

两个氮氧自由基的合成与晶体结构:双自由基与阳离子自由基

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摘要: 合成并表征了 2 个氮氧自由基: 2,2'-(2,5-二甲苯基)-1,4-双(4,4,5,5-四甲基咪唑啉-3-氧化-1-氧基)自由基 **1** 和水合碘化 *m*-*N,N',N''*-三甲基苯铵基)-4,4,5,5-四甲基咪唑啉-3-氧化-1-氧基自由基 **2**。双自由基 **1** 和阳离子自由基 **2** 均结晶于单斜晶系, $P2_1/c$ 空间群。通过分子间的氢键作用, 2 个化合物形成三维超分子体系。

关键词: 氮氧自由基; 双自由基; 阳离子自由基; 晶体结构

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Syntheses and Crystal Structures of Two Nitronyl Nitroxide: Biradical and Cationradical

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Abstract: Two nitronyl nitroxide radical $\text{NIT}_2\text{PhMe}_2$ (**1**), 2,5-dimethyl-1,4-bis(nitronyl nitroxide) benzene and $\text{NITPhNMe}_3 \cdot \text{I} \cdot \text{H}_2\text{O}$ (**2**), hydrous iodide *m*-*N,N',N''*-trimethyl-benzenaminium nitronyl nitroxide, have been synthesized and structurally characterized. The compound **1** crystallized in monoclinic, space group $P2_1/c$ with $a=0.613\,7(4)$ nm, $b=1.766\,2(12)$ nm, $c=1.180\,9(6)$ nm, $\beta=117.66(3)^\circ$, $V=1.133\,7(13)$ nm³, $M_r=416.52$, $Z=2$ and $F(000)=456$. The compound **2** also crystallized in monoclinic, space group $P2_1/c$ with $a=1.143\,47(11)$ nm, $b=1.119\,09(11)$ nm, $c=1.527\,38(15)$ nm, $\beta=101.766(2)^\circ$, $V=1.9134(3)$ nm³, $M_r=436.31$, $Z=4$ and $F(000)=884$. Through the weak hydrogen bond, **1** and **2** form three-dimensional supramolecular networks, respectively. CCDC: 749328, **1**; 749329, **2**.

Key words: crystal structure; nitronyl nitroxide; biradical; cationradical

Since Veyret et al. reported the magnetic behavior of several nitroxide radicals^[1] in the field of molecular magnetic materials, numerous important results have been obtained by constructing from metal and stable organic radicals^[2-8]. Amongst this field, the nitronyl nitroxide free radicals might play an essential role, thus are normally used due to their exceptional stability and ease chemical modification^[9] as well as their role of spin

carries to increase the spin density of magnetic system. In most of the system studied so far, the nitronyl nitroxides act in a bridging fashion and are found in axial position of the metallic coordination environments, thus leading to metal-radical alternating chain that may order ferromagnetically only at low critical temperatures (T_c)^[4,10]. In order to overcome this limitation to obtain comprising magnet of higher T_c , two basic

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strategies have been developed. One approach uses the functionalized nitronyl nitroxide radicals. The substituent groups on the radicals, such as benzaldehyde^[11], carboxyl^[12], mono-or multi-pyridine^[13], phosphine system^[14], triazole^[15] and others^[16], which contain ligated atoms can in principle enforce the coordination and connect different chains, giving rise to two-or hopefully three-dimensional structures^[7a,16b]. However, the cation radical can be regarded as expand functional one as result of two reasons: (1) stronger coordination owing to the electron draw of the cation group, (2) stronger supramolecular interaction due to the electrostatic attractability from the cation group. In the second approach, as bridging units, polyradicals^[5,17-18] which possess multi-nitroxide donors could also lead to obtain prospective high dimensional, stronger couple and higher T_c magnetic system. Despite the readily available synthetic procedures allowing the preparation of functionalized and poly-radicals, surprisingly multi- as well as cation nitroxides are less developed^[19]. Herein we report the syntheses and single-crystal structures of two new nitronyl nitroxides: biradical $\text{NIT}_2\text{PhMe}_2$ (**1**), 2,5-dimethyl-1,4-bis (nitronyl nitroxide) benzene and cation radical $\text{NITPhNMe}_3 \cdot \text{I} \cdot \text{H}_2\text{O}$ (**2**), hydrous iodide *m*-*N,N',N''*-trimethyl-benzenaminium nitronyl nitroxide.

1 Experimental

1.1 Materials and apparatus

The 2-nitro-propane,4-amino-bezenealdehyde and dimethyl sulfate were purchased from Acros company. All reagents were of analytic grade and were used without further purification. 2,3-bis (hydroxylamino)-2,3-dimethyl butane was prepared according to the literature^[20], and the 2,5-dimethyl-1,4-dialdehydebenzene was prepared according to literatures^[21,22]. Infrared spectra were recorded in the range of 400~4 000 cm^{-1} taken on a Nicolet FTIR 7199B spectrophotometer by using KBr pellets. The elements analyses of C, H and N contents were performed on a Carlo Erballo analyzer.

1.2 Synthesis of $\text{NIT}_2\text{PhMe}_2$ (**1**)

To a solution of 2,5-dimethyl-1,4-dialdehydebenzene (1.09 g) in anhydrous benzene (60 mL) was added 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2.0 g). The

resulting mixture was refluxed (80 $^{\circ}\text{C}$) for 12 h, then cooled to room temperature and filtered to afford light yellow residue. The remanent procedure was prepared following the Ullman method^[23]. Purple block single crystals suitable for X-ray analysis were obtained by slow evaporation solution of $\text{NIT}_2\text{PhMe}_2$ in $\text{MeOH}/\text{CH}_3\text{CN}$ (1:1) at -4°C for four weeks. Anal. Calcd (%) for $\text{C}_{22}\text{H}_{34}\text{N}_4\text{O}_4$: C, 63.13; H, 8.19; N, 13.39. Found (%): C, 63.43; H, 8.36; N, 13.27.

1.3 Synthesis of $\text{NITPhNMe}_3 \cdot \text{I} \cdot \text{H}_2\text{O}$ (**2**)

To a solution of 4-amino-bezenealdehyde (0.61 g) in MeOH (60 mL) was added 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2.0 g). The resulting mixture was refluxed for 12 h, then cooled to room temperature and filtered to afford light blue residue. The remanent procedure was prepared following the Ullman method^[23]. The intermediate radical was dissolved in 10 mL MeOH , and then 1 mL dimethyl sulfate dropwise added. Stirred rigorous and filtered, the filtrate kept at -4°C . Blue block single crystals suitable for X-ray analysis were obtained by slow evaporation solution for several weeks. Anal. Calcd (%) for $\text{C}_{16}\text{H}_{27}\text{IN}_3\text{O}_3$: C, 44.04; H, 6.24; N, 9.63. Found(%): C, 43.93; H, 6.36; N, 9.27.

1.4 Structure determination

A purple crystal of $\text{NIT}_2\text{PhMe}_2$ (**1**) with dimensions of 0.25 mm×0.20 mm×0.10 mm was mounted on the top of a glass fiber. X-ray diffraction intensity data were collected on Bruker SMART 1000 CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). A total of 4 571 reflections were collected in the $2.26^{\circ} \leq \theta \leq 25.03^{\circ}$ range at 273(2) K and 2 005 were independent ($R_{\text{int}}=0.057\ 1$), of which 1 068 were observed reflections with $I>2\sigma(I)$. The final $R=0.059\ 6$, $wR=0.139\ 2$ ($I>2\sigma(I)$) ($w=1/[\sigma^2(F_o^2)+(0.091\ 2P)^2]$, where $P=(F_o^2+2F_c^2)/3$).

A deep blue crystal of $\text{NITPhNMe}_3 \cdot \text{I} \cdot \text{H}_2\text{O}$ (**2**) with dimensions of 0.25 mm×0.22 mm×0.18 mm was mounted on the top of a glass fiber. X-ray diffraction intensity data were collected on Bruker SMART 1000 CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). A total of 15 202 reflections were collected in the $2.27^{\circ} \leq \theta \leq 26.99^{\circ}$ range at 273(2) K and 4 096 were independent

($R_{\text{int}}=0.035\ 5$), of which 3 310 were observed reflections with $I>2\sigma(I)$. The final $R=0.040\ 0$, $wR=0.090\ 7$ ($I>2\sigma(I)$) ($w=1/[\sigma^2(F_o^2)+(0.045\ 6P)^2+1.164\ 3P]$, where $P=(F_o^2+2F_c^2)/3$).

For both **1** and **2**, the empirical absorption corrections by SADABS were performed and the structures were solved by direct methods with SHELXS-97 program and refined with SHELXL-97 by full-matrix least-

squares techniques on F^2 ^[24]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically and refined isotropically. The crystallographic data and details on refinements for **1** and **2** are summarized in Table 1 and the selected bond distances and bond angles are listed in Table 2.

CCDC: 749328, **1**; 749329, **2**

Table 1 Crystal data and structure refinements for the two compounds

Empirical formula	C ₂₂ H ₃₄ N ₄ O ₄ (1)	C ₁₆ H ₂₇ IN ₃ O ₃ (2)
Crystal size / mm	0.25×0.20×0.10	0.25×0.22×0.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	0.613 7(4)	1.143 47(11)
b / nm	1.766 2(12)	1.119 09(11)
c / nm	1.180 9(6)	1.527 38(15)
β / (°)	117.66(3)	101.766(2)
V / nm ³	1.133 7(13)	1.913 4(3)
Z	2	4
θ range / (°)	2.26~25.03	2.27~26.99
Temperature / K	273(2)	273(2)
Radiation (Mo $K\alpha$), λ / nm	0.071 073	0.071 073
μ / mm ⁻¹	0.085	1.691
D_c / (g·cm ⁻³)	1.232	1.515
$F(000)$	448	884
Index ranges (h, k, l)	-7/7, -17/21, -6/14	14/-14, 14/-14, -19/19
Measured reflections	2 005	4 096
Observed reflections ($I>2\sigma(I)$) (R_{int})	1 068 (0.057 1)	3 310 (0.035 5)
Data / restraints / parameters	2 005 / 0 / 143	4 096 / 0 / 208
Goodness-of-fit on F^2	0.965	1.021
R, wR ($I>2\sigma(I)$)	0.059 6, 0.139 2	0.040 0, 0.090 7
R, wR (all data)	0.129 5, 0.168 9	0.052 4, 0.096 6
Largest diff. peak and hole / (e·nm ⁻³)	315 / -341	789 / -385

Table 2 Selected bond lengths (nm) and bond angles (°)

Compound 1					
O(1)-N(2)	0.126 9(3)	N(1)-C(5)	0.133 9(4)	N(2)-C(6)	0.150 3(4)
O(2)-N(1)	0.127 1(3)	N(1)-C(9)	0.150 8(3)	N(2)-C(5)	0.133 7(3)
O(2)-N(1)-C(9)	121.5(2)	O(1)-N(2)-C(6)	121.2(2)	N(2)-C(5)-C(3)	126.4(3)
C(5)-N(1)-C(9)	112.6(2)	C(5)-N(2)-C(6)	112.7(2)	N(1)-C(5)-C(3)	124.5(2)
O(1)-N(2)-C(5)	125.9(2)	N(2)-C(5)-N(1)	109.1(2)		
Compound 2					
O(1)-N(1)	0.127 6(3)	C(7)-N(2)	0.134 8(4)	C(14)-N(3)	0.150 6(4)
O(2)-N(2)	0.127 7(3)	C(8)-N(2)	0.150 0(4)	C(15)-N(3)	0.150 4(4)
C(7)-N(1)	0.134 2(4)	C(9)-N(1)	0.149 9(4)	C(16)-N(3)	0.151 4(4)

Continued Table 2

O(1)-N(1)-C(7)	126.5(3)	O(1)-N(1)-C(9)	120.9(2)	C(14)-N(3)-C(16)	110.2(3)
O(2)-N(2)-C(7)	125.9(2)	C(1)-N(3)-C(14)	109.3(2)	C(15)-N(3)-C(14)	107.5(2)
N(1)-C(7)-N(2)	108.9(3)	C(1)-N(3)-C(15)	112.5(2)	C(15)-N(3)-C(16)	107.8(2)
N(1)-C(7)-C(4)	125.3(3)	C(1)-N(3)-C(16)	109.6(2)		

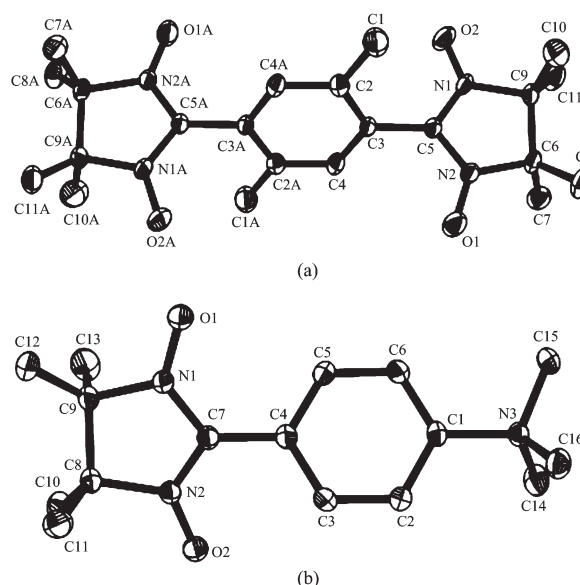
2 Results and discussion

2.1 Crystal structure

2.1.1 Compound 1

1 crystallizes in the monoclinic space group $P2_1/c$. The molecular structure of **1** is shown in Fig.1a. The X-ray crystal analyses reveal that the compound is central-symmetric molecule, which symmetric center locates the central of the phenyl. Both two methyl groups are coplanar with phenyl ring, but owing to the spatial baffle, the nitronyl nitroxide moieties are not coplanar with phenyl ring. The dihedral angle defined by the ONCNO plane and the phenyl ring is 65.53° , which is very closed to that one with carboxyl substitute^[12b]. The two N-O distances in the both nitronyl nitroxide moieties are very close, which are 0.126 9(3) (N(2)-O(1)) and 0.127 1(3) nm (N(1)-O(2)), respectively, as is generally observed^[3]. Shown in Fig.2a, the weak hydrogen bond between the C atom of methyl group in the nitronyl nitroxide moiety and O atom of N-O group between adjacent radicals led to form a chain (the distance of the C-H \cdots O is about 0.349 nm). Moreover, owing to the similar weak hydrogen bond between the C

atom of methyl group and O atom of N-O group from another chain, these chains form a supramolecular layer. Consequently, due to the similar mode hydrogen bond between O atom of N-O group and the C



Hydrogen atoms for **1** and **2**, iodine and lattice water for **2** were omitted for clarity

Fig.1 Drawing of molecule of **1** (a): NIT₂PhMe₂ and **2** (b): NITPhNMe₃⁺

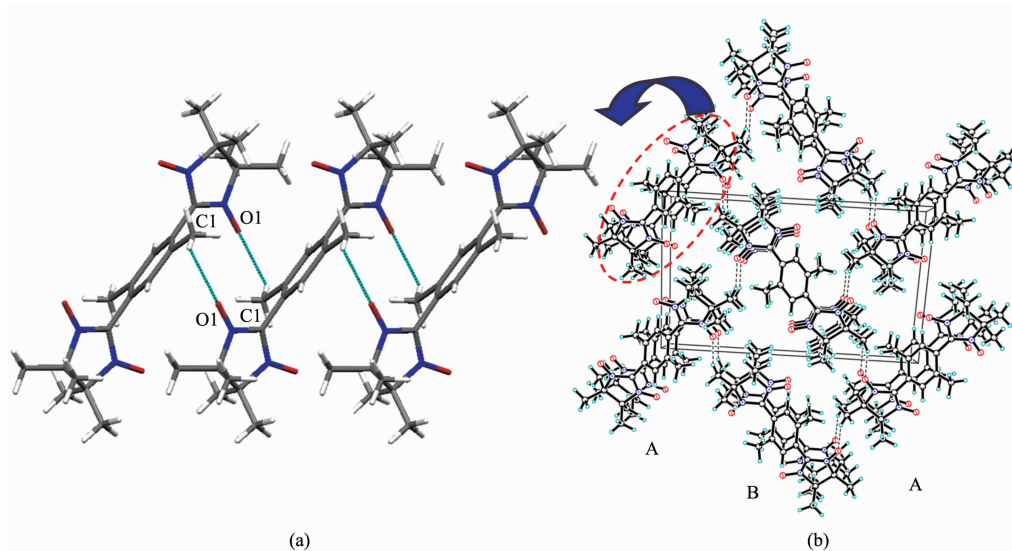


Fig.2 (a) C-H \cdots O hydrogen bonds (distance of C1 \cdots O1 is 0.349 nm) in chains, (b) Packing diagram of **1** with hydrogen bonds among immediate chains and the ABA stacking fashion

atom of methyl group (the distance of the C-H \cdots O is about 0.334 nm), the adjacent layers are stacked in an ABAB fashion into a supramolecular three-dimensional structure.

2.1.2 Compound 2

2 also crystallizes in the monoclinic space group $P2_1/c$. The partial molecular structure of NITPhNMe₃ cation of **2** is shown in Fig.1b. The two N-O distances are similar to that in **1**, which are 0.127 6(3) and 0.127 7(3) nm, respectively. If the I⁻ and lattice water are neglected, the NIT cations through the CH- π stacking of phenyl moieties (distance 0.399 7 nm, which is about 0.3 nm deducting the C-H length) and the weak hydrogen bond between the C atom of methyl from

N(Me)₃ group and O atom of N-O group in the nitronyl nitroxide moiety (the distance of the C-H \cdots O is about 0.368 and 0.388 nm, respectively) between adjacent radical cations by head-to-end fashion to form a chain. Moreover, these chains, owing to the weak hydrogen bonds between the C atom from N(Me)₃ moiety and O atom of N-O group to form a supramolecular layer, and the I⁻ and lattice water are located the interspace between the layers (Fig.3). The closest distance between the I⁻ ions, which clogged by lattice water, are about 0.615 nm. The distance between the I⁻ and O atom from adjacent lattice water is about 0.378 nm, indicated which possessing strong hydrogen bond with considering the big radii of I⁻ (0.216 nm)^[25].

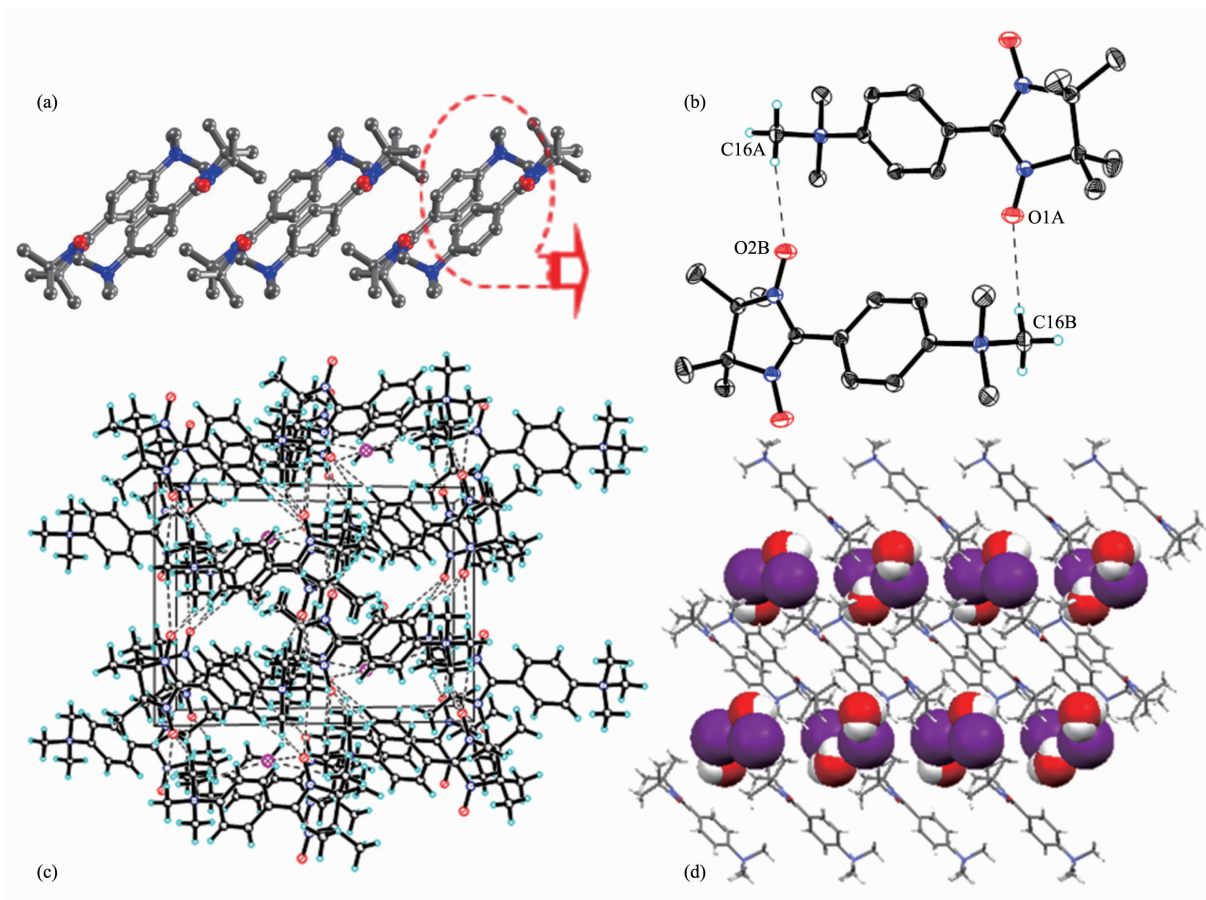


Fig.3 (a) Packing along b -axis of a NIT⁺ layer in **2**; (b) C-H \cdots O hydrogen bonds between NIT⁺ (the distances are 0.368 and 0.388 nm for O1 \cdots C16 and O2 \cdots C16, respectively); (c) Packing diagram of **2**; (d) Space-filling views of I⁻ (purple) and the lattice water between the NIT⁺ layers

2.2 FTIR spectroscopy

Fourier Transform Infrared (FTIR) spectra of both compounds were recorded in the range of 400~4 000 cm⁻¹ by using KBr pellets. The strong peak, at 1 371

cm⁻¹ for **1** and 1 365 cm⁻¹ for **2**, respectively, are belong to the symetric vibratoin of the N-O group from the nitronyl nitroxide partial, which is the characteristic vibratoin of the N-O group of nitronyl nitroxide free

radicals^[7,16c].

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