EFFECT OF ALKYL SUBSTITUENTS ON THE HYDROGEN BONDING AND MOLECULAR STRUCTURE OF BENZOPHENYLHYDROXAMIC ACIDS. CRYSTAL STRUCTURE OF UO_2 COMPLEX OF P-ISOPROPYLBENZOPHENYLHYDROXAMIC ACID

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ABSTRACT : *The effect of alkyl substituents on the C- phenyl and/or the N-phenyl ring of benzophenylhydroxamic acids on their molecular structure and hydrogen bonding has been investigated. The predominant configuration in $CHCl_3$ is determined by steric and electronic effects. Substituents on the C-phenyl ring favor the cis configuration, while substituents in the N-phenyl ring favor a trans configuration. These can be rationalized on the basis of electronic effects. Bulky substituents in the C-phenyl ring give rise to a mixture of cis and trans forms due to steric factors. When substituents are present on the C-phenyl ring and N-phenyl ring the trans configuration is preferred. The crystal and molecular structures of UO_2^{2+} complex of p-isopropylbenzophenylhydroxamic acid have been determined from a single crystal of this complex to elucidate the effect of complexation on the structure of this ligand which exists as a cis-trans mixture. Complexation occurs exclusively from the cis configuration.*

KEY WORDS : *Hydroxamic acids, Alkyl substituents, C-Phenyl ring effect, N-Phenyl ring effect, Hydrogen bonding, Molecular structure.*

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INTRODUCTION

Hydroxamic acids are an interesting class of compounds for a variety of reasons. They have found diverse applications as food additives, in metallurgy as inhibitors for copper corrosion, as antifungal agents, and in nuclear fuel processing [1]. Many naturally occurring low-molecular weight agents (siderphores) use hydroxamic acid functional groups for iron chelation and function as growth factors, antibiotics, and tumor inhibitors.

Hydroxamic acid derivatives have been used as extractants, as precipitating agents for niobium and tantalum, and as colorimetric reagents for a variety of metals [2-5]. There has been considerable interest in a class of hydroxamic acids, namely the benzophenylhydroxamic acids [6]. These can exist in the cis and trans forms with respect to the C=O and O−H groups. The cis and trans terminology stems from the partial double bond character of the C−N bond [6b]. We had investigated a series of alkyl substituted benzophenylhydroxamic acids for the extraction of transition metal ions and lanthanides [5a,b]. Hydroxamic acids with a substituent in the ortho positions of the C− or N−phenyl ring were not good extractants. This indicated that metal complexation occurs exclusively in the cis configuration, and that the ortho substituted compounds are poor ligands due to steric constraints [7]. The relative amount of cis and trans isomers in the uncomplexed ligand is an interesting problem. Experimentally this can be discerned by intramolecular vs. intermolecular hydrogen bonding. Previous attempts to determine the effect of substituents on the phenyl rings on the intramolecular vs. intermolecular hydrogen bonding did not provide definitive conclusions [6f,g]. We have conducted a systematic investigation of the effect of substituents on the hydrogen bonding characteristics of benzophenylhydroxamic acids by IR and ^{1}H-NMR. These results are presented.

Arylhydroxamic acids have been used for the spectrophotometric determinations of actinides like Th and U[6h]. The crystal structures of UO_2^{2+} complexes continue to attract interests. It is useful to investigate the crystal structure of UO_2^{2+} complex of hydroxamic acids in order to understand the mode of complexation and to understand their spectral properties. This in turn should aid in the design of appropriate ligands to improve detection limits in spectrophotometric determination of actinides. We have resolved the crystal and molecular structure of UO_2^{2+} complex of p-isopropyl benzophenylhydroxamic acid (pIPBPHA). We have also investigated the effect of substituent on the crystal structure of this complex and compared it with the unsubstituted complex [16,17].

EXPERIMENTAL

All hydroxamic acids were prepared from the appropriate hydroxylamines and acid chlorides, and their syntheses have been mentioned elsewhere [7]. All NMR data were obtained on a *Brucker* WM-250 instrument (Germany) in the FT mode in $CDCl_3$ solvent. IR spectra were recorded on a *Perkin-Elmer* FT-1800 (Norwalk, CT, U.S.A) instrument either as KBr pellets or as 0.1M solution in $CDCl_3$ using a 1 cm cell. All inorganic chemicals were purchased from Alfa Products (Danvers, MA) and were 99% pure. Organic chemicals were purchased from *Aldrich* Chemical Company (Milwaukee, WI, U.S.A) and American Scientific (Phoenix, AZ, U.S.A) and were appropriately distilled or recrystallized. Elemental analysis of UO_2^{2+} complex was performed by Galbraith Laboratories (Knoxville, TN, U.S.A).

Complexation of p- isopropylbenzophenylhydroxamic acid and $UO_2(NO_3)_2.6H_2O$

0.5g (10^{-3}mol) of $UO_2(NO_3)_2 .6H_2O$ was dissolved in 20mL water and equilibrated with 0.75g (3×10^{-3}mol) of p− isopropylbenzophenylhydroxamic acid in 20mL $CHCl_3$ at room temperature for 4 hrs. The red chloroform solution was evaporated to dryness. The solid was dissolved in minimum amount of hot absolute ethanol and cooled. Bright red crystals

of $UO_2(pIPBPHA)_2$. EtOH separated. Anal. Calcd. for $UO_7C_{34}H_{38}N_2$: C, 49.57; H, 5.5; N, 3.23; U(as UO_2), 32.7; O, 9.72.
Found: C, 49.85; H, 5.33; N, 3.23; U, 30.80; O, 10.25.

Crystal structure of uranyl p-isopropyl benzophenylhydroxamic acid

A dark red block shap crystal of dimension 0.18×0.24×0.33mm of this complex was mounted on a glass fiber in a random orientation on a Syntex-Nicolet P2 diffractometer (Modim, WI, U.S.A). Preliminary examination and data collection were performed with MoKα (0.71073Å) radiation on a Syntex P21 diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $20<2\theta<27°$. The monoclinic cell parameters and calculated volumes were a= 11.417Å, b= 30.154Å, c=17.566Å, β= 114.02°, and V= 3415.2Å^3 with four molecules of complex and one ethanol per unit cell. The density of the crystal, determined by flotation in carbontetrachloride and hexane, was 1.67g/cm^3 with the calculated value being 1.60. The monoclinic space group was determined to be P21/c (#14) from systematic absences and from the distribution of E values.

Intensity data were collected by using the $\theta/2\theta$ scan technique at 298K over the range $0°<2\theta<50°$ at a rate of 2−8°min^{-1}. A total of 6526 reflections were collected, 6048 of which were unique and not systematically absent. After every 97 reflections, the intensities of 3 standard reflections were monitored. As these showed no significant variation during the experiment, no decay correction was applied. Lorentz and polarization corrections were applied to the data. An analytical absorption correction was applied based on the crystal size and face indices. Relative transmission coefficients ranged from 9.985 to 48.774, with an average of 41.402.

The structure was solved using the *Patterson* heavy- atom method which revealed the position of the U atom. The remaining atoms were located in succeeding difference *Fourier* syntheses. The hydrogen atoms were added at idealized positions (C−H= 0.95Å) but constrained to ride on the atom to which they were bonded.

The structure was refined in full- matrix least- square, where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The standard deviation of F^2, $\sigma(F^2)$, is defined by $\sigma(F^2)=[\sigma(I)+(pF^2)^2]^{1/2}$. The weights for each reflection were calculated by using the counter weighting scheme, $w=4F^2/[\sigma(I)+pF^2)^2]$, which reduced to $w=4F^2/\sigma^2(F^2)$, where the uncertainty factor, p , was set to the value of 0.040.

Scattering factors were taken from *Cromer* and *Waber* [8]. Anomalous effects were included in F_c for all non- hydrogen atoms [9]. The values for $\Delta F'$ and $\Delta F''$ were those of *Cromer* [10]. Only 3361 reflections with intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 397 variable parameters and converged with unweighted and weighted agreement factors of:

$$R_1= \Sigma||F_o| - |F_c||/\Sigma F_o = 0.05$$

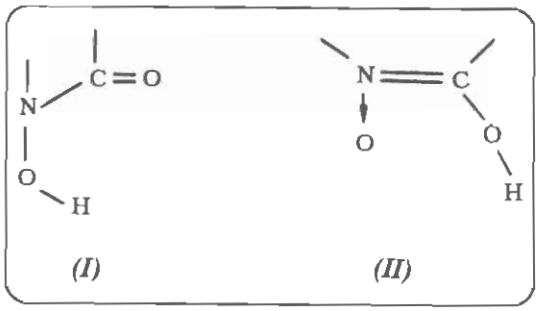
$$R_2= (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.054$$

The standard deviation of an observation unit weight was 1.82.

There were 149 correlation coefficients greater than 0.50. The highest peak in the final difference *Fourier* had a height of 1.52 e/Å^3, with an estimated error based on σ(F) of 0.17 [11]. The minimum negative peak had a height of −1.06 e/Å^3, with an estimated error based on σ(F) of 0.17. Plots of $\Sigma w(|F_o|-|F_c|)^2$, vs $|F_o|$, reflection order in data collection sin θ/λ, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using SDP/VAX [12].

RESULTS AND DISCUSSION

Although hydroxamic acids may be formulated as hydroxam- hydroxim tautomers I



(I) (II)

and II, form I is more probable [13].

The most striking differences between structures I and II is the presence of C=O and C=N groups, respectively. The shift of ν C=O of phenylhydroxamic acid in solution and the absence of this shift for ν C=N band in benzoimidates under similar conditions support structure I [6b]. In addition to structures I and II, these compounds may exist in two geometrical isomeric forms, cis or trans with respect to the carbonyl group and hydroxyl group in view of the partial double bond character of the C–N bond [6c]. The isolation of chromium complexes of both forms of benzophenylhydroxamic acid has been reported [6d]. Among these two isomeric forms, cis isomer favors intramolecular hydrogen bonding and is more stable in solid state and in solution while the trans form favors the intermolecular hydrogen bonding [6 b,e]. Previous studies have shown that all solid-state structures of hydroxamic acids are cis, although the trans isomer is expected to be more stable in the absence of intramolecular hydrogen bonding [6e].

The ν C=O frequencies of hydroxamic acids, in general, occur at 1610–1680 cm^{-1} and do not correspond to the free carbonyl frequencies (1700 cm^{-1}) indicating presence of hydrogen bonding [6b]. An intramolecular hydrogen bonded carbonyl group absorbs infrared radiation at a lower frequency than the corresponding intermolecular hydrogen bonded carbonyl group. In addition, when hydrogen bonding is intramolecular, the O–H stretching band is usually broad, whereas a relatively sharp hydroxyl absorption band is generally obtained when hydrogen bonding is intermolecular [14].

We have prepared a series of thirteen alkyl substituted benzophenyl hydroxamic acids by situating different alkyl groups on one or both of the aromatic rings, and we systematically studied the effect of these groups on the molecular structure and on the extent of intra- and intermolecular hydrogen bondings in these compounds. The frequencies of C=O and O–H stretching bands of these hydroxamic acids as their KBr pellets and as 0.1M solution in $CDCl_3$ are shown in Table 1. Representative examples of IR spectra of three hydroxamic acids, namely benzophenylhydroxamic acid, p–isopropylbenzophenylhydroxamic acid, and N–m–tolylbenzohydroxamic acid in the O–H and C=O regions are shown in Fig. 1. There are striking differences in the position of these bands based on the location of groups. Substituents on the N–phenyl rings, even in the case of methyl groups, shift the C=O frequencies to higher values by 60 to 70 cm^{-1}, as compared to the parent compound 1 or with compounds 2 and 3 where the methyl substituents are on the C–phenyl rings. When smaller substituents, such as methyl or trifluoromethyl are on the C–phenyl rings, regardless of the position of the substituent on this ring (ortho, meta or para), the C=O absorption frequencies are single and at lower frequencies (~1620 cm^{-1}). For these compounds, i.e. 2, 3 and 4, the ν_{O-H} are broad and at lower frequencies (~3200 cm^{-1}). The differences in $\nu_{C=O}$ for these compounds in the solid state as KBr pellets and in $CDCl_3$ solution are small (~5 cm^{-1}), indicating a strong intramolecular hydrogen bonding. However, when the methyl substituents are on the ortho, meta, or para positions of the N–phenyl rings, as in 9, 10 and 11, the C=O bands appear as single and sharp bands at higher frequencies (~1670 cm^{-1}). The O–H bands are also sharp at higher frequencies (~3400 cm^{-1}). The differences between the ν C=O and ν O–H bands from solid to liquids are greater (10–30 cm^{-1}). These results indicate the formation of an intermolecular hydrogen bonding in these compounds. As the bulk of substituents on the

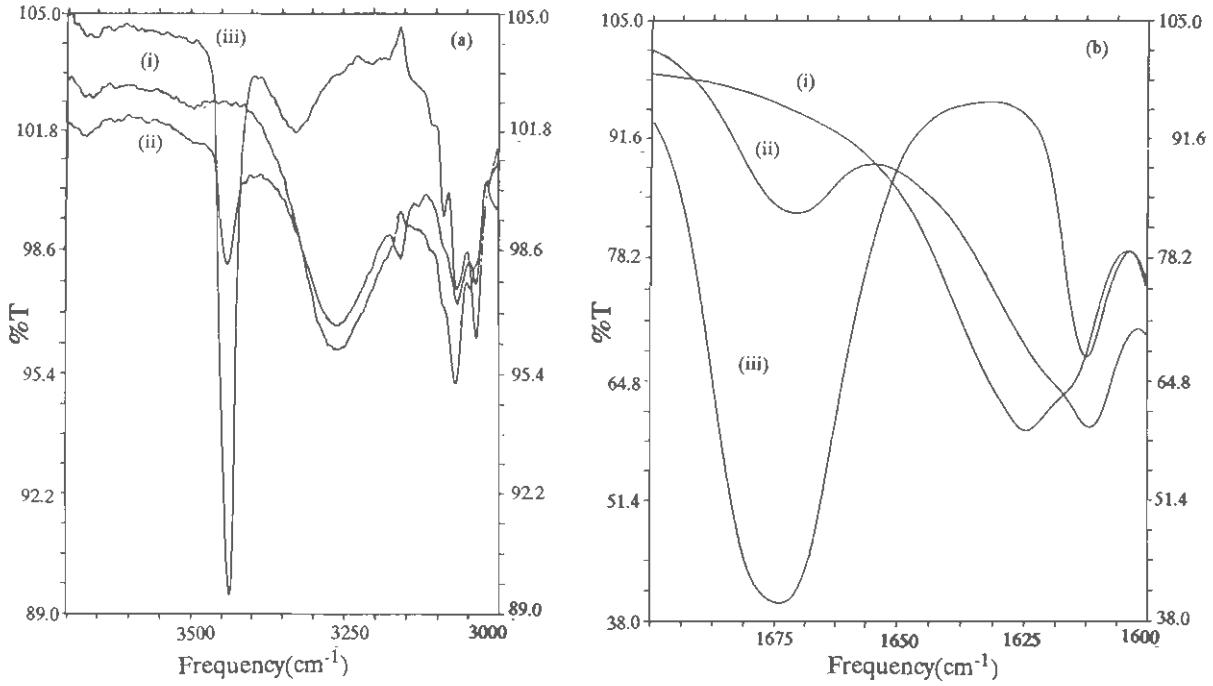
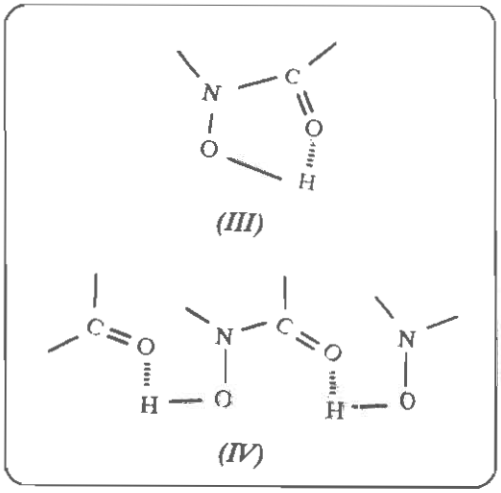


Fig.1 : Solvent subtracted and smoothed IR spectra of (i) benzophenyl hydroxamic acid, (ii) p- isopropylphenyl hydroxamic acid and (iii) N-m-tolylbenzophenyl hydroxamic. (a) O-H region and (b) C=O region.

C−phenyl rings increases from methyl to ethyl, n−propyl, isopropyl, and t−butyl, as in 5, 6, 7 and 8, a small amount of intermolecular hydrogen bonded isomer forms. This is evident from the doubling of the ν C=O and ν O−H bands in these compounds. From the ^{1}H-NMR data of these compounds (Table 1), the ratio of inter- to intramolecular hydrogen bonded isomers is about 13:87. The amount of intramolecularly hydrogen bonded and intermolecularly hydrogen bonded forms in benzophenylhydroxamic acids appears to be governed by both the steric and electronic factors. Alkyl substituents on the C−phenyl ring favor the intramolecularly hydrogen bonded form due to the inductive effect which increases the charge density on the C=O group, strengthening the intramolecular hydrogen bond. Increasing the bulk of alkyl substituents on the C−phenyl ring gives about 13% of the intermolecularly hydrogen bonded form with the intramolecularly hydrogen bonded form still the predominant species (Fig. 1). The alkyl substituent on the N−phenyl ring increases the electronic density due to the lone pair on the nitrogen leading to increased repulsion between the lone pair electrons and the hydrogen electron clouds at the ortho positions of the N− phenyl ring. This, in turn, favors the trans form as the stable configuration. When substituents are introduced both in the C− phenyl and N− phenyl rings (compounds 12 and 13, Table 1), the intermolecular hydrogen bonded is the predominant species. This is not a surprising result based on the above arguments.

From these results we conclude that substituents on the N− phenyl rings of benzophenylhydroxamic acids favor trans structure and intermolecular hydrogen bonding, such as IV, while these substituents on the C− phenyl rings favor intramolecular hydrogen bonding and cis configuration as in III. As the bulk of alkyl substituents on the C− phenyl ring increases, a small amount of IV begins to form. Tandon performed similar studies by recording the IR spectra as Nujol mulls. The C=O and



(III)

(IV)

O–H frequencies in every case correspond to intramolecular hydrogen bonding, irrespective of whether the substituents are on the C–phenyl or N–phenyl or both the rings [6f,g]. It is difficult to understand the discrepancy in these studies.

Crystal structure of UO_2(p-isopropylbenzophenylhydroxamic acid)$_2$. EtOH

The uranyl complex of this ligand was prepared in ethanol and characterized by elemental analysis and spectroscopic methods in order to study the effect of complexation on the

Table 1: IR and ^{1}H-NMR data of alkyl substituted benzophenylhydroxamic acids.

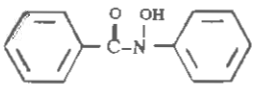
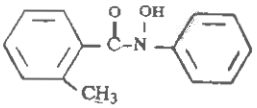
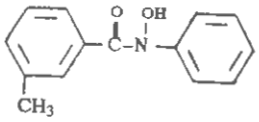
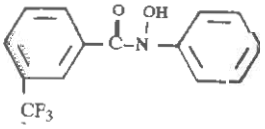
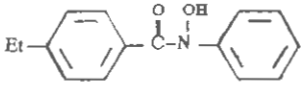
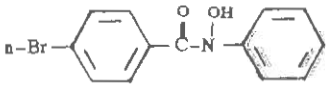
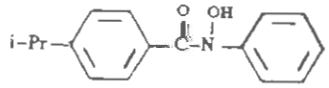
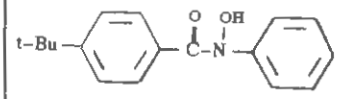
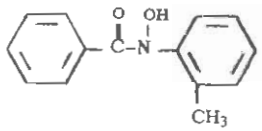
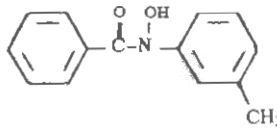
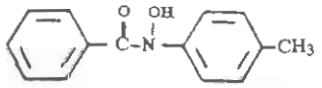
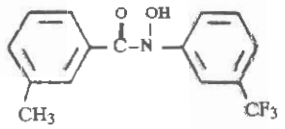
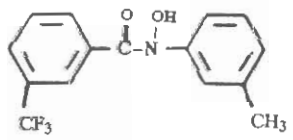
	Compound	$CDCl_3$ Solution		KBr pellets		Proton NMR		
		ν_{O-H}	$\nu_{C=O}$	ν_{O-H}	$\nu_{C=O}$	δ_{O-H}	δ_{Phenyl}	Alkyl
1		3260[a]	1623	3180[a]	1625	9.17	7.04-7.5	
2		3259[a]	1623	3061[a]	1623	9.45	7.06-7.25	2.25s
3		3252[a]	1623	3141[a]	1622	9.25	7.07-7.3	2.25s
4		3267[a]	1620	3143[a]	1613	9.25	7.19-7.7	
5		3438[b]	1669	3350[b]	1675	7.9	7.37-7.34	1.17t,2.58q
		3257[a]	1612	3143[a]	1604	9.2	7.38-7.8	1.25t,2.8q
6		3438[b]	1669	3346[b]	1640	8.0	7.6-7.9	0.93t,1.75m,2.62t
		3259[a]	1612	3189[a]	1622	9.35	7.6-7.9	0.87t,1.55m,2.52
7		3438[b]	1669	3352[b]	1643	7.95	7.6-7.8	1.25d,2.9m
		3256[a]	1614	3177[a]	1620	9.30	7.07-7.35	1.17d,2.8m

Table 1 continued:

	Compound	$CDCl_3$ Solution		KBr pellets		Proton NMR		
		ν_{O-H}	$\nu_{C=O}$	ν_{O-H}	$\nu_{C=O}$	δ_{O-H}	δ_{Phenyl}	Alkyl
8		3455[b]	1678	3386[b]	1640	8.0	7.4-7.6	1.31s
		3254[a]	1618	3184[a]	1613	9.25	7.22-7.6	1.31s
9		3447[b]	1674	3248[b]	1684	7.67	7.08-8.0	2.32s
10		3435[b]	1673	3265[b]	1648	7.92	6.9-7.71	2.17s
11		3435[b]	1676	3309[b]	1647	7.94	6.95-7.68	2.15s
12		3424[b]	1684	3241[b]	1653	7.90	7.2-7.84	2.44s
13		3423[b]	1682	3280	1647	7.89	7.19-7.81	2.46s
14	pIPBPHA-UO_2				1578			

a. Broad, b. Sharp, s. Singlet, d. Doublet, t. Triplet, q. Quartet, m. Multiplet.

molecular structure of these series of compounds. pIPEPHA is a mixture of intra- to intermolecular hydrogen bonding, as discussed above. This complex crystallized in monoclinic space group P21/c and with Z=4. An ORTEP [15] projection of this complex is shown in Fig.2.

Selected bond distances, bond angles, and the positional parameters are available on request. The equatorial plane of the uranyl cation is occupied by a planar set of five oxygen atoms provided by one ethanol molecule and two hydroxamic acid molecules. These form a pentagonal bipyramide along with the two uranyl oxygens. The coordinated solvent molecule confines with the CO group of one ligand and the NO group of the other so that the entire molecule is asymmetric. The UO_2^{2+} group is linear with the usual U–O bond distances (1.75Å). The mean value for the equatorial U–O (hydroxamic acid) distances and the U–O (solvent) distance of 2.38 and 2.37Å, respectively, are normal and similar with the values

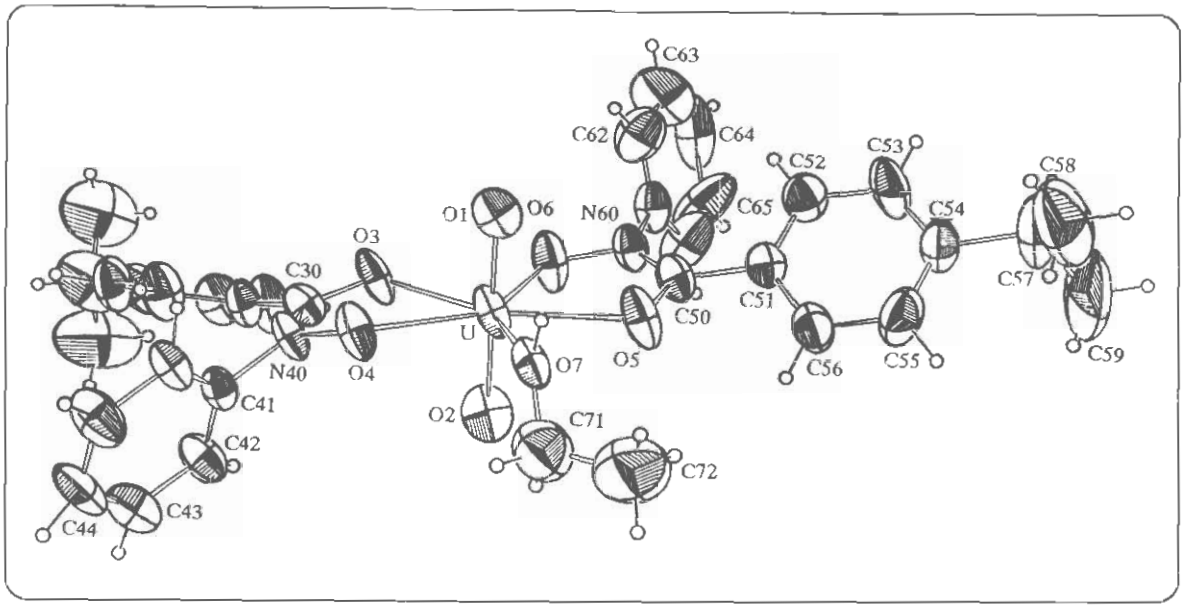


Fig.2 : ORTEP projection of UO_2 (p-isopropylbenzophenylhydroxamic acid)$_2$. EtOH.

reported by *Casellato*, et.al. [16], for the $UO_2(L)_2MeOH$(L=N−phenylbenzohydroxamic acid). The U−O(4) which forms a rather strong hydrogen bond with ethanol (2.55Å) has the longest bond distance (2.42Å). The mean values of C−O bond distances (1.28Å) and of the N−O bond distances (1.36Å) indicate the partial double bond nature of these groups. The plane of 01−U−02 and of 03−07, which form the pentagonal bipyramide, have a 90°C dihedral angle. The uranyl atom is situated out of the pentagonal plane by 0.03Å. The dihedral angle of the C−phenyl ring containing C31−C36 and the N−phenyl ring containing C41−C46 is 63°. However the dihedral angle of the C−phenyl ring, containing C51−C56, and the N−phenyl ring, containing C61−C66, is 76°. These angles are 72° and 63° respectively, for the unsubstituted ligand [16]. Differences are also observed in the dihedral angles between the plane of the pentagon and the C−phenyl and N−phenyl rings of the two hydroxamic acids for the same reason. These differences can be attributed to the bulkiness of the isopropyl groups.

The chelate is formed by the replacement of the hydroxylamino proton by uranyl ion and ring closure through coordination of the carbonyl oxygen. The frequency due to the O−H stretching vibration disappears in the complex and the C=O band frequency shifts to 1578cm^{-1}, indicating the complexation through C=O and N−O moieties.

This value shifted from 1635cm^{-1} in free BPHA, 1, to 1530cm^{-1} in the uranyl complex as it was reported by *Smith* and *Raymond* [17]. The shift to higher frequency in the substituted complex is due to the bulky isopropyl groups.

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