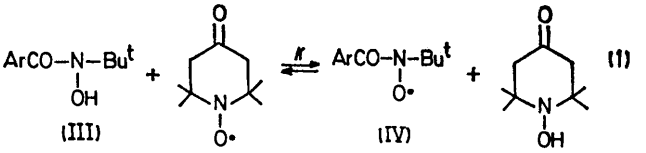
Structure and Stability of Acylnitroxyls

By TERENCE C. JENKINS, M. JOHN PERKINS,* and NANCY P. Y. SIEW
(*Department of Chemistry, Chelsea College, Manresa Road, London* SW3 6LX)

Summary The strengths of the O–H bonds in four *p*-substituted *N*-t-butylbenzohydroxamic acids [*p*-X-C_6H_4-CON(Bu^t)OH] have been estimated experimentally; together with the effect of substituent upon the a_N value of the resulting nitroxyls, the values obtained are taken to indicate that these nitroxyls are destabilised with respect to dialkyl nitroxides, and this conclusion finds some support in the results of INDO calculations on related structures.

ACYLNITROXYLS, *e.g.* (I), have lower a_N values than corresponding alkyl nitroxides, and this has been attributed to the competing amide resonance (Ia) which concentrates spin density on the nitroxyl oxygen.[1] A good correlation of a_N with σ^+ for the aroylphenylnitroxyls [ArCON(O·)Ph] is consistent with this,[1] electron-pair donating groups countering the amide resonance, *e.g.* (II).

However, an alternative explanation for the low a_N values has recently been implied in the use of acylnitroxyls to exemplify the concept of 'merostabilization', in which the importance of (Ib) is emphasised.[2]

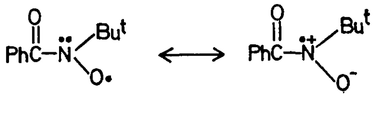

(III) (IV) (1)

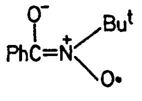
In the course of our studies of acylnitroxyls[3] we also have found an excellent correlation (r = 0·999) between a_N and σ^+_p for a series of 10 aroyl-t-butylnitroxyls [ArCON(O·)Bu^t], with substituents ranging from p-NMe_2 to p-NO_2, [a_N (PhH, in G) = 7·954 − 0·515 σ^+_p]. In addition, the stability of these radicals has enabled us to estimate the OH bond energy in the corresponding hydroxamic acids, by studying the equilibrium (1).

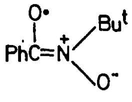
From a series of experiments in benzene at 15 °C, the ΔG values (in kcal mol^{-1}) are 8·41 ± 0·45 for Ar = p-$NO_2 \cdot C_6H_4$, 6·23 ± 0·07 for Ar = Ph, 5·74 ± 0·38 for Ar = p-$Ph \cdot C_6H_4$, and 4·13 ± 0·03 for Ar = p-$MeO \cdot C_6H_4$. Equating ΔG with the difference between the OH bond strengths of (III) and (IV),[4] we see (i) that these acylnitroxyls appear to be *destabilized* with respect to dialkyl nitroxides and simple alkyl nitroxides generally, and (ii) that the effect of substituents in the aroyl group on the radical stability is exactly as expected based on the importance of structures (Ia) and (II).

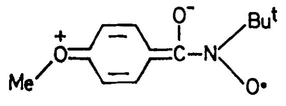
It should be noted that intramolecular hydrogen bonding in the hydroxamic acids (III), evident from the solvent-dependence of their i.r. spectra, may contribute to the observed ΔG for the reactions, but it is unlikely that this alone could account for the magnitude of the equilibrium constants, or their variation with substituent. Furthermore, radical association with the benzene solvent[5] is unlikely to be a significant factor since the equilibrium constant for the formation of the unsubstituted nitroxyl (I) was only slightly changed when the equilibration was repeated in CCl_4 (ΔG = 5·40 ± 0·08 kcal mol^{-1}) and in n-hexane (ΔG = 5·06 ± 0·17 kcal mol^{-1}). Neglecting these effects, the OH bond strengths in the hydroxamic acids can be deduced to lie in the range 76—80 kcal mol^{-1}, which compares with 72—74 kcal mol^{-1} estimated[4] for unhindered hydroxylamines.

Since the stabilizing effects of alkyl and acyl substituents on alkyl radicals are roughly comparable,[6] the effect of acyl seems to be out of line in the case of nitroxides. Some support for this conclusion comes from calculations using the INDO method on the most stable geometries of $H_2NO\cdot$ and HCONHO·, from which we have found that the p-orbital spin density on nitroxide oxygen is greater for the formylnitroxyl (0·749) than for $H_2NO\cdot$ itself (0·699). For these calculations, the bond lengths and angles were adjusted to give a minimum energy for planar $H_2NO\cdot$. Although in the best geometry obtained by the INDO method the NO bond is bent 38° out of the plane defined by the HNH atoms, the calculated energy of this structure is only *ca.* 2 kcal lower than that of the best planar structure.[7] For the formylnitroxyl, 120° angles were assumed, and bond lengths adjusted to give the minimum energy. In this case the planar structure lay at the bottom of a shallow potential well; the E-geometry was calculated to be very slightly more stable than the Z-geometry.


(I)


(Ia)


(Ib)


(II)

(*Received*, 15*th September* 1975; *Com.* 1047.)

---

[1] E. G. Janzen, *Accounts Chem. Res.*, 1969, **2**, 279; see also A. T. Balaban, H. G. Aurich, J. Trosken, F. Brugger, D. Dopp, and K. H. Sailer, *Tetrahedron*, 1974, **30**, 739.

[2] R. W. Baldock, P. Hudson, A. R. Katritzky, and F. Soti, *J.C.S. Perkin I*, 1974, 1422.

[3] M. J. Perkins and P. Ward, *J.C.S. Chem. Comm.*, 1973, 883.

[4] L. R. Mahoney, G. D. Mendenhall, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 8610.

[5] A. L. Buchachenko, O. P. Sukhanova, L. A. Kalashnikova, and M. B. Nieman, *Kinetika i Kataliz*, 1965, **6**, 601.

[6] H. E. O'Neal and S. W. Benson, in 'Free Radicals', ed. J. K. Kochi, Wiley, New York 1973, Vol. II p. 275.

[7] The most recent MO calculations on $H_2NO\cdot$ are those of Y. Ellinger, R. Subra, A. Rassat, J. Donady, and G. Berthier, *J. Amer. Chem. Soc.*, 1975, **97**, 476; an independent INDO study of this radical gives geometries similar, but not identical, to those found in the present work: I. A. Abronin, N. A. Sysoeva, M. Zhidomivov, A. L. Buchachenko, and N. D. Chuvylkin, *J. Struct. Chem. U.S.S.R.*, 1972, 907.