Hydrogen Chloride Treatment of Quinolinic Aminoxyls. Part 2.[1] Crystal Structures of 6-Chloro-1,2-dihydro-2,2-diphenyl- and 6,8-Dichloro-1,2-dihydro-2,2-diphenylquinoline

Liberato Cardellini,[a] Patricia Carloni,[a] Elisabetta Damiani,[a] Lucedio Greci,*[,a] Pierluigi Stipa,[a] Corrado Rizzoli[b] and Paolo Sgarabotto*[,b]
[a] *Dipartimento di Scienze dei Materiali e della Terra, Università, Via Brecce Bianche, I-60131 Ancona, Italy*
[b] *Istituto di Strutturistica Chimica, Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, I-43100 Parma, Italy*

Quinolinic aminoxyls **1a–c**, whose structures are similar to those formed from 1,2-dihydroquinolines, used as antioxidants and photostabilizers in plastics and rubbers, under hydrogen chloride treatment led to the formation of the corresponding mono- (**2**) and di-chlorinated (**3**) amines. The structures of the isolated compounds have been determined by X-ray analysis of 6-chloro-1,2-dihydro-2,2-diphenyl- and 6,8-dichloro-1,2-dihydro-2,2-diphenylquinoline (**2a** and **3a**). The mechanisms of chlorination and deoxygenation are discussed on the basis of the experimental results and literature reports.

Hindered secondary amines (HALS) are used as photostabilizers for polymers[2] and the mechanism of their stabilization is commonly explained through the formation of the corresponding aminoxyls[3] as intermediates. Most of the HALS used are 2,2,6,6-tetramethylpiperidine derivatives even though other kinds such as 2,2-disubstituted 1,2-dihydroquinolines,[4] acridans[5] and other secondary amines[6] are also used. Thus, all secondary amines that are precursors of stable aminoxyls may be regarded as potential photostabilizers.

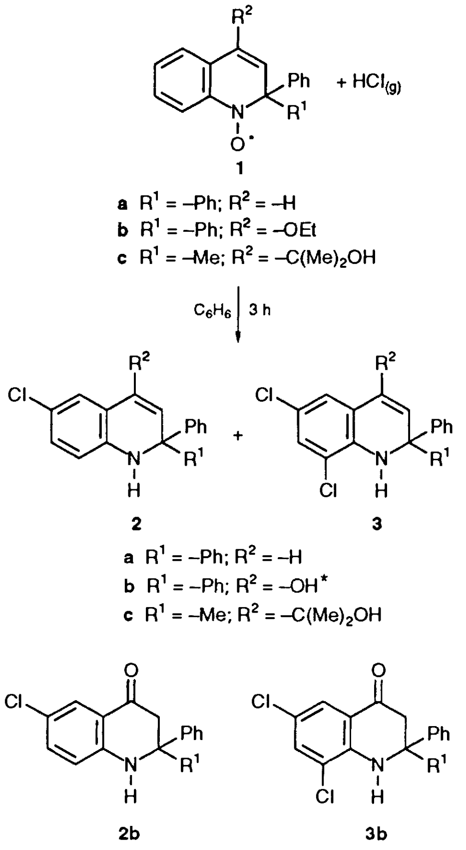
HALS are also used in halogenated polymers or with flame retardants (halogen containing compounds) for polymers, where hydrohalic acids are formed during the degradation. Furthermore, it is well known that aminoxyls under acid treatment give rise to different transformations depending on the type of aminoxyl and the acid used.[1,7]

In the present paper, the hydrochloric acid treatment of quinolinic aminoxyls in solution is described, taking into account that these aminoxyls are structurally similar to those formed from the commercial HALS, Anox HB (a mixture of 1,2-dihydro-2,2,4-trimethylquinoline oligomers) used as antioxidants and photostabilizers.†

Results

Benzene solutions of aminoxyls **1a–c** were saturated with gaseous hydrochloric acid at room temperature and stirred for 3 h. Working-up the reaction as described in the Experimental section, compounds **2a–c** and **3a–c** were isolated (Scheme 1). Compounds **2a** and **3a** were identified by X-ray analysis and the structures of **2b**, **2c**, **3b** and **3c** were determined by comparing their IR and ^1H NMR spectra with those of compounds **2a** and **3a** (Table 1). All mass spectra gave the expected molecular ion peaks.

Besides the transformation of the N–O$^•$ function and the chlorination of the benzene ring, compound **1b** undergoes hydrolysis of the vinyl ether group forming the 4-hydroxy substituted derivatives, since this gives rise to the more stable tautomeric ketone form as shown in Scheme 1; the same phenomenon was observed during treatment with trifluoroacetic acid.[1]



*Compounds **2b** and **3b** were isolated in the ketonic form.

Scheme 1

When the reaction of aminoxyl **1a** described above was stopped after a few minutes, the reaction products were a mixture of the two hydroxylamines **4a** and **5a** (Scheme 2), identified through the corresponding aminoxyls **1a** and **6a**

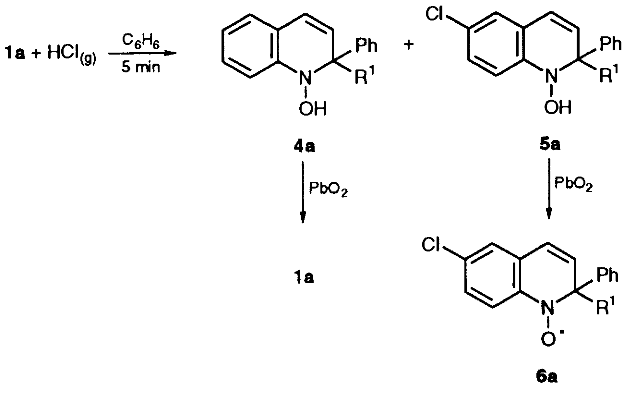
---

† This compound has different commercial names: Agerite resin D, Flectol H, Vulkanox HS and Anox HB.

Table 1 Analytical and spectroscopic data of compounds **2a–c**, **3a–c**

Cmpd.	$\delta_H(CDCl_3)$[a]	ν/cm^{-1}	MS (%)	M.p./°C	Found (%) (Calc.)
2a	4.32 (1 H, br s, NH), 5.96 (1 H, d, *J* 9.7, 3-H), 6.42 (1 H, d, *J* 8.3, 8-H), 6.44 (1 H, d, *J* 9.6, 4-H), 6.90 (1 H, d, *J* 2.3, 5-H), 6.95 (1 H, dd, *J* 8.3, 2.3, 7-H), 7.32 (10 H, m, Ar)	3410, 1645, 1600	317 (M$^+$, 15), 240 (100)	131	H: 5.0 (5.07) C: 79.55 (79.36) N: 4.3 (4.41)
2b	3.38 (2 H, s, 3-H_2), 5.20 (1 H, br s, NH), 6.70 (1 H, d, *J* 8.9, 7-H), 7.26 (11 H, m, Ar), 7.68 (1 H, d, *J* 2.7, 4-H)	3350, 1655, 1610	333 (M$^+$, 35), 256 (100)	210	H: 4.9 (4.83) C: 75.2 (75.56) N: 4.3 (4.20)
2c	1.58 [6 H, d, *J* 2.6, HO–C(CH_3)$_2$], 1.67 (3 H, s, CH_3), 4.89 (1 H, br s, NH), 5.81 (1 H, s, 3-H), 6.46 (1 H, d, *J* 8.5, 8-H), 6.96 (1 H, dd, *J* 8.5, 2.4, 7-H), 7.36 (5 H, m, Ar), 7.88 (1 H, d, *J* 2.4, 5-H)	3550, 3350, 1710, 1595	313 (M$^+$, 74), 298 (100)	55	H: 6.9 (6.42) C: 72.65 (72.72) N: 4.3 (4.46)
3a	4.90 (1 H, br s, NH), 6.07 (1 H, br d, *J* 9.9, 4-H), 6.44 (1 H, d, *J* 9.8, 3-H), 6.83 (1 H, d, *J* 2.3, 7-H), 7.11 (1 H, d, *J* 2.3, 5-H), 7.32 (10 H, m, Ar)	3420, 1645, 1595	351 (M$^+$, 22), 274 (100)	125	H: 4.4 (4.29) C: 71.45 (71.60) N: 3.85 (3.98)
3b	3.40 (2 H, s, 3-H_2), 5.52 (1 H, br s, NH), 7.30 (12 H, m, Ar)	3360, 1655, 1600	367 (M$^+$, 8), 349 (100)	145	H: 4.0 (4.11) C: 68.65 (68.49) N: 3.6 (3.80)
3c	1.57 [6 H, d, *J* 4.9, HO–C(CH_3)$_2$], 1.71 (3 H, s, CH_3), 4.82 (1 H, br s, NH), 5.91 (1 H, s, 3-H), 7.14 (1 H, d, *J* 2.3, 7-H), 7.33 (5 H, m, Ar), 7.87 (1 H, d, *J* 2.3, 5-H)	3560, 3410, 1720, 1595	347 (M$^+$, 60), 332 (100)	60	H: 5.7 (5.50) C: 65.3 (65.53) N: 3.9 (4.02)

[a] *J*-Values in Hz.



Scheme 2

respectively. The aminoxyl **6a** was identified by comparing its EPR signal with the one obtained by oxidation of the corresponding amine with *m*-chloroperbenzoic acid because the former shows a large linewidth and only the hyperfine coupling constants of the nitrogen (see Experimental) could be evinced.

Molecular Geometry.—Bond distances and angles are given in Table 2 and the arbitrary numbering scheme used in the crystal analysis is shown in Figs. 1 and 2, which represent perspective views of chloroquinolines **2a** and **3a**, respectively.*

A comparison between bond distances and angles, in line with the hybridization expected for the atoms, indicates that the geometry of the two molecules is similar and comparable with that found in related compounds previously studied.[1,8] The dihedral angle between the two mean planes of the fused six-membered rings of the quinoline moiety is also equal in the two compounds and is 1.5(1)°. This value falls in the range of those obtained in compounds previously described.[1,8]

The torsion angles of Table 2 and the analysis of the planarity reported in Table 3 show that the main peculiarities concerning the conformation of the two molecules are: (*a*) the two pyridine moieties are not planar within experimental error: the conformational analysis[9] indicates that these six membered rings adopt a half-boat conformation with C_s symmetry, the pseudo symmetry plane being located on N(1) and on C(2) in compounds **2a** and **3a** respectively;[10] and (*b*) the different orientation of the two phenyl rings in position 2 with respect to the quinoline ring (see angles between planes in Table 3) can be interpreted in terms of steric interactions.

Packing is consistent with van der Waals interactions.

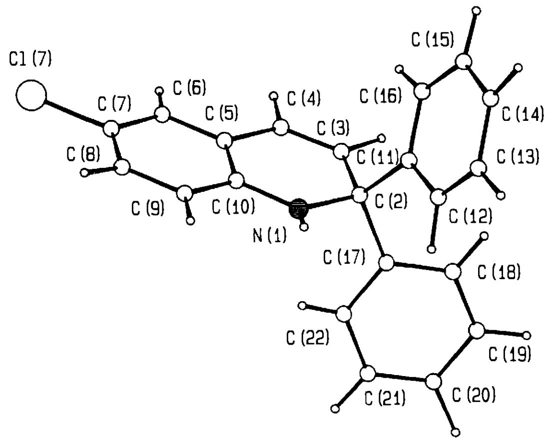


Fig. 1 Perspective view of 6-chloro-1,2-dihydro-2,2-diphenylquinoline

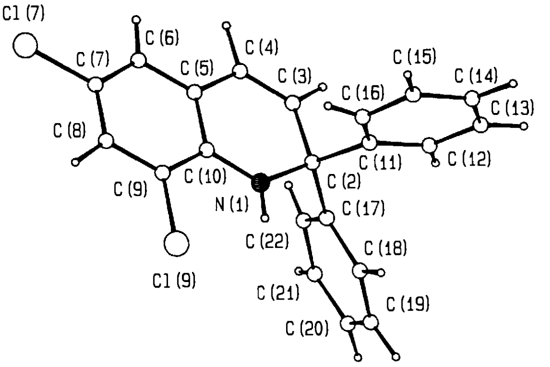


Fig. 2 Perspective view of 6,8-dichloro-1,2-dihydro-2,2-diphenylquinoline

---

* Atomic fractional coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, Issue 1.

Table 2 Bond distances (Å), angles (°) and selected torsion angles (°) with e.s.d.s in parentheses

	2a	**3a**
Cl(7)–C(7)	1.744(5)	1.747(4)
Cl(9)–C(9)		1.736(4)
N(1)–C(2)	1.479(5)	1.471(5)
N(1)–C(10)	1.376(6)	1.365(4)
C(2)–C(3)	1.512(7)	1.508(5)
C(2)–C(11)	1.548(6)	1.546(5)
C(2)–C(17)	1.547(5)	1.534(5)
C(3)–C(4)	1.316(7)	1.329(5)
C(4)–C(5)	1.450(6)	1.452(5)
C(5)–C(6)	1.388(6)	1.393(5)
C(5)–C(10)	1.404(6)	1.406(4)
C(6)–C(7)	1.370(7)	1.376(6)
C(7)–C(8)	1.386(8)	1.376(5)
C(8)–C(9)	1.384(7)	1.398(5)
C(9)–C(10)	1.394(6)	1.390(5)
C(11)–C(12)	1.383(6)	1.386(5)
C(11)–C(16)	1.394(7)	1.383(5)
C(12)–C(13)	1.368(8)	1.390(6)
C(13)–C(14)	1.404(10)	1.376(5)
C(14)–C(15)	1.363(10)	1.362(8)
C(15)–C(16)	1.390(9)	1.385(7)
C(17)–C(18)	1.364(6)	1.384(5)
C(17)–C(22)	1.392(7)	1.389(5)
C(18)–C(19)	1.388(8)	1.381(5)
C(19)–C(20)	1.380(10)	1.388(7)
C(20)–C(21)	1.366(9)	1.355(7)
C(21)–C(22)	1.404(10)	1.390(6)
C(2)–N(1)–C(10)	126.1(4)	126.3(3)
N(1)–C(2)–C(3)	108.9(4)	109.3(3)
N(1)–C(2)–C(11)	106.9(4)	110.5(3)
N(1)–C(2)–C(17)	109.6(4)	106.7(4)
C(3)–C(2)–C(11)	112.9(4)	105.4(3)
C(3)–C(2)–C(17)	107.1(3)	112.4(3)
C(11)–C(2)–C(17)	111.4(3)	112.5(3)
C(2)–C(3)–C(4)	125.0(5)	124.2(4)
C(3)–C(4)–C(5)	122.1(5)	122.0(4)
C(4)–C(5)–C(6)	123.2(4)	122.6(4)
C(4)–C(5)–C(10)	117.6(4)	117.4(3)
C(6)–C(5)–C(10)	119.2(4)	119.9(4)
C(5)–C(6)–C(7)	120.2(5)	119.8(3)
Cl(7)–C(7)–C(6)	119.7(4)	119.4(3)
Cl(7)–C(7)–C(8)	118.9(4)	118.8(3)
C(6)–C(7)–C(8)	121.4(5)	121.9(4)
C(7)–C(8)–C(9)	118.9(5)	118.2(4)
Cl(9)–C(9)–C(8)		118.9(3)
Cl(9)–C(9)–C(10)		119.4(3)
C(8)–C(9)–C(10)	120.6(5)	121.7(3)
N(1)–C(10)–C(5)	120.0(4)	120.3(4)
N(1)–C(10)–C(9)	120.4(4)	121.2(3)
C(5)–C(10)–C(9)	119.6(4)	118.5(3)
C(2)–C(11)–C(12)	120.0(4)	120.9(3)
C(2)–C(11)–C(16)	121.8(4)	121.0(4)
C(12)–C(11)–C(16)	118.0(5)	118.0(4)
C(11)–C(12)–C(13)	122.4(5)	121.2(4)
C(12)–C(13)–C(14)	119.0(6)	119.5(4)
C(13)–C(14)–C(15)	119.6(6)	119.9(4)
C(14)–C(15)–C(16)	121.0(6)	120.6(4)
C(11)–C(16)–C(15)	120.0(5)	120.7(4)
C(2)–C(17)–C(18)	122.0(4)	120.4(3)
C(2)–C(17)–C(22)	119.6(4)	122.4(3)
C(18)–C(17)–C(22)	118.2(4)	117.1(3)
C(17)–C(18)–C(19)	121.4(6)	121.8(3)
C(18)–C(19)–C(20)	120.7(6)	120.0(4)
C(19)–C(20)–C(21)	118.8(6)	119.0(5)
C(20)–C(21)–C(22)	120.7(7)	121.1(5)
C(17)–C(22)–C(21)	120.3(6)	121.0(4)
C(2)–N(1)–C(10)–C(5)	7.6(8)	4.2(6)
N(1)–C(2)–C(3)–C(4)	3.0(8)	7.6(6)
N(1)–C(2)–C(11)–C(16)	−105.7(5)	−30.0(4)
N(1)–C(2)–C(17)–C(22)	33.7(6)	99.1(5)
C(2)–C(3)–C(4)–C(5)	0.0(9)	−3.4(7)
C(4)–C(5)–C(10)–N(1)	−3.7(7)	1.3(6)

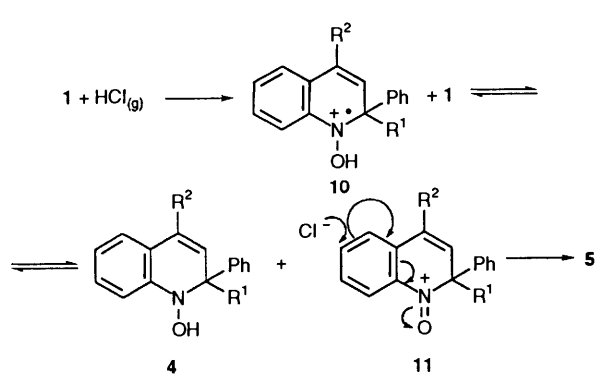
Table 3 Analysis of the planarity

	2a	**3a**
Plane A: C(5)–C(10)		
C(5)	−1(5)	4(4)
C(6)	−6(6)	−4(4)
C(7)	13(6)	0(4)
C(8)	−12(6)	4(4)
C(9)	3(5)	−4(4)
C(10)	2(5)	0(4)
Plane B: C(11)–C(16)		
C(11)	−9(4)	2(4)
C(12)	13(6)	9(4)
C(13)	−1(7)	−12(5)
C(14)	−16(7)	1(5)
C(15)	9(6)	13(6)
C(16)	7(6)	−8(5)
Plane C: C(17)–C(22)		
C(17)	0(4)	−7(5)
C(18)	−1(5)	8(5)
C(19)	1(5)	−5(6)
C(20)	0(5)	−3(6)
C(21)	−1(5)	5(6)
C(22)	1(5)	2(6)
Plane D: C(2), C(3), C(4), C(5), C(10)		
C(2)	0(4)	
C(3)	0(6)	
C(4)	0(6)	
C(5)	1(5)	
C(10)	0(5)	
N*(1)	74(5)	
Plane E: N(1), C(3), C(4), C(5), C(10)		
N(1)		1(4)
C(3)		−4(4)
C(4)		6(4)
C(5)		−7(4)
C(10)		4(4)
C*(2)		−103(4)
A–B	74.7(2)	83.8(1)
A–C	89.9(2)	70.5(1)
B–C	69.1(2)	65.3(1)

[a] Distances (Å × 10^3) of relevant atoms from the mean plane with e.s.d.s in parentheses: starred atoms were not used to define the plane.
[b] Angles (°) between planes.

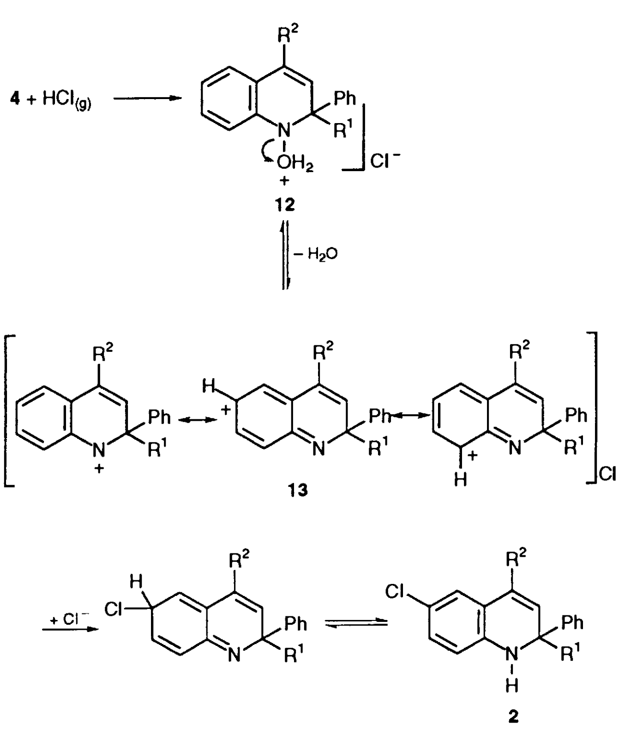
Discussion

It is well known that aminoxyls undergo a disproportionation reaction under acid treatment.[11] Aminoxyls such as 2,2,6,6-tetramethylpiperidine-1-oxyls give rise to the formation of an oxoammonium ion and an hydroxylamine,[12] instead those bearing the aminoxyl function in a conjugated position with a π-system, such as aryl aminoxyls, form a quinoneimine *N*-oxide and the corresponding amine.[13] In this study no quinoneimine *N*-oxide was found on HCl treatment of aminoxyls **1a–c**, despite the fact that their N–O˙ function is conjugated with a π-system. Therefore on the basis of the results obtained, it was assumed that aminoxyls **1a–c** give rise to a disproportionation reaction involving an oxoammonium ion and a hydroxylamine, as indicated in Scheme 3. To confirm this reaction mechanism, an experiment was carried out on aminoxyl **1a** for a few minutes where hydroxylamines **4** and **5** were identified (Scheme 2). According to this mechanism, the intermediate oxoammonium ion **11** could be the species which undergoes the chlorine anion attack to form the chlorinated hydroxylamine **5**. The probable mechanism for the deoxygenation of hydroxylamine **4** is shown in Scheme 4: the protonated hydroxylamine **12** could eliminate



Scheme 3

water thus forming the resonance stabilized cation **13**. This can then undergo nucleophilic attack by the chlorine anion at the conjugated 6-position to give the chlorinated amine **2**. The proposed mechanism may be considered similar to that reported in the literature for the reactions of phenylhydroxylamine with acids,[14–16] and could be also invoked for the formation of compounds **3** from monochlorinated hydroxylamines **5** (Scheme 4 where **12** is 6-chloro substituted).



Scheme 4

Experimental

Melting points were measured on an Electrothermal Melting Point Apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer model 298 spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 200 at 200 MHz and chemical shifts were reported downfield from $SiMe_4$. Mass spectra were recorded on a Carlo Erba QMD 1000 spectrometer. EPR spectra were recorded on a Varian E4 spectrometer.

Aminoxyls were prepared as reported in the literature.[1,17] All solvents were Fluka RP-ACS grade.

Reaction of Aminoxyls **1a–c** *with Hydrogen Chloride.*—Freshly prepared gaseous HCl was bubbled through a solution of aminoxyl **1a–c** (1 mmol) in 30 cm^3 of benzene for 5 min and stirred for 3 h. The aminoxyl solution turned from red to light yellow and no heat was given off. The mixture was then treated with 10% aqueous Na_2CO_3 (30 cm^3), washed twice with 20 cm^3 distilled water, dried (Na_2SO_4), filtered and concentrated to a small volume. The residue was chromatographed on preparative silica gel plates eluting with cyclohexane–ethyl acetate, 9:1, for reactions with aminoxyls **1a** and **b** and cyclohexane–ethyl acetate, 8:2, for those with aminoxyl **1c**. The two main fluorescent spots were extracted and crystallized from light petroleum (b.p. 60–80 °C). Yields as follows: **2a**, 47%; **3a**, 31%; **2b**, 35%; **3b**, 35%; **2c**, 37%; **3c**, 37%.

Another experiment starting from aminoxyl **1a** was stopped after a few minutes (1–2) by pouring the reaction mixture into 10% aqueous Na_2CO_3. The organic layer was checked by silica gel TLC and then oxidized with PbO_2 to transform hydroxylamines **4a** and **5a** into the corresponding aminoxyls **1a** and **6a**, which were separated by TLC eluting with cyclohexane–ethyl acetate, 9:1. Aminoxyl **1a** was identified by comparing the EPR signal with an authentic sample, instead aminoxyl **6a** ($a^N = 9.9$ G in benzene) was identified by comparing its EPR signal with that obtained from oxidation of the amine **2a** with *m*-chloroperbenzoic acid.

Crystal Structure of 6-*Chloro*-1,2-*dihydro*-2,2-*diphenylquinoline* (**2a**).—Crystals were colourless flattened prisms. Lattice parameters were determined using a program which repeatedly rectifies on the diffractometer the values of (θ, χ, φ) angles of 30 reflections to obtain the maximum of the peak when the angles are not moving more than 0.01°.

Crystal data. $C_{21}H_{16}ClN$, $M = 317.8$. Monoclinic $a = 9.888(2)$, $b = 9.678(2)$, $c = 17.456(3)$ Å, $\beta = 103.4(1)°$; $U = 1625.0(9)$ Å^3; $Z = 4$, $D_c = 1.30$ g cm^{-3}; Cu-Kα radiation $\lambda = 1.5418$ Å; $\mu = 20.6$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5 No. 14) from systematic absences.

X-Ray measurements were performed at $T = 295$ K on a Siemens AED single-crystal diffractometer in the range $3 \leqslant \theta \leqslant 70°$ using Ni-filtered Cu-Kα radiation. The angles for every reflection were determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in the θ–2θ step scanning mode using a scan width from (θ–0.60°) to ($\theta + 0.60 + \Delta\lambda/\lambda\ \mathrm{tg}\theta$)°. The intensities I_{hkl} were determined by analysing the reflection profiles.[18] 3468 Independent reflections ($0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 11$, $-21 \leqslant l \leqslant 20$) were measured of which 1367 (internal R merging factor 0.031) having $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ based on statistic counting] were used in the refinement. One standard reflection measured every 50 collected reflections to monitor crystal decomposition and instrumental linearity, showed no significant variations. Intensities I_{hkl} were corrected for Lorentz and polarization effects. The dimensions of the crystal were 0.14, 0.43, 0.04 mm. No absorption corrections were applied.

Structure analysis and refinement. The structure was solved by direct methods by use of the SHELXS86 program[19] and refined by SHELX76[20] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.048$, $R_w = 0.052$; the weighting function was of the form $w = 0.4725/[\sigma^2(F_0) + 0.0026F_0{}^2]$.

Crystal Structure of 6,8-*Dichloro*-1,2-*dihydro*-2,2-*diphenylquinoline* (**3a**).—Crystals were colourless hexagonal flattened prisms. Cell parameters were derived as before.

Crystal data. $C_{21}H_{15}Cl_2N$, $M = 352.3$. Monoclinic, $a = 11.164(3)$, $b = 18.004(4)$, $c = 8.682(2)$ Å, $\beta = 100.4(1)°$; $U = 1716.4(9)$ Å^3; $Z = 4$, $D_c = 1.36$ g cm^{-3}; Cu-Kα radiation $\lambda = 1.5418$ Å; $\mu = 34.5$ cm^{-1}. Space group $P2_1/n$ (C_{2h}^5 No. 14) from systematic absences.

Intensity data were collected as before. Of 3593 measured reflections ($-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 10$) 2076 symmetry-independent were used in the crystal analysis. The dimensions of the crystal were 0.10, 0.29, 0.33 mm. No absorption corrections were applied.

Structure analysis and refinement. The structure was solved as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.054$, $R_w = 0.056$. The weighting function was of the form $w = 0.2615/[\sigma^2(F_o) + 0.0127F_o^2]$.

All the hydrogen atoms were located in the difference-Fourier map. Atomic scattering factors from International Tables for X-ray Crystallography.[21]

All the calculations were carried out on the GOULD 6040 POWERNODE computer of the *Centro di Studio per la Strutturistica Diffrattometrica del CNR* of Parma and the Cambridge Crystallographic Data Files were used for bibliographic searches through the *Servizio Italiano di Diffusione Dati Cristallografici di Parma.*

Acknowledgements

The authors thank MURST (Rome) and Italian CNR (*Progetto Finalizzato Chimica Fine II*) for financial support.

References

1 P. Carloni, E. Damiani, L. Greci, P. Stipa, C. Rizzoli, P. Sgarabotto and F. Ugozzoli, *Tetrahedron*, 1993, **49**, 5099.

2 (*a*) S. Al-Malaika and G. Scott, *Degradation and Stabilization of Polyolefins*, ed. N. S. Allen, Applied Science Publishers, London, 1983, ch. 7; (*b*) D. J. Carlsson, A. Graton and D. M. Wiles, *Developments in Polymer Stabilization*—1, ed. G. Scott, Applied Science Publishers, London, 1979, ch. 7.

3 R. Bagheri, K. B. Chakraborty and G. Scott, *Polym. Deg. Stab.*, 1982, **4**, 1.

4 (*a*) J. Pospisil, *Oxidation Inhibition in Organic Material*, eds. J. Pospisil and P. P. Klemchuk, CRC Press, Boca Raton, FL, 1990, vol. 1, ch. 3; (*b*) R. G. Parker, USP 4, 1981, **247**, 664; (*c*) J. O. Harris, W. P. Metzner, Monsanto Chemical Co., USP 2, 1956, **748**, 100; (*d*) P. N. Son, *Polym. Deg. Stab.*, 1979, **2**, 295.

5 P. Carloni, L. Greci, A. Mar'in and P. Stipa, *Polym. Deg. Stab.*, in the press.

6 (*a*) J. Pospisil, *Developments in Polymer Stabilization*—7, ed. G. Scott, Applied Science Publishers, New York, 1984, ch. 1; (*b*) N. Grassie and G. Scott, Polymer Degradation and Stabilization, Cambridge University Press, London, 1985, ch. 5.

7 L. Greci, *Tetrahedron*, 1983, **39**, 677.

8 R. Benassi, F. Taddei, L. Greci, L. Marchetti, G. D. Andreetti, G. Bocelli and P. Sgarabotto, *J. Chem. Soc., Perkin Trans. 2*, 1980, 786.

9 D. Cremer and A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.

10 W. L. Duax, C. M. Weeks and D. C. Rohrer, *Top. Stereochem.*, 1976, **9**, 271.

11 A. R. Forrester, J. M. Hay and R. H. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press, London, 1968, p. 225.

12 E. G. Rozantsev and V. D. Sholle, *Synthesis*, 1971, 401.

13 A. R. Forrester and R. H. Thomson, *Nature*, 1964, **77**, 203.

14 H. E. Heller, E. D. Hughes and C. K. Ingold, *Nature*, 1951, **168**, 909.

15 T. Okamoto, K. Shudo and T. Ohta, *J. Am. Chem. Soc.*, 1975, **97**, 7184.

16 G. Kohnstam, W. A. Petch and D. L. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1984, 423.

17 C. Berti, M. Colonna, L. Greci and L. Marchetti, *Tetrahedron*, 1976, **32**, 2147.

18 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

19 G. M. Sheldrick, SHELXS86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

20 G. M. Sheldrick, SHELX76, System of Computer Programs for Crystal Structure Determination, University of Cambridge, 1976.

21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, England, 1974, Vol. IV.

Paper 3/07187A
Received 6*th December* 1993
Accepted 10*th January* 1994