X-Ray Structures of a Free Radical Nitronylnitroxide and Diamagnetic Succinimide

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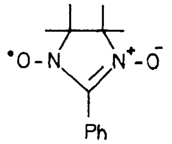
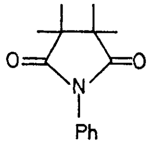
Summary The *X*-ray crystal structures of a stable free radical and its diamagnetic analogue are compared.

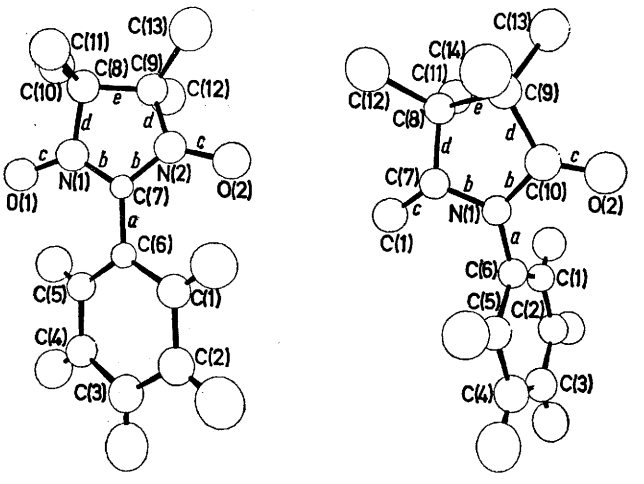
Since the reported synthesis[1] of the stable radical α-phenylnitronylnitroxide, considerable effort has been expended both in the physical characterization and the biological applications of this type of compound. For example, the nitronylnitroxide ring is similar to imidazole and has been used as a spin label in polypeptides containing histidine.[2] E.s.r. studies on solutions of nitronylnitroxides themselves have been carried out,[3] but single-crystal studies have met with little success. In particular, attempts to grow dilute single crystals of compound (I) in the analogous diamagnetic host, compound (II),[4] produced polycrystalline, highly disordered solids unsuitable for e.s.r. This, and the fact that few free radical *X*-ray structures of such biological importance are known, prompted us to investigate the crystal and molecular structures of (I) and (II).


(I)


(II)

Crystal data: (I) $C_{13}H_{17}N_2O_2$, blue-black, $M = 233{\cdot}32$, $a = 21{\cdot}14(1)$, $b = 10{\cdot}14(1)$, $c = 12{\cdot}22(1)$ Å, $\beta = 108{\cdot}09(6)°$, $U = 2493(1)$ Å^3, space group $P2_1/c$, $Z = 8$, $D_c = 1{\cdot}24$ g cm^{-3}, Mo-K_α (Zr filter). Of the 2105 independent reflections measured by the $\theta/2\theta$ scan technique on an Enraf-Nonius PAD-3 diffractometer, 937 were significantly above background $[I > 2\sigma(I)]$.

Crystal data: (II) $C_{14}H_{17}NO_2$, colourless, $M = 231{\cdot}32$, $a = 22{\cdot}497(2)$, $b = 6{\cdot}303(1)$, $c = 20{\cdot}409(3)$ Å, $\beta = 117{\cdot}662(8)°$, $U = 2563{\cdot}3(1)$ Å^3, space group $P2_1/c$, $Z = 8$, $D_c = 1{\cdot}20$ g cm^{-3}, Cu-K_α (Ni filter). 1974 of the 2992 independent reflections measured by the stationary crystal–stationary counter method on a G.E. XRD-490 diffractometer were significantly above background $[I > 2\sigma(I)]$.



a	1·42(1)	∠*bb*	108·9(12)
b	1·32(1)	∠*bc*	128·6(8)
c	1·27(1)	∠*bd*	111·5(8)
d	1·48(1)	∠*cd*	119·5(8)
e	1·51(2)	∠*de*	110·6(9)

(I)

a	1·419(4)	∠*bb*	112·6(4)
b	1·397(4)	∠*bc*	124·6(3)
c	1·207(4)	∠*bd*	107·5(3)
d	1·528(5)	∠*cd*	127·9(3)
e	1·554(6)	∠*de*	102·9(3)

(II)

Figure. Perspective drawings, average bond lengths and bond angles for (I) and (II).

Both structures were solved using the direct phasing program MULTAN.[5] Full-matrix least-squares refinement, including isotropic temperature factors for all atoms and rigid body constraints on the phenyl rings and methyl groups (including hydrogen atoms) has reduced the *R* values to 0·064 for (I) and 0·055 for (II). In (II) the two molecules in the crystallographically independent unit are almost exact enantiomers. The approximate molecular symmetry of (I) and (II) is C_2, but the molecules in the two crystals are oriented quite differently, a fact which is reflected in the non-equivalent unit-cell dimensions. Thus, while (I) and (II) have somewhat similar *molecular* structures, the *crystal* structures are entirely different, and the succinimide is not a proper diamagnetic host for the free radical nitronyl-nitroxide.

Some bond lengths and angles averaged over the two independent molecules in each crystal are shown in the Figure. In neither the succinimide nor the nitronyl-nitroxide are the five-membered rings planar. The tetramethylethylene group is twisted out of the plane of the five-atom π-system [O(1)–N(1)–C(7)–N(2)–O(2) and O(1)–C(7)–N(1)–C(10)–O(2)] about the molecular axis by *ca.* 19°, thus staggering the methyl groups relative to one another in order to relieve steric repulsion.

The most striking difference between the two molecules is in the dihedral angle between the phenyl ring and the plane of the five-membered π-system [29° in (I), 71° in (II)]. It is not clear how this difference is apportioned between crystal-packing effects and molecular-electronic effects, since few observations have been made in equivalent systems; a dihedral angle of 60° has been measured in *N*-(4-bromo-phenyl)succinimide.[6]

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