

constitution is best achieved by the addition of Cu(I) to the apoprotein, and then subsequent oxidation (Omura, 1961). Thus, a complex involving some ϵ -amino groups may be considered as a potential structural model for those copper binding sites that readily undergo reduction and oxidation. Such a binding site having 'unidentate' ligands would allow the ligands to move independently, and thus the coordination sphere can be rearranged or changed without any serious damage to the protein. For instance, a linear copper(I) complex, kept in position by two ϵ -amino groups, situated in a somewhat hydrophobic environment, may be readily transformed into a copper(II) complex *via* oxidation and the simultaneous approach of two carboxylate groups.

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The Crystal Structure of *p*-Nitroacetophenone

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p-Nitroacetophenone, $C_8H_7NO_3$, forms monoclinic crystals in the space group $P2_1/c$ with four molecules in a unit cell of dimensions: $a = 10.069$ (8), $b = 8.552$ (8), $c = 9.094$ (8) Å and $\beta = 93.85$ (1)°. The structure was refined by a full-matrix least-squares analysis of three-dimensional X-ray diffraction counter data to a final R value of 0.053. The molecule can be described as planar; the molecular plane lies close to the crystallographic (202) plane. The functional groups are slightly twisted about an axis that coincides approximately with the bond from the ring to the central atom of the group.

Introduction

A crystal structure determination of *p*-nitroacetophenone, $C_8H_7NO_3$, is of chemical interest since the compound contains two electron-withdrawing groups attached in competing positions to the benzene ring. The absence of major steric interactions ensures that the aromatic bond distances and the planarities of the functional groups with respect to the benzene ring will reflect primarily the inductive and resonance effects present.

Film techniques were initially employed to determine and refine the structure. When an automatic single-crystal diffractometer became available, a new set of intensity data was collected and the final refinement was based solely on these data.

Experimental

The compound was prepared by Dr T. T. Galkowski of Providence College. Three recrystallizations from anhydrous diethyl ether produced single crystals which

melted sharply at 80.5°C. Preliminary photographs showed the crystal system to be monoclinic with systematic absences uniquely specifying the space group as $P2_1/c$. Lattice parameter measurements and intensity data were taken on a Picker four-circle automatic X-ray diffractometer using Zr-filtered Mo $K\alpha$ radiation. A 2θ scan rate of 2° per min was employed over the range of 5.0 to 50.0°. The lattice constants were determined from measurements of the positions of 26 reflections on the diffractometer, and these are reported with the standard deviations given in parentheses.

Crystal data

$a = 10.069$ (8) Å	Space group $P2_1/c$
$b = 8.552$ (8)	$V = 781.3$ Å ³
$c = 9.094$ (8)	F.W. 165.15
$\beta = 93.85$ (1)°	$Z = 4$
$\mu(\text{Mo } K\alpha) = 1.20$ cm ⁻¹	$F(000) = 344$
$\lambda(\text{Mo } K\alpha) = 0.7107$ Å	$D_m = 1.44$ g cm ⁻³ (floatation)
	$D_x = 1.40$ g cm ⁻³

Sublimation of the crystal caused some difficulty and consequently a larger crystal (an approximate cube with 0.4 mm edges) was used than would normally be desirable. A decomposition study was carried out in which the intensities of four strong reflections were monitored over a 50 h period. It was found that the

decomposition rates were similar and a single linear correction was applied to all reflections. All the intensities were then adjusted for the background contributions and an estimated standard deviation for each reflection was obtained using the procedure of Busing & Levy (1957). No correction for absorption was made. The removal of the Lorentz-polarization led to a set of structure factors with individual estimated standard errors. A total of 1559 reflections was investigated and of these 917 had structure factors greater than twice their estimated standard errors. Within this group, there were 74 pairs of equivalent reflections, and the average relative deviation of the structure factor squared from the pair mean was 3.1%.

Structure determination and refinement

Patterson projections (film data) along the a and c axes were computed and these provided the approximate center of the benzene ring and molecular orientation. It was deduced that the plane of the molecule coincided with a (202) plane from the extreme strength of the corresponding reflection. A trial structure was developed from this information and a molecular model of the compound. The early refinement stages, based on film data, proceeded satisfactorily and the resulting structure became the initial approximation for the refinement based on the counter data.

Table 1. *Positional and thermal parameters*

The β_{ij} are given in Å² and are multiplied by 10⁴. The temperature-factor expression is $\exp[-(\beta_{11}a^{*2}h^2 + \dots + 2\beta_{12}a^*b^*hk \dots)]$. The numbers in parentheses are estimated errors.

	x/a	y/a	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.2956 (3)	-0.0050 (3)	-0.0241 (3)	107 (3)	119 (5)	130 (4)	23 (4)	27 (3)	-4 (4)
C(2)	0.3626 (3)	0.1128 (4)	-0.0904 (3)	113 (3)	144 (6)	119 (4)	18 (4)	27 (3)	3 (4)
C(3)	0.3298 (3)	0.2654 (4)	-0.0606 (3)	99 (3)	133 (5)	107 (4)	-3 (3)	-1 (3)	20 (4)
C(4)	0.1967 (3)	0.0276 (3)	0.0710 (3)	79 (3)	123 (5)	112 (4)	18 (3)	4 (3)	-7 (4)
C(5)	0.1655 (3)	0.1840 (4)	0.0969 (3)	100 (3)	130 (5)	137 (5)	22 (3)	29 (3)	-10 (4)
C(6)	0.2304 (3)	0.3021 (4)	0.0324 (4)	126 (4)	114 (5)	134 (4)	17 (4)	17 (3)	0 (4)
C(7)	0.1245 (3)	-0.0974 (4)	0.1482 (3)	86 (3)	141 (5)	144 (4)	-1 (3)	25 (3)	-2 (4)
C(8)	0.1555 (4)	-0.2638 (4)	0.1181 (5)	154 (4)	120 (5)	229 (6)	8 (4)	57 (4)	14 (5)
N	0.4022 (3)	0.3910 (4)	-0.1304 (3)	112 (3)	115 (5)	146 (4)	10 (4)	0 (3)	20 (4)
O(1)	0.4931 (3)	0.3551 (3)	-0.2054 (3)	158 (4)	231 (6)	228 (5)	-23 (4)	75 (4)	46 (4)
O(2)	0.3692 (3)	0.5261 (3)	-0.1097 (3)	189 (4)	133 (4)	225 (5)	-15 (4)	6 (3)	26 (4)
O(3)	0.0427 (3)	-0.0626 (3)	0.2335 (3)	159 (3)	172 (5)	249 (5)	-16 (3)	115 (4)	-14 (4)

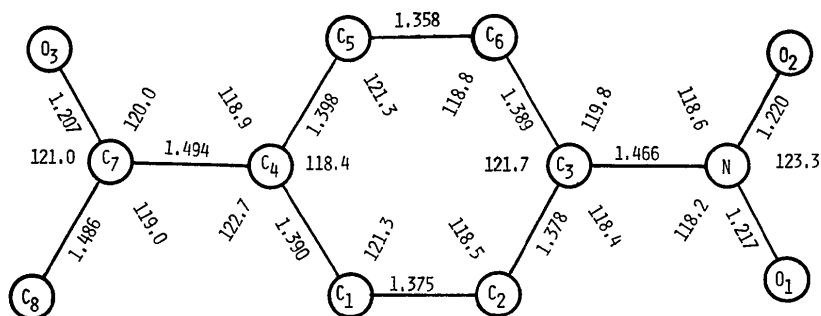


Fig. 1. Bond lengths and bond angles in *p*-nitroacetophenone.

The final structure was obtained by means of a full-matrix least-squares technique, *BULS*, the Brown University version of the Busing & Levy (1959) *ORFLS* program. The atomic scattering factors were taken from Cromer & Waber (1965) for nitrogen, oxygen and hydrogen and from *International Tables for X-ray Crystallography* (1962) for covalent carbon. Only those structure factors whose magnitude exceeded twice their estimated standard errors were used and the weights assigned were the squared reciprocals of these errors. Two iterations with isotropic temperature factors, followed by one with anisotropic temperature factors, produced a structure with a reliability index, *R* (observed reflections), of 0.085. A three-dimensional difference electron density synthesis was calculated and regions of high density were found where six of the seven hydrogens were to be expected. The seventh hydrogen, H(8c), was placed at the expected position. A least-squares cycle (anisotropic temperature factors) with the hydrogen atoms held fixed and assigned a temperature factor of 5.0 Å², lowered the *R* value to 0.053. As the shifts in the atomic coordinates and temperature factors were less than 20% of the indicated standard errors, with the exception of β₂₃ of C(8) which was 35%, it was concluded that the refinement process had fully converged. A difference synthesis was computed and the largest residual electron density found was 0.20 eÅ⁻³.

The final positional and thermal parameters with their estimated standard errors are given in Table 1; the hydrogen positions are given in Table 2. Table 3 contains a listing of the observed and calculated structure factors.

Description and discussion of the structure

The structure of the *p*-nitroacetophenone molecule is shown in Fig. 1, along with the bond lengths and angles. These values were computed using *BUFFE*, the Brown University version of the Busing, Martin & Levy (1964) *ORFFE* program. The estimated standard deviations are 0.004 Å in bond lengths and 0.3° in bond angles. The bond lengths and angles found here agree well with values reported previously for aromatic nitro-compounds (Trueblood, Goldish & Donohue 1961; Seff & Trueblood, 1968; Grant & Richards, 1969; Iwasaki & Saito, 1970) and for aromatic acetyl-compounds (Coppens & Schmidt, 1964; Sax & Desiderato, 1967; Young, Tollin & Sutherland, 1968).

Table 2. *Hydrogen positions*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)	0.328	-0.120	-0.050
H(2)	0.435	0.085	-0.170
H(5)	0.090	0.205	0.165
H(6)	0.210	0.415	0.030
H(8a)	0.105	-0.335	0.180
H(8b)	0.240	-0.290	0.150
H(8c)	0.145	-0.313	0.025

Table 3. *Observed and calculated structure factors* (× 10)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
001	1.00	1.00	001	1.00	1.00	001	1.00	1.00	001	1.00	1.00	001	1.00	1.00	001	1.00	1.00	001	1.00	1.00
010	1.00	1.00	010	1.00	1.00	010	1.00	1.00	010	1.00	1.00	010	1.00	1.00	010	1.00	1.00	010	1.00	1.00
020	1.00	1.00	020	1.00	1.00	020	1.00	1.00	020	1.00	1.00	020	1.00	1.00	020	1.00	1.00	020	1.00	1.00
030	1.00	1.00	030	1.00	1.00	030	1.00	1.00	030	1.00	1.00	030	1.00	1.00	030	1.00	1.00	030	1.00	1.00
040	1.00	1.00	040	1.00	1.00	040	1.00	1.00	040	1.00	1.00	040	1.00	1.00	040	1.00	1.00	040	1.00	1.00
050	1.00	1.00	050	1.00	1.00	050	1.00	1.00	050	1.00	1.00	050	1.00	1.00	050	1.00	1.00	050	1.00	1.00
060	1.00	1.00	060	1.00	1.00	060	1.00	1.00	060	1.00	1.00	060	1.00	1.00	060	1.00	1.00	060	1.00	1.00
070	1.00	1.00	070	1.00	1.00	070	1.00	1.00	070	1.00	1.00	070	1.00	1.00	070	1.00	1.00	070	1.00	1.00
080	1.00	1.00	080	1.00	1.00	080	1.00	1.00	080	1.00	1.00	080	1.00	1.00	080	1.00	1.00	080	1.00	1.00
090	1.00	1.00	090	1.00	1.00	090	1.00	1.00	090	1.00	1.00	090	1.00	1.00	090	1.00	1.00	090	1.00	1.00
100	1.00	1.00	100	1.00	1.00	100	1.00	1.00	100	1.00	1.00	100	1.00	1.00	100	1.00	1.00	100	1.00	1.00
110	1.00	1.00	110	1.00	1.00	110	1.00	1.00	110	1.00	1.00	110	1.00	1.00	110	1.00	1.00	110	1.00	1.00
120	1.00	1.00	120	1.00	1.00	120	1.00	1.00	120	1.00	1.00	120	1.00	1.00	120	1.00	1.00	120	1.00	1.00
130	1.00	1.00	130	1.00	1.00	130	1.00	1.00	130	1.00	1.00	130	1.00	1.00	130	1.00	1.00	130	1.00	1.00
140	1.00	1.00	140	1.00	1.00	140	1.00	1.00	140	1.00	1.00	140	1.00	1.00	140	1.00	1.00	140	1.00	1.00
150	1.00	1.00	150	1.00	1.00	150	1.00	1.00	150	1.00	1.00	150	1.00	1.00	150	1.00	1.00	150	1.00	1.00
160	1.00	1.00	160	1.00	1.00	160	1.00	1.00	160	1.00	1.00	160	1.00	1.00	160	1.00	1.00	160	1.00	1.00
170	1.00	1.00	170	1.00	1.00	170	1.00	1.00	170	1.00	1.00	170	1.00	1.00	170	1.00	1.00	170	1.00	1.00
180	1.00	1.00	180	1.00	1.00	180	1.00	1.00	180	1.00	1.00	180	1.00	1.00	180	1.00	1.00	180	1.00	1.00
190	1.00	1.00	190	1.00	1.00	190	1.00	1.00	190	1.00	1.00	190	1.00	1.00	190	1.00	1.00	190	1.00	1.00
200	1.00	1.00	200	1.00	1.00	200	1.00	1.00	200	1.00	1.00	200	1.00	1.00	200	1.00	1.00	200	1.00	1.00
210	1.00	1.00	210	1.00	1.00	210	1.00	1.00	210	1.00	1.00	210	1.00	1.00	210	1.00	1.00	210	1.00	1.00
220	1.00	1.00	220	1.00	1.00	220	1.00	1.00	220	1.00	1.00	220	1.00	1.00	220	1.00	1.00	220	1.00	1.00
230	1.00	1.00	230	1.00	1.00	230	1.00	1.00	230	1.00	1.00	230	1.00	1.00	230	1.00	1.00	230	1.00	1.00
240	1.00	1.00	240	1.00	1.00	240	1.00	1.00	240	1.00	1.00	240	1.00	1.00	240	1.00	1.00	240	1.00	1.00
250	1.00	1.00	250	1.00	1.00	250	1.00	1.00	250	1.00	1.00	250	1.00	1.00	250	1.00	1.00	250	1.00	1.00
260	1.00	1.00	260	1.00	1.00	260	1.00	1.00	260	1.00	1.00	260	1.00	1.00	260	1.00	1.00	260	1.00	1.00
270	1.00	1.00	270	1.00	1.00	270	1.00	1.00	270	1.00	1.00	270	1.00	1.00	270	1.00	1.00	270	1.00	1.00
280	1.00	1.00	280	1.00	1.00	280	1.00	1.00	280	1.00	1.00	280	1.00	1.00	280	1.00	1.00	280	1.00	1.00
290	1.00	1.00	290	1.00	1.00	290	1.00	1.00	290	1.00	1.00	290	1.00	1.00	290	1.00	1.00	290	1.00	1.00
300	1.00	1.00	300	1.00	1.00	300	1.00	1.00	300	1.00	1.00	300	1.00	1.00	300	1.00	1.00	300	1.00	1.00

The entire molecule is approximately planar. The least-squares plane through the benzene ring is described by the equation

$$6.359x + 0.124y + 6.648z - 1.722 = 0.$$

None of the ring atoms deviates more than 0.005 Å from this plane; deviations for the N and C(7) atoms are 0.018 and 0.043 Å, respectively. The functional groups are each slightly twisted about an axis that coincides approximately with the bond from the ring to the central atom of the group. The plane defined by O(1)-N-O(2) is twisted through -3.6°, and that defined by C(8)-C(7)-O(3) is twisted through -2.5°

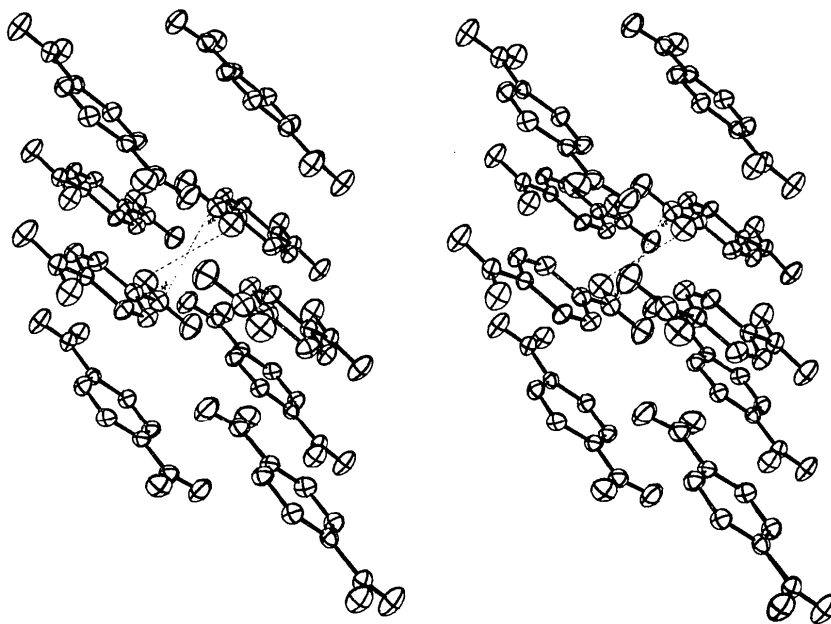


Fig. 2. Stereoscopic view of the molecular packing. The *a* axis runs left-to-right, *b* goes into the diagram, and *c* is vertical. The intersection of the dashed lines in the center indicates the center of symmetry at $\frac{1}{2}, \frac{1}{2}, 0$.

(thus the angle between the planes of the functional groups is 6.1°).

Since the molecule is nearly planar, both functional groups can participate in the delocalization of the π -electrons. The bonds C(1)–C(2) and C(5)–C(6) are significantly shorter than the average of the remaining four bonds in the ring; resonance theory predicts that these bonds will have increased double-bond character due to the presence of an electron-withdrawing group attached to either the C(3) or C(4) position.

The structure of the crystal is shown in Fig. 2. The plane of each molecule is within 1.3° of being parallel to the *b* axis. This produces a packing arrangement that is unusual for space group $P2_1/c$, and it precludes any weak hydrogen bonding of the type observed by Abrahams & Robertson (1948) in *p*-nitroaniline. No heavy atom interatomic distances between molecules are less than the sum of van der Waals radii.

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