Crystal and Molecular Structure of the *N*-Oxyl Radicals 1,2-Dihydro-3-oxo-2,2-diphenyl-3*H*-indole 1-Oxyl and 1,2-Dihydro-2,2-diphenylquinoline 1-Oxyl. Attempted Calculation of Hyperfine Coupling Constants by the INDO–SCF–MO Method

By **Rois Benassi** and **Ferdinando Taddei**, Istituto di Chimica Organica, Università di Modena, via Campi 183, 41100 Modena, Italy
Lucedio Greci and **Leonardo Marchetti**, Istituto Chimico, Facoltà di Ingegneria, Università di Bologna, viale Risorgimento 2, 40136 Bologna, Italy
Giovanni Dario Andreetti, Gabriele Bocelli, and **Paolo Sgarabotto**, Istituto di Strutturistica Chimica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., via D'Azeglio 85, 43100 Parma, Italy

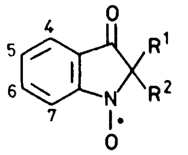
Theoretical calculations of hyperfine coupling constants of 1,2-dihydro-3*H*-3-oxoindole 1-oxyl and 1,2-dihydroquinoline 1-oxyl have been carried out using the semi-epirical INDO–SCF–MO method. The molecular geometries have been determined by *X*-ray analysis of 1,2-dihydro-3-oxo-2,2-diphenyl-3*H*-indole 1-oxyl and 1,2-dihydro-2,2-diphenylquinoline 1-oxyl. The application of the semi-empirical INDO–SCF–MO method is discussed.

An exhaustive review of the crystal and molecular structure of organic paramagnetic nitroxyl radicals determined by *X*-ray diffraction methods up to 1974 has been reported by Shibaeva.[1] The geometry of the $>$N–O functional group has been described for open-chain systems and in penta-atomic and hexa-atomic cyclic compounds. Apart from t-butylferrocenylnitroxyl[2] and phenylnitronylnitroxyl[3] no structures have been reported having a trigonal carbon atom in a position α to the nitroxyl group through which the p_z orbitals of the group could interact with the electrons of the whole molecule *via* a conjugated system. The structures reported here belong to a new class of nitroxyl radicals in which the $>$N∸O group is involved in conjugative interactions through an adjacent fused benzene ring.

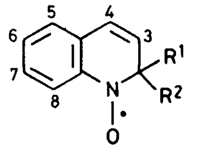
Calculation of hyperfine coupling constants of free radicals has been attempted by both semi-empirical (extended-Hückel, INDO, CNDO) and *ab-initio* MO approaches[4,5] and the results are mainly for radicals at the carbon atom. Much less attention has been devoted to radicals of atoms other than carbon, and so far little work has been done on nitroxide radicals which for various reasons, still merit theoretical and practical attention.[6,7]

The Hückel MO approach has been applied to *N*-oxide derivatives of pyrrole,[8] indole,[9] and quinoline.[10] The results were not satisfactory from the general point of view, since for reproducing the absolute experimental results the parameters to be introduced in the calculation (mainly exchange integrals and torsional angles for substituents) needed to be optimized for each class of compounds. On the other hand these results have been found to be very useful for assigning the experimental coupling constants to the different hydrogen atoms present in the molecule, since the trend of calculated values matches that of the experimental values.

Together with the results of an *X*-ray crystallographic determination of the structures of compounds (1c) and (2a), we also examine here the results obtained by applying the more sophisticated INDO–SCF–MO[5] approach to a number of nitroxide radicals, which we have studied experimentally,[10] of known molecular geometry, and, in particular, to test whether the calculated values as compared with the experimental ones may be considered to be more accurate than those derived from the Hückel approach. The compounds examined experimentally, and thus with known hyperfine coupling constants, are the series of indoline (1) and quinoline *N*-oxyl radicals (2).



(1)



(2)

a; $R^1 = Ph$; $R^2 = Me$
b; $R^1 = Ph$; $R^2 = Et$
c; $R^1 = R^2 = Ph$
d; $R^1 = Ph$; $R^2 = CH_2Ph$
e; $R^1 = Ph$; $R^2 =$ pyrrolidin-1-yl
f; $R^1 = Ph$; $R^2 = OPh$
g; $R^1 = Ph$; $R^2 = SPh$
h; $R^1 = Ph$; $R^2 = Cl$

a; $R^1 = R^2 = Ph$
b; $R^1 = Ph$; $R^2 = Me$
c; $R^1 = Ph$; $R^2 = Et$
d; $R^1 = Ph$; $R^2 = CH_2Ph$

Molecular Geometry.—1,2-Dihydro-2,2-diphenyl-3-oxo-3*H*-indole 1-oxyl (1c), the crystal structure of which is shown in (Figure 1), has the oxyl functional group in a five-membered ring in a 1,2-dihydroindole-like structure, and 1,2-dihydro-2,2-diphenylquinoline-1-oxyl (2a) (Figure 2) has the oxyl group in a six-membered ring in a 1,2-dihydroquinoline-like structure.

Tables 1 and 2 show the bond distances and angles for (1c) and (2a), respectively. The full covariance matrix was used in the estimation of standard deviations of bond distances and angles.

The configuration of the *N*-oxyl group is similar in the two compounds; the oxygen atom is out of the C–N–C plane by 0.071(4) and 0.089(2) Å, for (1c) and (2a), respectively, corresponding to angles of 3.5 and 4.0°,

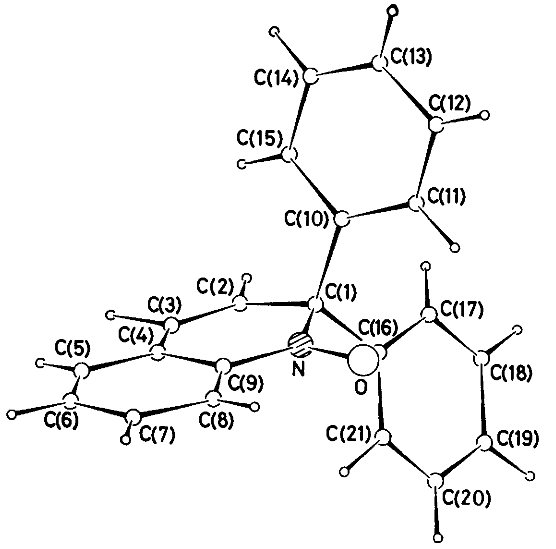


FIGURE 1 Projection of the molecular structure of the radical (1c) along [001], showing the crystallographic numbering

respectively, between the N–O bond and the C–N–C plane. The value of this angle for compound (1c) is in agreement with that found in radicals with the functional group in a five-membered heterocyclic ring [3.3° in (*R*)-(+)-3-carboxy-2,2,5,5-tetramethylpyrrolidine 1-oxyl[11] and 3.0° in 4,4,4″,4″-tetramethyloxazolidine-2-spiro-1′-cyclo-

TABLE 1

Bond distances (Å) and angles (deg.) with estimated standard deviations in parentheses for the radical (1c)

(a) Bond distances

O(1)–C(2)	1.243(6)	C(7)–C(8)	1.394(6)
O(2)–N	1.250(6)	C(9)–C(10)	1.396(6)
N–C(1)	1.528(6)	C(9)–C(14)	1.388(9)
N–C(8)	1.428(7)	C(10)–C(11)	1.403(8)
C(1)–C(2)	1.509(7)	C(11)–C(12)	1.387(10)
C(1)–C(9)	1.538(7)	C(12)–C(13)	1.384(7)
C(1)–C(15)	1.521(7)	C(13)–C(14)	1.400(9)
C(2)–C(3)	1.423(6)	C(15)–C(16)	1.385(7)
C(3)–C(4)	1.399(8)	C(15)–C(20)	1.390(9)
C(3)–C(8)	1.395(7)	C(16)–C(17)	1.396(8)
C(4)–C(5)	1.388(7)	C(17)–C(18)	1.401(11)
C(5)–C(6)	1.401(9)	C(18)–C(19)	1.370(8)
C(6)–C(7)	1.384(9)	C(19)–C(20)	1.392(8)

(b) Bond angles

O(2)–N–C(1)	124.0(11)	N–C(8)–C(3)	109.5(8)
O(2)–N–C(8)	126.5(11)	N–C(8)–C(7)	128.8(11)
C(1)–N–C(8)	109.4(7)	C(3)–C(8)–C(7)	121.6(10)
N–C(1)–C(2)	100.9(7)	C(1)–C(9)–C(10)	117.6(8)
N–C(1)–C(9)	112.7(7)	C(1)–C(9)–C(14)	122.2(11)
N–C(1)–C(15)	106.6(6)	C(10)–C(9)–C(14)	120.2(11)
C(2)–C(1)–C(9)	109.9(8)	C(9)–C(10)–C(11)	119.4(9)
C(2)–C(1)–C(15)	111.2(9)	C(10)–C(11)–C(12)	120.1(12)
C(9)–C(1)–C(15)	114.7(8)	C(11)–C(12)–C(13)	120.5(12)
O(1)–C(2)–C(1)	123.9(11)	C(12)–C(13)–C(14)	119.8(10)
O(1)–C(2)–C(3)	125.6(10)	C(9)–C(14)–C(13)	120.1(12)
C(1)–C(2)–C(3)	110.4(8)	C(1)–C(15)–C(16)	119.1(10)
C(2)–C(3)–C(4)	128.9(12)	C(1)–C(15)–C(20)	120.9(11)
C(2)–C(3)–C(8)	109.3(8)	C(16)–C(15)–C(20)	119.7(11)
C(4)–C(3)–C(8)	121.8(11)	C(15)–C(16)–C(17)	120.2(12)
C(3)–C(4)–C(5)	116.2(10)	C(16)–C(17)–C(18)	119.9(12)
C(4)–C(5)–C(6)	121.8(11)	C(17)–C(18)–C(19)	119.2(13)
C(5)–C(6)–C(7)	121.9(13)	C(18)–C(19)–C(20)	121.3(13)
C(6)–C(7)–C(8)	116.6(10)	C(15)–C(20)–C(19)	119.7(13)

(c) Carbon–hydrogen bonds

C(4)–H(4)	1.05(5)	C(13)–H(13)	1.05(7)
C(5)–H(5)	1.01(5)	C(14)–H(14)	1.02(4)
C(6)–H(6)	1.01(4)	C(16)–H(16)	1.02(7)
C(7)–H(7)	1.00(5)	C(17)–H(17)	1.01(4)
C(10)–H(10)	1.04(7)	C(18)–H(18)	1.00(5)
C(11)–H(11)	1.02(4)	C(19)–H(19)	1.02(8)
C(12)–H(12)	1.02(6)	C(20)–H(20)	1.00(4)

TABLE 2

Bond distances (Å) and angles (deg.) with estimated standard deviation in parentheses for radical (2a)

(a) Bond distances

O–N	1.286(5)	C(8)–C(9)	1.370(6)
N–C(1)	1.487(4)	C(10)–C(11)	1.374(9)
N–C(9)	1.399(5)	C(10)–C(15)	1.397(8)
C(1)–C(2)	1.520(8)	C(11)–C(12)	1.408(9)
C(1)–C(10)	1.515(5)	C(12)–C(13)	1.408(15)
C(1)–C(16)	1.539(5)	C(13)–C(14)	1.379(16)
C(2)–C(3)	1.277(10)	C(14)–C(15)	1.360(9)
C(3)–C(4)	1.430(9)	C(16)–C(17)	1.367(5)
C(4)–C(5)	1.366(8)	C(16)–C(21)	1.390(4)
C(4)–C(9)	1.427(9)	C(17)–C(18)	1.387(6)
C(5)–C(6)	1.339(17)	C(18)–C(19)	1.379(7)
C(6)–C(7)	1.383(21)	C(19)–C(20)	1.351(7)
C(7)–C(8)	1.436(10)	C(20)–C(21)	1.404(6)

(b) Bond angles

O–N–C(1)	116.3(6)	N–C(9)–C(8)	120.0(7)
O–N–C(9)	120.4(7)	C(4)–C(9)–C(8)	120.9(10)
C(1)–N–C(9)	123.2(6)	C(1)–C(10)–C(11)	120.8(9)
N–C(1)–C(2)	110.4(7)	C(1)–C(10)–C(15)	118.7(7)
N–C(1)–C(10)	107.4(5)	C(11)–C(10)–C(15)	120.5(11)
N–C(1)–C(16)	108.6(5)	C(10)–C(11)–C(12)	120.3(11)
C(2)–C(1)–C(10)	110.9(8)	C(11)–C(12)–C(13)	117.0(10)
C(2)–C(1)–C(16)	105.4(7)	C(12)–C(13)–C(14)	122.0(14)
C(10)–C(1)–C(16)	114.1(5)	C(13)–C(14)–C(15)	119.1(12)
C(1)–C(2)–C(3)	124.7(12)	C(10)–C(15)–C(14)	120.4(9)
C(2)–C(3)–C(4)	122.5(11)	C(1)–C(16)–C(17)	121.2(6)
C(3)–C(4)–C(5)	121.9(11)	C(1)–C(16)–C(21)	119.8(6)
C(3)–C(4)–C(9)	118.8(10)	C(17)–C(16)–C(21)	118.5(6)
C(5)–C(4)–C(9)	119.4(11)	C(16)–C(17)–C(18)	121.5(7)
C(4)–C(5)–C(6)	120.2(11)	C(17)–C(18)–C(19)	119.6(8)
C(5)–C(6)–C(7)	122.9(15)	C(18)–C(19)–C(20)	119.9(8)
C(6)–C(7)–C(8)	118.7(15)	C(19)–C(20)–C(21)	120.7(8)
C(7)–C(8)–C(9)	117.9(10)	C(16)–C(21)–C(20)	119.6(7)
N–C(9)–C(4)	119.1(8)		

(c) Carbon–hydrogen bonds

C(2)–H(2)	1.04(7)	C(13)–H(13)	0.92(9)
C(3)–H(3)	1.08(9)	C(14)–H(14)	1.08(10)
C(5)–H(5)	1.08(10)	C(15)–H(15)	0.79(11)
C(6)–H(6)	0.97(10)	C(17)–H(17)	0.82(7)
C(7)–H(7)	1.04(12)	C(18)–H(18)	1.08(5)
C(8)–H(8)	0.93(5)	C(19)–H(19)	1.10(5)
C(11)–H(11)	1.00(5)	C(20)–H(20)	0.92(7)
C(12)–H(12)	1.05(12)	C(21)–H(21)	1.07(4)

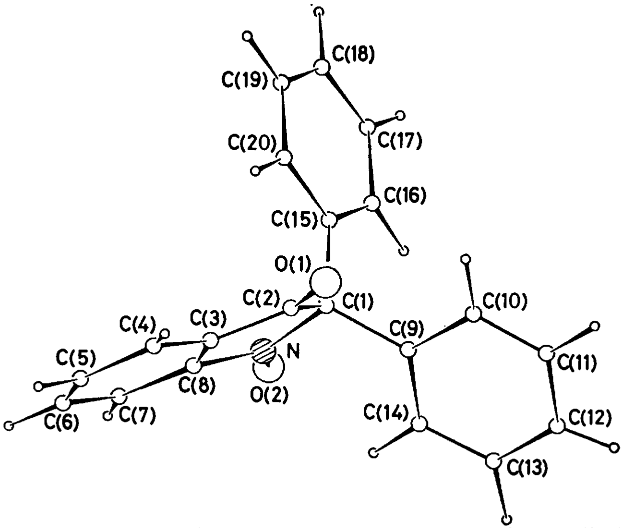


FIGURE 2 Projection of the molecular structure of the radical (2a) along [001] showing the crystallographic numbering

hexane-4′-spiro-2″-oxazolidine *N*,*N*″-dioxyl [12]. In compound (2a) this value is significantly different from that observed in all six-membered heterocyclic radicals for which the configuration of bonds at the nitrogen atom of the N–O fragment is non-planar with an out-of-plane angle in the range 16—22°. This is related to π delocalization in the heterocyclic ring. Indeed, analysis of the bond distances shows that the C(2)–C(3) bond [1.277(10) Å] is mainly double in character, but the π delocalization involves the paramagnetic $>$N$\dot{-}$O group *via* C(3)–C(4) [1.430(9)], C(4)–C(9) [1.427(9)], and C(9)–N [1.399(5) Å]. On the other hand the $>$N–O bond length of 1.286(5) Å is comparable to the average of 1.27—1.30 Å in previously studied radicals and is intermediate between lengths characteristic of NO double (1.20 Å) and single bonds (1.44 Å), corresponding in length to a three-electron bond: an electronic structure in which bonding σ and π orbitals are occupied by a pair of electrons and the unpaired electron occupies an antibonding π orbital formed from p_z nitrogen and oxygen orbitals.

The corresponding $>$N$\dot{-}$O bond length in (1c) of 1.250(6) is significantly shorter than that in (2a) but is comparable with that found in 4,4,4″,4″-tetramethyloxazolidine-2-spiro-1′-cyclohexane-4′-spiro-2″-oxazolidine *N*,*N*″-dioxyl [12] (1.25 Å).

A comparison of the C=O, N–O, and C–C bond lengths in the heterocyclic ring suggests a possible conjugative interaction between the *p* orbital of the two oxygen atoms through the adjacent fused benzene ring.

TABLE 3

Analysis of the planarity in radical (1c)

Equations of least-squares planes are in the form $lX + mY + nZ = p$ where X, Y, and Z are related to the crystallographic orthogonal axes by the transformation matrix:

$$|| \sin\gamma\ 0\ -\sin\alpha\cos\beta^*\ |\ \cos\gamma\ 1\ \cos\alpha\ |\ 0\ 0\ \sin\alpha\sin\beta^*\ ||$$

Distances (Å × 10^3) of atoms from the planes are given in square brackets

Plane A: C(3)—C(8)

$$-0.4483X + 0.8663Y - 0.2202Z = 5.9113$$

[C(3) −1(4),C(4) 2(6), C(5) −1(7), C(6) 0(6), C(7) 0(6), C(8) 1(4), N 25(4), C(2) 29(4)]

Plane B: C(9)—C(14)

$$0.2160X + 0.5023Y - 0.8373Z = 0.7348$$

[C(9) 0(4), C(10) 5(4), C(11) −5(5), C(12) −3(5), C(13) 11(5), C(14) −8(5), C(1) −37(4)]

Plane C: C(15)—C(20)

$$-0.7536X - 0.3865Y - 0.5317Z = -2.3668$$

[C(15) 3(4), C(16) 1(5), C(17) −5(5), C(18) 6(5), C(19) 0(6), C(20) −4(5), C(1) 158(4)]

Plane D: C(1)—C(3)

$$-0.4771X + 0.8688Y - 0.1323Z = 6.3793$$

[O(1) 61(4)]

Plane E: C(1)–N–C(8)

$$-0.5011X + 0.8181Y - 0.2823Z = 5.7236$$

[O(2) 71(4)]

Plane F: C(2)–C(3)–C(8)–N

$$-0.4661X + 0.8581Y - 0.2152Z = 5.9559$$

[C(2) 1(4), C(3) −2(4), C(8) 2(4), N −1(4), C(1) 121(4), O(1) −22(4), O(2) −16(4)]

Angles between planes

∠AB 58.5° ∠AC 83.1° ∠BC 84.9°

TABLE 4

Analysis of the planarity in radical (2a)

Equations of least-squares planes in the form $lX + mY + nZ = p$ where X, Y, and Z are related to the crystallographic orthogonal axes by the transformation matrix

$$|| 1\ 0\ \cos\beta\ |\ 0\ 1\ 0\ |\ 0\ 0\ \sin\beta\ ||$$

Distances (Å × 10^3) of atoms from the planes are given in square brackets

Plane A: C(4)—C(9)

$$-0.1456X + 0.9182Y - 0.3684Z = 2.7850$$

[C(4) 16(6), C(5) −12(8), C(6) −13(9), C(7) 14(7), C(8) 1(5), C(9) −5(4), N −1(4), C(3) 77(7)]

Plane B: C(10)—C(15)

$$-0.4141X - 0.1496Y - 0.8978Z = -5.5980$$

[C(10) −12(4), C(11) 16(5), C(12) −3(8), C(13) −54(8), C(14) 56(10), C(15) −3(8), C(1) −72(4)]

Plane C: C(16)—C(21)

$$0.7081X + 0.1098Y - 0.6975Z = -5.9750$$

[C(16) −12(4), C(17) 11(5), C(18) 1(5), C(19) −12(6), C(20) −2(6), C(21) 15(5), C(1) 115(4)]

Plane D: C(1)–N–C(9)

$$-0.0933X + 0.8762Y - 0.4727Z = 1.5920$$

[O −80(2)]

Plane E: C(2)–C(3)–C(4)–C(9)–N

$$-0.1544X + 0.9240Y - 0.3498Z = 2.9816$$

[C(2) −19(7), C(3) 28(7), C(4) −8(6), C(9) −2(4), N 3(4), C(1) −145(4)]

Angles between planes

∠AB 75.3° ∠AC 75.2° ∠BC 71.5°

Tables **3** and **4** report an analysis of the planarity of radicals (1c) and (2a), respectively. The dihydroindole ring adopts a flattened half-chair conformation C(1) being out of the plane of the other atoms by 0.121(4) Å; atoms O(1) and O(2) are out of this plane by −0.022(4) and by −0.017(4) Å respectively. The dihydroquinoline ring is rather flattened with a conformation close to a half-boat with C(1) as the bow (see plane E of Table **4**).

All the benzene rings are planar within experimental error. The reciprocal orientation of the planar parts of the molecules can be defined in terms of the dihedral angles reported in Table **3** and Table **4**.

For both compounds packing is consistent with van der Waals interactions. A contact at the limit of the sum of the van der Waals radii is observed in radical (1c) where $O(2) \cdots O(2)^i = 3.15$ Å and $i = -1 - x,\ 1 - y,\ -z$.

Theoretical Calculations.—The INDO-SCF-MO approach has been applied mainly to the calculation of e.s.r. hyperfine coupling constants of carbon radicals; for application to different nuclei it is necessary to parametrize the density of the valence *s* orbital at the nucleus of each atom.[5] To apply the method to nitroxide radicals we thus need to verify if the reported [5] parameter set may also be applied to this class of molecules.[4b] The experimental results we refer to are those for a series of indolinone nitroxide radicals (1), and quinoline nitroxide radicals (2), and the experimental hyperfine coupling constants are collected in Tables 5

TABLE 5

E.s.r. hyperfine coupling constants of the indolinone nitroxide radicals (1) [a]

Compound	a^{N}	$a^{H(5,7)}$	$a^{H(4,6)}$	a^{R}	Ref.
(1a)	9.58	3.15 (2 H)	1.05 (2 H)	0.12 (3 H)	b
(1b)	9.52	3.09 (2 H)	1.01 (2 H)	0.29 (1 H)	b
(1c)	9.52	3.04 (2 H)	1.01 (2 H)		b
(1d)	9.21	3.04 (2 H)	1.00 (2 H)	0.50 (1 H) 0.50 (1 H)	b
(1e)	10.56	3.36 (2 H)			c
(1f)	9.55	3.05 (2 H)	1.00 (2 H)		c
(1g)	9.20	3.02 (2 H)	0.98 (2 H)		c
(1h)	9.40	2.93 (2 H)	1.02 (2 H)		c

[a] In benzene solution. [b] Ref. 9. [c] This work.

TABLE 6

E.s.r. hyperfine coupling constants of the quinoline nitroxide radicals (2) [a]

Compd.	a^{N}	$a^{H(3)}$	$a^{H(4)}$	$a^{H(5,7)}$	$a^{H(6,8)}$	a^{R}
(2a)	10.17	1.42	0.53	1.07 (2 H)	3.20 (2 H)	
(2b)	10.15				3.20 (2 H)	
(2c)	10.15				3.25 (2 H)	
(2d)	10.31	1.36	0.55	1.02 (2 H)	3.25 (2 H)	0.55 (2 H)

[a] Ref. 10: in chloroform solution.

and 6. The values for each single nucleus are contained within a small interval for the different compounds even if they differ significantly because of the different positions and the different nuclei. When applying the calculation method, the systems examined experimentally turned out to be too large while the basic molecular skeleton according to the reported *X*-ray analysis was maintained. A reduction has been carried out for the dimensions of substituents R^1 and R^2 by introducing groups with similar electron effects but with a smaller number of atoms. The results of the calculation are reported in Table 7.

For the hyperfine coupling constants, a^N, the value calculated for the model compounds of type (1) are lower than that the experimental ones by a factor of 1.7; this might depend on the fact that the nitroxide derivatives were not included in the original parameter choice of the density value for the *s* valence orbital of the nitrogen nucleus; for different classes of compounds this value is not constant for a given atom. In fact for a radical of type (2) the quotient $(a^N_{\text{exp.}}/a^N_{\text{calc.}})$ is greater than 1.7. Furthermore, the presence of a strongly electronegative substituent, such as OR, on C-2 in compounds of type (1) does not seem to influence greatly the a^N coupling constants, whereas the corresponding calculated value is smaller than those of derivatives containing substituents on carbon atoms only; for compound (1e), in which the pyrrolidine group is bonded to C-2, the hyperfine coupling constant is higher than in the other compounds.

The calculated hyperfine coupling constants for the hydrogen nuclei are also lower than the experimental values and only the trend in these values (apart from the negative sign of the set relative to the hydrogen atoms that are *ortho–para* with respect to the nitroxide group) resembles that of experimental values. For 3- and 4-H compounds of type (2), the experimental and calculated values are closer, which means that these hydrogen atoms should be treated differently from those on the benzenoid ring with regard to the correlation between electron density and hyperfine coupling constants.

There are several reasons for this inconsistency, which have already been discussed in the literature,[4] and which do not permit the use of the INDO–SCF–MO method for predicting the hyperfine coupling constants even in a class of compounds such as nitroxide radicals.[4]

EXPERIMENTAL

Compounds (1a—d) and those of type (2) and their e.s.r. spectra have been reported elsewhere.[9,10] The e.s.r. spectra were recorded on a Varian E4 spectrometer.

1,2-*Dihydro*-3-*oxo*-2-*phenyl*-2-(*pyrrolidin*-1-*yl*)-3H-*indole* 1-*Oxyl* (1e).—Phenylisatogen (2.5 mmole) and pyrrolidine (7.5 mmol) were stirred for 1 h at room temperature in benzene solution (25 ml), then lead(II) dioxide (1 g) was added and the mixture was stirred for 3 h. The mixture was filtered and the solution, reduced to small volume, was chromatographed by silica preparative t.l.c., eluting with light petroleum–ethyl acetate (9 : 1). The head fraction, containing phenylisatogen also, was extracted with benzene and the e.s.r. signal of the nitroxide radical was obtained from this solution. Attempts to isolate the nitroxide from the solution failed because of its low stability.

1,2-*Dihydro*-3-*oxo*-2-*phenyl*-2-*phenoxy*-3H-*indole* 1-*Oxyl* (1f), *and* 1,2-*Dihydro*-3-*oxo*-2-*phenyl*-2-*thiophenoxy*-3H-*indole* 1-*Oxyl* (1g).—Phenylisatogen (200 mg) and phenol (500 mg) were left in benzene (10 ml) for 2 h. A portion of this solution was treated with lead(II) dioxide in the cavity of the e.s.r. spectrometer, and the signal due to compound (1f) was recorded. Compound (1g) was obtained by the same procedure from phenylisatogen (200 mg) and benzenethiol (500 mg).

2-*Chloro*-1,2-*dihydro*-3-*oxo*-2-*phenyl*-3H-*indole* 1-*Oxyl* (1h).—A solution containing phenylisatogen (200 mg) in benzene (10 ml) was saturated with gaseous HCl. A portion of this solution, when oxidized with chloroanil in the e.s.r. cavity, gave the signal for (1h). Compounds (1f—h) could not be isolated owing to their low stability.

Crystal Structure of 1,2-*Dihydro*-3-*oxo*-2,2-*diphenyl*-3H-*indole* 1-*Oxyl* (1c).—Crystals of (1c) are deep red tabular prisms. The preliminary cell dimensions and space group were obtained from rotation and Weissenberg photographs. Lattice parameters were refined by the use of 14 $(\sigma,\chi,\phi)_{hkl}$

TABLE 7

Hyperfine coupling constants by calculated the INDO-SCF-MO method for compounds of type (1) and (2)

Compound	R^1	R^2	a^{N}	$a^{H(3)}$	$a^{H(4)}$	$a^{H(5)}$	$a^{H(6)}$	$a^{H(7)}$	$a^{H(8)}$
(1)	H	H	5.085		0.855	−1.037	0.793	−1.215	
	Me	H	5.332		0.896	−1.074	0.826	−1.258	
	Me	Me	5.504		0.890	−1.069	0.827	−1.255	
	H	Ph	5.330		0.855	−1.032	0.803	−1.230	
	Me	OMe	5.262		0.852	−1.024	0.798	−1.208	
(2)	H	H	4.006	−1.052	0.502	0.851	−0.929	0.851	−0.929

measurements recorded on a Siemens single-crystal diffractometer.

Crystal data. $C_{20}H_{14}NO_2$, M = 300.3. Triclinic, a = 9.44(1), b = 8.59(1), c = 14.88(1) Å, α = 54.6(2), β = 128.5(2), γ = 109.1(2)°; Z = 2; D_m = 1.29 g cm^{-3}; U = 768.7 Å^3; Cu-K_α radiation, λ = 1.541 8 Å; μ (Cu-K_σ) = 6.8 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Intensity data were collected up to θ 70° by using the ω–2θ scan method and the five-points technique[13] with nickel-filtered Cu-K_α radiation on the same single-crystal diffractometer. 2 655 Independent reflections were measured of which 149 with $I \leqslant 2[\sigma^2(I) + 10^{-4}I^2]^{1/2}$ were not used in the analysis. The dimensions of the crystal were *ca.* 0.8 × 0.1 × 0.7 mm. No absorption correction was made.

Structure analysis and refinement. Structure amplitudes were put on an absolute scale by Wilson's statistical method[14] ($\bar{B}$ = 3.6 Å^2) and normalized structure factor magnitudes $|E_{hkl}|$ were then derived. The structure was solved by direct methods of use of the MULTAN program.[15] The structure was refined by block-diagonal least-squares cycles, first with isotropic and then with anisotropic thermal parameters; the R factor was reduced to 0.094. A difference-Fourier synthesis then showed significant residual peaks near all the positions where hydrogen atoms were expected. Two least-squares cycles were then computed including hydrogen atoms with isotropic thermal parameters and final R of 0.070 was obtained.

TABLE 8

Fractional atomic co-ordinates for radical (1c) with standard deviations in parentheses

	x	y	z
(a) Non-hydrogen atoms (× 10^4)			
O(1)	1 207(3)	3 573(4)	4 898(2)
O(2)	−3 020(3)	4 695(4)	501(2)
N	−2 234(4)	4 058(4)	1 714(3)
C(1)	−538(4)	4 885(4)	2 507(3)
C(2)	−140(4)	3 513(4)	3 888(3)
C(3)	−1 567(4)	2 239(4)	3 846(3)
C(4)	−1 816(5)	872(5)	4 873(4)
C(5)	−3 373(6)	−145(6)	4 531(5)
C(6)	−4 627(5)	185(5)	3 229(5)
C(7)	−4 381(5)	1 541(5)	2 213(4)
C(8)	−2 819(4)	2 567(4)	2 550(3)
C(9)	1 065(4)	4 822(4)	2 500(3)
C(10)	2 681(4)	5 566(5)	3 180(3)
C(11)	4 193(5)	5 481(5)	3 234(4)
C(12)	4 070(5)	4 685(6)	2 602(4)
C(13)	2 461(5)	3 971(6)	1 913(4)
C(14)	957(5)	4 015(5)	1 878(4)
C(15)	−1 105(4)	6 871(4)	1 965(3)
C(16)	−1 261(5)	8 380(5)	797(3)
C(17)	−1 952(5)	10 174(5)	207(4)
C(18)	−2 507(5)	10 446(5)	790(4)
C(19)	−2 334(6)	8 943(6)	1 950(4)
C(20)	−1 634(5)	7 152(5)	2 551(4)
(b) Hydrogen atoms (× 10^3)			
H(4)	−88(5)	61(6)	585(4)
H(5)	−358(5)	−119(6)	525(4)
H(6)	−572(5)	−62(5)	304(4)
H(7)	−527(5)	178(5)	128(4)
H(10)	276(5)	618(5)	364(4)
H(11)	536(5)	604(6)	373(4)
H(12)	528(5)	473(6)	274(4)
H(13)	235(5)	339(5)	142(4)
H(14)	−18(5)	341(5)	141(4)
H(16)	−90(5)	816(5)	36(4)
H(17)	−206(5)	1 130(5)	−64(4)
H(18)	−300(5)	1 173(5)	37(4)
H(19)	−273(5)	917(6)	−237(4)
H(20)	−150(5)	605(5)	340(4)

TABLE 9

Fractional atomic co-ordinates for radical (2a) with standard deviations in parentheses

	x	y	z
(a) Non-hydrogen atoms (× 10^4)			
O	403(4)	3 463(2)	7 759(2)
N	1 276(4)	3 350(2)	7 097(3)
C(1)	336(5)	2 939(2)	5 947(3)
C(2)	1 401(8)	2 967(4)	5 170(5)
C(3)	2 994(10)	3 193(4)	5 528(7)
C(4)	3 945(6)	3 479(3)	6 713(6)
C(5)	5 680(9)	3 676(4)	7 106(11)
C(6)	6 508(12)	3 972(4)	8 204(14)
C(7)	5 683(12)	4 094(3)	8 986(11)
C(8)	3 875(7)	3 872(3)	8 621(5)
C(9)	3 044(5)	3 566(2)	7 498(4)
C(10)	66(6)	2 119(2)	6 252(3)
C(11)	−1 103(10)	1 949(3)	6 770(4)
C(12)	−1 273(19)	1 191(4)	7 111(5)
C(13)	−198(15)	632(3)	6 899(6)
C(14)	836(12)	795(4)	6 270(9)
C(15)	1 047(9)	1 538(3)	6 012(7)
C(16)	−1 379(5)	3 372(2)	5 234(3)
C(17)	−2 794(6)	3 004(2)	4 406(4)
C(18)	−4 294(7)	3 401(3)	3 695(4)
C(19)	−4 359(8)	4 186(3)	3 807(5)
C(20)	−2 960(7)	4 564(3)	4 599(5)
C(21)	−1 434(7)	4 166(2)	5 317(4)
(b) Hydrogen atoms (× 10^3)			
H(2)	82(7)	271(4)	433(6)
H(3)	368(9)	316(4)	493(6)
H(5)	641(14)	360(5)	655(9)
H(6)	771(14)	404(6)	827(9)
H(7)	602(14)	424(6)	988(10)
H(8)	331(5)	390(2)	915(3)
H(11)	−188(6)	235(3)	689(4)
H(12)	−218(14)	88(7)	734(10)
H(13)	2(8)	12(5)	710(6)
H(14)	145(20)	33(12)	602(13)
H(15)	171(17)	171(7)	576(12)
H(17)	−273(8)	254(4)	432(5)
H(18)	−526(7)	304(3)	304(5)
H(19)	−561(7)	447(3)	328(5)
H(20)	−299(7)	509(4)	467(4)
H(21)	−24(6)	444)3)	588(4)

The final positional parameters and their standard deviations are given in Table 8.

Crystal Structure of 1,2-*Dihydro*-2,2-*diphenylquinoline* 1-*Oxyl* (2a).—Crystals are deep red prisms elongated on [1,0,0]. A crystal with dimensions *ca.* 0.4 × 0.2 × 0.2 mm was used for intensity measurements. The space group and initial unit-cell parameters were obtained as for (1c). Accurate unit cell parameters were obtained by a least-squares treatment of the $(\theta,\chi,\phi)_{hkl}$ values for 16 reflections.

Crystal data. $C_{21}H_{16}NO$, M = 298.4. Monoclinic, a = 8.264(5), b = 17.437(7), c = 12.115(6) Å; β = 113.0(1)°, U = 1 607.0 Å^3; Z = 4; D_m = 1.20 g cm^{-3}. Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 6.0 cm^{-1}. Space group $P2_1/c$, from systematic absences.

The diffraction data were collected as for (1c). Of 3 045 independent reflections measured ($\nu_{max.}$ 70°), 1 185 were considered unobserved and not used in the refinement. No absorption corrections were made.

Structure analysis and refinement. 400 Reflections with $E \geqslant 1.54$ were used for the phase determination. The structure was solved by direct methods. An E map, computed by using the most consistent phase set, revealed the whole structure. A structure-factor calculation based on the co-ordinates derived from E map with $\bar{B}$ = 6.3 Å^2 for all atoms gave R = 0.31. Refinement was carried out by full-matrix, least-squares cycles, first with isotropic and then with anisotropic thermal parameters, when R was reduced to 0.092. All hydrogen atoms were located from a difference-Fourier synthesis. Further least-squares cycles were computed, hydrogen atoms having been included with isotropic thermal parameters, and led to a final R of 0.076. Positional parameters and their standard deviations are given in Table 9.

The atomic scattering factors used for both crystal structure analyses were taken from ref. 16 for oxygen, nitrogen, and carbon, and from ref. 17 for hydrogen.

For both compounds the measured and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22674 (23 pp.).*

All the calculations were carried out on the CDC Cyber 76 computer at the Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

[8/2166 *Received*, 18*th December*, 1978]

---

* See Notice to Authors No. 7, *J.C.S. Perkin II*, 1979, Index issue.

REFERENCES

[1] R. N. Shibaeva, *Zhur. strukt. Khim.*, 1975, **16**, 330.

[2] A. R. Forrester, S. P. Hepburn, D. C. Dunlop, and H. H. Mills, *Chem. Comm.*, 1969, 698.

[3] J. H. Osiecki and E. F. Ullman, *J. Amer. Chem. Soc.*, 1968, **90**, 1078; W. Wong and S. F. Watkins, *J.C.S. Chem. Comm.*, 1973, 888.

[4] (*a*) F. W. King, *Chem. Rev.*, 1976, **76**, 157; (*b*) A. Rassat and J. Rounzaud, *J. Amer. Chem. Soc.*, 1973, **93**, 5041.

[5] (*a*) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026; (*b*) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201; (*c*) J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, London, New York, 1970.

[6] R. Bolton, D. Borg, and H. Swartz, eds. ' Biological Applications of Electron Spin Resonance Spectroscopy,' Wiley–Interscience, New York, 1972.

[7] B. Ranby and J. F. Rabek, ' ESR Spectroscopy in Polymer Research,' Springer–Verlag, Berlin, Heidelberg, New York, 1977.

[8] P. J. Grossi, L. Marchetti, R. Ramasseul, and A. Rassat, to be published; P. J. Grossi, Thèse 2559, Grenoble, 1968.

[9] C. Berti, M. Colonna, L. Greci, and L. Marchetti, *Tetrahedron*, 1975, **31**, 1745.

[10] C. Berti, M. Colonna, L. Greci, and L. Marchetti, *Tetrahedron*, 1976, **32**, 2147.

[11] J. B. Wetherington, S. S. Ament, and J. W. Moncriff, *Acta Cryst.*, 1974, **B30**, 568.

[12] W. B. Gleason, *Acta Cryst.*, 1973, **B29**, 2959.

[13] W. Hoppe, *Acta Cryst.*, 1969, **A25**, 67.

[14] A. J. Wilson, *Nature*, 1942, **150**, 151.

[15] P. Main, M. M. Woolfson, and G. Germain, MULTAN, a Computer Program for the Automatic Solution of Crystal Structures, University of York, 1971.

[16] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.