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AMINYLOXIDES[a] (NITROXIDES) FROM 1-HYDROXY-2-INDOLINONES

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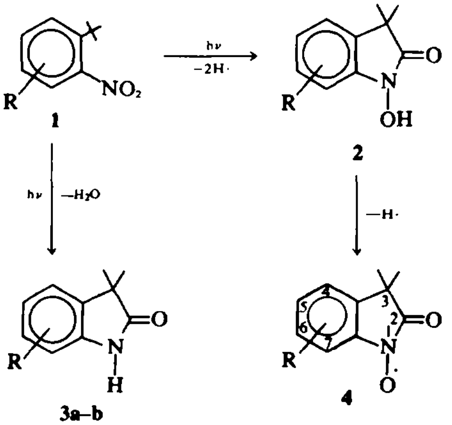
Abstract—1-Hydroxy-3,3-dimethylindolin-2-ones (2) formed by intramolecular photocyclisation of *o*-nitro-t-butylbenzenes (1) are oxidized to aminyloxides (4a–g). Their ESR spectra are reported and discussed.

A recently discovered[1-3] light-induced intramolecular cyclisation of *o*-nitro-t-butylbenzenes (**1**) afforded the possibility to synthesize variously substituted 1-hydroxy-3,3-dimethylindolin-2-ones (**2**) along with other products such as **3**.

Since such cyclic hydroxamic acids are known to, be easily oxidized to stable aminyloxides (nitroxides) which had been prepared by more cumbersome methods,[4] this photochemical cyclisation enabled us to investigate the properties and ESR spectra of free radicals **4** obtained from **2**.



a: R = H
b: R = 6-$C(CH_3)_3$
c: R = 6-C_6H_5
d: R = 6-$NHCOCH_3$
e: R = 6-Br
f: R = 6-NO_2
g: R = 5,7-$[C(CH_3)_3]_2$

RESULTS AND DISCUSSION

Solutions of **2** in 1,4-dioxane or benzene were prepared, degassed and oxidized to aminyloxides **4** by lead tetraacetate or lead dioxide. ESR spectra of these solutions afforded the hyperfine coupling constants and g-factors presented in Tables 1 and 2.

In all cases the ESR spectra show a 1 : 1 : 1 triplet (due to the ^{14}N nucleus) which is further split by interaction with the aromatic protons, and in some cases, with the Me protons. No coupling is observed with the R-group in position 6 of aminyloxides **4** (which, as can be seen from the data of **4a** and **4g**, has a very low spin density), except for **4d**.

The ESR spectra of **4b,c,e,f** are similar (Fig 1): each component of the triplet is further split owing to nearly equal coupling with the 5- and 7-protons situated *ortho* and *para* to the aminyloxide group, and each resulting energy level is further split into a doublet by a smaller coupling with the 4-proton lo-

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[a] Name according to IUPAC rule C 81.2.

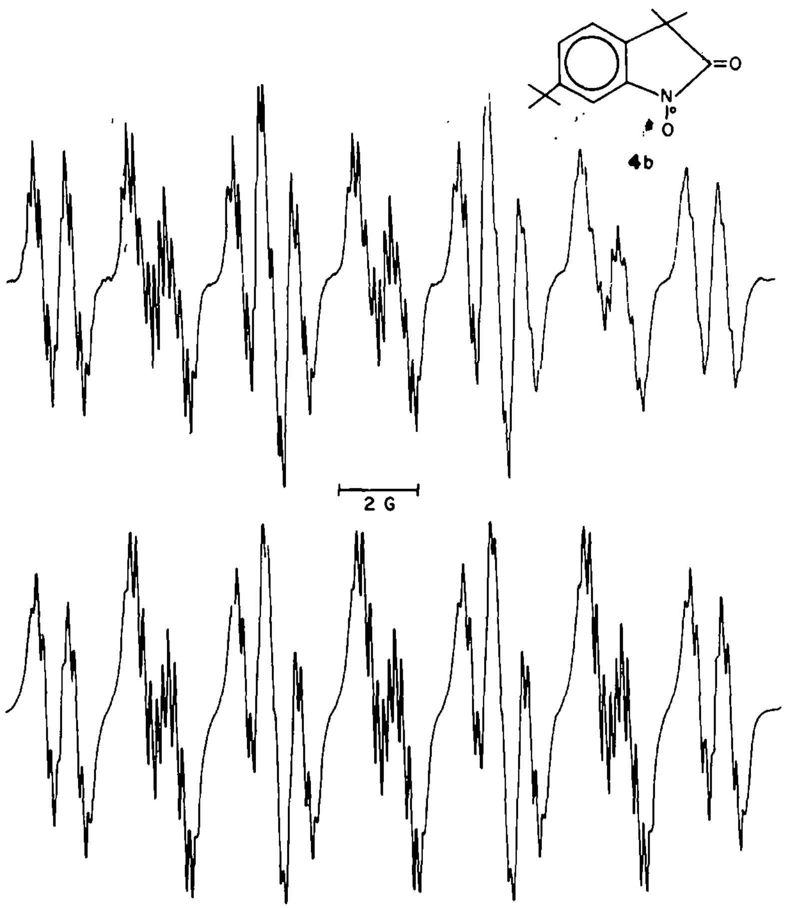


Fig 1. ESR first-derivative spectrum of **4b** in dioxane (above) with computer simulation (below).

Table 1. ESR data of aminyloxides **4** in dioxane at 25° (coupling constants in Gauss)

No.	R	$\sigma_{meta}{}^{a}$	$a_N{}^{NO}$	$a_H{}^{(5)}$	$a_H{}^{(7)}$	$a_H{}^{(4)}$	$a_H{}^{other}$	$a_H{}^{CH_3}$	g
4a	H	±0	5·80	2·69	2·47	0·86	0·74 $a_H{}^6$	0·15	2·0061
4b	6-CMe$_3$	−0·10	5·85	2·74	2·40	0·89	—	0·16	2·0061
4c	6-C$_6$H$_5$	+0·06	5·78	2·50	2·50	0·78	—	—	2·0061
4d	6-NHCOMe	+0·21	5·81	2·85	2·28	0·78	0·15 $a_H{}^{NHAc}$	0·14	2·0061
4e	6-Br	+0·391	5·69	2·54	2·54	0·77	—	0·14	2·0060
4f	6-NO$_2$	+0·71	5·58	2·63	2·38	0·71	—	0·15	2·0062
4g	5,7-(CMe$_3$)$_2$	—	6·00	—	—	0·86	0·63 $a_H{}^6$	—	2·0061

[a] values given *loc. cit.* Ref. 13.

Table 2. ESR hyperfine splitting constants of aminyloxides **4** in benzene at 25° (in Gauss)

No.	R	$\sigma_{meta}{}^{a}$	$a_N{}^{NO}$	$a_H{}^{(5)}$	$a_H{}^{(7)}$	$a_H{}^{(4)}$	$a_H{}^{other}$	$a_H{}^{CH_3}$
4a	H	±0	5·63	2·55	2·45	0·87	0·74 $a_H{}^6$	0·15
4b	6-CMe$_3$	−0·10	5·72	2·42	2·24	0·80	—	0·16
4c	6-C$_6$H$_5$	+0·06	5·60	2·50	2·50	0·76	—	—
4d	6-NHCOME	+0·21	5·64	2·82	2·26	0·76	0·15 $a_H{}^{NHAc}$	0·15
4e	6-Br	+0·391	5·48	2·55	2·55	0·87	—	—
4f	6-NO$_2$	+0·71	5·35	2·59	2·49	0·70	—	0·13
4g	5,7-(CMe$_3$)$_2$	—	5·95	—	—	0·63	0·63 $a_H{}^6$	—

[a] values given *loc. cit.* Ref 13.

cated *meta* to the radical function. Exact determination of the two coupling constants of the 5- and 7-protons could be achieved in some cases, in other cases only a mean value could be obtained owing to broad lines. Thus there result 16 groups of lines. In contrast **4d** with an acetylamino group in the 6-position shows an ESR spectrum with 19 groups of lines (Fig 2), indicating a greater difference in the coupling constants of the 5- and 7-protons. The larger a_H constant may tentatively be assigned to the 5-proton situated in *para* to the aminyloxide group.

Aminyloxide **4a**[4b] has an ESR spectrum (Fig 3) with 23 groups of lines in which each component of the 1 : 1 : 1 triplet is split into a 1 : 2 : 1 triplet of 1 : 2 : 1 triplets owing to the two sets of two protons in positions 5 and 7 (*ortho* and *para* to the aminyloxide group, hence larger coupling constants) and 4 and 6 (*meta* to the radical function, therefore smaller coupling constants). The larger one of the former couplings is attributed to the 5-proton in *para* to the nitroxide group using the same argument as above. By comparison with a_H(4) in the radicals **4b**–**4f** the larger of the two *meta*-couplings should be due to the 4-proton.

The correctness of the above assignment of coupling constants is confirmed by aminyloxide **4g**. Its 9-line ESR spectrum presents only the 1 : 1 : 1 triplet due to the nitrogen which is further split into a 1 : 2 : 1 triplet with a small coupling constant by the *meta*-standing 4- and 6-protons.

In addition the ESR spectra of **4a**–**d** and **4f** show a small splitting by interaction of the unpaired electron with the Me protons of the 3-position. Furthermore the proton of the acetylamino group in **4d** contributes to the splitting with the same coupling constant as the Me protons, as could be shown by deuterium exchange with D_2O.

The small value of a_N relatively to other aminyloxides[5-7] is due firstly to the fact that acylaminyloxides (**5**)[8-11] have lower unpaired spin density on the nitrogen relatively to radicals **6**. This is explained by the contribution of structures **5C**–**5E** and by the fact that structure **5B** with high spin density on the nitrogen is destabilized by the adjacency of two positive ends of dipoles.

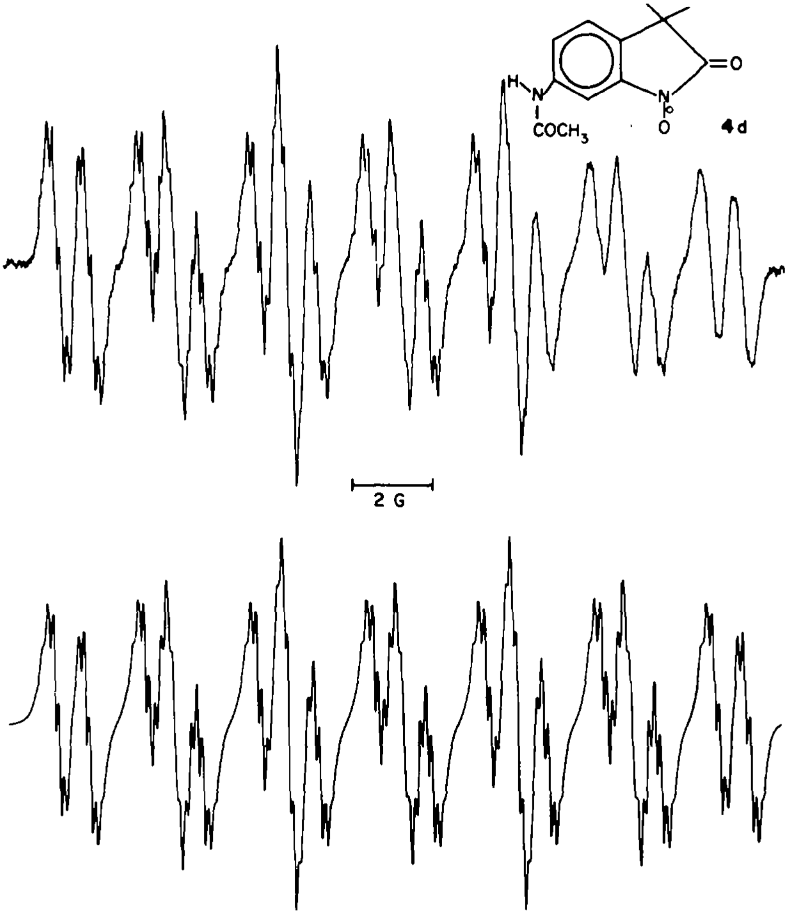


Fig 2. ESR first-derivative spectrum of **4d** in dioxane (above) with computer simulation (below).

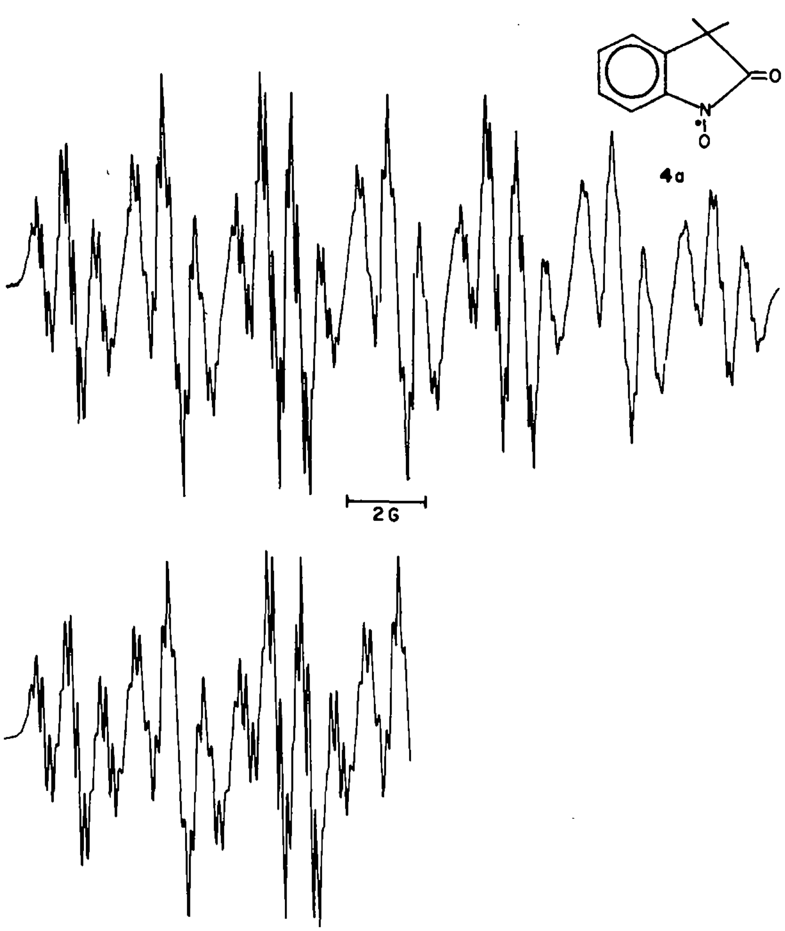
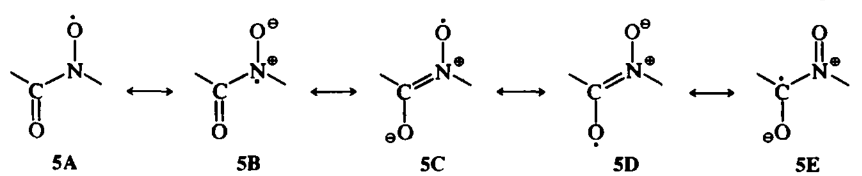


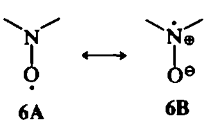
Fig 3. ESR first-derivative spectrum of **4a** in dioxane (above) with computer simulation of the low-field half of the spectrum.

A confirmation of this effect is provided by diacyl-aminyloxides **7**[11,12] which have still lower a_N values and higher g-factors. In fact, a_N values vary inversely to g-factors. The heavier the atom with highest spin density, the higher the g-factor: decreasing spin density on the nitrogen in the series aminyloxides–acylaminyloxides–diacylaminyloxides is achieved by increasing the spin density on oxygen atoms, causing the effects on a_N and g-factors.

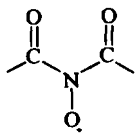
Secondly, a comparison between acylic (**5**) and cyclic acylaminyloxides (**8**) reveals that cyclisation lowers the nitrogen hyperfine coupling constant a_N. A rationalization of this effect is based on considering that acyclic aminyloxides are free to adopt the *anti* conformation **5**, whereas cyclic aminyloxides are compelled to exist in the *syn* conformation **8**.[14] Thus, the mutual orientations of the dipoles formed by the carbonyl and aminyloxide (nitroxide) groups as in **5** and **8** differ: the parallel orientation of the



5A **5B** **5C** **5D** **5E**



6A **6B**



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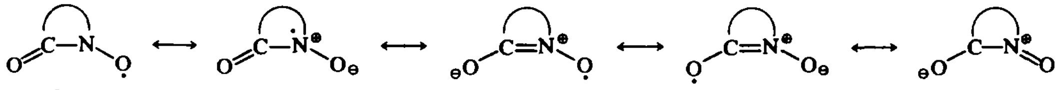
dipoles in the cyclic structure **8B** makes it less favourable energetically than the acyclic structure **5B** explaining thereby the different a_N values.



8A **8B** **8C** **8D** **8E**

Thirdly the nitrogen coupling constant depends on the nature of the substituent in the 6-position: the more electron attracting the substituent, the smaller the coupling constant. This can be easily explained considering that structure **A** is favoured over structure **B** with increasing possibility of the substituent to withdraw electron density from the aromatic ring.[15] These effects can be correlated by σ_m in the Hammett equation (Fig 4). There is no need however to use any modified parameter (e.g. σ_m^- or σ_m^+) which were found to give a better fit

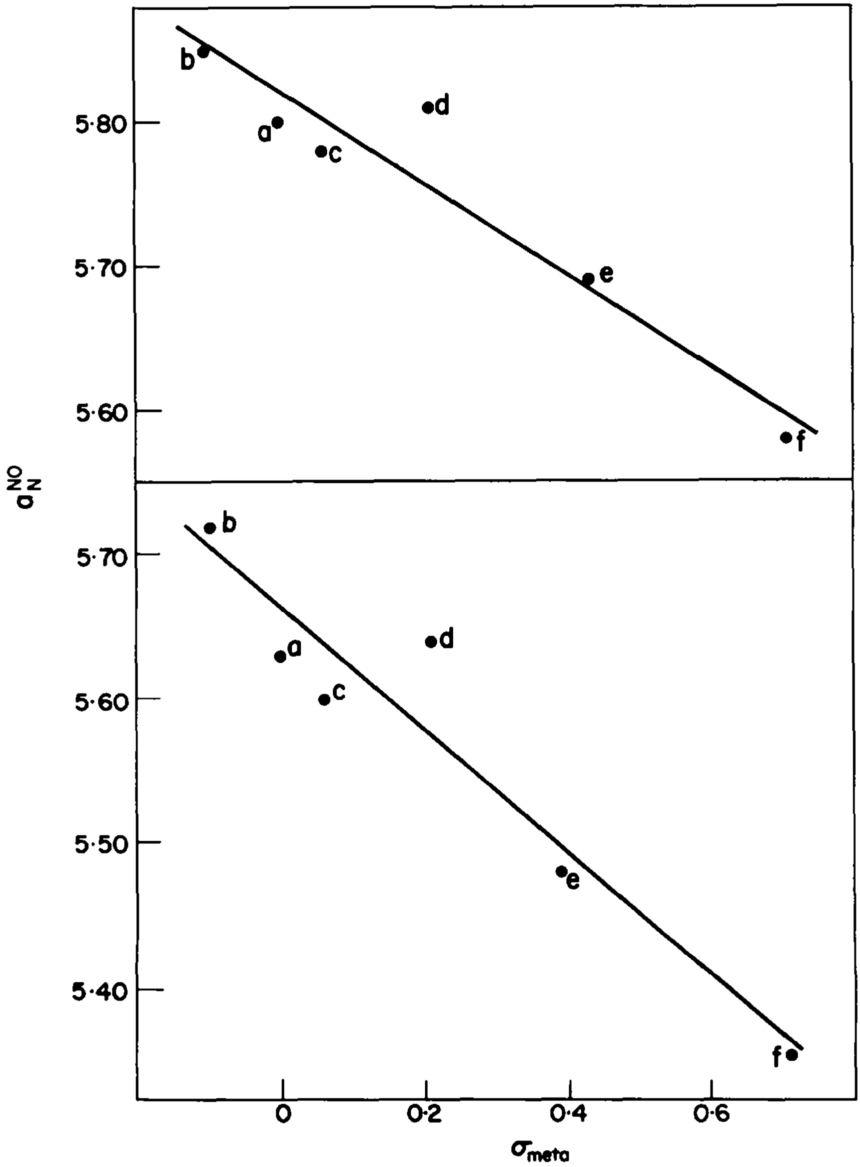


Fig 4. Plot of coupling constant a_N^{NO} of free radicals **4** *vs* σ_{meta} in 1,4-dioxane (above) and benzene (below).

with experimental data in phenylbenzoylaminyloxides.[15,16] The deviation in the case of **4d**, (R = $NHCOCH_3$) cannot however be explained at the moment.

As has already been known for other acylaminyloxides[8] the nitrogen hyperfine coupling constant a_N depends on solvent polarity. In the more polar solvent 1,4-dioxane the coupling constants are higher due to greater contribution of structure **B** relative to **A**, and less sensitive to changes in the nature of the substituent R as shown by the smaller variation in a_N values.

EXPERIMENTAL

The preparation of compounds **2a,b,d-f** has been described elsewhere: **2a**, *loc. cit.*[1] **2b,d-f** *loc. cit.*[2a] **2g**, *loc. cit.*[3] Compound **2c**[17] has been prepared by a procedure analogous to the preparation of **2a-f**.

The radicals were prepared as reported earlier.[4b,8] Deuteration of **4d** was achieved by treating a solution of **4d** in dioxane with *ca* 5% D_2O, drying over Na_2SO_4 and then degassing as usual. All surfaces were washed with D_2O prior to use to prevent re-exchange of deuterated material with the water film on vessel surfaces.

ESR spectra were recorded, using a Varian E9 spectrometer, operating at 9·5 GHz, and simulated by means of the Varian spectrosystem 100.

Potassium nitrosodisulphonate (Frémy's salt) in aqueous alkaline solution and a solution of the perylene cation radical in concentrated sulfuric acid were used to calibrate measurements of g-factors and coupling constants respectively.

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REFERENCES

[1] D. Döpp, *Chem. Ber.* **104**, 1035 (1971)

[2a] D. Döpp, *Ibid.* **104**, 1043 (1971); [b] D. Döpp, *Chem. Comm.* 1284 (1968); [c] D. Döpp, *Tetrahedron Letters* 2757 (1971)

[3] D. Döpp and K.-H.-Sailer, *Ibid.* 2761 (1971)

[4a] G. A. Russell, Ch. L. Myers, P. Bruni, F. A. Neugebauer and R. Blankespoor, *J. Am. Chem. Soc.* **92**, 2762 (1970); [b] A. T. Balaban, I. Pascaru and F. Cuiban, *J. Magn. Resonance* **7**, 241 (1972)

[5] A. R. Forrester, J. M. Hay and R. H. Thomson, *Organic Chemistry of Stable Free Radicals* Academic Press, New York (1968)

[6] A. L. Buchachenko, *Stable Radicals*, Consultants Bureau, New York (1965)

[7] E. G. Rozantsev, *Free Nitroxyl Radicals.* Plenum Press, New York (1970); E. G. Rozentsev and V. D. Sholle, *Synthesis* **190**, 401 (1971); *Usp. khim.* **40**, 417 (1971)

[8] H. G. Aurich and J. Trösken, *Liebigs Ann.* **745**, 159 (1971)

[9] H. G. Aurich and F. Bär, *Tetrahedron Letters* 3879 (1965)

[10] A. Mackor, Th. A. J. Wajer and Th. J. de Boer, *Tetrahedron* **24**, 1623 (1968)

[11] G. Chapelet-Letourneux, H. Lemaire and A. Rassat, *Bull. Soc. Chim. Fr.* 3283 (1965)

[12] H. Lemaire and A. Rassat, *J. Chem. Phys.* **61**, 1580 (1964)

[13] D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958)

[14] H. G. Aurich, J. Trösken and H. Forster, *Angew. Chem.* **83**, 892 (1971)

[15] E. G. Janzen, *Accounts Chem. Res.* **2**, 279 (1969)

[16] A. T. Balaban, N. Negoiţă and R. Baican, *J. Magn. Resonance* **9**, 1 (1973)

[17] D. Döpp and E. Brugger, unpublished