

## X-ray Crystallographic Studies of Two Acyl t-Butyl Nitroxides

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**Summary:** The X-ray structure of the stable aroyl nitroxide (1a) is consistent with significant electron delocalisation through the  $-CO.N(O^{\cdot})$ -unit; delocalisation is less important in the aminocarbonyl nitroxide (2a).

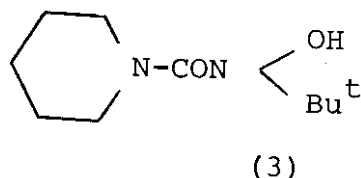
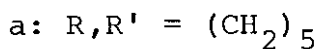
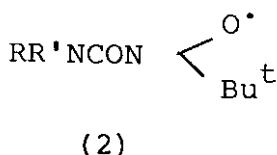
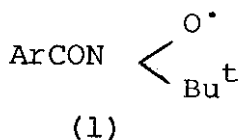
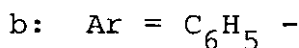
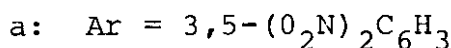
The isolation of several acyl t-butyl nitroxides has recently been reported [1]. Of these, the aroyl t-butyl nitroxides (1) are green with  $\lambda_{\max}$  ( $C_6H_{12}$ ) ca. 645 nm and their e.s.r. spectra show  $a_N$  values of ca. 8G; in contrast, we have found that di-

alkylaminocarbonyl t-butyl nitroxides, (2), are red [1b] with  $\lambda_{\max}$  ( $C_6H_{12}$ ) ca. 550 nm, and  $a_N$  ca. 11.7 G [2]. By these criteria, the aminocarbonyl nitroxides are intermediate between di-t-alkyl nitroxides ( $\lambda_{\max}$  ca. 430 nm; ca. 15.5 G) and (1). Also consistent with this conclusion are (i) the OH bond strength in (3), which we have found to be 74.4 kcal mol<sup>-1</sup>\*\*, and (ii) the results of the first crystallographic studies on acyl nitroxides presented here.

Single crystals of the 3,5-dinitrobenzoyl nitroxide (1a; Ar = 3,5-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-) and the piperidino-carbonyl nitroxide (2a; R, R' = (CH<sub>2</sub>)<sub>5</sub>), have been examined. Lattice parameters and intensity data were measured ( $\theta < 25^\circ$  in each case) on a Hilger/Watt fourcircle diffractometer with monochromated Mo-K $\alpha$  radiation. Lorentz and polarisation but not absorption correction were applied.

*Crystal data*<sup>†</sup>

(1a) C<sub>11</sub>H<sub>12</sub>N<sub>3</sub>O<sub>6</sub>,  $M = 282.2$ , triclinic  $a = 6.884(2)$ ,  $b = 11.617(3)$ ,



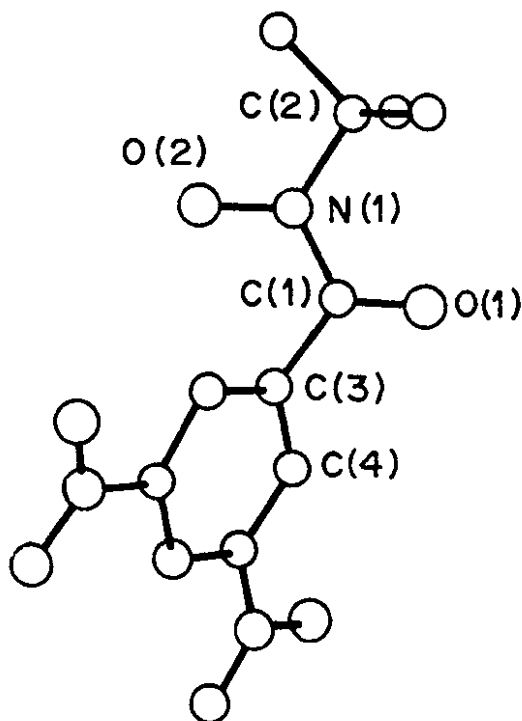
$c = 8.645(2)\text{\AA}$  :  $\alpha = 97.79(1)$ ,  $\beta = 110.64(1)$ ,  $\alpha = 90.79(1)^\circ$ ;  $U = 640.3\text{\AA}$ ;  
 [5]  $D_c = 1.46$   $D_m = 1.42$   $g\text{ cm}^{-3}$ ;  $z = 2$ ,  $F(000) = 249$ ; space group  $P1$  from  $\bar{E}$  statistics;  $\lambda = 0.71069\text{\AA}$ ;  $\mu = 2.6\text{ cm}^{-1}$ ; 1046 reflections were considered observed ( $I > 3$ ), and the final  $R$  value was 5.9%. (2a)  $C_{10}H_{19}N_2O_2$ ,  $M = 199.3$ , monoclinic  
 $a = 5.867(2)$ ,  $b = 9.471(2)$ ,  $c = 20.446(4)\text{\AA}$ ,  $\beta = 90.61(1)^\circ$ ;  $U = 1136.0\text{\AA}$ ; [5]  $D_c = 1.16$   $D_m = 1.11$   $g.\text{ cm}^{-3}$ ;  $z = 4$ ;  $F(000) = 436$ . Space group  $P2_1/n$  from systematic absences;  $\lambda = 0.71069\text{\AA}$ ;  $\mu = 0.88\text{ cm}^{-1}$ ; 1192 reflections were considered observed ( $I > 3$ ), and the final  $R$  value was 5.7%.

The structures are shown in Figures 1 and 2, together with selected interatomic distances, and bond and torsion angles. In both radicals the N-O bond lengths lie within the range found for other nitroxides [6], and the oxygen atoms are "anti" related [7]. The -CON(O<sup>•</sup>)-unit is however markedly twisted in the aminocarbonyl nitroxide crystal (2a), and the C(O)-N(O) bond length in this radical is appreciably greater than that in (1a). These results are consistent with marked delocalisation in the -CON(O<sup>•</sup>)-system of (1a), reduced somewhat in (2a) by competing interaction of the carbonyl group with the piperidine nitrogen. This supports the conclusion that the nitroxide moiety in (2a) is intermediate in character between that in (1a) and that in a dialkyl nitroxide<sup>++</sup>

It is of interest that the delocalisation in (1a) does not result in a longer carbonyl bond [ $\lambda_{\max}(\text{C}=\text{O})$  for (1b) is  $1687\text{ cm}^{-1}$  ( $\text{CCl}_4$ )]. Pre-

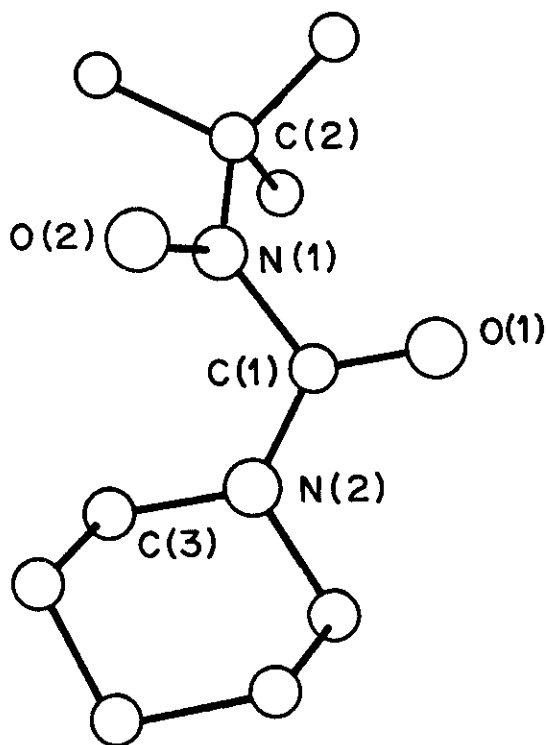
sumably this is a consequence of the dipolar character of the adjacent N-O bond.

\*\* This compares with D(OH) for PhCON (Bu)<sup>t</sup> OH of  $77.2\text{ kcal mol}^{-1}$  [3] and D(OH) for N-hydroxy-4-Oxo-2,2,6,6-tetramethylpiperidine of  $71.8\text{ kcal mol}^{-1}$ , [4].



C(1)-N(1)	1.384(7) $\text{\AA}$	<C(1)CN	117.5(5)°
C(1)-C(3)	1.498(8) $\text{\AA}$	<NCO	121.8(5)°
C(1)-O(1)	1.207(6) $\text{\AA}$	<CCO	120.7(5)°
N(1)-O(2)	1.275(6) $\text{\AA}$	<C(1)NO	118.0(5)°
N(1)-C(2)	1.526(7) $\text{\AA}$	<C(2)NO	119.3(5)°
		<CNC	122.6(5)°
$\phi$ O-N-C-O	166.3°		
$\phi$ O-C-C-C	38.6°		

Fig.1: Molecular structure (1a) with selected bond lengths and angles.



C(1)-N(1)	1.452(4) Å	<NCN	114.4(3)°
C(1)-N(2)	1.328(4) Å	<N(1)CO	119.4(3)°
C(1)-O(1)	1.205(4) Å	<N(2)CO	126.2(4)
N(1)-O(2)	1.276(4) Å	<C(1)NO	116.1(3)°
N(1)-C(2)	1.490(4) Å	<C(2)NO	119.2(3)°
		<C(1)NC(2)	123.0(3)°
$\phi$ O-N-C-O	116.9°		
$\phi$ O-C-N-C(3)	12.2°		

Fig.2: Molecular structure (2a) with selected bond lengths and angles.

<sup>+</sup>The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge. CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

<sup>++</sup>It has been reported [8] that substituted aminocarbonyl sulphonyl-

methyl nitroxides [RR'NCON(O')CH<sub>2</sub>SO<sub>2</sub>Ar] have lower  $a_N$  values (ca. 9 G) than the species (2). Possibly the electron-withdrawing sulphonyl group diminishes the contribution from the dipolar nitroxide structure  $>N^+-O^-$ ; alternatively, since other aminocarbonyl nitroxides have been reported with  $a_N$  values around 10 G [9], the difference might be a consequence of the bulk of the t-butyl group, which in (2) [but not in (1)] causes the CO-NO grouping to twist away from coplanarity.

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