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Structural Effects on Stabilities of Iminoxy Radicals

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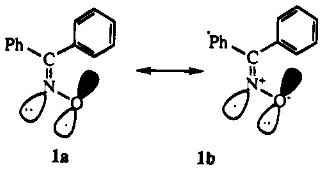
Abstract: The equilibrium acidities for the O−H bonds of seven ketoximes in dimethyl sulfoxide and the oxidation potentials of their conjugate anions have been measured. The combination of the pK_{HA} and $E_{ox}(A^-)$ values using eq 1 has allowed estimates to be made of the ethalpies for homolytic cleavage of the O−H bonds (BDEs). The BDEs estimated for the O−H bonds in t-Bu$_2$C=NOH and t-Bu(1-Ad)C=NOH by our simple method using eq 1, BDE = $1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3$, were found to be within experimental error of those obtained by a direct calorimetric method. The BDEs of the O−H bonds become progressively weaker as the size of the alkyl groups R and R′ in the RR′C=NOH oximes become larger. The BDEs cover a range of 14 kcal/mol from that of 95.8 kcal/mol for the BDE of the O−H bond in Me$_2$C=NOH to 81.7 kcal/mol for the BDE of the O−H bond in t-Bu(Ad)C=NOH. The effects are rationalized in terms of increasing ground state energies and decreasing BDEs with increasing size of the alkyl groups, as the result of progressively larger relief of steric strain as the O−H bond is broken homolytically. These and other effects of structural changes in oximes on BDEs of their O−H bonds are consistent with delocalization of the odd electron in a p orbital on oxygen to carbon. The X-ray crystal structure of di-*tert*-butyl ketoxime has been measured and compared with that of dimethyl ketoxime.

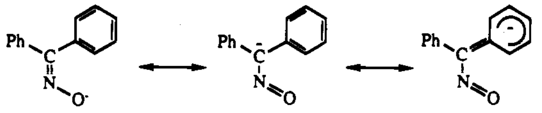
The unusual stability of iminoxy radicals formed by the oxidation of oximes has aroused considerable interest.[1] Their electronic structure, as deduced from ESR spectra, place the odd electron in a π-type orbital derived from a nitrogen sp^2 orbital and an oxygen p orbital. This π-type orbital is believed to lie in the nodal plane of the C=N π bond, which requires it to be orthogonal to the molecular π system, so that the radicals have been described as σ radicals, rather than π radicals. The radicals are best represented as hybrids, such as **1a** ↔ **1b**, for benzophenone oxime.[1]

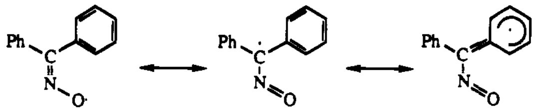

1a **1b**

By examining the ESR spectra of suitably-substituted benzophenone ketoximes, it was shown that the coupling of the odd electron involves two ortho protons on a single benzene ring. The results were deemed to be incompatible with the radicals being of a π-type. The ESR spectra of 28 iminoxy radicals were studied, and assignment as σ radicals was said to be apparent from all of the data obtained.[1d]

The di-*tert*-butyliminoxy radical has since been isolated and characterized. It was found to have a strong absorption at 1610 cm^{-1}, which is indicative of the presence of a C=N and/or an N=O bond.[2]

Recently we have measured acidities in DMSO and estimated homolytic bond dissociation enthalpies (BDEs) for the O−H bonds in 21 oximes. For example, the acidity of the O−H bond in benzophenone oxime was found to be 5.9 units (8.1 kcal/mol) stronger than that of the O−H bond in acetone oxime, and the BDE of the O−H bond in benzophenone oxime was found to be about 6.8 kcal/mol weaker than the O−H bond in acetone oxime.[3] (Henceforth, kcal/mol will be abbreviated as kcal.) These results were interpreted to mean that the corresponding iminoxy anions and radicals were stabilized by resonance delocalization as in **2a**$^-$ to **2c**$^-$ and **3a**• to **3c**•. In other words, these iminoxy radicals are acting as π radicals, rather than σ radicals.


2a' **2b'** **2c'**


3a **3b** **3c**

Measurements with aldoximes led to similar conclusions. The BDE of the O−H bond in an *E*/*Z* mixture of acetaldoximes, MeCH=NOH, was estimated by eq 1 to be 98 kcal, which is about 6 kcal less than that of the O−H bond in methanol.[4] Replacement of the Me group in acetaldoxime by a Ph group caused an 8 and 11 kcal decrease in BDE for the *Z* (anti) and *E* (syn) isomers, respectively. Replacement of the methyl group in acetaldoxime by NH$_2$ to give foramidoxime, H$_2$NCH=NOH (**4**) caused a 13 kcal decrease in the BDE of the O−H bond relative to that in CH$_3$O−H. Here, too, the sizable decrease in BDE is consistent with the formation of a π radical (**5a**• ↔ **5d**•).

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[4] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 473. The CH$_3$O−H BDE value of 104 kcal is used as a standard because the BDE value of 120 kcal for HO−H appears to be abnormally high.

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$$H_2N\text{-}CH{=}N\text{-}O^{\cdot} \longleftrightarrow H_2N\text{-}{}^{\cdot}CH\text{-}N{=}O \longleftrightarrow H_2\overset{+\cdot}{N}\text{-}\overset{-}{C}H\text{-}N{=}O \longleftrightarrow H_2\overset{+\cdot}{N}\text{-}CH{=}N\text{-}O^{\cdot}$$

5a· **5b·** **5c·** **5d·**

The BDEs of the O—H bonds in only a few oximes had been determined prior to our study. A direct calorimetric method had been devised, however, that can be used if the radicals formed are stable for many hours in concentrated solution at room temperature and undergo clean, rapid, exothermic, and reversible reactions with a suitable hydrogen donor.[5] These stringent requirements were found to be met for the iminoxy radicals derived from three oximes, t-Bu(i-Pr)C=NOH, t-Bu_2C=NOH, and t-Bu(1-Ad)C=NOH, for which BDEs of the O—H bonds were found to be 84.3 ± 3, 80.9 ± 3, and 80.0 ± 3 kcal, respectively.[4] These values are smaller than the BDEs we have reported[3] for the O—H bonds in oximes such as Me_2C=NOH, Et_2C=NOH, and c—$C_5H_{10}C$=NOH, by 6.3—15.8 kcal. These large differences indicate that either there is something wrong with our method or the BDEs of the O—H bonds in ketoximes are dramatically weakened by increasing the bulk of the alkyl groups.

Our method is based on the combination of pK_{HA} values in DMSO with the oxidation potentials of their conjugate bases $E_{ox}(A^-)$ according to eq 1. Comparisons of the BDEs for

$$BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + C \qquad (1)$$

the acidic H—A bonds in 18 weak acids where literature gas-phase values are available with estimates made using eq 1 have been shown to give general agreement to within ±3 kcal or better.[6] The BDE for phenol (90 kcal) is about 4 kcal higher than "best" literature value, but the effects of meta and para substituents on phenol BDEs agree well with literature values.[7] Nevertheless, it was clearly necessary to test our method further by applying it to t-Bu_2C=NOH and t-Bu(1-Ad)C=NOH oximes.

Results and Discussion

Synthesis of Di-*tert*-butyl Ketoxime and *tert*-Butyl-1-adamantyl Ketoxime. These two oximes have been prepared by reaction of the corresponding ketones with hydroxylamine at high pressure.[8] They have also been prepared by reaction by hydroxylamine with the corresponding ketimines, but no detailed procedure was given.[9] In our hands, di-*tert*-butyl ketoxime was prepared by the reaction of *tert*-butyllithium with trimethylacetonitrile, and the oxime was formed by reaction of the ketimine with hydroxylamine hydrochloride and sodium acetate. *tert*-Butyl-1-adamantyl ketoxime was prepared in a similar manner using 1-cyanoadamantane.

Acidities and BDEs of Di-*tert*-butyl and *tert*-butyl-1-adamantyl Ketoximes. The equilibrium acidities of these ketoximes were measured in DMSO by the overlapping indicator method,[10] using 1,1,3-triphenyl-2-aza-1-propene (pK_{HA} = 24.3) and 9-*tert*-butylfluorene (pK_{HA} = 24.35) as indicators. Their pK_{HA}s were found to be 24.4 and 24.3, respectively. The standard deviations in the runs were less than 0.1 pK_{HA} units. These oximes are each stronger acids in DMSO than Me_2C=NOH by about 1.7 pK_{HA} units (2.9 kcal).

Table 1. Equilibrium Acidities in DMSO and BDEs for the O—H Bonds in Oximes

no.	oxime	pK_{HA}	$E_{ox}(A^-)^b$ (eV)	BDE[c] (kcal)
1.	Me_2C=NOH[a]	26.0	−0.569	95.8
2.	Et_2C=NOH[a]	25.2	−0.673	92.3
3.	t-Bu(Me)C=NOH	24.4	−0.675	91.1
4.	4-t-Bu-c-C_5H_9C=NOH	23.7	−0.651	90.7
5.	c-$C_5H_{10}C$=NOH[a]	24.2	−0.700	90.3
6.	camphor	24.8	-0.829^R	88.1
7.	norcamphor	24.4	−0.827	87.6
8.	i-Pr_2C=NOH	24.2	-0.812^R	87.7
9.	t-Bu_2C=NOH	24.4	-0.977^R	84.2
10.	t-Bu(1-Ad)C=NOH	24.3	-1.078^R	81.7

[a] pK_{HA} and $E_{ox}(A^-)$ values taken from ref 3. [b] Oxidation potentials measured under the conditions previously described[6] and referenced to the ferrocene/ferrocenium couple. Values marked with a superscript R are reversible. [c] Calculated by using eq 1 with the empirical constant C = 73.3 kcal/mol.[5] The absolute values are probably no better than ±3 kcal/mol, but the relative values are believed to be accurate to better than 1 kcal/mol.

The BDEs estimated using eq 1 for the O—H bonds in t-Bu_2C=NOH and t-Bu(1-Ad)C=NOH ketoximes are 84.2 and 81.7 kcal, respectively, which agree within experimental error with the BDEs of the 80.9 ± 3 and 80.0 ± 3 kcal, respectively, obtained by the direct calorimetric method.[5] These results point to a remarkably large weakening of the O—H bonds in ketoximes brought about by increasing the bulk of the alkyl groups. This effect was examined further by measuring the acidities and BDEs of the ketoximes derived from pinacolone, 4-*tert*-butylcyclohexanone, diisopropyl ketone, camphor, and norcamphor. The results are summarized, along with data earlier reported, in Table 1.

There appears to be little or no relationship between a_N or a_H ESR coupling constants and BDEs of those ketoximes. Thus, all of the a_N coupling constants for the 28 ketoximes studied by Gilbert and Norman[1d] fall in the range of 28—32 G, with no obvious trends, whereas the BDEs for the 10 ketoximes in Table 1 cover a range from 82 to 96 kcal.

The Effects of Structural Changes on the Acidities and BDEs of Ketoximes. There is a dramatic, progressive weakening of the O—H bonds in these ketoximes as the size of the alkyl groups is increased. These effects must be associated with increased steric congestion in the region of the O—H function. This conclusion is supported by the reversibility of the cyclic voltammograms for the anions derived from four of the most sterically congested ketoximes (Table 1). The reversibility of these CVs means that the radical must have a sufficient lifetime on the electrode to be reduced back to the anion in the reverse sweep.

The steric hindrance effects in a bulky ketoxime can be illustrated by comparing the structure of the dimethyl ketoxime with that of di-*tert*-butyl ketoxime (**4**). The X-ray crystal structure of **4** is shown in Figure 1. A comparison of bond lengths and bond angles for di-*tert*-butyl ketoxime and dimethyl ketoxime is shown in Figure 2.

In dimethyl ketoxime the steric repulsion between the two methyl groups is small. This is evident from the small bond angle for CH_3—C—CH_3 of 116° (Figure 2), which is slightly *smaller* than that of a regular sp^2-hybridized carbon atom (120°). In di-*tert*-butyl ketoxime, the corresponding angle becomes 125° (Figures 1 and 2), i.e., 9° larger than that in dimethyl ketoxime, due to the large steric repulsions between the two *tert*-butyl groups, and the N—O bond is lengthened compared to that in Me_2C=NOH. Also, the NC_2C_3 angle (Figure 2) in di-*tert*-butyl ketoxime is reduced to 123°, i.e., 8° *smaller* than the corresponding angle in dimethyl ketoxime, which brings one of the methyl groups close to the oxygen atom. The large steric

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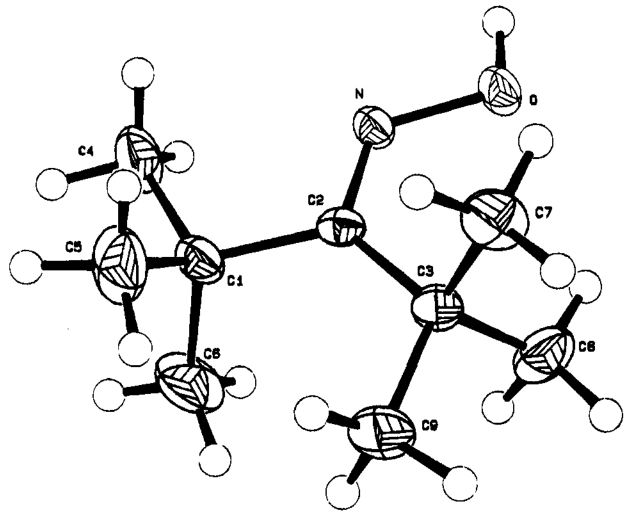


Figure 1. Molecular structure and atom-labeling scheme for t-Bu$_2$C=N–OH (50% probability ellipsoids.

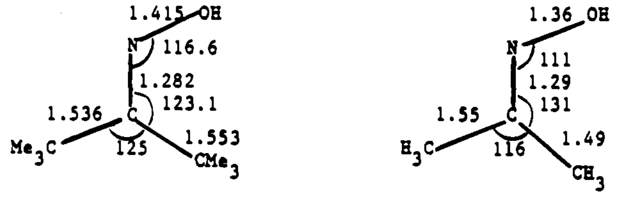


Figure 2. Structure of di-*tert*-butyl ketoxime and dimethyl ketoxime with bond lengths (Å) and bond angles (deg).

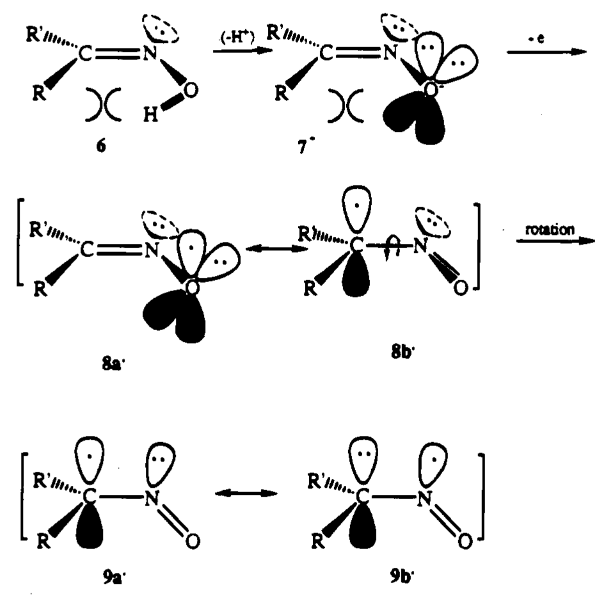
interaction between the *cis-tert*-butyl group and the hydroxyl group causes the ONC$_2$ angle (Figure 2) to increase by 6°, relative to the corresponding bond angle in dimethyl ketoxime.

In a general sense the progressive weakening of the O–H bonds in RR′C=NOH oximes with increasing alkyl size can be attributed to a progressive relief of steric strain on loss of a hydrogen atom to form an iminoxy radical.

Effects of Structural Changes on BDEs. Although the relative stabilities of the radicals formed by the oxidation of anions on an electrode provide important information concerning the weakening or strengthening of acidic H–A bonds resulting from structural changes, it is now clear that information obtained from a consideration of the effects on ground state energies (GSEs) may be at least of equal importance. In the present instance, *both* appear to be important.

Increases in GSEs are known to usually cause increases in the acidities of weak acids. For example, the substitution of an OMe group for one of the N–H hydrogen atoms of acetamide increases the acidity of the remaining N–H bond by 12.1 kcal, an effect believed to be caused primarily by an increase in the GSE, whereas a comparable phenyl substitution increases the acidity by only 5.9 kcal primarily by stabilizing the resulting anion.[11] Both of these structural changes cause cathodic shifts in the $E_{ox}(A^-)$ values and weaken the H–A bonds to homolytic cleavage as expected by the abilities of these functions to delocalize the odd electrons in the corresponding radicals.[11] Examination of Table 1 shows that Me$_2$C=NOH and Et$_2$C=NOH are *weaker* acids than the other eight oximes, which have acidities averaging 24.3 ± 0.06 pK_{HA} units, by 1.7 and 0.9 pK_{HA} units, respectively. The anions derived from these ketoximes must be subject to progressively larger steric hindrance to solvation as the bulk of the alkyl groups increase. Ordinarily, we would expect this to cause a progressive decrease in acidity, but this does not happen. Instead the acidity of the third member of the series *increases*, and those of all the subsequent members follow suit. We believe that an increase in GSE makes entry 3 more acidic than entries 1 and 2. As the alkyl groups get larger, increases in GSEs, caused by increased repulsions, keep pace with increased hindrance to solvation. As the anions become less solvated, their effective electron densities increase and there is a cathodic shift in their $E_{ox}(A^-)$ values that covers a range of 0.509 V (11.7 kcal). This will tend to weaken the O–H bonds and to decrease the BDEs.

Scheme 1



Stabilization of the corresponding radicals also provides information concerning the weakening of the O–H bonds. The formation of the iminoxy radicals in our experiments occurs on the electrode where a single electron is removed from an anion (7^-) generated by deprotonation of the oxime (Scheme 1). We assume that removal of an electron from the oxide ion occurs from an orbital so as to form an oxygen–carbon-centered allylic radical (**8**). Rotation around the C–N bond can occur, perhaps simultaneously with electron removal, to form the (more stable) radical (**9a**• ↔ **9b**•). This rotation is probably accompanied by relief of strain since the oxygen and R group can move away from one another. Note that the hybridization of the nitrogen atom does not change during these electronic transformations. It is perhaps for this reason that the ESR α_N coupling patterns remain nearly constant despite a substantial change in the overall structure of the radicals.[1b]

The overall effect reported in this paper of an increase in ground state energies of a series of weak acids being accompanied by a decrease in bond energies conforms to a rule that we have been using as a working hypothesis, namely, that *structural changes that decrease ground state energies tend to strengthen the BDEs of the acidic H–A bonds and vice versa.*[12]

Summary and Conclusions

The good agreement with literature values of the BDEs of the O–H bonds in t-Bu$_2$C=NOH and t-Bu(1-Ad)C=NOH oximes with the BDE values obtained by combining the pK_{HA} and $E_{ox}(A^-)$ values for the anions of these oximes using eq 1 has given further credence to this simple method of estimating

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BDEs. A progressive decrease in the BDEs of the O−H bonds in 10 RR′C=NOH ketoximes with progressive increases in the size of the R and R′ alkyl groups is rationalized in terms of progressive increases in ground state energies and the consequent increase in relief of steric strain in forming the iminoxy radicals by homolytic cleavage of the O−H bonds. The progressive cathodic shifts in $E_{ox}(A^-)$ values on homolytic bond cleavage are believed to be caused by progressive increases in effective electron densities of the anions as steric inhibition of solvation increases with increased alkyl size. The corresponding radicals are believed to be progressively stabilized also by delocalization involving a relief of strain.

Experimental Section

General. NMR spectra were recorded on a Varian Gemina-300 spectrometer using $CDCl_3$ as solvent and the chloroform peak (^1H, 7.2 ppm) as reference. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The procedure for electrochemical measurement has been described earlier.[6] All potentials are reported with reference to the formal potential ($E_{1/2}$) of ferrocene/ferrocenium couple. The equilibrium acidities in DMSO solution were determined by the indicator overlapping titration as described previously. All of the ketone oximes in Table 1 have pK_{HA} values between 23.7 and 24.8, and they were titrated using two common indicators: 1,1,3-triphenyl-2-aza-1-propene (pK_{HA} 24.3) and 9-*tert*-butylfluorene (pK_{HA} = 24.35). Agreement between titrations with different indicators were generally less than 0.1 pK_{HA} unit.

***tert*-Butyl Methyl Ketoxime, Diisopropyl Ketoxime, 4-*tert*-Butylcyclohexanone Oxime, Camphor Oxime, and Norcamphor Oxime** were prepared as follows. In a 250 mL round-bottom flask was dissolved 5 g of ketone in 150 mL of 95% ethanol. Two equivalents of hydroxylamine hydrochloride and 2 equiv of sodium acetate were dissolved in 10 mL of H_2O. The aqueous solution was mixed with the ethanol solution, and the solution was refluxed overnight. The solvent was removed on a rotavap, the residue was mixed with 50 mL of H_2O and extracted twice with 30 mL of diethyl ether. The combined ether solutions were dried over sodium sulfate, and the solvent was removed on a rotavap. Solid oximes were recrystallized from ethanol; liquid oximes were purified by silica gel column chromatography. Reactions were not optimized, but it was found that reactions gave over 70% yield, except for diisopropyl ketoxime, which was obtained in only 15% yield after 2 days of reflux.

Di-*tert*-butyl Ketone Imine. In a 250 mL three-neck round-bottom flask was dissolved 15 g of trimethylacetonitrile (0.18 mol) in 50 mL of anhydrous diethyl ether. *tert*-Butyllithium in 120 mL of pentane (1.7 M) was added dropwise into the ether solution cooled by an ice−water bath. The solution was stirred for 3 h at room temperature and poured onto about 100 g of ice. The organic layer was separated, and the aqueous solution was extracted twice with 20 mL of ether. The combined ether solutions were dried over sodium sulfate. After removal of the solvent on a rotavap, reduced pressure distillation (65 °C/0.2 mmHg) gave 20 g (78%) of di-*tert*-butyl ketone imine: ^1H NMR δ 1.22 (*t*-Bu), 1.24 (*t*-Bu), 9.3 (broad, NH).

Di-*tert*-butyl Ketoxime. In a 250 mL round-bottom flask was mixed 9 g (64 mmol) of di-*tert*-butyl ketone imine with 100 mL of 95% ethanol. To the above solution was added 20 mL of an aqueous solution containing 7.5 g (108 mmol) of hydroxylamine hydrochloride and 5.4 g (64 mmol) of sodium acetate. A white precipitate formed immediately. The solid was collected on a filter and recrystallized from acetone and H_2O. Di-*tert*-butyl ketoxime (9 g, 90%) was obtained: ^1H NMR δ 1.26 (*t*-Bu), 1.42 (*t*-Bu), 9.8 (OH); mp 157 °C.

1-Adamantyl *tert*-Butyl Ketoxime. The same procedure was used to prepare 1-adamantyl *tert*-butyl ketone imine from 1-cyanoadamantane and *tert*-butyllithium. The crude 1-adamantyl *tert*-butyl ketone imine was used in the reaction with hydroxylamine hydrochloride without further purification. 1-Adamantyl *tert*-butyl ketoxime was obtained as white crystals in an overall yield of 85%: ^1H NMR δ 1.25, 1.44 (*t*-Bu's), 1.69, 1.97, 2.35 (Ad's), 9.7 (OH, broad); mp 196−197 °C.

X-ray Crystallography. A transparent, colorless prismatic crystal of di-*tert*-butyl ketoxime, $C_9H_{19}ON$, having approximate dimensions of 0.46 × 0.39 × 0.26 mm was mounted using oil (Paratone-N, Exxon) on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of 25 carefully centered reflections in the range $22.1 < 2\theta < 23.8°$, corresponded to a monoclinic cell with dimensions: $a = 11.239(2)$ Å, $b = 8.373(2)$ Å, $\beta = 102.12(2)°$, $c = 10.698(3)$ Å, $V = 984.3(8)$ Å. For $Z = 4$ and FW = 157.26, the calculated density is 1.061.

The data were collected at 120 ± 1 °C using the $\omega-\theta$ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.25° with a take-off angle of 2.8°. Scans of $(1.00 + 0.35 \tan \theta)°$ were made at speeds ranging from 3.0 to 16.0 deg/min (in ω). Moving-crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm, and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with isotropic thermal parameters. The final cycle of full-matrix least-squares refinement was based on 1323 observed reflections ($I > 3.00\sigma(I)$) and 177 variable parameters and converged (largest parameter shift was 0.08 times its esd) with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.048$. All calculations were performed using the TEXSAN software.

Acknowledgment. We are grateful to the National Science Foundation for support of this research. We are indebted to Charlotte L. Stern (Northwestern University) for carrying out the X-ray analysis.

Supplementary Material Available: Experimental details of X-ray diffraction for di-*tert*-butyl ketoxime (23 pages); tables of observed and calculated structure of factors (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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