of starting materials, was also performed. The purities of the isolated samples were checked by GC and found to be quite high in all cases except one. By using an internal standard and response factors, we were able to determine the concentrations of the various samples in ethanol prior to determination of the rotations. The results of the optical activity measurements, done in absolute ethanol, were as follows: 7, $[\alpha]_D$ +107°, +104°; 8, $[\alpha]_D$ +34°, +32°; lactone 9, $[\alpha]_D$ −52° (the second sample of 9 was contaminated).

Thermal Reaction of Tri-*n*-butyltin Hydride with Methyl 5-Bromopentanoate (15). Into a 50-mL, round-bottomed flask fitted with a magnetic stirrer, a pressure-equalizing addition funnel, a condenser and an inlet for nitrogen were placed 0.5480 g (2.810 mmol) of methyl 5-bromopentanoate and 15 mL of reagent grade benzene. The flask was placed in an oil bath maintained at 80 °C, the apparatus was deoxygenated, and a solution containing 0.8675 g (2.981 mmol) of tri-*n*-butyltin hydride and 0.0008 g (0.0049 mmol) of azobis(isobutyronitrile) in 15 mL of benzene was added over a period of 6 h. The reaction mixture was allowed to reflux at 80 °C for an additional 10 h. A variety of reaction times, dropping rates, and concentrations were also employed; comparable results were obtained.

The crude product was analyzed directly by GC, using a 3% OV-17 on 100–120-mesh Gas Chrom Q for support in a $^1/_8$ in. × 5 ft column, a carrier gas flow of 30 mL/min, and a temperature program consisting of an initial 10-min isothermal period at 70 °C followed by a 10 °C/min increase to 230 °C and a final 10-min period at 230 °C. The identity of the products was based on GC retention time comparison with known samples and mass spectra (by using the Du Pont GC/MS described earlier). Yields were determined from response factors for samples which were available and estimated, based on the number of carbons, for the other reaction products.

The compounds identified were the following (name, retention time, yield): methyl pentanoate, 1.4 min, 30.5%; methyl 5-bromopentanoate, 13.9 min, 19.7%; tri-*n*-butyltin hydride, 15.2 min, 5.5%; tetrabutyltin, 18.5 min, 1.3%; unidentified tin compound, 19.5 min, 1.8%; tributyltin bromide, 20.1 min, 35.7%; hexabutylditin, 25.8 min, 5.5%.

A sample of tetrahydropyran-2-one (**6a**) was available and was shown by GC retention time to not be a part of the above reaction mixture.

Irradiation of Methyl 5-Bromopentanoate (15). A solution consisting of 0.0171 g (0.0877 mmol) of methyl 5-bromopentanoate in 15 mL of *tert*-butyl alcohol was placed in a quartz tube fitted with a serum seal and magnetic stirrer. Two needle tubes were passed through the seal to permit the bubbling of nitrogen through the solution and venting. The reaction vessel was deoxygenated for a period of 0.5 h, the inlet and outlet tubes were removed, and GC analyses were run for samples after periods of 1.5, 13.5, 24.5, 39, and 63.5 h of irradiation in the Rayonet reactor described earlier.

The GC analysis and procedures were the same as those described in the previous experiment. The compounds identified from the 63.5-h sample were the following (name, retention time, yield): methyl pentanoate, 1.4 min, 40.6%; methyl 5-bromopentanoate, 13.9 min, 53.9%; dimethyl decanedioate, 21.7 min, 2.5%; unidentified component, which, on the basis of its long retention time, was assumed to be a branched isomer of **16**, 22.4 min, 3.0%.

Registry No. [4]a, 624-34-8; *cis*-(±)-**7**, 76024-08-3; (2*S*,6*S*)-(+)-[7], 76024-09-4; *trans*-(±)-**8**, 76024-10-7; (2*R*,6*S*)-(−)-**8**, 76024-11-8; (2*S*,6*R*)-(+)-**8**, 58801-54-0; (6*S*)-(−)-**9**, 16320-13-1; **10**, 106-70-7; **11**, 13317-80-1; **12**, 75993-77-0; **13**, 75993-78-1; **14**, 1636-34-6; **15**, 5454-83-1; **16**, 106-79-6; 2-methoxy-6-methyl-2,3-dihydropyran, 28194-35-6; 2-hydroxy-6-methyltetrahydropyran, 18545-19-2; methyl 5-oxohexanoate, 13984-50-4; methyl 5-phenyl-5-hydroxyhexanoate, 75993-79-2; 6-methyl-6-phenyltetrahydropyran-2-one, 28771-65-5; 5-phenylhexanoic acid, 2972-25-0; Acetophenone, 98-86-2; tri-*n*-butyltin, 688-73-3; tetrabutyltin, 1461-25-2; tributyltin bromide, 1461-23-0; hexabutylditin, 4808-30-4.

Stereochemistry of Iminoxy Radicals

Angelo Alberti, Gaetano Barbaro, Arturo Battaglia, and Maurizio Guerra

Laboratorio dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni, 40064 Ozzano Emilia, Italy

Fernando Bernardi

Istituto di Chimica Organica, 40136 Bologna, Italy

Alessandro Dondoni

Laboratorio di Chimica Organica, Facoltà di Scienze, Università di Ferrara, Italy

Gian Franco Pedulli*

Istituto Chimico dell'Università, 09100 Cagliari, Italy

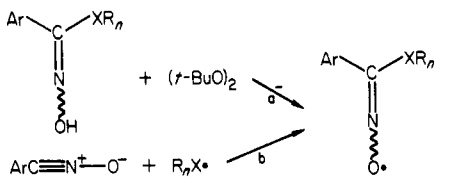
Received September 12, 1980

Iminoxy radicals of general structure Ar—C(X)=N—O·, where X = H, CH_2OH, *n*-Bu, *t*-Bu, $SiEt_3$, $SiPh_3$, $GePh_3$, $SnMe_3$, $SnBu_3$, $SnPh_3$, SMe, SBu, SPh, Cl, and Br, have been photolytically generated from the parent oximino compounds or from aromatic nitrile *N*-oxides in an aprotic solvent. Two configurational isomers, interconvertible in solution, have been detected by electron spin resonance spectroscopy for the majority of these radicals. The preferred geometry of iminoxyls derived from ortho-unsubstituted benzaldoximes is that which places the aryl ring and the oxygen atom on the same side of the C=N double bond (anti). Substitution of the azomethine proton leads to a stabilization of the syn configuration, the effect being larger the greater the atomic number of the leading atom of the substituent group. The relative stability of the syn isomer is also increased by substitution of the aromatic ortho protons. INDO calculations have been carried out on several model systems in order to rationalize the experimental results. The effects responsible for the configurational preference of the different terms of this series of radicals are discussed in terms of a perturbation molecular orbital (PMO) approach.

Iminoxyls belong to one of the few classes of σ radicals long lived enough to be studied in solution under different experimental conditions.[1] Owing to their persistency, they are especially suitable substrates to investigate the char-

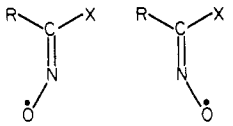
0022-3263/81/1946-0742$01.00/0

Scheme I



acteristics of σ as opposed to π radicals which are by far more common and whose properties are well understood. In iminoxyls the unpaired electron is contained in an orbital which is made up of the nonbonding sp^2 orbital on nitrogen and a p orbital on oxygen and which lies on the nodal plane of the C–N π bond. Approximately 45% of the total spin density is associated with the nitrogen atom.[2]

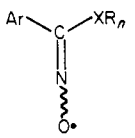
When the substituents bonded to the azomethine carbon are different, syn and anti isomers can be formulated for



anti syn

these radicals, depending on whether the one selected of these groups, say X, is on the same or on the opposite side of the oxygen atom with respect to the C=N double bond. The energy barrier for the interconversion of these isomers is large enough to allow the detection of distinct ESR signals from each of them.[3]

Although a large number of studies on iminoxyls has been reported,[1-7] these were mainly concerned with the structural dependence of the hyperfine splittings measured at the nuclei of the R and X groups rather than with the factors responsible for the configurational preference of these radicals. We have therefore undertaken an approach to this problem and report here the results from this study. We have examined a series of iminoxyls bearing two different substituents at the azomethine carbon. One of them is constantly an aryl ring and the other can be a hydrogen, an alkyl, a group 4B organometallic substituent, a thioalkyl, a thioaryl, or a halogen atom.



Ar = Ph, 4-ClPh, 2-ClPh, 2-BrPh, 2,6-Cl_2Ph, 2-Cl,6-FPh, mesityl, 3,5-dichloromesityl, pentafluorophenyl

XR_n = H, CH_2OH, Et, *n*-Bu, *t*-Bu, $SiEt_3$, $SiPh_3$, $GePh_3$, $SnMe_3$, $SnBu_3$, $SnPh_3$, SMe, SEt, S-*t*-Bu, SPh, Cl, Br

Most of these radicals are new, and a few data are available in the literature for XR_n = alkyl, Cl, and H.[1,4-6]

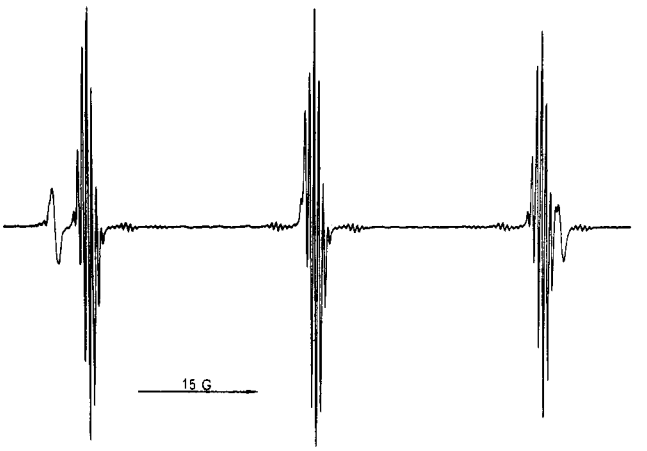


Figure 1. Room-temperature ESR spectrum of (2,6-dichlorophenyl)(triethylsilyl)methaniminoxyl (**7f**) in *tert*-butylbenzene.

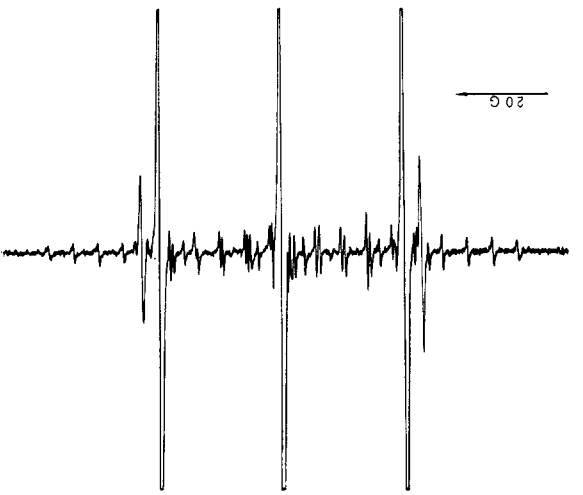


Figure 2. Room-temperature ESR spectrum of (2,6-dichlorophenyl)(triphenylgermyl)methaniminoxyl (**7g**) in *tert*-butylbenzene.

SCF-MO calculations have also been performed on model systems to get a deeper understanding of the experimental results.

Experimental Section

Generation of the Radicals. The iminoxyls have been produced by two distinct methods: either by photolytic abstraction of the hydroxylic hydrogen (route a[1c] Scheme I) from the parent oximino compounds with di-*tert*-butyl peroxide (DTBP) or by addition of $R_nX\cdot$ radicals generated in situ to aromatic nitrile oxides (route b).[5] In both cases *tert*-butylbenzene was used as solvent unless otherwise specified. The $R_nX\cdot$ radicals next trapped by nitrile oxides have been produced by photolytic hydrogen abstraction with DTBP from triethylsilane, triphenylsilane, triphenylgermanium hydride, trialkyl- or triphenyltin hydride, or methanol ($R_nX\cdot$ = $R_3Si\cdot$, $R_3Ge\cdot$, $R_3Sn\cdot$, $\cdot CH_2OH$), by photolytic cleavage of the S–S bond of disulfides ($R_nX\cdot$ = RS·), or by reaction of alkyl bromides with triethylsilyl radicals ($R_nX\cdot$ = alkyl).

Photolysis was performed using a high-pressure mercury lamp (1 kW) focused within the ESR cavity.

Organometallic radicals gave the most intense and better resolved ESR signals, so that satellite lines due ^{29}Si(4.70%, $I = {}^1/_2$), ^{73}Ge(7.61%, $I = {}^9/_2$), ^{117}Sn(7.67%, $I = {}^1/_2$), and ^{119}Sn(8.68%, $I = {}^1/_2$) could be easily detected. As examples, Figures 1 and 2 show the ESR spectra of (2,6-dichlorophenyl)(triethylsilyl)methaniminoxyl (**7f**) and (2,6-dichlorophenyl)(triphenylgermyl)methaniminoxyl (**7g**).

Materials. The silicon, germanium, tin, and sulfur derivatives employed for the generation of the radicals $R_nX\cdot$ were commercially available as was unsubstituted benzaldoxime.

(1) (a) B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 234 (1964); (b) H. Lemaire and A. Rassat, *Tetrahedron Lett.*, 2245 (1964); (c) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 7090 (1972).
(2) M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963); 2276 (1965).
(3) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 1446 (1964).
(4) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).
(5) T. Caronna, A. Quilico, and F. Minisci, *Tetrahedron Lett.*, 3633 (1970); B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Am. Chem. Soc.*, **93**, 3290 (1971).
(6) A. Dondoni, G. F. Pedulli, and G. Barbaro, *J. Org. Chem.*, **37**, 3564 (1972).
(7) J. J. Zeilstra and J. B. F. N. Engberts, *Tetrahedron*, **29**, 4299 (1973).

Table I. Room-Temperature Hyperfine Splitting Constants (Gauss), g Factors, and Isomer Ratios of $ArC(XR_n)=NO\cdot$ Iminoxyls in *tert*-Butylbenzene

radical	Ar	XR_n	isomer	a_N	a_{Ar}	a_X	a_R	g	syn/anti ratio
1a	Ph	H	anti	31.20	1.4 (2 H)	5.9 (H)		2.0057	0
1b	Ph	SEt	syn	28.52	0.55 (2 H), 0.20 (1 H)		2.92 (2 H)	2.0058	>20
1c	Ph	SPh	syn	28.10	*a*		*a*	2.0060	>20
2	4-MePh	H	anti	31.14	1.37 (2 H)	5.78 (H)		2.0057	0
3a	4-ClPh	H	anti	31.45	1.30 (2 H)	5.88 (H)		2.0057	0
3b		CH_2OH	anti	31.34	1.31 (2 H)		0.88 (2 H)[b]	2.0058	0.3[c]
			syn	29.89	0.40 (2 H)			2.0060	
3c		$SiPh_3$	anti	34.30	1.33 (2 H)			2.0045	0.59
			syn	28.17	0.31 (2 H)	11.0 (Si)		2.0044	
3d		$SiEt_3$	anti	33.50	1.30 (2 H)				1.41
			syn	28.41	0.26 (2 H)	10.1 (Si)	0.63 (6 H)		
3e		$GePh_3$	anti	34.12	1.30 (2 H)			2.0046	1.66
			syn	27.37	0.29 (2 H)	5.62 (Ge)		2.0053	
3f		$SnMe_3$	anti	33.75	1.30 (2 H)			2.0042	15.1
			syn	26.37	*a*	92.5 (Sn)	0.75 (9 H)	2.0078	
3h		SMe	syn	28.62	*a*		2.05 (3 H)		>20
3i		S-*t*-Bu	syn	26.30	0.35 (2 H)				>20
3j		SPh	anti	33.37	1.33 (2 H)			2.0054	~40
			syn	27.9	0.42 (2 H)		0.42 (3 H)	2.0060	
3k		Cl	syn	29.02	0.65 (2 H)[d]	1.40 (^{35}Cl), 1.16 (^{37}Cl)		2.0067	>30

[a] Splitting not resolved. [b] Splitting assigned by deuterium substitution. [c] In methanol. [d] Splitting measured at −60 °C.

All oximes,[8] *S*-ethylbenzothiohydroximate,[9] *S*-phenylbenzothiohydroximate,[9] 4-chlorobenzohydroxymoyl chloride,[10] mesitylhydroxymoyl chloride,[11] 3,5-dichloro-2,4,6-trimethylbenzohydroxymoyl bromide,[13] and pentafluorobenzohydroxymoyl chloride,[14] were prepared by methods reported in the literature.

Isomerization of the oximes was accomplished as described.[15]

Nitrile *N*-oxides were prepared by two alternative methods:[16] either by reaction of the corresponding hydroxymoyl chloride with triethylamine (4-chlorobenzonitrile oxide and pentafluorobenzonitrile oxide) or by dehydrogenation of the parent oxime with hypobromite.

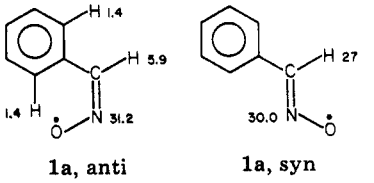
Results

Before proceding to discuss the assignment of the ESR spectra to the geometrical isomers and the configurational preference of iminoxyls, we need to be certain that the observed ratio of the two isomers reflects the actual thermodynamic stability, instead of being kinetically controlled. In other words, the geometrical forms of the radicals should be interconvertible in solution. This, of course, is not obvious, particularly when it is recalled that the corresponding isomers of the parent oximino compounds may be separated by chemical methods and kept for months when stored in the dark.

Several experimental results reported by other authors[4,17] suggest that the isomerization of iminoxyls is a much faster process than that for oximino derivatives. However, conclusive evidence in this direction is provided by the following observations: (i) when a mixture of the syn and anti isomers of benzaldoxime is photolized in the presence of di-*tert*-butyl peroxide, the corresponding radical is obtained only in the configuration placing the oxygen atom on the opposite site of the azomethine proton (anti); (ii) in the case of alkylthio- and arylthio-substituted iminoxyls (XR_n; X = S, R = alkyl or Ph), which could be produced either by hydrogen abstraction from the parent oximino compounds or by addition of thiyl radicals to nitrile oxides, the same isomeric composition was obtained.

It should also be emphasized that the relative stability of the two geometric forms of iminoxyls is, in some cases, remarkably solvent dependent. For instance, benzaldoxime gives a mixture of the two geometrical forms of the corresponding iminoxyl in water solution,[3,17] while only the anti isomer is obtained in *tert*-butylbenzene. For this reason the data have been collected in a low-polarity solvent which seems more adequate than polar solvents for comparison of the experimental results with theoretical predictions.

Assignment of the ESR Spectra. To make clearer the line of reasoning we adopted to solve this problem, the examined radicals have been divided in two groups: (i) iminoxyls without substituents at the ortho positions of the aryl ring, whose hyperfine splitting constants and g factors are reported in Table I, and (ii) iminoxyls bearing ortho substituents, whose ESR parameters are listed in Table II. As far as the first group of radicals is concerned, a convenient starting point for proceeding to the configurational assignment is represented by the two isomeric forms of phenylmethaniminoxyl (**1a**) which are characterized by very different hyperfine splittings (given in gauss) at the proton attached to the azomethine carbon.[3] The larger one has been assigned by several authors to the



1a, anti 1a, syn

(8) A. I. Vogel, "Practical Organic Chemistry", Longmans, London, 1961.
(9) M. H. Benn, *Can. J. Chem.* **42**, 2393 (1964).
(10) A. Battaglia, A. Dondoni, and O. Exner, *J. Chem. Soc., Perkin Trans. 2*, 1911 (1972).
(11) C. Grundman and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).
(12) P. Beltrame, C. Veglio, and M. Simonetta, *J. Chem. Soc. B*, 867 (1967).
(13) P. Beltrame, A. Dondoni, G. Barbaro, G. Gelli, A. Lai, and S. Steffè, *J. Chem. Soc., Perkin Trans. 2*, 607 (1978).
(14) J. J. Wakefield and D. J. Wright, *J. Chem. Soc. C*, 1165 (1970).
(15) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1491 (1955).
(16) C. Grundman and P. Grunanger, "The Nitrile Oxides", Springer-Verlag, Heidelberg, 1971.
(17) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966); K. U. Ingold and S. Brownstein, *J. Am. Chem. Soc.*, **97**, 1817 (1975); T. S. Dobashi, D. R. Parker, and E. J. Grubbs, *ibid.*, **99**, 5382 (1977); J. A. Villarreal, T. S. Dobashi, and E. J. Grubbs, *J. Org. Chem.*, **43**, 1890 (1978); J. A. Villarreal and E. J. Grubbs, *ibid.*, **43**, 1896 (1978).

isomer placing the proton syn to the oxygen atom, on the basis of a variety of MO calculations[18] and of spectroscopic data from related derivatives.[4] We may be reasonably confident that this attribution is correct.

In the same isomeric radicals the ortho hydrogens are also coupled to a different extent with the unpaired electron. The measured splitting in the anti form is, in fact, 1.4 G and, more important for us, is practically independent of the nature of the atom or group directly bonded at the azomethine carbon. In the syn isomer, on the other hand, this coupling constant never exceeds 0.5–0.6 G.[19] Therefore, the magnitude of the ortho-proton splitting may be used as a criterion for determining the geometry of the radical species when the aryl ring does not bear substituents at this position. The assignments reported in Table I have been made on this basis for the iminoxyls of the first group.

An examination of Table I shows other interesting features characteristic of the two series of isomeric radicals. These can be summarized as follows.

(i) In the syn isomers the unpaired electron is always coupled with the leading atom of the XR_n substituent, while in the anti forms the corresponding splitting is undetectably small. This is in agreement with the fact that in phenylmethaniminoxyl (**1a**) the larger azomethine proton splitting is observed in the syn isomer.

(ii) The protons of the alkyl chain of the XR_n group show hyperfine splitting only in the syn configuration as a consequence of the direct spin transfer resulting from the overlap of the oxygen p orbital containing the unpaired electron and the hydrogen 1s orbitals. The same protons do not show any coupling in the anti configuration.

(iii) The g factors are practically constant in the anti isomers of the organosilyl, organogermyl, and organotin derivatives, while they show a progressive increase on descending the periodic table within the series of the syn isomeric radicals. This again is a consequence of the larger spin density at the metal atom in the latter configuration and of the increasing spin–orbit coupling with increasing atomic number.

(iv) In the organometallic iminoxyls the nitrogen splitting in the syn configuration is always smaller than that in the anti form, the marking line being ca. 30 G. Thus, a clear distinction between the two isomers of the latter class of radicals may be made from the value of a_N.

On the basis of these findings, we may now assign the configuration also to iminoxy radicals where the ortho protons of the aryl ring are substituted by other groups. The pertinent data are reported in Table II. For the majority of these radicals the assignment is straightforward in the light of the previous considerations; for others a more detailed discussion may be convenient. Thus, the syn geometry has been attributed to arylchloromethaniminoxyls because of the similarity of the a_{Cl} splitting with the value measured in the (4-chlorophenyl)chloromethaniminoxyl (**3k**) where the magnitude of the ortho proton coupling is indicative of the syn configuration. Also consistent with this geometry is the absence of meta-proton splitting in the mesitylchloromethaniminoxyl (**4i**), since in the anti isomers of other radicals containing the mesityl group and where the assignment is unambiguous, a^H_m is always clearly measurable and of the order of 0.2–0.3 G.

With (3,5-dichloromesityl)bromomethaniminoxyl (**5b**) the large g value suggests that the radical adopts the syn configuration if it is assumed that for arylhalomethaniminoxyls the dependence of the g factor on the atomic number of the atom attached to the azomethine carbon is similar to that found for group 4B organometallic iminoxyls. Finally, the syn geometry has been assigned to the 2-hydroxy-1-(2-chlorophenyl)ethan-1-iminoxyl (**9b**) on the basis of the absence of hyperfine splitting at the methylene protons, by analogy with radical **3b**.

It should be mentioned that the configurational assignment of arylchloromethaniminoxyls given here is reversed with respect to that reported in a previous paper.[6] A more detailed discussion on the more stable geometry of the above and other iminoxyls not described here is reported in another paper.[19]

Configurational and Conformational Preference of Iminoxyls. Tables I and II report, besides the spectral parameters, also the measured ratio between the syn and anti isomers of each radical. Since in the majority of cases the two isomeric species are characterized by different multiplicity of the spectral lines and different line widths, an estimate of the relative amount of each isomer could be made only by computer simulations of the superposition of the two ESR spectra. This procedure is the only one which can provide reliable data; nevertheless it is subject to large errors mainly when the line widths of the two configurational isomers are very different. This situation occurs in the derivatives ortho substituted with chlorine atoms, for which the accuracy of the syn/anti ratio is extremely poor (presumably not more than 50%). In all the other cases the estimated error should not exceed 15–20%. When only one species could be observed, a lower limit of the isomer ratio has been given. This is related to the intensity of the ESR signals and to the predictable multiplicity of the spectrum of the undetected isomer. Thus, large values indicate good quality spectra and/or a low number of lines expected for the unobserved radical.

An examination of the tables shows that the configurational stability of the investigated iminoxyls is strongly dependent both on the nature of the XR_n group attached to the azomethine carbon and on the presence of substituents at the ortho positions of the aryl ring. As far as the effect of the XR_n group is concerned, the larger amount of the anti isomer is always found when X is a proton, the radical being totally in this configuration in iminoxyls unsubstituted in at least one of the ortho positions. Substitution of the azomethine proton with alkyl or organometallic groups produces a stabilization of the syn configuration, which is larger the greater the atomic number of the group 4B atom or the hindrance of the alkyl is. When the substituent is an alkylthio group or a halogen atom, the radical exists essentially in the syn configuration. Therefore, the order of increasing stability of the syn isomer as a function of the leading atom of the XR_n substituent follows the sequence H < C < Si < Ge < Sn < S < Cl $\simeq$ Br. Also, the R groups have some effect on the syn/anti ratio; thus, larger values are found in triethylsilyl than in triphenylsilyl derivatives. However, the differences are smaller than those obtained by changing X.

Substitution of the ortho protons of the aryl ring has the effect of promoting a stabilization of the syn configuration. Thus, the relative amount of the syn isomer is slightly increased by methyl substituents, as is shown by the data for the mesityl derivatives, but it is significantly enhanced in the halogenated radicals. The effect is particularly evident in the series of arylmethaniminoxyls (XR_n = H), where the configurational preference is reversed on going

(18) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964); G. Berthier, H. Lemaire, A. Rassat, and A. Veillard, *Theor. Chim. Acta*, **3**, 213 (1965); R. E. Cramer and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 4790 (1968); M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, *J. Phys. Chem.*, **76**, 553 (1972).

(19) A. Alberti, G. Barbaro, A. Battaglia, A. Dondoni, and G. F. Pedulli, *J. Org. Chem.*, **45**, 4223 (1980).

Table II. ESR Spectral Parameters of Ortho-Substituted $ArC(XR_n)=NO\cdot$ Iminoxyls in *tert*-Butylbenzene

radical	Ar	XR_n	isomer	a_N	a_{Ar}	a_X	a_R	g	syn/anti ratio
4a	Mes[f]	H	anti	31.12	*a*	6.28 (H)		2.0052	0.3
			syn	30.80	0.88 (6 H)	28.8 (H)		2.0056	
4b		CH_2OH	anti	30.26	0.23 (2 H)		1.16 (2 H)[b]	2.0057	0.3[c]
			syn	30.47			0.40 (2 H)[b]	2.0056	
4c		*n*-Bu	anti	29.90	0.27 (2 H)		1.43 (2 H)		0.7
			syn	30.85			0.92 (4 H)		
4d		CMe_3	anti	29.38	0.25 (2 H)				0.9
			syn	30.56			0.87 (9 H)		
4e		$SiPh_3$	anti	32.12	0.27 (2 H)			2.0045	0.84
			syn	28.90		14.07 (Si)		2.0041	
4f		$SiEt_3$	anti	32.02	0.22 (2 H)				1.7
			syn	29.02		11.75 (Si)	0.60 (6 H)		
4g		$GePh_3$	anti	32.25	0.29 (2 H)			2.0047	2.1
			syn	28.25		7.25 (Ge)		2.0049	
4h		$SnMe_3$	anti	32.75	0.26 (2 H)			2.0045	42
			syn	27.03		118 (Sn)	0.71 (9 H)	2.0077	
4i		Cl	syn	29.50		1.77 (^{35}Cl), 1.48 (^{37}Cl)			>30
5a	3,5-Cl_2Mes	Cl	syn	29.53		1.63 (^{35}Cl), 1.36 (^{37}Cl)		2.0063	>30
5b		Br	syn	28.3		6.25 (Br)		2.0082	>10
6a	F_5Ph	H	anti	32.02	0.92 (2 F), 0.41 (1 F)	5.68 (H)		2.0051	2.9
			syn	31.23	7.20 (2 F), 0.55 (1 F)	26.76 (H)		2.0054	
6b		$SiPh_3$	syn	29.0	0.35 (2 F)			2.0039	>20
6c		$SiEt_3$	syn	28.9	0.64 (2 F)		0.64 (6 H)	2.0039	>20
6d		$GePh_3$	syn	28.45	0.50 (2 F)			2.0047	>30
6e		Cl	syn	29.88	1.60 (2 F), 0.20 (1 F)	1.25 (^{35}Cl), 1.04 (^{37}Cl)		2.0058	>20
7a	2,6-Cl_2Ph	H	anti	31.5	0.17 (2 Cl)[d]	5.60 (H)		2.0052	2.2
			syn	32.25	1.55 (2 Cl)	27.65 (H)		2.0054	
7b		CH_2OH	anti	30.86	0.13 (2 Cl)[d]		1.22 (2 H)[b]	2.0056	1.6[c]
			syn	30.35			0.48 (2 H)[b]	2.0054	
7c		Et	syn	30.82			0.88 (2 H), 1.25 (3 H)		*e*
7d		CMe_3	syn	30.35			0.87 (9 H)		*e*
7e		$SiPh_3$	anti	32.60	0.15 (2 Cl)[d]			2.0047	2.6
			syn	29.22		12.0 (Si)		2.0042	
7f		$SiEt_3$	anti	32.42	0.16 (2 Cl)[d]			2.0048	4.2
			syn	29.25		9.86 (Si)	0.58 (6 H)	2.0041	
7g		$GePh_3$	anti	32.68	0.15 (2 Cl)[d]			2.0049	7.7
			syn	28.53		5.92 (Ge)		2.0049	
7h		$SnMe_3$	syn	27.62			0.70 (9 H)	2.0068	>10
7i		$SnBu_3$	syn	27.46		73.5 (Sn)	*a*	2.0069	>10
7j		SMe	syn	29.81	*a*		1.80 (3 H)	2.0053	>10
7k		SPh	syn	29.13	*a*			2.0052	>10
8a	2-F,6-ClPh	H	anti	31.50	6.0 (1 F)	6.0 (H)		2.0052	1.7
			syn	31.98	1.23 (1 Cl), 9.96 (1 F)	27.56 (H)		2.0053	
8b		$SiPh_3$	anti	33.12	*a*			2.0045	3.0
			syn	29.25		11.5 (Si)		2.0039	
8c		$GePh_3$	anti	33.0	*a*			2.0044	7.8
			syn	28.62		5.75 (Ge)		2.0046	
9a	2-ClPh	H	anti	32.15	2.51 (1 H)	6.60 (H)		2.0052	0
9b		CH_2OH	syn	31.32	1.10 (1 Cl)			2.0054	*e*
9c		CMe_3	syn	30.50			0.88 (9 H)	2.0050	*e*
9d		$SiPh_3$	anti	33.12	0.90 (1 H), 0.49 (1 Cl)[d]			2.0043	2.0
			syn	29.31	0.26 (1 Cl)[d]			2.0041	
9e		$SiEt_3$	anti	32.60	0.70 (1 H), 0.40 (1 Cl)[d]				3.7
			syn	29.25	0.30 (1 Cl)[d]	10.25 (Si)	0.62 (6 H)		
9f		$GePh_3$	anti	32.90	0.80 (1 H), 0.45 (1 Cl)[d]			2.0046	5.5
			syn	28.50	0.33 (1 Cl)[d]			2.0048	
10	2-BrPh	H	anti	31.98	2.40 (1 H)	6.64 (H)		2.0055	0

[a] Splitting not resolved. [b] Splitting assigned by deuterium substitution. [c] In methanol. [d] Splitting determined by computer simulation. [e] Signals due to the anti isomer were observed but not interpreted. [f] Mes = mesityl.

from unsubstituted to ortho-substituted derivatives. An exception to this behavior is represented by iminoxyls bearing halogens at only one of the two ortho positions (**9a** and **10**) in which only the anti isomer is observed. However, this is due to the conformation adopted by the aryl ring which, as shown by the absence of coupling at the chlorine or bromine nuclei and by the large splitting at the ortho hydrogen, is the one placing the latter atom close

to the iminoxy oxygen. In this conformation the most important interactions determining the configurational preference of the examined radicals, which we believe to be those between the iminoxy function and the aryl ring as discussed later on, are practically unchanged with respect to the situation in which no ortho substituents are present.

The conformational preference of the aryl ring with respect to the CNO fragment is also strongly affected by the nature of the XR_n group and the ortho substituents. This problem may be discussed by assuming that the hyperfine splittings at the ortho nuclei result mainly from direct overlap of the appropriate s orbital of these atoms and the orbital containing the unpaired electron.[4] Thus, the larger splittings are expected for the ortho nucleus lying on the CNO plane and on the same side of the iminoxy function.

In iminoxyls containing protons at the ortho positions, the practical invariance of the splitting at the latter nuclei suggests that they adopt the coplanar geometry as in phenylmethaniminoxyl, independent of the size of the XR_n group attached to the azomethine carbon. The mesityl derivatives presumably deviate from planarity, even though the experimental data do not provide elements which may substantiate this guess. With the ortho-halogenated radicals, the coupling at fluorine or chlorine is either undetectable or very small, and therefore the aryl ring is out of the CNO plane in both configurations for any XR_n group different from hydrogen. A planar or nearly planar geometry is instead found in the syn isomer of ortho-halogenated arylmethaniminoxyls, i.e., for XR_n = H, as indicated by the large values of a_F and a_{Cl} in **6a** and **7a**, respectively.

In iminoxyls where the aryl ring bears only one ortho halogen we may define a cisoid or transoid conformation, depending on whether the chlorine atom lies on the same or on the opposite side of the C=N double bond with respect to the C(aryl)–C(azomethine) bond. The conformational preference of these radicals is substantially different in the syn and anti configurations. Thus, in the series of the syn isomers the cisoid structure is always more stable. However, the decreasing values of a^{Cl} when the XR_n group is changed along the sequence $CH_2OH > SiR_3 \simeq GeR_3 > t$-Bu suggest progressive deviation of the radicals from planarity. In the anti configuration, on the other hand, the observed coupling with the unpaired electron of both chlorine and an ortho proton when XR_n is an organometallic group indicates that the cisoid and transoid conformations, with the aromatic nucleus slightly out of the CNO plane, have comparable stabilities. With XR_n = H instead, evidence of the strong preference for a planar transoid structure is provided by the large ortho proton splitting.

Computational Results. In order to obtain information about the factors that cause the observed structural differences of iminoxyls, INDO calculations[20] have been carried out on several model systems.

We have at first studied the methaniminoxyl, H_2C=NO·, to test the validity of the computational procedure on this class of radicals. For this purpose the unpaired electron has been forced to reside in the lowest vacant orbital of either σ or π symmetry, and the geometry was optimized in both cases. Since the σ radical is computed to be more stable than the π one by ca. 20 kcal/mol, in agreement with experiment, the theoretical investigation on the other systems has been confined to the case in which the unpaired electron occupies a σ orbital.

Chart I

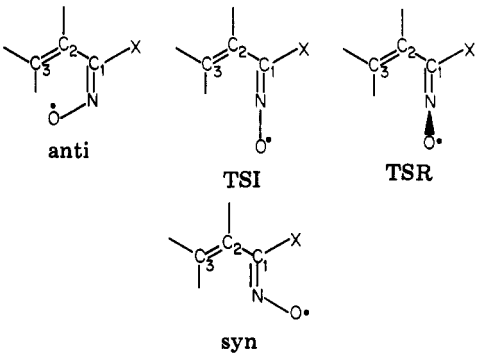


Table III. Geometrical Parameters and Relative Energies, Computed at the INDO Level, for Various Configurations of the Model Radical H_2C=CHC(X)=NO·[a]

optimized parameters	X = H				X = Cl		
	anti	TSI	TSR	syn	anti	TSI	syn
r(N–O), Å	1.22	1.20	1.20	1.22	1.23	1.21	1.23
$r(C_1$–N), Å	1.31	1.30	1.37	1.31	1.31	1.29	1.31
$<C_2C_1N$, deg	122	122	123	122	123	125	122
$<C_1NO$, deg	125	180	126	135	124	180	136
ΔE[b]	0	8.92	36.5	2.45	0	8.11	1.24

[a] See Chart I for definitions. [b] $\Delta E = E - E_{anti}$ (in kcal/mol).

Actual computations have been performed on radicals of general structure H_2C=CHC(X)=NO· (with X = H or Cl) which differ from those experimentally investigated in that the phenyl ring has been replaced with an ethylene group; this approximation should not affect significantly the validity of the results and reduces considerably the computing time. The choice of hydrogen and chlorine for X is due to the fact that they represent the two limiting cases of configurational stability of the examined iminoxyls.

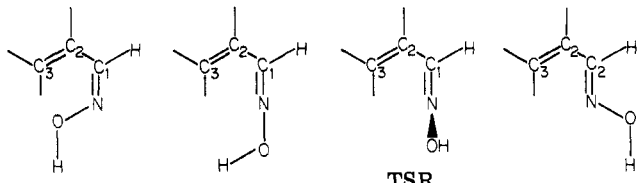
In order to establish the computed configurational preference of these radicals and also to establish which is the lowest energy path to isomerization between planar inversion at the nitrogen atom and rotation around the C=N double bond, we have optimized the geometry of the syn and anti configurations as well as of the two transition states (see Chart I). Optimization has been made on the C_1–N and N–O bond distances and the C_2C_1N and C_1NO bond angles, while the other parameters have been kept fixed at standard values [r(C–H) = 1.08 Å, $r(C_1$–$C_2)$ = 1.47 Å, $r(C_1$–Cl) = 1.72 Å, ∠HCH = 120°] except for the C_2–C_3 bond length which was set equal to 1.39 Å as in benzene.

The computed energies and geometrical parameters for the radical with X = H are listed in Table III. These data show the anti isomer to be more stable than the syn by 2.45 kcal/mol and the lowest energy path to the anti–syn isomerization to be nitrogen inversion which requires 8.92 kcal/mol, while the rotation about the C=N double bond is characterized by a much larger energy barrier (36.5 kcal/mol). With the chlorine derivative (X = Cl) the anti configuration is again computed to be more stable as shown in Table III, although in this case the syn–anti energy gap is lower (1.24 kcal/mol). Chlorine substitution has a negligible effect on the height of the inversion barrier. The isomerization process through rotation has not been considered in the latter radical because of the larger energy required.

To check whether the replacement of the phenyl ring with an ethylene group may somehow modify the com-

(20) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

Chart II



puted conformational stability of iminoxyls, we have repeated the calculations on the radicals PhC(X)=NO· (with X = H, Cl) which are more similar to those examined experimentally, keeping unchanged the geometrical parameters reported in Table III for the iminoxy moiety. Optimization has been performed only on the dihedral angle ϑ formed by the phenyl ring and the C_1NO plane. This angle is computed as 1.8° in the syn and 0° in the anti configuration of phenylmethaniminoxyl (X = H) and as 9.3° and 0°, respectively, in the same configurations of phenylchloromethaniminoxyl (X = Cl). The computations show that in both radicals the anti isomer is again more stable, although the presence of the phenyl instead of the ethylene group reduces the syn–anti energy separation to 1.5 kcal/mol for X = H and 0.2 kcal/mol for X = Cl.

In conclusion, the INDO calculations predict the anti configuration to be lower in energy in all the examined cases. This result agrees with experiment only when X = H, while the reverse is true for X = Cl. Nevertheless, these calculations show that the syn–anti energy gap decreases on substitution of the azomethine proton with chlorine: so the trend, at least, is correct.

As it has already been pointed out, the isomerization of iminoxyls seems to be much faster than that for the parent oximino compounds. With the purpose to explain the origin of this different behavior, we have performed SCF–MO ab initio calculations on the precursors of the theoretically investigated radicals, shown in Chart II.

All these computations have been carried out with the Gaussian 70 series of programs[21] at the STO-3G level.[22] The energy required for both isomerization processes is computed to be much larger than in the related radicals, in agreement with the expectations based on the experimental results, the inversion process being slightly favored (62.1 kcal/mol for inversion and 70 kcal/mol for rotation). The computations also give the syn isomer as more stable than the anti isomer by 5.5 kcal/mol.

Since, when calculating rotational barriers about a formal double bond a single determinantal approach may not be sufficient, we have reoptimized the geometry of the four configurations of Chart II, using a 3 × 3 CI which includes the three singlets arising from the HOMO–LUMO pair. From the computed data, listed in Table IV, it turns out that the CI procedure lowers slightly the barriers, which now become 60.8 kcal/mol for inversion and 60.9 kcal/mol for rotation, and increases the syn–anti energy separation to 6.6 kcal/mol.

Discussion

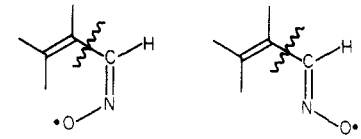
In this section we shall try to rationalize, in terms of a perturbation molecular orbital (PMO) approach,[23] the experimental and computational results previously described.

Table IV. Geometrical Parameters and Relative Energies, Computed at the ab initio Level STO-3G with a 3 × 3 CI, for Various Configurations of the Model Molecule $H_2C{=}CHCH{=}NOH$

geometrical parameters	configuration			
	anti	TSI	TSR	syn
r(N-O), Å	1.392	1.361	1.333	1.402
$r(C_1\text{-}N)$, Å	1.299	1.259	1.459	1.249
r(O-H), Å	0.996	1.006	0.996	0.996
$<C_2C_1N$, deg	129.4	121.6	121.6	121.6
$<C_1NO$, deg	122.2	180	103.3	109.2
<NOH, deg	100.9	104.6	105.4	101.3
ΔE^a	6.62	60.8	60.9	0

[a] $\Delta E = E - E_{syn}$ (in kcal/mol).

Chart III



	anti	syn
with π interactions	E = 0 kcal/mol	E = 2.45 kcal/mol
without π interactions	E = 0 kcal/mol	E = 0.54 kcal/mol

The first problem we shall examine is the origin of the configurational preference of iminoxyls. The interactions which can play a certain role with this respect are π nonbonded interactions, hydrogen bonding between oxygen and the ortho hydrogens, and σ conjugative interactions. We discuss briefly the effect of each type of interaction upon the conformational preference.

(i) π Nonbonded Interactions. The effect of π nonbonded interactions has been estimated quantitatively by using a procedure[24] recently suggested by some of us that provides in the framework of an INDO scheme the total energy of the radical under investigation in the absence of selected π interactions.

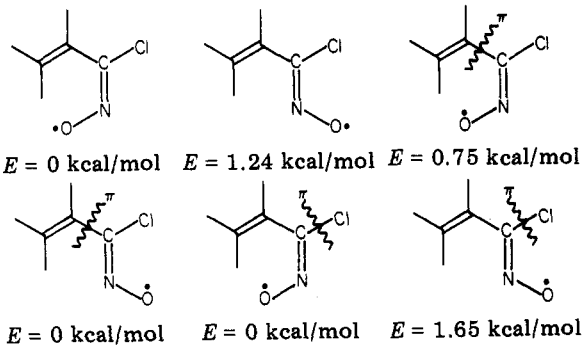
In our discussion we consider first the radical in which the atom attached to the azomethine carbon is a proton. As previously pointed out, for this radical the INDO calculations predict correctly the anti isomer to be more stable. Since the latter isomeric radical can be regarded as a six-electron aromatic system made up of the two double bonds and the oxygen $2p_\pi$ lone pair, while in the syn configuration we have a nonaromatic situation, it is presumable that π interactions stabilize the anti isomer. This expectation is supported by the results of the quantitative analysis carried out for the situation where the π interactions between the ethylenic and CNO fragments are interrupted.

As shown in Chart III the anti isomer is computed to be still more stable, but the energy gap with respect to the syn isomer is reduced from 2.45 to 0.54 kcal/mol. This means that π nonbonded interactions are important, even though they are not the only factor controlling the preferred configurational stabilization.

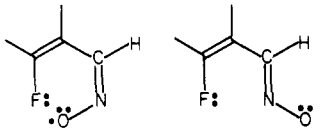
On the basis of π interactions we may also understand the decreased stability of the anti configuration after substitution of the ortho protons of the aryl ring. Deviations of the aromatic nucleus from coplanarity with the CNO fragment, and therefore reduction of the energy gap between the two configurations, are expected as the result

(21) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, "Quantum Chemistry Program Exchange", University of Indiana, Bloomington, IN, Program No. 236.
(22) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).
(23) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1978.
(24) F. Bernardi, M. Guerra, and G. F. Pedulli, *Tetrahedron*, 34, 2141 (1978).

Chart IV



of both steric and electronic interactions. The former ones should prevail in the mesityl derivatives and the latter ones in halogenated radicals. Evidence for a nonplanar geometry in the anti isomers of the latter iminoxyls is provided by the measured values of the hyperfine couplings and can be rationalized on the following basis. If coplanarity is assumed for the aromatic ring and the iminoxy moiety, the anti configuration may be regarded as an eight-electron

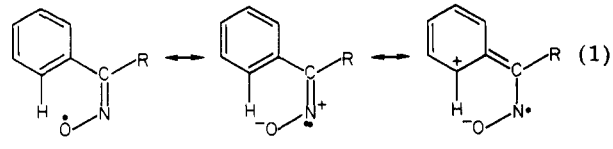


antiaromatic system arising from the two double bonds and the oxygen and halogen p lone pairs, and therefore destabilization is expected. On the other hand, in the syn configuration, coplanarity is favored by an almost aromatic situation. With bulky XR_n groups, the steric interaction with the ortho substituents may induce out of plane rotation of the ring even in the syn isomeric radicals.

Substitution of the azomethine proton with a group whose leading atom has a p lone pair as a thio group or a halogen produces a stabilization of the syn configuration. The INDO calculations made for the chlorine derivative do not reproduce this experimental result; however, they predict at least that the energy gap between the two geometries should decrease. Actually, in this case π nonbonded interactions should differentiate less substantially the two configurations, since they can operate in both isomers because of the presence of the p lone pair of chlorine. The relative importance of this effect is shown by the calculations where π interactions between the appropriate fragments have been truncated (see Chart IV). In both cases we have a reduction of stabilization of the configuration which can be regarded as a six-π-electron ring. The effect, however, is smaller for chlorine than for the ethylenic double bond.

(ii) Hydrogen Bonding. Another interaction which may be of some relevance in the derivatives unsubstituted at the ortho positions of the aryl ring is hydrogen bonding between oxygen and the ortho protons. Two different effects will contribute to this interaction, i.e., the electrostatic and the charge-transfer effects.

The electrostatic interaction in iminoxyls should be more important than that in oximino compounds given the different orbital occupancy. In fact, for the radicals we may write polar structures (eq 1) where attractive forces


(1)

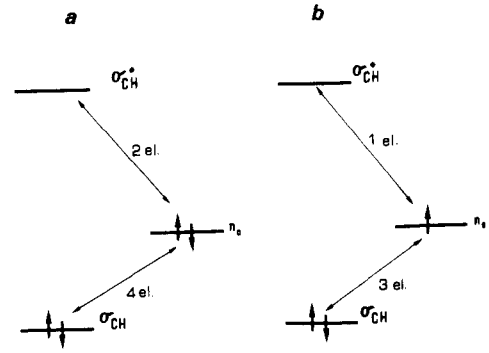


Figure 3. Interaction diagram of the oxygen p orbital of σ symmetry and the ortho proton C–H bond orbitals in the syn configuration of (a) oximino compounds and (b) iminoxy radicals.

between oxygen and the ortho hydrogen can operate, while similar structures cannot be written for oximino compounds. Also, charge transfer may be different in the two cases, as shown in Figure 3, and should favor the radical species. In order to estimate the effect of hydrogen bonding in iminoxyls, we have carried out a computation of the total energy of the syn and anti configurations of the unsubstituted radical by setting equal to zero the matrix elements related to the interaction between the 1s AO of the ortho proton and the AO's of oxygen. The difference between this energy value and the total energy provides an estimate of the stabilizing effect associated with hydrogen bonding. The computations show that the stabilization energy is significant in the anti isomer (−4.4 kcal/mol) but negligible in the syn isomer (0.03 kcal/mol).

Indirect evidence that hydrogen bonding is important in the radicals can be obtained from the optimized geometries of the neutral and paramagnetic species. For the oximino derivative the computed CNO bond angle is smaller in the syn than in the anti configuration, thus suggesting that, in the latter, repulsive interactions prevail. In the radical the reverse is true (see Table III), since the calculated angle is 135° in the syn and 125° in the anti isomer. So hydrogen bonding may well be responsible for this attractive interaction in the radical.

The different conformational preference of iminoxyls with and without halogen substituents at the ortho positions may also be understood in terms of the absence of hydrogen bonding in the halogenated radicals. The latter effect should produce a destabilization of the anti configuration, as π nonbonded interactions, with respect to the unsubstituted iminoxyls. Less effective intramolecular hydrogen bonding in the anti configuration may also explain the larger stability of the syn isomer of the radical from benzaldoxime observed in protic solvents.

(iii) σ Conjugative Interactions. Another important interaction which should be considered is the n–σ^* conjugative interaction between the sp^2 lone pair of the nitrogen atom and the σ^* orbital of the C–X or C–aryl bonds. As shown in Figure 4, the σ–σ^* interaction between the N–O and C–X bonds should be less important because of the large energy gap.

It is known that this interaction favors the configuration which places the lone pair and the σ^* orbital lower in energy in the anti geometry because the overlap integral is larger than that in the alternative syn geometry.[25] The preference toward the syn configuration, which corresponds to the anti geometry of the n_O and σ^*_{CX} orbitals, will therefore increase as the C–X bond becomes an in-

(25) N. D. Epiotis, W. R. Cherry, S. Shaik, R. L. Yates, and F. Bernardi, *Top. Curr. Chem.*, **70** (1977).

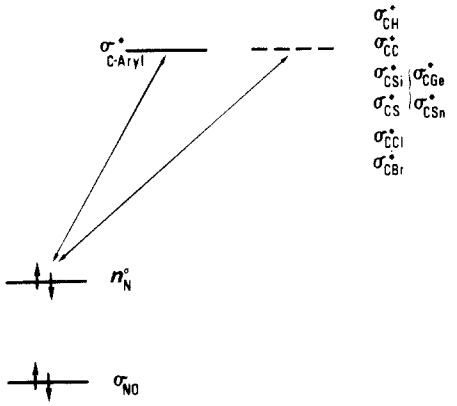


Figure 4. Diagram of the σ conjugative interactions in iminoxyls. The electron-acceptor ability of the σ^*_{CX} bond orbital increases from top to bottom.

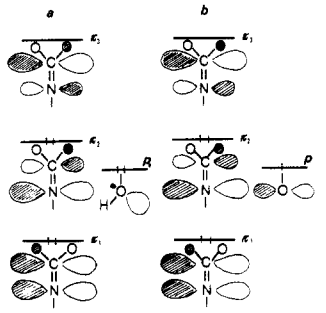


Figure 5. Orbital interactions, occurring in the transition state to inversion, between the π MO's lying in the molecular plane (a) in oximino compounds and (b) in iminoxyls. The positioning of the MO's is schematic.

creasingly better acceptor with respect to the C–aryl bond. From known data the electron-acceptor ability of C–X bonds is that shown in Figure 4 and parallels quite nicely the order of increasing stabilities of the syn configuration of iminoxy radicals.

It seems, therefore, that the following conclusion may be drawn: both π nonbonded interactions and hydrogen bonding favor the anti configuration, which is the preferred one in all the cases where the C–X bond is a poor acceptor. However, when the latter bond becomes a good acceptor, as for X = Ge, Sn, S, Cl, and Br, the dominant interaction is the n–σ^*_{CX} and consequently the syn isomer becomes more stable.

Another problem of interest concerns the origin of the large decrease in the energy barrier for the preferred isomerization pathway, i.e., planar inversion at nitrogen, on going from oximino compounds to iminoxyls. This problem can be discussed by comparing the effects of the dominant orbital interactions occurring in the two transition states. The orbital analysis is based upon a dissection of the molecular species into a common >C=N fragment and an OH or O· fragment in the diamagnetic and paramagnetic derivatives, respectively. The interactions subject to the largest change on going from the oximino compound to the corresponding radical are those involving the π MO's lying in the plane of the molecule and are depicted in Figure 5. The largest energy effect in oximino derivatives is associated with the four-electron, two-orbital interaction π_2–p_σ, which is highly destabilizing. In the radicals the same orbitals give origin to a three-electron interaction which, according to our quantitative analysis, is stabilizing. This change is the main factor responsible for the large variation in the energy barrier to isomerization. The energy effects associated with the other two interactions play only a minor role.

Acknowledgment. Financial support from CNR (Rome) is gratefully acknowledged by F.B., A.D., and G.F.P.

Registry No. *anti*-**1a**, 15013-89-5; *syn*-**1b**, 15013-88-4; *syn*-**1c**, 75781-14-5; *anti*-**2**, 75781-15-6; *anti*-**3a**, 10507-33-2; *anti*-**3b**, 74346-84-2; *syn*-**3b**, 74346-85-3; *anti*-**3c**, 75781-16-7; *syn*-**3c**, 75781-17-8; *anti*-**3d**, 75781-18-9; *syn*-**3d**, 75781-19-0; *anti*-**3e**, 75781-20-3; *syn*-**3e**, 75781-21-4; *anti*-**3f**, 75781-22-5; *syn*-**3f**, 75781-23-6; *syn*-**3h**, 75781-24-7; *syn*-**3i**, 75781-25-8; *anti*-**3j**, 75781-26-9; *syn*-**3j**, 75781-27-0; *syn*-**3k**, 74346-75-1; *anti*-**4a**, 75781-28-1; *syn*-**4a**, 75781-29-2; *anti*-**4b**, 74346-86-4; *syn*-**4b**, 74346-86-4; *anti*-**4c**, 75781-30-5; *syn*-**4c**, 75781-31-6; *anti*-**4d**, 75781-32-7; *syn*-**4d**, 75781-33-8; *anti*-**4e**, 75781-34-9; *syn*-**4e**, 75781-35-0; *anti*-**4f**, 75781-36-1; *syn*-**4f**, 75781-37-2; *anti*-**4g**, 75781-38-3; *syn*-**4g**, 75781-39-4; *anti*-**4h**, 75781-40-7; *syn*-**4h**, 75781-41-8; *syn*-**4i**, 74346-76-2; *syn*-**5a**, 74346-77-3; *syn*-**5b**, 75781-42-9; *anti*-**6a**, 74346-80-8; *syn*-**6a**, 74346-81-9; *syn*-**6b**, 75781-43-0; *syn*-**6c**, 75781-44-1; *syn*-**6d**, 75781-45-2; *syn*-**6e**, 75781-46-3; *anti*-**7a**, 74346-82-0; *syn*-**7a**, 74346-83-1; *anti*-**7b**, 74346-88-6; *syn*-**7b**, 74346-89-7; *syn*-**7c**, 75781-47-4; *syn*-**7d**, 75781-48-5; *anti*-**7e**, 75781-49-6; *syn*-**7e**, 75781-50-9; *anti*-**7f**, 75781-51-0; *syn*-**7f**, 75781-52-1; *anti*-**7g**, 75781-53-2; *syn*-**7g**, 75781-54-3; *syn*-**7h**, 75781-55-4; *syn*-**7i**, 75781-56-5; *syn*-**7j**, 75781-57-6; *syn*-**7k**, 75781-58-7; *anti*-**8a**, 75781-59-8; *syn*-**8a**, 75781-60-1; *anti*-**8b**, 75781-61-2; *syn*-**8b**, 75781-62-3; *anti*-**8c**, 75781-63-4; *syn*-**8c**, 75781-64-5; *anti*-**9a**, 14941-21-0; *syn*-**9b**, 74346-90-0; *syn*-**9c**, 74346-91-1; *anti*-**9d**, 75781-65-6; *syn*-**9d**, 75781-66-7; *anti*-**9e**, 75781-67-8; *syn*-**9e**, 75781-68-9; *anti*-**9f**, 75781-69-0; *syn*-**9f**, 75781-70-3; *anti*-**10**, 14941-28-7; *anti*-(ethenyl)methaniminoxyl, 75781-71-4; *syn*-(ethenyl)methaniminoxyl, 75781-72-5; *anti*-(ethenyl)(chloro)-methaniminoxyl, 75781-73-6; *syn*-(ethenyl)(chloro)methaniminoxyl, 75781-74-7; *anti*-2-propenal oxime, 39847-72-8; *syn*-2-propenal oxime, 28051-67-4.