

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) $^\circ$. 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 (flotation)
	$D_x = 1.40$ 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 $\exp [-(\beta_{11}a^2h; + \dots 2\beta_{12}a^*b^*hk\dots)]$. 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)

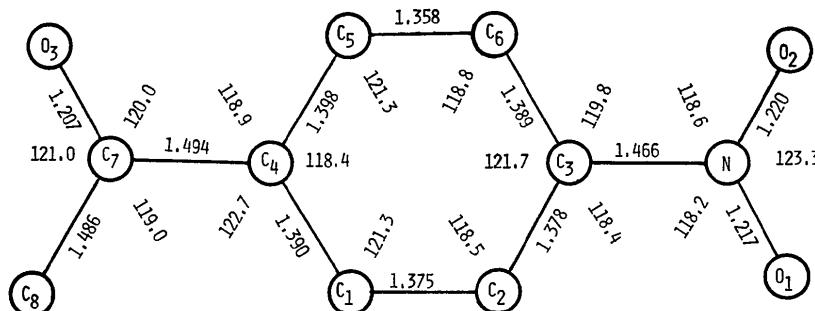


Fig. 1. Bond lengths and bond angles in *p*-nitroacetophenone.

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 \AA^2 , 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 β_{23} 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 e\AA^{-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*

	x/a	y/b	z/c
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 ($\times 10$)

L	PO	PC	L	PO	PC	L	PO	PC	L	PO	PC	L	PO	PC	L	PO	PC	L	PO	PC
-11	0	149	8	125	136	1	22	20	-2	1	31	-51	2	71	62	2	21	25	2	25
-11	1	150	8	126	137	1	23	21	-2	1	32	-52	2	72	63	2	22	26	2	26
-11	2	151	8	127	138	2	24	22	-2	2	33	-53	3	73	64	3	23	27	3	27
-11	3	152	8	128	139	3	25	23	-2	3	34	-54	4	74	65	4	24	28	4	28
-11	4	153	8	129	140	4	26	24	-2	4	35	-55	5	75	66	5	25	29	5	29
-11	5	154	8	130	141	5	27	25	-2	5	36	-56	6	76	67	6	26	30	6	30
-11	6	155	8	131	142	6	28	26	-2	6	37	-57	7	77	68	7	27	31	7	31
-11	7	156	8	132	143	7	29	27	-2	7	38	-58	8	78	69	8	28	32	8	32
-11	8	157	8	133	144	8	30	28	-2	8	39	-59	9	79	70	9	29	33	9	33
-11	9	158	8	134	145	9	31	29	-2	9	40	-60	10	80	71	10	30	34	10	34
-11	10	159	8	135	146	10	32	30	-2	10	41	-61	11	81	72	11	31	35	11	35
-11	11	160	8	136	147	11	33	31	-2	11	42	-62	12	82	73	12	32	36	12	36
-11	12	161	8	137	148	12	34	32	-2	12	43	-63	13	83	74	13	33	37	13	37
-11	13	162	8	138	149	13	35	33	-2	13	44	-64	14	84	75	14	34	38	14	38
-11	14	163	8	139	150	14	36	34	-2	14	45	-65	15	85	76	15	35	39	15	39
-11	15	164	8	140	151	15	37	35	-2	15	46	-66	16	86	77	16	36	40	16	40
-11	16	165	8	141	152	16	38	36	-2	16	47	-67	17	87	78	17	37	41	17	41
-11	17	166	8	142	153	17	39	37	-2	17	48	-68	18	88	79	18	38	42	18	42
-11	18	167	8	143	154	18	40	38	-2	18	49	-69	19	89	80	19	39	43	19	43
-11	19	168	8	144	155	19	41	39	-2	19	50	-70	20	90	81	20	40	44	20	44
-11	20	169	8	145	156	20	42	40	-2	20	51	-71	21	91	82	21	41	45	21	45
-11	21	170	8	146	157	21	43	41	-2	21	52	-72	22	92	83	22	42	46	22	46
-11	22	171	8	147	158	22	44	42	-2	22	53	-73	23	93	84	23	43	47	23	47
-11	23	172	8	148	159	23	45	43	-2	23	54	-74	24	94	85	24	44	48	24	48
-11	24	173	8	149	160	24	46	44	-2	24	55	-75	25	95	86	25	45	49	25	49
-11	25	174	8	150	161	25	47	45	-2	25	56	-76	26	96	87	26	46	50	26	50
-11	26	175	8	151	162	26	48	46	-2	26	57	-77	27	97	88	27	47	51	27	51
-11	27	176	8	152	163	27	49	47	-2	27	58	-78	28	98	89	28	48	52	28	52
-11	28	177	8	153	164	28	50	48	-2	28	59	-79	29	99	90	29	49	53	29	53
-11	29	178	8	154	165	29	51	49	-2	29	60	-80	30	100	91	30	50	54	30	54
-11	30	179	8	155	166	30	52	50	-2	30	61	-81	31	101	92	31	51	55	31	55
-11	31	180	8	156	167	31	53	51	-2	31	62	-82	32	102	93	32	52	56	32	56
-11	32	181	8	157	168	32	54	52	-2	32	63	-83	33	103	94	33	53	57	33	57
-11	33	182	8	158	169	33	55	53	-2	33	64	-84	34	104	95	34	54	58	34	58
-11	34	183	8	159	170	34	56	54	-2	34	65	-85	35	105	96	35	55	59	35	59
-11	35	184	8	160	171	35	57	55	-2	35	66	-86	36	106	97	36	56	60	36	60
-11	36	185	8	161	172	36	58	56	-2	36	67	-87	37	107	98	37	57	61	37	61
-11	37	186	8	162	173	37	59	57	-2	37	68	-88	38	108	99	38	58	62	38	62
-11	38	187	8	163	174	38	60	58	-2	38	69	-89	39	109	100	39	59	63	39	63
-11	39	188	8	164	175	39	61	59	-2	39	70	-90	40	110	101	40	60	64	40	64
-11	40	189	8	165	176	40	62	60	-2	40	71	-91	41	111	102	41	61	65	41	65
-11	41	190	8	166	177	41	63	61	-2	41	72	-92	42	112	103	42	62	66	42	66
-11	42	191	8	167	178	42	64	62	-2	42	73	-93	43	113	104	43	63	67	43	67
-11	43	192	8	168	179	43	65	63	-2	43	74	-94	44	114	105	44	64	68	44	68
-11	44	193	8	169	180	44	66	64	-2	44	75	-95	45	115	106	45	65	69	45	69
-11	45	194	8	170	181	45	67	65	-2	45	76	-96	46	116	107	46	66	70	46	70
-11	46	195	8	171	182	46	68	66	-2	46	77	-97	47	117	108	47	67	71	47	71
-11	47	196	8	172	183	47	69	67	-2	47	78	-98	48	118	109	48	68	72	48	72
-11	48	197	8	173	184	48	70	68	-2	48	79	-99	49	119	110	49	69	73	49	73
-11	49	198	8	174	185	49	71	69	-2	49	80	-100	50	120	111	50	70	74	50	74
-11	50	199	8	175	186	50	72	70	-2	50	81	-101	51	121	112	51	71	75	51	75
-11	51	200	8	176	187	51	73	71	-2	51	82	-102	52	122	113	52	72	76	52	76
-11	52	201	8	177	188	52	74	72	-2	52	83	-103	53	123	114	53	73	77	53	77
-11	53	202	8	178	189	53	75	73	-2	53	84	-104	54	124	115	54	74	78	54	78
-11	54	203	8	179	190	54	76	74	-2	54	85	-105	55	125	116	55	75	79	55	79
-11	55	204	8	180	191	55	77	75	-2	55	86	-106	56	126	117	56	76	80	56	80
-11	56	205	8	181	192	56	78	76	-2	56	87	-107	57	127	118	57	77	81	57	81
-11	57	206	8	182	193	57	79	77	-2	57	88	-108	58	128	119	58	78	82	58	82
-11	58	207	8	183	194	58	80	78	-2	58	89	-109	59	129	120	59	79	83	59	83
-11	59	208	8	184	195	59	81	79	-2	59	90	-110	60	130	121	60	80	84	60	84
-11	60	209	8	185	196	60	82	80	-2	60	91	-111	61	131	122	61	81	85	61	85
-11	61	210	8	186	197	61	83	81	-2	61	92	-112	62	132	123	62	82	86	62	86
-11	62	211	8	187	198	62	84	82	-2	62	93	-113	63	133	124	63	83	87	63	87
-11	63	212	8	188	199	63	85	83	-2	63	94	-114	64	134	125	64	84	88	64	88
-11	64	213	8	189	200	64	86	84	-2	64	95	-115	65	135	126	65	85	89	65	89
-11	65	214	8	190	201	65	87	85	-2	65	96	-116	66	136	127	66	86	90	66	90
-11	66	215	8	191	202	66	88	86	-2	66	97	-117	67	137	128	67	87	91	67	91
-11	67	216	8	192	203	67	89	87	-2	67	98	-118	68	138	129	68	88	92	68	92
-11	68	217	8	193	204	68	90	88	-2	68	99	-119	69	139	130	69	89	93	69	93
-11	69	218	8	194	205	69	91	89	-2	69	100	-120	70	140	131	70	90	94	70	94
-11	70	219	8	195	206	70	92	90	-2	70	101	-121	71	141	132	71	91	95	71	95
-11	71	220	8	196	207	71	93	91	-2	71	102	-122	72	142	133	72	92	96	72	96
-11	72	221	8	197	208	72	94	92	-2	72	103	-123	73	143	134	73	93	97	73	97
-11	73	222	8	198	209	73	95	93	-2	73	104	-124	74	144	135	74	94	98	74	98
-11	74	223	8	199	210	74	96	94	-2	74	105	-125	75	145	136	75	95	99	75	99
-11	75	224	8	200	211	75	97	95	-2	75	106	-126	76	146	137	76	96	100	76	100
-11	76	225	8	201	212	76	98	96	-2	76	107	-127	77	147	138	77	97	101	77	101
-11	77	226	8	202	213	77	99	97	-2	77	108	-128	78	148	139	78	98			

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°

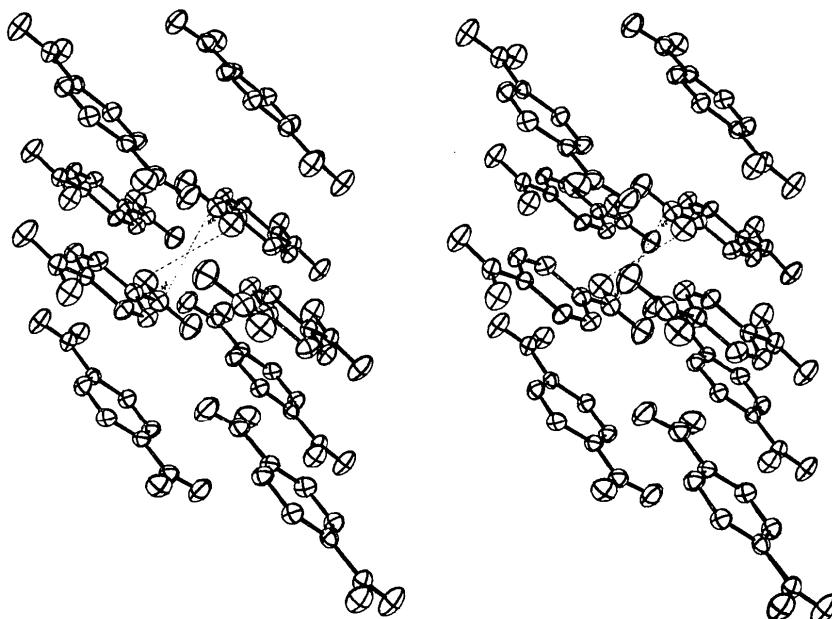


Fig. 2. Stereoscopic view of the molecular packing. The **a** axis runs left-to-right, **b** goes into the diagram, and **c** is vertical. The intersection of the dashed lines in the center indicates the center of symmetry at $\frac{1}{2}, \frac{1}{2}, 0$.

(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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