17.46; S, 0. Found: C, 59.82; H, 6.53; N, 17.21; S, <0.07.

N-Butyl-N'-(6-methoxy-3-pyridinyl)thiourea (22). A. From 10. A solution of 12.1 g (0.097 mol) of **10** and 11.5 g (0.10 mol) of butyl isothiocyanate in 100 mL of benzene was allowed to stand at room temperature overnight and then evaporated under vacuum. The residue was recrystallized from CH_2Cl_2–ether to give 12.5 g (54%) of **14b** as colorless crystals: mp 87.5–89.5 °C; UV (C_2H_5OH) 243 nm (ϵ 20 000), 270 (infl, 1000), 300 (infl, 3200); NMR ($CDCl_3$) δ 8.34 (s, 1, NH), 8.20 (d, 1, J = 2.5 Hz, 2-H), 7.63 (dd, 1, J = 2.5, 8.5 Hz, 4-H), 6.87 (d, 1, J = 8.5 Hz, 5-H), 6.10 (m, 1, NH), 4.00 (s, 3, OCH_3), 3.64 (m, 2, NCH_2C), 1.45 (m, 4, $NCH_2CH_2CH_2CH_3$), 0.92 (t, 3, J = 7 Hz, CCH_3); mass spectrum, m/z 239. Anal. Calcd for $C_{11}H_{17}N_3OS$: C, 55.22; H, 7.16; N, 17.56; S, 13.38. Found: C, 55.30; H, 7.12; N, 17.72; S, 13.47.

B. From 11. A 1.662-g (10 mmol) sample of **11** was dissolved in 15 mL of CH_2Cl_2 with some heat. Butylamine (1.10 mL, 0.81 g, 11 mmol) was added, and the reaction was allowed to stand at ambient temperature for 2 h and then concentrated under vacuum. The residue was chromatographed over silica gel. Elution with CH_2Cl_2 followed by crystallization from ether gave 1.598 g (1.34 mol/mol of **11**) as colorless crystals, mp 87.5–89 °C, undepressed on mixture with material prepared in A.

N,N'-Bis(6-methoxy-3-pyridinyl)thiourea (23). A. From 11. Further elution of the silica gel column from the isolation of **22** from **11** with 5% methanol in $CHCl_3$ followed by crystallization from $CHCl_3$ gave 158 mg (5%) of **23** as colorless crystals: mp 174–175 °C; compatible IR, UV, NMR, and mass spectra. Anal. Calcd for $C_{13}H_{14}N_4O_2S$: C, 53.77; H, 4.86; N, 19.30; S, 11.04. Found: C, 53.57; H, 4.86; N, 19.02; S, 11.14.

B. From 10. A solution of 12.41 g (0.10 mol) of **10** and 15.8 mL (15.5 g, 0.20 mol) of pyridine in 50 mL of CS_2 was heated under reflux while a solution of 12.7 g (0.05 mol) of I_2 in 125 mL of CS_2 was added over 15 min. The mixture was stirred an additional 30 min at ambient temperature. The precipitate of pyridine hydriodide was removed by filtration and washed with CH_2Cl_2. The filtrate was concentrated under vacuum, and the residue was heated with xylene on the steam bath. The insoluble solid was collected and heated with $CHCl_3$. The solution was treated with charcoal and concentrated. Recrystallization of the resulting solid from $CHCl_3$ gave 1.60 g (11%) of **23** as pale pink crystals, mp 173–174 °C, undepressed on mixture with a sample from A.

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Registry No. 10, 6628-77-9; **11**, 74763-57-8; **12a**, 52023-93-5; **13**, 74763-58-9; **13**·HCl, 74763-59-0; **14**, 74763-60-3; **20**, 74763-61-4; **21**, 74763-62-5; **22**, 74763-63-6; **23**, 74763-64-7.

Notes

Configuration of Arylchloromethaniminoxy Radicals. A Reassignment

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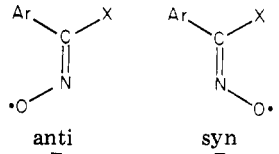
In a previous article some of us[1] reported that iminoxy radicals **1** obtained by oxidation of benzohydroxymoyl chlorides with lead tetraacetate in benzene solution exist in only one of the two possible configurations which, on the basis of the ESR spectral parameters, was assigned to be anti (*E*).[2] In a more recent study on the stereochemistry of a variety of iminoxyls,[3] we have found that in aprotic solvents the preferred geometry of the radicals derived from ortho-unsubstituted benzaldoximes is anti (*Z*), viz., that the aryl group and the oxygen are on the same side of the plane defined by the C=N bond, while substitution of the ortho positions of the aryl ring leads to a stabilization of the syn isomer. Stabilization of the syn configuration is also observed by substitution of the azomethine proton by an XR_n group (X = Si, Sn, and Ge; R_n are alkyls or aryls), the effect being that the larger the atomic number of X the greater the stabilization. In contradiction with these new findings, it appeared to be the assignment previously made for arylchloromethaniminoxyls. We therefore collected further experimental data on these radicals and on related iminoxyls with the aim of establishing on more firm grounds their preferred geometry.



	anti	syn
1; X = Cl	*E*	*Z*
2; X = Me	*Z*	*E*
3; X = H	*Z*	*E*
4; X = CH_2OH	*E*	*Z*
5; X = *t*-Bu	*Z*	*E*

The assignment of the anti configuration to arylchloromethaniminoxyls (**1**) was based[1] on the following arguments: (i) the magnitude of the hyperfine splitting at the chlorine atom (ca. 1.7 G) in radicals **1** appeared to be small for the syn configuration in comparison with a value of ca. 27 G which was reported for the coupling at the azomethine hydrogen in the syn isomeric radical (*E*)-**3** (Ar = Ph) from benzaldoxime;[4] (ii) the splittings to the halogen of the phenyl ring in iminoxyls **1** containing a chlorine or a bromine atom in one of the ortho positions (a_{Cl} = 2.15 G, a_{Br} = 9.8 G) were *large* and *similar* to the values reported by Norman and Gilbert[4] for the radicals from *o*-chloro- and *o*-bromoacetophenone oximes **2** which were assigned the anti configuration (**Z**).

We now have several indications that neither the magnitude of the hyperfine splitting at the azomethine chlorine

(1) A. Dondoni, G. F. Pedulli, and G. Barbaro, *J. Org. Chem.*, 37, 3564 (1972).

(2) Due to the variable priority order between the groups Ar and X (X = H, alkyl, Cl, CH_2OH) on the iminoxy radicals **1–5**, the *E* and *Z* notation may indicate opposite stereochemistry. This may be misleading for the objectives of the present work and clarity of the discussion. Therefore, in order to keep a uniform notation, we used the classical term syn to indicate compounds where X and O are on the *same* side with respect to the plane defined by the C=N double bond and the term anti for compounds where X and O are on *opposite* sides.

(3) A. Alberti, G. Barbaro, A. Battaglia, M. Guerra, F. Bernardi, A. Dondoni, and G. F. Pedulli, submitted for publication in *J. Org. Chem.*

(4) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 71, 14 (1967); B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc B*, 981 (1967).

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Table I. Hyperfine Splitting Constants (G) and g Values of the Isomeric Iminoxy Radicals 3-5

radical	Ar	X	isomer	a_N	a_{Ar}	a_X	g
3a	F_5Ph	H	anti	32.0	0.92 (2 F), 0.42 (1 F)	5.68	2.0051
			syn	31.20	7.20 (2 F), 0.55 (1 F)	26.76	2.0054
3b	2,6-Cl_2Ph	H	anti	31.50	0.17 (2 Cl)[b]	5.60	2.0052
			syn	32.25	1.55 (2 Cl)	27.65	2.0054
3c	2-ClPh	H	anti	32.15	2.51 (1 H)	6.60	2.0052
4a	4-ClPh	CH_2OH	anti	31.34	1.31 (2 H)	0.88 (2 H)[a]	2.0058
			syn	29.89	0.40 (2 H)		2.0061
4b	Mes	CH_2OH	anti	30.26[c]		1.16 (2 H)[a]	2.0057
			syn	30.47		0.40 (2 H)[a]	2.0056
4c	2,6-Cl_2Ph	CH_2OH	anti	30.86	0.13 (2 Cl)[b]	1.22 (2 H)[a]	2.0056
			syn	30.35		0.48 (2 H)[a]	2.0054
4d	2-ClPh	CH_2OH	syn	31.32	1.10 (1 Cl)		2.0054
5	2-ClPh	t-Bu	syn	30.50		0.88 (9 H)	2.0050

[a] Hyperfine splitting constants attributed by full deuteration of the CH_2OH group. [b] Coupling determined by computer simulation of the experimental ESR spectrum. [c] A 0.23-G splitting from the two meta protons of the mesityl group is also observed.

nor the coupling at the ortho halogens can be used as an evidence for the proposed configuration. Actually, our recent results[3] show that the percentage of spin density on the pertinent s orbital of the atom bonded to the iminoxy carbon decreases sharply with an increase of the atomic number in the syn configuration. The small value of the chlorine splitting in arylchloromethaniminoxyls (1) may therefore also be consistent with the latter geometry. In addition, we have collected, data on ortho-substituted iminoxyls **3–5** which suggest that values as large as those observed for the ortho halogen couplings in radicals 1 have to be expected for the syn more than for the anti configuration. The relevant ESR spectral parameters substantiating the latter point are reported in Table I.

The arylchloromethaniminoxyls (1) and arylmethaniminoxyls (**3**) were obtained from the corresponding oximino compounds by photolytically induced hydrogen abstraction with di-*tert*-buty peroxide,[5] while radicals 4 and **5** resulted from the addition of $\cdot CH_2OH$ and $\cdot CMe_3$ radicals to the appropriate nitrile oxides.[6]

We will examine first the configuration of iminoxyls **3** and **4** which is the basis for our further discussion. The geometry of radicals **3a–c** obtained from benzaldoximes could be established straightforwardly from the hyperfine splitting at the azomethine hydrogen which is known to have values of ca. 6 G for anti isomers and ca. 27 G for syn isomers.[4] The assignment of the syn configuration to the *tert*-butyl derivative **5** parallels that reported for the 2,2-dimethyl-1-phenylpropan-1-iminoxyl[6b] and is based on the observation that the aliphatic protons are coupled with the unpaired electron only when the *tert*-butyl group lies on the same side of the iminoxy oxygen. The two isomers of the hydroxymethyl derivative **4a** were identified on the basis of the different splittings at the ortho hydrogens of the aryl ring, which are typical of the two geometric forms.[7] The structural assignment for the mesityl derivative **4b** was obtained from the coupling at the meta protons of the mesityl ring, the observed values being characteristic of the two configurations.[8]

It is relevant to point out that in both **4a** and **4b** the hyperfine splitting at the methylenic protons is ca. 1 G in the anti isomers and smaller than 0.5 G in the syn isomers. The magnitude of the latter coupling has therefore been employed to assign the configurations of 2-hydroxy-1-(2,6-dichlorophenyl)ethan-1-iminoxyl (**4c**) and 2-hydroxy-1-(2-chlorophenyl)ethan-1-iminoxyl (**4d**). The similarity of the methylenic proton splittings in the related isomers of the iminoxyls **4b** and **4c** on one side and of **4a** and **4d** on the other, which are comparable on steric grounds, gives us confidence that the assignment of the syn configuration to the only observed isomer of **4d** is correct.[9]

We may now proceed to analyze the splittings of the phenyl ring halogens starting from iminoxyls **3a** and **3b** where both ortho positions are substituted by fluorine and chlorine, respectively. In contrast with logical expectations, in both cases the halogen splitting that results is much larger for the syn than for the anti isomers. This indicates that in the anti configuration the direct overlap between the orbital containing the unpaired electron and the s orbital of the halogen, determining the transmission of spin density, is less effective than that in the syn form. A simple explanation is that in the anti configuration the aryl group deviates significantly from coplanarity with the C=NO moiety, because of the steric repulsions between the ortho halogens and the oxygen atom. The importance of this repulsive interaction is also demonstrated by the absence of chlorine splitting and by the concomitantly large coupling (2.51 G) to the ortho proton in (2-chlorophenyl)methaniminoxyl (**3c**). Since the latter value is about twice as large as that of the two ortho protons in the anti radical from benzaldoxime, it has been taken as evidence[4] that radical **3c** adopts the coplanar conformation where the ortho proton is close to the iminoxy oxygen. Therefore, these results suggest that in the anti isomers of ortho-halogen-substituted aryl iminoxyls, the halogen hyperfine splitting should be very small or even absent.

The situation is somehow more complex in the syn isomers as the coupling at the ortho halogens strongly depends on whether the X substituent allows the aryl ring to be coplanar with the iminoxy function or not. In the coplanar arrangement, which is favored by unhindering X groups such as H, the overlap between the nitrogen sp^2 hybrid and the halogen s orbital is at maximum and leads to a significant splitting from the latter atom, as is shown

(5) The ESR parameters indicate that radicals 1 obtained by this procedure are identical with those from lead tetracetate oxidation.

(6) (a) T. Caronna, A. Quilico, and F. Minisci, *Tetrahedron Lett.*, 3633 (1970); (b) B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Am. Chem. Soc.*, **93**, 3290 (1971).

(7) The ortho proton splittings of arylmethaniminoxyls currently reported in the literature are in the range 1.2–1.5 G in the anti isomers and 0.3–0.5 G in the syn isomers. See F. A. Neugebauer in "Magnetic Properties of Free Radicals", Vol. 9, Landolt-Börnstein, Springer-Verlag, West Berlin, 1979, Part C1.

(8) Iminoxyls bearing a mesityl group invariably show a small but resolvable (ca. 0.25 G) coupling at the meta protons of the mesityl ring in the anti configuration, while no splitting is observed in the syn isomers.[3]

(9) It is worth noting that the hindered iminoxyls **4b** and **4c** show a larger coupling at the CH_2 protons than do the presumably planar compounds **4a** and **4d**. We agree with the suggestion of one of the reviewers that this may be related to some twisting of the phenyls in the former iminoxyls.

Table II. Hyperfine Splitting Constants (G) and g Values of Substituted Phenylchloromethaniminoxyls (1) and 1-(2-Chlorophenyl)ethan-1-iminoxyl (2)

radical	Ar	a_N	a_{Cl}	a_{Ar}	g
1a	4-ClPh	29.02	1.40 (^{35}Cl), 1.16 (^{37}Cl)	0.65 (2 H)	2.0067
1b	Mes	29.50	1.77 (^{35}Cl), 1.48 (^{37}Cl)		
1c	Cl_2Mes	29.50	1.63 (^{35}Cl), 1.36 (^{37}Cl)		2.0063
1d[a,b]	2,4-Cl_2Ph	32.00	1.76[d]	2.15 (1 Cl)[d]	
2[a,c]	2-ClPh	33.50	1.40 (CH_3)	1.55 (1 Cl)[d]	2.0056

[a] Values measured in methylene chloride. [b] Reference 1. [c] Reference 4. [d] Mean for ^{35}Cl and ^{37}Cl.

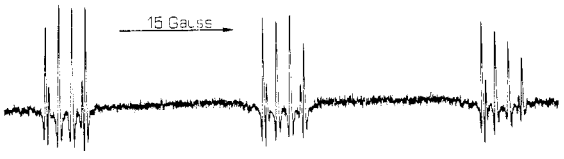

Figure 1. Second-derivative ESR spectrum of mesitylchloromethaniminoxyl (**1b**) recorded at room temperature.

by radicals **3a** and **3b**. By contrast, bulky X substituents destabilize the coplanar conformation and prevent the halogen nuclei from coupling with the unpaired electron. This repulsive effect is more important, as expected, in the ortho-disubstituted than in the monosubstituted derivatives. Actually, when the phenyl ring bears two ortho halogens, the hindrance exerted by the hydroxymethyl group is sufficient to induce significant deviations from coplanarity, as is demonstrated by the absence of chlorine splitting in radical **4c**. In ortho-monohalogenated aryl iminoxyls, this situation is found when X is the bulkier *tert*-butyl group (see radical **5**), while for X = CH_2OH the observed splitting of 1.10 G at chlorine indicates that the out of plane rotation of phenyl is not very large (radical **4d**). We may then conclude that the coupling at the ortho halogens in aryl iminoxyls is mainly determined by the size of the X group in the syn isomers, whereas it is always expected to be small in the anti isomers.

In the light of the above considerations, the value of 2.15 G for a_{Cl} (ortho) observed in the (2,4-dichlorophenyl)-chloromethaniminoxyl **1d** (see Table II) is consistent with a syn configuration and a conformation about the Ar—C=N single bond where the chlorine is close to the iminoxy nitrogen and the phenyl ring slightly deviates from coplanarity.[10] On the other hand, we cannot find any plausible explanation for the magnitude of this splitting if the anti configuration is assumed. On the same basis, the a_{Cl} value of 1.55 G measured in 1-(2-chlorophenyl)-ethan-1-iminoxyl (**2**) is also more consistent with the syn than with the anti configuration assigned by Norman and Gilbert.[4] It may be added that the *o*-chlorine splitting in radicals **4d**, **2**, and **1d** increases along the sequence CH_2OH < CH_3 < Cl for the azomethine substituent, i.e., with decreasing the size of the X group in accord with expectations for the syn configuration. Similarly to the case of **2**, a reassignment may also be required for the radicals from *o*-fluoro-, *o*-bromo-, and *o*-iodoacetophenone oximes.[4]

Further, evidence in favor of the syn configuration of radicals **1** comes from the absence of the ca. 0.25-G splitting from the meta protons in mesitylchloromethaniminoxyl (**1b**). This splitting is usually observed in the anti isomers of the mesitylmethaniminoxyls.[8] The ESR spectrum of **1b**, reported in Figure 1, shows, in fact, well-resolved lines due to the isotopes ^{35}Cl and ^{37}Cl. Since the separation between the outer lines of the two quartets is only 0.15 G, any hyperfine splitting of the order of 0.2–0.3 G should be, if present, clearly observable.

(10) For a planar conformation one should in fact expect a_{Cl} (ortho) to be twice as large as it is in radical **3b**, i.e., 3.1 G.

Another indication is provided by the value of the coupling at the ortho protons in the (4-chlorophenyl)chloromethaniminoxyl (**1a**). The ESR spectrum of this radical consists at room temperature of three broad multiplets which, in our previous study,[1] we were not able to resolve. However, when the spectrum was recorded at lower temperature (ca. −40 °C), the resulting lines were relatively sharp, and all coupling could be determined. The ortho-proton splitting in **1a** is 0.65 G, a value which although rather unusual in iminoxyls supports the syn more than the anti configuration.[7]

In conclusion, the results now available uniformly favor the syn (*Z*) configuration for arylchloromethaniminoxy radicals (**1**), in contrast with the geometry previously proposed. A similar reassignment in favor of the *Z* configuration has been reported[11] by some of us for the precursors of radicals **1**, i.e., benzohydroxymoyl chlorides. Finally, our results also suggest that the configuration of 1-(2-halophenyl)ethan-1-iminoxyls[4] has to be reconsidered.

Experimental Section

Arylchloromethaniminoxy radicals (**1**) were generated by photolysis of solutions of the corresponding hydroxymoyl chlorides[12] in a 2:1 (by volume) mixture of *tert*-butylbenzene and di-*tert*-butyl peroxide. The same procedure was employed for the production of radicals **3** by starting from the corresponding substituted benzaldoximes. Radicals **4** and **5** were obtained in the same solvent by reaction of the proper benzonitrile oxides[12b,13] with photolytically generated hydroxymethyl (or $\cdot CD_2OD$) and *tert*-butyl radicals.[6]

A high-pressure 1-kW mercury lamp was used as UV source, and the temperature was controlled with standard accessories.

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

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(12) (a) A. Battaglia, A. Dondoni, and O. Exner, *J. Chem. Soc., Perkin Trans. 2*, 1911 (1972); (b) C. Grundman and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).
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A Novel and Inexpensive Synthesis of Ethyl 4-Methyl-2,4-pentadienoate[1]

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While investigating the reaction of 3,4-dibromo-4-methyl-2-pentanone with bases,[2] we encountered small

