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SOME MAGNETIC RESONANCE PARAMETERS FOR ACYL NITROXIDES : A COMMENT ON NITROXIDE CONFIGURATION.

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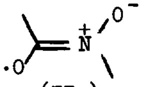
In recent studies of several ^{17}O-labelled nitroxides,[1,2] the hyperfine splittings a_N and a_O have been regarded as directly proportional to ρ_N and ρ_O respectively (the π-electron spin densities on N and O). This neglects any contributions to the splittings from spin densities on adjacent atoms; such effects were considered negligibly small.[1]

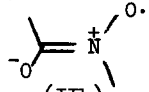
Extrapolation of the proportionality relationships from dialkyl nitroxides to the acyl nitroxide (I; R = CH_3)[a_N = 7.75G; a_O(Nitroxide) = 20.3G], led to the conclusion that ca. 19% of the π-electron spin density must reside in the carbonyl group. Since any splittings from the acetyl protons are too small to resolve,[3] and splitting from the formyl proton in (I; R = H) is also very small (ca. 1.5G),[4] much of this spin density must be on carbonyl oxygen. INDO calculations on HCONHO·,[5] and analogy with α-iminoalkyl nitroxides [RC(= NR')N(Bu^t)O·],[1] both suggest that any spin density on carbon may actually be negative; **therefore ρ_O carbonyl might be eve** greater than 19% (structure IIa), This contrasts with the view that the dominant effect of carbonyl in (I) is to delocalise the nitrogen lone pair (IIb).[6]

RCON(Bu^t)O·

(I)



(IIa)



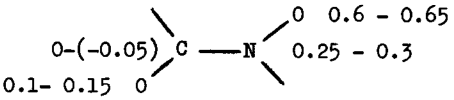
(IIb)

To investigate this point we have generated carbonyl ^{17}O-labelled benzoyl t-butyl nitroxide (I; R = Ph);[7] the a_O-value for this radical is 4.4G (PhH, 293K). This corresponds to ρ_O(Carbonyl) of ca.12%[8][any contribution to a_O from ρ_C is probably negligible[9]]. This agrees with the earlier data only if ρ_C is positive. The following considerations suggest that this may not be the case, and that the spin on the NO group in (I) may have been underestimated.

(i) Direct proportionality of the nitroxide a_O-values gives ρ_O = 0.575 for (I; R = CH_3).[1] Earlier workers[9] had concluded that there is a small <u>positive</u> contribution to a_O from ρ_N. Since ρ_N is significantly smaller in acyl than in alkyl nitroxides, to accommodate the observed a_O it would then be necessary for ρ_O to be larger than that deduced by simple proportionality. Furthermore, the reported sign of the contribution from ρ_N is surprising and may reflect out-of-plane deformation at nitrogen in the dialkyl nitroxides studied.[9] Assumption that the (strongly π-bonded) acyl nitroxides are more rigidly planar, so that ρ_N may make a small negative contribution to a_O, would necessitate an even larger ρ_O. A value of at least 0.6-0.65 seems plausible.

(ii) The value of ρ_N in I (0.234) was obtained from the ratio a_N (I; R = Me)/a_N (dialkyl nitroxide), which is ca. 0.52.[1] Now the π-electron spin density on an sp^2-hybridised atom is normally reflected also in the splittings of substituent atoms; the ratio $a_{\alpha\text{-}C}$[PhCO($^{13}CMe_3$)O·]/$a_{\alpha\text{-}C}$[Bu^{t}N($^{13}CMe_3$)O·] is 0.66,[10] and the ratio a_H[PhCONHO·]/a_H[Bu^{t}NHO·] is ca. 0.9.[11] The discrepancy between ρ_N ratios based on nitrogen splittings, and those based on α-atom splittings may again be associated with non-planarity at N in the alkyl nitroxides; the a_N- ratio would then give a minimum value for the ρ_N-ratio, whilst splittings from the α-substituents should set upper limits. On this basis, a ρ_N for (I) of 0.25 - 0.3 seems reasonable.

Our conclusions regarding "reasonable" values for π-electron spin densities in (I) are summarised in (III). Significantly, the spin on carbonyl oxygen is appreciably less than that (ca. 0.2) deduced for the less electronegative imine nitrogen of the α-iminoalkyl nitroxides.[1]



(III)

Breakdown of the proportionality between oxygen and nitrogen splittings and spin densities has already been used to infer non-planarity at nitrogen in strained cyclic nitroxides.[2] The present work suggests that strain-free dialkyl nitroxides used as reference points for the proportionality relationships, may themselves be appreciably non-planar. This is not inconsistent either with calculations on nitroxide geometry or with crystallographic studies.[12]

In the course of investigations of acyl nitroxides we have for the first time recorded n.m.r. spectra of these radicals. For several acyl nitroxides it was observed that the t-butyl protons experience downfield shifts; the magnitudes of these correspond to $a_{\gamma-H}$= +0.054 and +0.069 G for (I) R=Ph and $4O_2N-C_6H_4$ respectively ($CDCl_3$,308K). This contrasts with a negative $a_{\gamma-H}$ for di-t-butyl nitroxide.[13] Although γ-hydrogen splittings in nitroxides are markedly dependent on nitrogen geometry,[14] it is not yet clear whether the sign difference noted here is to be construed as further evidence for out-of-plane bending in the dialkyl nitroxides.

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1. H.G.Aurich, K.Hahn, K.Stork, and W.Weiss, Tetrahedron, 1977, 33, 969.
2. H.G.Aurich and H.Czepluch, Tetrahedron Letters, 1978, 1187.
3. A.Mackor, Th.A.J.W.Wajer, and Th.J.de Boer, Tetrahedron, 1968, 24, 1623.
4. J.W.Hartgerink, J.B.F.N.Engberts, and Th.J.de Boer, Tetrahedron Letters, 1971, 2709.
5. N.P.Y.Siew, Ph.D. Thesis, London, 1976.
6. D.F.Minor, W.A.Waters, and J.V.Ramsbottom, J.Chem.Soc.B, 1967, 180; E.G.Janzen, Accounts Chem.Res., 1969, 2, 279; T.C.Jenkins, M.J.Perkins, and N.P.Y.Siew, Chem.Comm. 1975, 880.
7. Prepared from PhCOCl + $H_2{}^{17}O$ in dry THF, reaction of the resulting acid with $SOCl_2$ and subsequent ^{17}O-benzoylation of t-butylhydroxylamine. Oxidation of the crude product gave spectra showing well resolved ^{17}O-satellites. The comparison of the benzoyl nitroxide with the acetyl nitroxide seems justified on the basis of their similar a_N, g, and λ_{max}[649 and 646 nm (cyclohexane) respectively; T.C.Jenkins Ph.D. Thesis, London 1977] values.
8. K.Scheffer and H.B.Stegmann, "Electronenspinresonanz", Springer-Verlag, Berlin, 1970, 194.
9. H.Cohen and B.M.Hoffman, J.Phys.Chem., 1974, 78, 1313.
10. G.F.Hatch and R.W.Kreilick, Chem.Phys.Letters, 1971, 10, 490, and this work. ^{13}C-satellites are observed in the spectrum of (I; R=Ph); those due to carbonyl carbon show a_C 5.0 G(by isotopic enrichment), with a_C (t-Bu-α) = 4.16 G and a_C (t-Bu-β) 3.2G. The value of a_C(CO) is considered relatively uninformative in view of the contribution from the greater spin density on two adjacent atoms.
11. 0.95 (Bu^tOOBu^t) this work; 0.75 (H_2O), Th.A.J.W.Wajer, A.Mackor and Th.J.de Boer, Tetrahedron 1969, 25, 175, and C.J.W.Gutch and W.A.Waters, J.Chem.Soc., 1965, 751.
12. J.Lajzerowicz-Bonneteau, in "Spin Labelling" L.J.Berliner Ed. A.P., New York, 1976.
13. K.H.Hausser, H.Brunner, and J.C.Jochims, Mol.Phys., 1966, 10, 253; R.W.Kreilick, J.Chem. Phys., 1966, 45, 1922.
14. A.Rassat and J.Ronzaud, J.Am.Chem.Soc., 1971, 93, 5041.