Supplementary Material (ESI) for Chemical Communications

Supporting Material

for

6-Uradinyl-4,4,5,5-tetramethyl-4,5-dihydro-*1H*-imidazole-1-oxyl – hydrogen-bonding and molecular recognition in stable organic radicals.

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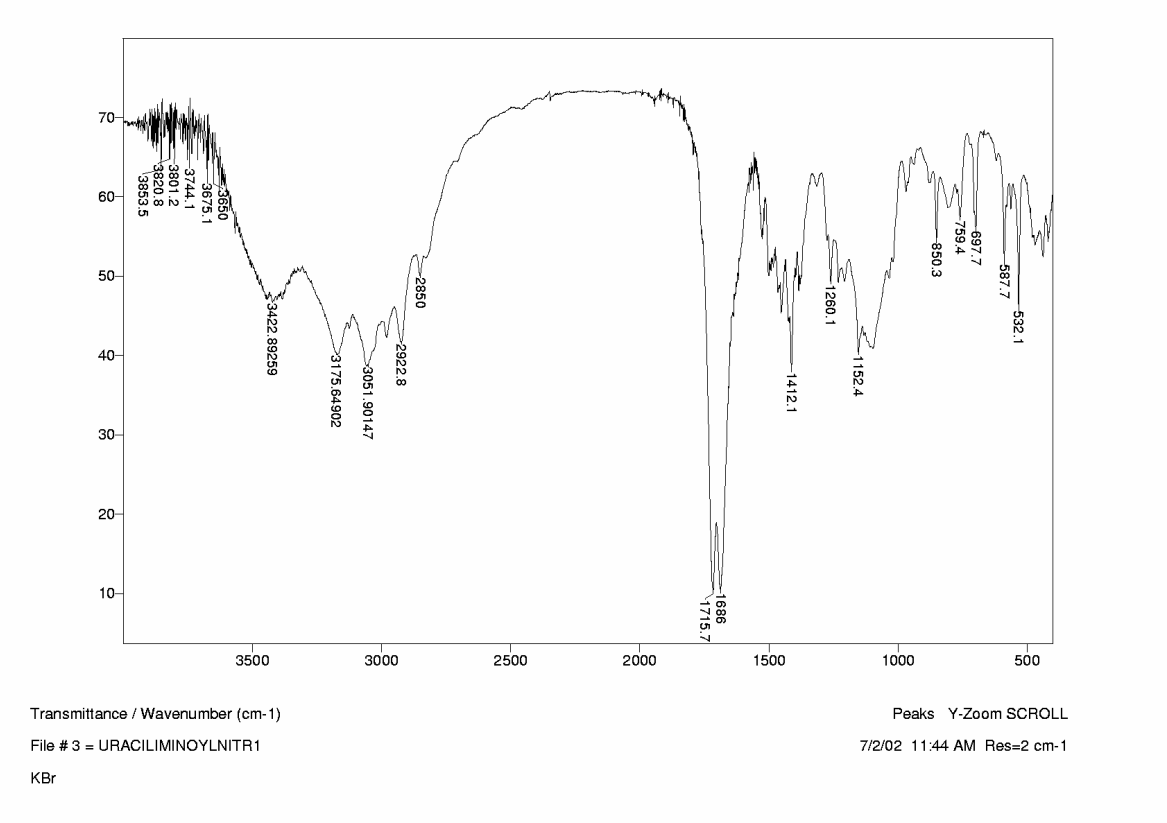
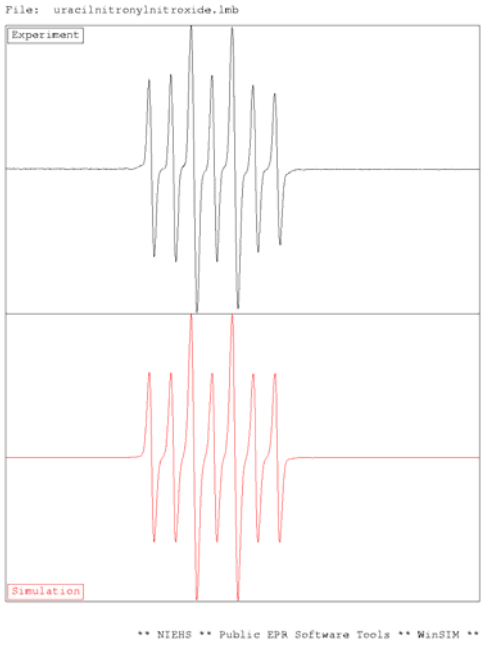
Experimental

6-Formyluracil. Following the procedure of Bocca, *et al*. [Bocca, M.; De Angelis, F.; Corelli, F.; Menichincheri, M.; Nicoletti, R.; Marongiu, M.; Pani, A.; La Colla, P. *Arch. Pharm.* **1991**, *324*, 203-207] a solution of 6-methyluracil (Lancaster, 2.0 g, 0.016 mol) in 50 mL of glacial acetic acid was treated with selenium oxide (2.64 g, 0.024 mol). The resulting suspension was heated at reflux with vigorous stirring for 24 h. The reaction mixture was filtered hot through Celite, and and the filter plug rinsed with warm acetic acid. Silica (10 g, 230-400 mesh) was added to the combined filtrates, and the solvent removed under reduced pressure. This adsorbed product with then chromatographed on silca gel using 9:1 $CHCl_3$:MeOH solution to yield one major fraction. Removal of the solvents afforded the desired aldehyde as an off-white solid, (1.2 g, 55%, mp 278-280 ºC, lit mp 274-275 ºC). ^{1}H-NMR (200 MHz, DMSO-d_6, δ): 6.29 (1H, vinylic CH), 9.55 (1H, aldehyde CH), 11-12 (tautomeric NH/OH peaks?).

6-Uradinyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl (2). A solution of 2,3-bis(hydroxylamino)2,3-dimethylbutane hydrogen sulfate (0.328 g, 1.33 mmol)[Ovcharenko, V.; Fokin, S.; Rey, P.; *Mol. Cryst. Liq, Cryst.* **1999**, *334*, 109-119] in argon-purged methanol (50 mL) was treated with triethylamine (0.74 mL, 5.30 mmol) with stirring. Once the salt had completely dissolved, 6-formyluracil (0.371 g, 2.65 mmol) was added to the reaction. The resulting light brown suspension was heated at reflux for 2 days under argon, following which the solvent was removed under vacuum to leave an orange, oily residue. The crude product was dissolved in 25 mL of dichloromethane and oxidized by stirring with an aqueous solution of sodium periodate (0.213 g in 25 mL water, 1.5 mmol). The organic phase was separated and evaporated. The crude solid product was purified by column chromatography (silica, 1:9 hexanes: ethyl acetate) to give **2** as a brick red powder (0.05 g, 19%, mp 186-188 ºC[d]). FTIR (KBr, cm^{-1}): 3423 (broad, NH), 3175, 3051, 2923 2830 (CH stretch), 1716, 1686 (amide N-C=O modes), 1412. MS(ESI, m/z): 252 (parent + H). ESR (9.645 GHz, chloroform): seven lines, a_N = 8.67, 4.58 G. Analysis calc'd for $C_{11}H_{15}N_4O_3$; C 52.58, H 6.02, N 22.30: found C 52.81; H 6.07; N 20.49. Crystals suitable for X-ray analysis[†] were obtained by slow evaporation of a layered 1:1 $CHCl_3$:H_2O solution.





FTIR is a KBr wafer at room temperature obtained on a Midac 2000 spectrometer.
ESR simulation with WINSIM [Duling, D. R. *J. Magn. Res.* **1994**, *B104*, 105-110]; 8.67 G (2N), 4.58 G (2N), correlation coefficient is 0.994.

Table S1. Crystal data and structure refinement for uracilin.

Empirical formula	C11 H15 N4 O3
Formula weight	251.266
Temperature	293 K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Crystal size	0.20 X 0.20 X 0.35
Unit cell dimensions	a = 13.3744(9) A alpha = 90 deg. b = 13.6012(9) A beta = 109.701(3) deg. c = 15.1086(13) A gamma = 90 deg.
Volume	2587.5(3) A^3
Z, Calculated density	8, 1.290 Mg/m^3
Absorption coefficient	0.096 mm^-1
F(000)	1064
Theta range for data collection	4.30 to 25.05 deg.
Limiting indices	-15<=h<=15, -15<=k<=16, -17<=l<=17
Reflections collected / unique	4041 / 2244 [R(int) = 0.0249]
Completeness to theta = 25.05	97.7 %
Reflections with I>2sigma(I)	1643
Absorption correction	None
Data / restraints / parameters	2244 / 0 / 163
Goodness-of-fit on F^2	1.111
Final R indices [I>2sigma(I)]	R1 = 0.0865, wR2 = 0.2416
R indices (all data)	R1 = 0.1110, wR2 = 0.2667
Largest diff. peak and hole	0.397 and -0.296 e.A^-3

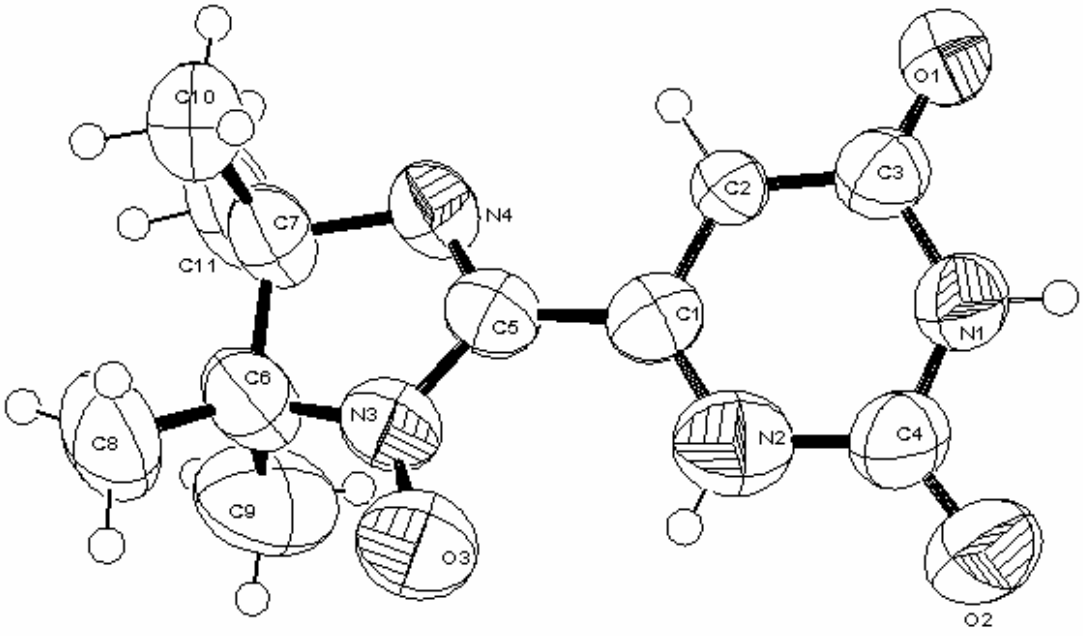


Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for uracilin.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5472(2)	4106(2)	5844(2)	92(1)
O(2)	1992(2)	4827(3)	4392(2)	120(1)
O(3)	1227(2)	2218(3)	6269(2)	118(1)
N(1)	3725(2)	4485(2)	5145(2)	82(1)
N(2)	2428(3)	3638(3)	5602(3)	100(1)
N(3)	2105(2)	2097(2)	6921(2)	82(1)
N(4)	3850(2)	2197(2)	7681(2)	76(1)
C(1)	3216(3)	3147(2)	6243(2)	67(1)
C(2)	4247(2)	3304(2)	6304(2)	55(1)
C(3)	4542(3)	3967(3)	5767(2)	75(1)
C(4)	2662(3)	4351(3)	4992(3)	84(1)
C(5)	3078(3)	2472(3)	6953(2)	69(1)
C(6)	2224(3)	1631(4)	7848(3)	93(1)
C(7)	3437(3)	1478(3)	8225(3)	84(1)
C(8)	1558(4)	696(5)	7670(4)	137(2)
C(9)	1834(5)	2395(6)	8386(4)	149(2)
C(10)	3792(4)	470(4)	8000(4)	112(2)
C(11)	3966(4)	1676(4)	9272(3)	123(2)

Table S3. Bond lengths [A] for **2.**

O(1)-C(3)	1.225(4)
O(2)-C(4)	1.223(4)
O(3)-N(3)	1.263(4)
N(1)-C(3)	1.372(4)
N(1)-C(4)	1.374(5)
N(2)-C(1)	1.344(5)
N(2)-C(4)	1.442(5)
N(3)-C(5)	1.384(4)
N(3)-C(6)	1.495(5)
N(4)-C(5)	1.285(4)
N(4)-C(7)	1.498(4)
C(1)-C(2)	1.368(4)
C(1)-C(5)	1.469(5)
C(2)-C(3)	1.358(4)
C(6)-C(9)	1.516(7)
C(6)-C(8)	1.525(7)
C(6)-C(7)	1.541(6)
C(7)-C(11)	1.524(6)
C(7)-C(10)	1.526(6)

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for uracilin. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	79(2)	105(2)	98(2)	28(2)	38(1)	9(1)
O(2)	102(2)	153(3)	104(2)	45(2)	32(2)	41(2)
O(3)	76(2)	128(3)	133(3)	13(2)	13(2)	-13(2)
N(1)	89(2)	89(2)	74(2)	14(2)	36(2)	16(2)
N(2)	94(2)	108(3)	98(2)	-9(2)	33(2)	9(2)
N(3)	62(2)	90(2)	90(2)	-1(2)	20(2)	-9(1)
N(4)	74(2)	88(2)	69(2)	0(1)	29(2)	-11(1)
C(1)	72(2)	66(2)	61(2)	-7(1)	20(2)	7(2)
C(2)	52(2)	64(2)	54(2)	9(1)	23(1)	8(1)
C(3)	79(2)	80(2)	70(2)	5(2)	29(2)	13(2)
C(4)	88(3)	96(3)	69(2)	12(2)	31(2)	19(2)
C(5)	66(2)	73(2)	70(2)	-10(2)	26(2)	-2(2)
C(6)	77(2)	115(3)	94(3)	6(2)	37(2)	-17(2)
C(7)	80(2)	98(3)	78(2)	7(2)	34(2)	-16(2)
C(8)	93(3)	146(5)	156(5)	43(4)	22(3)	-44(3)
C(9)	133(4)	205(7)	134(4)	-12(4)	80(4)	32(4)
C(10)	119(3)	100(3)	128(4)	27(3)	55(3)	0(3)
C(11)	117(3)	171(5)	79(3)	20(3)	31(2)	-53(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for uracilin.

	x	y	z	U(iso)
H(1)	3894	4935	4820	98
H(2)	1780	3526	5555	120
H(2)	4775	2936	6736	66
H(8A)	818	864	7425	205
H(8B)	1701	341	8249	205
H(8C)	1735	292	7223	205
H(9A)	1076	2454	8115	223
H(9B)	2157	3018	8353	223
H(9C)	2021	2196	9031	223
H(10A)	4552	424	8262	168
H(10B)	3571	386	7331	168
H(10C)	3477	-33	8266	168
H(11A)	4717	1569	9445	185
H(11B)	3678	1239	9624	185
H(11C)	3835	2344	9407	185

Spin Density Computations for **2**.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 Test job not archived.
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 15N4O3)]\\@
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Total atomic spin densities:

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1	O	-0.007355
2	C	0.000700
3	C	-0.019698
4	H	-0.000387
5	C	0.011623
6	N	0.002653
7	H	-0.000999
8	C	-0.000289
9	O	0.001292
10	N	-0.001029
11	H	0.000027
12	C	-0.061536
13	N	0.289529
14	C	-0.009582
15	C	0.025272
16	H	-0.000675
17	H	0.001253
18	H	-0.001740
19	C	0.006960
20	H	-0.001354
21	H	-0.000234
22	H	0.000048
23	C	-0.007911
24	C	0.003879
25	H	0.001071
26	H	0.001460
27	H	-0.000381
28	C	0.018038
29	H	-0.000663
30	H	0.002894
31	H	-0.000149
32	N	0.311056
33	O	0.436228