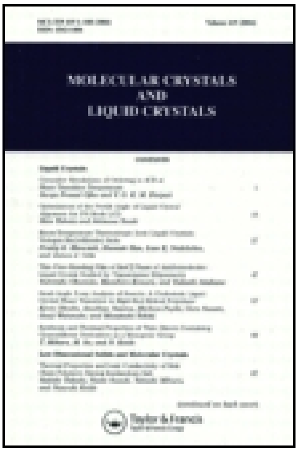

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PREPARATION AND PROPERTIES OF CHIRAL NITROXIDE RADICALS WITH HELICAL CRYSTAL STRUCTURE

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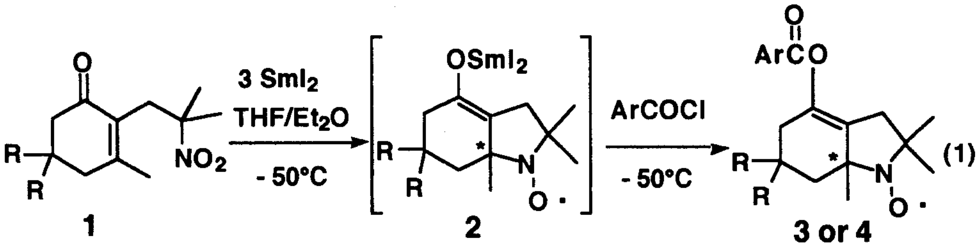
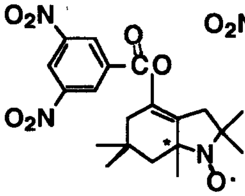
Abstract A new type of α-asymmetric bicyclic nitroxides were synthesized by three electron reduction of certain homoallylic nitroenones followed by the reaction with nitro-substituted benzoyl chlorides. Some nitroxides thus obtained turned out to exist as a conglomerate (racemic mixture), an equimolecular mixture of two crystalline enantiomers, and hence induced spontaneous optical resolution upon recrystallization. The relationship between the formation of conglomerates and their molecular and crystral structures is described, together with the preliminary results of their paramagnetic susceptibility mesurements.

INTRODUCTION

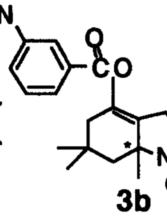
Besides the utilization of nitroxides as the stable free radical for spin-labeling[1] and trapping experiments[2] and as the precursor for organic oxidants,[3] they have been regarded as the potential component for elaboration of purely organic, paramagnetic advanced materials.[4] In this context, chiral nitroxide radical compounds bearing the quarternary asymmetric carbon center adjacent to the N-O radical moiety[5] are expected to exhibit unique optoelectronic properties by the appropriate molecular design owing to the large dipole moment ($\mu \fallingdotseq 3$ D) and magnetic moment of the N-O radical moiety and the molecular chirality. In this connection, we have found a new synthetic method of stable α-asymmetric bicyclic nitroxides by three electron reduction of the homoallylic nitroenone **1** giving the fairly stable radical anion intermediate **2** and the subsequent reaction with nitro-substituted benzoyl chlorides as the electrophile (Eq. 1).[6] During investigation of the scope and limitations of this synthetic method and the properties of the obtained nitroxides,[7] we observed that spontaneous optical resolution occurred upon recrystallization of some nitroxides. It is quite rare to obtain stable free radicals as conglomerates.[8] Therefore, in order to seek the source of the formation of conglomerate free radicals, we focused our attention on the relationship between the molecular and crystal structures of conglomerate nitroxide radicals. In this account we describe these results along with the preliminary results of their paramagnetic susceptibility mesurements by means of a SQUID magnetometer (T > 1.8 K).



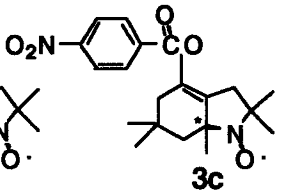
3a, 75%; 3b, 65%; 3c, 45%; 4, 70%



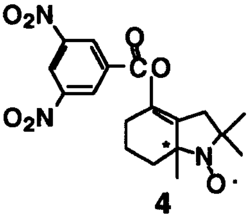
3a



3b



3c



4

PREPARATION OF α-ASYMMETRIC BICYCLIC NITROXIDES

To a solution of the nitroenone **1** (2.00 mmol) in the mixed solvent of ether (25 mL) and THF (15 mL) was dropwise added a freshly prepared THF solution of SmI_2 (ca. 0.10 M solution; 60 mL)[9] at -50°C under argon atmosphere, followed by stirring for additional 10 min at the same temperature. The powdered nitro-substituted benzoyl chloride (3.00 mmol) was added all at once to the yellowish brown solution at -50°C. The resulting red solution was slowly allowed to warm to room temperature over 1 h. After removal of the yellowish brown precipitate by filtration in the air, the filtrate was concentrated to give viscous oily red material, which was dissolved in chloroform and applied to short flash column chromatography on silica gel (19:1 hexane/ethyl acetate) to remove Sm-containing components. The crude products were purified by flash column chromatography on silica gel (19:1 hexane/ethyl acetate) judging the eluent by means of HPLC (a silica gel stationary-phase column; 97:3 hexane/2-propanol; UV-detector: 254 nm) analysis to give analytically pure **3a**, **3b**, **3c** and **4**.[7]

MOLECULAR AND CRYSTAL STRUCTURES OF CONGLOMERATES

Among a variety of nitroxides synthesized, **3a**,[6a] **3b**, **3c** and **4**[6a] were obtained as crystalline solids. The single crystals of the nitroxides **3a**, **3b** and **3c** of good quality and the fine crystals of **4** of poor quality for X-ray structure analysis were prepared by recrystallization from Et_2O. The crystals of **3a** and **3b** were needles, while **3c** was plate. The crystal data for **3a**, **3b** and **3c** are summarized in Table I. Apparently the single crystals of **3a** and **3b** consisted of the single enantiomer, while that of **3c** existed as the racemate. As reported recently, in the chiral molecule **3a**, the mean plane of the fused ring forms an angle of 76° with the 3,5-dinitrobenzoyl group so as to avoid steric repulsion between two ring systems.[6a] The similar dihedral angle of 78° was observed with **3b**, while the orthogonal dihedral angle of 91° was noted with **3c**. As to the crystal structure, **3a** possesses two threefold screw axes along the c axis in the trigonal unit cell (Figure 1).[6a] The molecules are arranged around one axis because of the electrostatic intermolecular interaction between the nitroxide oxygen atom and the nitrogen atom of one of two nitro groups on the benzene ring (2.87Å), eventually resulting in a head-to-tail arrangement around this axis. The other axis is surrounded by the other nitro groups owing to another electrostatic intermolecular interaction between the nitro groups (3.02Å), giving a tail-to-tail arrangement. Figure 2 represents a schematic diagram of the same view of the crystal structure of **3a** as that of Figure 1 to emphasize the helical structure. The chiral molecule **3b** also possesses four twofold screw axes along the c axis in the orthorhombic unit cell (Figure 3). In this case there still exists a weak electrostatic intermolecular interaction between the neighboring nitroxide and nitro groups (4.80Å). Therefore, the unique molecular asymmetry and arrangement of **3a** and **3b** seem to be responsible for their helical crystal structure. For this reason the formation of conglomerates of the stable free radicals of **3a**, **3b** and **4**[6a] and their spontaneous optical resolution should occur. In contrast, there are four sets of (±)-pairs in the orthorhombic

TABLE I Selected crystallographic parameters for **3a**, **3b** and **3c**.

	3a	**3b**	**3c**
space group	$P3_1$ or $P3_2$ (h)	$P2_12_12_1$	*Pbca*
a, Å	17.274 (6)	15.625 (5)	24.173 (2)
b, Å	17.274 (6)	21.282 (6)	13.6395 (9)
c, Å	6.166 (2)	5.917 (3)	11.935 (1)
Z	3	4	8
R/Rw	0.045/0.041	0.046/0.041	0.092/0.102

unit cell of **3c**, where no appreciable electrostatic intermolecular interaction between the nitroxide and nitro portions was noted (Figure 4). Thus, the position of the nitro group on the benzene ring turned out to play a crucial role with respect to the type of enantiomers mixture, as far as the α-asymmetric nitroxide radicals **3a**, **3b**, **3c** and **4** are concerned.

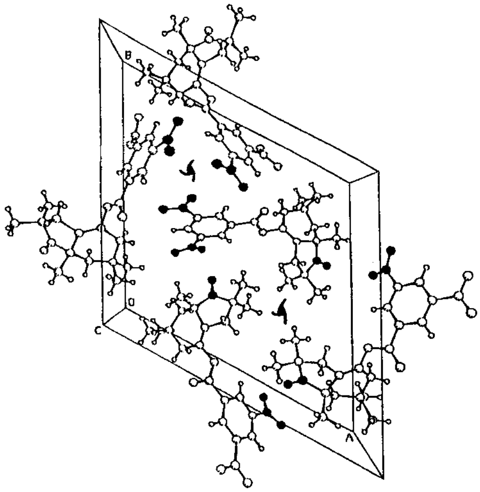


FIGURE 1 Crystal structure of **3a**.

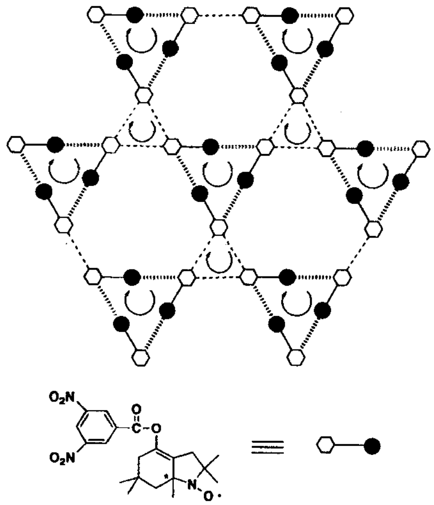


FIGURE 2 Schematic diagram of molecular packing of **3a**.

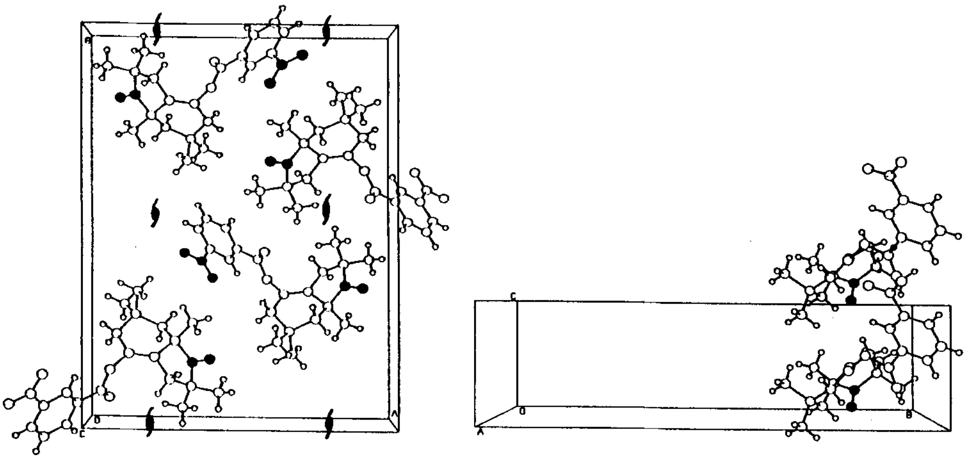
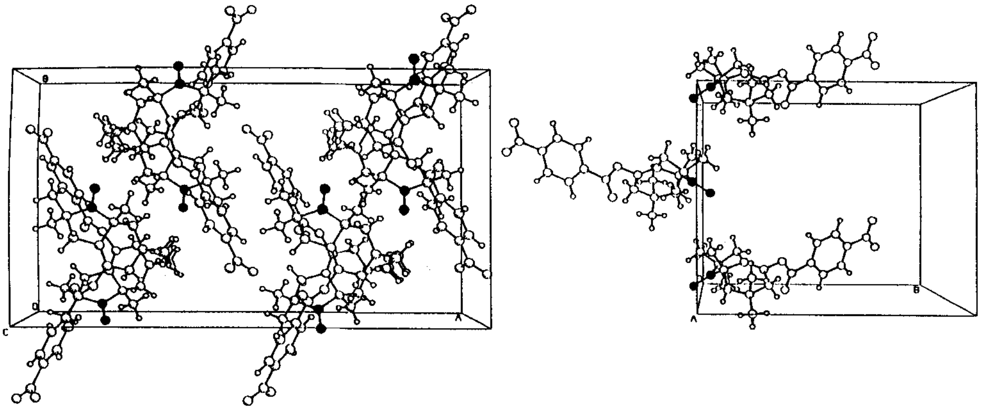


FIGURE 3 Crystal structure of **3b**.



FIFURE 4 Crystal structure of **3c**.

PARAMAGNETIC SUSCEPTIBILITY

Preliminary paramagnetic susceptibility of the conglomerates **3a**, **3b** and **4** was measured by means of a SQUID magnetometer (T > 1.8 K). As represented in Figure 5, the temperature dependence of the static magnetic susceptibility of **3a** and **3b** followed the Curie law, showing no appreciable intermolecular spin-spin coupling ($\theta \fallingdotseq 0$) at the temperature range of 1.8 to 300 K. These results were well in accordance with fairly large intermolecular distances between the nearest-neighbouring N-O portions; 6.17Å and 5.92Å along the c axis for **3a** and **3b**, respectively. A similar result was obtained for **4** at the same temperature range.

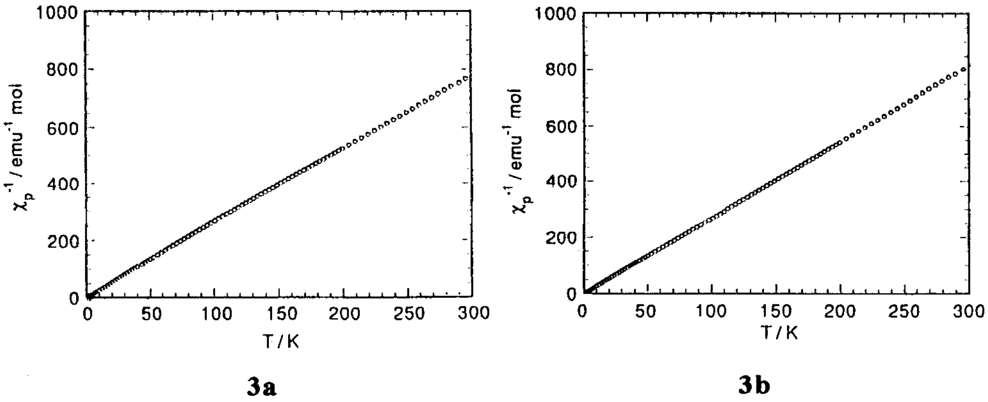


FIGURE 5 The $\chi_p{}^{-1}$ vs. T plot for **3a** and **3b**.

ACKNOWLEDGMENT

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