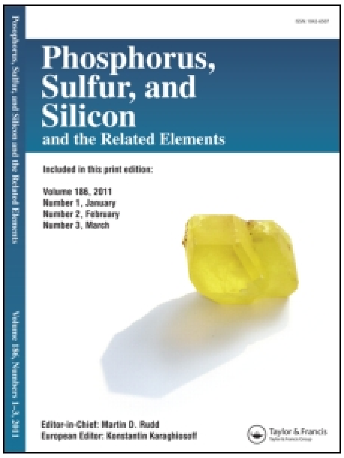

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SYNTHESIS AND STRUCTURE OF AROMATIC COMPOUNDS CARRYING TWO 1-ADAMANTYLS ON ADJACENT POSITIONS: 3,4-DI-1-ADAMANTYLTHIOPHENE, *o*-DI-1-ADAMANTYLBENZENE, AND 4,5-DI-1-ADAMANTYLPYRIDAZINE

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Abstract 3,4-Di-1-adamantylthiophene, *o*-di-1-adamantylbenzene, and 4,5-di-1-adamantylpyridazine, which carry two bulky 1-adamantyl groups on adjacent positions, were satisfactorily synthesized starting from 1,5-di-1-adamantyl-3-thiapentane-1,5-dione. Synthesis, properties, and single crystal structure analysis of these compounds are described.

1-Adamantyl is a very bulky substituent similar to *tert*-butyl. It can be considered a kind of "tied-back" *tert*-butyl group but is far less flexible and thus might behave as a bulkier substituent than *tert*-butyl. To our knowledge, no report has appeared on the successful synthesis of five- or six-membered aromatic rings carrying two 1-adamantyl groups on adjacent positions. These would be sterically more strained than the corresponding di-*tert*-butyl-substituted compounds. We report here the synthesis and structure of such molecules, 3,4-di-1-adamantylthiophene (**3**), *o*-di-1-adamantyl benzene (**5**), and 4,5-di-1-adamantyl pyridazine (**8**).[1]

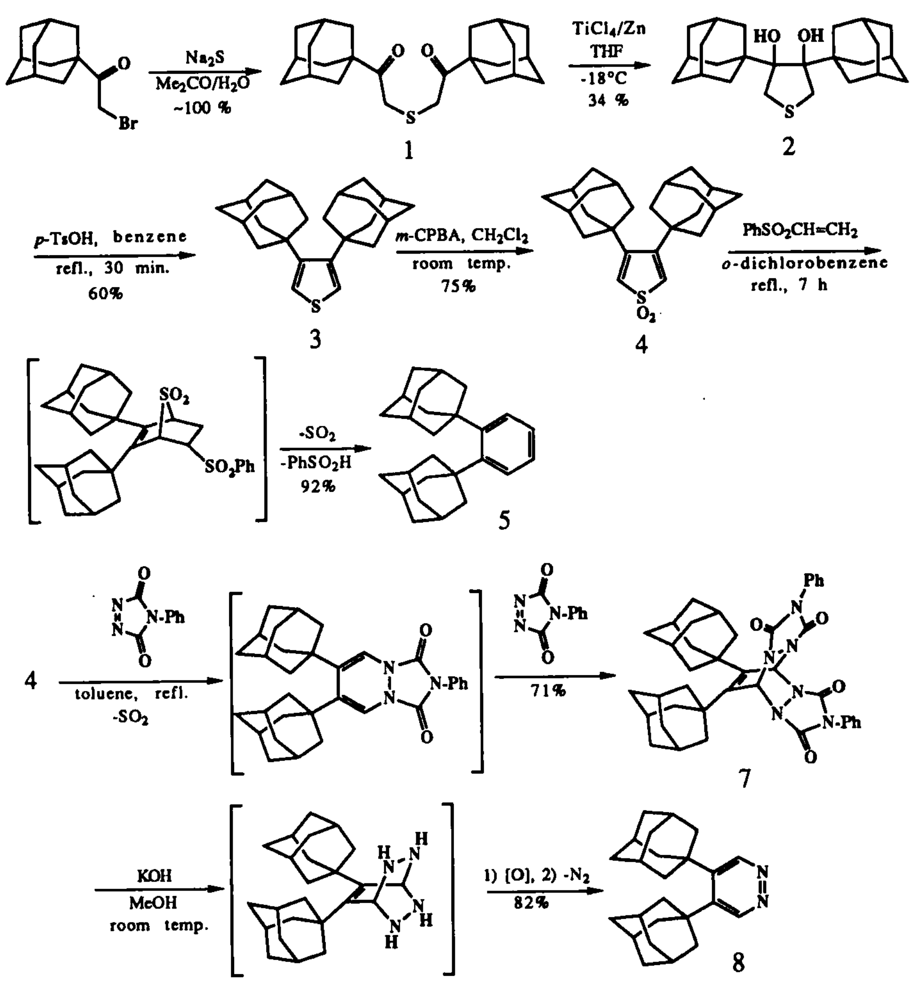
Diketo sulfide **1** is easily obtainable[2] by reaction of sodium sulfide with commercially available 1-adamantyl bromomethyl ketone. Intramolecular pinacol reduction of **1** by a low valent titanium reagent, prepared from titanium(IV) chloride and zinc powder, at -18 °C for 9 h in THF afforded the diol **2** in 34% yield.[3] *p*-Toluenesulfonic acid catalyzed dehydration of **2** in refluxing benzene for 0.5 h produced the expected thiophene **3** in 60% yield.[3a,c] Oxidation of **3** with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at room temperature gave the corresponding 1,1-dioxide **4** in 75% yield.[3c]

The Diels-Alder reaction of dioixde **4** with phenyl vinyl sulfone (3 equiv) in refluxing *o*-dichlorobenzene for 24 h afforded *o*-di-1-adamantylbenzene (**5**) in 92% yield with loss of sulfur dioxide and benzenesulfinic acid from the initial adduct.[4] Similarly, the reaction of **4** with dimethyl acetylenedicarboxylate (DMAD) in refluxing *o*-dichlorobenzene for 7 h furnished dimethyl 4,5-di-1-adamantylphthalate (**6**) in 90% yield with extrusion of sulfur dioxide from the initial adduct.[4]

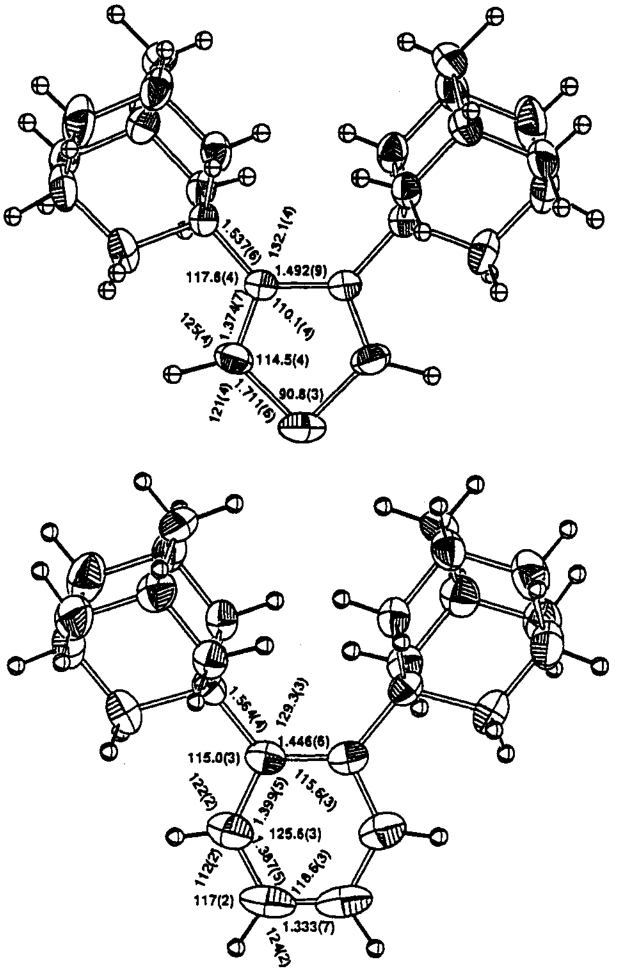
The reaction of **4** with excess 4-phenyl-1,2,4-triazoline-3,5-dione (7.5 equiv) in refluxing toluene afforded the bis-adduct **7** in 72% yield. Treatment of **7** with potassium hydroxide in methanol at room temperature followed by air oxidation and nitrogen extrusion led directly to 4,5-di-1-adamantylpyridazine (**8**) in 82% yield (Scheme 1).[5]

The two 1-adamantyl substituents of **3**, **5**, and **8** are equivalent in the ^1H NMR spectra, which confirms that rotation about the bond from the aromatic ring to adamantyl is fast on the ^1H NMR time scale at room temperature. A similar conclusion is reached from ^{13}C NMR analysis.

Treatment of **3** with aluminum chloride in carbon disulfide at room temperature for 6 days brought about quantitative isomerization to 2,4-di-1-adamantylthiophene.[3c] Treatment of **5** under similar conditions resulted in exhaustive deadamantylation, although the use of benzene as the solvent gave 1-adamantylbenzene in 41% yield.



ORTEP drawings of compounds **3** and **5** are given below with relevant bond lengths and angles. The C(3)-C(4) bond of **3** is longer than that of the parent thiophene by *ca.* 0.07 Å and the adamantyl-C(3)-C(4) bond angle is larger than the H-C(3)-C(4) bond angle of the parent thiophene by *ca.* 9°. Two adamantyls are twisted with a torsion angle of 13.1°. In compound **5** the adamantyl-C(1)-C(2) bond angle is 129.3° and *two adamantyls are twisted with a torsion angle of 16.6°, thus making the benzene ring nonplanar!* The C(1)-C(2) bond of **5** is as long as 1.446 Å and the C(4)-C(5) bond as short as 1.333 Å.



Torsion Angles

S1-C2-C3-C3'	-0.8(5)
C2-C3-C3'-C2'	1.0(5)
C3-C2-S1-C2'	0.3(4)
S1-C2-C3-C11	174.2(2)
C11-C3-C3'-C11'	13.1(6)

Torsion Angles

C11-C1-C1'-C11'	-16.7(4)
C11-C1-C2-C3	-170.8(2)

ORTEP Drawings of 3,4-Di-1-adamantylthiophene (top) and *o*-Di-1-adamantylbenzene (bottom)

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