

Synthesis, Structure, and Ring Inversion of a Trithiolane (6b,12b-Epitrithioacenaphtho[1,2-a]acenaphthylene)

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ABSTRACT: Reduction of 6b,12b-epipentathioacenaphtho[1,2-a]acenaphthylene **2**, prepared by sulfuration of acenaphtho[1,2-a]acenaphthylene **1**, with LiEt_3BH , followed by air-oxidation, resulted in the desulfuration that led to 6b,12b-epitrithioacenaphtho[1,2-a]acenaphthylene **7** in 87% yield. The trithiolane ring of **7** adopts an envelope conformation both in solution at -40°C (NMR) and in crystals (X-ray). The ring inversion of the trithiolane ring is frozen at low temperature, but begins to take place as the temperature rises. Activation energy (E_a) of the ring inversion was determined to be 58 kJ mol^{-1} , based on dynamic ^{13}C NMR analyses. © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:638–643, 1999

INTRODUCTION

Cyclic oligosulfides have been attracting much interest not only in their physical and chemical properties but also in biological activities [1–4]. Thus, 1,2,3-trithioles [1–3] and 1,2,3,4,5-pentathiepins [3,4], unsaturated five-membered trisulfides and seven-membered

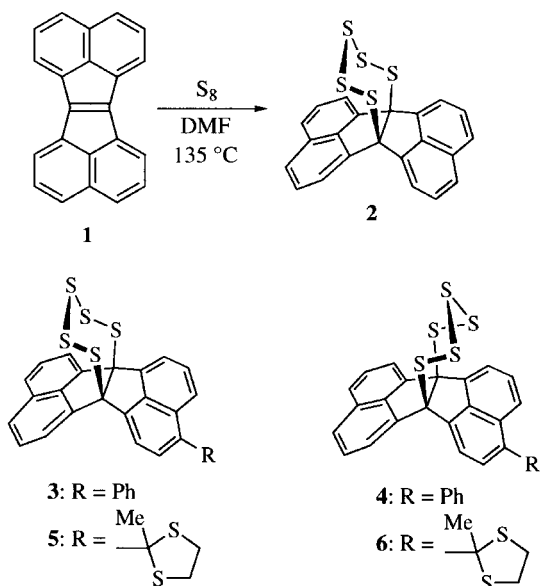
pentasulfides, respectively, were investigated briskly in syntheses, reactions, and structures, since naturally occurring benzotrithioles and benzopentathiepins were isolated [5]. 1,2,3-Trithiolanes [1,2] and 1,2,3,4,5-pentathiepanes [4,6–9], which are saturated analogs of trithioles and pentathiepins, respectively, were also studied mainly on preparations and reactions. A few reports dealt with the crystal structure of 1,2,3-trithiolanes [10–12] and 1,2,3,4,5-pentathiepanes [13]. To our knowledge, however, conformational studies of 1,2,3-trithiolanes and 1,2,3,4,5-pentathiepanes in solution have never been reported [1,14], though those of benzopentathiepins were reported in some detail [15–17]. Recently, we reported the preparation and the conformational study of 6b,12b-epipentathioacenaphtho[1,2-a]acenaphthylene **2** and the related compounds **3–6**, which possess a [5.3.3] propellane structure (Scheme 1) [18,19]. The C_s symmetry of **2** made its conformational analysis easier. In an extension of this study, we now report the preparation and conformational analysis of 6b,12b-epitrithioacenaphtho[1,2-a]acenaphthylene **7**.

RESULTS AND DISCUSSION

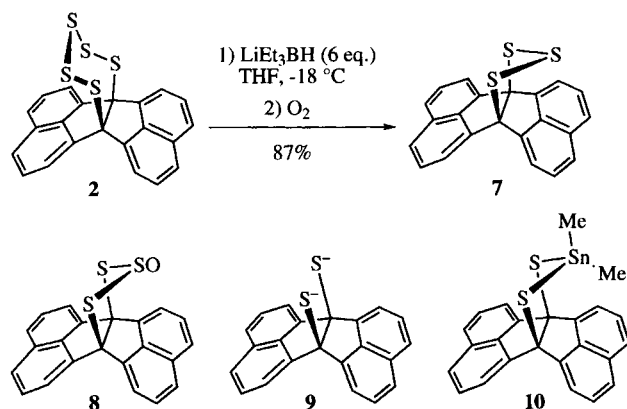
Synthesis of the Trithiolane **7**

1,2,3-Trithiolanes are often formed, along with 1,2,3,4,5-pentathiepanes, by sulfuration of cyclic alkenes such as norbornene [7] and dibenzobarrelene [8]. In general, trithiolanes are thermodynamically more stable than the corresponding pentathiepanes, which occasionally decompose to trithiolanes and

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SCHEME 1



SCHEME 2

sulfur when dissolved in polar solvents or on attempted purification by silica-gel column chromatography [7] or distillation [9]. In contrast to these results, the pentathiepane **2** was produced as the sole product for the sulfuration of acenaphtho[1,2-*a*]acenaphthylene **1** with elemental sulfur in dimethylformamide (DMF) at 135°C [18,19]. The trithiolane **7** was never formed. This probably indicates that in the angle-strained propellane system the trithiolane **7** is thermodynamically less stable than the pentathiepane **2**. Taking this into account, the synthesis of **7** was planned by deoxygenation of 6b,12b-epitrithioacenaphtho[1,2-*a*]acenaphthylene 2-oxide **8**, which might be derived from **2**. The previous study showed that the reduction of **2** with LiEt₃BH led to the formation of the 1,2-dithiolate **9** [18,19]. Therefore, treatment of **2** with LiEt₃BH followed by suc-

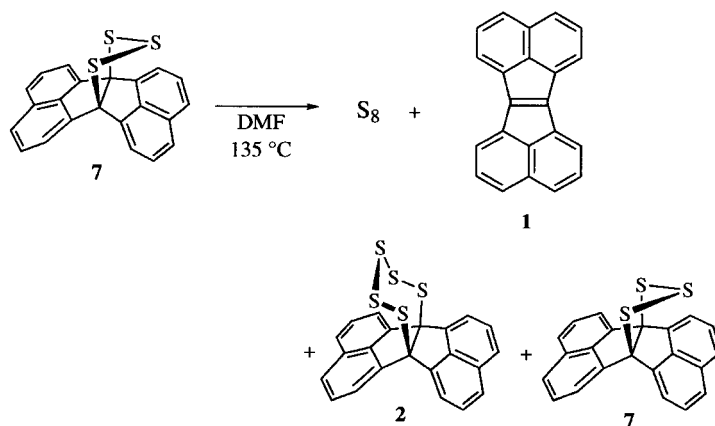
cessive addition of Me₂SnCl₂ and SOCl₂ was expected to give the trithiolane 2-oxide **8**. Unexpectedly, however, these treatments furnished **7** directly in 19% yield. Neither 1,3-dithia-2-stannolane **10** nor **8** was formed [20]. Encouraged with these results, we then reduced **2** by use of six molar amounts of LiEt₃BH at -18°C in tetrahydrofuran (THF). After quenching of the reaction with ice water, molecular oxygen was bubbled into the mixture. This furnished **7** in 87% yield (Scheme 2) [21]. At present, the mechanism of the formation of **7**, including the precursor compound that leads to **7**, is uncertain. The trithiolane **7**, obtained in this way, forms faint yellow crystals and decomposed at 230°C to form acenaphtho[1,2-*a*]acenaphthylene **1** and sulfur. When **7** was heated under the same conditions as those used for the preparation of **2** (DMF at 135°C for 22 hours), it decomposed to give **1**, **2**, and **7** in 42, 22, and 11% yields, respectively, in addition to sulfur in 18% yield (Scheme 3). The formation of **2** would be the result of the reaction of **1** and sulfur, which were formed by the decomposition.

NMR Analysis of the Trithiolane 7

The ¹H NMR spectrum of **7** at -40°C showed one doublet of doublets at δ 7.64 and four doublets at δ 7.74, 7.82, 7.86, and 7.87. The ¹³C NMR spectrum showed twelve aromatic carbon peaks in the range δ 119.9–140.6 and one bridgehead carbon peak at δ 97.2. These spectra reveal the nonequivalency of the two naphthalene rings at low temperature and are in harmony with an envelope conformation of the trithiolane ring of **7** with a C_s symmetry. ¹H NMR data at -40°C, which were assigned based on ¹H-¹H COSY correlation and coupling constant values [22] are summarized in Figure 1. Slight differences in the chemical shift values are observed between H¹ (δ 7.86) and H⁷ (7.87) and between H³ (δ 7.82) and H⁹ (7.74) because of the influence of the ring sulfur atoms [7,12,19]. However, we cannot determine whether the trithiolane ring lies over the H¹ or H⁷ side. The ¹H NMR spectrum at room temperature is simpler and showed one doublet of doublets at δ 7.64, one broad doublet at δ 7.78, and one doublet at δ 7.86, suggesting the presence of the only three nonequivalent hydrogen atoms, that is, the occurrence of the inversion of the trithiolane ring. Further details of the ring inversion will be discussed later.

X-Ray Crystallographic Analysis of the Trithiolane 7

The molecular structure of **7** was determined by X-ray single crystallographic analysis. An ORTEP



SCHEME 3

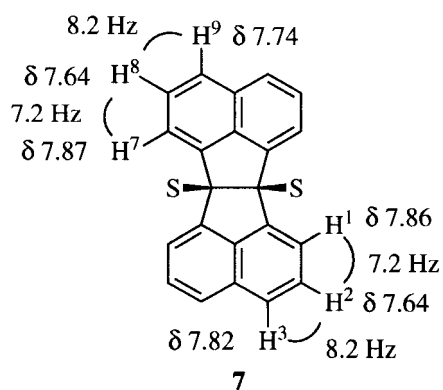
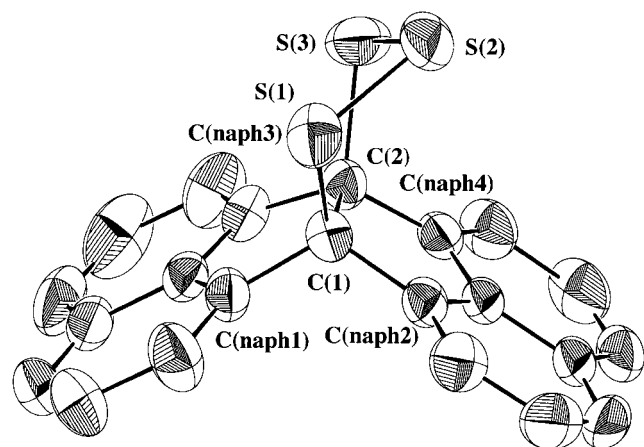
FIGURE 1 ¹H NMR assignments of 7.

FIGURE 2 An ORTEP drawing of 7 (50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å): C(1)–C(2), 1.613(4); C(1)–S(1), 1.843(3); C(2)–S(3), 1.835(3); S(1)–S(2), 2.056(2); S(2)–S(3), 2.035(2). Selected bond angles (°): C(1)–C(2)–S(3), 111.5(2); C(2)–C(1)–S(1), 111.1(2); C(1)–S(1)–S(2), 95.6(1); C(2)–S(3)–S(2), 93.9(1); S(1)–S(2)–S(3), 92.5(1); S(1)–C(1)–C(naph1), 108.9(2); S(1)–C(1)–C(naph2), 113.1(2); S(3)–C(2)–C(naph3), 110.9(2); S(3)–C(2)–C(naph4), 112.5(2).

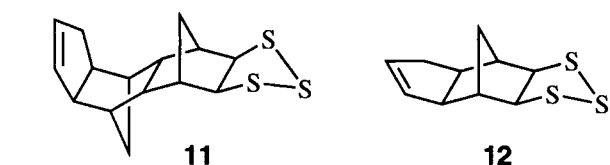


FIGURE 3

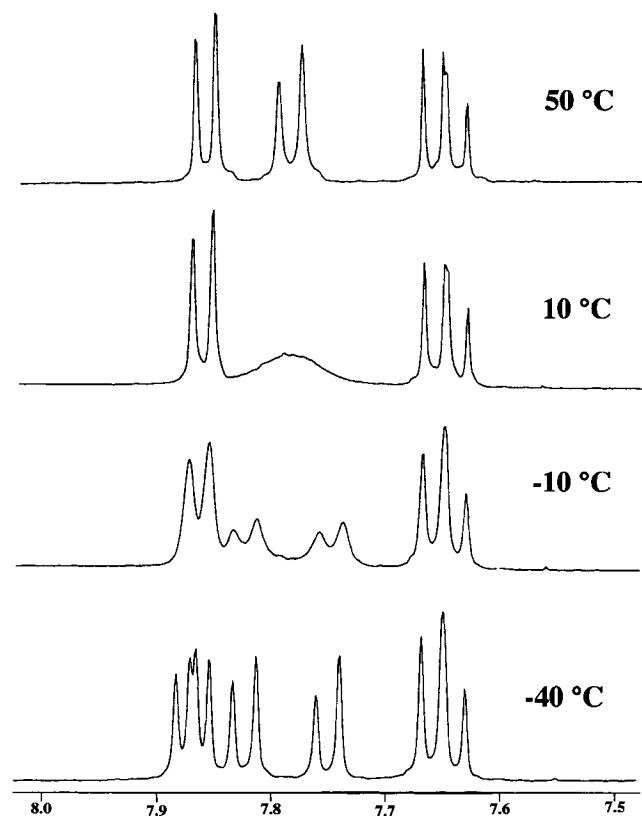


FIGURE 4 Dynamic ¹H NMR spectra of 7 (CDCl₃ as solvent).

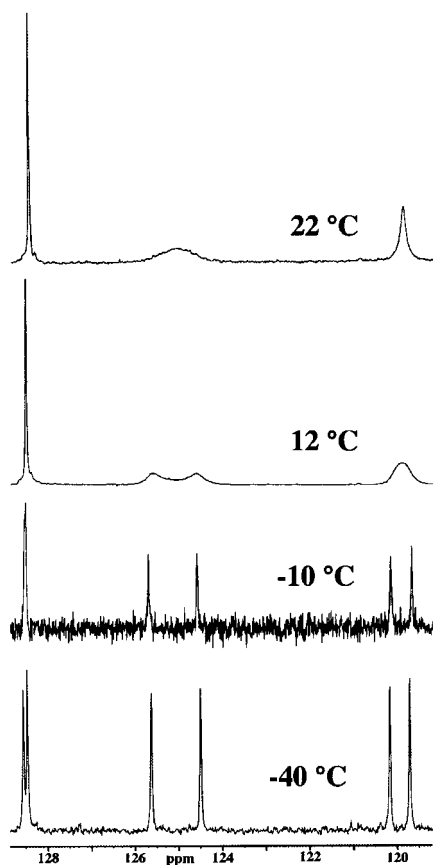


FIGURE 5 Dynamic ^{13}C NMR spectra of **7** (CDCl_3 as solvent).

drawing of **7** is given in Figure 2 with the selected bond lengths and angles data. In agreement with the NMR analyses at -40°C , the trithiolane ring of **7** adopts an envelope conformation. The C(1)–C(2) bond length, 1.61 Å, is much longer than those of trithiolanes, **11** [10] and **12** [11], which are 1.56 and 1.57 Å, respectively (Figure 3). The C–C bond lengthening would be the result of the angle strains originating from the [3.3.3]propellane structure, as true for **2** (1.63 Å) with a [5.3.3]propellane structure. The S(1)–C(1)–C(naph1) bond angle (108.9°) and the S(3)–C(2)–C(naph3) bond angle (110.9°) are much larger than the corresponding angles of **2** (about 103°), whereas the S(1)–C(1)–C(naph2) bond angle (113.1°) and the S(3)–C(2)–C(naph4) bond angle (112.5°) are comparable with those of **2**. These observations suggest that the repulsive interactions between the trithiolane ring and the naphthalene ring containing the C(naph2) and C(naph4) atoms in **7** are not as serious as those in the pentathiepane **2**.

Ring Inversion of the Trithiolane Ring of **7**

The two naphthalene rings of the trithiolane **7** were found to be nonequivalent at -40°C , suggesting that

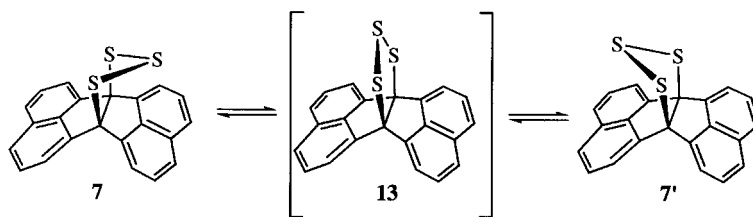
the ring inversion of the trithiolane ring of **7** is frozen at that temperature. The hydrogen signals of the two naphthalene rings of **7** commenced broadening and coalescing with a rise in temperature in the ^1H NMR spectra (Figure 4). This is in contrast to the results with the pentathiepane **2**, in which the hydrogen signals neither broaden nor coalesce up to 100°C [19]. The activation energy of the ring inversion of **7** was investigated by dynamic ^{13}C NMR experiments. Three pairs of the signals that are assigned to the aromatic carbons carrying a hydrogen are shown in Figure 5. They commence broadening and coalescing with a rise in temperature. A pair of signals at δ 128.77 and 128.83 coalesced at -10°C . The other two pairs of signals at δ 119.9 and 120.4 and at δ 124.9 and 126.0 coalesced at 12°C and 22°C , respectively. These results lead to the activation energy E_a of 58 kJ mol^{-1} for the ring inversion of the trithiolane ring [24]. The most likely mechanism of the ring inversion involves the planar conformation **13** at the transition state (Scheme 4). The activation energy is much smaller than those ($104\text{--}109\text{ kJ mol}^{-1}$) observed between **3** and **4** and between **5** and **6** [19]. We suggest that these differences in activation energies are a result of the number of S–S bonds involved that encounter increasing repulsive interactions between lone pair electrons on adjacent sulfur atoms in the planar transition state [15–17].

EXPERIMENTAL

Solvents were dried and purified in the usual manner. All the reactions were performed under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70–230 mesh). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 or a Bruker AM 400 spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard (400 MHz for ^1H and 100.6 MHz for ^{13}C). IR spectra were recorded on a Hitachi 270-50 spectrophotometer. UV–vis spectra were recorded on a JASCO V-560 spectrophotometer. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Formation of **7** in an Attempted Synthesis of 1,2,3-Trithiolane 2-Oxide **8**

To a suspension of **2** (100 mg, 0.23 mmol) in THF (4 mL) was added a 1.0 M THF solution of LiEt_3BH (2.3 mL, 2.3 mmol) at 0°C . After the mixture was stirred



SCHEME 4

at room temperature for 2 hours and then cooled at 0°C, Me_2SnCl_2 (50 mg, 0.23 mmol) was added. After the mixture was stirred at 0°C for 1 hour, SOCl_2 (20 μL , 0.25 mmol) was added, and the resulting mixture was stirred at room temperature for 45 hours. The insoluble materials were collected by filtration and washed with ether to give 50 mg (50%) of the unreacted **2**. The filtrate and washings were combined, diluted with cold water, extracted with ether, dried over MgSO_4 , and evaporated. Chromatography was performed on the residue on a silica-gel column, and the column was eluted with CCl_4 -hexane (1:3) to give 16 mg (19%) of 6b,12b-epitritioacenaphtho[1,2-*a*]acenaphthylene **7**: faint yellow plates; m.p. > 230°C (dec.); $^1\text{H NMR}$ (233 K) δ 7.64 (dd, $J = 7.2, 8.2$ Hz, 4H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.87 (d, $J = 7.2$ Hz, 2H); $^{13}\text{C NMR}$ (233 K) δ 97.2, 119.9, 120.4, 124.9, 126.0, 128.77, 128.83, 129.6, 131.7, 133.7, 137.2, 139.2, 140.6; IR (KBr) 3048, 2356, 1626, 1594, 1496, 1418, 1360, 1220, 786 cm^{-1} ; UV-vis (CHCl_3) λ_{max} (log ϵ) 224 (4.38), 226 (4.43), 232 (4.53), 295.5 (4.08), 318.5 (4.08), 332.5 (4.07) nm; MS m/z 372 (M^+), 276 (100%). Anal. calcd for $\text{C}_{22}\text{H}_{12}\text{S}_3$: C, 70.93; H, 3.25; Found: C, 70.55; H, 3.17.

Preparation of **7** by Reduction of **2** with LiEt_3BH Followed by Air-Oxidation

To a suspension of **2** (179 mg, 0.41 mmol) in THF (10 mL), a 1.0 M THF solution of LiEt_3BH (2.5 mL, 2.5 mmol) was slowly added at -18°C . After the mixture was stirred at -18°C for 8 hours, the reaction was quenched by addition of ice water. The mixture was extracted with ether, dried over MgSO_4 , and evaporated. Oxygen gas was bubbled into the water layer, and the resulting precipitate was collected by filtration. The materials obtained by both operations were combined, and chromatography was performed on a silica-gel column, and the column was eluted with CCl_4 -hexane (1:3) to give 133 mg (87%) of **7**.

Pyrolysis of **7**

A solution of **7** (38 mg, 0.10 mmol) in DMF (2.5 mL) was heated at 135°C for 22 hours. After the mixture was cooled at room temperature, the resulting crystals were collected by filtration and washed with Et_2O . The filtrate was washed with water, dried over MgSO_4 , and evaporated. The materials obtained by both operations were combined and purified by silica-gel column chromatography with CCl_4 -hexane (1:5) to give 5 mg (18%) of sulfur, 12 mg (42%) of **1**, 10 mg (22%) of **2**, and 4 mg (11%) of **7**.

X-Ray Crystallographic Analysis of **7**

A single crystal with crystal dimensions 0.2 mm \times 0.18 mm \times 0.11 mm was grown by slow diffusion of hexane into a CS_2 solution of **7** at room temperature. The crystal was mounted on a glass fiber with epoxy cement. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of a MAC Science DIP3000 diffractometer by using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 23°C , and the data collection was made by the XDIP program system. Cell parameters were determined and refined by using the DENZO for all observed reflections. Formula: $\text{C}_{22}\text{H}_{12}\text{S}_3$; monoclinic, space group $P2_1/c$, $a = 13.727(2)$; $b = 9.941(1)$; $c = 13.470(1) \text{ \AA}$; $\beta = 111.217(7)^\circ$; $V = 1713.5(4) \text{ \AA}^3$; $Z = 4$, $d_{\text{calcd}} = 1.444 \text{ Mg m}^{-3}$, $\mu = 4.155 \text{ mm}^{-1}$. The structure was solved by direct methods using SIR92²⁵ in the CRYSTAN-GM program system. All nonhydrogen atoms were refined with anisotropic thermal parameters using full-matrix least-squares procedures on F_0^2 with $I > 2\sigma(I)$ [26]. Hydrogen atoms were placed in ideal positions with isotropic thermal parameters fixed at 0.1. The refinement converged to $R(F_0) = 0.067$, $wR(F_0^2) = 0.067$, and $S = 1.731$ for 2581 reflections with 271 parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.71 and -0.56 eV^{-3} , respectively.

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- [26] Mallinson, P. R.; Muir, K. W. *J Appl Crystallogr* 1985, 28, 31.
- [27] The following tables concerning the crystal and molecular structure of trithiolene are available on request to Professor Nakayama: (a) Crystal Data, (b) Data Collection, (c) Fractional Atomic Coordinates and U(150), (d) Anisotropic Thermal Parameters, (e) Intramolecular Bond Lengths (H omitted), (f) Intramolecular Bond Angles (H omitted), (g) Intramolecular Torsion Angles (omitted).