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UNPAIRED ELECTRON DISTRIBUTION IN ACYLAMINYLS

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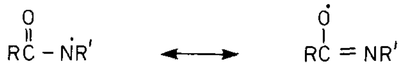
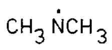
Unpaired electron distribution in acylaminyls and acylalkoxyaminyls has been investigated by e.s.r. measurements of ^{17}O labelled radicals. Delocalisation of free spin onto carbonyl oxygen has been established for the former and onto carbonyl and etherial oxygens for the latter.

Existing evidence indicates that in their ground state amidyls (1a↔1b) have a π-electronic structure.[1] However, in some cases at least the extent of delocalisation is reduced by "twisting" of the N-C(O) bond rendering the RC(O) and $\overset{\prime}{R}N$ groups in different planes. The extent of twisting depends mainly on the bulk of R'.[1] In no case has it been possible to quantify the extent of delocalisation onto the carbonyl oxygen, irrespective of the degree of twist. In this respect both the a_N and $a_H^{NCH_3}$ values appear to be poor indicators of ρ_N^{π}. Thus, the radicals (2) and (3) have remarkably similar a_N and $a_H^{NCH_3}$ values despite obvious differences in their electronic structures.[1,2]



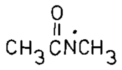
$$R\overset{\overset{O}{\|}}{C}-\dot{N}R' \longleftrightarrow R\overset{\overset{\dot{O}}{|}}{C}=NR'$$

(1a) (1b)



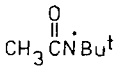
$CH_3\dot{N}CH_3$

(2)



$CH_3\overset{\overset{O}{\|}}{C}\dot{N}CH_3$

(3)



$CH_3\overset{\overset{O}{\|}}{C}\dot{N}Bu^t$

(4)

$a_N = 14.8G$
$a_H = 27.4G$

$a_N = 14.96G$
$a_H = 29.5G$

We have now attempted to quantify the relative importance of structures (1a) and (1b) by labelling the carbonyl oxygen with ^{17}O and measuring the resulting $a_{^{17}O}$ value. The high spin (5/2) of ^{17}O limited us to examine amidyls which give spectra sufficiently intense to allow detection of ^{17}O satellite lines. In this report we describe results for the amidyl (4) in which the degree of twist about the N-C(O) bond is considered[1] to be relatively high due to steric repulsion between O and Bu^t (relatively large g- and $a_{^{13}C}^{\gamma-C}$ values measured)

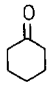
From the e.s.r. spectrum measured at -90°C $a_{^{17}O}$ = 5.3G was evaluated. Above -60°C signals became too weak to measure accurately the ^{17}O satellite lines but there was little change in $a_{^{17}O}$ (5.3 → 5.15G) over this narrow range. The value ρ^π_C of the carbonyl carbon is almost certainly small and is likely to be less than the value 0.04 calculated for amidyl (3) (based on $a_H^{COCH_3}$ = 1.3G and Q_β = 29.3G) since (4) is more "twisted" than (3). Hence, using equation (i)[3,4]

$$a_O = (S^O + Q^O_{OC})\rho^\pi_O + Q^O_{CO}\,\rho^\pi_C \qquad \text{(i)}$$

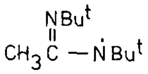
and $(S^O + Q^O_{OC})$ = -44.5G, Q^O_{CO} = -14.3G, the spin density on oxygen is 0.13.

Interestingly, using Q^C_{CO} = -25.1G and Q^C_{NC} = -20.5G the spin polarisation contributions to $a^{CO}_{^{13}C}$ from adjacent N and O are -9.4 and -3.0G, respectively. The sum of these -12.4G is slightly larger than the value 11.0G measured for N-alkyl formamidyls[5] [e.g.$HC(O)\dot{N}CH_2Bu^t$] which is reasonable because "twisting" in (4) should lead to higher values of $a^{CO}_{^{13}C}$.

Values of ρ^π_O (0.13), ρ^π_C (0.04) and hence ρ^π_N ca. 0.9 agree remarkably well with those derived by STO 3G calculation[6] for a π-allyl state of $HCO\dot{N}H$ (ρ_O = 0.152, ρ^{CO}_C = 0.009, ρ_N = 0.839). Comparison with the cyclohexanonyl radical[3,7] which has $O_{^{17}O}$ = 9.3G and ρ^π_O = 0.21 indicates that delocalisation onto oxygen in the amidyl (4) is significantly less than it is in (5) which is thought to have about 30% allylic character.



(5)



$CH_3C(=NBu^t)-\dot{N}Bu^t$

(6)

A further useful comparison of (4) can be made with the amidinyl[8] (6) which has a_N = 8.6G (2N) and $a_H^{CH_3}$ = 2.4G [cf., (4) which has $a_H^{CH_3}$ = 2.5G]. Spin density on the imino-carbon of (6) like that on the carbonyl-carbon of (4) will be small and negative making ρ^π_N on each of the nitrogens ca. 0.5. Hence, on this basis ρ^π_N for the structurally similar amidyl (4) may be estimated from its a_N value (15.8G) as 0.92 which is in good agreement with the previously derived value.

Alkoxyamidyls

Comparison of the a_N and a_H values of the aminyls[2,9] (2) and (7) indicates that the introduction of an oxygen adjacent to nitrogen reduces the π spin density on nitrogen as in (7a↔7b). The extent to which this occurs is more difficult to ascertain. Assuming that

$$CH_3\dot{N}CH_3 \qquad CH_3\dot{N}OCH_3 \longleftrightarrow CH_3\overset{-+\cdot}{NO}CH_3$$

(2) (7a) (7b)

$$a_N = 14.8G \qquad a_H^{CH_3} = 27.4G$$

$$a_N = 14.3G \qquad a_H^{CH_3} = 21.85G \qquad a_H^{OCH_3} = 2.62G$$

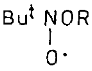
ρ_N^π = 1 for the aminyl (2) and equation (ii) (Q_{NCH_3} = 27.4) then for the alkoxyaminyl (7)

$$a_H^{NCH_3} = Q_{NCH_3}\,\rho_N^\pi \qquad \text{(ii)}$$

ρ_N^π = ca. 0.8 and hence ρ_O^π = ca. 0.2. An alternative approach with such radicals is to measure $a_{^{17}O}$ from which ρ_O^π may be calculated. To date $a_{^{17}O}$ values have been measured for only a short series of t-butylalkoxyaminyls[10] (8). For these (8; R=t-alkyl) $a_{^{17}O}$ = 11.4G

$Bu^t\dot{N}OR$

(8)



$$Bu^t\underset{O\cdot}{\underset{|}{N}}OR$$

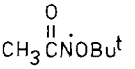
(9)

and ρ_O^π has been calculated as 0.28 using the simplified equation (iii) and Q_O = 41G.

$$a_{^{17}O} = Q_O\,\rho_O^\pi \qquad \text{(iii)}$$

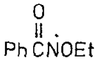
However, if Aurich's[11] Q_O values of 35.3G is used ρ_O^π = 0.32 and if Silver's[12] full equation and parameters are used then ρ_O^π becomes 0.43. It is also the case that a surprisingly large variation in $a_{^{17}O}$ values have been measured for the alkoxynitroxides[13] (9; R=Bu^t and Pr^i) 1.03 and 4.6G, respectively. This difference has been attributed to differences in conformation arising from the bulk of R in (9) which affects overlap of the half-filled orbital on nitrogen with a lone pair orbital on oxygen. Hence, we conclude that (a) ρ_O^π may well vary substantially in alkoxyamidyls depending on the size of the alkyl substituents; (b) the most accurate means of conversion of $a_{^{17}O}$ values into ρ_O^π densities has still to be established.

It was with this knowledge that we labelled (^{17}O) the precursors of the alkoxyamidyls (10) and (11) with a view to comparing ρ_N^π and ρ_O^π spin densities in amidyls, alkoxyaminyls and alkoxyamidyls. The observed values of 4.25G and 4.0G for the amidyls (10) and (11), correspond to ρ_O^π carbonyl of 0.1 and 0.095, respectively. Both values are slightly less than that of the corresponding amidyl (4) and the absence of a splitting due to the acetyl protons again indicates negligible spin density on carbonyl carbon.



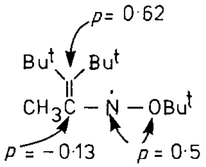
$CH_3\overset{O}{\overset{\|}{C}}\dot{N}OBu^t$

(10)



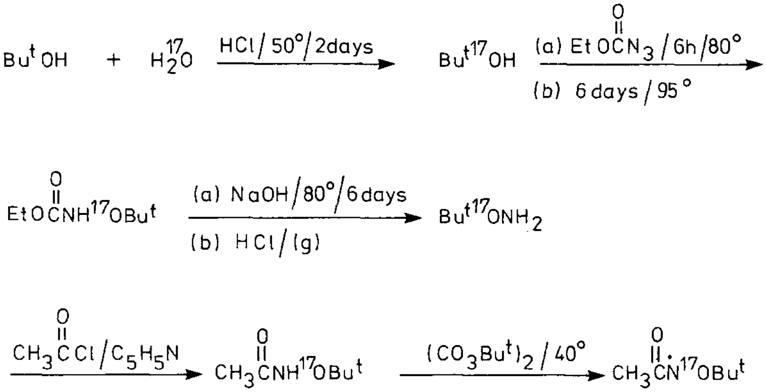
$Ph\overset{O}{\overset{\|}{C}}\dot{N}OEt$

(11)



(12)

Labelling of the etherial oxygen was achieved as shown in the Scheme.[15] The incorporation of the label was low ($\sim$5%) in this case and full analysis required a lengthy accumulation experiment. The measured $a^{OR}_{^{17}O}$ value of 3.95G corresponds to ρ^{π}_{O} = 0.095. Comparison with the related t-butoxyaminyls[14] (12), and (8) (ρ_O = 0.3, ρ_N = 0.7) shows significant differences in unpaired electron distribution in these three radicals. However, examination of molecular models indicates that non-bonding interactions between alkyl groups is much greater in (8) than in (12) and almost negligible in (10). Hence, conformational preferences about the N-O bonds in (8), (10), and (12) are likely to be very different and the observed spin densities on N and O reflect these.



Scheme (10)

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