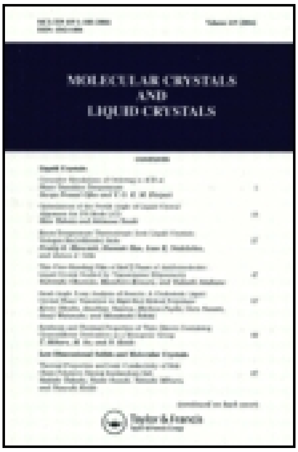

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Crystal Structure and Electronic State of the Organic Ferromagnet, Nitrophenyl α-Nitronyl Nitroxide Radical

Kunio Awaga [a], Tamotsu Inabe [b], Toshihiko Yokoyama [c] & Yusei Maruyama [d]

[a] Department of Pure and Applied Sciences, University of Tokyo, Komaba, Meguro, 153, Japan

[b] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan

[c] Department of Materials Science, Faculty of Science, Hiroshima University, Hiroshima, 730, Japan

[d] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

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CRYSTAL STRUCTURE AND ELECTRONIC STATE OF THE ORGANIC FERROMAGNET, NITROPHENYL α-NITRONYL NITROXIDE RADICAL

KUNIO AWAGA
Department of Pure and Applied Sciences, University of Tokyo, Komaba, Meguro 153, Japan

TAMOTSU INABE
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

TOSHIHIKO YOKOYAMA
Department of Materials Science, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

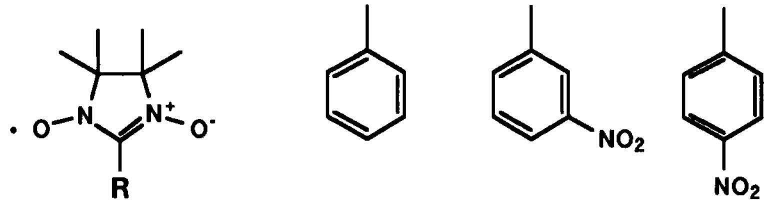
YUSEI MARUYAMA
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract Three kinds of α-nitronyl nitroxides, including the organic ferromagnet, p-nitrophenyl α-nitronyl nitroxide, have been structurally characterized. MO calculation has indicated that both of the spin and electronic polarization effects are much enhanced in this radical family, and that the spin density distribution depends little on the substituent at the α position. The magneto-structural correlation is discussed, based on the difference in the crystal structure.

INTRODUCTION

While the majority of organic radicals exhibit antiferromagnetic (AFM) intermolecular interaction, a few radicals have been confidently proved to possess ferromagnetic (FM) interactions. The galvinoxyl radical belongs to the latter category.[1] The FM interaction in galvinoxyl has been interpreted by the cooperation between the intramolecular spin polarization effect and the intermolecular charge-transfer (CT) interaction.[2,3] The spin polarization effect stabilizes the triplet CT excited state, and admixture of this state to the ground state results in the FM coupling. This mechanism has been originally proposed by McConnell.[4]

Recently, we have started a study of the magneto-structural correlation in the crystals of α-nitronyl nitroxides. This radical family is known to possess a strong spin polarization effect,[5] because of the spatial closeness between the unpaired π electron and the non-bonding electrons. We have already reported[6-9] the magnetic properties of some



1 2 3

SCHEME I

α-nitronyl nitroxides, including the three shown in Scheme I. The intermolecular magnetic coupling is FM in the crystal of 3, while it is AFM in 1 or 2.[6] Their Weiss constants have been determined to be -1.4K (1), -0.5K (2) and +0.9K (3), respectively. The intermolecular magnetic interaction in the α-nitronyl nitroxide changes from AFM to FM, depending on the substituent at the α-carbon. We have also described the two-dimensional (2D) intermolecular network in the crystal of the nitroxide 3, briefly.[10] Recently, it has been reported that the nitroxide 3 has two more polymorphs which have 1D stacking structures and also show weak FM couplings.[11,12] The first 2D network phase is now called β-one, and the other 1-D stacking phases are α- and γ-phases. Furthermore, the β-phase has been found to have an FM ordered state below T_C=0.65 K by Kinoshita et al.[13]

In this paper, we describe the molecular and crystal structures of 1, 2 and the organic ferromagnet, 3(β-phase), in detail. Structural conditions for the FM coupling are discussed, based on the difference in molecular and crystal structure among 1-3(β) and on the results of the molecular orbital (MO) calculation.

EXPERIMENTAL

The nitroxides 1-3 were prepared according to the method described in ref. 5. Single crystals were obtained by recrystallization from the benzene solutions.

X-Ray diffraction data at room temperature were recorded on RIGAKU AFC-5 (1 and 3) and ENRAF NONIUS CAD4 (2) four-circle diffractometers using Mo-K_α radiation. The refined cell constants from 20 reflections with 20<2θ<30° and additional relevant crystal data are given in Table I.

MOLECULAR STRUCTURE AND ELECTRONIC STATE

The results obtained by single-crystal X-ray studies at room temperature for 1 are in agreement with those reported in ref. 14, where there is no description for the solid-state

TABLE I Summary of crystal data.

compound	1	2	3 (β)
formula	$C_{13}H_{17}N_2O_2$	$C_{13}H_{16}N_3O_4$	$C_{13}H_{16}N_3O_4$
space group	$P2_1/c$	$P2_1$	$Fdd2$
a, Å	21.070(3)	10.314(3)	10.960(3)
b, Å	10.239(5)	11.130(2)	19.350(3)
c, Å	12.311(2)	6.138(2)	12.347(5)
β, deg	105.56(1)	106.70(1)	
V, Å^3	2558(1)	674.9(3)	2618(1)
Z	8	2	8

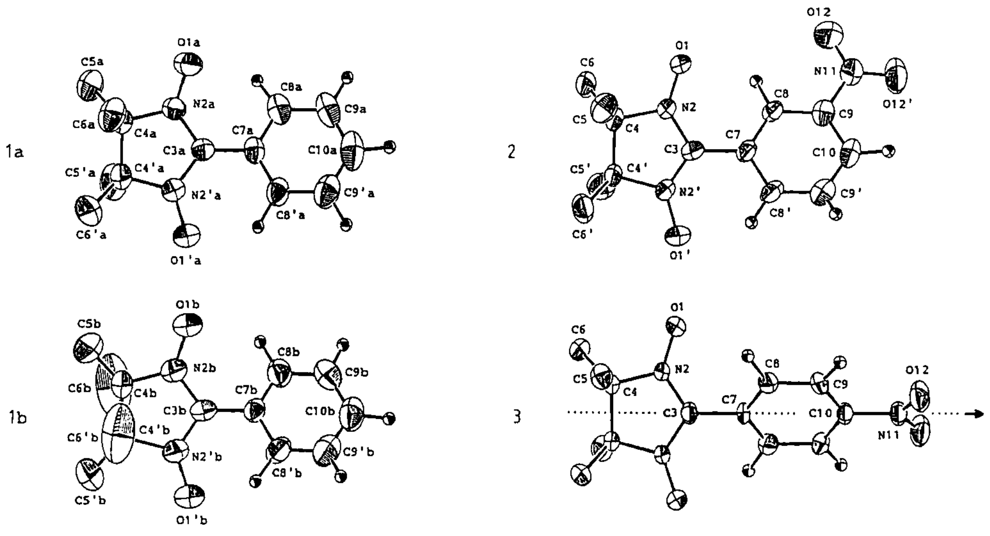


FIGURE 1 ORTEP drawing and atom numbering schemes of the nitroxides **1**-**3**(β).

structure. In this paper we use our data just for the comparison of the solid-state structure with those for **2** and **3**(β).

Molecular Structure

ORTEP views of the molecular structures of the nitroxides are shown in Figure 1. There are two crystallographically-independent molecules, **1a** and **1b**, in the crystal of **1**, while one molecule is independent in **2** and a half of molecule is independent in **3**(β). Table II shows the dihedral angles between the following three planes: (1) Nitronyl nitroxide, O1, O1', N2, N2', C3; (2) Phenyl ring, C7, C8, C8', C9, C9', C10; (3) Nitro group, N11, O12, O12'. The dihedral angle between the planes (1)-(2) is about 30° for the molecule **1a**, **1b** or **2**. On the other hand, the (1)-(2) dihedral angle of **3**(β) is about 50°. Further, the (2)-(3) dihedral angle of **3**(β) is about twice as large as that of **2**. The (1)-(2) dihedral angles have been reported to be *ca.* 12° for **3**(α-phase)[8] and *ca.* 30° for **3**(γ-phase)[9],

TABLE II Dihedral angles (deg) between planes for the molecules, **1**-**3**(β).

plane no.	plane no.	**1a**	**1b**	**2**	**3**(β)
(1)[a]	(2)[b]	24.8(2)	31.3(2)	26.0(1)	51.0(3)
(2)	(3)[c]			7.9(3)	16.3(5)
(1)	(3)			25.2(5)	67.2(5)

a) Plane (1): O1, O1', N2, N2', C3.
b) Plane (2): C7, C8, C8', C9, C9', C10.
c) Plane (3): N11, O12, O12'.

respectively. The nitroxide **3**(β) is extremely-twisted, compared with the other ones. The molecular distortion in **3**(β) may be ascribed to the effect of an intermolecular interaction, as is shown later.

MO calculation

Spin densities and atomic charges have been calculated based on the determined molecular structures, **1a**, **2**, and **3**(β), by UHF- and RHF-CNDO methods, respectively. Results are listed in Table III. There is little difference in the spin density distribution among them: the spin densities are localized on the side of the nitronyl nitroxide and have little distribution in the phenyl or the nitrophenyl ring. This fact agrees well with the results of the magnetic resonance studies.[5,15] Each radical molecule has an anomalously-large negative spin density on C3, the α-carbons, reflecting the strong spin polarization effect in this radical family.

In the spin-restricted picture, the SOMO[16] of **1**, **2**, or **3**(β) originates from the anti-bonding combination between the π* orbitals of the NO groups with a node at the α-carbon atom. There is little penetration of the SOMO into the phenyl or nitrophenyl ring. However, the other frontier π-orbitals, for example NHOMO, NLUMO and so on, have population in the both sides of the molecule. It is characteristic of the α-substituted nitronyl nitroxide that the SOMO is localized in the extended π-conjugation system. We have reported the UV-VIS spectra of **1**-**3** in ref. 6, where we have tried to interpret the spectra by assuming the quinoid structure in **3**. However, the MO calculation in this study revealed that this assumption is invalid. The UV-VIS spectra should be interpreted by the substituent dependence of the frontier orbitals which have population in the α-substituents.

Both of the spin and electronic polarization effects are much enhanced in this radical family. The atomic charge calculation indicates large negative charges on the O-atoms in the NO and NO_2 groups, and large positive charges on the N- and H-atoms. The positive charge on N11, the N-atom in the NO_2 group, is much larger than those on N2 and N2' in the NO group, in **2** or **3**(β). This electronic polarization effect plays an important role to determine the molecular arrangements in the crystal, as is shown later.

TABLE III Calculated spin densities[a] and atomic charges[b] for the nitroxides **1a**, **2**, and **3**(β).

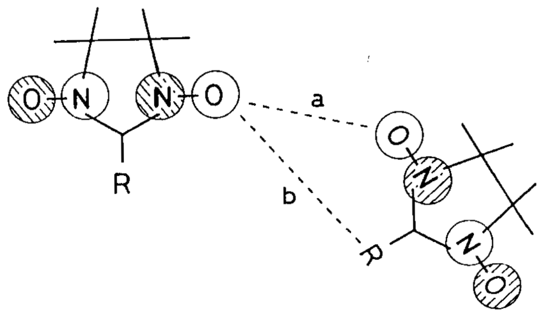
atom	spin densities			atomic charges		
	1 a	**2**	**3**(β)	**1 a**	**2**	**3**(β)
O1	0.423	0.437	0.442	-0.396	-0.382	-0.387
O1'	0.414	0.417		-0.403	-0.402	
N2	0.335	0.321	0.318	0.137	0.143	0.142
N2'	0.342	0.308		0.129	0.146	
C3	-0.474	-0.448	-0.498	0.056	0.043	0.026
C7	0.077	0.062	0.040	0.018	0.018	0.062
C8	-0.088	-0.067	-0.046	-0.083	-0.057	-0.080
C8'	-0.082	-0.066		-0.086	-0.070	
C9	0.050	0.038	0.025	-0.079	-0.033	-0.060
C9'	0.051	0.037		-0.088	-0.098	
C10	-0.071	-0.060	-0.045	-0.083	-0.062	-0.033
N11		-0.001	0.001		0.578	0.574
O12		0.002	-0.002		-0.355	-0.362
O12'		0.002			-0.372	
H8	0.000	0.000	0.000	0.121	0.143	0.117
H8'	0.000	0.000		0.123	0.131	
H9	0.000	0.000	-0.001	0.087		0.123
H9'	0.000	0.000		0.089	0.120	
H10	0.000	0.000		0.089	0.122	

a) by UHF-CNDO method.
b) by RHF-CNDO method.

CRYSTAL STRUCTURE

There is little difference in the spin density distribution among the nitroxides **1**-**3**(β). The difference in their magnetic coupling could not result from their intramolecular electronic states, but from their crystal structures. In this section, we discuss the magneto-structural correlation in the α-nitronyl nitroxide radicals, with respect to the conclusion of the MO calculation; localization of the SOMO in the extended π-conjugation.

The intermolecular contacts of the NO group can be classified into two types, as is illustrated in Scheme II. The contact (a) is between the NO groups (NO···NO), and the contact (b) is between the NO group and the substituent at the α-carbon (NO···R). We ignore the contact from the NO group to the atom without π orbital, C4-C6 and H-atoms, because they would make little contribution to the intermolecular magnetic coupling. The NO···NO contact (a) usually means the direct overlap between the SOMO's, with the exception of the case of the tanol suberate radical. In the crystalline state, this nitroxide radical takes an intermolecular mutual conformation in which the neighboring SOMO orbitals are orthogonal, and has an FM intermolecular interaction.[17] The nitroxides **1**-**3**(β) do not have such conformation as seen in the crystal of tanol suberate. Therefore, the type (a) contact in the crystals of **1**-**3**(β) means the intermolecular SOMO-SOMO



SCHEME II

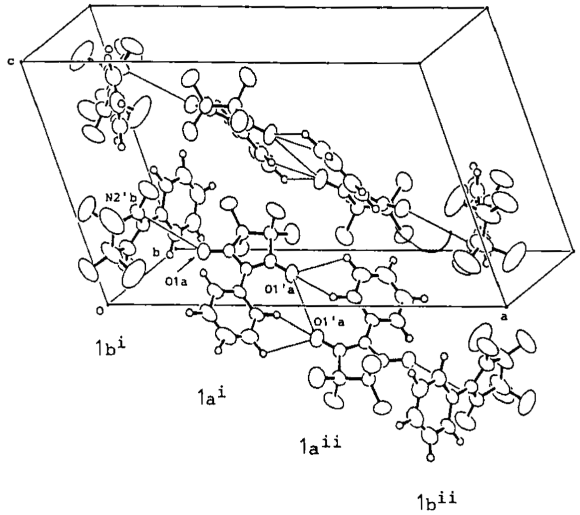


FIGURE 2 View of the unit cell of the nitroxide **1**.

overlap which always contributes to the AFM coupling.[2] On the other hand, the type (b) contact means the intermolecular orbital overlaps between the SOMO and the other orbitals. There is a possibility that such contacts contribute to the FM intermolecular interaction.[2]

Nitroxide **1**

Figure 2 shows a view of the unit cell of the nitroxide **1** which has the strongest AFM coupling among **1**-**3**(β). The shortest intermolecular, interatomic distance which belongs to the type (a) is 3.721(6) Å of $O1'a^{i}\cdots O1'a^{ii}$ (Symmetry operations; (i) x, y, z; (ii) -x+1, -y, -z). Since the type (a) distances in **2** or **3**(β) are longer than 4.9 Å, the NO···NO contact in **1** is much shorter than those in the other two. The distance of 3.721(6) Å is somewhat larger than the sum of the van der Waals radii, but it would be short enough to explain the AFM coupling of 1 K. The intermolecular arrangement between the molecules (i) and (ii) also includes the shortest distance of the type (b); 3.300(7) Å of $\mathrm{O1'a^{i}\cdots C8'a^{ii}}$.

Nitroxide 2

The crystal of 2 exhibits a 2D layer structure parallel to the *bc* plane. Figures 3(a) and (b) show the projections of the layer along the *c* axis and onto the *ac* plane, respectively. In this layer, each molecule is arranged with its aromatic part turned inside and its aliphatic

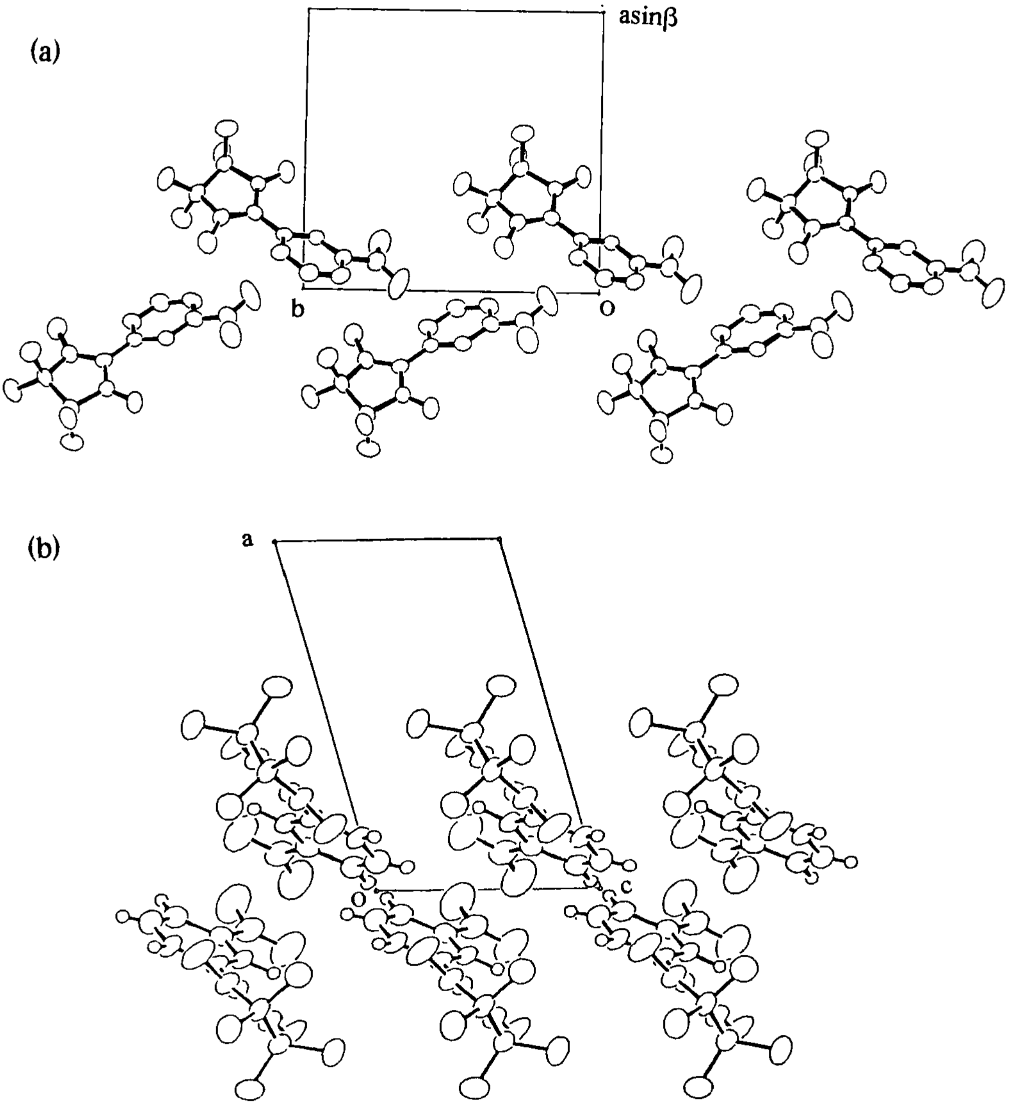


FIGURE 3 Projection of the 2D layer structure in 2, along the *c* axis (a) and onto the *ac* plane (b).

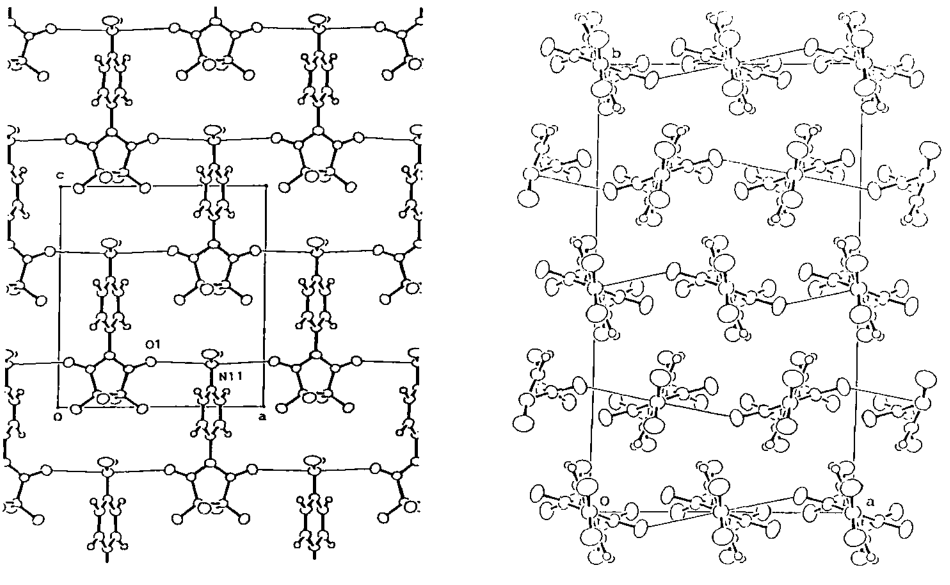
part turned outside. This 2D layer could be formed by the Coulombic interactions between the polar parts in the molecule 2, reflecting the strong electronic polarization effect.

In the crystal, the shortest intermolecular, interatomic distance which belongs to the type (b), is 3.176(7) Å of $O1'^{i}\cdots C10^{iii}$ (Symmetry operations; (iii) -x, y+0.5, -z+2). On the other hand, the shortest distance in the type (a) is 4.938(5) Å of $N2^{i}\cdots O1'^{ii}$ (Symmetry operations; (i) x, y, z; (ii) x, y, z-1). The former distance is much shorter than the latter one, but the nitroxide 2 exhibits the weak AFM interaction.

Nitroxide 3

The organic ferromagnet, nitroxide 3(β) has a complex 3D structure. Figure 4(a) shows the 2D network parallel to the *ac* plane.[10] Figure 4(b) shows the projection of the unit cell onto the *ab* planes. The 2D network is formed by the type (b) contacts between N11 and O1. The nitrophenyl ring is almost perpendicular to the $O1^{ii}\cdots N11^{i}\cdots O1^{iii}$ vector (Symmetry operations; (i) x, y, z; (ii) -x,-y+0.5 z+0.5 (iii) x+0.5, y, z+0.5). The intermolecular, interatomic distance between O1 and N11 is 3.369(3) Å, which could be due to the Coulombic attractive force, $O^{\delta-}\cdots N^{\delta+}$.

As are shown in Figure 5, there are molecular stackings along both of the [110] and [$\bar{1}$10] directions, which are crystallographically-equivalent. Each molecule is connected by the intermolecular contacts between O1 in the NO group and the phenyl ring.



(a) (b)

FIGURE 4 (a) 2D network in 3(β) parallel to the *ac* plane. (b) Projection of the unit cell in 3(β) onto the *ab* plane.

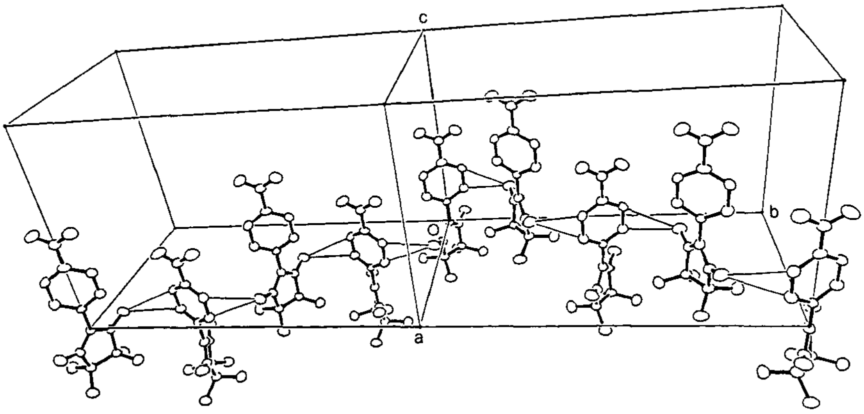


FIGURE 5 View of the molecular stackings along both of the [110] and $[\bar{1}10]$ directions in 3(β).

When the NO groups in one molecule have contacts with the phenyl rings in the two neighboring molecules along the [110] direction, its phenyl ring does with the NO groups along the $[\bar{1}10]$ direction, and *vice versa* (see the central molecule in Figure 5). The molecular distortion in 3(b) should be ascribed to these intermolecular contacts, in addition to the $O^{\delta-}\cdots N^{\delta+}$ contacts in the 2D network. The two directional molecular stackings are reticulately combined, forming a 3D lattice. The type (b) distances from $O1^{i}$ to $C8^{iv}$ and $C9^{iv}$ in the phenyl ring, are 3.218(5) Å and 3.247(5) Å, respectively (symmetry operation; (iv) x-0.25,-y+0.25, z-0.25).

Magneto-structural correlation

There are some type (a) contacts less than 4 Å in the crystal of **1** which includes the strongest AFM coupling among **1**-**3**(β), while the shortest NO···NO distance in **2** or **3**(β) is longer than 4.9 Å. There seems to be a relation between the NO···NO distance and its magnetic coupling: the shorter the distance between the NO groups, the stronger the AFM interaction. The FM nitroxide **3**(β) confidently has the type (b) contacts (NO···NO_2 contact and so on) less than 3.5 Å, but the AFM nitroxides **1** and **2** also do. Unfortunately, the correlation between the magnetic interaction and the NO···R distance is not so clear, at least in the studies for **1**-**3**(β). The idea that the magneto-structural correlation in the α-nitronyl nitroxide radical family is dominated by the competition between the AFM interaction due to the NO···NO contacts and the FM one due to the NO···R contacts, is supported in the studies for *m*-*N*-methylpyridinium α-nitronyl nitroxide with a stronger FM coupling.[9]

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REFERENCES

1. K. Mukai, H. Nishiguchi and Y. Deguchi, J. Phys. Soc. Jpn., 23, 125 (1967); K. Mukai, Bull. Chem. Soc. Jpn., 42, 40 (1969); K. Awaga, T. Sugano and M. Kinoshita, J. Chem. Phys., 128, 587 (1986).
2. K. Awaga, T. Sugano and M. Kinoshita, Chem. Phys. Lett., 141, 540 (1987).
3. K. Awaga, T. Sugano and M. Kinoshita, Synth. Metal, 27, B631 (1988).
4. H. M. McConnell, Proc. Robert A. Welch Found. Chem. Res., 11, 141 (1967).
5. D. G. B. Boocock and E. F. Ullman, J. Am. Chem. Soc., 90, 6873 (1968); E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, J. Am. Chem. Soc., 194, 7049 (1972).
6. K. Awaga and Y. Maruyama, Chem. Phys. Lett., 158, 556 (1989); J. Chem. Phys., 91, 2743 (1989).
7. K. Awaga, T. Inabe and Y. Maruyama, Mat. Res. Soc. Symp. Proc., 173, 33 (1990).
8. K. Awaga, T. Inabe and Y. Maruyama, Chem. Phys. Lett., 190, 349 (1992).
9. K. Awaga,T. Inabe, T. Nakamura, M. Matsumoto and Y.Maruyama, Chem. Phys. Lett., 195, 21 (1992).
10. K. Awaga, T. Inabe, U. Nagashima and Y. Maruyama, J. Chem. Soc. Chem. Commun., 1617 (1989). In this paper, we have taken an incorrect space group. See the Corrigenda, J. Chem. Soc. Chem. Commun., 520 (1990).
11. P. Turek, K. Nozawa, D. Shiomi, K.; Awaga, T. Inabe, Y. Maruyama and M. Kinoshita, Chem. Phys. Lett., 180, 327 (1991).
12. P. -M. Allemand, C. Fite, P. Canfield, G. Srdanov, N. Keder, and F. Wudl, Synth. metal, 41-43, 3291 (1991).
13. M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe and Y. Maruyama, Chem. Lett., 1225 (1991); M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa, M. Kinoshita, Phys. Rev. Lett., 67, 746 (1991); M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita,.Chem. Phys. Lett., 186, 401 (1991).
14. W. Wang and S. F. Watkins, J. Chem. Soc. Chem. Commun., 888 (1973).
15. M. S. Davis, K. Morokuma and R. W. Kreilick, J. Am. Chem. Soc., 94, 5588 (1972); J. W. Neely, G. F. Hatch and R. W. Kreilick, J. Am. Chem. Soc., 96, 652 (1974).
16. SOMO is the singly-occupied MO. NHOMO and NLUMO are defined as the highest doubly-occupied and the lowest unoccupied MO, respectively.
17. C. Veyret and A. Blaise, Mol. Phys., 25, 873 (1973); G. Chouteau and C. Veyret-Jeanday, J. Phys. (Paris), 42, 1441 (1981); A. Capiomont, Acta Crystallogr., B28, 2298 (1972); P. J. Brown, A. Capiomont, B. Gillon and J. Schweizer, J. Mag. Mag. Mat., 14, 289 (1979).
18. G. M. Sheldrick, G. M. SHELXS-86 (1986). Program for crystal structure determination. Univ. of Göttingen, FRG.