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4-크로로-4'-메톡시-2-니트로디페닐아민의 X-선 결정 및 분자구조 결정

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The Crystal and Molecular Structure of the 4-Chloro-4'-Methoxy-2-Nitro-Diphenylamine($C_{13}H_{11}N_2O_3CL$)

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요 약

4-크로로-4'-메톡시-2-니트로디페닐아민, ($C_{13}H_{11}N_2O_3Cl$, FW=278.70)의 단위세포 상수는 a=8.169(3), b=8.883(1), c=9.150(1)Å, α=82.98(1), β=104.80(2), γ=101.43(2)°, V=627.3 Å^3, F(000)=288.0, Dc=1.48 g/cm^3, μ=3.06cm^{-1}, T=295° K, 공간군 P$\bar{1}$, 번호 2, 삼사 정계이며, Z=2이다. λ(Mo-K$_\alpha$)=0.7107Å을 사용하여 수집한 독립적인 회절 반점 1541개로 구조분석한 최종 신뢰도 값은 각각 R=0.032, Rw=0.033이며, S=0.46이다. 본 화합물은 암모니아의 두개의 수소 대신에 4-크로로-페닐기와 4-메톡시 페닐기로 치환된 물질로써, 질소와 두 페닐기 사이의 각과 결합거리 들은 각각 125.42°, 1.362 및 1.428 Å 인바 수소와 함께 SP^2-혼성결합을 하고있다. 질소를 포함한 두 면간 각은 63.29°이다. 분자간 어떠한 수소결합을 하고 있지않다.

Abstract

4-Chloro-4'-Methoxy-2-Nitrodiphenylamine, $C_{13}H_{11}N_2O_3Cl$, FW=278.70, Tricline, P$\bar{1}$ (SG=2), a=8.169(3), b=8.883(1), c=9.150(1)Å, α=82.98(1), β=104.80(2), γ=101.43(2)°, V=627.3Å^3, Z=2, Dc=1.48 g/cm^3, λ(Mo-K$_\alpha$)=0.7107Å, μ=3.06cm^{-1}, F(000)=288.0, T=295°K, final R=0.032, Rw=0.033, S=0.46 for 1541 unique observed reflections. As a compound substituted from two hydrogen of ammonia with two phenyl-derivatives, the bond lengths and angle in amine group are 125.4°, 1.362, 1.428Å, and then respond to SP^2-hybride bond. The molecular structure shows a twisted conformation in the essentially planar aromatic rings giving a dihedral angle of 63.29°. The packing of the molecules is due to van der Waals forces and there are no intermolecular hydrogen bonds.

INTRODUCTION

This compound is one of a series of intermediates obtained by synthesis of planar N-Methyl phenazine(NMP)-derivatives which can be assumed to form the one dimensional molecular complex as a highly conducting NMP·TCNQ (Tetracyanoquinodimethan).[1-2] By reduction of 4-chloro-4'-methoxy-2-nitro-diphenylamine with ferrous oxalate, 4-chloro-4'-methoxy-phenazine is formed with elimination

of water and oxygen of this compound.[3] The crystal and molecular structure of the title compound has been determined as an attempt to correlate the ring closure and molecular conformation.

EXPERIMENT

Red single crystals of this compound suitable for an X-ray analysis was obtained by reaction of p-anisidine 9.6 g (0.078mol) and 2, 5-dichloronitrobenzene 9.6 g (0.05mol) with anhydrous sodium acetate 10.25 g (0.125mol) in an oil-bath at 205° -215℃ during 40 hours.[3] Analysis ; calc. : C=55.9%, H=3.85%, N=9.50%, meas. : C=55.8%, H=3.97%, N=9.88%. Unit cell parameters were calculated from an orientation matrix derived from the setting angles of 25 reflection with $20^{o}<2\theta<29^{o}$ centered on an Enraf-Nonius CAD4-diffractometer using graphite monochromatized Mo-K_{α} radiation.

Data collection (θ-2θ scans background-peak-background, $2\theta_{max}=50^{o}$) yielded 2198 unique reflections after averaging(R_{int}=0.012). Four standard reflections showed no variation during the 35.4 hr of X-ray exposure time. The intensities were corrected for Lp and the small decay but not for absorption. The 1541 reflecttions with $I>4.0\sigma(I)$ were used in the subsequent analysis. The structure was solved by direct methods and subsequent maps using SHELXS[4] and SDP package programs [5] on a PDP 11/23+ computer. All the nonhydrogen atoms were found from a three dimensional Fourier map and were refined anisotropically by full-matrix least squares calculations on F's. The function minimised $\Sigma w(F_o-F_c)^2$ with unit weights. The convergence was reached at R=0.066, R_w=0.074, 172 parameters, S=0.99. Eight of eleven all hydrogen aroms were found from difference Fourier synthese and the rest three H atoms were calculated on the basis of standard geometry. The structure was refined with anisotropic temperature factors for nonhydrogen and isotropic for all hydrogen atoms. The final results for 216 variables were R=0.032, R_w=0.033, S=0.46, $(\triangle/\sigma)_{max}$=0.00, $(\triangle\rho)_{max}$=0.175 e A^{-3}. *

*List of observed and calculated structure factors, anisotropic and isotropic thermal parameters of the atoms are aviliable from the auther(HNM).

DISCUSSION

The final positional and anisotropic thermal parameters are listed in Table 1 and 2 respectively and the bond lengths and angles in Table 3. The corresponding e.s.d.'s are shown in parentheses. The molecular structure with atomic numbering scheme are shown in Figure 1. The two least square phenylamine rings in Table 4 are essentially planar with atom N(1) deviating as much as 0.112(2) and 0.009(2).

Their bond lengths and angles were similar by comparsion with corresponding structures of Bis(p-met-

Table 1. Positional parameters and their estimated standard derivations.

Atom	X	Y	Z	B Å^2
N1	0.4888(3)	-.1440(2)	0.7991(3)	3.86(5)
C2	0.3921(3)	-.2737(3)	0.8668(3)	3.35(6)
C3	0.4397(3)	-.3068(3)	1.0225(3)	3.45(6)
C4	0.3602(3)	-.4390(3)	1.0891(3)	3.55(6)
C5	0.2321(3)	-.5396(3)	0.9998(3)	3.34(6)
C6	0.1799(3)	-.5042(3)	0.8461(3)	3.65(6)
C7	0.2615(3)	-.3715(3)	0.7798(3)	3.85(6)
O8	0.1696(3)	-.6725(2)	1.0755(2)	4.39(5)
C9	0.0321(4)	-.7752(3)	0.9916(4)	4.53(7)
C10	0.4245(3)	-.0205(3)	0.7193(3)	3.10(5)
C11	0.5237(3)	0.1039(3)	0.6504(3)	2.89(5)
C12	0.4528(3)	0.2294(3)	0.5690(3)	3.17(5)
C13	0.2836(3)	0.2334(3)	0.5561(3)	3.37(6)
C14	0.1820(3)	0.1143(3)	0.6239(3)	3.67(6)
C15	0.2506(3)	-.0083(3)	0.7022(3)	3.58(6)
CL	0.1938(1)	0.38793(9)	0.45560(9)	5.10(2)
N17	0.7047(3)	0.1115(2)	0.6634(2)	3.44(5)
O18	0.7759(2)	0.0046(2)	0.7330(2)	4.85(5)
O19	0.7849(2)	0.2242(2)	0.6058(2)	5.02(5)
H1	0.593(3)	-.138(3)	0.807(3)	2.0(6)*
H2	0.534(3)	-.235(3)	1.084(3)	1.2(5)*
H3	0.385(3)	-.464(3)	1.192(3)	1.5(6)*
H4	0.100(3)	-.573(3)	0.790(3)	1.5(6)*
H5	0.234(3)	-.353(3)	0.679(3)	0.9(5)*
H6	0.004(4)	-.867(3)	1.055(3)	3.3(7)*
H7	0.069(3)	-.812(3)	0.913(3)	2.8(7)*
H8	-.068(4)	-.734(3)	0.941(3)	3.1(7)*
H9	0.529(3)	0.311(3)	0.528(3)	1.4(6)*
H10	0.069(3)	0.120(3)	0.613(3)	2.3(6)*
H11	0.175(3)	-.089(3)	0.744(3)	1.5(6)*

Starred atoms were refined isotropically. Anisotropically equivalent displacement parameter defined as : (4/3) × [a2 B(1,1)+b2×B(2,2)+c2×B(3,3)+ab(cos gamma)×B(1,2)+ab(cos beta)×B(1,3)+bc(cos alpha)×B(2,3)]

Table 2. General displacement parameter expressions –B's.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
N1	2.87(8)	3.19(9)	5.3(1)	0.33(7)	1.23(7)	0.82(8)	3.86(5)
C2	3.10(9)	2.73(9)	4.2(1)	0.53(8)	1.05(8)	0.21(9)	3.35(6)
C3	3.3(1)	3.0(1)	4.0(1)	0.40(8)	0.78(8)	–.63(9)	3.45(6)
C4	4.1(1)	3.6(1)	3.0(1)	0.74(9)	0.91(8)	–.15(9)	3.55(6)
C5	3.4(1)	2.9(1)	3.8(1)	0.63(8)	1.18(8)	0.10(9)	3.34(6)
C6	3.4(1)	3.2(1)	3.7(1)	–.10(9)	0.25(9)	–.14(9)	3.65(6)
C7	3.9(1)	3.7(1)	3.3(1)	0.36(9)	0.39(9)	0.45(9)	3.85(6)
O8	4.83(9)	3.58(8)	4.13(8)	–.28(7)	1.17(7)	0.58(7)	4.39(5)
C9	4.0(1)	3.4(1)	5.7(1)	–.1(1)	1.2(1)	0.2(1)	4.53(7)
C10	3.11(9)	2.84(9)	3.3(1)	0.26(8)	0.73(8)	–.44(8)	3.10(5)
C11	2.55(8)	3.06(9)	3.02(9)	0.25(7)	0.75(7)	–.34(8)	2.89(5)
C12	3.3(1)	3.0(1)	3.1(1)	0.29(8)	0.84(8)	–.12(8)	3.17(5)
C13	3.6(1)	3.3(1)	3.3(1)	1.01(8)	0.64(8)	–.18(9)	3.37(6)
C14	2.86(9)	4.0(1)	4.4(1)	0.69(8)	1.04(8)	–.4(1)	3.67(6)
C15	3.03(9)	3.2(1)	4.5(1)	0.07(8)	1.42(8)	–.10(9)	3.58(6)
CL	5.02(3)	5.01(3)	5.40(3)	2.24(2)	1.24(3)	1.42(3)	5.10(2)
N17	2.86(8)	3.59(9)	3.72(9)	0.26(7)	0.8(7)	–.10(8)	3.44(5)
O18	2.95(7)	4.20(8)	7.0(1)	0.90(6)	1.07(7)	1.29(8)	4.85(5)
O19	3.36(7)	4.88(9)	6.6(1)	0.21(7)	2.12(7)	1.76(8)	5.02(5)

The form of the anisotropic displacement parameter is : exp[–0.25 < h2a2B(1,1)+k2b2B(2,2)+l2c2B(3,3)+2hkabB(1,2)+2hlacB(1,3)+2klbcB(2,3) >] where a,b and c are reciprocal lattice constants.

Table 3. Bond distances in Å and Bond angles in°

N1 – C2	1.428(5)	C10 – C11	1.414(6)
N1 – C10	1.362(5)	C10 – C15	1.414(5)
C2 – C3	1.388(6)	C11 – C12	1.406(6)
C2 – C7	1.372(6)	C11 – N17	1.441(5)
C3 – C4	1.374(6)	C12 – C13	1.365(5)
C4 – C5	1.386(6)	C13 – C14	1.390(6)
C5 – C6	1.378(6)	C13 – CL	1.741(4)
C5 – O8	1.366(4)	C14 – C15	1.367(6)
C6 – C7	1.383(6)	N17 – O18	1.239(5)
O8 – C9	1.412(5)	N17 – O19	1.219(4)
N1 – H1	0.83(5)	C9 – H7	0.96(5)
C3 – H2	0.99(4)	C9 – H8	0.95(5)
C4 – H3	0.92(4)	C12 – H9	0.96(5)
C6 – H4	0.90(4)	C14 – H10	0.92(4)
C7 – H5	0.89(4)	C15 – H11	0.97(5)
C9 – H6	0.96(6)		
C2 – N1 – C10	125.4(4)	C11 – C10 – C15	115.3(3)
N1 – C2 – C3	119.1(4)	C10 – C11 – C12	122.0(3)
N1 – C2 – C7	121.1(4)	C10 – C11 – N17	121.9(3)
C3 – C2 – C7	119.7(4)	C12 – C11 – N17	116.1(3)
C2 – C3 – C4	120.4(4)	C11 – C12 – C13	119.6(4)
C3 – C4 – C5	119.5(4)	C12 – C13 – C14	120.3(4)
C4 – C5 – C6	120.2(4)	C12 – C13 – CL	120.1(4)
C4 – C5 – O8	114.9(4)	C14 – C13 – CL	119.6(3)
C6 – C5 – O8	124.9(4)	C13 – C14 – C15	120.1(4)
C5 – C6 – C7	119.8(5)	C10 – C15 – C14	122.7(4)
C2 – C7 – C6	120.3(5)	C11 – N17 – O18	119.7(3)
C5 – O8 – C9	117.2(3)	C11 – N17 – O19	118.9(3)
N1 – C10 – C11	123.6(4)	O18 – N17 – O19	121.4(3)
N1 – C10 – C15	121.0(4)		
C2 – N1 – H1	121(3)	O8 – C9 – H7	110(3)
C10 – N1 – H1	114(3)	O8 – C9 – H8	117(3)
C2 – C3 – H2	119(2)	H6 – C9 – H7	104(4)
C4 – C3 – H2	121(2)	H6 – C9 – H8	111(4)
C3 – C4 – H3	123(3)	H7 – C9 – H8	105(4)
C5 – C4 – H3	117(3)	C11 – C12 – H9	117(2)
C5 – C6 – H4	120(3)	C13 – C12 – H9	123(2)
C7 – C6 – H4	121(3)	C13 – C14 – H10	118(3)
C2 – C7 – H5	120(2)	C15 – C14 – H10	122(3)
C6 – C7 – H5	120(2)	C10 – C15 – H11	121(2)
O8 – C9 – H6	110(3)	C14 – C15 – H11	117(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

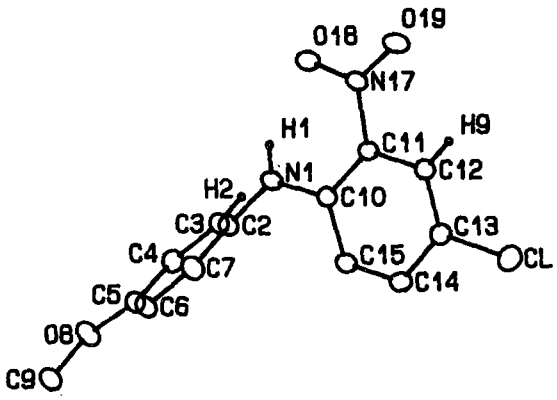

Fig. 1: A molecular drawing of 4-chloro-4'-methoxy-2-nitrodiphenylamine with atomic numbering scheme.

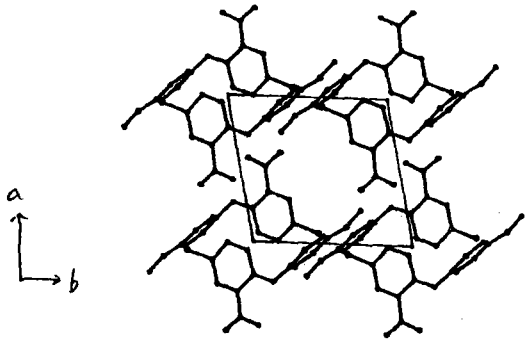

Fig. 2: Projection of unit cell content on ab Plane.

Table 4. Least squares planes

Plane No. 1

0.8510X − 0.5078Y − 0.1341Z − 1.3454=0			
Atom	Distance	Atom	Distance
N1	0.112	C6	-0.052
C2	-0.024	C7	-0.044
C3	-0.041	C8	0.077
C4	-0.039	C9	0.028
C5	-0.016		

Plane No. 2

0.0764X − 0.5350Y − 0.8414Z + 5.3671=0			
Atom	Distance	Atom	Distance
N1	0.009	C15	-0.020
C10	0.012	CL	0.008
C11	0.025	N17	-0.002
C12	0.027	O18	0.001
C13	0.001	O19	-0.034
C14	-0.027		

Table 5. Selected torsion angles

C10 - N1 - C2 - C3	-120.0(3)
C10 - N1 - C2 - C7	64.6(4)
C2 - N1 - C10 - C11	-178.2(2)
C2 - N1 - C10 - C15	2.7(4)
C10 - C11 - N17 - O18	2.1(4)
C10 - C11 - N17 - O19	-177.6(2)
C12 - C11 - N17 - O18	-179.7(2)
C11 - C12 - C13 - CL	-179.8(2)
CL - C13 - C14 - C15	179.4(2)

hoxyphenyl) Nitric-oxide[6] and m-Chloro-nitrobenzene[7]. The intramolecular hydrogen bond of N1-H1-O18 (0.83, 1.96, 2.620 Å, 136.5°) contributes to stabilization of twisted conformation in order to minimize the repulsions between the nonbonded atoms. The ring closure, as described in introduction, is possible through these twist conformation and intramolecular hydrogen bond. The torsion angles C10-N1-C2-C3 and C10-N1-C2-C7 in Table 5 are -120.0 and 64.6° respectively and the dihedral angle between two least square planes is 63.29(5)°. An ORTEP- plot[8] of the unit cell content projected on the ab plane is shown in Figure 2. The molecules are packed in parallel stacks at noraml van der Waals distances. Any unusually short intermolecular contacts were not observed.

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