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α-Nitronyl Nitroxide Cation Radicals: Crystal Engineering for the Molecular Based Organic Ferromagnetism

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α-NITRONYL NITROXIDE *CATION* RADICALS: CRYSTAL ENGINEERING FOR THE MOLECULAR BASED ORGANIC FERROMAGNETISM

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Abstract Magnetic properties and crystal structures of *N*-alkylpyridinium α-nitronyl nitroxide *cation* radicals, has been studied. Some of them have been found to have ferromagnetic intermolecular interaction which are much stronger than those in the α-nitronyl nitroxide free radicals. Further, a *m*-*N*-methylpridinium α-nitronyl nitroxide salt crystallizes into a trigonal space group with a triangular lattice, which includes both of the ferromagnetic and antiferromagnetic interactions.

INTRODUCTION

Search for molecular/organic ferromagnetism is of current interest.[1] In this search, it is important to determine the factor controlling the intermolecular magnetic coupling in the solid state. An organic radical, galvinoxyl, has been confidently proved to possess a ferromagnetic intermolecular interaction.[2] This interaction has been interpreted by the cooperation between the intramolecular spin polarization effect and the intermolecular charge-transfer (CT) interaction.[3,4] The spin polarization effect stabilizes the triplet CT excited state, and the admixture of this state results in the ferromagnetic coupling. This mechanism has been originally proposed by McConnell,[5] and the importance of the spin polarization effect has been theoretically pointed out by Yamaguchi et al.[6]

Recently, we have started a study of the magneto-structural correlation in the crystals of α-nitronyl nitroxides. This radical family is known[7] to possess a strong spin polarization effect, because of the spatial closeness between the unpaired π electron and

the non-bonding electrons (n-π exchange interaction). We have already reported the magnetic properties of some α-nitronyl nitroxide free radicals.[8-10] We found weak ferromagnetic interactions in the crystals of *p*-nitrophenyl[8] and *p*-pyridyl[10] α-nitronyl nitroxides (abbreviated as *p*-NPNN and *p*-PYNN, respectively). Last year, the β-phase of *p*-NPNN has been revealed to have a ferromagnetic ordered state below T_c=0.65 K, by Kinoshita et al.[11]

CRYSTAL ENGINEERING

The crystal structure of the ferromagnetic *p*-PYNN radical consists of an one-dimensional (1D) linear chain, as is shown in Figure 1.[10] The molecules are arranged side-by-side and head-to-tail in the chain. There are short intermolecular, interatomic distances from the oxygen atom in the NO group to the pyridyl ring. Since the oxygen atom in the NO group is equipped with a large negative charge, resulting from the electronic polarization in the NO bond, namely $N^{\delta+}O^{\delta-}$, this structure could be realized by the hydrogen bonds between the negative oxygen atom and the hydrogen atoms on the pyridyl ring.

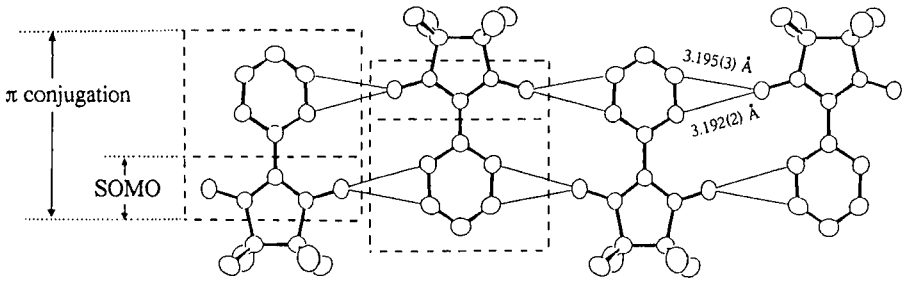


FIGURE 1 View of the chain structure in the crystal of *p*-PYNN.

The SOMO of *p*-PYNN is considered to be localized on the side of the nitronyl nitroxide, O-N-C-N-O, and has little population in the pyridine ring, while the other frontier π orbitals are distributed on both sides of the molecule.[10] In the molecular

arrangement of *p*-PYNN shown in Figure 1, the overlap between the SOMOs is much smaller than those between the SOMO and the other frontier orbitals. It is thought that the former overlap always makes the intermolecular interaction antiferromagnetic and the latter ones bring about the ferromagnetic coupling.[3] Therefore, the ferromagnetic interaction is expected to operate in the chain. In fact, the temperature dependence of magnetic properties of *p*-PYNN can be interpreted in terms of an 1D ferromagnetic chain.[10]

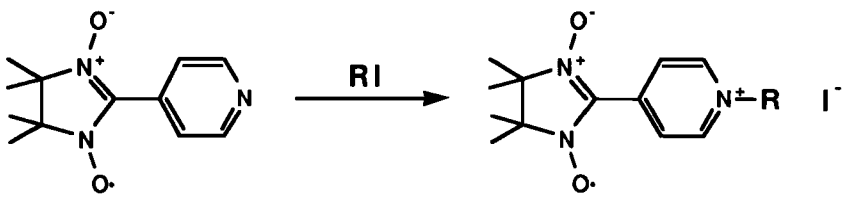
If the distance between the NO group and the pyridyl ring becomes short, the ferromagnetic intermolecular interaction could be enhanced. To examine it, we have moved into a study of pyridinium α-nitronyl nitroxide *cation* radicals. They are expected to have a shorter intermolecular contact between the NO group and the pyridinium ring in the solid state, due to the Coulombic attraction force between the negative charge on the oxygen and the positive charge on the pyridinium ring.

PYRIDINIUM α-NITRONYL NITROXIDE

para-Isomers

The *p*-pyridinium α-nitronyl nitroxide cation radicals were prepared by the *N*-alkylation of *p*-PYNN, as is shown in Scheme I. The iodide salts of methyl, ethyl and *n*-propyl derivatives (abbreviated as *p*-MPYNN, *p*-EPYNN and *p*-PrPYNN, respectively), were separated from the solutions of *p*-PYNN in the alkyl iodides. *p*-EPYNN crystallized with water in the solvent or in the air as $(p\text{-EPYNN}\bullet I)_2\bullet H_2O$, while *p*-MPYNN•I and *p*-PrPYNN•I did not include crystal water. Results of the elemental analyses are listed in Table I. The IR spectrum of the *p*-EPYNN salt is clearly different from those of the other two, due to the crystal water.

Temperature dependence of the molar paramagnetic susceptibilities, χ_p, of *p*-MPYNN•I is shown in Figure 2.[12] χ_p increases with decreasing temperature down to *ca.* 90 K, and after going through a maximum, χ_p begins to decrease, approaching to zero at



SCHEME I

TABLE I Results of the elemental analyses.

		C	H	N
p-MPYNN•I	Calc.	41.50	5.09	11.17
$C_{13}H_{19}N_3O_2I$	Found	41.35	5.00	11.29
(*p*-EPYNN•I)$_2$•H_2O	Calc.	42.12	5.55	10.52
$C_{28}H_{44}N_6O_5I_2$	Found	42.51	5.32	10.59
p-PrPYNN•I	Calc.	44.57	5.73	10.39
$C_{15}H_{23}N_3O_2I$	Found	44.29	5.69	10.33
m-MPYNN•I•$(H_2O)_2$	Calc.	37.88	5.62	10.19
$C_{13}H_{23}N_3O_4I$	Found	38.08	5.02	10.16
(*m*-EPYNN•I)$_2$•$(H_2O)_3$	Calc.	40.30	5.80	10.07
$C_{30}H_{48}N_6O_7I_2$	Found	40.13	5.43	9.85
(*m*-PrPYNN)$_2$•H_2O	Calc.	43.59	5.85	10.17
$C_{30}H_{48}N_6O_5I_2$	Found	43.68	5.72	10.45

0 K. Below 15 K, χ_p shows a slight increase again, which could be due to the Curie spins on the lattice defects. The observed temperature dependence is well understood by the combination of the singlet-triplet model and a small amount of the Curie component, as is written by

$$\chi_p = \frac{C}{T}\frac{4\exp(-2J_{AF}/k_BT)}{1+3\exp(-2J_{AF}/k_BT)} + \frac{C_{def}}{T} \quad . \tag{1}$$

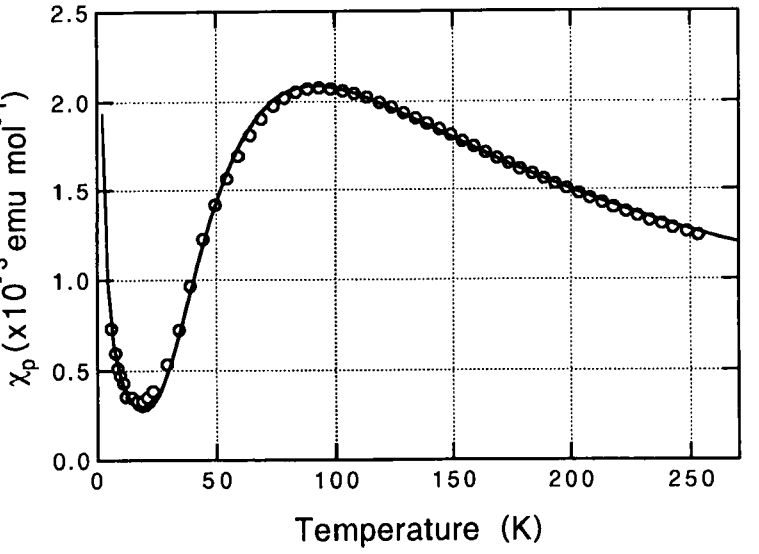


FIGURE 2 Temperature dependence of χ_p of *p*-MPYNN•I. The solid curve is the theoretical one of Eq. (1).

The solid curve in Figure 2 represents the best fit of the experimental data obtained with C= 0.378 emu K mol^{-1}, $2J_{AF}/k_B$=149 K and C_{def}=0.005 emu K mol^{-1}. This antiferromagnetic coupling constant is larger by two order of magnitude than those in the nitroxide free radicals.[9] From the magnetic point of view, the nitroxide *p*-MPYNN is concluded to exist as dimers formed by the strong antiferromagnetic interaction. Temperature dependence of χ_p of *p*-EPYNN•I follows the Curie-Weiss law with a negative Weiss constant of θ=-1.8 K in the whole temperature range below 260 K (not shown).[12] This indicates the weak antiferromagnetic intermolecular interaction in *p*-EPYNN•I.

Figure 3 shows the temperature dependence of χ_pT of *p*-PrPYNN•I. χ_pT increases gradually, as the temperature is decreased down to 4 K. However, χ_pT shows a quick decrease below 4 K. The observed dependence was found to be well interpreted by the modified singlet-triplet model;

$$\chi_p = \frac{C}{T-\theta}\frac{4}{3+\exp(-2J_F/k_BT)}, \qquad (2)$$

in which coexistence of a intradimer ferromagnetic interaction and a interdimer antiferromagnetic interaction is assumed. The solid curve in Figure 3 is the theoretical best fit with the parameter listed in Table II. The magnetic couplings of the *p*-isomer changes from antiferromagnetic to ferromagnetic, with changing the *N*-alkyl substituent.

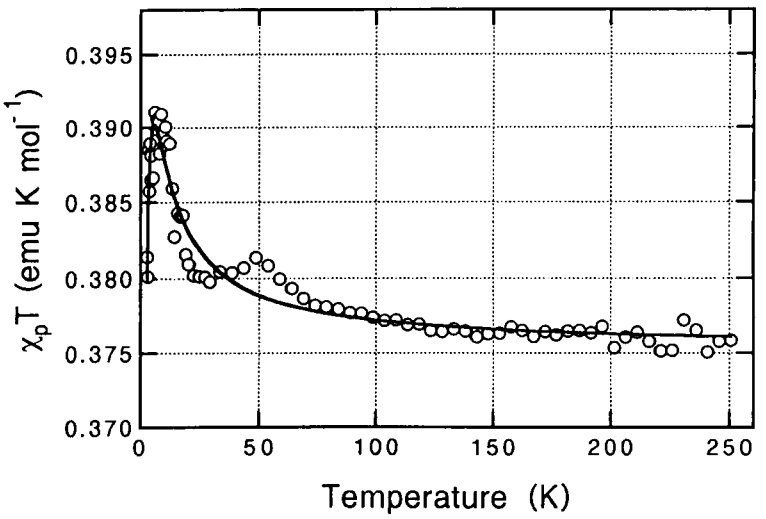


FIGURE 3 Temperature dependence of χ_pT of *p*-PrPYNN•I. The solid curve is the theoretical one of Eq. (2).

TABLE II. Fitting parameters for the Eq. (2).

	C (emu K mol^{-1})	$2J_F / k_B$ (K)	θ (K)
p-PrPYNN•I	0.375	4.8	-0.7
m-MPYNN•I•$(H_2O)_2$	0.370	21.5	-0.2
m-EPYNN•I•$(H_2O)_{1.5}$	0.370	25.0	-3.1
m-PrPYNN•$(H_2O)_{0.5}$	0.383	21.3	-1.2
m-MPYNN•$(BF_4)_{0.72}$•$I_{0.28}$ •$(H_2O)_{0.17}$	0.377	24.0	-1.6

meta-Isomers

The iodide salts of *m*-MPYNN, *m*-EPYNN and *m*-PrPYNN were obtained by the same procedure as those for the *p*-isomers. Elemental analysis and the spin concentration determined by the magnetic measurements indicated that they crystallized with water, as *m*-MPYNN•I•$(H_2O)_2$, (*m*-EPYNN•I)$_2$•$(H_2O)_3$ and (*m*-PrPYNN•I)$_2$•H_2O (See Table I). The IR spectra clearly indicated their crystal waters.

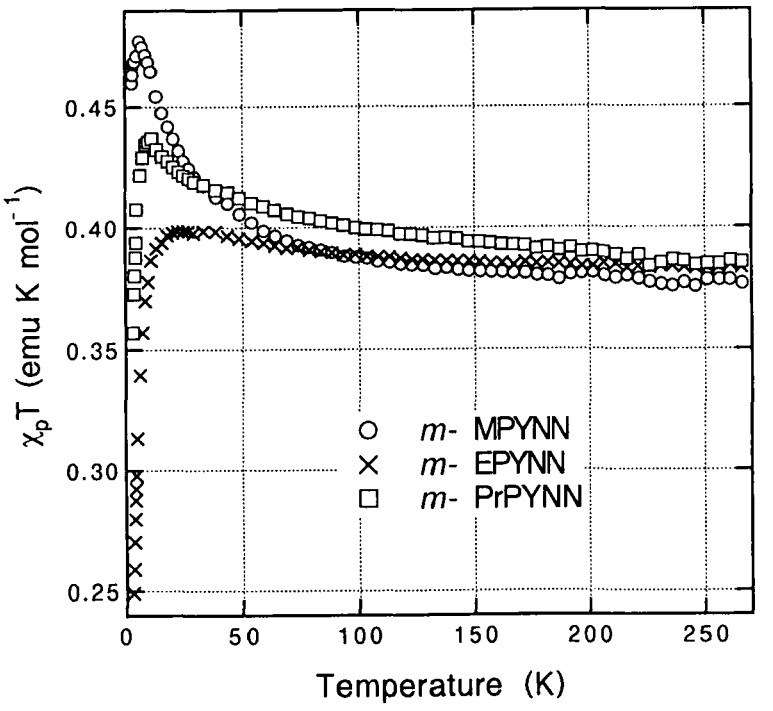


FIGURE 4 Temperature dependence of χ_pT of *m*-MPYNN•I•$(H_2O)_2$, *m*-EPYNN•I•$(H_2O)_{1.5}$ and *m*-PrPYNN•I•$(H_2O)_{0.5}$.

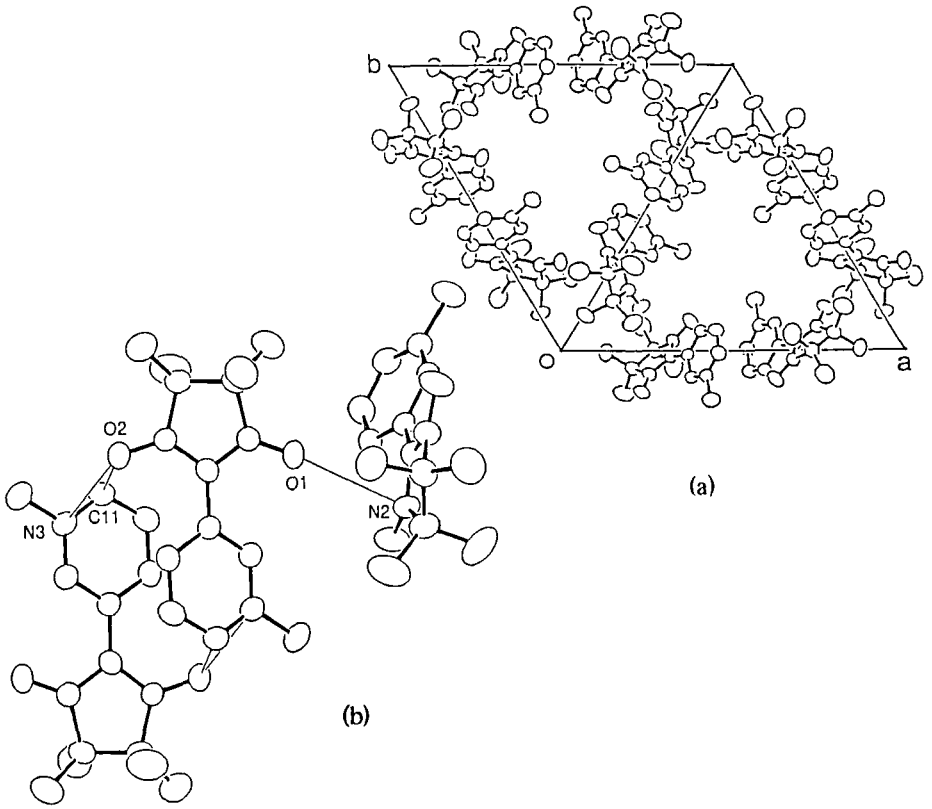


FIGURE 5 (a) 2D triangular lattice of the *m*-MPYNN dimers. (b) Intradimer and interdimer molecular arrangements.

Figure 4 shows the temperature dependence of $\chi_p T$ of the three *m*-isomers. They show similar temperature dependence as that seen in *p*-PrPYNN•I, which indicates coexistence of the ferromagnetic and antiferromagnetic interactions. All of the three can be well interpreted by Eq. (2) with the parameters in Table II. Their ferromagnetic coupling constants are much larger than that of *p*-PrPYNN•I and those of the other α-nitronyl nitroxide free radicals.[8-10] As far as the three iodide salts of the *m*-isomers, the relative change in the interdimer antiferromagnetic coupling constant, θ, is larger than that in the intradimer ferromagnetic coupling constant, J_F.

Recrystallization of *m*-MPYNN•I•$(H_2O)_2$ from an acetone solution gave hexagonal-plate single crystals including both of water and acetone as crystal solvents.[13] In the air they immediately turn into mosaic by the evaporation of the crystal solvents. Recrystallization with the presence of excess TBA•BF_4 or TBA•ClO_4 (TBA=tetrabutylammonium) gave a crystalline solid solution, *m*-MPYNN•X_x•I_{1-x}

($X=BF_4$ or ClO_4), which is free from the evaporation. X-ray diffraction data were collected using a stable crystal, *m*-MPYNN•$(BF_4)_{0.72}$•$I_{0.28}$•$(H_2O)_{0.17}$, whose crystal data are as follows; trigonal $P\bar{3}c1$, $Z=12$, $a=15.938(1)$, $c=23.615(1)$ Å.[13] The occupation numbers of the anions and water were determined through a least square structure refinement. There is an occupancy disorder of counter parts (anions and water) and the refinement is still in progress, while this development would give little change in the molecular structure and arrangement of *m*-MPYNN.

The *m*-MPYNN molecules exist as a dimer and, surprisingly, the solid state structure consists of a 2D triangular lattice of the dimer units. Figure 5(a) shows a view of the triangular lattice projected onto the *ab* plane. The radical dimer is located on each side of the triangles. The intradimer and the interdimer molecular arrangements are shown in Figure 5(b). In the intradimer arrangement, there are very short intermolecular, interatomic distances between the NO group and the pyridinium ring; 2.995 Å of O2•••C11 and 3.188 Å of O2•••N3. This is a wanted arrangement, as is discussed before. These short contacts would be caused by the Coulombic attraction force between the positive charge on the pyridinium ring and the negative charge polarized on the oxygen atom. Such overlap is considered to contribute to the ferromagnetic coupling. In the interdimer arrangement, on the other hand, there is a weak contact between the NO groups; 3.217 Å of O1•••N2. The NO•••NO contact means the overlap between SOMOs, and should contribute to the antiferromagnetic coupling.

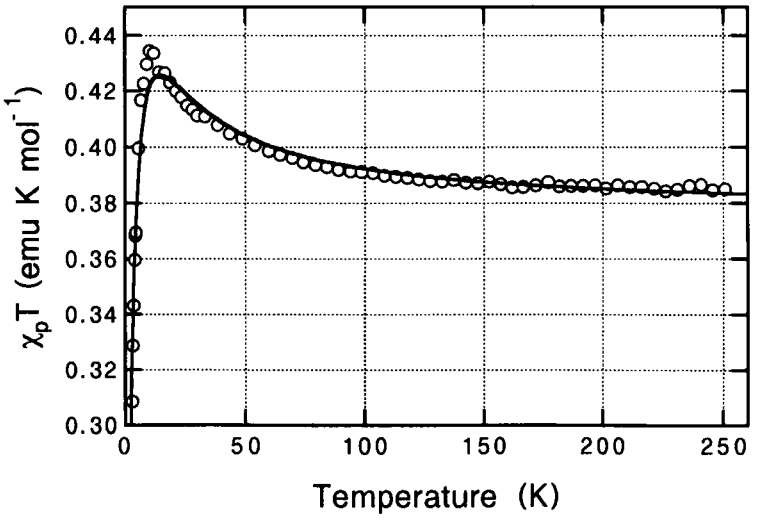


FIGURE 6 Temperature dependence of χ_pT of *m*-MPYNN•$(BF_4)_{0.72}$•$I_{0.28}$•$(H_2O)_{0.17}$.

Figure 6 shows the temperature dependence of $\chi_p T$ of *m*-MPYNN•$(BF_4)_{0.72}$•$I_{0.28}$•$(H_2O)_{0.17}$,[13] which can be also understood by Eq. (2). This is quite consistent with the discussion on the intermolecular arrangements described just above. There is a possibility that the spin system in *m*-MPYNN could be characterized in terms of a 2-D triangular lattice of antiferromagnetic S=1 spins[14] at very low temperatures (less than ca. 2 K).

o-Isomers

Figure 7 shows the temperature dependence of $\chi_p T$ of *o*-MPYNN•I and *o*-EPYNN•I. They can be interpreted by the Curie-Weiss law with the parameters of θ=-1.9 K for *o*-MPYNN•I and θ=-0.1 K for *o*-EPYNN•I.

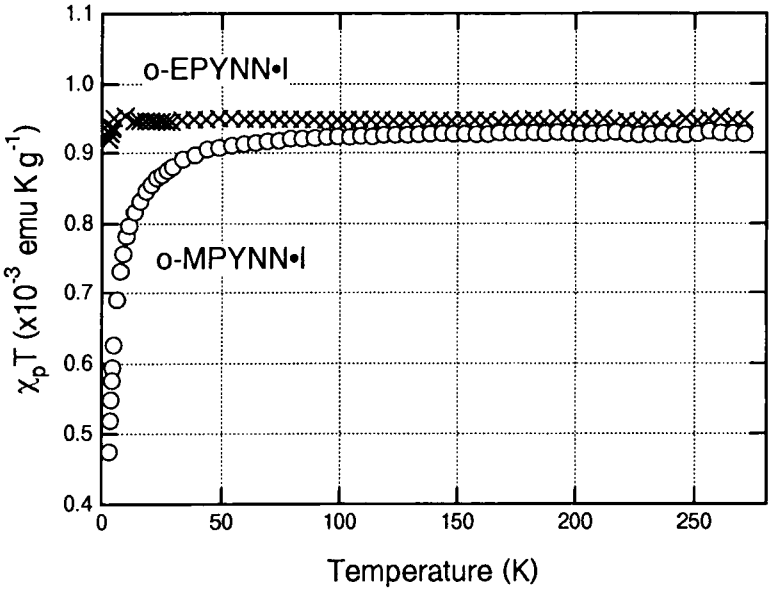


FIGURE 7 Temperature dependence of $\chi_p T$ of *o*-MPYNN•I and *o*-EPYNN•I..

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