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Molecular Structure of 2'-Hydroxy-3'-Methoxy-5'-Allyl -4-Methylazobenzene

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2'-hydroxy-3'-methoxy-5'-allyl-4-methylazobenzene was synthesized in two steps: 4-methylbenzenediazonium chloride was prepared by the reaction of 4- methylaniline, HCL and $NaNO_2$, and was then reacted with eugenol to give 2'-hydroxy-3'-methoxy-5'-allyl-4-methylazobenzene. The molecular structure was identified by UV/VIS, IR, ^{1}H-NMR and elemental analysis. The crystal structure was determined as monoclinic by single crystal X-ray diffraction technique. The final R values was found to be 0. 078 for 1065 observed reflections. The structure consists of isolated molecules with van der Waals contacts and the molecule is essentially planar in the solid state. There is a strong intramolecular hydrogen bond in which the hydroxyl group serves as a donor to the N1 atom.

Introduction

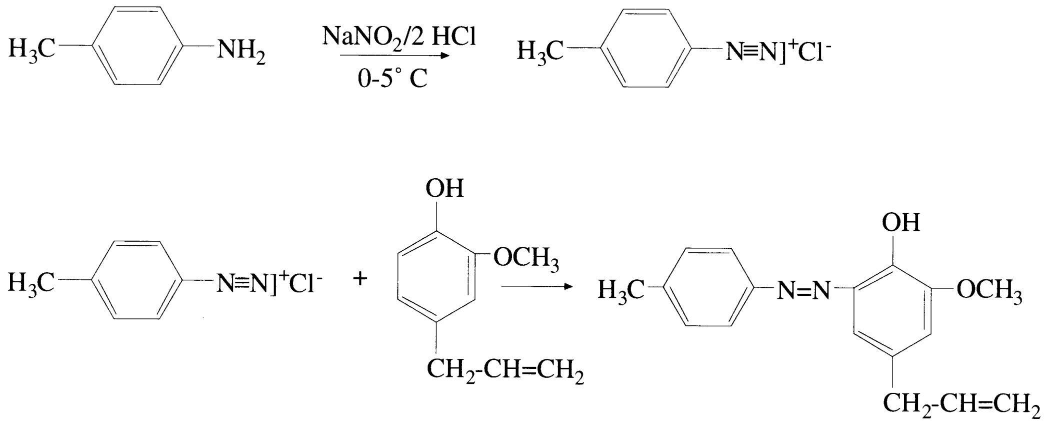
Azo compounds are an important class of organic colorants and consist of at least a conjuge chromophore azo (N=N) group and two or more aromatic rings. The colour properties of organic dyes depend both on the presence of the chromophores and the crystallographic arrangement of molecules in the solid state. The colour of azo dyes is mainly due to the interaction of the $N = N$ group and incident light.

This work is a part of synthesis of novel azobenzene compounds containing substituted phenols[1]; and this paper reports the synthesis, molecular and crystal structure of 2'-hydroxy-3'-methoxy-5'-allyl-4-methylazobenzene. Although the molecular structure of such compounds may readily be identified by spectroscopic techniques such as UV-VIS, IR and NMR,the x-ray crystallographic work was especially carried out to solve the crystal structure of the compound and to illustrate the orientation of the functional groups present in this molecule.

Experimental

synthesis

A solution of 0.04 mol 4-methylaniline and 20 ml of distilled water was mixed with 10 ml concentrated HC1 solution in a beaker to obtain 4- methylanilinium chloride solution. Then the solution was placed in an ice bath and a cold solution of 0.04 mol $NaNO_2$ and 20 ml of distilled water was added dropwise to the solution to give 4-methylbenzenediazonium chloride solution. 0.04 mol eugenol was dissolved in 20 ml 2M NaOH solution and this solution was slowly added to the solution of 4- methylbenzenediazonium chloride solution by stirring. The solution was stirred about 30 min. and the solid product formed was filtered off and washed with water. After that the solid product was dissolved in acetic acid and the brown-red coloured azo compound was precipitated by adding distilled water to the acetic acid solution. The azo dye, 2'-hydroxy-3'-methoxy-5'-allyl-4-methylazobenzene, was crystallized from diethylether to obtain suitable crystals for X-ray and spectral analysis.



2'-Hydroxy-3'-methoxy-5'-allyl-4-methylazobenzene: Yield (70) % of brown-red crystal: mp. 82-84°C; IR (KBr): 3500-3200 (OH), 3100- 2870 (alkyl), 1635 (C=C, allyl), 1600-1450 (aromatic rings), 1450-1400 (N=N), 1380 (OCH_3) cm^{-1}; UV/VIS ($CHCl_3$) λ max ($\sum$): 351 nm (20782), 263 nm (1905); ^{1}H NMR ($CDCl_3$) $- d_6$: δ13.2 (s, 1H, -OH), 7.8-6.8 (m, 6H, aromatic), 6,2-5,5 (m, 1H, =CH), 5.2-5.0 (m, 2H, $= CH_2$), 3.9 (s, 3H, $-OCH_3$), 3.6-3.4 (d, 2H, CH_2), 2.4 (s, 3H, CH_3).

$$\begin{aligned} \text{Anal. Calcd. for} C_{17}H_{18}N_2O_2 &: C, 72.34; H, 6.38; N, 9.93 \\ \text{Found} &: C, 72.12; H, 6.46; N, 9.82. \end{aligned}$$

X-ray diffraction

X-ray diffraction (XRD) data were obtained from a suitable tabular crystal (0.6 x 0.4 x 0.16 mm) on a Nicolet P3 four-circle diffractometer with MoK_α radiation (λ = 0.71043Å) and graphite monochromator at 293 K. Nicolet P3 software was used for data collection and cell refinement. Data collection used 2Θ scan rates of 5.33 ($Ip < 150$)° to 58.6 ($Ip > 2500$)°min^{-1}, where Ip is the prescan intensity. Scan widths were 2.4 to 2.7°2Θ. A local program was used for data reduction^2. The cell parameters were calculated and refined from the setting angles of 14 reflection with Θ ranging from 8.5° to 11.5°. A total of 2941 reflections were measured, of which 1065 with $F > 4\sigma$ (F) were considered and used for refinement without absorption correction. The unit weighting scheme (ω) was used as $\omega = 1/[\sigma^2(F) + 0.009926F^2]$. The structure was solved using the direct methods on F^2 by Shelx86[3] and refinement was carried out by Shelx 76[4]. All non-H were refined anistropically. Difference maps revealed the position of the hydroxyl hydrogen (HO) which was then refined isotropically. The terminal H of the vinyl group attached to C were placed in calculated positions with C-H 0.95$\AA$ and refined riding upon the atoms to which they were attached with separate group isotropic thermal vibrations parameters for methyl, methylene and aryl including H14 of the vinyl group. The methyl groups involving C16 and C17 were treated as rigid bodies. All computations were performed on a SUNSPARC server (UNIX operating system) at the computing centre of University of Aberdeen. The scattering factors for C, O, N and H atoms were taken from the International Tables for X-ray crystallography [5]. The molecular graphic was obtained by using the ORTEX graphic program[6].

Results and Discussion

The lattice parameters of the azo compounds are given in Table 1. The parameters clearly reveal that the compound has a monoclinic crystal structure with $P2_1/C$ space group and each unit cell contains four molecules of the compound.

Table 1. Cell parameters of 2'-hydroxy-3'-methoxy-5'-allyl-4- methylazobenzene

$a(\AA)$	9.553 (10)	$\alpha(\circ)$	90.0
$b(\AA)$	16.452 (16)	$\beta(\circ)$	115.28(8)
$c(\AA)$	10.601 (14)	$\gamma(\circ)$	90.0
$V(\AA^3)$	1503 (3)	D(Mg m^{-3})	1.247
Space group	P2$_1$/C	Z*	4

* number of molecules in the unit cell

Table 2 lists final atomic coordinates of non-H atoms and selected bond lengths and angles are given in Table 3. A plot of the molecule with the atomic numbering scheme is shown in Figure 1.

The lengths of the two C-N bonds are almost identical, giving an average C-N bond lenght of 1.418(9)$\AA$. The average value of the C-N-N angles is 115.1(6)^0. The planes 1 and 2 were defined as C1, C2, C3, C4, C5, C6 and C7, C8, C9, C10, C11, C12, respectively. The angle between perpendiculars of planes 1 and 2 is 169.7^0 which suggests that the molecule is practically planar in the solid state. There are some azobenzene derivatives similar to the title compounds, showing significant conjugation of the whole azobenzene system as evidenced by planarity. The average C-N bond length (1.410(5) $\AA$) and the C-C-N-N torsion angles ($< 8^0$) of some of these compounds[7] are comparable with the title compound while in the other structures the average C-N lengths are slightly shorter and the C-C-N-N torsion angles are much greater (usually over 30^0)[8-10].

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\AA^2$)

	x/a	y/b	z/c	Ueq^*
N1	0.1317(7)	0.6216(4)	0.2040(6)	0.048(2)
N2	0.1943(7)	0.5744(4)	0.1478(6)	0.051(2)
O1	-0.0812(6)	0.6690(3)	-0.0288(6)	0.059(2)
02	-0.1825(7)	0.6656(4)	-0.3011(6)	0.072(2)
C1	0.1500(10)	0.6806(5)	0.4144(8)	0.060(3)
C2	0.2201(11)	0.6932(5)	0.5566(9)	0.068(3)
C3	0.3574(10)	0.6569(5)	0.6402(8)	0.057(3)
C4	0.4217(10)	0.6044(6)	0.5841(9)	0.070(3)
C5	0.3496(10)	0.5891(5)	0.4323(8)	0.064(3)
C6	0.2130(8)	0.6290(4)	0.3515(7)	0.040(2)
C7	0.1219(9)	0.5722(4)	0.0005(7)	0.046(2)
C8	0.1922(9)	0.5201(4)	-0.0597(8)	0.051(2)
C9	0.1374(9)	0.5165(5)	-0.2031(8)	0.050(2)
C10	0.0099(9)	0.5654(5)	-0.2866(8)	0.054(2)
C11	-0.0597(8)	0.6156(5)	-0.2269(8)	0.052(2)
C12	-0.0082(9)	0.6197(5)	-0.0833(8)	0.048(2)
C13	0.2039(10)	0.4591(5)	-0.2762(9)	0.064(3)
C14	0.3516(16)	0.4187(10)	-0.1940(9)	0.143(6)
C15	0.4165(15)	0.3534(8)	-0.1699(10)	0.103(5)
C16	-0.2407(11)	0.6657(6)	-0.4508(9)	0.077(3)
C17	0.4366(12)	0.6714(6)	0.7939(8)	0.081(3)
HO	-0.0030	0.6623	0.0930	

$^*Ueq = (1/3)\sum_i \sum_j U_{ij}a_i^* a_j^* a_i \cdot a_j$

Table 3. Selected Geometric Parameters

Bond distances ($\AA$)			
N1-N2	1.272 (8)	C11-O2	1.370 (9)
C6-N1	1.423 (9)	O1-HO	1.189 (10)
C7-N2	1.413 (9)	HO-N1	1.480 (11)
C12-O1	1.349 (9)	O1... N1	2.558 (8)
Bond angles (o)			
C6-N1-N2	115.0 (6)	C7-C12-O1	122.6 (7)
C7-N2-N1	115.3 (6)	C11-C12-O1	119.5(7)
C1-C6-N1	116.2 (7)	C12-C11-O2	114.6 (7)
C5-C6-N1	124.6 (7)	C10-C11-O2	124.0 (7)
N2-C7-C8	114.6 (7)	C12-O1-H	102.1(5)
N2-C7-C12	124.3 (7)	O1-H-N1	146.5 (9)
N1-N2-C7-C8	179.9 (1)	C5-C6-N1-N2	-0.14 (1)
N1-N2-C7-C12	1.7 (2)	C6-N1-N2-C7	-174.6 (8)
C1-C6-N1-N2	178.8 (2)		

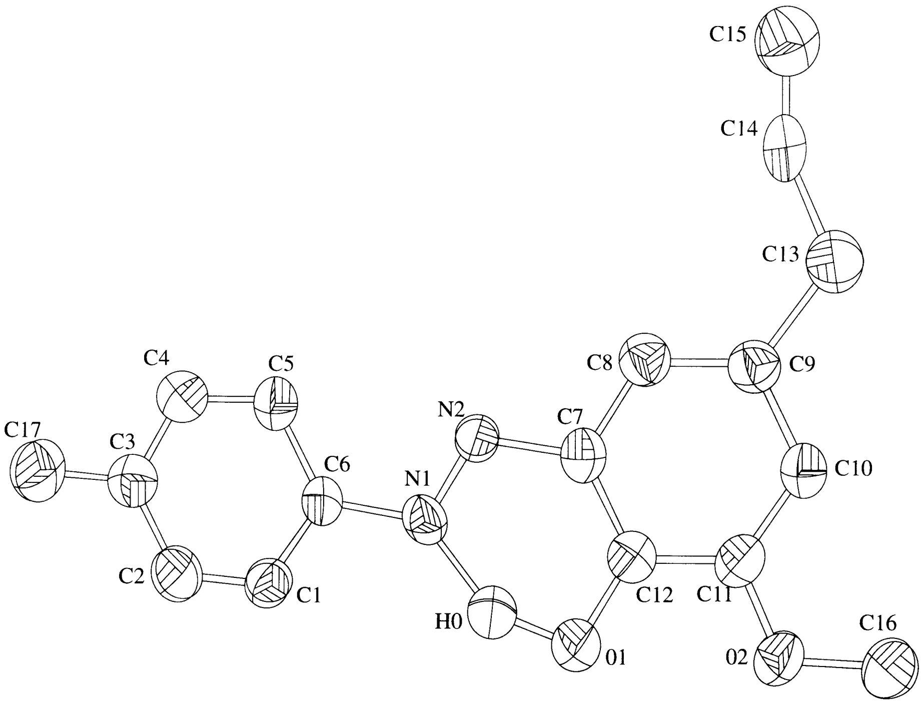


Figure 1. A molecule of $C_{17}H_{18}N_2O_2$ showing the atom numbering scheme. Ellipsoids are shown at the 40% probability level and all H other than hydroxyl H(HO) have been omitted for clarity

The planarity of the molecule facilitates an intramolecular hydrogen bond, completing the six-membered ring, in which the hydroxyl group (HO) adjacent to the -N=N- bond serves as the donor to the N1 atom. The $HO \ldots N1$ angle is 146,5(9)° The length of the hydrogen bond ($HO \ldots N1$) in the molecule is 1.480(11) Å and the distance between O1 and N1 is 2.558(8) Å, which is much shorter than a typical hydrogen bond [$N \ldots HO$ = 2.78Å(10)] as explained by Vinogradov and Linnell[11]. This shows the presence of a very strong intramolecular interaction in the molecule, the strong intramolecular hydrogen bonding was also confirmed by IR and ^{1}H-NMR spectroscopy. In the IR spectra of the title compound the broadening of the OH band was observed in the range of 3500-3200 cm^{-1} while the OH resonance in the ^{1}H-NMR spectra was greatly shifted to downfield. ^{1}H-NMR spectra of the starting compound, eugenol, which does not exhibit a strong intramolecular hydrogen bonding, shows OH resonance in the range of δ 6.0-5.0 ppm. However in the title compound this resonance shifts to 13.2 ppm due to the presence of the hydrogen bond. It is evident that this strong intramolecular hydrogen bond tend to keep the molecule planar. However, there is no intermolecular interaction other than van der Waals contacts between the molecules which are therefore present as isolated individuals within the crystal.

There is evidence of some disorder in the positions of atoms C14 and C15 of the vinyl group. The slightly high R-value (0.078) and the significantly large displacement parameters of the atoms C14 and C15 are attributed to the presence of the disorder rather than to the quality of the crystal. The disorder in the atoms of the vinyl group may also account for the failure to find positions for the 2H atoms attached to C15.

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