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Exceptionally Persistent Nitrogen-Centered Free Radicials. Magnetic Behaviour and X-Ray Crystallo Graphy Structures of N-(Arylthio)-2-Tert-Butyl-4,6-Diarylphenylaminyl and N-(Aryl-Thio)-4-Tert-Butyl-2,6-Diarylphylphenylaminyl Radicals

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EXCEPTIONALLY PERSISTENT NITROGEN-CENTERED FREE RADICALS. MAGNETIC BEHAVIOR AND X-RAY CRYSTALLOGRAPHIC STRUCTURES OF *N*-(ARYLTHIO)-2-*TERT*-BUTYL-4,6-DIARYLPHENYLAMINYL AND *N*-(ARYL-THIO)-4-*TERT*-BUTYL-2,6-DIARYLPHENYLAMINYL RADICALS

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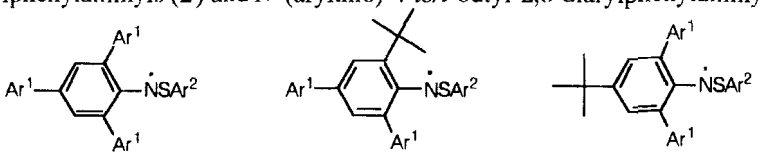
Abstract The generation, isolation, X-ray crystallographic structures, and magnetic behavior of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**2**) and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**3**) are described. Radicals **2** and **3** were generated by PbO_2 oxidation of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylanilines and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylanilines, and seven radicals were isolated as the pure radical crystals. The X-ray crystallographic structures of *N*-[(4-nitrophenyl)thio]-6-*tert*-butyl-2,4-diphenylphenylaminyl and *N*-[(4-nitrophenyl)thio]-4-*tert*-butyl-2,6-diphenylphenylaminyl radicals were determined. The magnetic susceptibility measurements for the isolated radicals were carried out in the temperature range 1.8 - 300 K with a SQUID magnetometer. Among the four radicals studied the two were analyzed by an alternating one-dimensional Heisenberg model with J_1/k = -1.8 (α = 0.86) and -18.2 K (α = 0.16), and the other two were analyzed by a one- dimensional regular Heisenberg model with J_1/k = -30.8 K or a singlet-triplet dimer model with J_1/k = -45.2 K

INTRODUCTION

For recent years the chemistry of stable free radicals have been largely stimulated by the expectation that organic free radicals might have ferromagnetic properties.[1] However, most of the stable free radicals investigated from the viewpoints of magnetism have been limited to nitroxides and nitronyl nitroxides which have a localized unpaired electron spin. We have therefore made an effort to search for a new class of stable free radicals. Our extensive studies on thioaminyls[2] (RNSR') have shown that *N*-(arylthio)-2,4,6-triarylphenylaminyls (**1**) are exceptionally stable and can be isolated as pure radical

crystals.[3] The magnetic studies have shown that three aminyls exhibit ferromagnetic coupling with the J_1/k values of 1.8 - 14.0 K.[4] Herein we report generation, isolation, X-ray crystallographic structures, and magnetic behavior of *N*-(arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**2**) and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**3**).

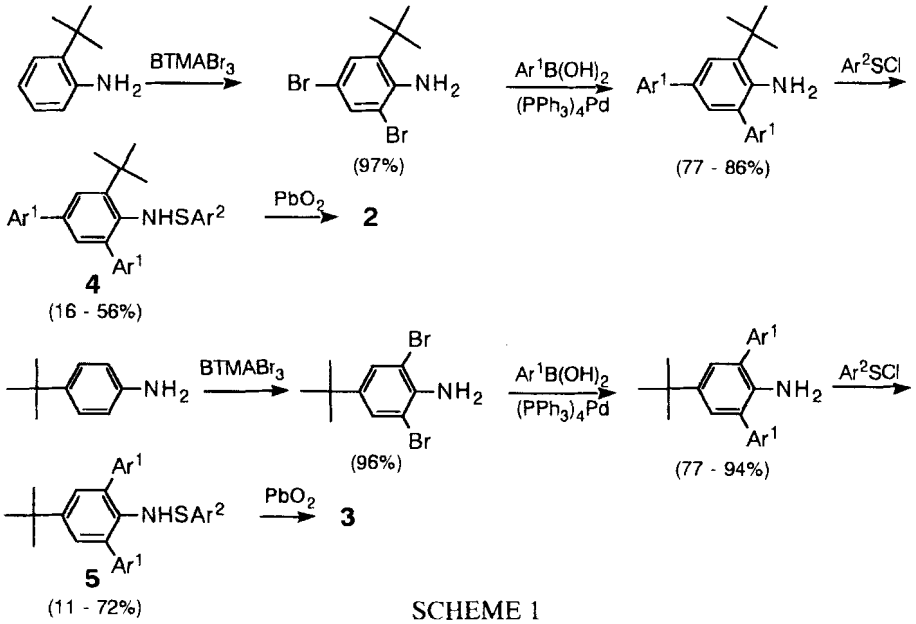


1 **2** **3**

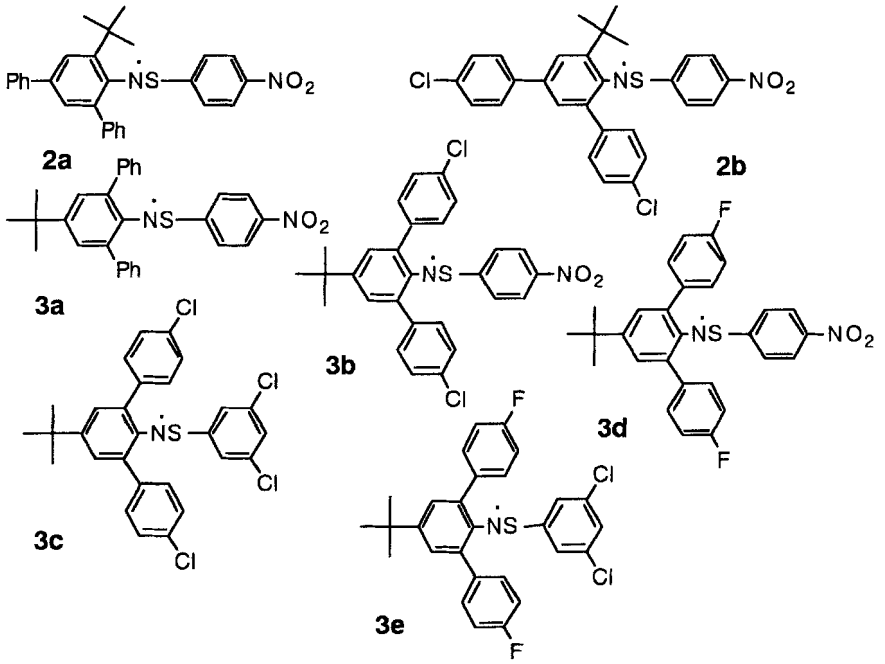
RESULTS AND DISCUSSION

Preparation of Thioaminyl Radicals

Precursors **4** and **5** were prepared according to Scheme 1. Radicals **2** and **3** were generated by oxidation of **4** or **5** with PbO_2 in benzene. Like **1**, aminyls **2** and **3** were quite stable, even in the presence of oxygen, and showed that they existed in the individual radical form even at low temperatures. Their isolation was tried, and radicals **2a**, **2b**, **3a** - **3e** were isolated as pure radical crystals in 33 - 56% yields. The stabilities of the solid radical crystals depended on the crystal conditions. Although the powdery microcrystals decomposed slowly even on storage at 0 °C, sufficiently big crystals showed no decomposition on storage of a long period at 0°C.



SCHEME 1



ESR Spectra of **2** and **3**

ESR measurements of **2** and **3** were performed at room temperature using benzene as a solvent. In Figure 1, an ESR spectrum of *N*-[(3,5-dichlorophenyl)thio]-2-*tert*-butyl-4,6-di(phenyl-d_5)phenylaminyl (**2c**) is illustrated. As can be seen from Figure 1, all the ESR spectra are split into a 1 : 1 : 1 triplet, and in some spectra each of the triplet is further split by the interaction with aromatic protons. Upon deuteration of the phenyl groups at the anilino group satellite lines due to ^{33}S at natural abundance (0.76%) could be detected in the both wings, on recording at high gain. The hyperfine coupling constants obtained from the ESR measurements of **2** and **3** are summarized in Figure 2.

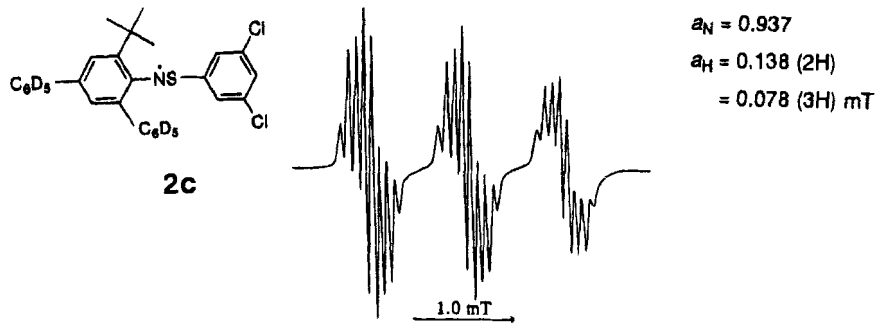


FIGURE 1. ESR spectrum of **2c** in benzene at 20 °C. The hyperfine coupling constants were determined by computer simulations.

It is obvious from Figure 2 that the unpaired electron spin is extensively delocalized over the whole of the radicals. Furthermore, no observation of the hyperfine couplings due to the 2,4- or 2,6-diaryl protons indicates that the delocalization of the unpaired electron spin onto the 2,4- or 2,6-diaryl groups is very or negligibly small. This spin density distribution pattern is supported by the McLachlan MO calculations.

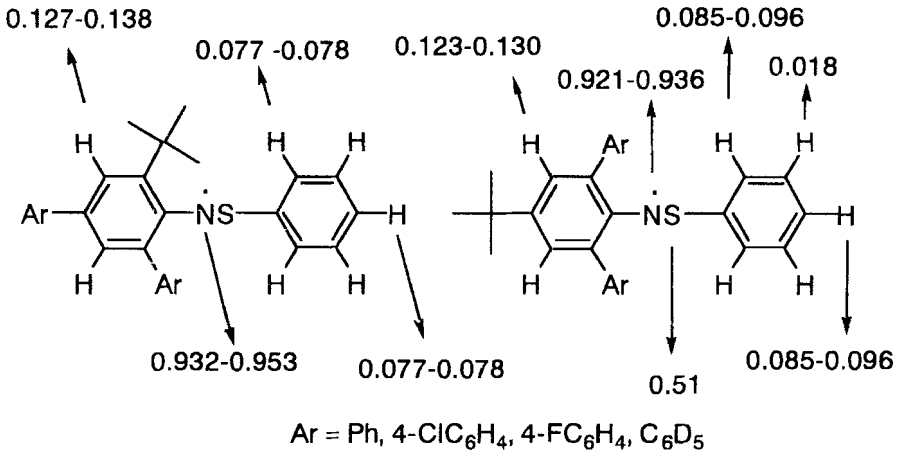


FIGURE 2. Observed hyperfine coupling constants (mT) for **2** and **3**

X-ray Crystallographic Analyses of **2a** and **3a**

Upon recrystallization from ethanol (**2a**) or hexane (**3a**), a sufficiently large single crystal suitable for X-ray crystallographic analysis was provided. Figures 3 and 4 show molecular and crystal structures of **2a** and **3a**.[5,6]

Figure 3 shows the following structural features: The N and S atoms are coplanar with the benzene ring A. This planar group makes a dihedral angle of 21° with the benzene ring D. The dihedral angle between the benzene rings A and C is 34°, while that between the benzene rings A and B is 87°, indicating that there are serious steric congestions around the N-S bond surrounded by a phenyl group and a *tert*-butyl group. On the other hand, Figure 4 shows the following structural features. The N and S atoms are coplanar with the benzene ring D (not A), and this planar group makes a dihedral angle of 21° with the benzene ring A. The benzene ring A makes a dihedral angles of 64° with the benzene ring B and 45° with the benzene ring C. Therefore, the steric congestions around the N-S bond surrounded by the two benzene rings are serious, but less than in **2a**. On the basis of the above X-ray results it is concluded that both radicals have an approximately planar π–framework consisting of the A and D benzene rings and N and S atoms. This conclusion is in accordance with the ESR results of **2** and **3** that show an

extensive delocalization of the unpaired electron spin to the anilino and phenylthiyl groups.

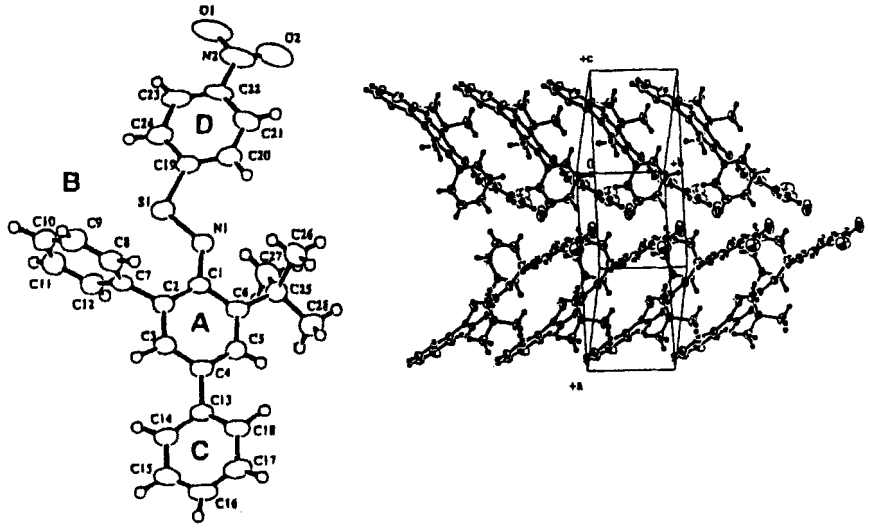


FIGURE 3. Molecular and crystal structures of **2a**.

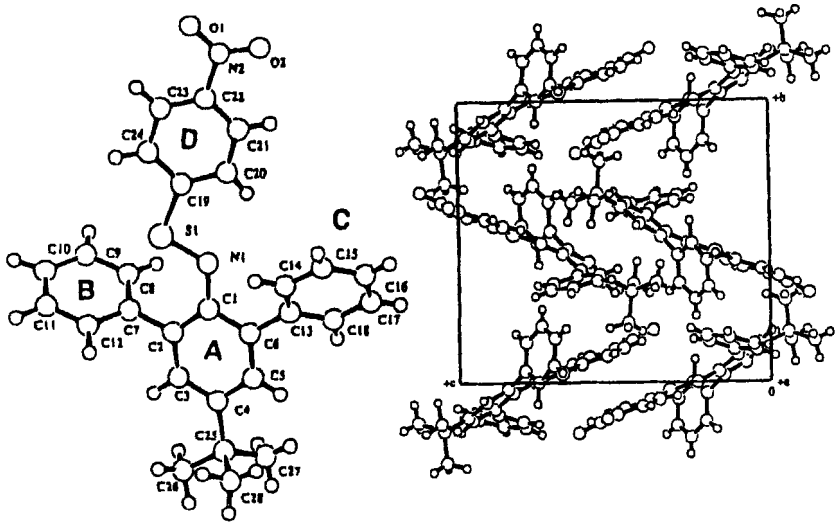


FIGURE 4. Molecular and crystal structures of **3a**.

Magnetic Behavior of the Isolated Thioaminyl Radicals.

The temperature dependence of the molar magnetic susceptibilities (χ_{mol}) of **2a**, **3a**, **3d**, and **3e** were investigated in the temperature range 1.8 - 300 K with a Quantum-Design

MPMS2 SQUID magnetometer. The correction of the diamagnetic components for the susceptibility was carried out by Pascal's sum rule.

Figure 5 shows χ_{mol} vs T plots of **2a** obtained. As found in the figure, the χ_{mol} vs T plots show a maximum at ca.40 K and give 3.0 x 10^{-3} emu mol^{-1} at 1.8 K. This experimental data was fitted by a one-dimentional regular (α = 1) Heisenberg model with J_1/k = -30.8 K. Further detailed magnetic studies of this radical at further low temperatures are in progress.

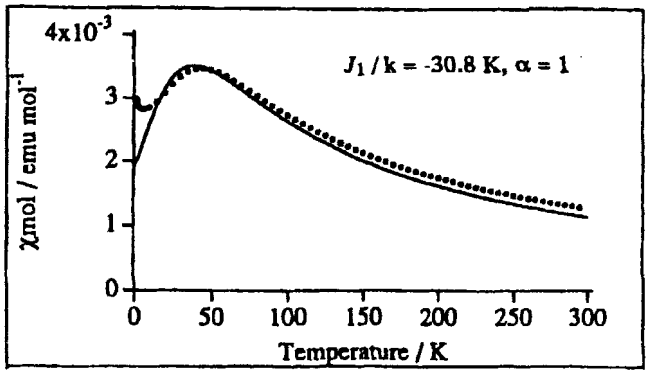


FIGURE 5. χ_{mol} vs T plots of **2a**

Figure 6 slows $\chi_{mol}T$ vs T plots of **3a**. In the Figure, the χ_{mol} T values are decreased with decreasing temperature, indicating that the unpaired electron spins couple antiferromagnetically in the low temperature region. This experimental curve was well analyzed by an alternating linear-chain model with J_1/k = -18.2 K and α = 0.16.

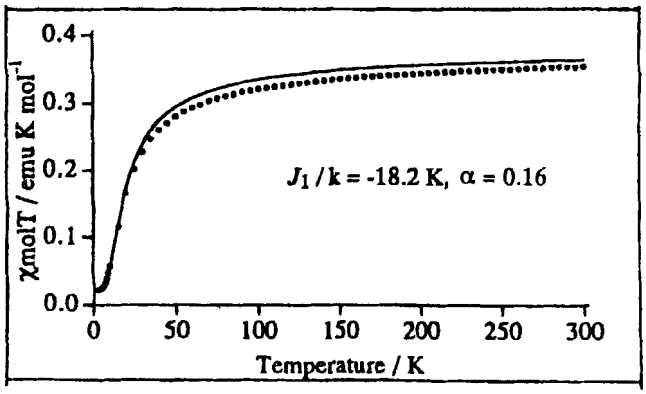


FIGURE 6. $\chi_{mol}T$ vs T plots of **3a**

The χ_{mol} T vs T plots for **3d** and **3e** are shown in Figures 7 and 8. In both figures, the χ_{mol} T values are decreased with decreasing temperature, indicating that both radicals couple antiferromagnetically. The experimental data of **3d** were analyzed in terms

of an alternating linear-chain Heisenberg model with J_1/k = -1.8 K and α = 0.86. On the other hand, those of **3e** were analyzed in terms of a singlet-triplet dimer model with J/k = -45.2 K.

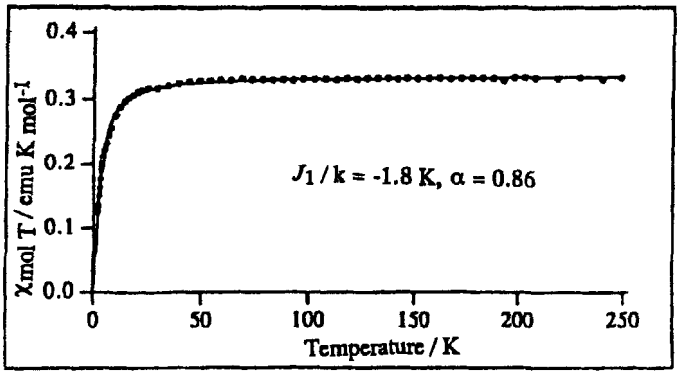


FIGURE 7. $\chi_{mol}T$ vs T plots of **3d**

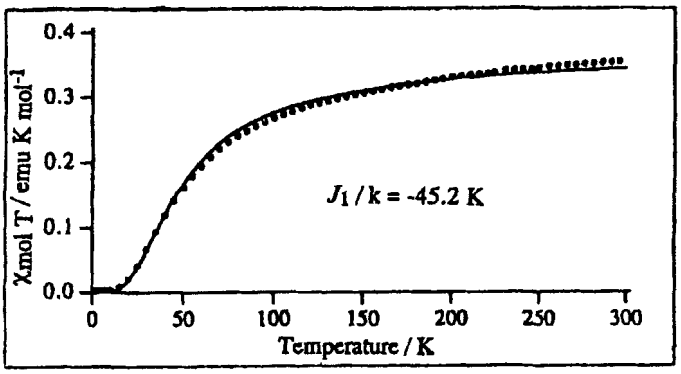


FIGURE 8. $\chi_{mol}T$ vs T plots of **3e**

CONCLUSIONS

N-(Arylthio)-2-*tert*-butyl-4,6-diarylphenylaminyls (**2**) and *N*-(arylthio)-4-*tert*-butyl-2,6-diarylphenylaminyls (**3**) were generated by PbO_2 oxidation of the corresponding precursors. Seven thioaminyls were isolated as pure radical crystals. The single crystal X-ray crystallographic analyses were performed for **2a** and **3a** and showed that the anilino benzene ring, N atom, and phenylthiyl group are almost coplanar. This conformation agreed with the ESR results for **2** and **3**. The SQUID magnetic studies of thioaminyl radicals were carried out. The χ_{mol} vs T and χ_{mol} T vs T plots showed the unpaired electron spins coupled antiferromagnetically to each other.

ACKNOWLEDGMENT

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5. The crystal data of **2a**: $C_{28}H_{25}N_2O_2S$ (453.58), monoclinic, space group $P2_1$, a = 14.095(5), b = 5.855(4), c = 14.124(3) Å, β = 90.92(2)°, V = 1165.5(8) Å^3, Z = 2, D_c = 1.29 g cm^{-3}.
6. The crystal data of **2a**: $C_{28}H_{25}N_2O_2S$ (453.58), monoclinic, space group $P2_1/n$, a = 11.434(2), b = 13.453(2), c = 15.860(2) Å, β = 101.46(1)°, V = 2390.9(6) Å^3, Z = 4, D_c = 1.268 g cm^{-3}.