

Geometrical Isomerization and Restricted Rotation in Iminoxyl Radicals from Benzaldoximes

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The *E* geometrical isomers of benzaldoxime, *p*-chlorobenzaldoxime, and *p*-methylbenzaldoxime have been oxidized to the corresponding iminoxyl radicals within the cavity of an EPR spectrometer by using photolytically produced *tert*-butoxy radicals. The observed iminoxyls retain the same geometry (*E*) of the starting oximes at low temperature (ca. 190 K), while at room temperature they are almost completely converted to the more stable *Z* isomers. At an intermediate temperature (233 K), where both isomeric species were simultaneously detected, the rate of geometrical isomerization could be determined as $18 \pm 6 \text{ s}^{-1}$ for the radical from *p*-chlorobenzaldoxime. The estimated energy barrier (ca. 12 kcal mol⁻¹) is much lower than that calculated in the parent oximino compounds (ca. 60 kcal mol⁻¹). A rationalization of this effect in terms of Molecular Orbital theory is given. In the *Z* isomers of the examined iminoxyls, selective broadening of the EPR lines due to restricted rotation of the aryl ring was observed in the temperature range from 250 to 330 K. An analysis of the line shape variations with temperature performed on iminoxyl 5 provided a value of the rotational barrier of 6.18 kcal mol⁻¹.

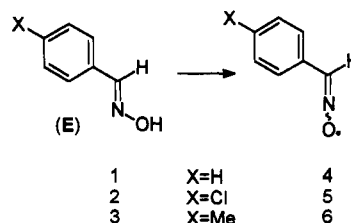
Iminoxyls are long-lived σ -radicals where the unpaired electron is located in an orbital which is made by the nonbonding nitrogen sp² orbital and an oxygen p-orbital lying in the nodal plane of the C-N π bond.¹ When two different groups are linked to the azomethine carbon, these radicals, likewise the parent oximes, may exist either in the *E* or in the *Z* geometry. Several experiments indicate that the geometrical isomerization of iminoxyls is much faster than in the parent oximes, even though the reported rate constants are scattered over a wide range of values. Norman and Gilbert have placed a lower limit of about 30 s⁻¹ for the interconversion of the iminoxyl radical from benzil monoxime at room temperature.² By assuming a preexponential factor of 10¹³, this corresponds to an activation energy $E_a \leq 16 \text{ kcal mol}^{-1}$. Grubbs and co-workers estimated the rate of *E*-*Z* isomerization of phenyl- (*p*-tolyl)iminoxyl as $4 \times 10^{-4} \text{ s}^{-1}$ at room temperature; this implies that E_a should be ca. 22 kcal mol⁻¹.³ Ingold and Brownstein determined the rate of geometrical interchange of di-*tert*-butyl iminoxyl as $6 \times 10^5 \text{ s}^{-1}$ at 14 °C, which corresponds to an activation energy of 9.5 kcal mol⁻¹.⁴

Geometrical isomerization of the parent oximino derivatives, on the other hand, takes place at much lower rates; the *E* and *Z* isomers of these compounds may actually be separated by chemical methods and kept for months when stored in the dark. Consistently, *ab initio* calculations carried out on acrolein oxime, CH₂=CH-CH=NOH, predict a barrier of ca. 60 kcal mol⁻¹ for geometrical isomerization, irrespective of the pathway followed, i.e. inversion at nitrogen or rotation about the C=N double bond.⁵

In iminoxyl radicals containing at least an aromatic ring

linked to the azomethine carbon, restricted rotation, or conformational isomerism is also possible. Despite the relative wealth of information concerning these radicals, little is known about the ease at which internal rotation of aryl rings takes place. Actually, to the best of our knowledge, the only report is the one concerning the iminoxyl from 2-naphthaldehyde oxime, which at room temperature showed a line width alternation effect attributed to restricted rotation of the naphthalene ring.⁶ Iminoxyl radicals derived from benzaldehyde and benzophenone oximes did not show selective line broadening at the same temperature.

In the present paper we report an EPR investigation on the iminoxyl radicals (4-6) derived from the *E* conformers of substituted benzaldoximes (1-3) and on the determination of the energy barriers to geometrical isomerization and to rotation of the aryl ring for *p*-chlorophenyl methaniminoxyl (5).



Results and Discussion

The iminoxyl radicals 4-6 were generated within the EPR cavity by photolyzing deoxygenated solutions of the parent oximes and di-*tert*-butyl peroxide in *tert*-butyl alcohol/*tert*-butylbenzene (1/4) or toluene. The geomet-

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.
(1) Norman, R. O. C.; Gilbert, B. C. *J. Phys. Chem.* 1967, 71, 14, and references therein.

(2) See second paragraph at page 5385 of ref 3.

(3) Dobashi, T. S.; Parker, D. R.; Grubbs, E. J. *J. Am. Chem. Soc.* 1977, 99, 5382.

(4) Ingold, K. U.; Brownstein, S. *J. Am. Chem. Soc.* 1975, 97, 1817.

(5) Alberti, A.; Barbaro, G.; Battaglia, A.; Guerra, M.; Bernardi, F.; Dondoni, A.; Pedulli, G. F. *J. Org. Chem.* 1981, 46, 742.

(6) Hyperfine splittings at the *ortho* protons result mainly from direct overlap of their 1s orbital with the orbital containing the unpaired electron.¹ Thus, only the *ortho* proton on the same side of the iminoxyl function is expected to be coupled with the unpaired electron.

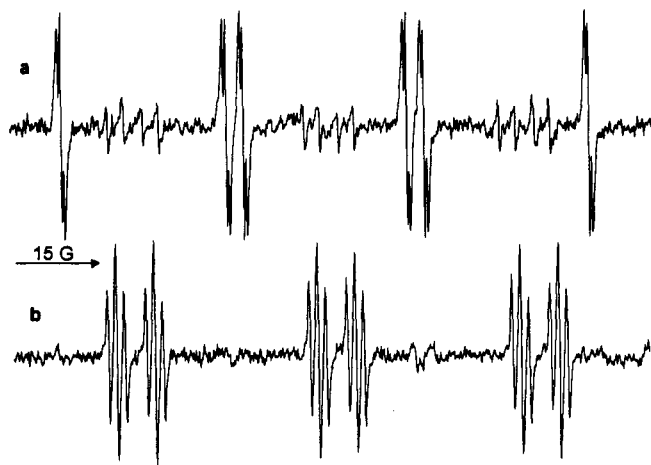


Figure 1. EPR spectra of the *Z* and *E* iminoxyl radical from *p*-Cl-benzaldoxime recorded at 210 K (a) and at 320 K (b).

Table 1. EPR Parameters for the Iminoxyl Radicals from 4-Substituted-*E*-benzaldoximes *p*-X-C₆H₄CH=NOH (1-3) in Toluene Solution

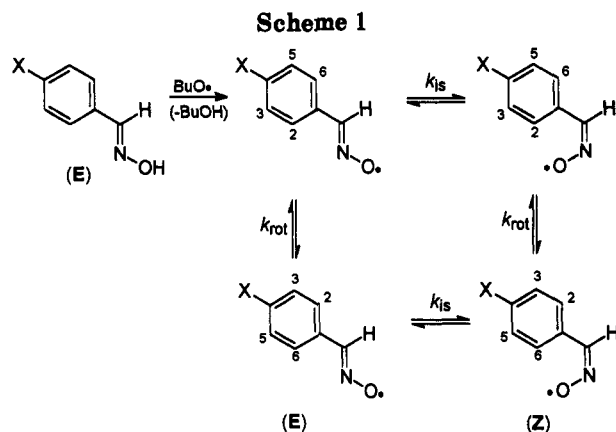
radical	X	isomer	T, K	a_N , G	a_H , G	a_{Ar} , G	g
4	H	<i>E</i>	193	29.40	26.96	0.47 (3H)	2.0060
		<i>Z</i>	223	31.80	5.97	2.68 (1H)	2.0057
		<i>Z</i>	298	31.20	5.90	1.40 (2H)	2.0057
5	Cl	<i>E</i>	193	29.50	26.79	0.48 (2H)	2.0059
		<i>Z</i>	223	31.49	5.89	2.60 (1H)	2.0057
		<i>Z</i>	298	31.45	5.88	1.30 (2H)	2.0057
6	Me	<i>E</i>	193	29.32	26.97	nr ^a	2.0061
		<i>Z</i>	223	30.98	5.71	2.74 (1H)	2.0057
		<i>Z</i>	298	31.14	5.78	1.37 (2H)	2.0057

^a nr = not resolved.

rical *E* isomers of the starting oximino compounds were used in each case.

When the photolysis was carried out at low temperature ($T \leq 193\text{K}$), the spectrum was dominated by the *E* isomer retaining the geometry of the starting oxime, but traces of the *Z* isomer were also observed as it is shown in Figure 1 for a representative example. Interestingly the two isomeric radicals, beside showing very different splittings at the azomethine proton (ca. 27 G in the *E* and ca. 6 G in the *Z* isomer)^{1,5} and slightly different couplings at the nitrogen atom (see Table 1), exhibited also a marked difference in the ring protons' splittings. In particular, at these temperatures, the *Z* isomer showed an additional doublet (ca. 2.7 G) which, by comparison with the known data for aryl iminoxyls, was assigned to one of the *ortho* protons. This indicates that, in the EPR time scale, the aromatic ring is locked in the plane containing the CNO moiety; otherwise identical splittings from the two *ortho* protons would be observed.⁶ In agreement with this interpretation, when raising the temperature the doublet evolved to a 1:2:1 triplet whose line separation was half that of the initial doublet, as it should be expected if the increasing rate of rotation of the aromatic ring rendered the *ortho* hydrogens magnetically equivalent.

At variance with what was observed with the *Z* isomer, the low-temperature EPR spectrum of the *E* isomer of 5 (see Figure 1) did not show any selective line broadening. In this latter radical the unpaired electron was coupled with the nitrogen atom, the azomethine proton, and two equivalent protons (0.48 G) which, by comparison with previously reported data,⁷ could be unambiguously iden-



tified as the *ortho* protons of the phenyl ring. Although their equivalence might be taken as an indication that the aromatic ring is freely rotating in the EPR time scale even at 190 K, we believe this is not the case and that the equivalence is accidental since there is no apparent reason why internal rotation in the *E* isomer should be so much faster than in the other one. A more likely explanation is that the *ortho* protons are equivalent because transmission of spin density to them from the N-O moiety takes place through the bonds by means of a spin polarization mechanism rather than through the space¹ as in the *Z* isomeric radicals. The much lower splitting at these protons, detected in the *E* (ca. 0.5 G) with respect to the *Z* isomer and the fact that in the *E* iminoxyl (4) from benzaldoxime the *para* hydrogen has the same splitting as the two *ortho* protons, are consistent with the above interpretation.

Another effect observed when increasing the temperature was the reduction of the intensity of the signals due to the *E* isomer which were gradually replaced by those of the *Z* isomer. In the three examined cases the *Z* isomer became largely dominant at $T \geq 300\text{K}$, as it is shown in Figure 1 for the iminoxyl radical 5 from *p*-chlorobenzaldoxime. Similar changes in the relative stability of the two possible geometrical isomers of the iminoxyl radicals with respect to the parent oximes have been reported in previous papers,^{8,9} and a rationalization of this effect in terms of molecular orbital theory has been given.⁵

The various processes taking place in our system are exemplified in Scheme 1. To determine the rates at which rotation and geometrical isomerization are taking place, the variations with temperature of the EPR spectra of these species were investigated.

The rate constants for rotation could be easily determined from the line shape in those spectra where selective broadening of some of the EPR lines was observed. These were analyzed, in the case of the *Z* isomer of *p*-chlorophenyl iminoxyl 5, by comparison with spectra simulated by using the density matrix theory^{10,11} according to well-established procedures.¹² The Arrhenius plot of the resulting rate constants, reported in Figure 2, provides an activation energy of $6.18 \pm 0.20\text{ kcal mol}^{-1}$ and a $\log(A/s^{-1}) = 12.80 \pm 0.14$ for the rotation of the aryl ring.

We are not aware of any determination of the barrier to internal rotation in benzaldehyde oxime or related

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(8) Thomas, J. R. *J. Am. Chem. Soc.* 1964, 86, 1446.
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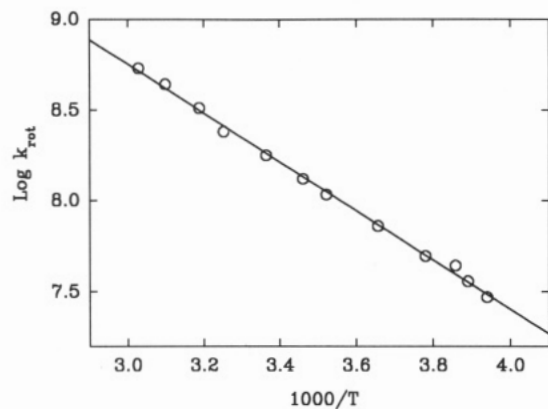
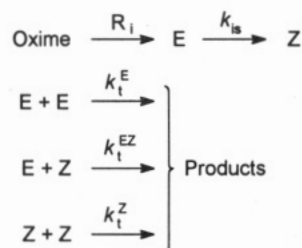


Figure 2. Arrhenius plot of the rate constant for internal rotation of the aryl ring in the *Z* isomer of the (*p*-chlorophenyl)-methaniminoxyl radical (5).

compounds; however, we can compare the value of E_a measured here with the reported free energy of activation ($\Delta G^\ddagger = 7.6 \text{ kcal mol}^{-1}$) for the rotation of the aryl ring in *p*-chlorobenzaldehyde^{13,14} which is the precursor of oxime 3. The similarity of this barrier in the iminoxyl radical and in the corresponding diamagnetic aldehyde is not surprising in view of the fact that the unpaired electron occupies a molecular orbital having σ character. Since the rotational barrier is essentially determined by the π conjugative interactions between the aryl ring and the C=N double bond, it is reasonable that the barrier height is not affected to a large extent by the change in the occupancy of a σ orbital.

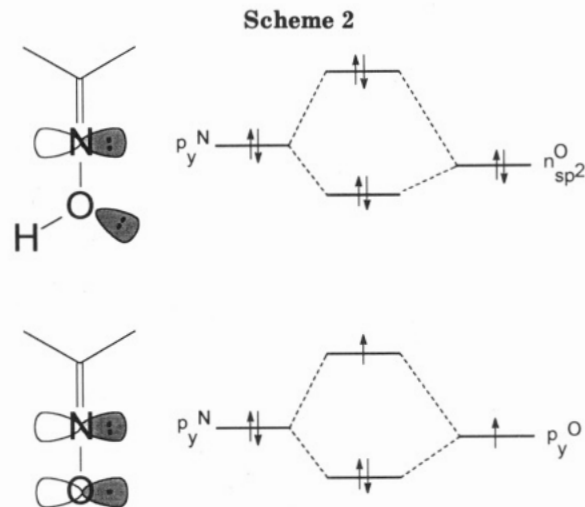
The rate constants for geometrical isomerization were more difficult to measure. This, however, could be done by taking advantage of the fact that, at certain temperatures, both the *E* and *Z* isomeric iminoxyls were observed simultaneously when one of the oximes 1–3 was photolyzed within the EPR cavity in the presence of $(\text{Me}_3\text{CO})_2$. This allowed k_{is} to be determined from the concentrations of the two isomeric radicals under steady state conditions (continuous photolysis) provided the overall reaction scheme can be represented as follows.



Under the steady-state approximation and by making the reasonable assumption that $k_t^E = k_t^{EZ} = k_t^Z$, it is easy to show that k_{is} is given by eq 1.^{15,16}

$$k_{is} = 2k_t[Z] \left\{ \frac{[Z]}{[E]} + 1 \right\} \quad (1)$$

Phenyliminoxyl radicals have been shown to decay with first-order kinetics at high temperature but with second-



order kinetics at or below room temperature, where their self-reaction leads to the formation of dimers. A rate constant of $9 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ has been reported for the bimolecular decay of phenylmethaniminoxyl (4) at 25 °C.¹⁷ To apply eq 1 we had to repeat the determination of $2k_t$ at a temperature where the *E* and *Z* isomers were present in comparable amounts. We choose the iminoxyl giving the more intense EPR spectrum, that is (*p*-chlorophenyl)-methaniminoxyl (5), and the temperature of 233 K at which the *E* and *Z* isomers were present in concentration of 2.5×10^{-7} and $4.2 \times 10^{-7} \text{ M}$, respectively. The second-order decay of radical 5 at 233 K was fitted with a rate constant $2k_t$ of $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ which, when introduced in eq 1, provides a value of $18 \pm 6 \text{ s}^{-1}$ for the rate constant to geometrical isomerization, k_{is} .

This value, which is not far from those reported in ref 2 and 4 when taking into account the different experimental temperatures, indicates that the activation energy for the geometrical isomerization of iminoxyl radicals is in the range 10–15 kcal mol⁻¹. Actually, if a preexponential factor of 10^{13} is assumed, the presently determined rate constant k_{is} at 233 K corresponds to $E_a = 12.5 \text{ kcal mol}^{-1}$.

It is therefore apparent that in iminoxyl radicals the interconversion between the *E* and *Z* isomers is much easier than in the corresponding oximes for which an isomerization barrier of ca. 60 kcal mol⁻¹ has been computed.⁵ INDO calculations on the vinyliminoxyl radical previously reported are in agreement with that finding; these also suggested that geometrical isomerization should take place via inversion at nitrogen rather than rotation about the C=N double bond, because the former process is much less expensive in energetic terms (8.92 kcal mol⁻¹) than the latter one (36.5 kcal mol⁻¹).⁵ The greater ease of geometrical isomerization via nitrogen inversion for iminoxyls has been explained on electronic grounds in terms of the change of orbital occupancy with respect to parent oximes. As shown in Scheme 2, the transition state of oximino compounds involves a strongly destabilizing four electron–two orbital interaction between the doubly occupied p_y orbital on nitrogen and sp^2 on oxygen, while the three electron–two orbital interaction occurring in the iminoxyl radical between the nitrogen and oxygen p_y orbitals is instead slightly stabilizing.⁵ This favorable interaction is expected to produce a marked reduction of the energy barrier to inversion on passing from oximes to

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the corresponding iminoxy radicals. On the other hand, the different occupancy of a σ orbital in oximes and iminoxyls should only have a small effect on the isomerization barrier via rotation about the π C=N double bond, in agreement with the above computations.

Experimental Section

The *E* isomer of benzaldoxime was a commercial product, while (*E*)-4-chloro- and (*E*)-4-methylbenzaloxime were prepared according to standard procedures described in the literature¹⁸ and purified by column chromatography; all other chemicals were commercially available and were used as received.

Typical samples consisted of nitrogen-purged toluene or *tert*-butyl alcohol/*tert*-butylbenzene solutions of the oximes con-

taining some di-*tert*-butyl peroxide and were photolyzed with the light from a 1-kW high-pressure mercury lamp directly inside the cavity of either a Bruker ER 200D or a Bruker ESP 300 EPR spectrometer. These were fitted with standard variable-temperature accessories, with an NMR gaussmeter for field calibration and a frequency counter for the determination of *g*-factors, that were corrected with respect to that of the radical cation from perylene in concentrated sulfuric acid (2.00258).

The decay traces of the EPR signals necessary for kinetic measurements were acquired by means of a dedicated computer, radical concentrations were measured with respect to a solution of DPPH of known concentration using the signal from a ruby crystal as internal standard, and line-shape analysis was carried out by simulating the spectra by means of a program based on the density matrix theory.¹²

Acknowledgment. Financial support from MURST and CNR (Rome) is gratefully acknowledged.

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