCUSSION

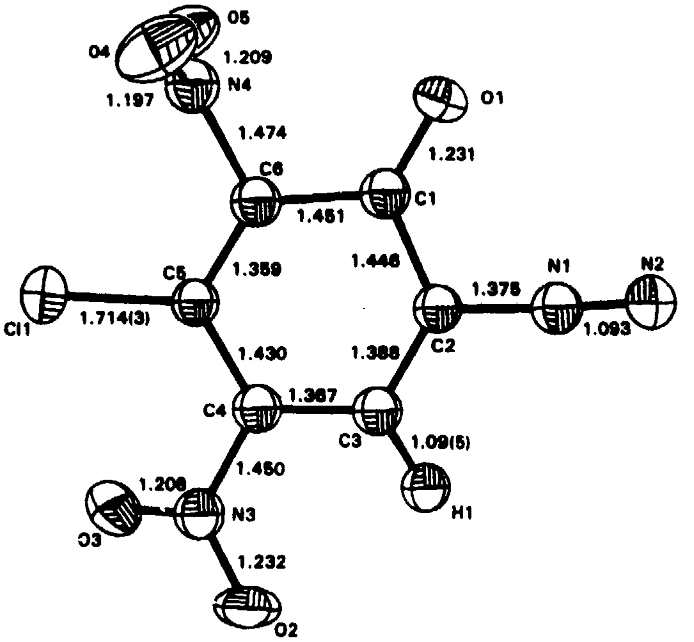
Bond lengths, bond angles, and atom labelling for DDNP and 5-Cl-DDNP are shown in Figures 1 and 2. Atomic coordinates, thermal parameters, bond lengths, and bond angles for each molecule, hydrogen atom coordinates, and thermal parameters are listed in Appendixes A and B.

The most striking feature of these structures is their resemblance to each other and their similarity to 7 (Reference 16), the fact that the latter compound is a para-diazophenol notwithstanding. Indeed the resemblance to the related 6 is also noteworthy (Reference 17). The C(1)-O(1) bond lengths for DDNP and 5-Cl-DDNP (1.220, 1.231 Å) are typical of a carbonyl double bond, as are the values of 1.221 and 1.208 Å for 7 and 6, respectively. A bond length of about 1.42 Å would be expected for a carbon-oxygen single bond. The N(1)-N(2) bonds (1.081 and 1.093 Å) are very short, as are those for 7 and 6, and are similar to the N-N bond length for molecular nitrogen (1.0976 Å). This is the same as the bond length observed for aryl diazonium salts (1.09 to 1.11 Å). The C(2)-N(1) bond length (1.379 and 1.375 Å) may be compared with a value of about 1.40 Å obtained for benzenediazonium chloride. The C(1)-C(6) and C(1)-C(2) bonds are longer than is normally found in aromatic rings (ca. 1.39 Å), while the other carbon-carbon bonds (with the possible exception of C(4)-C(5) in 5-Cl-DDNP) are typical of aromatic rings (References 18 through 20). The C(6)-C(1)-C(2) interior ring bond angle in each molecule is significantly less than the other bond angles of the ring system.

Listed in Table 3 are the results of the best-plane calculations for the six carbon atoms for each molecule. In DDNP, O(1), N(1), and N(4) are approximately in the plane of the ring; in 5-Cl-DDNP, O(1), N(3), and the chlorine atom lie in the plane of the ring, while N(1) is marginally out of plane (0.067 Å). The oxygen atoms of the nitro groups in each molecule are out of plane, indicating that the nitro groups are rotated. In DDNP the plane of the nitro group O(2)-N(3)-O(3) is rotated by 3.7 deg; the O(4)-N(4)-O(5) plane is rotated by 28.8 deg. In 5-Cl-DDNP the O(2)-N(3)-O(3) plane is rotated by 29.3 deg from the plane of the ring, and the O(4)-N(4)-O(5) plane by 87.0 deg.

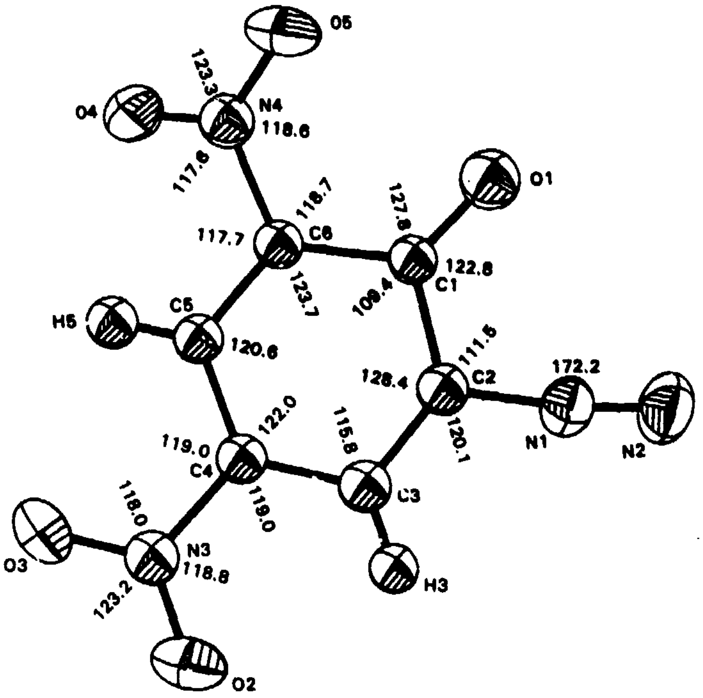


DDNP

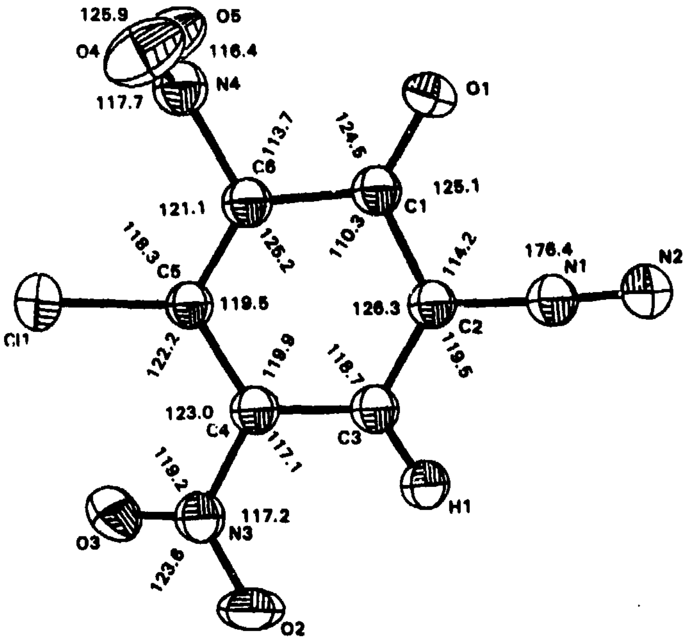


5-Cl-DDNP

FIGURE 1. Bond Lengths of DDNP and 5-Cl-DDNP. Esds for DDNP and 5-Cl-DDNP are 0.004 to 0.005 and 0.005 to 0.006 Å, respectively.



DDNP



5-Cl-DDNP

FIGURE 2. Bond Angles of DDNP and 5-Cl-DDNP. Esds for DDNP and 5-Cl-DDNP are 0.3 to 0.4 and 0.3 to 0.5 deg, respectively.

TABLE 3. Best Planes for DDNP and 5-Cl-DDNP.

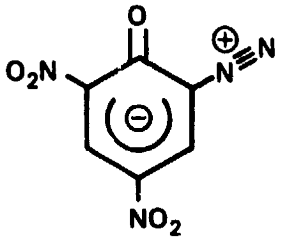
DDNP[a]			5-Cl-DDNP[b]		
Atom	Deviations from plane	Weight	Atom	Deviations from plane	Weight
C(1)	-0.0268	1.0000[c]	C(1)	-0.0000	1.0000[c]
C(2)	0.0200	1.0000[c]	C(2)	-0.0115	1.0000[c]
C(3)	0.0048	1.0000[c]	C(3)	0.0144	1.0000[c]
H(3)	0.0130	1.0000	C(4)	-0.0061	1.0000[c]
C(4)	-0.0222	1.0000[c]	C(5)	-0.0054	1.0000[c]
C(5)	0.0118	1.0000[c]	C(6)	0.0086	1.0000[c]
H(5)	0.0359	1.0000	H(1)	-0.0426	1.0000
C(6)	0.0124	1.0000[c]	N(1)	-0.0672	1.0000
N(1)	0.0598	1.0000	N(2)	-0.1168	1.0000
N(2)	0.0926	1.0000	N(3)	-0.0310	1.0000
N(3)	-0.0915	1.0000	N(4)	0.0801	1.0000
N(4)	0.0586	1.0000	O(1)	-0.0201	1.0000
O(1)	-0.0508	1.0000	O(2)	0.4704	1.0000
O(2)	-0.1249	1.0000	O(3)	-0.5776	1.0000
O(3)	-0.1272	1.0000	O(4)	1.1651	1.0000
O(4)	0.6037	1.0000	O(5)	-0.9729	1.0000
O(5)	-0.4366	1.0000	Cl(1)	0.0121	1.0000

[a] Equation of plane number 1 for DINOL. 2.996(0.038) X + 7.235(0.019) Y + (3.775(0.012) Z = 6.4971(0.0103).

[b] Equation of plane number 1 for 5-Cl-DDNP. 3.623(0.011) X + 2.463(0.030) Y + -6.654(0.019) Z = 0.3149(0.0067).

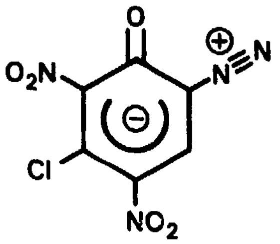
[c] Atoms contributing to the best-plane calculations.

From these results it may be concluded that neither the quinonoid structure of **1b** nor the zwitterionic form **1c** provides a satisfactory model for the ortho-diazophenols DDNP and 5-Cl-DDNP, nor indeed does some tautomeric structure intermediate between the two. Rather, these molecules appear to contain discrete features of each structure. On the one hand, the short C(1)-O(1) bond length, the long C(6)-C(1) and C(1)-C(2) bond lengths, and the smaller C(6)-C(1)-C(2) bond angle are indicative of a carbonyl function. On the other hand, the remaining ring bond lengths and angles seem typical of a benzenoid aromatic system, while the C(2)-N(1) and N(1)-N(2) bond lengths are those anticipated for an aryl diazonium moiety. Piecing these features together leads to the structures **11** and **12** for DDNP and 5-Cl-DDNP, and by analogy to the structure **13** for 3-Me-5-NO$_2$-DDNP. Such structures resemble closely those proposed by Kazitsyna and co-workers (Reference 14). The out of plane distortion of the nitro groups, previously observed in nitroaromatics (Reference 21), may be understood in terms of the steric interaction between adjacent substituents about the carbocyclic rings.



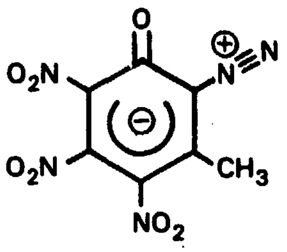
DDNP

11



5-Cl-DDNP

12



3-Me-5-NO_2-DDNP

13

^{13}C NUCLEAR MAGNETIC RESONANCE

EXPERIMENTAL SECTION

^{13}C Nuclear magnetic resonance spectra of DDNP, 5-Cl-DDNP, and 3-Me-5-NO_2-DDNP were recorded using an IBM NR-80 instrument operating at 20 MHz and a Nicolet NT-200 instrument operating at 50 MHz. Samples were prepared as saturated solutions in acetone-d_6 and filtered through a glass wool plug into 10 and 12 millimeter NMR tubes. The spectra were recorded under broad band proton decoupling conditions, with pulse width of 30 deg and recycle time of 9 s for the IBM spectrometer and pulse width of 45 deg and recycle time of 7.4 s for the Nicolet instrument. With the exception of the 3-Me-5-NO_2-DDNP spectrum on the Nicolet instrument, which was run at 0°C to minimize decomposition during recording, all spectra were run at ambient temperature, about 40°C. Chemical shifts were referenced secondarily to tetramethylsilane (TMS) through the carbon signals for the solvent (acetone-d_6). Scans were accumulated overnight (16 to 18 hours) to achieve a satisfactory signal to noise ratio. In certain cases broad peaks were identified by signal enhancement techniques using exponential multiplication. Gaussian multiplication was applied where necessary to enhance resolution and to allow separation of overlapping peaks.

DISCUSSION

The ^{13}C NMR data obtained on both the IBM and the Nicolet instruments for DDNP, 5-Cl-DDNP, and 3-Me-5-NO_2-DDNP are assembled in Table 4 and are assigned on the basis of both chemical shifts and peak shapes and intensities. ^{13}C Nuclear magnetic resonance chemical shifts are particularly sensitive to changes in electron density, and simple additive relationships have been developed to predict chemical shifts in certain series based solely on the type and position of the substituents. These predictive relationships have proven remarkably accurate, provided the effects of steric crowding are not too severe. ^{13}C Chemical shifts for benzenoid aromatics can be predicted accurately if there is no ortho substitution (Reference 22). Thus, prediction of chemical shifts could be made for the zwitterionic structures of the diazophenols (**8**, **9**, and **10**, respectively); these are also presented in Table 4. (It will be noted, of course, that there is significant steric crowding in the diazophenols, which limits the accuracy of the predictions.) However, the use of such relationships depend on the existence of an appropriate data base, and unfortunately, no data base exists for the easy prediction of ^{13}C chemical shifts for the quinonoid models.

TABLE 4. ^{13}C NMR Spectra of Diazophenols.

Compound	Carbon	^{13}C Chemical Shift, ppm		
		IBM	Nicolet	Calculated[a]
DDNP	1	165.8	165.69	174.8
	2	98.3	98.36	109.2
	3	134.7	134.20	137.1
	4	130.6	130.89	141.0
	5	131.1	131.10	135.8
	6	142.6	142.58	146.4
5-Cl-DDNP	1	164.1	164.35	175.8
	2	93.9	94.28	107.2
	3	131.9	132.22	138.1
	4	131.5	131.55	141.4
	5	131.4	131.40	142.2
	6	146.9	147.20	146.6
3-Me-5-NO_2-DDNP	Me	17.9	17.96	
	1	164.0	163.74	175.6
	2	101.9	102.44	115.8
	3	145.3	145.73	147.2
	4	126.7	126.25	136.3
	5	146.3	146.05	151.6
	6	136.7	135.65	138.0

[a] Calculated for the zwitterionic structures **8**, **9**, and **10**, respectively.

The ^{13}C NMR spectra recorded on the IBM instrument were repeated using the Nicolet spectrometer in order to confirm broad nitro-aromatic peaks and to help resolve overlapping signals. As indicated by the data in Table 4, the correlation between the spectra obtained using the two instruments was excellent. Furthermore, there was general agreement of chemical shifts with those anticipated for such compounds, although there is sufficient deviation from the calculated values to allow comment and speculation. First, the signals are generally downfield from the positions predicted for the zwitterionic model. This observation is indicative of a higher electron density in the carbon ring and consistent with the bonding postulated on the basis of the X-ray structure determination. Second, the difference between the calculated and experimental chemical shifts is greatest for C(1), C(2) and C(4), again consistent with the postulated bonding. It is perhaps surprising that there is not a similar discrepancy for C(6), but this may be attributable to the lack of planarity of the nitro group on C(6) with the ring system.

MOLECULAR ORBITAL CALCULATIONS

Very recently, Professor K. N. Houk and Mr. Wang Xuebao of the University of California, Los Angeles, carried out molecular orbital calculations for us on DDNP using both the MNDO (Reference 23) and AM-1 (Reference 24) semi-empirical methods. Their results will not be discussed in any detail here, but suffice it to say that these methods appear to be quite applicable to this system. Both methods predicted geometries in excellent qualitative agreement with those obtained experimentally by X-ray crystallography, despite the fact that AM-1 systematically overestimates bond lengths and MNDO does a little worse. Bond lengths and net atomic charges calculated are entirely consistent with the essential features of the deduced structures, namely a carbonyl C–O bond, a positive charge on the diazonium function with essentially a C-N single bond and a N-N triple bond, and the negative counter charge distributed over the carbocyclic ring system.

EXPLOSIVE PROPERTIES

During the synthesis of polynitroaromatics (References 1 through 3), the formation of diazophenols was regarded as bothersome since they were manifested as highly colored, sensitive impurities. However, the development of an efficient route to diazophenols via the polynitroaromatic nitramines (Reference 4) made available a new class of sensitive explosives. Indeed, under the names DDNP and DINOL (the latter name should not be used, to avoid confusion with another material of the same name), 2-diazo-4,6-dinitrophenol has already found application as a primary explosive ingredient for use in electrical detonators (Reference 6). Therefore, selected diazophenols were screened for explosive sensitivity prior to further evaluation. Elsewhere, the diazophenols were selected as a class of compounds with which to examine the sensitization of lead azide to stab and percussion initiaion. These latter experiments have already been reported (Reference 25), but relevent data are included in this report for the sake of completeness.

As already noted, diazophenols decompose with various degrees of vigor in the temperature range of about 130 to 180°C. 2-Diazo-4,6-dinitrophenol melts in a capillary tube at 157°C and then decomposes; 5-Cl-DDNP decomposes in the solid phase at 178°C without the formation of liquid; 3-Me-5-NO_2-DDNP explodes at 157°C to leave a liquid residue. These results are also reflected in differential scanning calorimetry (DSC) results (Perkin-Elmer DSC-2 equipped with a scanning autozero SAZ accessory) illustrated in Figure 3 and listed in Table 5. The latter shows a single exotherm corresponding to decomposition immediately preceded by a sharp melting endotherm for DDNP, a simple broad decomposition exotherm for 5-Cl-DDNP, and a sharper exotherm for 3-Me-5-NO_2-DDNP with a shoulder corresponding with liquid formation on the leading edge. Also included in Table 5 are the ignition temperatures for the three diazophenols. In this test the sample explosive (50 mg) is heated in a glass tube at 5°C/min until ignition (in this case with a sharp report and shattering of the glass tube). The differences in the results of the three tests are, of course, attributable to differences in sample size and heating rate.

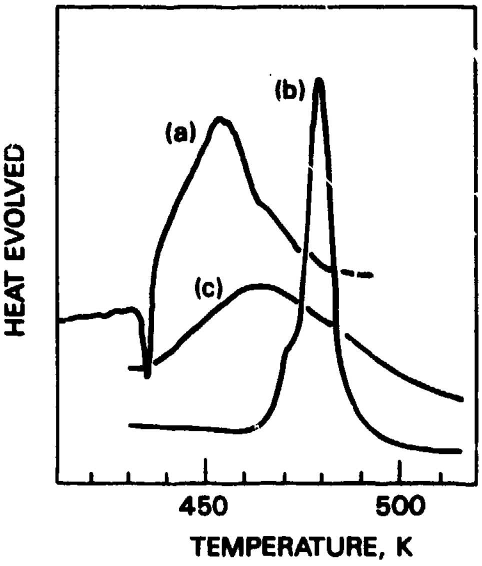


FIGURE 3. DSC Thermograms for Diazophenols, Heating Rate 20 K/min, (a) DDNP, (b) 5-Cl-DDNP, and (c) 3-Me-5-NO_2-DDNP.

TABLE 5. Thermochemical Data for Diazophenols.

Compound	Ignition temperature, T of I, °C	DSC data		
		Thermogram, T_{max}, °C	H_{decomp}	
			kJ/g	kJ/mol
DDNP	157	168.8	1.641	387
5-Cl-DDNP	178	192.6	1.883	460
3-Me-5-NO_2-DDNP	157	177.3	2.343	630

The sensitivity of explosives to impact may be illustrated in a simple hammer/anvil test, with the response varying from a mild explosion to a sharp, ringing report customarily associated with primary explosives. Each of the diazophenols under discussion produced the more vigorous response in this crude screening test, and this sensitivity was reflected in more rigorous test results. Thus, when these materials were subjected to impact testing on the B of M (Bureau of Mines, Pittsburgh, Penna.) machine using the Type 12 tool and a 2.0-kg drop weight, each was initiated at a 50% drop height in the range of about 8 to 10 cm. This may be compared with lead azide, for which a value of 15 to 16 cm is commonly obtained. In the ABL (Allegany Ballistics Laboratory, Cumberland, Md.) pendulum friction test, the 50% load for DDNP was 436 lbs, with 5-Cl-DDNP being somewhat more sensitive at 120 lbs and 3-Me-5-NO_2-DDNP rather less sensitive at 691 lbs. In each case a "fire" was characterized by a dim flash in which most of the explosive was consumed, leaving a residual smudge. In the ERL (Explosives Research Laboratory, Bruceton, Penna.) electrostatic test, DDNP was initiated at 0.09 J, while 5-Cl-DDNP is rather less sensitive at 0.17 J, and 3-Me-5-NO_2-DDNP is slightly more sensitive at 0.08 J. In this test a "fire" was typified by a bright flash, smoke, and a residual smudge. These results are collated in Table 6.

TABLE 6. Sensitivity Data for Diazophenols.

Compound	B of M impact sensitivity, cm	ABL friction sensitivity, lb	ERL electrostatic sensitivity, J	Stab sensitization, mJ
DDNP	9.4	436	0.09	4.0
5-Cl-DDNP	8.0	120	0.17	4.0
3-Me-5-NO_2-DDNP	7.7	691	0.08	7.6
Lead azide	15.0-16.0	...	...	~ 1000
RDX	25.0	407	>0.25	
Tetracene	14.0	...	...	3.3

Also included in Table 6 are the results obtained in experiments designed to investigate the sensitization of lead azide to stab initiation and to develop an alternative to tetracene for use in stab and percussion devices. These results were obtained in a wider project to examine the stab initiation process (Reference 25) but are included for completeness. In these tests compositions were prepared by mixing the diazophenol with lead azide in the ratio 1:10, and the composition (40 mg) was pressed into an experimental detonator tube already containing a "back filling" of lead monoxide (280 mg). This inert "back filling" ensured that the explosive pellet remained intact during testing. The experimental detonator was supported in an aluminum holder held in a mild steel base. A free falling striker weighing 14.5 g fitted with a needle was dropped from a preset height to impact on the detonator. The needle was silver steel hardened to 650 Vickers Hardness Number (VHN) with a 0.08 to 0.20 mm flat on the tip. The striker was fitted with a new needle after every test, and the drop height was varied following the Bruceton staircase method, depending on whether the result of the previous test was a "fire" or not. The 50% fire level was calculated using standard Bruceton statistical analysis and then converted to impact energies. The stab initiation energy for pure lead azide is about 1000 mJ, and the values of 4.0, 4.0, and 7.6 mJ for mixtures of lead azide with 10% of added diazophenol represent substantial sensitization. Indeed these values may be compared favorably with values of about 3 mJ for commonly used stab and percussion mixes such as "L" mix and NOL 130.

CONCLUSION

The bonding structure of diazophenols (diazo oxides, diazonium phenolates, diazoquinones, or quinone diazides) has been assigned on the basis of X-ray crystal structure determinations. These compounds are comprised of a carbonyl C-O bond, a diazonium function with a C-N single bond and a N-N triple bond, and the negative counter charge distributed over the carbocyclic ring system. This conclusion is fully in accord with ^{13}C NMR spectra and molecular orbital calculations (MNDO and AM-1) reported here and with previously reported spectral and physical data. Furthermore, this bonding description is reminiscent of those obtained previously for **6** (Reference 15) and 7 (Reference 16) but regarded as atypical (Reference 10) and with that proposed by Kazitsyna on the basis of Hückel molecular orbital calculations (Reference 14).

The diazophenols considered here also show properties of thermal stability and explosive sensitivity typical of primary explosives, and may find application as detonants or stab sensitizing additives for use in stab or percussion initiated compositions.

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Appendix A

ATOMIC COORDINATES AND THERMAL PARAMETERS, BOND LENGTHS, BOND ANGLES, ANISOTROPIC THERMAL PARAMETERS, AND HYDROGEN COORDINATES AND THERMAL PARAMETERS FOR DDNP

TABLE A-1. Atom Coordinates, x 10^4, and Thermal Parameters, $Å^3$ x 10^3.

Atom	x	y	z	U
C(1)	-198(5)	4647(4)	8391(2)	29(1)
C(2)	-1349(6)	5537(4)	7722(2)	32(1)
C(3)	-3304(6)	6288(4)	7794(3)	33(1)
C(4)	-4263(6)	6227(4)	8601(2)	30(1)
C(5)	-3279(6)	5492(4)	9319(2)	30(1)
C(6)	-1364(6)	4750(4)	9223(2)	29(1)
N(1)	-245(5)	5545(5)	6935(2)	41(1)[a]
N(2)	787(7)	5462(7)	6363(2)	63(1)[a]
N(3)	-6367(5)	6941(4)	8719(2)	36(1)
N(4)	-425(5)	4019(4)	10000(2)	36(1)
O(1)	1508(5)	3983(3)	8246(2)	44(1)
O(2)	-7221(5)	7575(4)	8094(2)	52(1)[a]
O(3)	-7207(4)	6861(4)	9445(2)	47(1)[a]
O(4)	-862(5)	4581(4)	10715(2)	52(1)[a]
O(5)	735(6)	2906(4)	9902(2)	62(1)[a]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE A-2. Bond Lengths, Å.

Bond	Length, Å	Bond	Length, Å
C(1)-C(2)	1.460(5)	C(1)-C(6)	1.460(5)
C(1)-O(1)	1.220(4)	C(2)-C(3)	1.376(5)
C(2)-N(1)	1.379(5)	C(3)-C(4)	1.365(5)
C(4)-C(5)	1.401(5)	C(4)-N(3)	1.450(5)
C(5)-C(6)	1.355(5)	C(6)-N(4)	1.461(5)
N(1)-N(2)	1.081(5)	N(3)-O(2)	1.219(5)
N(3)-O(3)	1.223(4)	N(4)-O(4)	1.222(4)
N(4)-O(5)	1.208(5)		

TABLE A-3. Bond Angles, degrees.

Bond angle	Deg	Bond angle	Deg
C(2)-C(1)-C(6)	109.4(3)	C(2)-C(1)-O(1)	122.8(3)
C(6)-C(1)-O(1)	127.8(3)	C(1)-C(2)-C(3)	128.4(3)
C(1)-C(2)-N(1)	111.5(3)	C(3)-C(2)-N(1)	120.1(3)
C(2)-C(3)-C(4)	115.8(3)	C(3)-C(4)-C(5)	122.0(3)
C(3)-C(4)-N(3)	119.0(3)	C(5)-C(4)-N(3)	119.0(3)
C(4)-C(5)-C(6)	120.6(3)	C(1)-C(6)-C(5)	123.7(3)
C(1)-C(6)-N(4)	118.7(3)	C(5)-C(6)-N(4)	117.7(3)
C(2)-N(1)-N(2)	172.2(4)	C(4)-N(3)-O(2)	118.8(3)
C(4)-N(3)-O(3)	118.0(3)	O(2)-N(3)-O(3)	123.2(3)
C(6)-N(4)-O(4)	117.6(3)	C(6)-N(4)-O(5)	118.6(3)
O(4)-N(4)-O(5)	123.8(4)		

TABLE A-4. Anisotropic Thermal Parameters, $\text{Å}^2 \times 10^3$.[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	39(2)	50(2)	34(2)	-1(2)	2(1)	-6(2)
N(2)	53(2)	98(3)	39(2)	2(2)	11(2)	-2(3)
O(2)	42(2)	47(2)	69(2)	7(2)	-13(2)	7(1)
O(3)	36(2)	48(2)	58(2)	-6(2)	7(1)	5(1)
O(4)	56(2)	66(2)	34(1)	4(2)	-4(1)	11(2)
O(5)	66(2)	59(2)	62(2)	12(2)	-4(2)	31(2)

[a] The anisotropic temperature factor exponent takes the form: $-2\Pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2\,hka^*b^*U_{12})$.

TABLE A-5. Hydrogen Coordinates, x 10^4, and Thermal Parameters, $\text{Å}^2 \times 10^3$.

Atom	x	y	z	U
H(3)	-3952	6822	7308	30(10)
H(5)	-3969	5516	9883	33(9)

Appendix B

ATOMIC COORDINATES AND THERMAL PARAMETERS, BOND LENGTHS, BOND ANGLES, ANISOTROPIC THERMAL PARAMETERS, AND HYDROGEN COORDINATES AND THERMAL PARAMETERS FOR 5-Cl-DDNP.

TABLE B-1. Atom Coordinates, x 10^4, and Thermal Parameters, $Å^2$ x 10^3.

Atom	x	y	z	U
C(1)	7330(9)	802(4)	3815(5)	31(1)
C(2)	7786(7)	2067(4)	4548(4)	30(1)
C(3)	6269(8)	3184(4)	4097(5)	31(1)
C(4)	4045(8)	3106(4)	2888(5)	32(1)
C(5)	3382(7)	1901(4)	2080(4)	29(1)
C(6)	4968(8)	838(5)	2529(5)	32(1)
N(1)	9935(7)	2108(4)	5818(4)	35(1)
N(2)	11660(8)	2076(4)	6819(5)	50(1)[a]
N(3)	2449(8)	4282(4)	2492(4)	35(1)
N(4)	4437(8)	-403(4)	1673(4)	37(1)
O(1)	8707(7)	-177(3)	4233(4)	42(1)
O(2)	3659(7)	5326(4)	2783(4)	48(1)[a]
O(3)	19(7)	4195(4)	1958(4)	51(1)[a]
O(4)	5490(9)	-569(4)	555(4)	61(1)[a]
O(5)	3041(9)	-1184(4)	2206(5)	60(1)[a]
Cl(1)	675(2)	1749	524(1)	46(1)[a]
H(1)	6774(91)	4069(48)	4785(53)	33(11)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE B-2. Bond Lengths, Å.

Bond	Length, Å	Bond	Length, Å
C(1)-C(2)	1.446(6)	C(1)-C(6)	1.451(6)
C(1)-O(1)	1.231(5)	C(2)-C(3)	1.388(6)
C(2)-N(1)	1.375(5)	C(3)-C(4)	1.367(5)
C(4)-C(5)	1.430(6)	C(4)-N(3)	1.450(6)
C(5)-C(6)	1.359(6)	C(5)-Cl(1)	1.714(3)
C(6)-N(4)	1.474(6)	N(1)-N(2)	1.093(5)
N(3)-O(2)	1.232(5)	N(3)-O(3)	1.208(5)
N(4)-O(4)	1.197(6)	N(4)-O(5)	1.209(6)
H(1)-C(3)	1.09(5)		

TABLE B-3. Bond Angles, degrees.

Bond angle	Deg	Bond angle	Deg
C(2)-C(1)-C(6)	110.3(4)	C(2)-C(1)-O(1)	125.2(4)
C(6)-C(1)-O(1)	124.5(4)	C(1)-C(2)-C(3)	126.3(3)
C(1)-C(2)-N(1)	114.2(4)	C(3)-C(2)-N(1)	119.5(4)
C(2)-C(3)-C(4)	118.7(4)	C(3)-C(4)-C(5)	119.9(4)
C(3)-C(4)-N(3)	117.1(4)	C(5)-C(4)-N(3)	123.0(3)
C(4)-C(5)-C(6)	119.5(3)	C(4)-C(5)-Cl(1)	122.2(3)
C(6)-C(5)-Cl(1)	118.3(3)	C(1)-C(6)-C(5)	125.2(4)
C(1)-C(6)-N(4)	113.7(4)	C(5)-C(6)-N(4)	121.1(3)
C(2)-N(1)-N(2)	176.4(5)	C(4)-N(3)-O(2)	117.2(3)
C(4)-N(3)-O(3)	119.2(4)	O(2)-N(3)-O(3)	123.6(4)
C(6)-N(4)-O(4)	117.7(4)	C(6)-N(4)-O(5)	116.4(4)
O(4)-N(4)-O(5)	125.9(4)	C(2)-C(3)-H(1)	118.9(2.3)
		C(4)-C(3)-H(1)	122.2(2.4)

TABLE B-4. Anisotropic Thermal Parameters, $Å^2 \times 10^3$.[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	49(2)	40(2)	51(2)	-3(2)	-11(2)	2(2)
O(1)	47(2)	29(2)	45(2)	-3(1)	-3(1)	12(1)
O(2)	56(2)	23(2)	64(2)	5(1)	11(2)	1(1)
O(3)	43(2)	45(2)	60(2)	7(2)	-1(1)	11(2)
O(4)	79(3)	55(2)	54(2)	-20(2)	29(2)	-8(2)
O(5)	79(3)	40(2)	66(2)	-8(2)	24(2)	-21(2)
Cl(1)	48(1)	44(1)	40(1)	-3(1)	-10(1)	-1(1)

[a] The anisotropic temperature factor exponent takes the form: $-2\Pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2\,hka^*b^*U_{12})$.

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