Rotation barriers in aryl- and heteroaryldi(1-adamantyl)methyl systems; the ionic hydrogenation of heteroaryldi-(1-adamantyl)methanols

John S. Lomas,*[a] Jean-Christophe Lacroix[a] and Jacqueline Vaissermann[b]

[a] *Institut de Topologie et de Dynamique des Systèmes, Université de Paris 7, associé au C.N.R.S., 1 rue Guy de la Brosse, 75005 Paris, France*
[b] *Laboratoire de Chimie des Métaux de Transition, Université de Paris 6, associé au C.N.R.S., Case 42, 4 place Jussieu, 75252 Paris Cedex 05, France*

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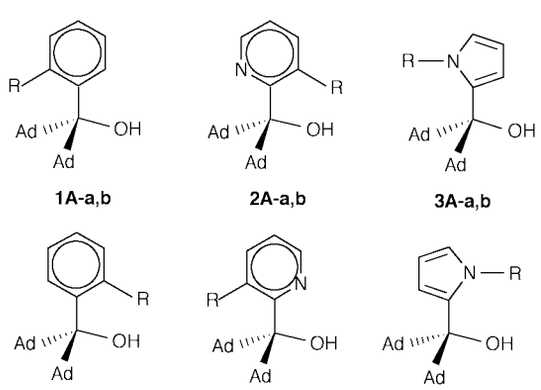
[2-(3-Methylthienyl)]di(1-adamantyl)methanol is synthesized as a 1 : 1 mixture of the *anti* and *syn* isomers; the latter rotates incompletely to the more stable isomer upon heating, the equilibrium constant ranging from about 5 to 10 at 150 °C, depending on the solvent. Ionic hydrogenation (deoxygenation) of the 2-(3-methylthienyl) alcohols gives a single product, the *syn* isomer, in which the methyl group is close to the adamantyls; the *anti*/*syn* ratio at equilibrium is substantially higher than for the alcohol. Activation energies (at 157 °C) for *syn*→*anti* rotation in this alcohol and its deoxygenation product are 32.1 and 34.4 kcal mol^{-1}, respectively. The analogous 2-(3-methylfuryl) derivatives have much lower rotation barriers, the alcohol being isolated as the stable, *anti* rotamer; deoxygenation gives predominantly the corresponding methane. The *anti*→*syn* rotation barriers for (2-furyl)-, (2-thienyl)- and (thiazol-2-yl)diadamantylmethanols, measured by DNMR, are 16.3, 20.0 and 18.2 kcal mol^{-1}, respectively. Deoxygenation of the 2-furyl alcohol or its 4-methyl derivative gives in both cases two isomers in a ratio of 2 : 1, mainly the *syn* isomer. For the corresponding 2-thienyl alcohols the two isomers are obtained in equal amounts, while the 2-selenienyl analogue shows a preference for the *anti* isomer (1.8 : 1). Rotation barriers (*anti*→*syn*) for the (2-furyl)-, (2-thienyl)- and (2-selenienyl)diadamantylmethanes are 16.9, 20.2 and 22.1 kcal mol^{-1}, respectively, and about 1 kcal mol^{-1} higher for the 4-methyl derivatives of the first two.

Introduction

The search for molecules or supramolecules capable of mimicking mechanical devices has led in the past few years to the description of molecular gears,[1] brakes,[2] ratchets[3] and turnstiles.[4] In other work an attempt was made to control a molecular rotor by a chiroptical switch.[5] What these devices have in common is that their operation depends critically on intramolecular rotation about sp^3–sp^3 or sp^2–sp^3 carbon–carbon bonds. It is interesting to consider therefore how rotation barriers could be tailored for different applications.

Rotation barriers of interest to organic chemists generally lie above about 5 kcal mol^{-1}, in which case they can be measured by conventional low-temperature DNMR spectroscopy, and rise to a maximum of about 45 kcal mol^{-1}, beyond which C–C bonds may become fragile.[6]† In the upper half of this range it becomes possible to isolate rotamers (atropisomers or conformational isomers) as distinct chemical species, with significant spectroscopic differences and, in some cases, different patterns of chemical reactivity.[7] Most barriers are associated with steric interactions between the various groups attached to the carbon atoms at the ends of the bond about which rotation is considered.

Oki's extensive work on triptycenes (sp^3–sp^3) and 9-arylfluorenes (sp^2–sp^3) is well documented.[7,8] If in the latter the aryl group "rotor" is conserved and the 9-fluorenyl "stator" is replaced by a dialkylmethanol group we get another sp^2–sp^3 system, aryldialkylmethanols, in which wide variations in rotation barriers can be achieved by simple modifications of readily synthesized materials. The barrier in arylalkyl(*tert*-butyl)methanols rises from 9.4 to 21.4 kcal mol^{-1} as the second alkyl group is varied from methyl to *tert*-butyl.[9] This upper value can be raised to 29 kcal mol^{-1} by introducing an *ortho*-methyl substituent[10] and even further, to 39 kcal mol^{-1}, if the *tert*-butyl groups are then replaced by 1-adamantyls (**1-b**).[11] Introduction of the methyl group in the *ortho* position[11,12] leads also to a very marked difference (*ca.* 6 kcal mol^{-1}) in the steric energies of the *syn* and *anti* isomers, **1S-b** and **1A-b**, essentially because of unfavourable interactions between the methyl and adamantyl groups in the *anti* isomer.



a: R = H; **b**: R = Me **a**: R = H; **b**: R = Me **a**: R = Me; **b**: R = Et

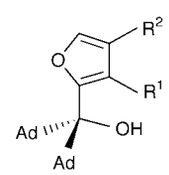
More recent work has been devoted to heteroaryldi(1-adamantyl)methyl systems. In the 2-pyridyl derivatives (**2**) there is strong hydrogen bonding between the hydroxy group hydrogen and the heteroatom.[13] It was expected that the resulting stabilization of the **2S** ground state would raise the rotation barriers and reduce the energy difference between **2S-b** and

† 1 cal = 4.184 J.

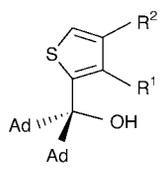
2A-b to somewhat less than 6 kcal mol^{-1}. However, attempts to measure these effects were frustrated by the thermal decomposition of **2S-b** and the very low equilibrium level of **2A-a**.[13] ‡

In contrast, the (*N*-alkylpyrrol-2-yl)diadamantylmethanols (alkyl = Me or Et), **3**, behave very much like the phenyl analogues. The product of synthesis is the *anti* isomer, **3A**, which by rotation about the sp^2–sp^3 C–C bond (activation energy *ca.* 31 kcal mol^{-1}) gives the more stable, *syn* isomer, **3S**.[14] Ionic hydrogenation[16] of **3A-a** gives a single isomer, again the less stable, and its rotation barrier is some 4 kcal mol^{-1} higher than for the alcohol. A similar difference is seen for alcohol **1A-b** and its deoxygenation product.[6,11] The prime effect of replacing the *o*-methyl-substituted benzene ring by the *N*-methyl-substituted five-membered heterocyclic ring is therefore to reduce the rotation barriers by 8–10 kcal mol^{-1}.

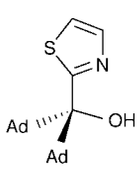
However, when the heteroaryl is 2-furyl, 2-thienyl or thiazol-2-yl (**4-a**, **5-a** or **6**, respectively) the apparent rotamer composition, as determined by NMR spectroscopy, depends on the solvent used, the *syn* isomer generally being the more stable.[13] Contrary to expectation, the reason for this proves not to be hydrogen bonding, except perhaps in the case of thiazol-2-yl, but more probably solvent effects. What is important, however, is the fact that the isomer ratio can be changed simply by going from one solvent to another (this could be considered as a rudimentary "switch"), which indicates that the rotamers are in dynamic equilibrium, though the exchange rate must be low on the NMR time-scale. Nevertheless, this means that we are now dealing with rotation barriers of the order of 20 kcal mol^{-1}, perhaps less, which is a far cry from the 39 kcal mol^{-1} of **1A-b**.[11]



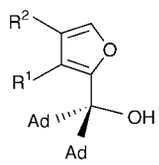
4A-a,b,c



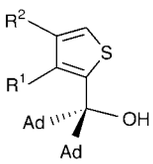
5A-a,b,c



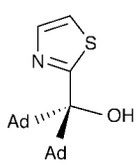
6A



4S-a,b,c



5S-a,b,c



6S

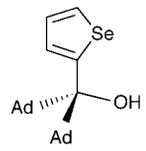
a: $R^1 = R^2 = H$; **b**: $R^1 = Me$; $R^2 = H$; **c**: $R^1 = H$; $R^2 = Me$

Though none of the heteroaryl- or aryldiadamantylmethyl species described above would aspire to micromechanical applications, the wide variety of potential "rotors" makes this a model system for the investigation of the factors which determine the magnitude of rotation barriers. In this work we shall consider the new heteroaryldi(1-adamantyl)methanols, some methyl-substituted derivatives and the corresponding deoxygenation products.

Results

Synthesis and structure of heteroaryldiadamantylmethanols

The synthesis of several heteroaryldiadamantylmethanols has been described elsewhere.[13] The selenium analogue, **7S**, of the



7S

2-furyl and 2-thienyl derivatives was readily prepared by lithiation of selenophene with *n*-butyllithium followed by reaction with di(1-adamantyl) ketone.[17,18] 2-Furyl and 2-thienyl derivatives methyl-substituted at the 3- or 4-position were prepared as described below. NMR and IR spectroscopic data on all new alcohols are presented in Table 1.

[2-(3-Methylthienyl)]di(1-adamantyl)methanol, 5-b. By reaction of 2-lithio-3-methylthiophene with diadamantyl ketone, the 2-(3-methylthienyl) derivative, **5-b**, is obtained as a 1 : 1 mixture of the *syn* and *anti* isomers, **5S-b** and **5A-b**. These were readily distinguished by ^{1}H NMR NOE experiments in which the α-methylene hydrogens of the adamantyl groups were irradiated. Heating the *syn* isomer at 150 °C gives mainly the *anti* isomer. The equilibrium constant for this reaction in benzene at 135–180 °C is about 9, which means that the *anti* isomer, with the methyl group remote from the adamantyls, is only 1.8–1.9 kcal mol^{-1} more stable than the *syn*, a much smaller difference than in **1-b** and **3**.[11,12,15] As observed for unsubstituted heteroaryldiadamantylmethanols,[13] the equilibrium constant is solvent-dependent, ranging from 5 (DMSO) to 10 (isooctane) at 150 °C, corresponding to free energy differences of 1.3 to 1.9 kcal mol^{-1}.

[2-(4-Methylthienyl)]di(1-adamantyl)methanol, 5-c. Direct lithiation of 3-methylthiophene, by exchange with *n*-butyl- or *tert*-butyllithium in the presence of TMEDA, and reaction with diadamantyl ketone gives [2-(4-methylthienyl)]diadamantylmethanol, **5-c**, as a 5 : 1 rotamer mixture in benzene. This is in agreement with previous reports that 3-methylthiophene lithiation and subsequent reaction with carbonyl compounds leads mainly to products with the methyl group remote from the new substituent, essentially for reasons of steric hindrance.[17] Given the bulk of the diadamantylmethyl moiety, it is not surprising that only one positional isomer, the least strained, is obtained.

[2-(3-Methylfuryl)]- and [2-(4-methylfuryl)]di(1-adamantyl)-methanols, 4-b and 4-c. Attempts to synthesize the 2-(3-methylfuryl) derivative, **4-b**, by lithiation of 2-bromo-3-methylfuran[19] were unsuccessful, but direct lithiation of 3-methylfuran,[20] as for 3-methylthiophene, followed by addition of diadamantyl ketone, gives a mixture of two alcohols in a ratio of 2 : 1. The coupling constants for the heteroaromatic protons are 1.1 and 1.7 Hz for the major and minor isomers, respectively, suggesting that they are the 4-methyl and 3-methyl derivatives.[21] The minor component has a strong IR (CCl_4) absorption band at 3627 cm^{-1} with a shoulder at 3612 cm^{-1} while the other has a broad OH absorption (Table 1). By analogy with other alcohols in which the OH group is in close proximity to a methyl,[10–13,15] these results indicate that the minor component is most probably the 2-(3-methylfuryl) derivative, **4A-b**. This was established unambiguously by a single crystal X-ray diffraction study (Fig. 1).

The main structural features of the 2-(3-methylfuryl) alcohol (Table 2) are very similar in general outline to results on aromatic-[22–26] and heteroaromatic[15] analogues. Bonds to the C–OH carbon are uniformly long and the plane of the furan ring roughly bisects the very large Ad–C–Ad angle. Nevertheless, the two adamantyl groups are distinct as regards their orientation with respect to the sp^2–sp^3 bond, that which is slightly further from the furan plane being almost perfectly

‡ Confusion may arise here because the nitrogen atom has priority;[14] this means that the **2-b** rotamer which has the methyl group close to the adamantyl groups is now *syn*, **2S-b**, whereas in the *ortho*-tolyl derivatives it is *anti*,[11] the 2-methyl group having priority. The same problem arises with all the heteroaryl systems described below, except *N*-alkylpyrrol-2-yl, where the alkyl group is on the heteroatom.[15]

Table 1 Solvent dependence of hydroxy proton NMR chemical shifts (in ppm) in heteroaryldi(1-adamantyl)methanols; temperature coefficient (25–55 °C) of chemical shift in pyridine (*ca*. 0.05 M; in ppb °C^{-1}); OH stretching frequencies in carbon tetrachloride (*ca*. 0.01 M)

Compound	$\delta(CDCl_3)$	$\delta(C_6D_6)$	$\delta(C_5D_5N)$	$-\Delta\delta/\Delta T$	δ(DMSO-d_6)	ν_{OH}
4A-b	—[a]	—[a]	4.72	21.7	3.89	3612sh, 3627
4S-c	—[a]	—[a]	5.04	22.1	4.06	3608, 3618, 3628
5A-b	2.08	1.84	4.61	20.1	3.95	3617sh, 3628
5S-b	2.49	2.26	5.85	21.5	—[b]	3600, 3624
5S-c	—[a]	—[a]	5.03	22.1	4.07	3607, 3626
7S	2.54	2.22	5.78	19.6	4.71	3608sh, 3624
7A	2.08	—[a]	5.29	22.1	4.38	—[b]

[a] The signal fell in the range of the adamantyl protons (1.6–2.1 ppm) but could not be located unambiguously. [b] Not detected.

Table 2 Selected bond lengths, bond angles and torsion angles for *anti*-[2-(3-methylfuryl)]di(1-adamantyl)methanol, **4A-b**

Bond lengths/Å		Bond angles/°		Torsion angles/°	
O1–C2	1.378(3)	C2–O1–C5	106.6(2)	C3–C2–C10–O11	−10
O1–C5	1.380(3)	C2–C3–C30	130.6(3)	C3–C2–C10–C101	103
C2–C3	1.364(4)	C4–C3–C30	123.8(3)	C3–C2–C10–C201	−123
C3–C4	1.429(4)	O1–C2–C3	109.4(2)	O1–C2–C10–O11	167
C4–C5	1.314(4)	C2–C3–C4	105.2(2)	O1–C2–CC10–C101	−80
C3–C30	1.490(4)	C3–C4–C5	108.4(3)	O1–C2–C10–C201	54
C2–C10	1.516(4)	O1–C5–C4	110.0(2)	C2–C10–C101–C102	180
C10–C101	1.606(4)	O1–C2–C10	115.8(2)	C2–C10–C101–C108	56
C10–C201	1.604(4)	C3–C2–C10	134.8(2)	C2–C10–C101–C109	−62
		C2–C10–C101	109.0(2)	C2–C10–C201–C202	157
		C2–C10–C201	109.3(2)	C2–C10–C201–C208	40
		C101–C10–C201	120.9(2)	C2–C10–C201–C209	−80

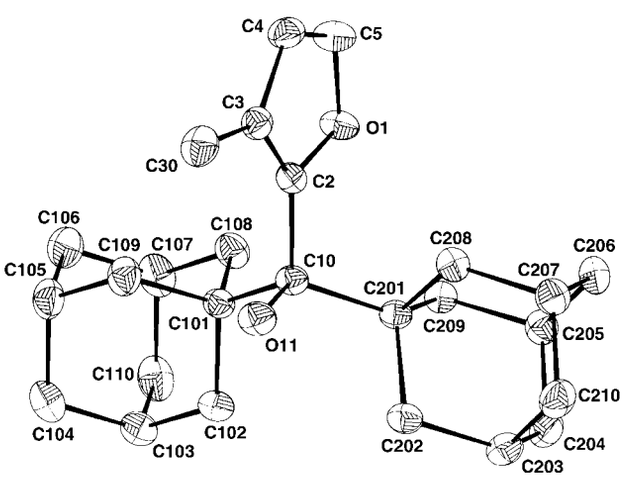


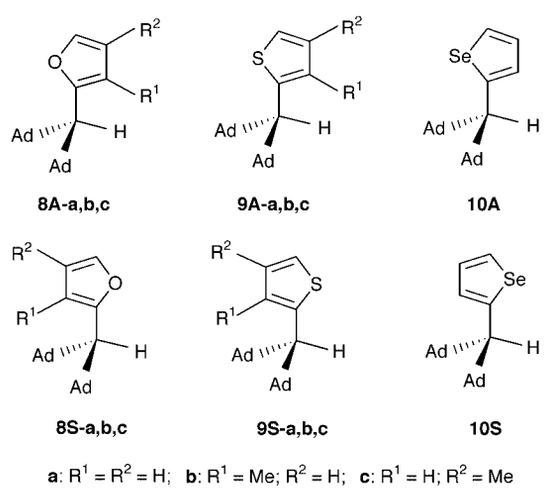
Fig. 1 CAMERON diagram for *anti*-[2-(3-methylfuryl)]di(1-adamantyl)methanol, **4A-b**, showing 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

staggered, while the other is rotated by about 20°. The furan ring is slightly deformed in the plane.

The major component was identified as the 2-(4-methylfuryl) alcohol, **4-c**, by comparison of its spectroscopic properties and chemical behaviour with those of the parent (2-furyl)-diadamantylmethanol, **4-a** (*vide infra*).[13]

Ionic hydrogenation

Carbocations derived from congested aryl-substituted tertiary alcohols in dichloromethane–TFA mixtures can be reduced stereoselectively by hydrosilanes or sodium borohydride, the steric requirements of the reactants determining how the hydride donor approaches.[25] Though the intermediate carbocation cannot be observed directly, certain heteroaryl derivatives undergo the same reaction.[15] The 2-pyridyl and thiazol-2-yl derivatives, **2S-a** and **6**, could not be reduced in this way, the electron-attracting nitrogen atom presumably preventing carbocation formation.



(2-Thienyl)di(1-adamantyl)methane, 9-a. The 2-thienyl derivative, **5S-a**, was reduced cleanly by treatment with TES and TFA in dichloromethane, giving a 1 : 1 mixture of two isomers, **9A-a** and **9S-a**.§ By NOE and COSY experiments as well as ^{1}H–^{13}C correlation the various ^{1}H and ^{13}C NMR signals were attributed to the *anti* and *syn* (2-thienyl)diadamantylmethanes, **9A-a** and **9S-a**. Only a few signals for quaternary carbons and adamantyl CH_2 groups could not be unambiguously assigned. Long-range couplings between the heteroaromatic protons and the $Ad_2C\mathbf{H}$ proton were observed in both isomers.

[2-(3-Methylthienyl)]di(1-adamantyl)methane, 9-b. Reduction of either of the 2-(3-methylthienyl) alcohols, **5A-b** or **5S-b**, gives a single product which was identified by NOE as the *syn* isomer, **9S-b**. The rates of reaction of the *syn* and *anti* alcohols are

§ In the past[6,12,13,22,23,25] we have systematically used the same conformational descriptor, *anti* or *syn*, for an alcohol and the alkane obtained by removal of the oxygen atom, despite the fact that OH and H do not have the same priority with respect to carbon.[14] This practice, though incorrect, has the advantage that analogous structures bear the same descriptor, and we shall continue to employ it here.

Table 3 Rotation barriers (activation energies, $\Delta G^{\ddagger}$/kcal mol^{-1}) for heteroaryl- and aryldi(1-adamantyl)methanols and the corresponding methanes

Compound	Aryl or heteroaryl	X in Ad_2C–X	Solvent	Temp./°C	$\Delta G^{\ddagger}$/*anti*→*syn*	$\Delta G^{\ddagger}$/*syn*→*anti*
1-a	3-Methylphenyl[a]	OH	Chloroform	85–118	27.6 (100 °C)	27.8 (100 °C)
	3-Methylphenyl[a]	H	Chloroform	100–130	28.2 (115 °C)	28.4 (115 °C)
1-b	2-Methylphenyl[b]	OH	Dodecane	205–265	39.1 (200 °C)	
	2-Methylphenyl[b]	H	Toluene	257–285	45.3 (271 °C)	
3-a	(*N*-Methylpyrrol-2-yl)[c]	OH	Benzene	113–157	31.0 (135 °C)	
	(*N*-Methylpyrrol-2-yl)[c]	H	Benzene	150–195	34.9 (172 °C)	
8-b	[2-(3-Methylfuryl)]	H	Chloroform	30–50		24.3 (40 °C)
5-b	[2-(3-Methylthienyl)]	OH	Benzene	134–180	34.0 (157 °C)	32.1 (157 °C)
9-b	[2-(3-Methylthienyl)]	H	Chloroform	154–201	38.5 (178 °C)	34.6 (178 °C)
4-a	(2-Furyl)	OH	Chloroform	17–52	16.3 ± 0.2	17.4 ± 0.2
8-a	(2-Furyl)	H	Benzene	32–62	16.9 ± 0.2	17.3 ± 0.2
8-a	(2-Furyl)	H	Nitrobenzene	37–57	17.0 ± 0.3	17.4 ± 0.3
5-a	(2-Thienyl)	OH	DMSO	77–147	20.0 ± 0.2	21.1 ± 0.2
9-a	(2-Thienyl)	H	Nitrobenzene	87–137	20.2 ± 0.2	20.2 ± 0.2
8-c	[2-(4-Methylfuryl)]	H	Chloroform	32–52	17.8 ± 0.2	18.1 ± 0.2
5-c	[2-(4-Methylthienyl)]	OH	Nitrobenzene	97–167	21.5 ± 0.3	22.5 ± 0.4
9-c	[2-(4-Methylthienyl)]	H	Nitrobenzene	117–147	21.8 ± 0.1	21.8 ± 0.1
10	(2-Selenienyl)	H	Nitrobenzene	107–177	22.1 ± 0.2	21.7 ± 0.2
6	(Thiazol-2-yl)	OH	Toluene	47–87	18.2 ± 0.2	18.7 ± 0.2

[a] Ref. 12. [b] Ref. 11. [c] Ref. 15.

significantly different, and the *syn* isomer gives substantial amounts of diadamantyl ketone in addition to the expected deoxygenation product. The reactivity difference is obviously related to the difference in the thermodynamic stabilities of the two rotamers, the more strained giving the intermediate carbocation more readily. In the case of the more stable isomer, carbocation formation is competing with nucleophilic substitution at the heterocyclic nucleus, as has been observed in the corresponding reaction of (*N*-methylpyrrol-2-yl)diadamantylmethanol, **3-a**, where even the less stable isomer gives essentially diadamantyl ketone.[15]

Infinity samples for the rotation of the deoxygenation product (*vide infra*) show a very small amount (about 1.3%) of residual *syn* isomer, indicating that the energy difference between the rotamers is at least 4 kcal mol^{-1}, in any case significantly higher than for the alcohols.

(2-Furyl)di(1-adamantyl)methane, 8-a. The 2-furyl derivative, **4S-a**, was reduced by TES to a 2:1 mixture of isomers, obviously **8A-a** and **8S-a**, but the NOE experiment was equivocal, both protons in the 3-position showing a small enhancement when the α-methylene groups of the adamantanes were irradiated. If, however, we assume that sulfur and oxygen have similar effects upon the proton and carbon NMR shifts for the Ad_2C**H** group, then since both are smaller for the major component, as they are for *syn*-(2-thienyl)diadamantylmethane, **9S-a**, as compared to the *anti* isomer, **9A-a**, the conclusion is that this isomer is *syn*, **8S-a**. Again, assuming substituent effects are additive in ^{13}C NMR[27] and that the effects of replacing S by O on going from the *syn* 2-thienyl to the *syn* 2-furyl alcohol (**5S-a** to **4S-a**) are transferable to the methanes, we can predict the shifts for the aromatic CH carbons of the *syn* 2-furyl deoxygenation product, **8S-a**; compared to the experimental values for the major and minor isomers the rms values are 0.7 and 3.2 ppm, respectively.

[2-(3-Methylfuryl)]- and [2-(4-methylfuryl)]di(1-adamantyl)-methanes, 8-b and 8-c. Deoxygenation of **4-c**, the major product from the lithiation of 3-methylfuran and subsequent reaction with diadamantyl ketone, gives a 2:1 mixture of two isomers, with NMR spectra, particularly that of ^{13}C, very similar to those of the isomeric methanes, **8A-a** and **8S-a**, obtained from the parent compound, **4-a**. This confirms that **4-c** is the 2-(4-methylfuryl) derivative. The same treatment of **4-b** gives a small yield of a mixture of [2-(3-methylfuryl)]diadamantylmethanes, **8-b**, the major component of which proves to be the more stable, *anti* isomer, **8A-b**.

(2-Selenienyl)di(1-adamantyl)methane, 10. Deoxygenation of the 2-selenienyl derivative, **7S**, gives a 1.8:1 mixture of products, with the isomer having the higher NMR shifts for the Ad_2C**H** carbon and hydrogen predominating. The reasonable conclusion is that this is the *anti* isomer, **10A**, and that there is a smooth progression in the isomer ratio on going from the 2-furyl to the 2-thienyl to the 2-selenienyl system (2:1 to 1:1 to 1:1.8). Regularities in the shifts of the quaternary carbon atoms then appear, making it possible to complete the attribution for the 2-thienyl derivatives.

Rotation barriers in alcohols and the corresponding deoxygenation products

Rotation barriers were measured either by the conventional sampling technique, where ^{1}H NMR is used simply as an analytical method, or by dynamic NMR, where exchange is observed as it happens. It is convenient to refer to the phenomena concerned as "slow rotation" and "fast rotation", respectively. Data from this and previous work are summarized in Table 3.

Slow rotation. Rotation barriers for [2-(3-methylthienyl)]-diadamantylmethanol, **5S-b**, and the corresponding deoxygenation product, **9S-b**, are about 32 kcal mol^{-1} (benzene, 134–180 °C) and 34.6 kcal mol^{-1} (chloroform, 178 °C), respectively, the difference being consistent with previous work.[6,12,15]

[2-(3-Methylfuryl)]diadamantylmethane, **8S-b**, has an intermediate rotation barrier and was studied directly in the NMR probe. In chloroform at 30–50 °C the *syn*→*anti* rotation barrier is 24.3 kcal mol^{-1}, only 7 kcal mol^{-1} greater than for the parent compound (*vide infra*). This is much smaller than the difference, about 14 kcal mol^{-1}, for the corresponding 2-thienyl derivatives.

Fast rotation. *(i) Deoxygenation products.* Simulation of the exchange spectra (in nitrobenzene) for the aromatic and Ad_2C**H** protons in the 1:1 mixture of (2-thienyl)diadamantylmethanes, **9A-a** and **9S-a**, by means of the gNMR program[28] leads to an activation energy of 20.2 kcal mol^{-1} at 87–137 °C. For the 4-methyl derivative, **9-c**, the rotation barrier, measured in the same solvent, is slightly higher, 21.8 kcal mol^{-1}.

For (2-furyl)diadamantylmethane, **8-a**, the equilibrium con-

stant is not unity but is close to 2. The rate constant given by spectrum simulation, k_{ex}, is half the sum of the two, now different, rate constants involved in the equilibrium,[29] and the activation energies for rotation differ by the free energy difference between the two isomers. In nitrobenzene or benzene the activation energies are about 17.0 (*anti*→*syn*) and 17.4 (*syn*→*anti*) kcal mol^{-1}, substantially smaller than for the thiophene derivative. Again, the 4-methyl derivative, **8-c**, has higher rotation barriers: 17.8 (*anti*→*syn*) and 18.1 (*syn*→*anti*) kcal mol^{-1}.

Rotation barriers for (2-selenienyl)diadamantylmethane, **10**, are higher than for the 2-furyl (**8-a**) and 2-thienyl (**9-a**) analogues, the values being 22.1 (*anti*→*syn*) and 21.7 (*syn*→*anti*) kcal mol^{-1}.

(ii) Alcohols. The 2-furyl alcohol is obtained mainly as the *syn* isomer, **4S-a**, with at the most about 15% of the *anti* isomer in chloroform. Simulation of the variable-temperature spectra by gNMR gives an *anti*→*syn* value of 16.3 kcal mol^{-1} (17–52 °C), obtained on the basis of the coalescence of the 4-proton signals, the 3- and 5-proton signals being almost coincident in the two isomers. The *anti*/*syn* isomer ratio for (2-thienyl)-diadamantylmethanol, **5-a**, is slightly higher in DMSO (1 : 4.2) than in other solvents and, moreover, DMSO has a long liquid range; the activation energies (77–147 °C) for *anti*→*syn* and *syn*→*anti* rotation are 20.0 and 21.1 kcal mol^{-1}, respectively. The 4-methyl derivative, **5-c**, like the corresponding deoxygenation product, gives higher values than the parent alcohol, 21.5 and 22.5 kcal mol^{-1}. In similar experiments on the thiazol-2-yl alcohol, **6**, in toluene at 47–87 °C, where the *anti*→*syn* equilibrium constant is about 2, activation energies for rotation of 18.2 (*anti*→*syn*) and 18.7 (*syn*→*anti*) kcal mol^{-1} were found. Attempts to determine the rotation barriers for the 4-methyl-substituted furyl alcohol, **4-c**, and the 2-selenienyl alcohol, **7**, were thwarted by the lack of significant amounts of the minor, *anti* component in any solvent with an appropriate liquid temperature range.

Discussion

This study raises a number of issues concerning hydrogen bonding in heteroaryl-substituted alcohols, the stereoselectivity of organolithium addition to carbonyl bonds, that of ionic hydrogenation and the effects of steric size upon rotation barriers. Semi-empirical quantum mechanical calculations have been used to explain differences in rotamer stabilities, with somewhat limited success. The results are not sufficiently encouraging to warrant any attempt to interpret rotation barriers by this means.

Hydrogen bonding in heteroaryldiadamantylmethanols

None of the new alcohols gives evidence for significant inter- or intramolecular hydrogen bonding (the case of **5S-b** will be discussed in detail below) (Table 1). The OH stretching region of the IR spectrum consists generally of two sharp bands characteristic of free OH, separated by 10–20 cm^{-1}. The chemical shift of the OH proton in the ^{1}H NMR spectrum is highly solvent- and temperature-dependent, indicating hydrogen bonding (if any) with the solvent rather than intramolecular.

Usually, when there is a methyl group in proximity to the two adamantyl groups in one isomer, as in the *ortho*-tolyl[11,12] and *N*-methylpyrrol-2-yl[15] analogues, **1** and **3**, respectively, this isomer is considerably less stable than the other, by some 5–7 kcal mol^{-1}, according to molecular mechanics and semi-empirical quantum mechanical calculations. It is tempting, therefore, to attribute the much smaller difference in the stabilities of the isomeric [2-(3-methylthienyl)]diadamantylmethanols (1.3–1.9 kcal mol^{-1}) to compensatory hydrogen bonding between the sulfur atom and the OH hydrogen in the *syn* alcohol, **5S-b**. However, there is no spectroscopic evidence to support this view, the IR spectra and the NMR spectra showing no exceptional frequency shifts (Table 1). The OH region of the IR spectrum of the *syn* isomer consists of two bands, at 3600 and 3624 cm^{-1}, very similar in intensity, while the *anti* isomer has a peak at 3628 cm^{-1} with a shoulder at 3617 cm^{-1}. The separation in **5S-b** is admittedly slightly greater than is usual, but indicates at the most very weak hydrogen bonding. The difference between the shifts of the hydroxy proton in **5A-b** and **5S-b** (1.84 and 2.26 ppm, respectively, in benzene) is too small to support hydrogen bonding in **5S-b**. Moreover, the temperature dependence of the chemical shift in pyridine is high ($\Delta\delta/\Delta T = -21.5$ ppb °C^{-1}), which is characteristic of hydrogen bonding to the solvent.[13,30] We shall see that PM3 calculations on the relative stabilities of the two rotamers give a result in tolerable agreement with the experimental observation (*vide infra*).

Stereoselectivity in heteroaryllithium addition to di(1-adamantyl) ketone

An unexpected feature of the reaction of [2-(3-methylthienyl)]-lithium with diadamantyl ketone is that the *anti* and *syn* [2-(3-methylthienyl)]diadamantylmethanols, **5A-b** and **5S-b**, are formed in equal amounts, whereas in the reaction of *o*-tolyllithium[11,12] or (*N*-methylpyrrol-2-yl)lithium[15] the main, almost exclusive, product is the *anti* isomer. Normally, this addition is a kinetically controlled process, the less stable isomer being formed preferentially. In the present case addition is unselective. A rationale for this observation may be that the position of the transition state and, consequently, the importance of the interactions between the adamantyl and methyl groups depends on the nature of the nucleophile. *Ab initio* calculations on organolithium addition to a carbonyl group suggest that the transition state is early,[31] but this result may be in part an artefact attributable to the neglect of solvation.

No datum is available for the 2-(3-methylfuryl) alcohol, **4-b**, since only the stable, *anti* isomer was isolated. Either the alcohol is formed as the *anti* isomer or the initial *syn* product rotates during work-up. Since rotation barriers are usually lower for alcohols than for the corresponding methanes,[6,12,15] and as that for **8S-b** is already low (24.3 kcal mol^{-1}), the latter is a real possibility.

Clearly, the isomer ratios observed for the parent alcohols studied here, **4-a**, **5-a**, **6** and **7**, reflect the thermodynamic stabilities of the two isomers in a given solvent, the half-lives for rotation corresponding to a few seconds at room temperature. There is no way of knowing whether one isomer is formed preferentially; the NMR spectra only tell us what the rotamer equilibrium is in solution.[13]

Stereoselectivity in the ionic hydrogenation of heteroaryl-diadamantylmethanols

In previous work it was found that a methyl group at the 2-position of a benzene ring or on the pyrrolyl nitrogen directed hydride transfer to the opposite face of the intermediate carbocation.[15,25] The reduction of the 2-(3-methylthienyl) alcohols, **5-b**, to **9S-b** is consistent with this pattern of behaviour. In contrast, the major component of the [2-(3-methylfuryl)]-diadamantylmethanes, **8-b**, is the more stable, *anti* isomer. However, since the half-life for rotation of the *syn* isomer at room temperature is about 12 h, while the total time of reaction, work-up and chromatography is of the order of 24 h, the initial product could be largely, though not necessarily entirely, the *syn* isomer.

Semi-empirical quantum mechanical calculations

Optimized semi-empirical quantum mechanical calculations were run on as many of the alcohols and the corresponding methanes as possible. The PM3 parametrization was used for the sulfur-containing species, as it is generally preferable to AM1 for this purpose.[32]

AM1 calculations on the [2-(3-methylfuryl)]diadamantylmethanol rotamers, **4A-b** and **4S-b**, give a gas-phase energy difference of 2.6 kcal mol^{-1} in favour of the *anti* isomer. AM1 underestimates the relative stability of the *syn* isomer, **4S-a**, of the parent compound (by 1–3 kcal mol^{-1}, depending on the solvent),[13] but for the 3-methyl derivative no such "error" is apparent, there being no evidence for significant amounts of the *syn* isomer, **4S-b**, in any solvent. PM3 results for the [2-(3-methylthienyl)]diadamantylmethanols, **5A-b** and **5S-b**, give a very similar energy difference of 2.8 kcal mol^{-1}, again in favour of the *anti* isomer, and substantially less than previously found for methyl-substituted rotamer pairs.[11,12,15] This estimate is in fair agreement with the experimental datum (1.3–1.9 kcal mol^{-1}), though it overestimates the relative stability of the *anti* isomer by 0.9 kcal mol^{-1} (if we consider the least solvating solvent). In previous work on **5A-a** and **5S-a** a very similar "error" in the same direction was found (0.8 kcal mol^{-1} for benzene), the greater stability of the *syn* isomer in solution being underestimated by PM3.[13]

PM3 calculations agree with the experimental observation that there is very little difference in the stabilities of the two (2-thienyl)diadamantylmethane isomers, **9A-a** and **9S-a**, the calculated heat of formation of the *anti* isomer, **9A-a**, being the lesser by only 0.1 kcal mol^{-1}. AM1 calculations on the 2-furyl derivatives, **8S-a** and **8A-a**, indicate a slight preference (0.3 kcal mol^{-1}) for the *syn* isomer, in agreement with our interpretation of the NMR data.

According to molecular mechanics calculations (MMP2)[33] on *ortho*-tolyl derivatives,[12] **1**, and, more recently, AM1 calculations on *N*-methylpyrrolyl analogues,[14] **3-a**, the energy difference is greater for the rotameric alcohols than for the corresponding deoxygenation products by about 1 kcal mol^{-1}. The AM1-calculated gas-phase energy difference between the deoxygenated 3-methylfuryl compounds, **8A-b** and **8S-b**, is somewhat smaller (1.6 kcal mol^{-1}) than that for the corresponding alcohols, **4A-b** and **4S-b** (2.6 kcal mol^{-1}). This would suggest that there should be about 6% of the minor isomer, **8S-b**, at equilibrium at 25 °C; in fact, it cannot be detected. PM3 calculations make *anti*-[2-(3-methylthienyl)]diadamantylmethane, **9A-b**, only 0.8 kcal mol^{-1} more stable than **9S-b**, less than the calculated difference between the corresponding alcohols, **5A-b** and **5S-b** (2.8 kcal mol^{-1}). However, the experimental finding is that the difference between the alcohols is less than calculated and that between the deoxygenation products greater.

It has to be concluded that these semi-empirical quantum mechanical calculations of the gas-phase energy differences between rotamers are an unreliable guide to what is observed in solution, though they give good results for some deoxygenation products. This may be due to the lack of solvation or to inherent defects in the parametrizations, neither of which is easy to remedy for molecules of this degree of complexity.

Steric effects on rotation barriers

Generally, increasing the steric size of the groups at either end of the bond about which slow rotation is considered to occur results in an increase in the rotation barrier, destabilization of the transition state being greater than that of the ground state.[7,8] In our first studies of di(1-adamantyl)benzyl derivatives the accent was on very high rotation barriers, up to about 45 kcal mol^{-1} for *o*-tolyldi(1-adamantyl)methane,[6] making it possible to separate rotamers in several cases. Replacing the aromatic group by a five-membered heteroaromatic ring leads to much lower barriers, both for the 3-methyl-substituted and the unsubstituted compounds, though rotation is in all cases slow on the NMR time-scale at room temperature. The differences between the benzenoid aromatic and the corresponding heteroaromatic compounds can be attributed mainly to the larger exterior ring angles in these latter compounds and hence to the decreased non-bonded interactions with the adamantyl groups.

Rotation barriers for the five-membered heteroaryl systems are sensitive to the ring size, the larger heteroatom and, therefore, the smaller exterior ring angles being associated with the higher barriers. This is best illustrated by the regular increase in going from **8-a** to **9-a** to **10**, corresponding to the successive replacement of oxygen by sulfur and selenium in the heteroaryldiadamantylmethanes. The values are all smaller than that for the six-membered ring system, *m*-tolyldiadamantylmethane[12] (about 28 kcal mol^{-1} at 100–130 °C). The effect of introducing a methyl substituent at the carbon atom adjacent to that which bears the diadamantylmethyl group is to increase the barrier considerably, by 10–15 kcal mol^{-1} for the benzene and thiophene derivatives, but somewhat less (*ca*. 7 kcal mol^{-1} for the deoxygenation product) for the relatively unstrained 2-furyl system. The smallness of this difference is no doubt due to the lesser size of the furan ring and the fact that the methyl group is withdrawn from the locus of the adamantyl groups much more than for the sulfur-containing ring. That the introduction of a 4-methyl group, remote from the sterically demanding adamantyl groups, leads to a small increase in the rotation barriers can only be explained by differential effects upon the energies of the ground and transition states. The methyl group not only deforms the ring in the ground state (closure of the C3–C4–C5 bond angle) but must increase the energetic cost of deformation in the rotation transition state.

The effect of varying the "second" substituent at the 9-position in 9-arylfluorenes from H to OH to Cl is to reduce the rotation barrier.[34] This is attributed to increasing destabilization of the ground state, any effects on the transition state being implicitly smaller. Previous experience on aryldiadamantylmethyl derivatives has been that the alcohols have substantially lower barriers than the deoxygenation products.[6,12,15] but the difference is much greater for the very strained *o*-tolyldiadamantylmethyl system[6,6] than for the less strained phenyl[12] and *N*-methylpyrrolyl[15] analogues. The *anti*→*syn* rotation barriers for 2-furyl (and 2-thienyl) methanols and their deoxygenation products are very similar. The difference between alcohols and methanes, therefore, appears to decrease as the rotation barriers become smaller. Surprisingly, the *syn*→*anti* barriers for the 2-thienyl and 2-(4-methylthienyl) alcohols are higher than for the corresponding methanes. Given the polar character of the solvents used (DMSO and nitrobenzene) this may be due to stabilization of the *syn* isomer of the alcohols by solvation.

Conclusion

In conclusion, we now have a variety of aryl- and heteroaryldiadamantylmethyl derivatives with rotation barriers ranging from 16 to 45 kcal mol^{-1} and a qualitative understanding of the observed trends. The next question is whether it is possible to exploit the chemistry of the heteroaryl systems, in particular, in order to create species which will undergo a detectable and preferably reversible rotation when subjected to a chemical stimulus, such as radiation, oxido-reduction, solvent or pH change, and thereby to construct molecular-scale micromechanical devices.

Experimental

General methods

NMR measurements were performed on a Bruker AS 200 FT instrument operating at 200 MHz (proton) or 50 MHz (carbon). Chemical shifts are given in ppm and *J* values in Hz. All measurements were made in hexadeuteriobenzene, deuteriochloroform, pentadeuteriopyridine or hexadeuteriodimethyl sulfoxide (reference values: δ_H = 7.16, 7.26, 8.71 and

2.50 ppm for ^{1}H; δ_C = 128.0, 77.0, 149.9 and 39.5 ppm for ^{13}C, all relative to TMS). Carbon and hydrogen shifts of the heterocyclic system are numbered: C2, C3, *etc*. Generally, the proton signals were assigned on the basis of shifts, coupling constants,[21] and spectrum simulation by the gNMR program (Cherwell Scientific).[28] The corresponding ^{13}C signals were identified by heteronuclear correlation (XHCORR) experiments. Samples for NOE experiments were solutions in deuteriochloroform degassed by several freeze–pump–thaw cycles before sealing under vacuum. Measurements were made on a Bruker AM-500 spectrometer at 500 MHz using the NOEDIFF pulse sequence.[13] IR spectra were measured in carbon tetrachloride on a Nicolet 60SX FTIR spectrometer with 2 cm^{-1} resolution. Lorentzian deconvolution was used to locate shoulders and to resolve broad absorptions. Gas chromatography was performed on a 30 cm 10% SE30 on Chrompack column. Column chromatography was performed on silica gel 60 (Merck) in light petroleum (boiling range 35–60 °C)–dichloromethane mixtures. Melting points were determined in capillary glass tubes on a Mettler FP5 instrument with a heating rate of 3 °C min^{-1}.

Synthesis of heteroaryldi(1-adamantyl)methanols

[2-(3-Methylfuryl)]di(1-adamantyl)methanol, 4-b and [2-(4-methylfuryl)]di(1-adamantyl)methanol, 4-c. A solution of 3-methylfuran[20] (1.35 cm^3, 15 mmol) and TMEDA (2.3 cm^3, 15 mmol) in sodium–dry diethyl ether (50 cm^3) was stirred at 0 °C under argon while a solution of *n*-butyllithium in hexane (1.6 M, 9.3 cm^3, 15 mmol) was added. The cooling bath was removed and the temperature allowed to rise during 30 min, after which a solution of di(1-adamantyl) ketone (0.5 g, 1.7 mmol) in diethyl ether (60 cm^3) was added in about 10 min. After 1 h the reaction mixture was quenched with water, the organic layer washed with water, dried ($MgSO_4$) and the solvent evaporated off at reduced pressure. The residue consisted of a 2:1 mixture of isomeric [2-(X-methylfuryl)]diadamantylmethanols which were separated by chromatography on silica gel. Faster-running (210 mg, 33%) and slightly slower fractions (389 mg, 61%), consisting of almost pure materials, were obtained. The latter, [2-(4-methylfuryl)]diadamantylmethanol, was identified by NOE as the *syn* isomer, **4S-c**: mp 170 °C; ν_{OH}/cm^{-1} (CCl_4) 3608, 3618, 3628; δ_C (chloroform) 9.8 (CH_3), 29.1 (6 CH), 37.1 (6 CH_2), 38.6 (6 CH_2), 44.4 (2 C_q), 82.4 (COH), 110.8 (C4), 119.4 (C3), 136.7 (C5) and 159.9 (C2); δ_H (chloroform) 1.62 (br s, Ad), 1.7–2.0 (br m, Ad), 2.01 (CH_3, *J* 0.6 and 1.2), 6.02 (H3, *J* 0.6 and 1.1) and 7.11 (H5, *J* 1.1 and 1.2) (Found: C, 81.7; H, 9.6. $C_{26}H_{36}O_2$ requires C, 82.06; H, 9.53%). The minor component, [2-(3-methylfuryl)]diadamantylmethanol, was identified by single crystal X-ray diffraction as the *anti* isomer (the cyclic oxygen has priority), **4A-b**: mp 169 °C; ν_{OH}/cm^{-1} (CCl_4) 3612sh, 3627; δ_C (chloroform) 12.1 (CH_3), 29.1 (6 CH), 37.1 (6 CH_2), 38.6 (6 CH_2), 45.8 (2 C_q), 84.8 (COH), 113.9 (CH), 117.7 (C3), 137.9 (CH) and 152.4 (C2); δ_H (chloroform) 1.62 (br s, Ad), 1.7–2.0 (br m, Ad), 2.15 (CH_3, *J* 0.3 and 0.3), 6.11 (H4, *J* 0.3 and 1.7) and 7.24 (H5, *J* 0.3 and 1.7) (Found: C, 81.7; H, 9.4. $C_{26}H_{36}O_2$ requires C, 82.06; H, 9.53%).

[2-(3-Methylthienyl)]di(1-adamantyl)methanol, 5-b. 2-Bromo-3-methylthiophene (0.25 cm^3, 2.2 mmol) was stirred in sodium–dry diethyl ether (10 cm^3) under argon at −15 °C. A solution of *tert*-butyllithium in pentane (1.5 M, 2.5 cm^3, 3.8 mmol) was added dropwise in about 1 min and the cooling bath removed. After stirring for 1 h, a solution of di(1-adamantyl) ketone (0.15 g, 0.5 mmol) in diethyl ether (20 cm^3) was added in about 10 min. After 3–4 h the reaction mixture was quenched with water, and worked up as for **4-b** and **4-c**. ^{1}H NMR showed the crude product to consist mainly of a 1:1 mixture of two isomeric alcohols. Chromatography separated cleanly the faster running *anti*, **5A-b** (89 mg, 45%) from the slower *syn* isomer, **5S-b** (98 mg, 49%). **5A-b**: mp 192 °C (methanol); ν_{OH}/cm^{-1} (CCl_4) 3617sh, 3628; δ_C (benzene) 18.6 (CH_3), 29.6 (6 CH), 37.3 (6 CH_2), 39.1 (6 CH_2), 46.4 (2 C_q), 88.3 (COH), 120.6 (C5), 131.3 (C4), 136.7 (C2 or C3) and 138.0 (C2 or C3); δ_H (benzene) 1.60 (br s, Ad), 1.8–2.2 (br m, Ad), 1.84 (OH), 2.50 (CH_3), 6.62 (H4, *J* 5.1) and 6.83 (H5, *J* 5.1) (Found: C, 78.5; H, 9.2; S, 8.0. $C_{26}H_{36}OS$ requires C, 78.73; H, 9.15; S, 8.08%). **5S-b**: mp 171 °C (methanol); ν_{OH}/cm^{-1} (CCl_4) 3600, 3628; δ_C (benzene) 21.3 (CH_3), 29.6 (6 CH), 37.2 (6 CH_2), 39.5 (6 CH_2), 46.1 (2 C_q), 87.3 (COH), 122.3 (C5), 129.6 (C3), 133.4 (C4) and 149.0 (C2); δ_H (benzene) 1.57 (br s, Ad), 1.8–2.2 (br m, Ad), 2.26 (OH), 2.34 (CH_3), 6.71 (H4, *J* 5.2) and 6.95 (H5, *J* 5.2) (Found: C, 78.6; H, 9.3; S, 8.2. $C_{26}H_{36}OS$ requires C, 78.73; H, 9.15; S, 8.08%).

Samples of alcohol **5S-b** in various, generally deuteriated, solvents were sealed under vacuum in small tubes and heated at 150 °C for 8 h. In the case of isooctane the solvent was evaporated off and the residue taken up in chloroform for NMR analysis. *Anti*/*syn* ratios determined by ^{1}H NMR were as follows: DMSO, 4.9; $CDCl_3$, 7.2; pyridine, 6.6; benzene (see below), 9.0; isooctane, 9.8.

[2-(4-Methylthienyl)]di(1-adamantyl)methanol, 5-c. A solution of 3-methylthiophene (0.5 cm^3, 5 mmol) and TMEDA (0.75 cm^3, 5 mmol) in sodium–dry diethyl ether (10 cm^3) was stirred at 0 °C under argon while a solution of *n*-butyllithium in hexane (1.6 M, 3.1 cm^3, 5 mmol) was added dropwise in about 1 min. The cooling bath was removed and the temperature allowed to rise during 30 min, after which a solution of di(1-adamantyl) ketone (0.15 g, 0.5 mmol) in diethyl ether (20 cm^3) was added in about 10 min. After 1 h the reaction mixture was quenched with water and worked up as usual. The product after purification by column chromatography and crystallization from hexane (138 mg, 67%; mp 241 °C) consisted of two isomers in a ratio of 5:1 in benzene. Major isomer, **5S-c**: ν_{OH}/cm^{-1} (CCl_4) 3607, 3626; δ_C (benzene) 16.3 (CH_3), 29.5 (6 CH), 37.2 (6 CH_2), 39.1 (6 CH_2), 45.2 (2 C_q), 84.6 (COH), 118.2 (CH), 125.0 (CH), 136.7 (C4) and 152.1 (C2); δ_H (benzene) 1.60 and 1.8–2.2 (br m, Ad), 2.11 (CH_3, *J* 1.1), 6.62 (H, *J* 1.1 and 1.1) and 6.79 (H, *J* 1.1). Minor isomer, **5A-c**: δ_C (benzene) 17.9 (CH_3), 29.6 (6 CH), 37.2 (6 CH_2), 39.1 (6 CH_2), 44.7 (2 C_q), 85.3 (COH), 119.2 (CH), 129.7 (CH), 134.7 (C4) and 156.8 (C2); δ_H (benzene) 1.60 and 1.8–2.2 (br m, Ad), 2.08 (CH_3, *J* 1.0), 6.56 (H, *J* 1.0 and 1.6) and 6.95 (H, *J* 1.6); OH proton signals could not be located (Found: C, 78.8; H, 9.2; S, 8.3. $C_{26}H_{36}OS$ requires C, 78.73; H, 9.15; S, 8.08%).

(3-Selenienyl)di(1-adamantyl)methanol, 7. To a solution of selenophene (0.43 cm^3, 0.65 g, 5 mmol) in sodium–dry diethyl ether (10 cm^3) stirred at room temperature under argon was added a solution of *n*-butyllithium in hexane (1.6 M, 3.1 cm^3, 5 mmol). After 30 min a solution of di(1-adamantyl) ketone (0.45 g, 1.5 mmol) in diethyl ether (50 cm^3) was added in about 10 min. After 2 h the reaction mixture was quenched with water, the organic material extracted with hexane, worked up as usual and purified by column chromatography to give the required alcohol (0.54 g, 83%), identified by NOE as the *syn* isomer, **7S**: mp 224 °C (hexane); ν_{OH}/cm^{-1} (CCl_4) 3608sh, 3624; δ_C (chloroform) 29.1 (6 CH), 36.9 (6 CH_2), 38.1 (6 CH_2), 45.1 (2 C_q), 85.7 (OH), 123.9 (C3), 126.9 (C5), 129.2 (C4) and 160.1 (C2); δ_H (chloroform) 1.61 and 1.8–2.1 (br m, Ad), 2.54 (OH), 7.09 (H3, *J* 0.8 and 3.9), 7.28 (H4, *J* 3.9 and 5.7) and 7.85 (H5, *J* 0.8 and 5.7) (Found: C, 69.5; H, 8.0; Se, 17.9. $C_{25}H_{34}SeO$ requires C, 69.91; H, 7.98; Se, 18.38%).

Ionic hydrogenation of heteroaryldi(1-adamantyl)methanols

(2-Furyl)di(1-adamantyl)methane, 8-a. Treatment of alcohol **4S-a** (100 mg, 0.27 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temper-

ature for 3 h gave a 2 : 1 mixture of two (2-furyl)di(1-adamantyl)-methanes (82 mg, 86%, mp 143 °C). Major product, **8S-a** (*i.e.* oxygen *syn* to Ad_2CH hydrogen): δ_C (chloroform) 29.2 (6 CH), 37.0 (6 CH_2), 38.9 (2 C_q), 42.7 (6 CH_2), 61.5 (CH), 108.9 (C4), 109.5 (C3), 140.2 (C5) and 157.5 (C2); δ_H (chloroform) 1.62 and 1.89 (br m, Ad), 1.97 (CH), 5.85 (H3, *J* 1.1 and 3.0), 6.25 (H4, *J* 1.8 and 3.0) and 7.35 (H5, *J* 1.1 and 1.8). Minor product, **8A-a**: δ_C (chloroform) 29.0 (6 CH), 37.0 (6 CH_2), 39.1 (2 C_q), 42.3 (6 CH_2), 62.3 (CH), 105.7 (C3), 110.2 (C4), 138.6 (C5) and 156.9 (C2); δ_H (chloroform) 1.62 and 1.89 (br m, Ad), 2.23 (CH), 6.04 (H3, *J* 0.7 and 3.0), 6.33 (H4, *J* 1.8 and 3.0) and 7.28 (H5, *J* 0.7 and 1.8) (Found: C, 86.0; H, 9.7. $C_{25}H_{34}O$ requires C, 85.66; H, 9.78%).

The same reaction performed with TTMSS (0.15 cm^3, 0.49 mmol) instead of TES gave after 12 h a 40% yield of the same isomer mixture.

[2-(3-Methylfuryl)]di(1-adamantyl)methane, 8-b. Treatment of alcohol **4A-b** (205 mg, 0.54 mmol) in dichloromethane (20 cm^3) with TES (0.25 cm^3, 1.6 mmol) and TFA (1.0 cm^3) at room temperature for 20 h gave after silica chromatography in pentane (care should be taken not to heat the material at any stage of the work-up) a mixture of two [2-(3-methylfuryl)]-diadamantylmethanes in a ratio ranging from about 3 : 1 to 1 : 1 (58 mg, 30%). In most experiments the major deoxygenation product was **8A-b** (*i.e.* oxgyen *anti* to Ad_2CH hydrogen): mp 161 °C (after trituration with methanol); δ_C (benzene) 11.0 (CH_3), 29.6 (6 CH), 37.3 (6 CH_2), 40.3 (2 C_q), 43.1 (6 CH_2), 58.6 (CH), 112.3 (C4), 116.9 (C3), 139.1 (C5) and 153.5 (C2); δ_H (benzene) 1.64 and 1.7–2.1 (br m, Ad), 1.87 (CH_3), 2.06 (CH), 6.05 (H4, *J* 1.7) and 7.16 (H5, masked by solvent). Minor product, **8S-b**: δ_C (benzene) 14.1 (CH_3), 29.6 (6 CH), 37.2 (6 CH_2), 39.9 (2 C_q), 43.4 (6 CH_2), 64.2 (CH), 114.1 (C3), 115.0 (C4), 138.5 (C5) and 153.5 (C2); δ_H (benzene) 1.63 and 1.7–2.1 (br m, Ad), 2.09 (CH_3), 2.55 (CH), 6.07 (H4, *J* 1.7) and 7.11 (H5, *J* 1.7) (Found: C, 85.5; H, 10.1. $C_{26}H_{36}O$ requires C, 85.66; H, 9.95%).

[2-(4-Methylfuryl)]di(1-adamantyl)methane, 8-c. Treatment of alcohol **4-c** (100 mg, 0.26 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temperature for 2 h gave a 2 : 1 mixture of two [2-(4-methylfuryl)]diadamantylmethanes (56 mg, 58%, mp 155 °C after chromatography and recrystallization from a mixture of methanol and diethyl ether). Major product, **8S-c** (*i.e.* oxygen *syn* to Ad_2CH hydrogen): δ_C (chloroform) 9.9 (CH_3), 29.2 (6 CH), 37.0 (6 CH_2), 38.9 (2 C_q), 42.8 (6 CH_2), 61.5 (CH), 112.6 (C3), 119.2 (C4), 136.8 (C5) and 157.5 (C2); δ_H (chloroform) 1.61 and 1.7–2.0 (br m, Ad), 1.88 (CH), 2.00 (CH_3, *J* 1.2), 5.70 (H3, *J* 0.9 and 1.2) and 7.10 (H5, *J* 0.9). Minor product, **8A-c**: δ_C (chloroform) 10.2 (CH_3), 29.1 (6 CH), 37.0 (6 CH_2), 39.0 (2 C_q), 42.3 (6 CH_2), 62.6 (CH), 108.8 (C3), 120.5 (C4), 135.2 (C5) and 156.8 (C2); δ_H (chloroform) 1.61 and 1.7–2.0 (br m, Ad), 2.04 (CH_3, *J* 0.5 and 1.2), 2.12 (CH), 5.89 (H3, *J* 0.7 and 1.2) and 7.03 (H5, *J* 0.5 and 0.7) (Found: C, 85.7; H, 9.8. $C_{26}H_{36}O$ requires C, 85.66; H, 9.95%).

(2-Thienyl)di(1-adamantyl)methane, 9-a. Treatment of alcohol **5S-a** (100 mg, 0.26 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temperature for 4 h gave a 1 : 1 mixture of two (2-thienyl)di(1-adamantyl)methanes (78 mg, 81%, mp 192 °C). On the basis of NOE, COSY and HETCOR experiments the ^1H and ^{13}C NMR spectra were assigned as follows. **9A-a** (*i.e.* sulfur *anti* to Ad_2CH hydrogen): δ_C (chloroform) 29.2 (6 CH), 36.9 (6 CH_2), 38.7 (2 C_q), 42.7 (6 CH_2), 65.4 (CH), 123.3 (C5), 124.4 (C4), 129.2 (C3) and 144.3 (C2); δ_H (chloroform) 1.60 and 1.88 (br m, Ad), 2.45 (CH, *J* 1.1), 6.59 (H3, *J* 1.3 and 3.4), 6.90 (H4, *J* 3.4 and 5.1) and 7.16 (H5, *J* 1.1, 1.3 and 5.1). **9S-a**: δ_C (chloroform) 29.2 (6 CH), 36.9 (6 CH_2), 39.5 (2 C_q), 42.8 (6 CH_2), 62.5 (CH), 120.7 (C5), 124.2 (C3), 126.7 (C4) and 144.5 (C2); δ_H (chloroform) 1.60 and 1.88 (br m, Ad), 2.18 (CH, *J* 0.3, 0.45 and 0.55), 6.84 (H3, *J* 0.45, 1.1 and 3.4), 6.98 (H4, *J* 0.3, 3.4 and 5.2) and 7.05 (H5, *J* 0.55, 1.1 and 5.2) (Found: C, 81.7; H, 9.6; S 8.6. $C_{25}H_{34}S$ requires C, 81.91; H, 9.35; S, 8.75%).

The same reaction performed with TTMSS (0.15 cm^3, 0.49 mmol) instead of TES gave after 16 h an 80% yield of the same isomer mixture.

[2-(3-Methylthienyl)]di(1-adamantyl)methane, 9-b. Treatment of alcohol **5S-b** (100 mg, 0.25 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temperature for 2 h, followed by column chromatography gave a single deoxygenation product (90 mg, 93%), identified by NOE as the *syn* isomer, **9S-b** (*i.e.* sulfur *syn* to Ad_2CH hydrogen): mp 132 °C (methanol-washed); δ_C (benzene) 19.3 (CH_3), 29.7 (6 CH), 37.16 (6 CH_2), 40.2 (2 C_q), 43.8 (6 CH_2), 64.8 (CH), 120.9 (C5), 131.4 (C3), 132.7 (C4) and 139.5 (C2); δ_H (benzene) 1.60 and 1.8–2.2 (br m, Ad), 2.28 (CH_3), 2.41 (CH), 6.68 (H4, *J* 5.0) and 6.78 (H5, *J* 5.0). The ^1H NMR spectrum is considerably different in chloroform: δ_H 1.63 and 1.7–2.0 (br m, Ad), 2.30 (CH), 2.36 (CH_3), 6.77 (H4, *J* 5.2) and 6.94 (H5, *J* 5.2) (Found: C, 81.7; H, 9.4; S, 8.5. $C_{26}H_{36}S$ requires C, 82.04; H, 9.53; S, 8.42%).

Heating the material in benzene at 150 °C for 10 h gave about 50% conversion to the *anti* isomer, **9A-b**: δ_C (benzene) 15.5 (CH_3), 29.6 (6 CH), 37.25 (6 CH_2), 40.0 (2 C_q), 42.9 (6 CH_2), 60.9 (CH), 121.1 (C5), 128.8 (C4), 135.2 (C_q) and 138.3 (C_q); δ_H (benzene) 1.60 and 1.8–2.2 (br m, Ad), 2.10 (CH_3, *J* 0.7), 2.58 (CH), 6.71 (H4, *J* 5.1) and 6.90 (H5, *J* 0.7 and 5.1).

Ionic hydrogenation of the *anti* isomer, **5A-b**, under the same conditions as for **5S-b** gave after 16 h the deoxygenation product (54 mg, 56%), diadamantyl ketone (20 mg, 27%) and residual alcohol (5 mg, 5%).

[2-(4-Methylthienyl)]di(1-adamantyl)methane, 9-c. Treatment of alcohol **5-c** (124 mg, 0.31 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temperature for 4 h, followed by column chromatography gave a 1 : 1 mixture of two isomeric compounds (97 mg, 82%, mp 217 °C). The NMR spectra (except for the quaternary carbons) were attributed by comparison with those of the parent compounds, **9A-a** and **9S-a**. **9A-c**: δ_C (chloroform) 16.3 (CH_3), 29.2 (6 CH), 36.9 (6 CH_2), 38.6 (2 C_q), 42.7 (6 CH_2), 65.4 (CH), 118.5 (C5), 131.9 (C3), 134.8 (C4) and 144.1 (C2); δ_H (benzene) 1.60 and 1.90 (br m, Ad), 2.07 (CH_3, *J* 0.2 and 1.0), 2.36 (CH, *J* 1.0), 6.37 (H3, *J* 0.2 and 1.6) and 6.56 (H5, *J* 1.0, 1.0 and 1.6). **9S-c**: δ_C (chloroform) 15.6 (CH_3), 29.2 (6 CH), 36.9 (6 CH_2), 39.5 (2 C_q), 42.8 (6 CH_2), 63.0 (CH), 116.1 (C5), 126.7 (C3), 137.2 (C4) and 144.4 (C2); δ_H (benzene) 1.60 and 1.90 (br m, Ad), 2.10 (CH_3, *J* 0.3 and 1.0), 2.16 (CH, *J* 0.2 and 0.3), 6.49 (H3, *J* 0.3, 1.0 and 1.2) and 6.74 (H5, *J* 0.2, 0.3 and 1.2) (Found: C, 82.0; H, 9.5; S, 8.3. $C_{26}H_{36}S$ requires C, 82.04; H, 9.53; S, 8.42%).

(3-Selenienyl)di(1-adamantyl)methane, 10. Treatment of alcohol **7S** (100 mg, 0.24 mmol) in dichloromethane (10 cm^3) with TES (0.1 cm^3, 0.63 mmol) and TFA (0.5 cm^3) at room temperature for 3 h gave a 1.8 : 1 mixture (51 mg, 53%) of two (2-selenienyl)di(1-adamantyl)methanes, mp 199 °C (methanol–chloroform). Major product, **10A** (*i.e.* selenium *anti* to Ad_2CH hydrogen): δ_C (chloroform) 29.2 (6 CH), 36.9 (6 CH_2), 38.4 (2 C_q), 42.7 (6 CH_2), 67.5 (CH), 127.0 (C4), 128.5 (C5), 131.1 (C3) and 150.9 (C2); δ_H (chloroform) 1.6–2.1 (br m, Ad), 2.51 (CH), 6.77 (H3, *J* 1.1 and 3.6), 7.16 (H4, *J* 3.6 and 5.6) and 7.84 (H5, *J* 1.1 and 5.6). Minor product, **10S**: δ_C (chloroform) 29.2 (6 CH), 36.9 (6 CH_2), 39.6 (2 C_q), 42.9 (6 CH_2), 63.9 (CH), 126.4 (C3), 126.4 (C5), 129.4 (C4) and 152.1 (C2); δ_H (chloroform) 1.6–2.1 (br m, Ad), 2.34 (CH), 7.02 (H3, *J* 0.8 and 3.7), 7.25 (H4, *J* 3.7 and 5.6) and 7.75 (H5, *J* 0.8 and 5.6) (Found: C,

72.7; H, 8.4; Se, 18.7. $C_{25}H_{34}Se$ requires C, 72.62; H, 8.29; Se 19.10%).

Rotation kinetics

Slow rotation. Aliquots (0.1 cm^3) containing about 2 mg (*ca.* 0.05 M) of *syn* [2-(3-methylthienyl)]diadamantylmethanol, **5S-b**, in hexadeuteriobenzene were sealed under vacuum in 5 mm o.d. glass tubes. Batches of tubes (8 samples per run on average) were thermostatted in an oil bath and samples withdrawn at convenient intervals. Each sample was made up to 0.45 cm^3 with hexadeuteriobenzene for ^{1}H NMR analysis, the methyl group peaks at 2.34 (*syn*) and 2.50 (*anti*) ppm being used to estimate the progress of the reaction. A further two samples taken after 10 half-lives were used to determine the equilibrium constant. First-order rate constants were determined from plots of log [%*syn*(t) − %*syn*(∞)] *vs.* time (t). Rate constants were as follows (T/°C, k/s^{-1},%*syn* at equilibrium), the error limits being the standard deviations on single runs: 133.7, $5.74 \pm 0.03 \times 10^{-5}$, 10.1 ± 0.1; 149.7, $2.54 \pm 0.03 \times 10^{-4}$, 10.1 ± 0.1; 164.6, $9.13 \pm 0.11 \times 10^{-4}$, 10.2 ± 0.1; 180.0, $3.13 \pm 0.02 \times 10^{-3}$, 10.3 ± 0.2, giving for the forward reaction: $\Delta H^{\ddagger} = 30.8 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.1 \pm 0.2$ cal mol^{-1} K^{-1}, with $\Delta G^{\ddagger}$(157 °C) = 32.1 kcal mol^{-1}; for the reverse reaction: $\Delta H^{\ddagger} = 31.1 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.8 \pm 0.7$ cal mol^{-1} K^{-1}, with $\Delta G^{\ddagger}$(157 °C) = 34.0 kcal mol^{-1}.

The rotation of *syn*-[2-(3-methylthienyl)]diadamantylmethane, **9S-b**, was studied in deuteriochloroform (because of peak overlap in benzene), the methyl signals at 2.36 (*syn*) and 2.14 (*anti*) ppm being used to follow the reaction; (T/°C, k/s^{-1}): 154.1, 2.28×10^{-5}; 170.0, $8.86 \pm 0.04 \times 10^{-5}$; 186.0, $3.19 \pm 0.03 \times 10^{-4}$; 200.6, $9.65 \pm 0.05 \times 10^{-4}$ giving: $\Delta H^{\ddagger} = 31.5 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.8 \pm 0.2$ cal mol^{-1} K^{-1}, with $\Delta G^{\ddagger}$(178; 157 °C) = 34.6; 34.4 kcal mol^{-1}. Infinity samples (10 half-lives) taken at 200.6 °C showed 1.3 ± 0.1% residual *syn* isomer, corresponding to an energy difference of 4.1 kcal mol^{-1}.

[2-(3-Methylfuryl)]diadamantylmethane was obtained as a mixture of *anti* and *syn* isomers, **8A-b** and **8S-b**, the less stable, *syn* isomer representing 25–50% of the total. The methyl group signal at 2.16 ppm of a solution of this material in deuteriochloroform (*ca.* 7 mg in 0.5 cm^3; initial **8S-b** concentration *ca.* 0.01 M) was monitored in the NMR probe, 2,5-dimethylfuran (methyl signal at 2.25 ppm) being used as internal standard; (T/°C, k/s^{-1}): 30.0, $1.38 \pm 0.01 \times 10^{-5}$; 40.0, $5.06 \pm 0.04 \times 10^{-5}$; 45.0, $9.59 \pm 0.09 \times 10^{-5}$; 50.0, $1.75 \pm 0.03 \times 10^{-4}$ giving: $\Delta H^{\ddagger} = 23.6 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.2 \pm 0.5$ cal mol^{-1} K^{-1}, with $\Delta G^{\ddagger}$(30–50 °C) = 24.3 kcal mol^{-1}.

Fast rotation. While the rotation activation energy can be estimated from the coalescence temperature in the case of **9-a** and **9-c**, where the equilibrium constant, K, is close to unity, this is not possible for **6**, **8-a** and **8-c**, where the value is close to 2, or for **4-a** and **5-a**, where it is over 4. For this reason activation energies were determined at all experimental temperatures by simulating the exchange spectra with the gNMR program using full lineshape analysis. A "low-temperature" spectrum (no exchange) was first simulated to determine shifts, coupling constants, line-widths and relative concentrations. Variations in the last three parameters at higher temperatures were neglected, but shifts were observed to be temperature-dependent and were, therefore, optimized at each temperature at the same time as the exchange rate constant, k_{ex}. This latter is the rate constant for the conversion of A to S or S to A when the equilibrium constant is unity. When this is not the case, there are different rate constants for A and S, with $k_A/k_S = K = ([S]/[A])_{eq}$ and $k_A + k_S = 2\ k_{ex}$.[29] The activation energies are not sufficiently regular for activation enthalpies and entropies to be determined; the values listed are mean activation energies based on 5–8 measurements at 5 or 10 °C intervals in the ranges indicated. Results are given in Table 3.

X-Ray crystallography¶

***anti*-[2-(3-Methylfuryl)]di(1-adamantyl)methanol, 4A-b: $C_{26}H_{36}O_2$.** *Crystal data.* $M = 380.6$. Triclinic, $a = 6.663(4)$, $b = 11.047(3)$, $c = 15.062(8)$ Å, $\alpha = 68.89(4)$, $\beta = 87.16(5)$, $\gamma = 80.26(3)°$, $V = 1019(1)$ Å^3 (by least squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group P-1, $Z = 2$, $D_x = 1.24$ g cm^{-3}. Colourless prismatic crystals, ν(Mo-Kα) = 0.7 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.8 + 0.345 tan θ, graphite-monochromated Mo-Kα radiation. 3899 reflections measured ($1 \leq \theta \leq 25°$), 3563 unique, giving 2289 with $I > 3\sigma(I)$.

Structure analysis and refinement. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic; hydrogens located from Fourier difference map with one, overall, refined isotropic thermal parameter (255 refinable parameters). No absorption correction. Final R and R_w (Chebyshev series) values are 0.073 and 0.085. Programs used are the PC version of CRYSTALS[35] for refinements and CAMERON[36] for views.

Semi-empirical quantum mechanical calculations

The Spartan package[32] with AM1 and PM3 (for sulfur-containing species) was used for semi-empirical calculations. The heats of formation (kcal mol^{-1}) listed are those for the lowest-energy conformations within the different conformers: **4S-b** (AM1), −98.9; **4S-b** (AM1), −96.3; **5A-b** (PM3), −54.0; **5S-b** (PM3), −51.2; **8A-a** (AM1), −55.9; **8S-a** (AM1), −56.2; **8A-b** (AM1), −63.7; **8S-b** (AM1), −62.1; **9A-a** (PM3), −30.3; **9S-a** (PM3), −30.2; **9A-b** (PM3), −24.1; **9S-b** (PM3), −23.3.

¶ CCDC reference number 188/183. See http://www.rsc.org/suppdata/p2/1999/2001 for crystallographic files in .cif format.

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