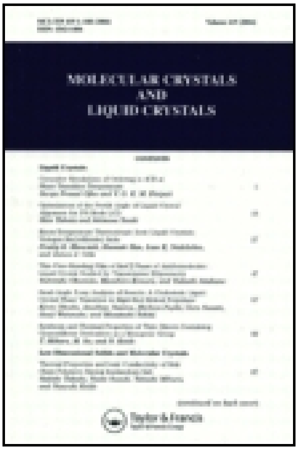

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A Uracil-Substituted α-Nitronyl Nitroxide

Robert Feher [a] , David B. Amabilino [a] , Klaus Wurst [b] & Jaume Veciana [a]

[a] Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193, Bellaterra, Spain

[b] Institut für Allgemeine Anorg. und Theoret. Chemie. Universität Innsbruck., A-6020, Innrain, 52a, Austria

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A Uracil-Substituted α-Nitronyl Nitroxide

ROBERT FEHER[a], DAVID B. AMABILINO[a], KLAUS WURST[b] and JAUME VECIANA[a]

[a]*Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193-Bellaterra, Spain and* [b]*Institut für Allgemeine Anorg. und Theoret. Chemie. Universität Innsbruck. A-6020, Innrain 52a, Austria*

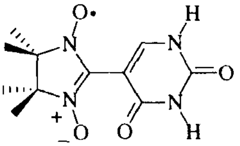
We have synthesized and chemically as well as structurally characterized a new α-nitronyl nitroxide. The spin density distribution in this uracil-substituted nitronyl nitroxide Ur-NN was examined as well as its correlation with the molecular structure, together with a study of the formation of aggregates of Ur-NN in solution.

Keywords: supramolecular engineering; α-nitronyl nitroxides; uracil derivatives

INTRODUCTION

The α-nitronyl nitroxides have proven to be suitable candidates for the preparation of organic ferromagnets in which the magnitude of the intermolecular interaction depends on the distance and relative orientation between the free radical moieties[1]. Hydrogen bonds can play a specific role in crystal packing[2] and propagation of magnetic interactions, as has been described for the bishydroxyphenyl radicals[3], [4], [5]. In these cases spin density spreads out over the α-nitronyl nitroxide part as well as to the substituted aromatic rings, and is propagated via intermolecular hydrogen bonding to the next radical moiety. Another example, where the hydrogen bonding of substituted aromatic rings leads to a ferromagnetic behaviour is N-protonated *m*-pyridinium α-nitronyl nitroxide bromide, where the proton is N···H···N bonded between the two nitrogen atoms of two neighbouring pyridine rings[6]. As a linker between two spin carrying organic radicals a diamagnetic molecule can also be used[7]. When phenylboronic acid is used to link phenyl α-nitronyl nitroxides, chains are formed, where the NO groups of two α-nitronyl nitroxides are connected by hydrogen bonding with the B-OH function of the phenylboronic acid, thus leading to ferromagnetic interactions, albeit between chains[8],[9].

To extend these studies to compounds with non-aromatic substituents laced with many hydrogen bond accepting and donating groups, we are investigating a uracil-substituted α-nitronyl nitroxide Ur-NN.



Ur-NN

FIGURE 1.

The thymine analogues in general show interesting regular packed structures[10] and have a great tendency to form H-bonds in solution[11],[12]. Various possibilities for the packing of the uracil derivatives have been found, depending on the substituents at the 5 and 6 positions on the uracil ring. The head-to-tail arrangement of NH donors and C=O acceptors can lead to tape, ribbon (Fig. 2) and two dimensional layer structures[13],[14] (Fig. 3). Therefore changing the substituents offers a possibility for designing a variety of supramolecular structures of radical substituted uracil molecules which may show a variety of intermolecular magnetic interactions. Thus, the functionality of the uracil together with the radical carrying substituents permits the control of crystalline molecular arrangements suitable for constructing magnets made out of purely organic open shell molecules.

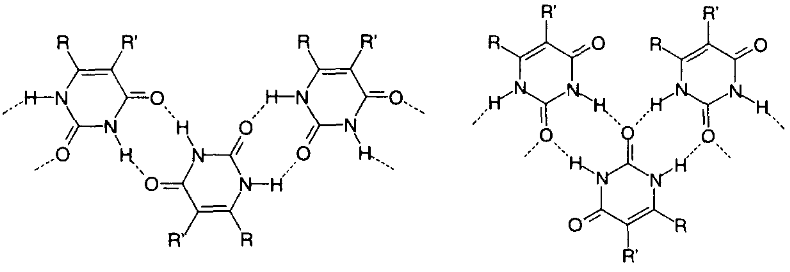


FIGURE 2. Tape structures of 5-methyl-6-ethyluracil (R=Et, R'=Me, left side) and 5-bromo- and 5-chlorouracil (R=H, R'=Br/ Cl, right side).

It was generally found that for the formation of tapes, applying an equal number of N-H donors and C=O acceptors is the best strategy. When the number of C=O acceptors exceeds the number of N-H functions, chains or dimers are preferred, where the excess C=O functions remain unbonded. In the opposite case when there are more N-H donors than C=O acceptors, the oxygen of the C=O group is able to form hydrogen bonds to two NH groups, involving both lone pairs of the acceptor. Where the number of donor and acceptor groups is balanced, as in 5-chlorouracil , 5-bromouracil[15], 5-methyl-6-ethyl-uracil[16] and thymine[10], tape like structures form (Fig. 2), whereas uracil[17], 5-(diphenylphosphino)uracil[18], 5-iodouracil[19] and 5-nitro-6-methyluracil[20] form layers (Fig. 3).

In all the examples given, the self-assembly of the molecules is primarily determined by the strong N-H--O hydrogen bonds between the oxygen atoms of the carbonyl group and the hydrogen atoms of the amide groups of two interacting uracil moieties. In none of the cases were found strong hydrogen bonds between the substituents in the 5- or 6-position even when the substituent was NO_2.

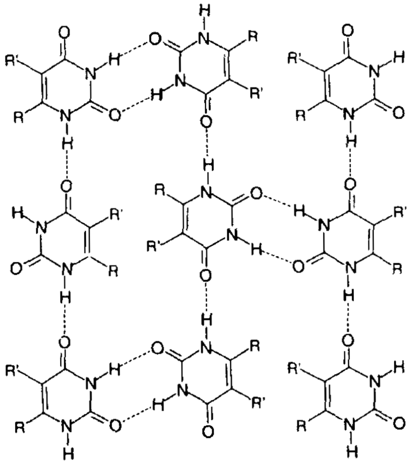


FIGURE 3. Layer structure of 5-(diphenylphosphino)uracil (R=H, R'=PPh_2).

The supramolecular structure in the next step is determined by weaker C-H--X bonds, where the H atom belongs to an alkyl group. Even a small change in size or electronegativity of substituents greatly influences the tape or layer motif during crystallization.

These results encouraged us to synthesize a new family of α-nitronyl nitroxide substituted uracils which could be changed by substitution of the hydrogen atom in the 6-position of the uracil with other functional groups. An interesting question is how the two additional NO groups of the α-nitronyl nitroxide, which can act as acceptors, might influence the packing of the molecule.

Another reason for our attraction to the uracil derivatives is the possibility for the formation of cyclic hexameric aggregates in solution (Fig. 4), which are favoured thermodynamically over their linear homologues. The characterization of magnetic interactions in solution is an appealing way to uncover supramolecular motifs for propagation of ferromagnetic interactions between radicals. Here, we present the preparation of the first example of this family of radicals, Ur-NN as well as an examination of its spin density distribution along with its correlation with the molecular structure, and a preliminary study of the formation of aggregates of Ur-NN in solution.

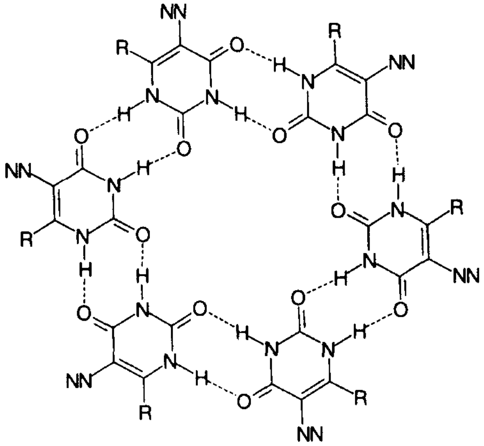


FIGURE 4. Possible cyclic structure of a hexameric aggregate of Ur-NN

Electronic structure of Ur-NN

A very important feature for the propagation of a magnetic interactions between the unpaired spins of these hydrogen bonded molecules is the amount of spin density which spreads from the two NO groups to the N and O atoms of the uracil ring, which build hydrogen bonds to the next molecule. The spin density of the free molecule was examined by ESR spectroscopy in solution. The ESR spectrum of the compound in water at room temperature shows the regular splitting pattern of five lines due to the coupling of the unpaired electron with two equivalent nitrogen nuclei. These lines are further split by the interaction of the unpaired electron with the twelve equivalent hydrogen nuclei of the α-nitronyl nitroxide methyl groups, one hydrogen atom at the conjugated double bond and the two nitrogen nuclei in the uracil ring.

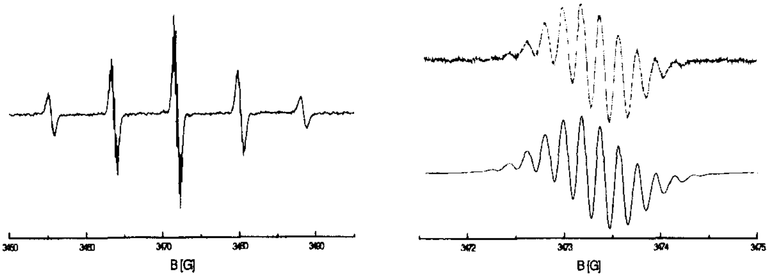


FIGURE 5. ESR spectrum of the deprotonated Ur-NN in water (left side); central line (right side) and simulation of it (below)

A significant amount of spin density is only transferred to the hydrogen attached to the double bond in the uracil ring (Table I) as confirmed by the simulation of the experimental ESR spectra. When NaOH is added to the solution, the colour turns from deep purple to dark blue indicating a better conjugation and thus a smaller torsion angle between the two rings. This hypothesis is supported by the change of the hydrogen and nitrogen coupling constants of the uracil ring, which are increased by adding a base. The better resolution of the ESR spectra (Fig. 5) of the deprotonated compound stems from the fact, that the coupling constant of the hydrogen atom at the double bond is more similar to the one of the twelve hydrogen atoms of the α-nitronyl nitroxide part, thus leading to a more regular pattern. The greater distribution of spin density being transferred from the α-nitronyl nitroxide part to the uracil ring depends strongly on the conjugation taking place between the two rings. For a maximum overlap of the p orbitals on both rings, the molecule has to be planar.

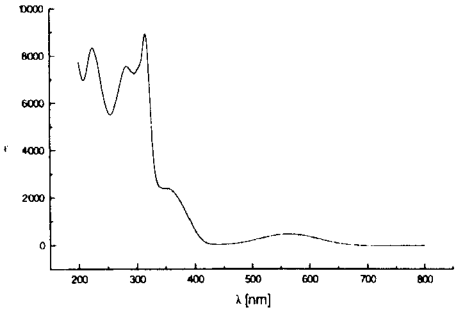
The crystal structure of the compound (vide infra)[21] shows that the torsion angle between the two ring planes (64.9 °) is relatively high. This explains why only little spin density is transferred to the uracil ring, thus leading to small coupling constants.

TABLE I Coupling constants of Ur-NN radical in [G]

	in H_2O	in H_2O / OH^-
$a_{N,\ \text{nitronyl nitroxide}}$	8.16	8.26
a_{Me}	0.176	0.190
a_{H7}	< 0.1	0.149
a_{N4}	< 0.15	< 0.1

Aggregation of Ur-NN in Solution

We first studied the aggregation of Ur-NN by absorption spectroscopy. The UV-VIS spectrum (Fig. 6) of radical Ur-NN shows absorption bands in the region between 200 - 250 nm and 300 - 360 nm corresponding to the π→π* and n→π* transitions of the carboxyl groups of the uracil ring, respectively, and the n→π* absorption on the α-nitronyl nitroxide moiety. A broader band between 500 - 650 nm can be assigned to the π→π* transition of the α-nitronyl nitroxide part.



UV-VIS:
225 nm ⇒ Ur-ring π→π* (ε=8300)
283 nm ⇒ C=O n→π*
315 nm ⇒ ONCNO n→π*
352 nm ⇒ C=O (conjugated) n→π*
565 nm ⇒ ONCNO π→π* (ε=450)

FIGURE 6. UV-VIS spectrum of Ur-NN in a 2×10^{-4} M solution in acetonitrile

The temperature dependence of the absorption coefficient of Ur-NN was analyzed in the visible region when recorded in acetonitrile (Fig. 7). Isosbestic points were found at 450 nm and 650 nm. Going to lower temperatures leads to an increase of the signal intensity, strongly indicating the formation of supramolecular aggregates. The spectra also show a slight concentration dependence, in support of this conclusion. The character of the aggregates is weak as a result of competition of the solvent, a good hydrogen bond acceptor. The poor solubility of the compound in less polar solvents precluded studying the aggregates in conditions in which they would be more favoured.

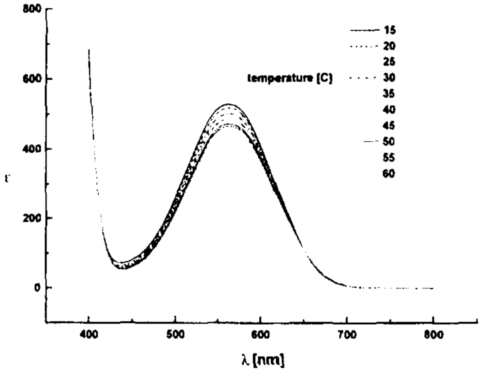


FIGURE 7. Temperature dependence of UV-VIS spectra of Ur-NN in a 10^{-3} M solution in acetonitrile.

The aggregates were also studied by ESR spectroscopy. In a frozen solution (CH_2Cl_2 / MeOH, 160 K), only the signal of the monomer and no signal at half field is observed which would stem from the possible formation of dimers with triplet ground state. The dependence of the intensity of the main signal with temperature has been evaluated showing a decrease of signal intensity when going to lower temperatures. These facts in combination with the results of the UV-VIS spectroscopy contribute to the conclusion that aggregates are formed in solution, which could be comprised of anti-ferromagnetically interacting radicals. Examples for possible aggregates of this type of compounds are linear oligomeric (Fig. 2) or cyclic hexameric species (Fig. 4), sustained by hydrogen bonds.

An X-ray analysis of the compound confirms the existence of hydrogen bonds between the NO groups one α-nitronyl nitroxide and the N-H donor groups of two flanking molecules, thus leading to a chain like structure (Fig. 8). The further packing of the chains themselves is determined by weaker C-H---O=C hydrogen bonds (see Table II for the geometry of the different bond types.)

TABLE II Different hydrogen bridging motifs in crystals of Ur-NN

type of H-bond	[H···O] (Å)	[X-H-O] angle [°]
N-H···O intrachain	1.907	164.7
N'-H···O intrachain	2.114	154.4
C-H···O interchain	2.754	164.0
C'-H···O interchain	2.765	171.3

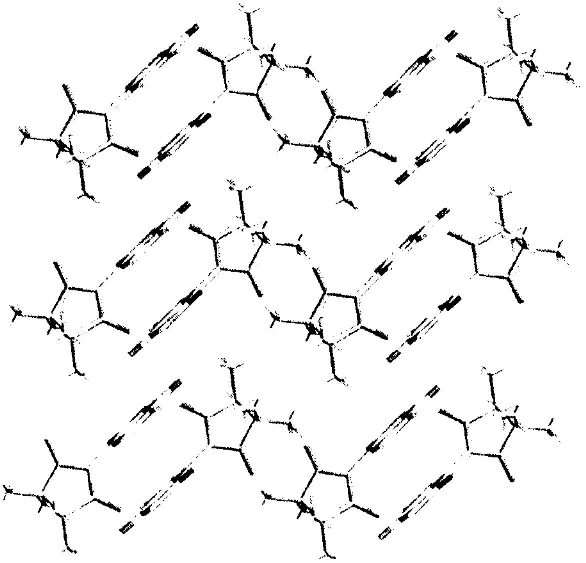


FIGURE 8. A view down the zig-zag chain in the crystal structure of Ur-NN

Magnetic Properties of Ur-NN

The paramagnetic susceptibility of the UR-NN radical measured on a SQUID magnetometer shows a paramagnetic behaviour down to very low temperatures (10 K) and then sharply decreases (Fig. 9). This kind of behaviour cannot be fitted to a 1D antiferromagnetic Heisenberg spin chain, because the decrease in this case is more gradual. It could be explained by a first order transition ocurring below 5 K, that leads to a contraction of the structure and a sudden change of the antiferromagnetic interaction between the neighbouring molecules.

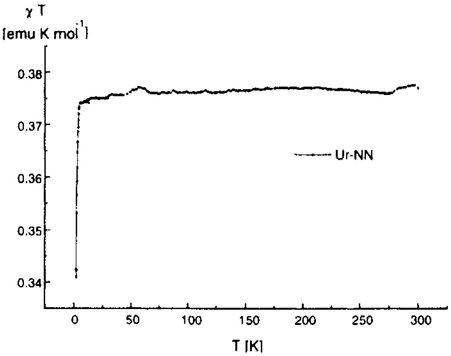


FIGURE 9. χT vs. T plot of the radical

CONCLUSION

The uracil-substituted α-nitronyl nitroxide radical described shows little distribution of the free electron density as a result of a high torsion angle between the component heterocyclic rings. It does indeed form aggregates in solution, although its poor solubility in apolar solvents prohibited their full structural characterization. While the crystal packing of other uracil derivatives is dominated by hydrogen bonds between the oxygen and NH groups of the uracil ring, in the case of UR-NN, the strongest interaction is found between the uracil NH group and the NO moiety of the α-nitronyl nitroxide ring. Whether this situation pertains in solution is presently unclear. The aggregates formed in solution appear to be antiferromagnetically coupled, while in the solid state the material behaves as a quasi-ideal paramagnet down to very low temperatures. By cooling down below 10 K a phase change occurs which is accompanied by an increase of antiferromagnetic interactions. Uracil derivatives form well-defined complexes with a variety of host molecules, such as melamine. We are currently investigating Ur-NN complexes, seeking to modify its magnetic properties by this supramolecular approach.

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