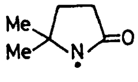
E.S.R. Spectra of Cyclic Oxyamidyls

By Alexander R. Forrester* and Hajime Irikawa
(*Chemistry Department, University of Aberdeen, Old Aberdeen,* AB9 2UE, *Scotland*)

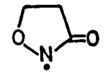
Summary Oxoisoxazolidinyl, dioxoisoxazolidinyl, and dioxo-oxadiazolidinyl radicals have been detected by e.s.r. spectroscopy and $a_{\text{oxygen-17}}$(C=O) has been measured for an acyclic analogue of the first-mentioned radical.

Following the recent first detection[1] by e.s.r. spectroscopy of a cyclic amidyl (**1**) we now communicate our results on a set of analogous oxyamidyls (**2**)—(**5**). The radicals (**2**)—(**5**) were generated by u.v. photolysis of the corresponding *N*-chloro-compounds in carbon tetrachloride–chloroform (1 : 1) at 233—273 K. Alternatively, radicals (**4**) and (**5**) were also detected when the parent heterocycles were photolysed in di-t-butyl peroxide–t-butyl alcohol at 243—273 K.


(1)

a_{N} 11·2

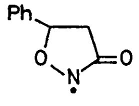
a_{H} unresolved


(2)

a_{N} 9·3

$a_{\mathrm{H}}^{\mathrm{OCH_2}}$ 7·5

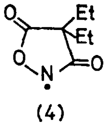
$a_{\mathrm{H}}^{\mathrm{COCH_2}}$ 2·3


(3)

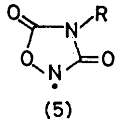
a_{N} 9·2

$a_{\mathrm{H}}^{\mathrm{OCHPh}}$ 7·6

$a_{\mathrm{H}}^{\mathrm{COCH_2}}$ 1·8 and 1·3


(4)

a_{N} 10·8


(5)

a_{N} 11·3

$a_{\mathrm{N}}^{\mathrm{NR}}$ 0·9

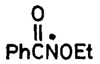
a values are given in G (= 10^{-4} T).


$\mathrm{Me\overset{\overset{O}{\|}}{C}\dot{N}Pr^{i}}$

(6)

a_{N} 14·7

$a_{\mathrm{H}}^{\mathrm{Me}}$ 1·6

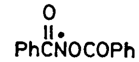

$\mathrm{Ph\overset{\overset{O}{\|}}{C}\dot{N}OEt}$

(7)

a_{N} 9·9

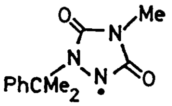
$a_{\mathrm{H}}^{\mathrm{OCH_2}}$ 4·3

$a_{\text{oxygen-17}}^{\mathrm{C=O}}$ 4·0


$\mathrm{Ph\overset{\overset{O}{\|}}{C}\dot{N}OCOPh}$

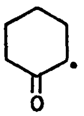
(8)

a_{N} 11·7


(9)

a_{N} 7·7

$a_{4\text{-N}}$ 1·47


(10)

$a_{\text{oxygen-17}}^{\mathrm{C=O}}$ 9·4

a values are given in G (= 10^{-4} T).

As in the case of (**1**), a_{N} values of the radicals (**2**)—(**5**) are smaller than those of their acyclic analogues[1–3] (**6**)—(**8**). For the amidyls (**1**) and (**6**) this was attributed[1] to increased unpaired electron delocalisation from N to C=O in the enforced planar cyclic radical. This may also be the case for the cyclic radicals (**2**)—(**5**) but the situation is complicated by the oxygen adjacent to nitrogen. Significantly the a_{H} ($\mathrm{OCH_2}$) and a_{H} (OCHPh) values for (**2**) and (**3**) respectively are almost twice as large as that of the analogous acyclic radical[3] (**7**). Hence, these protons must be favourably disposed for hyperconjugative interaction with the half-filled orbital on oxygen. The protons adjacent to carbonyl in (**2**) and (**3**) give rise to splittings similar to those of the acyclic amidyl (**6**) but presumably much larger than those of (**1**), which could not be resolved. The non-equivalence of the methylene protons in (**3**) is due to the adjacent CHPh group. The small splitting (0·5 G) due to 4-N in (**5**; R = Ph and Me) was not unexpected in view of the reported value (a_N = 1·47 G) for 4-N in the related urazolyl[4] (**9**). The coupling constants of the radicals (**2**)—(**5**) did not vary appreciably in the temperature range quoted.

The unpaired electron delocalisation pattern in cyclic and acyclic oxyamidyls and amidyls will not be fully elucidated until all ^{17}O coupling constants have been evaluated. Present indications are that delocalisation on to carbonyl oxygen is slight, especially for the acyclic radicals. So far we have measured $a_{\text{oxygen-17}}$ (C=O) to be 4·0 G for (**7**) using an ^{17}O-enriched sample (*ca.* 15%). This corresponds[5] to ρ_0 (carbonyl) of *ca.* 11% assuming that there is a negligible contribution to a_0 from ρ_C. This value is remarkably similar to that found[5] (4·4 G) for a member $[\mathrm{PhC({=}O)N}(\dot{\mathrm{O}})\mathrm{Bu}^t]$ of the isomeric series of acyl nitroxides, but significantly very much smaller than that of the analogous carbon radical[6] (**10**) which has $a_{\text{oxygen-17}}$ (C=O) = 9·4 G.

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