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The conformational effects of the quaternary centre in  $(RCH_2CH_2)_4X_q$  species are studied by molecular mechanics calculations on hydrocarbons, ammonium ions, and related species, and the results verified by data on quaternary ammonium ions from the Cambridge Structural Database.  $Pr^*_4C$  and  $Pr^*_4N^+$  have just two low-energy structures, with  $D_{2d}$  or  $S_4$  symmetry. All other conformations suffer from  $g^+g^-$  non-bonding interactions and will be populated to the extent of <5% at ambient temperatures. These non-bonding interactions affect both the inner torsion angles,  $CH_2-CH_2-X_q-CH_2$  and the next set of torsions,  $-CH_2-CH_2-CH_2-X_q$ , but the third set of torsions away from the quaternary centre is unaffected. Two competitive mechanisms for interconversion of the  $D_{2d}$  and  $S_4$  conformations are proposed on the basis of molecular mechanics calculations. Polymers  $[(RCH_2CH_2)_2C(CH_2)_2]_n$  and  $[(RCH_2CH_2)_2C(CH_2)_3]_n$  are strain-free with controlled conformations for the  $-(CH_2)_2-$  and  $-(CH_2)_3-$  segments. In polymers containing simple alkyl side chains, there are two energetically similar conformations associated with the  $D_{2d}$  local structure which have  $aaaa$  and  $ag^+g^+a$  torsion angle sequences for the polymer chain, and two comparable sequences  $ag^+aa$  and  $ag^+g^+a$  associated with  $S_4$  local symmetry. Poly[(1,1-di-R)butane-1,4-diyl]s ( $R = Et, Pr, Bu$  and  $PhCH_2CH_2$ ) have been prepared by ring opening metathesis polymerisation of 3,3-dialkylcyclobutenes, followed by diimide reduction, and their physical properties are in accord with these predictions. More highly structured side groups can act as extra conformational control elements, and the preparation of monomers and some polymers with these extra features is reported. Planar aromatic side groups like fluorene favour  $aaaa$  conformations, cyclohexyl side groups disfavour  $aaaa$ , but do not strongly discriminate between  $ag^+aa$  and  $ag^+g^+a$ , adamantane side groups strongly favour  $ag^+g^+a$ , and a chiral  $ag^+aa$  sequence is favoured for a polymer from (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene, itself derived from  $\alpha$ -pinene. Studies directed at preparing some structurally-related ketal polymers and a potential covalent ketal network are also described.

### Introduction

Methods for controlling the conformations around C–C bonds have wide significance since many important properties are crucially dependent on molecular shape. While conformational control of a structure by the incorporation of rings is very well known, methods for the control of conformation in acyclic molecules have been less thoroughly investigated. Simple acyclic molecules can be surprisingly complex conformationally. Thus  $n$ -hexane has 12 distinct conformations, of which 6 will be populated to the extent of 4% or more at 298 K, according to *ab initio* MP4SDQ/6-31G\*\*/6-31G\* calculations.<sup>1</sup> The complexity of this case is in striking contrast to cyclohexane, where only two conformations are possible (Fig. 1). Fig. 1 also shows the calculated conformational energy level diagram for  $Et_4C$ , the simplest example of the type of molecule discussed in this paper, and it can be seen that two conformations are dominant, a much simpler regime than for  $n$ -hexane.

In general, the conformations of acyclic molecules can only be controlled by using non-bonding interactions, and a number of examples of this control have appeared in recent years,<sup>2</sup> especially in the elegant work of Still<sup>3</sup> and Hoffmann.<sup>4,5</sup> It is important to realise that building conformational control into a structure involves designing a structure which has one, or at least only a few, structures which have much lower strain energy than all the alternatives. Hoffmann has discussed the use of conformational control elements or locks in three interesting reviews,<sup>4,6,7</sup> and has demonstrated their occurrence in many natural products. He pointed out that the most effective control often amounts to the creative use of two types of non-bonded

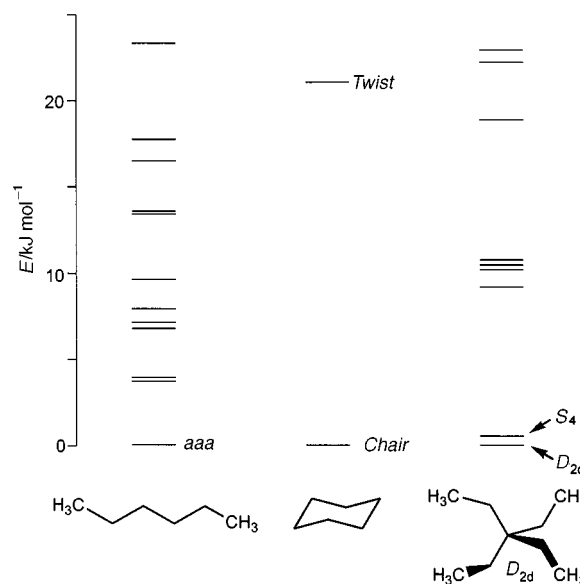


Fig. 1 Conformational energy levels for hexane, cyclohexane and tetraethylmethane ( $D_{2d}$  conformer shown)

interactions (a)  $g^+g^-$  or *syn*-pentane<sup>8</sup> interactions which produce a destabilisation of between 6 and 13  $kJ\ mol^{-1}$ , and (b) the closely related allylic  $A^{(1,3)}$ -strain<sup>9,8</sup> effects (Fig. 2). Hoffmann gives an example of the control of  $n$ -heptane conformer populations by methyl substitution or ring annulation so that each of

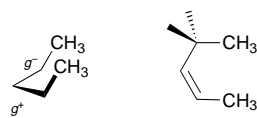


Fig. 2 *syn*-Pentane ( $g^+g^-$ ) and  $A^{(1,3)}$ -strain effects

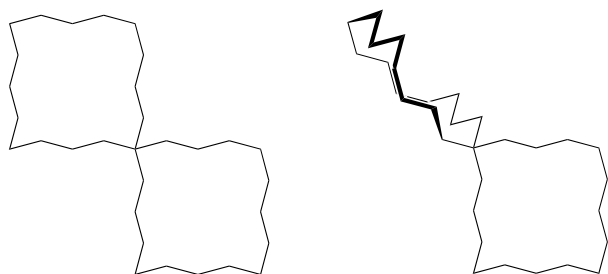


Fig. 3 Stable coplanar and perpendicular [4444] conformations for spiro[15.15]untriacontane

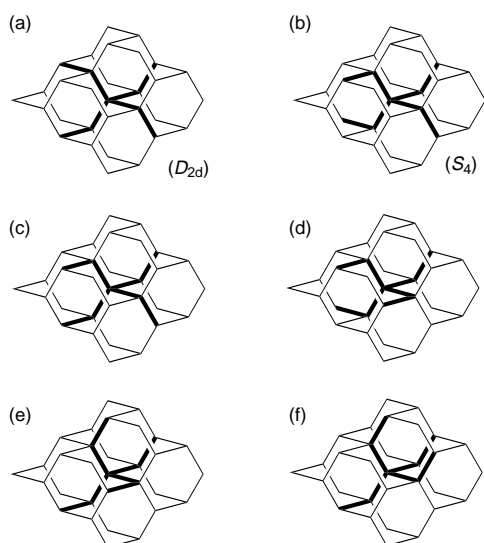


Fig. 4 Idealised diamond lattice conformations for  $\text{Et}_4\text{C}$

the possible conformations can be made to be preferred in turn.<sup>5</sup>

During some modelling work directed at other ends, we were very surprised to find that a spirane with two 16-membered rings in their most stable [4444] conformation could be constructed in two ways, such that the average planes of the two rings were either co-planar or exactly perpendicular, Fig. 3. Both structures fit on the diamond lattice and simple counting of *gauche* interactions indicates that they should have the same strain energy to a first approximation; MM2 calculations predict the  $D_2$  conformation to be more stable than the  $S_4$  by  $0.85 \text{ kJ mol}^{-1}$ , an energy difference well below that for a single *gauche* interaction! These conformations only differed around the quaternary (spiran) carbon atom and led to a realisation that there are two low-energy conformations for 3,3-diethylpentane,  $\text{Et}_4\text{C}$ , as was pointed out by Wait and Powell<sup>10</sup> for the iso-structural  $\text{Et}_4\text{N}^+$  ion as long ago as 1958. The obvious conformation is shaped like a cross and has  $D_{2d}$  symmetry. The other low-energy conformation has the relatively uncommon  $S_4$  symmetry, and is much harder to find by inspection. All other conformations have one or more  $g^+g^-$  interactions and should be much higher in energy. Idealised diamond lattice conformations for  $\text{Et}_4\text{C}$  are shown in Fig. 4. Therefore although it was clearly stated in the literature that the quaternary centre provides conformational control over the bonds directly attached to it, this control takes a rather subtle form and has been more or less ignored by organic chemists. We then realised that quaternary centres also provide the same level of control around  $\text{C}_q\text{-CH}_2\text{-CH}_2\text{-C}$

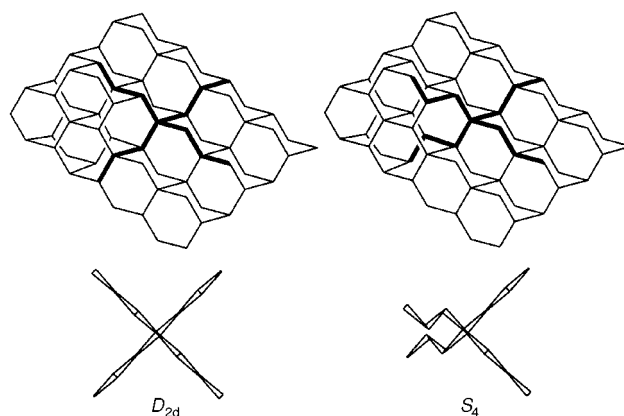


Fig. 5 The two lowest energy conformations for  $\text{Pr}_4\text{C}$

torsions, but here the regime is simpler; these must be *anti* to avoid  $g^+g^-$  interactions. This is really a manifestation of the long-known *tert*-butyl effect.<sup>11</sup> This means that 4,4-dipropylheptane has only two conformations within  $9 \text{ kJ mol}^{-1}$  of the global minimum (Fig. 5), and thus is remarkably simple conformationally for a  $\text{C}_{13}$  molecule.<sup>12</sup> In this paper, we examine the origins of this conformational control in the light of force field (molecular mechanics) calculations, and provide experimental evidence for the control, as shown by the conformations of tetraalkylammonium ions in the Cambridge Structural Database. We also discuss some limitations of these methods of conformational control, and mechanisms for interconversion of the low-energy  $D_{2d}$  and  $S_4$  conformers.

These effects might be put to use as conformational control elements in various situations. Controlling the secondary structure of polymers is an important target, so we have applied these ideas to design polymers containing repeating quaternary centres (Fig. 6). Cases (a) and (b) in Fig. 6 are clearly highly strained in all conformations, and are not of interest here. In case (e), the central bond is not subject to control, so the cases where the quaternary centres provide proper control are (c) and (d). In this paper, we will only consider case (d). We have recently developed a route to polymers based on case (c) with fluorene side groups where there is excellent NMR evidence for a very strong preference for the type of structure shown in Fig. 6(c).<sup>13</sup>

Fig. 6 illustrates the case where the polymer chain is all-*anti*, but this is not the only possibility. Starting from the basis  $D_{2d}$  and  $S_4$  structure around a quaternary centre, four structures for  $\text{PCH}_2\text{CH}_2\text{CPr}_2\text{CH}_2\text{CH}_2\text{P}$  can be developed (Fig. 7); in general extremely small energy differences between these possibilities are to be expected, well below the cost of one *gauche* interaction. There appears to have been only one previous study of structures of this kind; two forms of poly(3,3-diethyloxetane) have been observed; the higher melting form is believed to adopt the *aaaa* (a)-type structure in Fig. 7, while the lower melting form is thought to be  $ag^+g^+a$  [either type (b) or type (c)].<sup>14-16</sup> In order to overcome this problem, we discuss various methods of introducing additional conformational control elements to design polymer structures like those shown in Fig. 8. As we will show, a polymer with rigid aromatic side groups should prefer the *aaaa* structure in Fig. 8(a), while adamantyl side groups strongly favour the  $ag^+g^+a$  structure in Fig. 8(b). A polymer derived from  $\alpha$ -pinene should have a chiral  $ag^+aa$  secondary structure [Fig. 8(c)], and polymers with cyclohexyl groups should strongly avoid *aaaa* structures, and show a preference for  $ag^+g^+a$  [Fig. 8(d)], but with  $ag^+aa$  relatively favourable also.

In practical applications of these ideas, we first describe the preparation of simple 3,3-disubstituted cyclobutene monomers **1** which can be subjected to ring opening polymerisation (ROMP) with well-defined Schrock catalysts such as  $\text{Mo}[\text{=CHCPh}(\text{Me}_2)](\text{=N-2,6-di-Pr}^i\text{C}_6\text{H}_3)(\text{Bu}^t\text{O})_2$ <sup>17-20</sup> to form

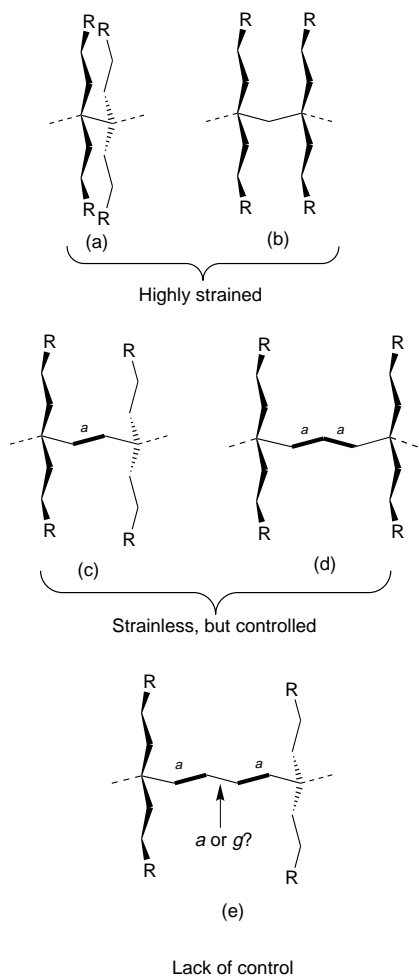


Fig. 6 Polymer structures with repeating quaternary centres

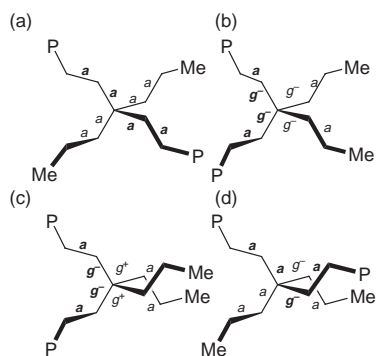


Fig. 7 The four possible conformations, (a)–(d), around a quaternary centre in the polymer  $(\text{Pr}_2\text{CCH}_2\text{CH}_2\text{CH}_2)_n$ ; **P** is the remaining polymer chain. Torsion angles along the main chain are shown **bold**, those in the  $\text{Pr}-\text{C}-\text{Pr}$  unit are not bold.

poly[(1,1-dialkyl)but-2-en-1,4-diy]s followed by diimide reduction to generate poly[(1,1-dialkyl)butane-1,4-diy]s.<sup>21</sup> Physical data on these polymers are reported. We then describe the preparation of monomers **2a**, and **3–5** and some polymers from these which employ additional conformational control elements to achieve the selective conformational control shown in Fig. 8.

All the structures discussed above are based on the diamond lattice, the ideal structure for  $\text{sp}^3$  carbon. All-*anti* polymethylene [Figs. 7(a) and 8(a)] can be seen as a one-dimensional linear thread through the diamond lattice. As we pointed out in our preliminary paper, it is intriguing to speculate on open two- and three-dimensional structures based on the diamond lattice and utilising multiple quaternary centres.<sup>22</sup> For example, spiro-fused 16-membered rings, as shown in Fig. 3, can, in principle, be built into the two- and three-dimensional structures shown

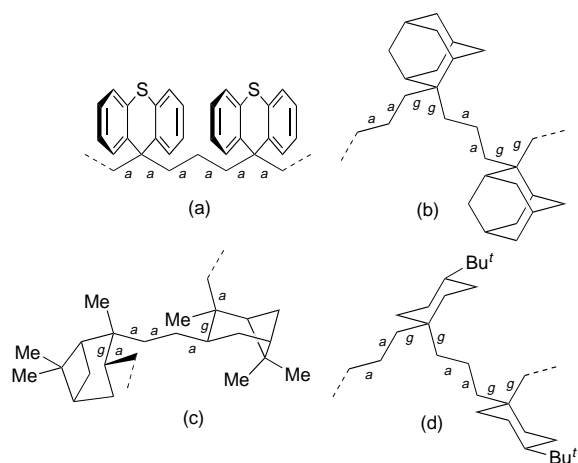
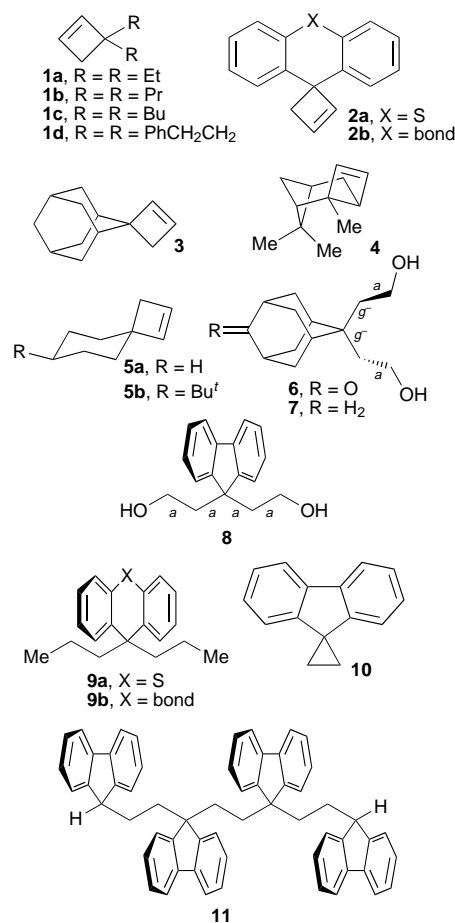


Fig. 8 Polymer structures with additional conformational locks, derived from monomers **2** (a), **3** (b), **4** (c) and **6** (d)



diagrammatically in Fig. 9. It is obvious that any material based on the structures shown in Fig. 9 will be totally insoluble, and it appeared to us that the only hope for synthesis of such a material lay in using reactions which were under equilibrium control, so that any mistakes made in assembling the structure could potentially be repaired as the system moved towards equilibrium.<sup>23</sup> It was hoped that solvents and reagents would be able to gain access to the cavities in the relatively open network we aimed to assemble. Two reactions which appeared to offer some hope for the construction of saturated lattices of the types envisaged are the formation of tetraalkylborate anions from borates and polyols under alkaline conditions, and ketal formation under acid catalysis. We have put considerable effort into trying to realise this aim,<sup>24</sup> for example by examining the reaction of  $(\text{HOCH}_2\text{CH}_2)_4\text{N}^+$  with  $\text{B}(\text{OMe})_3$  and  $\text{NaOMe}$ . However we could not prepare any products which did not still show

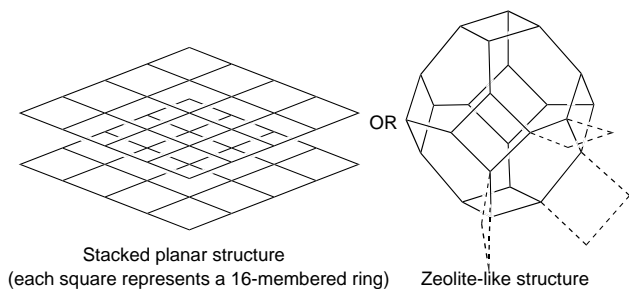


Fig. 9 Two- and three-dimensional lattice derived for spiro/fused 16-membered rings

large amounts of free HO groups by IR. Using intermolecular ketal formation,  $(\text{HOCH}_2\text{CH}_2)\text{C}=\text{O}$  could, in principle, form a ketal network of the types shown in Fig. 9. Undoubtedly, however, the many alternative reactions open to this molecule will make this a hopeless case. In the hope of overcoming these problems, we designed a monomer **6** which cannot enolise and which can only ketalise intermolecularly, and where the additional conformational control provided by the adamantane moiety would reduce the number of possible structures to the point where formation on a network such as those in Fig. 9 could become practical. The synthesis of **6**, by no means a trivial task, has been completed and self-ketalisation experiments are reported. In order to explore reversible ketal formation in simpler systems, we have also prepared diols **7** and **8**, and studied the potential for formation of linear polymers from them with several ketones.

## Results and discussion

### Conformational control about a single quaternary centre

**Molecular mechanics calculations.** In the idealised diamond lattice conformations for  $\text{Et}_4\text{C}$  shown in Fig. 4, two basic conformations [(a) and (b)] are free of  $g^+g^-$  non-bonding interactions, two conformations [(c) and (d)] have one  $g^+g^-$  interaction, one (e) has two, and one (f) has three  $g^+g^-$  interactions. A molecular mechanics conformation search<sup>25</sup> actually located 10 conformers, with there being two minima close to each of the idealised (c) and (d) conformers and three minima close to (e). These extra minima are associated with distortions to lessen the  $g^+g^-$  interactions and give rise to extra minima in non-symmetrical situations (see below). The relative energies of the conformations were calculated using MM2 force fields, and have been checked with MM3 calculations. The  $\Delta\Delta H$  between the lowest energy conformations and the (c) and (d) type conformations as calculated by MM2 and MM3 is in good agreement. MM3 does reverse the ordering of the lowest (d) and (c) conformations, but the small difference in energy between this group of conformations makes this reversal relatively unimportant. Osawa<sup>1</sup> has stated that for hydrocarbons 'good agreement is found for the order of MM2 and *ab initio* conformational energies'. It was found that the relative energies of the two lowest energy conformations were similar with MM2 and MM3, with the  $D_{2d}$  conformer being slightly favoured by 0.67  $\text{kJ mol}^{-1}$  (MM2) and 0.85  $\text{kJ mol}^{-1}$  (MM3). Although this energy difference is quite small it can be rationalised by conformational considerations. Osawa<sup>1</sup> found a 0.67  $\text{kJ mol}^{-1}$  stabilising energy increment for the  $g^+g^+$  torsion sequence in a study of the conformations of ethane to *n*-hexane by MP4SDQ/6-31G\*\*/6-31G\* calculations. This effect has also been noted in molecular mechanics calculations (MM2 and MM3). It is suggested that the source of this effect is a 1,5-nonbonded attractive interaction between  $\text{CH}_2-\text{CH}_3$ ,  $\text{CH}_3-\text{CH}_2$  and  $\text{CH}_2-\text{CH}_2$  groups. In  $D_{2d}$  there are four such  $\text{CH}_3-\text{CH}_3$  interactions but in  $S_4$  there are only two. This interaction is maximised when the carbons in the 1,5- $\text{CH}_3$  groups are twice their van der Waals radii apart, that is  $\sim 3.8 \text{ \AA}$ . In  $D_{2d}$  they are

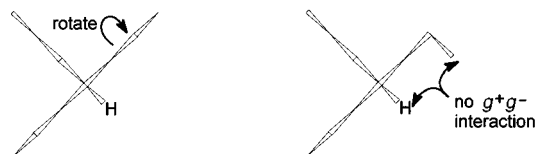


Fig. 10 Tertiary centres do not control  $\text{C}_1-\text{CH}_2-\text{CH}_2-\text{C}$  conformations

calculated to be 3.76  $\text{\AA}$  apart. This attractive force can also rationalise the observed distortion from idealised *gauche* values in the  $\text{CH}_3-\text{CH}_2-\text{C}_q-\text{CH}_2$  torsion angles. In the  $D_{2d}$  structure, there are two different angles around the quaternary carbon; the  $\text{C}-\text{C}_q-\text{C}$  angle involving two bonds which are part of an *aa* sequence is around  $107^\circ$ , while the other angle is around  $111^\circ$ . Although these distortions are small, they will lead to quite pronounced cumulative effects in polymer chains containing quaternary centres. In particular, the chain in a structure like that shown in Fig. 6(d) is not straight but curves significantly when viewed from the side. The curvature is such that the planes through successive pairs of side chains make an angle of  $16^\circ$  with each other. This means that about 22 monomer units would describe a cylinder containing an 88-membered ring, with all the side chains on the outer surface. The  $S_4$  conformer should be favoured by entropy, being of lower symmetry. Calculations were carried out on all the conformations of  $\text{Et}_4\text{C}$  to determine the relative Gibbs free energy ( $\Delta\Delta G$ ) of the series of conformers. The rotational and vibrational contributions were calculated using the Free Energy utility in MacroModel V2.5. The calculations were calibrated by the calculation of  $\Delta\Delta G$  for hexane. The free energies calculated were of the same order as those found in the *ab initio* calculations by Osawa,<sup>1</sup> and the same conformational hierarchy was found. As predicted,  $S_4$  is favoured by entropy, but  $D_{2d}$  and  $S_4$  should contribute about equally to the conformational mix. More importantly the  $\Delta\Delta G$  calculations retained the significant energy gap between the two lowest energy conformers and the (c) and (d) types. An electron diffraction study of  $\text{Et}_4\text{C}$  at 298 K has been completed recently.<sup>26</sup> The data are well fitted to a mixture of 67%  $D_{2d}$  and 33%  $S_4$ , with other conformations not making a significant contribution.

The next symmetrical homologue,  $\text{Pr}^n_4\text{C}$ , provides an important lesson, because it shows that the quaternary centre controls not only the conformations about the  $\text{C}-\text{C}_q-\text{CH}_2-\text{C}$  bonds, but also those about the  $\text{C}_q-\text{CH}_2-\text{CH}_2-\text{C}$  bonds. Conformational searching and molecular mechanics minimisation on  $\text{Pr}^n_4\text{C}$  using MM2 produce only two low energy conformers of  $D_{2d}$  and  $S_4$  symmetry, illustrated in Fig. 5, the  $D_{2d}$  being lower in energy by 1.06  $\text{kJ mol}^{-1}$ ; the next lowest conformation lies at 9.69  $\text{kJ mol}^{-1}$ . It is easy to see why the  $\text{C}_q-\text{CH}_2-\text{CH}_2-\text{CH}_3$  torsion is held in an *anti*-conformation, because a *gauche* conformation here produces a  $g^+g^-$  interaction between the  $-\text{CH}_3$  and a methylene group of one of the other chains. This conformational control over  $\text{C}_q-\text{CH}_2-\text{CH}_2-\text{C}$  bonds is unique to quaternary centres, and gives them considerable scope for controlling larger structures. Tertiary centres cannot control the conformation of the  $\text{C}_t-\text{CH}_2-\text{CH}_2-\text{C}$  torsions; they are free to adopt *gauche* configurations without forming  $g^+g^-$  interactions, see Fig. 10. Tertiary centres do provide some control over the conformation of  $\text{CH}_2-\text{CH}_t-\text{CH}_2-\text{CH}_2$  bond torsions, but the energetic cost of introducing  $g^+g^-$  interactions is not as high as for quaternary centres because there is more room for unfavourable non-bonding interactions to be relieved by distortion away from idealised diamond lattice conformations.

Simple conformational analysis and calculations reveal that the control does not extend to the terminal torsion in the  $\text{C}_q-\text{CH}_2-\text{CH}_2-\text{CH}_3$  chain in  $\text{Bu}^n_4\text{C}$ . These bonds can adopt *gauche* conformations without causing any  $g^+g^-$  interactions, but the two sets of inner torsion angles are still held in local  $D_{2d}$  and  $S_4$  conformations, as in  $\text{Pr}^n_4\text{C}$ .

In conclusion, quaternary centres in simple hydrocarbons exert conformational control over the surrounding chains so that the inner  $\text{CH}_2\text{-C}_q\text{-CH}_2\text{-C}$  bonds adopt local  $D_{2d}$  or  $S_4$  symmetry, and the next set of bonds ( $\text{C}_q\text{-CH}_2\text{-CH}_2\text{-C}$ ) simply show a strong preference for *anti* conformations. Conformational control stops abruptly at these bonds.

Finally, it is important to remember that conformational control relies on the precise limitation of non-bonding interactions; our remarks apply to  $(\text{RCH}_2\text{CH}_2)_4\text{C}_q$ , and possibly to structures where the  $\text{CH}_2$  groups are replaced by  $\text{NH}$  or  $\text{O}$ , but replacement of hydrogen atoms on these  $\text{CH}_2$  groups by larger atoms (e.g. methyl groups), will rapidly destroy the control.

**The effect of other central elements,  $\text{N}^+$  and  $\text{Si}$ .** Replacing the central quaternary carbon with a heteroatom will affect the relative energies of the conformers, reflecting the differing  $\text{X}_q\text{-C}$  bond lengths. Calculations were therefore carried out on some iso-structural species where  $\text{X}_q = \text{N}^+$  and  $\text{Si}$ . The bond lengths for  $\text{C-N}^+$ ,  $\text{C-C}$  and  $\text{C-Si}$  are 1.49, 1.54 and 1.89 Å respectively. Shortening the bond length to the quaternary atom may be expected to increase the energetic cost of  $g^+g^-$  interactions, and this is seen with the quaternary ammonium ions. For the ion  $\text{Pr}^n_4\text{N}^+$ , the  $\text{-CH}_2\text{-C-N-C-CH}_2\text{-}$   $g^+g^-$  interaction greatly increases as the two 1,5-methylene groups are brought closer together. In  $\text{-CH}_2\text{-N-C-CH}_3$ , the  $g^+g^-$  interaction of the  $\text{-CH}_2\text{-}$  and  $\text{-CH}_3$  groups can be relieved by torsional distortions which increase the 1,5-non-bonded distance found in the hydrocarbons. The same basic conformations were found from conformational searches of  $\text{Et}_4\text{N}^+$  and  $\text{Pr}^n_4\text{N}^+$  as for the corresponding hydrocarbons, with the energy gaps between sets of conformers containing a different number of  $g^+g^-$  interactions reflecting the altered bond lengths. The same basic principles apply where  $\text{X}_q = \text{Si}$ , but the longer  $\text{Si-C}$  bond lengths decrease the steric repulsion of the  $g^+g^-$  interactions to the point where the silicon quaternary centre provides little useful conformational control. This is unfortunate, since quaternary silanes are particularly easy to prepare.

**Database studies.** There is a wealth of experimental evidence on the conformations of quaternary ammonium ions in the solid state available in the Cambridge Structural Database (CSD).<sup>27</sup> These ions are commonly used as counterions for obtaining structural data on anions of interest and so structures have been obtained in many different environments. It has been shown by Allen *et al.*<sup>27</sup> that although individual structural determinations may be affected by several factors, experimental errors or crystal packing forces for example, the averaging of collected molecular parameters for a given fragment smooths out these non-systematic influences. Conformational analysis using the CSD was performed on tetraethyl-, tetrapropyl- and tetrabutyl-ammonium ions. For  $\text{Et}_4\text{N}^+$  ions there were, at the time of these studies, 361 structure determinations in the database containing 351 fragments for which geometric parameters were available. These were filtered to remove those that showed disorder and/or insufficient accuracy, leaving a working set of 208 fragments. The conformations of the fragments were determined by examining the improper torsion angle  $\tau$  formed by the terminal  $\text{-CH}_3$  groups, as detailed in the Experimental section (see Fig. 17). Every one of the fragments found was of either  $S_4$  or  $D_{2d}$  conformation, with no other conformations located in the search. The relative proportions of  $D_{2d}$  and  $S_4$  conformers were 163:45.

A search for  $\text{Pr}^n_4\text{N}^+$  ions gave 31 references, and 41 fragments giving 35 fragments of sufficient precision, and all these were either  $D_{2d}$  and  $S_4$  conformations with the relative proportions of the two conformations being 13:22 respectively. Note that this proves that the control provided by the quaternary centre extended to the  $\text{N-CH}_2\text{-CH}_2\text{-CH}_3$  torsion angles, holding them *anti*. The search for  $\text{Bu}^n_4\text{N}^+$  ions gave 170 references and 184 fragments, giving 176 fragments of sufficient accuracy. On considering the conformation around the  $\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-}$  torsions, only local  $D_{2d}$  and  $S_4$  conformations are found as

**Table 1** Calculated barriers for  $D_{2d}$  to  $S_4$  interconversion

	MM2/kJ mol <sup>-1</sup>	MM3/kJ mol <sup>-1</sup>
Two-step mechanism	30.17	32.84
Three-step mechanism	27.49	36.90

expected, the relative proportions being 127:49 respectively. The  $\text{N-CH}_2\text{-CH}_2\text{-CH}_2$  torsions were all held *anti*, but the  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$  torsions were not controlled, and examples with one, two, three and four *gauche* conformations were found for ions of both central local  $D_{2d}$  and  $S_4$  types.

We draw attention to the  $D_{2d}:S_4$  ratios observed for  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}^n_4\text{N}^+$  and  $\text{Bu}^n_4\text{N}^+$ : 163:45, 13:22 and 127:49. The preference for  $D_{2d}$  structures for  $\text{Et}_4\text{N}^+$  and  $\text{Bu}^n_4\text{N}^+$ , but  $S_4$  for  $\text{Pr}^n_4\text{N}^+$  seems remarkable and is surely statistically significant. We can see no simple explanation for this; indeed we have even wondered if the 'cause' is human selection!  $\text{Pr}^n_4\text{N}^+$  is clearly the least commonly used cation; perhaps chemists only resort to it in difficult cases where  $\text{Et}_4\text{N}^+$  and  $\text{Bu}^n_4\text{N}^+$  are unsuccessful; these might involve anions which pack better with the  $S_4$  conformer.

**Mechanisms for interconversion of  $D_{2d}$  and  $S_4$  conformers of  $\text{Et}_4\text{C}$ .** (a) Distortions in conformers containing  $g^+g^-$  interactions: Conformers containing  $g^+g^-$  interactions are always distorted; small changes in the *gauche* torsion angles decrease the high steric strain whilst not initially increasing the torsional strain to the same degree. This distortion is calculated to be asymmetric by MM2<sup>28</sup> and *ab initio* studies (6-31G\*\*),<sup>29</sup> giving two minima. One torsion angle increases to around  $\pm 90^\circ$  while the other remains close to  $\pm 60^\circ$ . It has been noted that if both angles are distorted by small and equal amounts the 1,5- $\text{CH}_3$  groups are initially brought closer together. The exact nature of the interaction has been under discussion, and MM3 calculations have located a near  $C_s$  symmetrical conformation in *n*-pentane for the  $g^+g^-$  interaction.<sup>30</sup> However in our study MM3 gave distorted  $g^+g^-$  interactions in  $\text{Et}_4\text{C}$ , producing asymmetric (c) and (d) conformers (see Fig. 4). Probably the main point is that the energy surface in this region is very flat.

(b) Pseudorotation between non-symmetric forms: The *ab initio* study of pentane cited above<sup>29</sup> located a saddle point between the two enantiomeric minima of approximately  $C_s$  symmetry with torsion angles of  $\pm 77^\circ$ , which was 1.17 kJ mol<sup>-1</sup> higher in energy; the process is similar to that in cyclopentane rings.<sup>31</sup> We calculated the barrier for *n*-pentane pseudo-rotation to be 1.40 kJ mol<sup>-1</sup> by MM2. These barriers are so small that the existence of the calculated minima as separate conformational entities may be doubtful.<sup>32</sup> The two (c) and the two (d) conformations of  $\text{Et}_4\text{C}$  (Fig. 4) are interconverted by similar pseudo-rotation-like processes, which occur by opening up the small internal torsion angle to reach an early transition state, followed by further outward motion of that torsion angle and an associated inward motion of the other torsion.

(c) Two- and three-step mechanisms for interconversion of  $D_{2d}$  and  $S_4$  conformers: The mechanism for interconversion for the two low energy conformers  $S_4$  and  $D_{2d}$  conformers is simplified by two factors. Firstly, due to the high symmetry of the  $D_{2d}$  conformer, there is only one torsional motion that can occur starting from this conformer, and this leads to a conformer of type (c). Secondly, starting from  $S_4$ , there are only two different torsional motions leading to either (c) or (d) type conformers. The simplest pathway is therefore  $S_4$  to (c) to  $D_{2d}$ . An alternative pathway involves three steps, where  $S_4$  initially converts to a (d) conformation,  $S_4$  to (d) to (c) to  $D_{2d}$ .

The barriers for the differing mechanisms have been estimated using both MM2 and MM3 calculations and dihedral drivers and the results are presented in Table 1. MM2 shows a small preference for the three-step mechanism. The two pathways are illustrated in Figs. 11 and 12. It has been pointed out that barriers calculated by MM2 can in some instances be up

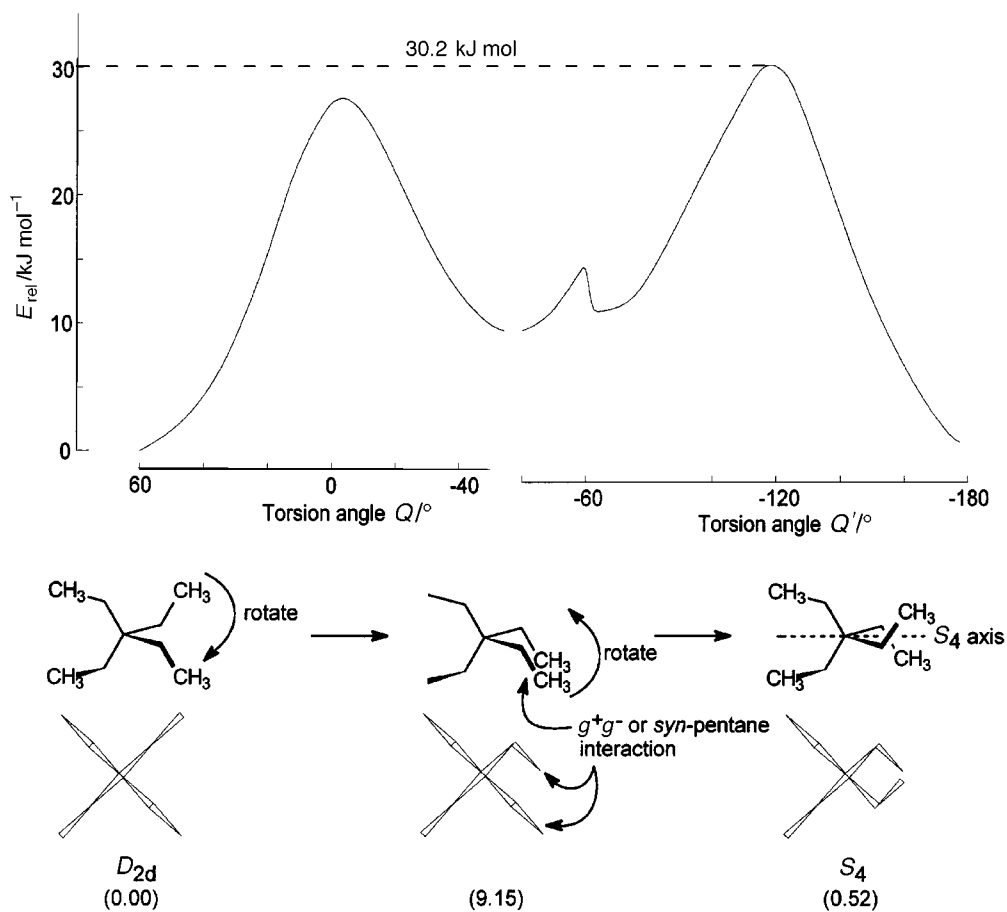


Fig. 11 Two-step mechanism for inter-conversion of  $D_{2d}$  and  $S_4$  conformations of  $\text{Et}_4\text{C}$

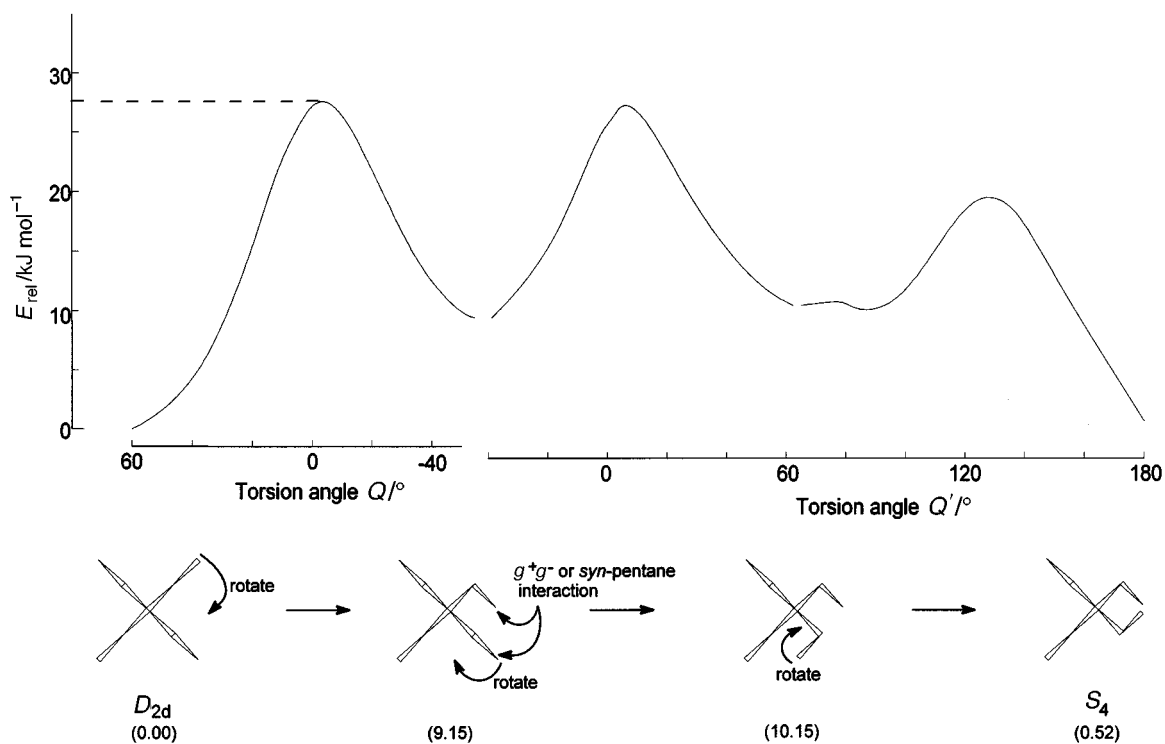


Fig. 12 Three-step mechanism for inter-conversion of  $D_{2d}$  and  $S_4$  conformations of  $\text{Et}_4\text{C}$

to 40% lower in value than free energy barriers measured experimentally. This is particularly relevant for crowded hydrocarbons.<sup>33-35</sup> At least half of this difference is due to the exclusion of the entropy of activation. The other part is due to an error in the torsional potential.

There have been many attempts to re-parametrise MM2 for this error,<sup>33,36</sup> including the developments which led to the MM3 force field. It is interesting that in our calculations, MM3 favours the two-step process. The calculated barriers are close to the limit of what can be observed by low temperature

dynamic NMR, but our attempts to observe the interconversion of  $D_{2d}$  and  $S_4$  conformers of  $\text{Et}_4\text{C}$  in solution by  $^1\text{H}$  NMR only led to line broadening down to the lowest temperatures we could attain. The spectra are complicated by the small range of chemical shifts and it is likely that the spectroscopic differences between the two stable conformers are quite small. In the solid state,  $\text{Et}_4\text{C}$  shows several phase changes, and these might be associated with conformational changes. The solid state  $^{13}\text{C}$  NMR of  $\text{Et}_4\text{C}$  has been studied by Riddell and Cameron,<sup>37</sup> who have observed several interesting effects which will be discussed elsewhere. We also note that barriers have been calculated and experimentally determined for rotation about the torsion adjacent to the quaternary centre in 2,2-dimethylbutane. Bushweller and Anderson<sup>38</sup> gave a barrier of  $21.73 \pm 0.8$  kJ mol<sup>-1</sup> at 100 K. *Ab initio* calculations<sup>29</sup> located the barrier at 23.9 kJ mol<sup>-1</sup> (including zero point energy).

(e) A 'three-dimensional domino mechanism' for interconversion of  $D_{2d}$  and  $S_4$  conformers: Narasimhamurthy *et al.*<sup>39</sup> studied the routes to interconversion between  $S_4$  (most stable) and  $D_{2d}$  conformations for tetramethoxymethane using an extended MM2 force field. The two-step mechanism above gave a barrier of 35.6 kJ mol<sup>-1</sup>. An appealing four-step process described as a 'three-dimensional domino motion' was also described in which one 120° rotation of the C–C<sub>q</sub>–C–C torsion is supposed to 'set off' the motion of the adjacent torsion. For  $\text{C}(\text{MeO})_4$  this  $D_{2d}$  to (c) to (d) to (d') to  $S_4$  mechanism was the lowest energy pathway, with the rate-determining step being the conversion of  $D_{2d}$  to C with the saddle point lying 27.6 kJ mol<sup>-1</sup> and 27.5 kJ mol<sup>-1</sup> above  $S_4$  and  $D_{2d}$  respectively. The last step of (d') to  $S_4$  was calculated to be barrierless. The 'three-dimensional domino motion' implies that the conversion of (d) to (d') occurs by a standard 120° torsion rotation *via* an eclipsed transition state. We believe however that the low barrier pseudo-rotation process described above will always provide a more economical mechanism for the conversion of (d) to (d'), and so this mechanism will reduce to the three-step mechanism described above.

#### Multiple quaternary centres; X-ray structure of $\text{Me}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{Me}_2(\text{CH}_2)_3\text{N}^+\text{Me}_3$ ( $\text{BPh}_4^-$ )<sub>2</sub> I<sup>-</sup>

As discussed in the Introduction, the maximum number of intervening  $-\text{CH}_2-$  groups which gives full control of the intervening chain is three, Fig. 6(d). An early NMR study of ions of the type  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_x\text{N}^+(\text{CH}_3)_3$  showed that all the methylene groups in between the two quaternary centres are held *anti* when  $x = 2, 3$  but flexibility was introduced when  $x = 4$ .<sup>40</sup> We therefore sought to examine the possibilities shown in Fig. 7, by obtaining crystal structures for salts of the trication  $\text{Me}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{Me}_2(\text{CH}_2)_3\text{N}^+\text{Me}_3$  with various anions. We were only able to solve one structure, for the salt  $\text{Me}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{Me}_2(\text{CH}_2)_3\text{N}^+\text{Me}_3$  ( $\text{BPh}_4^-$ )<sub>2</sub> I<sup>-</sup>. In this structure, the trication adopts the lowest energy conformation predicted by MM2 with the two methylene chains in *anti* conformations and an  $ag^+g^+a$  conformation at the central nitrogen, as illustrated in Fig. 13. The N–C–C–C torsion angles are distorted slightly away from  $\pm 180^\circ$  to reduce the non-bond interactions. This results in the N1–N2–N3 inter-quaternary centre angle being opened up from the idealised 90° to 103.2°. The C5–C6–N2–C9 and C6–N2–C9–C10 torsion angles are measured at  $-63.1^\circ$  and  $-61.5^\circ$ .

#### Designing systems with additional conformational control.

It is clear from the discussion above that simple alkyl chains in association with quaternary centres cannot provide complete control of polymer secondary structures, so we set out to design systems incorporating additional conformational controls. Ideally, one would like to select a set of side groups which would lead to strong preferences for each of the possible conformations for the main chain: *aaaa*,  $ag^+aa$  and  $ag^+g^+a$ . We describe below our solutions to this problem.

**All-*anti* (*aaaa*) conformations.** There is one simple way to

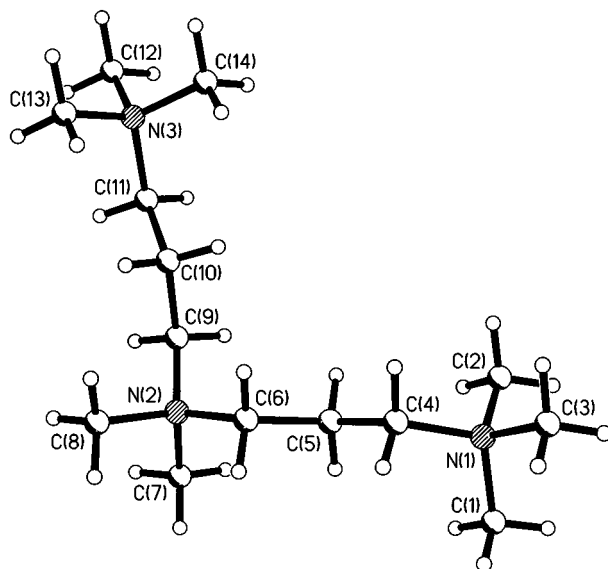


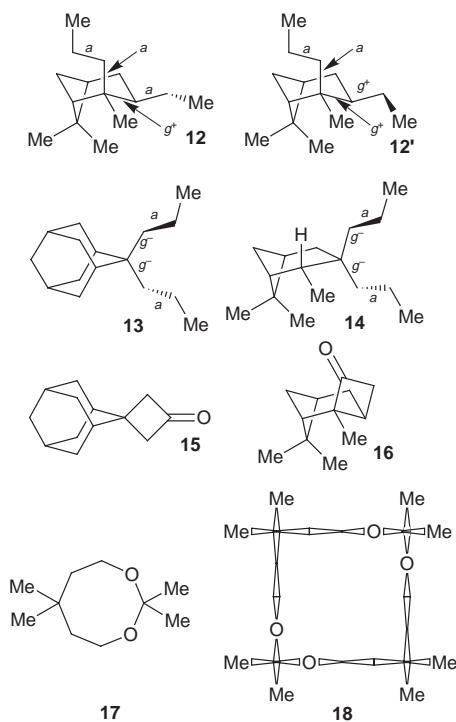
Fig. 13 Structure of the tri-cation in 2,2,6,6,10,10-hexamethyl-2,6,10-triazoniaundecane iodide di(tetraphenylborate)

impose an *aaaa* on the main chain in a polymer with repeating quaternary centres: fix the side chains (or groups) themselves in an *aaaa* conformation within a local  $D_{2d}$  symmetry! There is no way to do this with simple alkyl groups, but a rigid aromatic ring system should be relatively similar from the point of view of non-bonding interactions. Thus fluorene attached through the 9,9-positions to the polymer chain, imposes an *aaaa* conformation on that chain. Calculations show that the *aaaa* conformation of 9,9-dipropylfluorene **9b** is preferred over the  $ag^+aa$  by 8.1, and over the  $ag^+g^+a$  by 15.7 kJ mol<sup>-1</sup>. The familiar *gem*-dialkyl effect<sup>11</sup> is often said to favour conformations which may undergo ring closure, but in this case the effect is almost the exact opposite! Thus a target monomer for ROMP was spiro[cyclobut-2-ene-1,9'-9*H*-fluorene], **2b**. We also looked at alternative tricyclic ring systems like xanthene or thioxanthene; these might behave similarly sterically, but could be more complicated, since the central ring can flex to become non-planar. Calculation showed that the relative energies for the conformations of 9,9-dipropylthioxanthene **9a** are *aaaa*: 0.0;  $ag^+aa$ : 10.3;  $ag^+g^+a$ : 42.7 kJ mol<sup>-1</sup>. In one respect, the increased energy difference between *aaaa* and  $ag^+aa$  is reasonable in view of the enlarged size of the central ring which brings the 1,8-hydrogen atoms on the thioxanthene into greater contact with the propyl chains. However, in the thioxanthene  $aag^+a$  structure the aromatic rings do fold so that the benzene rings are pointing away from the *gauche* central bond, so the gain is not as great as might be expected. Folding is not possible in the  $ag^+g^+a$  structure and this explains the massive increase in energy. One other point should be made about all these structures; control is somewhat lacking over the outer bonds. The *gaaa* conformations for both thioxanthene and fluorene cases are relatively lower in energy than most other 4,4-disubstituted heptanes at 6.2 and 6.6 kJ mol<sup>-1</sup> respectively. Not unexpectedly, the planar nature of the aromatic rings does reduce the effect of the  $g^+g^-$  interactions which are generated.

As described below, the synthesis of the required monomer, spiro[cyclobut-2-ene-1,9'-9*H*-xanthene], **2a**, for the thioxanthene polymer was achieved, but ROMP of this failed. We have recently described the anionic ring opening polymerisation of spiro[cyclopropane-1,9'-fluorene], **10**, leading to a different type of polymer with quaternary centres every three atoms down the main chain.<sup>13</sup> The  $^1\text{H}$  NMR shifts of oligomers like tetramer **11** provide very strong evidence for the almost exclusive all-*anti* conformation of these oligomers. We also reported the X-ray structure of 9,9-bis(2-hydroxyethyl)fluorene, **8**, which shows that the O–C–C–C–C–C–O chain adopts the

predicted all-*anti* conformation.<sup>13</sup> These results represent the most successful application of this type of conformational control element to date.

**A chiral  $ag^+aa$  conformation.** An  $ag^+aa$  conformation is chiral and we performed conformational searches on derivatives containing heptane chains (as models for the polymer chain) built onto various bicyclic monoterpenes which might be used as sources of suitable chiral enantiopure monomers. The result of the conformational search on **12** (global minimum



shown), potentially derivable from  $\alpha$ -pinene, was encouraging. In this molecule part of the heptane chain is fused into the cyclohexane ring of the side group. As a consequence the fused bond is held in a  $g^+$  arrangement. To avoid a  $g^+/g^-$  interaction the other bond next to the quaternary centre must adopt an *anti* conformation as shown. A polymer adopting this conformation should exist as a chiral helix. A conformer **12'** where one of the outer bonds exists as *gauche* is 6 kJ mol<sup>-1</sup> higher in energy. All other conformations are >10 kJ mol<sup>-1</sup> higher in energy. The preparation of this polymer is described below.

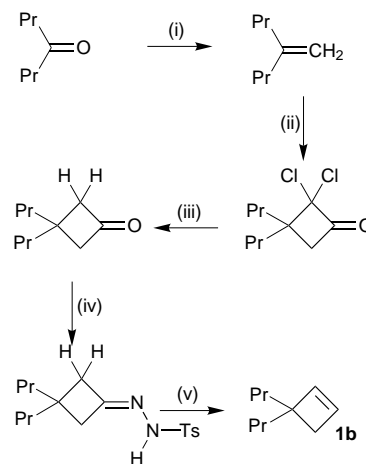
**The zig-zag ( $ag^+g^+a$ ) conformation.** As discussed by Hoffmann, 2,2-dipropyladamantane **13** has a racemic pair of strongly preferred conformations, in which the two propyl chains avoid interacting with the cyclohexane rings. This implies that a polymer with adamantyl side groups will adopt a zig-zag conformation with an  $ag^+g^+a$  sequence about each quaternary centre. In later sections, we describe the preparation of spiro[adamantane-2,1'-cyclobut-2-ene], **3**, a ROMP monomer for such a polymer. We were able to polymerise this but the resultant unsaturated polymer was so insoluble that it could not be reduced. Of course in this case  $ag^+g^+a$  and  $ag^-g^-a$  sequences are equally probable, and we therefore sought an enantiopure case. The most promising example was **14** derived from isopinocamphe, for which the conformation shown is 10.2 kJ mol<sup>-1</sup> lower in energy than any other. Attempts to prepare the required monomer failed however.

**Avoiding all-*anti* ( $aaaa$ ) conformations; cyclohexyl rings as side groups.** A chair cyclohexyl group as side group does not provide the same level of control as an adamantyl group. The chain which is axial is strongly constrained, but there are alternatives for the equatorial chain. 1,1-Dipropylcyclohexane was modelled and the findings were consistent with those outlined by Hoffman; the relative potential energies of three conform-

ations are  $aaaa$ : 24.5;  $ag^+aa$ : 4.7;  $ag^+g^+a$ : 0.0 kJ mol<sup>-1</sup>. Thus both  $ag^+g^+a$  and  $ag^+aa$  should be populated, but  $aaaa$  will be strongly avoided.

### Synthesis of cyclobutene monomers for ROMP

The syntheses of 3,3-dipropylcyclobutene **1b** for ring opening metathesis polymerisation (ROMP) *via* dichloroketene cycloaddition (Scheme 1) was described in our preliminary



**Scheme 1** Reagents and conditions: (i)  $\text{Ph}_3\text{P}=\text{CH}_2$ , 60%; (ii)  $\text{Cl}_2\text{C}=\text{C}=\text{O}$  from Zn powder and  $\text{Cl}_3\text{CCOCl}$  with sonication,  $\text{Et}_2\text{O}$ , 60%; (iii) Zn/HOAc, 90%; (iv) toluene-*p*-sulfonylhydrazide, THF, 70%; (v) lithium 2,2,6,6-tetramethylpiperidide, THF, 60%

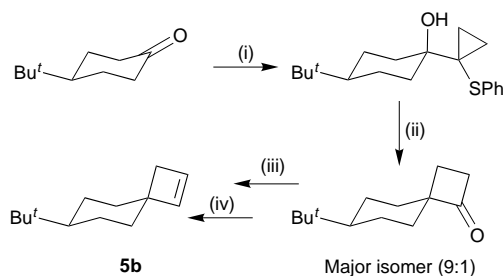
communication.<sup>21</sup> Full details of the preparation of 3,3-diethyl-**1a**, 3,3-dipropyl-**1b**, 3,3-dibutyl-**1c** and 3,3-di(2-phenylethyl)cyclobutene **1d** using this approach are given in the Experimental section. The only major problem in these syntheses was that the cycloaddition of dichloroketene to the 1,1-disubstituted alkenes was found to be sluggish, and was not satisfactorily competitive with the self-reactions of the ketene under the usual conditions, when the ketene was generated by reaction of zinc with trichloroacetyl chloride. For this reason the reactions were carried out by sonicating<sup>41</sup> a suspension of zinc powder in an ethereal solution of the alkene, while adding a diethyl ether solution of  $\text{Cl}_3\text{CCOCl}$  slowly<sup>42</sup> by syringe pump.

The synthesis of spiro[adamantane-2,1'-cyclobut-2-ene] **3** and (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene **4** were also accomplished by the dichloroketene route from methyleneadamantane and  $\alpha$ -pinene respectively. The synthesis of spiro[adamantane-2,1'-cyclobutan]-3'-one **15** has been reported by Farcasiu *et al.*<sup>43</sup> and we followed their procedures closely. Both the benzenesulfonyl- and toluene-*p*-sulfonylhydrazones of **15** were surprisingly unstable and the conditions given in the Experimental section, in which the compounds were precipitated, but not recrystallized, provided the purest samples. The decomposition of these compounds will be discussed elsewhere.

The main difficulty in the preparation of **4** was found to be the cycloaddition step, which proceeded in 19% yield at best. Bak and Brady<sup>42</sup> also reported a low yield in this reaction, and did not give any evidence concerning the regio- and stereo-chemistry of the cycloaddition. Analysis of the <sup>1</sup>H NMR spectrum of the dehalogenated cyclobutanone suggests that it is (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one, **16**, the product resulting from cycloaddition to the less hindered face of the double bond, but with the unexpected regio-chemistry. The two protons at C4 adjacent to the ketone are each coupled to one other proton at  $\delta$  2.90, which we assign to the proton on C5. Formation of the benzenesulfonylhydrazone of **16**, and the Shapiro reaction proceeded without difficulty to give **4**.

The remaining cyclobutenes **2a**, **5a** and **5b** were prepared by



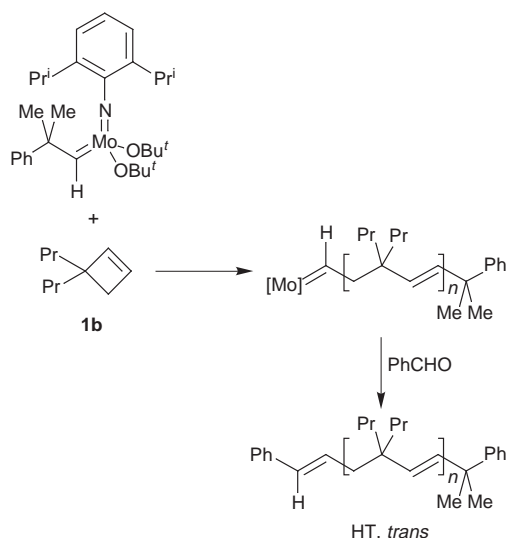


**Scheme 2** Reagents and conditions: (i) Bu<sup>t</sup>Li, cyclopropyl phenyl sulfide, THF, 51%; (ii) SnCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 45%; (iii) toluene-*p*-sulfonohydrazide, EtOH, 87%; (iv) LDA, THF, 30%

an alternative route, based on work of Trost,<sup>44,45</sup> as shown for **5b** in Scheme 2. As described by Trost, addition of lithio-cyclopropyl phenyl sulfide to 4-*tert*-butylcyclohexanone, gives mainly the isomer with the carbonyl group as an equatorial substituent. This cyclobutanone could be obtained free of the minor isomer by flash chromatography, and carried through without incident to give a single cyclobutene. Full details of this synthesis and of the syntheses of **2a**, **5a** and **5b** are given in the Experimental section.

### ROMP and the hydrogenation of ROMP polymers

As described in our preliminary communication,<sup>21</sup> the simple cyclobutene monomers **1** were efficiently polymerised by Schrock catalysts,<sup>17,18</sup> such as Mo[=CHCPh(Me<sub>2</sub>)](=N-2,6-di-Pr<sup>t</sup>C<sub>6</sub>H<sub>3</sub>)(Bu<sup>t</sup>O)<sub>2</sub> (Scheme 3). As the polymerisation is a living



**Scheme 3** ROMP polymerisation of 3,3-dipropylcyclobutene

process, the disappearance of the monomer and appearance of the propagating chain could be followed by <sup>1</sup>H NMR. In particular, the alkylidene proton in the initiator has a characteristic chemical shift of δ 11.31. In the mono-insertion product, this proton is observed at about δ 11 as a triplet, due to coupling of the alkylidene proton with the methylene protons next to the quaternary centre. The molecular weights of the polymers were in satisfactory accord with the starting monomer: initiator ratio, and the polymers were finally capped with benzaldehyde. The <sup>13</sup>C NMR spectrum of the polymer from **1b** showed only two strong signals in the alkene region which indicates that the polymer obtained was clearly head-to-tail (HT) and stereospecific (*trans*, IR out-of-plane vinyl absorption at 977 cm<sup>-1</sup>). ROMP of **1b** using Mo[=CHCPh(Me<sub>2</sub>)](=N-2,6-di-Pr<sup>t</sup>C<sub>6</sub>H<sub>3</sub>)[O-C(CF<sub>3</sub>)<sub>2</sub>Me]<sub>2</sub><sup>46</sup> as initiator gave a polymer which was largely *cis* but did contain some *trans* alkene. In general, the *M<sub>w</sub>* and polydispersity (*M<sub>w</sub>*/*M<sub>n</sub>*) values for the polymers are in accord with these polymerisations being living processes. Polymeris-

ation of the monomer containing butyl side chains, **1c**, was less successful, with a large polydispersity; we have no explanation for this (but see below concerning the polymerisation of **4**).

Polymerisation of monomers **4**, **5a** and **5b** with Mo[=CHCPh(Me<sub>2</sub>)](=N-2,6-di-Pr<sup>t</sup>C<sub>6</sub>H<sub>3</sub>)(Bu<sup>t</sup>O)<sub>2</sub> proceeded in a similar fashion to **1**. The polydispersity of the polymer from **4** was high (3.5), and the gel permeation chromatography (GPC) trace indicated a bimodal molecular weight distribution. In studying this polymerisation at ambient temperature, it was noted that unreacted monomer was present in the reaction mixture prior to the capping reaction with benzaldehyde. This suggested that a very fast polymerisation had occurred, and so the reaction was repeated at -78 °C. Under these conditions, the polydispersity was reduced to 1.8.

The polymerisation of the adamantane monomer **3** was complicated by precipitation of the polymer (which is totally insoluble up to 200 °C in all organic solvents we have tested). Thus addition of 50 equivalents of monomer to the catalyst over a 20 min period led to precipitation 10 min after the addition of all the monomer. The reaction was stirred overnight and benzaldehyde was then added. Not surprisingly, 50% of the total material by weight was recovered as unreacted monomer. However, the expected polymer structure was confirmed by solid state <sup>13</sup>C NMR spectroscopy; the presence of just two signals in the alkene region indicated that the polymerisation process was regiospecific. The insolubility of this product precluded molecular weight determination or subsequent diimide reduction. We can only speculate that we have been too efficient in designing a polymer with such a high degree of organisation that it packs very effectively in the solid!

The thioxanthene monomer **2a** was completely unreactive to the Schrock catalysts, as shown by the unchanging <sup>1</sup>H NMR signal at δ 11.31 for initiator during attempted polymerisation reactions. Although these catalysts are sensitive to various functional groups, Schrock has reported the successful polymerisation of a norbornene monomer containing a phenothiazene.<sup>47</sup> The ruthenium catalysts developed by Grubbs and co-workers<sup>48</sup> have been reported to be more tolerant of varied functionality, and we hoped to use these to overcome this problem. The polymerisation of one cyclobutene derivative, bicyclo[3.2.0]hept-6-ene has been reported,<sup>49</sup> but this is additionally strained, and we found that none of the 3,3-dialkylcyclobutene monomers was polymerised by either RuCl<sub>2</sub>(=CHPh)(PPh<sub>3</sub>)<sub>2</sub> or RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>. Wu and Grubbs have reported ROMP on 3-methyl- and 3,3-dimethyl-cyclobutene, but they used Schrock catalysts for this.<sup>50</sup>

We wished to prepare saturated polymers to test our predictions concerning secondary structures. All our attempts to hydrogenate the polymers from our cyclobutenes with standard heterogeneous catalysts failed completely. In the hope that this was due to inaccessibility of the double bonds in the polymer to the catalyst, we tried two homogeneous catalysts, [RhCl(PPh<sub>3</sub>)<sub>3</sub>] and [Ir(cod)py(PCy<sub>3</sub>)<sub>3</sub>]PF<sub>6</sub> but without success. Reductions were therefore carried out with diimide, generated from the thermal decomposition of toluene-*p*-sulfonohydrazide.<sup>51,52</sup> This is an inherently inefficient process and it is necessary to add a large excess of the hydrazide, but complete hydrogenation can be achieved, as shown by the absence of alkene carbon absorptions in the <sup>13</sup>C NMR of the products. In spite of the relatively brutal conditions for the diimide reduction, the GPC results show that there was little chain scission or cross-linking during the reduction process.

### Polymer characterisation

Tables 2 and 3 summarise the general properties of the polymers from monomers **1** and **3–5** respectively. Due to the limited solubility of some of the polymers, all GPC analyses were carried out at 140 °C in 1,2-dichlorobenzene to ensure comparability. In general the molecular weights were consistent with the monomer: initiator ratios, but the polydispersities were

**Table 2** Properties of the polymers from ROMP of 3,3-dialkylcyclobutenes **1**

Polymer side chain		Monomer/ catalyst ratio	$M_w$	$M_w/M_n$	Solubility	TGA (2%/96% weight loss)	DSC/°C
Et	Unsat.	113	41 000	1.89	Good	>250/—	$T_g$ -9, $T_m$ 75, 95
	Sat.				Low	400/500	$T_m$ 133, 143, 152
Pr	Unsat.	208	52 000	1.27	Good	290/380	$T_m$ 102 (54 J g <sup>-1</sup> )
	Sat.				Good	349/456	$T_m$ 135 (36 J g <sup>-1</sup> )
Bu	Unsat.	156	15 000	3.82	Good	300/380	$T_g$ -4
	Sat.				Good	315/654	$T_g$ 10
PhCH <sub>2</sub> CH <sub>2</sub>	Unsat.	48	26 000	1.79	Good	>250/—	$T_g$ 49, $T_m$ 60
	Sat.				Good	192/300	$T_m$ 66

**Table 3** Properties of the polymers from ROMP of fused and spirocyclobutenes **3–5**

Polymer side groups		Monomer/ catalyst ratio	$M_w$	$M_w/M_n$	Solubility	TGA (2% weight loss)	DSC/°C
Adamantyl (from <b>3</b> )	Unsat.	50	Insol.	Insol.	Very low	340	
<i>a</i> -Pinene-derived (from <b>4</b> )	Unsat.	50	24 800	1.8	Good	430	$T_m$ 150; decomp. 225
	Sat.				Very low	440	$T_m$ >320
Cyclohexyl (from <b>5a</b> )	Unsat.	50	12 300	1.3	Good		$T_m$ 50
	Sat.				Low	455	$T_m$ 127 (35 J g <sup>-1</sup> )
4- <i>tert</i> -Butylcyclohexyl (from <b>5b</b> )	Unsat.	50	17 600	1.7	Good	435	$T_g$ ~90
	Sat.				Low	465	$T_m$ 291 (33 J g <sup>-1</sup> )

significantly higher than reported for the living ROMP of norbornenes.<sup>18</sup> The thermal gravimetric analysis (TGA) results show that these polymers are thermally stable, especially after removal of the double bonds.

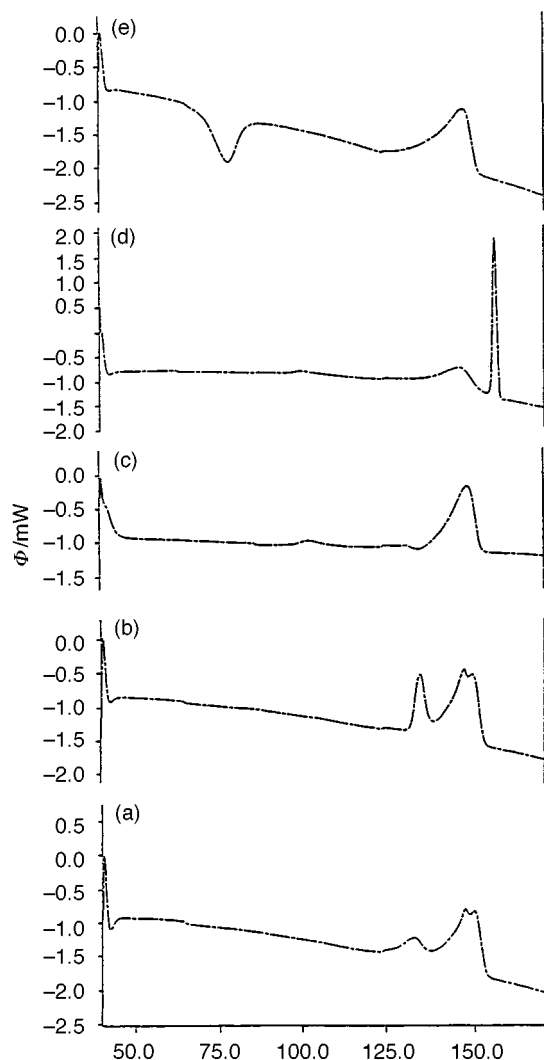
A major goal in our studies of the polymers obtained from ROMP of the cyclobutenes **1**, **3**, **4**, **5a** and **5b** was identification of their secondary structure and we will first look at the qualitative evidence from  $T_m$  and DCS. In general, saturated polymers show lower solubility and higher  $T_m$  than their unsaturated precursors. This is particularly noticeable for the polymers derived from **4**, **5a** and **5b**. Intuitively, one might expect that double bonds would stiffen up the chain and thus lower the solubility and raise  $T_m$ , but this is clearly not the case. We believe that the explanation lies in there being many possible conformations around the C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bonds. Multiple minimum searches for short oligomeric models of the polymers from **4** and **5** showed the presence of many more low energy conformations than for the saturated models.

The most interesting data concerning these polymers come from differential scanning calorimetry (DSC) measurements. A DSC experiment gives information about the exothermic and endothermic transitions which occur on heating a polymer sample under an inert atmosphere. The presence of different crystalline forms can be detected in many polymers by the observance of multiple melting endotherms. Perez *et al.*<sup>14</sup> found that the two melting point endotherms observed for poly-3,3-diethyloxetane corresponded to two distinct crystalline forms as determined by X-ray powder diffraction.<sup>15,16</sup> Our DSC experiments were initially carried out on the native polymers with a heating rate of 10 °C per minute. The unsaturated polymers all showed very broad and rather small melting point endotherms on initial heating, suggesting very little crystallinity. In contrast, the DSC traces obtained for saturated polymers with cyclohexyl and 4-*tert*-butylcyclohexyl side chains had single and much more distinct endothermic peaks. It is interesting that the melting point of the polymer with 4-*tert*-butylcyclohexyl side chains (290 °C) is significantly higher than that of polymer with cyclohexyl side chains (128 °C). The melting point of the latter is similar to those of polymers [R<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]<sub>n</sub> (R = Et, Pr<sup>n</sup>). A second heating of the polymer with cyclohexyl side chains showed no melting point endotherm which indicated that no crystallinity had reformed. This is in contrast to the 4-*tert*-butylcyclohexyl case where on re-heating the same endotherm with a similar enthalpy was noted. This suggests that in the

4-*tert*-butylcyclohexyl case, crystallinity is re-established much faster than in the cyclohexyl case.

In order to further explore the thermal properties of these polymers, annealing studies were carried out. Annealing polymers can in some cases induce crystallinity and, if suitable temperatures are used, preference for different crystalline forms can be achieved. An example of this is poly-3,3-diethyloxetane which Perez *et al.*<sup>14</sup> annealed at temperatures ranging from 0 to 50 °C. Annealing at 0 °C produced a single melting point endotherm which was shown by X-ray analysis to correspond to the *ag<sup>±</sup>g<sup>±</sup>a* structure. Annealing at 50 °C produced a higher melting endotherm corresponding to the *aaaa* structure. The temperatures used for annealing in our studies were always at least 20 °C below the onset of the lowest endotherm. Annealing times of 20 h, 3 days, 5 days and 8 days were used. A separate sample was used for each of the runs. Before annealing, each polymer sample was heated at 20 °C above its melting point for 5 min under an atmosphere of nitrogen and then cooled rapidly to room temperature by removing the heat source. The samples were then heated at the appropriate annealing temperatures. The samples were allowed to cool to room temperature before being exposed to the air and a DSC experiment run. The results for [Pr<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>]<sub>n</sub> are particularly interesting and are shown in Fig. 14. Annealing at 85 °C for 20 h resulted in the growth of the lower melting form (135 °C) although no significant increase in the combined enthalpies of the endotherms was noted. However, after annealing for 3 days the endotherm at 135 °C had disappeared and only the endotherm at 147 °C was present. It seems likely that the crystalline form corresponding to the lower melting endotherm had changed into the higher melting form. After annealing the polymer for 8 days the endotherm at 147 °C was much reduced, being replaced by a new, very sharp endotherm at 155 °C. Again no significant increase in energy of the combined endotherms was apparent. On reheating samples rapidly cooled from the melt, only the endotherm at 147 °C was observed. Interestingly, an exotherm at 75 °C caused by cold crystallisation was also observed. This feature probably indicates that one crystalline form can be generated with relative ease.

For the polymer containing cyclohexyl side chains, notable crystallinity did not reappear after 20 h annealing at 85 °C. After 3 days and 8 days, a notable endotherm was apparent. It was lower in temperature and it occurred over a narrower temperature range than the endotherm observed for the native



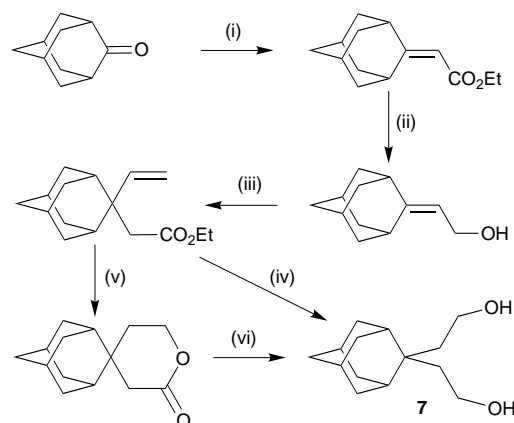
**Fig. 14** DSC traces for  $[\text{Pr}'_2\text{CCH}_2\text{CH}_2\text{CH}_2]_n$  annealed for various lengths of time. (a)  $[\text{PrCCH}_2\text{CH}_2\text{CH}_2]_n$ , polymer precipitated from MeOH,  $\Delta H$   $48 \text{ J g}^{-1}$ ; (b) annealed at  $85^\circ\text{C}$  for 20 h,  $\Delta H$   $54 \text{ J g}^{-1}$ ; (c) annealed at  $85^\circ\text{C}$  for 3 days,  $\Delta H$   $38 \text{ J g}^{-1}$ ; (d) annealed at  $85^\circ\text{C}$  for 8 days,  $\Delta H$   $48 \text{ J g}^{-1}$ ; (e) second heating of any sample,  $\Delta H$   $44 \text{ J g}^{-1}$ .

polymer. For the polymer containing 4-*tert*-butylcyclohexyl side chains, the crystallinity of the polymer appeared to be unchanged after annealing. Indeed the DSC trace obtained on reheating a sample cooled rapidly from the melt is nearly identical to that obtained for the sample which had been annealed for 8 days at  $200^\circ\text{C}$ . The differences between the DSC traces for the cyclohexyl and 4-*tert*-butylcyclohexyl cases is notable. The tertiary butyl group is remote from the polymer chain but the steric bulk of this group could have a significant effect on inter-chain packing. If the 4-*tert*-butylcyclohexyl case were to adopt the lowest energy  $ag^+g^+a$  conformation, the tertiary butyl groups would force the cyclohexane rings on the polymer chain to all orientate in the same direction [see Fig. 8(d)]. For the cyclohexyl case randomisation in the orientation of the cyclohexane rings along the polymer chain could be expected to lead to less favourable packing of the polymer chains.

In summary, the DSC behaviour of these polymers suggests that interesting structural changes do occur in the solid, and we hoped to link this to convincing identification of their secondary structure from X-ray diffraction studies. However, while it proved possible to pull fibres from several of our polymers, Professor E. D. T. Atkins (Bristol) was not able to observe diffraction from any of the samples.

#### Monomers for ketal and ether polymers

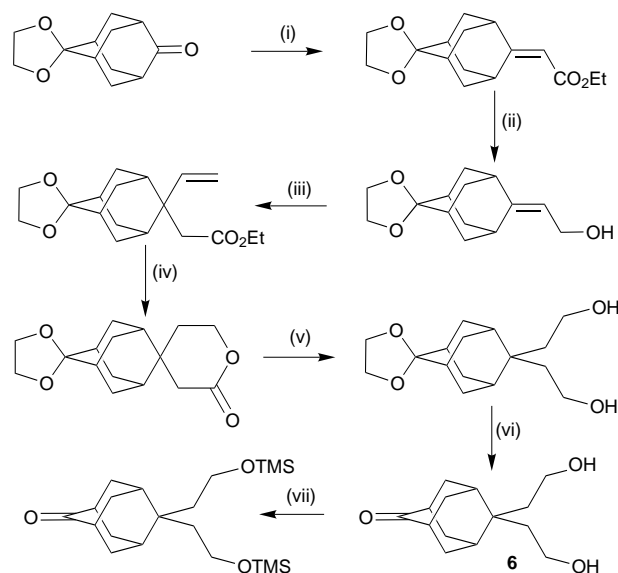
The syntheses of the diols **6**, **7** and **8** will be discussed in reverse



**Scheme 4** Reagents and conditions: (i) triethyl phosphonoacetate anion; (ii)  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; (iii) triethyl orthoacetate, propionic acid; (iv) (a)  $\text{BH}_3\cdot\text{Me}_2\text{S}$ , (b)  $\text{NaOH}$ , 35% aq.  $\text{H}_2\text{O}_2$ ; (v) (a) catecholborane,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , (b)  $\text{EtOH}$ -THF,  $\text{NaOH}$ , 35% aq.  $\text{H}_2\text{O}_2$ ; (vi)  $\text{LiAlH}_4$

order, since **8** is easiest to make, followed by **7**. The fluorene-based diol **8** was readily prepared from fluorene,  $\text{Bu}^n\text{Li}$ , and ethylene oxide in 72% yield, and the X-ray crystal structure has been reported.<sup>13</sup> Synthesis of the adamantane-based diols proved much more challenging; the successful route to **7** shown in Scheme 4 is based on the use of the Johnson ortho ester rearrangement<sup>53</sup> to establish the quaternary centre at the 2-position. All attempts at introducing the second two-carbon chain by Michael addition to the unsaturated ester (Scheme 4) failed. We also experienced difficulties with the hydroboration of the vinyl group; to our surprise,  $\text{BH}_3\cdot\text{Me}_2\text{S}$  was not highly regioselective and the unwanted isomer could not be separated easily; we also found that 9-BBN failed to react. Eventually it was found that catalytic hydroboration with catecholborane<sup>54</sup> was reasonably satisfactory.

Synthesis of **6** was carried out by a similar route, Scheme 5,



**Scheme 5** Reagents and conditions: (i) triethyl phosphonoacetate anion; (ii)  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; (iii) triethyl orthoacetate, propionic acid; (iv) (a) catecholborane,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , (b)  $\text{EtOH}$ -THF,  $\text{NaOH}$ , 35% aq.  $\text{H}_2\text{O}_2$ ; (v)  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; (vi) 25%  $\text{HCl}$ , acetone; (vii) BSA,  $\text{CH}_2\text{Cl}_2$

starting from the monoketal of adamantane-2,6-dione, which is itself available in a seven-stage synthesis from 4-methoxyphenol,<sup>55</sup> so this is a 13-step synthesis in all. As a consequence only limited quantities of **6** were available for experiments directed at network formation. The structure of **6** has been determined by X-ray crystallography and is shown in Fig. 15(a); as expected, the conformation of the  $\text{HOCH}_2\text{CH}_2\text{CCH}_2\text{CH}_2\text{OH}$

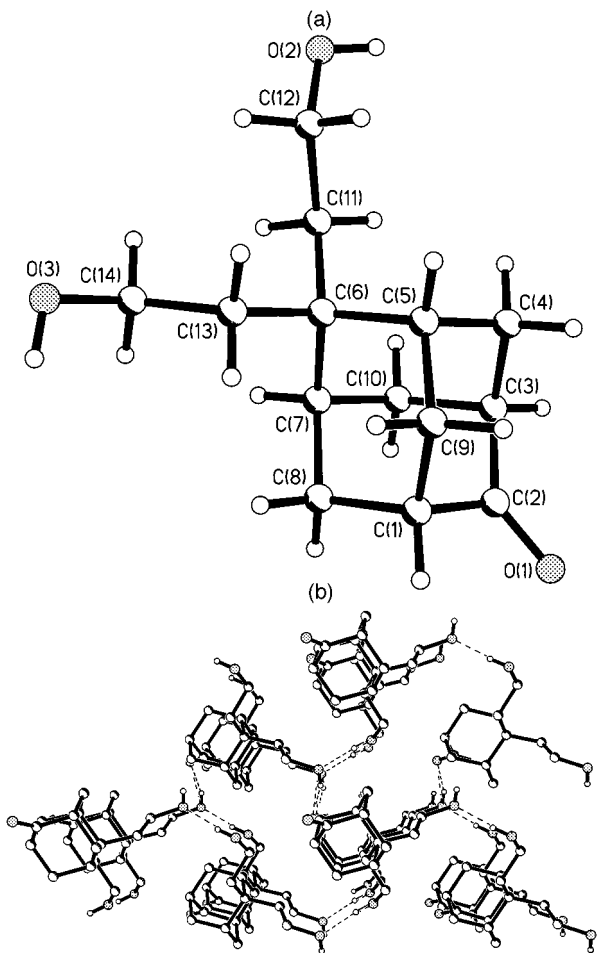


Fig. 15 (a) Structure of 6,6-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one **6**, (b) hydrogen bonding network in the crystals of **7**

chain is  $ag^+g^+a$ . This compound shows an interesting network of hydrogen bonding involving both the hydroxy and ketone groups, Fig. 15(b).

#### Polymer and network formation from diols and ketones

Before investigating network formation from **6**, available in very limited quantities, we examined ketal formation by **7** and **8** with various ketones. It was hoped that diol **7** would give rise to polymeric ketals with  $ag^+g^+a$  segments derived from the conformational effect of the adamantyl group, while diol **8** should introduce  $aaaa$  segments. Dale and Ekeland<sup>56</sup> investigated the formation of ketals from 3,3-dimethylpentane-1,5-diol and 2,2-dimethoxypropane. The monomeric ketal **17**, containing an eight-membered ring, was formed first, and this was subsequently converted completely to the dimeric ketal **18**, after stirring the monomer with an acid catalyst in hexane. No larger ring products or polymer were seen. Note that in the preferred [4444] conformation for **18**, and probably in **17** too, the ketals are able to adopt the  $g^+g^+$  (or  $g^-g^-$ ) conformation about the C–O bonds favoured by the anomeric effect. We found that reaction of adamantanone with 3,3-dimethylpentane-1,5-diol was similar to Dale's case. The monomeric ketal was formed first, and this equilibrated with the dimer over a period of 4 h with *p*-TsOH in benzene, however the equilibrium constant,  $K = [16\text{-ring}]/[8\text{-ring}]^2$  under these conditions was only 0.4.

Brief reaction of adamantanone with **7** in benzene with *p*-TsOH produced the (soluble) monomeric ketal, but when this was stood in benzene with *p*-TsOH for prolonged periods, insoluble material was formed. While this material was clearly a ketal (IR), and could well have been the desired polymer, it was so insoluble that we were unable to get any information on its structure.

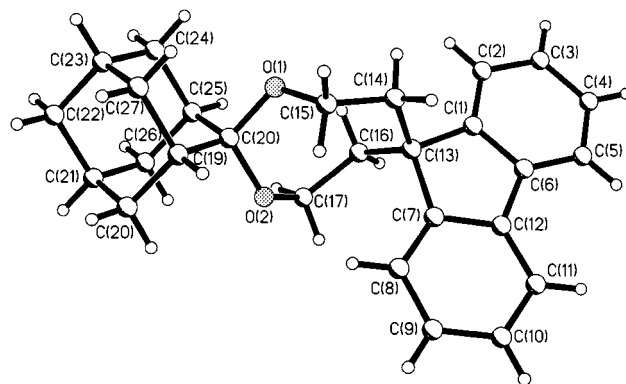
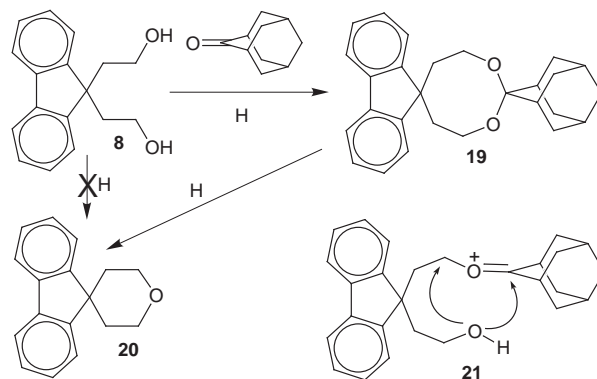


Fig. 16 Structure of dispiro[1,3-dioxacyclooctane-2,2'-adamantane-6,9'-9H-fluorene] **19**

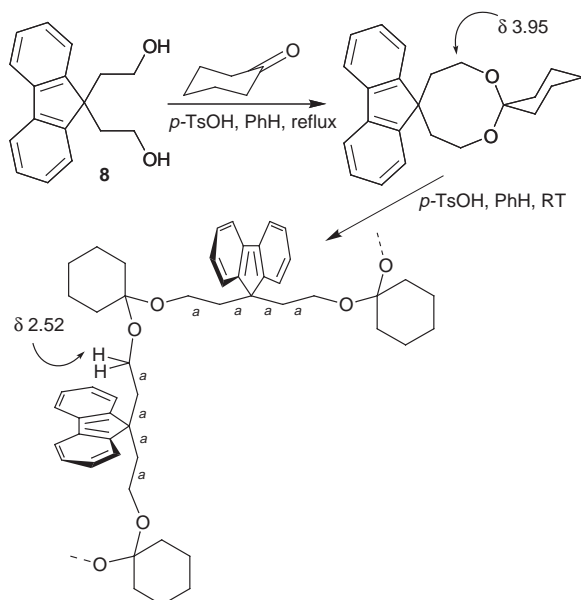


Scheme 6 Reactions of **8** with adamantanone

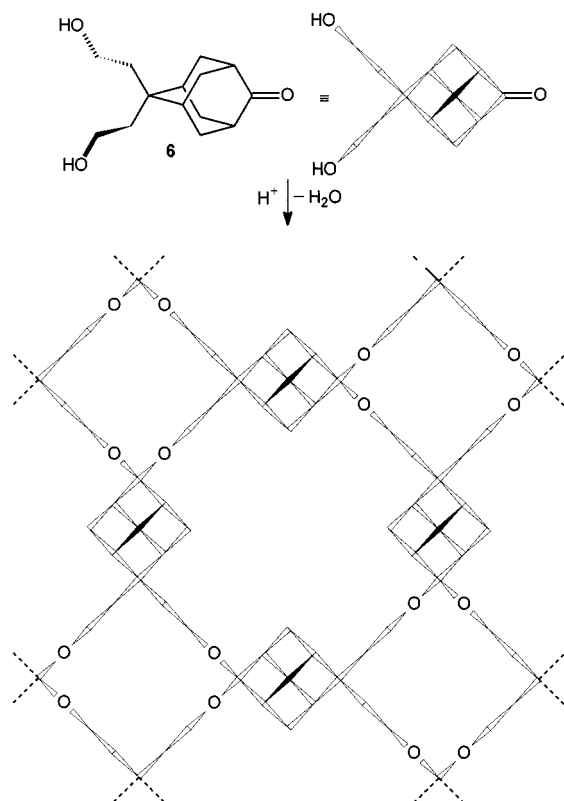
Reaction of adamantanone with **8** gave ketal **19** (Scheme 6), whose monomeric structure was established by X-ray crystallography. As shown in Fig. 16, the eight-membered ring is in an unsymmetrical boat-chair conformation. The formation of **19** surprised us, since there have to be  $g^+g^-$  interactions between the 1,8-fluorene centres and the eight-membered ring, in addition to the strain in the latter. When we heated this with acid under more vigorous conditions, the only observable reaction was the formation of the tetrahydropyran derivative **20**, and the reformation of adamantanone. We find that **20** is not formed when **8** is treated with acid in the absence of adamantanone, but it seems that **20** arises from  $S_N2$  displacement of adamantanone from **21** (Scheme 6), *i.e.* that the ketone is a better leaving group than water, and therefore acts as a catalyst for this reaction.

More promising results were obtained when cyclohexanone was reacted with **8** (Scheme 7). Again the monomeric ketal was formed initially, but stirring this in benzene with 1/100th equivalent of *p*-TsOH resulted in complete conversion to a polymeric product which precipitated from solution (Scheme 8). Fortunately the product was soluble in chloroform and could be characterised. It was shown by vapour pressure osmometry to have an average molecular weight of 3850 (corresponding to approximately 11 monomer units). The product was pure by both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and, significantly, no **20** was detected. The most interesting feature of the <sup>1</sup>H NMR spectra of the monomer and polymer was the chemical shift of the protons of the CH<sub>2</sub>O groups, which occurred at  $\delta$  3.95 in the monomer and  $\delta$  2.52 in the polymer, where they are clearly in a shielding zone of the fluorene rings. The chemical shift of these protons in the starting diol **8** is  $\delta$  2.85, whereas they occur at  $\delta$  4.01 in tetrahydropyran **20**. We believe that this is strong evidence for the  $aaaa$  conformation about the fluorenes shown in Scheme 7.

We have made various attempts to induce the formation of a covalent network product from 6,6-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one **6**. In principle, intermolecular ketal



Scheme 7 Reaction of **8** with cyclohexanone



Scheme 8 Attempted network formation from **6**

formation could give a two-dimensional network, as shown in Scheme 8, although a three-dimensional alternative based on the zeolite-like structure shown in Fig. 9 is also possible. Both reaction of **6** with *p*-TsOH and treatment of 6,6-bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one with Me<sub>3</sub>Si-OTf led to the precipitation of insoluble material which showed no significant absorptions corresponding to siloxy groups, and only minor OH and C=O absorption but which appeared to be amorphous. Further treatment with acid catalysts, which we hoped might lead to annealing towards some strongly preferred structure, led instead to the re-dissolution of the insoluble material with formation of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one-6-spiro-4'-tetrahydropyran. Thus the formation of this cyclic ether, perhaps catalysed by the ketone group, as discussed for

**8** above, seems to preclude the development of an ordered structure by equilibration.

## Conclusions

The conformational effects of a quaternary centre in structure (RCH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>X<sub>q</sub> are now clearly defined. Inner torsion angles, CH<sub>2</sub>-CH<sub>2</sub>-X<sub>q</sub>-CH<sub>2</sub>, adopt *D*<sub>2d</sub> or *S*<sub>4</sub> local symmetries to avoid *g*<sup>+</sup>*g*<sup>-</sup> non-bonding interactions, while the next set of torsions, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-X<sub>q</sub> are strongly constrained to be *anti* by the same effects. However, the third set of torsions away from the quaternary centre are unaffected and are free to adopt *gauche* conformations. The maximum length of a polymethylene chain between quaternary centres which can be controlled by these effects is therefore -(CH<sub>2</sub>)<sub>3</sub>-. In polymers containing simple alkyl side chains, PCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>2</sub>CH<sub>2</sub>R)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, there are four energetically similar conformations associated with the *D*<sub>2d</sub> or *S*<sub>4</sub> local structures, but the introduction of more highly structured side groups which can act as extra conformational control elements allows the design of polymers with predictable secondary structures. Several polymers with these features have been prepared, and are shown to display interesting physical properties, although it has proved difficult to provide unequivocal evidence (*e.g.* from X-ray data) that these polymers do have the proposed conformations.

## Experimental

All reactions were carried out under an atmosphere of dry nitrogen and all solvents were purified by literature procedures.<sup>57</sup> Melting points were obtained on a Reichert apparatus, using a thermocouple and a digital readout, and are corrected. Elemental analyses and vapour pressure osmometry molecular weight determinations using a Perkin-Elmer 115 molecular weight apparatus were carried out by the staff of the micro-analytical laboratory of the School of Chemistry, University of Bristol.

NMR spectra were recorded using JEOL JNM-GX270, JEOL L300 and JEOL JNM-GX400 instruments. NMR spectra of the polymer samples were recorded using a JEOL A-500 (University of Bristol) and a Varian VXR400S (University of Durham). Chemical shifts are reported in ppm relative to an internal tetramethylsilane reference for both <sup>1</sup>H and <sup>13</sup>C spectra. *J* values are given in Hz. Infrared spectra were recorded using a Perkin-Elmer 881. Low and high resolution electron impact mass spectra were recorded by Dr K. MacNeil of the mass spectrometry service at the School of Chemistry, University of Bristol. Sonications were carried out using a Sonicor SC 120H apparatus. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and gel permeation chromatography analysis (GPC) were recorded by the staff of the IRC in Polymer Science at the University of Durham or at RAPRA.

### Note concerning trichloroacetyl chloride

Some batches of trichloroacetyl chloride purchased from the Aldrich Chemical Company during 1995–1996 failed to generate dichloroketene when reacted with various specimens of zinc, although the NMR and IR spectra of these batches of Cl<sub>3</sub>CCOCl were apparently identical to other batches purchased earlier, which behaved normally. We draw attention to this problem but have not been able to identify the impurity or inhibitor responsible.

### 1,5-Diphenylpentan-3-one

1,5-Diphenylpenta-1,4-dien-3-one<sup>58</sup> (10.0 g, 42.7 mmol), in a 1% solution of acetic acid in ethyl acetate (150 cm<sup>3</sup>), was hydrogenated under 3.5 bar of hydrogen with platinum oxide (Adam's catalyst, 100 mg) using a Parr hydrogenation apparatus; the reaction was complete in approximately 1 h. The solution was filtered to remove most of the catalyst, and the solvent

removed under reduced pressure. Chromatography on silica gel with pentane–diethyl ether (5:1) as the eluent yielded 1,5-diphenylpentan-3-one<sup>59</sup> as a colourless oil (7 g, 69%);  $\nu_{\max}$  (liquid film)/ $\text{cm}^{-1}$  1713 (C=O);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 7.13–7.29 (10H, m), 2.88 (4H, t,  $J$  7.5) and 2.69 (4H, t,  $J$  7.3);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 209.02, 140.96, 128.45, 128.26, 126.05, 44.44 and 29.66.

### 1,1-Dialkylethenes

**2-Ethylbut-1-ene.** Sodium hydride (60% dispersion in oil, 10 g, 0.25 mol) was washed with dry diethyl ether. Dry DMSO (200  $\text{cm}^3$ ) was added and the mixture heated with stirring to 60–70 °C. When hydrogen evolution stopped (after *ca.* 50 min) it was left to cool to room temperature and methyltriphenylphosphonium iodide (100.4 g, 0.248 mol) was added slowly in a stream of nitrogen. Stirring was continued for 10 min to allow the ylide to form, then pentan-3-one (21.36 g, 26.4  $\text{cm}^3$ , 0.248 mol) was added dropwise at 0 °C. A fractional distillation column with condenser was fitted to the reaction flask and after heating the mixture for 2 h at 50 °C, the temperature was raised to *ca.* 100 °C at which point the product distilled at 66 °C (lit.<sup>60</sup> bp 66.2–66.7 °C) as a colourless liquid (8.2 g, 38%);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 4.68–4.70 (2H, m), 1.99–2.08 (4H, m) and 1.03 (6H, t,  $J$  7.5);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 153.34, 106.16, 28.89 and 12.39.

**2-Propylpent-1-ene.** The procedure described above applied to heptan-4-one yielded a product which was collected from the reaction mixture by distillation (50 °C, 100 mbar) to give a colourless liquid (60% yield) (lit.<sup>61</sup> bp 60–61 °C at 76 mmHg);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 4.70 (2H, s), 1.98 (4H, t,  $J$  7.6), 1.38–1.51 (4H, m) and 0.90 (6H, t,  $J$  7.3);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 149.85, 108.62, 38.17, 20.89 and 13.88.

**2-Butylhex-1-ene.** The procedure described above applied to nonan-5-one yielded a product which was collected from the reaction mixture by distillation (55 °C, 30 mbar) to give a colourless liquid (58% yield) (lit.<sup>62</sup> bp 163.6–163.7 °C),  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 4.68–4.69 (2H, m), 1.98–2.03 (4H, m), 1.24–1.46 (8H, m) and 0.91 (3H, t,  $J$  7.1);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 150.37, 108.32, 35.80, 30.08, 22.53 and 13.98.

**2-Phenylethyl-4-phenylbut-1-ene.** The procedure described above was applied to 1,5-diphenylpentan-3-one. The reaction mixture was diluted with pentane (100  $\text{cm}^3$ ) and washed with water (3  $\times$  50  $\text{cm}^3$ ), dilute HCl (50  $\text{cm}^3$ ), neutralised with saturated sodium bicarbonate solution and washed with brine. The organic layer was dried ( $\text{MgSO}_4$ ) and the solvent removed under reduced pressure. Distillation of the crude product in a short-path apparatus (0.1 mbar, 200 °C) yielded 2-phenylethyl-4-phenylbut-1-ene<sup>59</sup> as a colourless oil (68% yield). HRMS; found for  $\text{M}^+$ : 236.156 498, calculated for  $\text{C}_{18}\text{H}_{20}$ : 236.156 501.  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 7.17–7.30 (10H, m), 4.81 (2H, t,  $J$  1.0), 2.73–2.79 (4H, m) and 2.33–2.39 (4H, m);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 148.64, 142.13, 128.30 (double intensity), 125.80, 109.64, 38.09 and 34.36.

### 2,2-Dichloro-3,3-dialkylcyclobutanones

**2,2-Dichloro-3,3-diethylcyclobutanone.** 2-Ethylbut-1-ene (3.22 g, 37.4 mmol) in dry, degassed diethyl ether (100  $\text{cm}^3$ ) was sonicated, using a Sonicor SC 120H apparatus, with zinc dust (4.9 g, 74.8 mmol) as a solution of trichloroacetyl chloride (10.2 g, 6.3  $\text{cm}^3$ , 56.1 mmol) in dry, degassed diethyl ether (20  $\text{cm}^3$ ) was added over a period of 1 h *via* a syringe pump. Iced water was added to the sonic bath at intervals to maintain the temperature below 30 °C. After the addition was complete, sonication was continued for a further 1 h. The reaction mixture was quenched with water (20  $\text{cm}^3$ ) added dropwise at 0 °C, and was then washed with water (2  $\times$  50  $\text{cm}^3$ ), saturated sodium bicarbonate solution (50  $\text{cm}^3$ ) and brine (50  $\text{cm}^3$ ), dried ( $\text{MgSO}_4$ ) and the solvent removed under reduced pressure to give a dark brown oil. Distillation in a short-path distillation apparatus (150 °C, 20 mbar) yielded 2,2-dichloro-3,3-diethylcyclobutanone as a colourless liquid (4.1 g, 56%);  $\nu_{\max}$  (liquid

film)/ $\text{cm}^{-1}$  1810 (C=O) and 752 (C–Cl);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 2.96 (2H, s), 1.95–2.08 (2H, m), 1.53–1.66 (2H, m) and 0.98 (6H, t,  $J$  7.3);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 193.18, 92.24, 52.04, 48.89, 26.14 and 9.05. Satisfactory elemental analysis results could not be obtained for this compound.

**2,2-Dichloro-3,3-dipropylcyclobutanone.** The procedure described above, applied to 2-propylpent-1-ene, yielded a crude product which on distillation of the crude product in a short-path distillation apparatus (180 °C, 10 mbar) yielded 2,2-dichloro-3,3-dipropylcyclobutanone as a colourless liquid (73% yield);  $\nu_{\max}$  (liquid film)/ $\text{cm}^{-1}$  1807 (C=O) and 750 (C–Cl);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 2.95 (2H, s), 1.87–1.95 (2H, m), 1.29–1.56 (6H, m) and 0.98 (6H, t,  $J$  7.1);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 193.31, 92.51, 52.71, 48.21, 36.24, 18.17 and 14.38;  $m/z$  182.1 ( $\text{M}^+$ , 63%), 180.1 (97), 138.0 (57), 124.0 (41), 97.1 (56), 84.2 (84), 79.1 (46), 54.9 (100), 42.8 (93), 41.8 (56) and 40.8 (91). Satisfactory elemental analysis results could not be obtained for this compound.

**2,2-Dichloro-3,3-dibutylcyclobutanone.** The procedure described above, applied to 2-butylhex-1-ene, yielded a crude product which was distilled in a short-path distillation apparatus (175 °C, 20 mbar) to give 2,2-dichloro-3,3-dibutylcyclobutanone as a colourless liquid (66% yield);  $\nu_{\max}$  (liquid film)/ $\text{cm}^{-1}$  1805 (C=O) and 752 (C–Cl);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 2.95 (2H, s), 1.88–1.93 (2H, m), 1.22–1.57 (10H, m), 0.92–0.97 (6H, m);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 193.29, 92.52, 52.71, 48.14, 33.73, 26.90, 23.0 and 13.95. Satisfactory elemental analysis results could not be obtained for this compound.

**2,2-Dichloro-3,3-di(2-phenylethyl)cyclobutanone.** The procedure described above, applied to 2-phenylethyl-4-phenylbut-1-ene, yielded a crude brown solid which was recrystallised twice from diethyl ether to give colourless crystals of 2,2-dichloro-3,3-di(2-phenylethyl)cyclobutanone (37% yield) mp 99 °C;  $\nu_{\max}$  (liquid film)/ $\text{cm}^{-1}$  1800 (C=O) and 703 (C–Cl);  $\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ) 7.21–7.35 (10H, m), 3.06 (2H, s), 2.61–2.88 (4H, m), 2.31–2.42 (2H, m) and 1.91–2.02 (2H, m);  $\delta_{\text{C}}$  (68 MHz;  $\text{CDCl}_3$ ) 192.41, 140.82, 128.67, 128.24, 126.39, 92.27, 52.77, 48.07, 36.08 and 31.31;  $m/z$  306 ( $\text{M}^+$ , 3%), 304 (5), 268 (2), 233 (4), 221 (3) and 91 (100). Satisfactory elemental analysis results could not be obtained for this compound.

**2,2-Dichlorospiro[adamantane-2,1'-cyclobutan]-3'-one.** Trichloroacetyl chloride (5.2  $\text{cm}^3$ , 46 mmol) in diethyl ether (60  $\text{cm}^3$ ) was added to a solution of 2-methyleneadamantane<sup>63</sup> (5 g, 34 mmol) and zinc (4.03 g, 62 mmol) in diethyl ether (75  $\text{cm}^3$ ) over a 4 h period *via* a syringe pump. During the addition, the suspension was sonicated whilst the temperature was maintained below 30 °C. One hour after the addition was completed, the brown suspension was added to water and extracted with diethyl ether. The extract was washed with saturated sodium hydrogen carbonate, dried with magnesium sulfate, and evaporated to dryness. Recrystallisation from heptane yielded 2,2-dichlorospiro[adamantane-2,1'-cyclobutan]-3'-one (6.2 g, 71%). Analytically pure material could be obtained by distillation (200 °C, 0.2 mbar) (Found: C, 60.15; H, 6.45.  $\text{C}_{13}\text{H}_{16}\text{Cl}_2\text{O}$  requires C, 60.25; H, 6.2%). All spectral data obtained were consistent with the literature.<sup>43</sup>

**(1R,2R,5R,7R)-4,4-Dichloro-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]-nonan-3-one.** (1R)-(+)- $\alpha$ -Pinene **36** (15  $\text{cm}^3$ , 94 mmol, 97% ee) was added to a suspension of zinc (19 g, 290 mmol) in diethyl ether (300  $\text{cm}^3$ ). A solution of trichloroacetyl chloride (15.78  $\text{cm}^3$ , 141 mmol) in diethyl ether (34  $\text{cm}^3$ ) was added to the suspension over a period of 4 h *via* a syringe pump. The brown solution was then added to water and extracted with diethyl ether. The extract was washed with saturated sodium carbonate, dried with magnesium sulfate and evaporated to dryness. The crude product was then absorbed onto silica gel (30 g). This was placed on top of another 50 g of silica gel. By eluting with petroleum spirit (bp 40–60 °C), starting material (typically about 10  $\text{cm}^3$ ) was recovered with the first 400  $\text{cm}^3$  of petroleum spirit. Eluting with a further 4 l of petroleum spirit yielded

(1*R*,2*R*,5*R*,7*R*)-4,4-dichloro-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]-nonan-3-one as a clear oil (4.5 g, 19%). A sample of analytical purity was obtained by cooling a concentrated petroleum spirit solution to -78 °C and decanting off the solvent from the precipitate (Found: C, 58.0; H, 6.8. C<sub>12</sub>H<sub>16</sub>Cl<sub>2</sub>O requires C, 58.3; H, 6.5%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1803 (C=O);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 0.98 (3H, s, Me), 1.31 (1H, br d, *J* 13, C9-H<sub>a</sub>), 1.32 (3H, s, Me), 1.52 (3H, s, Me), 1.86 (1H, br m), 2.05–2.38 (4H, m), 3.35 (1H, br d, *J* 10, C5-H);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 21.6, 23.7, 26.8, 26.9, 27.6, 38.2, 39.2, 48.9, 49.2, 54.7, 92.8, 200.1.

### 1-(1-Phenylthiocyclopropyl)-1-hydroxycycloalkanes

**1-(1-Phenylthiocyclopropyl)-1-hydroxycyclohexane.** Following the procedure of Trost,<sup>44</sup> *n*-butyllithium [34 cm<sup>3</sup>, 86 mmol (2.5 M in hexanes)] was added to a solution of cyclopropyl phenyl sulfide (12.8 cm<sup>3</sup>, 89 mmol) in THF (170 cm<sup>3</sup>) at 0 °C. The solution was stirred at 0 °C for 90 min. Cyclohexanone (7 g, 71 mmol) was added dropwise and the solution stirred at 0 °C. After 30 min the reaction mixture was added to water and extracted with diethyl ether. The organic layer was dried with magnesium sulfate and evaporated to dryness. Distillation of the crude product (160 °C, 0.1 mbar) yielded 1-(1-phenylthiocyclopropyl)-1-hydroxycyclohexane (9.5 g, 54%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.93 (2H, dd, *J* 8, 5, cyclopropane-H), 1.13 (2H, dd, *J* 8, 5, cyclopropane-H), 1.4–1.8 (11H, m), 7.05 (1H, m, Ph), 7.15 (2H, m, Ph), 7.42 (2H, m, Ph).

**1-(1-Phenylthiocyclopropyl)-1-hydroxy-4-*tert*-butylcyclohexane.** The same basic procedure was employed as for 1-(1-phenylthiocyclopropyl)-1-hydroxycyclohexane described earlier but using: *n*-butyllithium [25 cm<sup>3</sup>, 62 mmol (2.5 M in hexanes)], cyclopropyl phenyl sulfide (9.3 cm<sup>3</sup>, 65 mmol), THF (130 cm<sup>3</sup>) and *tert*-butylcyclohexanone (8 g, 52 mmol). Excess cyclopropyl phenyl sulfide and unreacted *tert*-butylcyclohexanone were removed by short-path distillation (100 °C, 0.1 mbar) yielding 1-(1-phenylthiocyclopropyl)-1-hydroxy-4-*tert*-butylcyclohexane (8.1 g, 51%). The product was shown by NMR spectroscopy to consist of two isomers and was not further purified at this stage.

**9-(1-Phenylthiocyclopropyl)-9-hydroxy-9*H*-thioxanthene.** The same basic procedure was employed as for 1-(1-phenylthiocyclopropyl)-1-hydroxycyclohexane described earlier but using: *n*-butyllithium [12 cm<sup>3</sup>, 30 mmol (2.5 M in hexanes)], cyclopropyl phenyl sulfide (5 g, 33 mmol), THF (130 cm<sup>3</sup>) and thioxanthone (5.4 g, 25 mmol). Dry-flash column chromatography on silica gel eluting with diethyl ether–hexane (1:3) yielded 9-(1-phenylthiocyclopropyl)-9-hydroxy-9*H*-thioxanthene (8.6 g, 92%). An analytically pure sample was prepared by recrystallisation from chloroform–hexane (1:5), mp 90–92 °C (Found: C, 72.9; H, 4.8. C<sub>22</sub>H<sub>18</sub>OS<sub>2</sub> requires C, 72.9; H, 5.0%);  $\nu_{\max}$ (nujol mull)/cm<sup>-1</sup> 3426 (OH);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.93 (2H, dd, *J* 7, 5, cyclopropane-H), 1.07 (2H, dd, *J* 7, 5, cyclopropane-H), 3.20 (1H, s, OH), 7.05 (5H, m, Ar-H), 7.25–7.40 (6H, m, Ar-H), 7.90 (2H, dd, *J* 8, 2, Ar-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 13.9, 34.7, 76.6, 124.9, 125.8, 126.2, 127.4, 127.7, 127.9, 131.5, 132.1, 135.7, 136.4.

### 3,3-Dialkylcyclobutanones

**3,3-Diethylcyclobutanone.** A solution of 2,2-dichloro-3,3-diethylcyclobutanone (3.92 g, 20.1 mmol) in acetic acid (10 cm<sup>3</sup>) was added dropwise to a vigorously stirred suspension of zinc dust (8.1 g) in acetic acid (20 cm<sup>3</sup>) at 0 °C. After the addition the reaction mixture was heated at 70 °C for 50 min. The mixture was allowed to cool to room temperature and then poured into a separating funnel containing diethyl ether (50 cm<sup>3</sup>) and water (50 cm<sup>3</sup>). The organic layer was washed with water (3 × 50 cm<sup>3</sup>), saturated sodium bicarbonate solution (2 × 50 cm<sup>3</sup>) and brine (50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure to give 3,3-diethylcyclobutanone as a colourless liquid (2.2 g, 87%). This was used without further purification (Found: C, 75.9; H, 11.5. C<sub>8</sub>H<sub>14</sub>O requires C, 76.14; H,

11.18%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1782 (C=O);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 2.70 (4H, s), 1.62 (4H, q, *J* 7.4), 0.89 (6H, t, *J* 7.4);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 208.79, 55.83, 33.06, 29.63, 9.09.

**3,3-Dipropylcyclobutanone.** The procedure described above, applied to 2,2-dichloro-3,3-dipropylcyclobutanone, yielded 3,3-dipropylcyclobutanone as a colourless liquid (92% yield);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1785 (C=O);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 2.71 (4H, s), 1.52–1.58 (4H, m), 1.23–1.37 (4H, m) and 0.94 (6H, t, *J* 7.2);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 209.01, 56.81, 40.11, 32.27, 18.27 and 14.52; *m/z* 154.1 (M<sup>+</sup>, 2%), 139.1 (3), 84.1 (81), 70.1 (39), 69.0 (63), 56.0 (100), 55.0 (80) and 41.0 (67); HRMS: Found for [M - 1]<sup>+</sup>: 153.128 223, calculated for C<sub>10</sub>H<sub>17</sub>O: 153.127 940.

**3,3-Dibutylcyclobutanone.** The procedure described above, applied to 2,2-dichloro-3,3-dibutylcyclobutanone, yielded 3,3-dibutylcyclobutanone as a colourless liquid (90% yield);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1784 (C=O);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 2.71 (4H, s), 1.53–1.59 (4H, m), 1.18–1.38 (8H, m) and 0.92 (6H, t, *J* 7.1);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 208.91, 56.74, 37.44, 32.17, 27.22, 23.09 and 14.01; *m/z* 183 (M<sup>+</sup>, 45%), 165 (34), 140 (28), 125 (51), 109 (46), 95 (41), 83 (62), 69 (80), 56 (100). Satisfactory elemental analysis results could not be obtained for this compound.

**3,3-Di(2-phenylethyl)cyclobutanone.** The procedure described above, applied to 2,2-dichloro-3,3-di(2-phenylethyl)cyclobutanone, yielded 3,3-di(phenylethyl)cyclobutanone as a colourless liquid (86% yield) (Found: C, 86.0; H, 7.9. C<sub>20</sub>H<sub>22</sub>O requires C, 86.29; H, 7.97%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1778 (C=O);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.18–7.33 (10H, m), 2.80 (4H, s), 2.61–2.68 (4H, m) and 1.96–2.03 (4H, m);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 207.56, 141.58, 128.53, 128.23, 126.05, 56.92, 39.62, 32.51 and 31.60.

### Spiro[adamantane-2,1'-cyclobutan]-3'-one

2,2-Dichlorospiro[adamantane-2,1'-cyclobutan]-3'-one (5 g, 19 mmol) was dissolved in acetic acid (20 cm<sup>3</sup>) and zinc (4.94 g, 76 mmol) was added. The solution was stirred for 40 min at 70 °C. On cooling the suspension was added to water and extracted with hexane. The extract was washed with saturated sodium hydrogen carbonate, dried with magnesium sulfate and evaporated to dryness. Sublimation (80–90 °C, 0.1 mbar) yielded spiro[adamantane-2,1'-cyclobutan]-3'-one (3.2 g, 87%), mp 125–127 °C (lit.,<sup>43</sup> 130 °C).

### (1*R*,2*R*,5*R*,7*R*)-2,8,8-Trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one

The same basic procedure was employed as for spiro[adamantane-2,1'-cyclobutan]-2'-one described earlier but using: (1*R*,2*R*,5*R*,7*R*)-4,4-dichloro-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one (5 g, 20 mmol), acetic acid (60 cm<sup>3</sup>) and zinc (7.8 g, 120 mmol). The product was purified by short-path distillation (80–90 °C, 0.2 mbar) yielding (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one (2.6 g, 80%),  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 1781 (C=O);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 0.96 (3H, s, Me), 1.16 (1H, d, *J* 12, C9-H<sub>a</sub>), 1.28 (3H, s, Me), 1.46 (3H, s, Me), 1.8–2.35 (5H, m, includes C9-H<sub>b</sub>), 2.75 (1H, dd, *J* 18, 3, C4-H), 2.90 (1H, br m, C5-H), 3.01 (1H, dd, *J* 18, 3, C4-H);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 23.2, 26.3, 26.9, 27.0, 28.1, 34.0, 39.5, 40.6, 49.6, 57.6, 57.8, 214.4; *m/z* (CI) 179.1428 ([M + 1]<sup>+</sup>, 25%), calc. mass for C<sub>12</sub>H<sub>19</sub>O: 179.1436 (+4.4 ppm).

### 2,2-Dialkylcyclobutanones

**Spiro[cyclobutane-1,1'-cyclohexan]-2-one.** Following the procedure of Trost,<sup>45</sup> 1-(1-phenylthiocyclopropyl)-1-hydroxycyclohexane (8.5 g, 34 mmol) was dissolved in dichloromethane (250 cm<sup>3</sup>) at 0 °C. Stannic chloride [34 cm<sup>3</sup>, 34 mmol (1 M in dichloromethane)] was added and after 30 s the ice bath was removed. After 4 min, water (100 cm<sup>3</sup>) was added and the suspension poured into a separating funnel containing sodium hydroxide solution (250 cm<sup>3</sup>, 2 M) and diethyl ether (600 cm<sup>3</sup>). The organic layer was extracted with sodium hydroxide (3 × 250 cm<sup>3</sup>, 2 M), water (250 cm<sup>3</sup>) and evaporated to dryness. Distillation of the crude material (80 °C, 20 mbar) yielded spiro[cyclobutane-1,1'-cyclohexan]-2-one (2.67 g, 57%);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>)

1.25–1.75 (10H, m), 1.80 (2H, t, *J* 8, C4-H), 2.96 (2H, t, *J* 8, C3-H).

**4'-tert-Butylspiro[cyclobutane-1,1'-cyclohexan]-2-one.** The same basic procedure was employed as for spiro[cyclobutane-1,1'-cyclohexan]-2-one described earlier but using: 1-(1-phenylthiocyclopropyl)-1-hydroxy-4-tert-butylcyclohexane (8.1 g, 27 mmol), dichloromethane (200 cm<sup>3</sup>) and stannic chloride [27 cm<sup>3</sup>, 27 mmol (1 M in dichloromethane)]. Distillation of the crude material (70 °C, 0.1 mbar) yielded a mixture of both cyclobutanone isomers. These were separated by column chromatography using silica gel (150 g), eluting with diethyl ether–hexane (1:9). From the column, 0.35 g (yield 7%) of the minor isomer and 1.22 g (yield 25%) of the major isomer 4'-tert-butylspiro[cyclobutane-1,1'-cyclohexan]-2-one were obtained cleanly whilst 1.14 g of mixed product (mostly major isomer) was also obtained. NMR data for the major isomer:  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 0.84 (9H, s, Me), 0.9–1.1 (3H, m), 1.45–1.55 (2H, m), 1.6–1.7 (4H, m), 1.84 (2H, t, *J* 6, C4-H), 2.97 (2H, t, *J* 6, C3-H).

**Spiro[cyclobutane-1,9'-9H-thioxanthen]-2-one.** 40% Aqueous tetrafluoroboric acid (13 cm<sup>3</sup>, 4.5 M) was added to a solution of 9-(1-phenylthiocyclopropyl)-9-hydroxy-9H-thioxanthen (8.2 g, 23 mmol) in dioxane (190 cm<sup>3</sup>) and water (90 cm<sup>3</sup>). The solution was heated at reflux for 16 h. The solution was poured onto aqueous saturated sodium hydrogen carbonate and extracted with diethyl ether. The extract was dried and evaporated to dryness. Dry-flash column chromatography on silica gel with diethyl ether–hexane (1:6) as the eluent yielded spiro[cyclobutane-1,9'-9H-thioxanthen]-2-one (3.3 g, 58%),  $\nu_{\text{max}}$ (liquid film)/cm<sup>-1</sup> 1782 (C=O);  $\delta_{\text{H}}$ (400 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 2.29 (2H, t, *J* 8.7, C4-H), 3.16 (2H, t, *J* 8.7, C3-H), 6.95–7.10 (4H, m, Ar-H), 7.22 (2H, m, Ar-H), 7.33 (2H, m, Ar-H);  $\delta_{\text{C}}$ (100 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 27.2, 43.4, 73.6, 124.7, 127.1, 127.3, 128.0, 132.8, 137.8, 209.1; *m/z* (CI) 253.0693 ([M + 1]<sup>+</sup>, 100%). Calc. mass for C<sub>16</sub>H<sub>13</sub>OS: 253.0687 (–2.3 ppm).

### Dialkylcyclobutanone toluene-*p*-sulfonylhydrazones

**3,3-Diethylcyclobutanone toluene-*p*-sulfonylhydrazone.** Toluene-*p*-sulfonohydrazide (2.8 g, 15 mmol) was added to a stirred solution of 3,3-diethylcyclobutanone (1.81 g, 14.4 mmol) in dry, degassed THF (25 cm<sup>3</sup>). The solution was left to stir overnight. The solvent was removed under reduced pressure and the white solid residue recrystallised from methanol–water to give colourless needle-like crystals of 3,3-diethylcyclobutanone toluene-*p*-sulfonylhydrazone (mp 130 °C with decomposition) which were dried overnight *in vacuo* over P<sub>2</sub>O<sub>5</sub> (3.21 g, 76%) (Found: C, 61.1; H, 7.9; N, 9.8; S, 11.1 C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 61.20; H, 7.53; N, 9.58; S, 10.89%);  $\nu_{\text{max}}$ (nujol mull)/cm<sup>-1</sup> 3199 (N–H), 1689 (C=N), 1335, 1168 (SO<sub>2</sub>) and 814 (*para*-disubstituted benzene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.84 (2H, d, *J* 8.4), 7.69 (1H, s), 7.32 (2H, d, *J* 8.1), 2.50 (2H, t, *J* 2.5), 2.43 (3H, s), 2.37 (2H, t, *J* 2.5), 1.43 (4H, q, *J* 7.3) and 0.75 (6H, t, *J* 7.3);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 158.53, 143.97, 135.40, 129.60, 127.90, 43.29, 40.96 (double intensity), 36.75, 29.43, 21.58 and 8.36; *m/z* 295 (M<sup>+</sup>, 3%) 265 (1), 139 (100) and 91 (33).

**3,3-Dipropylcyclobutanone toluene-*p*-sulfonylhydrazone.** The procedure described above, applied to 3,3-dipropylcyclobutanone, yielded 3,3-dipropylcyclobutanone toluene-*p*-sulfonylhydrazone as colourless needles (74% yield) mp 115 °C with decomposition (Found: C, 63.5; H, 8.4; N, 8.6. C<sub>17</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 63.32; H, 8.13; N, 8.69%);  $\nu_{\text{max}}$ (liquid film)/cm<sup>-1</sup> 3197 (N–H), 1693 (C=N), 1335, 1168 (SO<sub>2</sub>) and 816 (*para*-disubstituted benzene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.84 (2H, d, *J* 8.3), 7.67 (1H, s), 7.32 (2H, d, *J* 8.3), 2.51 (2H, s), 2.43 (3H, s), 2.39 (2H, s), 1.33–1.39 (4H, m), 1.08–1.21 (4H, m), 0.86 (6H, t, *J* 7.1);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 158.78, 143.96, 135.39, 129.61, 127.92, 44.27, 41.89 (double intensity), 39.98, 36.08, 21.60, 17.51 and 14.49; *m/z* 323 (M<sup>+</sup>, 1%), 293 (1), 279 (1), 167 (100) and 91 (35).

**3,3-Dibutylcyclobutanone toluene-*p*-sulfonylhydrazone.** The

procedure described above, applied to 3,3-dibutylcyclobutanone, yielded 3,3-dibutylcyclobutanone toluene-*p*-sulfonylhydrazone as colourless needles (54% yield) mp 113 °C, decomposition (Found: C, 65.1; H, 8.8; N, 7.9; S, 9.3. C<sub>19</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 65.10; H, 8.63; N, 7.99; S, 9.15%);  $\nu_{\text{max}}$ (nujol mull)/cm<sup>-1</sup> 3203 (N–H), 1688 (C=N), 1339, 1161 (SO<sub>2</sub>), 819 (*para*-disubstituted benzene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.84 (2H, d, *J* 8.4), 7.72 (1H, s), 7.32 (2H, d, *J* 8.1), 2.50 (2H, d, *J* 2.2), 2.43 (3H, s), 2.38 (2H, d, *J* 2.0), 1.06–1.40 (12H, m) and 0.87 (6H, t, *J* 7.1);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 158.78, 143.92, 135.42, 129.60, 127.88, 44.19, 41.91, 37.29, 35.90, 26.40, 23.04, 21.55 and 13.98; *m/z* 351 (M<sup>+</sup>, 18%) 336 (13), 196 (36), 195 (100), 180 (11), 155 (20), 139 (21) and 91 (28).

**3,3-Di(2-phenylethyl)cyclobutanone toluene-*p*-sulfonylhydrazone.** The procedure described above, applied to 3,3-di(2-phenylethyl)cyclobutanone, yielded 3,3-di(2-phenylethyl)cyclobutanone toluene-*p*-sulfonylhydrazone as colourless needles (75% yield) mp 100 °C (Found: C, 72.8; H, 7.0; N, 6.5; S, 7.3. C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 72.61; H, 6.77; N, 6.27; S, 7.18%);  $\nu_{\text{max}}$ (liquid film)/cm<sup>-1</sup> 3205 (N–H), 1693 (C=N), 1594 (N–H), 1330, 1170 (SO<sub>2</sub>) and 817 (*para*-disubstituted benzene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.84 (2H, d, *J* 8.4), 7.60 (1H, s), 7.11–7.31 (12H, m), 2.64 (2H, s), 2.48–2.54 (4H, m), 2.48 (3H, s), 2.36 (2H, s) and 1.79–1.85 (4H, m);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 157.49, 144.13, 141.60, 135.28, 129.65, 128.48, 128.20, 127.90, 126.00, 44.28, 41.94, 39.56, 36.20, 30.85 and 21.53.

**Spiro[adamantane-2,1'-cyclobutan]-3'-one benzenesulfonylhydrazone.** Spiro[adamantane-2,1'-cyclobutan]-3'-one (7.25 g, 38 mmol) was dissolved in diethyl ether (500 cm<sup>3</sup>) and benzenesulfonohydrazide (6.58 g, 38 mmol) added in portions over a 10 min period. After 18 h of stirring a stream of nitrogen was passed over the suspension reducing the volume of the diethyl ether to 250 cm<sup>3</sup>. After cooling to –10 °C the precipitate was filtered and dried under vacuum to yield spiro[adamantane-2,1'-cyclobutan]-3'-one benzenesulfonylhydrazone (8.2 g, 63%), mp 101–102 °C (Found: C, 66.6; H, 7.25; N, 8.25. C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 66.3; H, 7.0; N, 8.15%);  $\nu_{\text{max}}$ (nujol mull)/cm<sup>-1</sup> 3202 (N–H), 1676w (C=N), 1586w (N–H), 1166s (SO<sub>2</sub>);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.5–1.9 (14H, m), 2.48 (2H, s, CH<sub>2</sub>), 2.64 (2H, s, CH<sub>2</sub>), 7.56 (3H, m, Ph), 7.96 (2H, m, Ph), 8.25 (1H, br s, NH);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 26.8, 33.2, 33.8, 36.4, 36.9, 40.6, 42.2, 44.4, 127.9, 128.9, 133.0, 138.5, 158.6.

**(1*R*,2*R*,5*R*,7*R*)-2,8,8-Trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one benzenesulfonylhydrazone.** (1*R*,2*R*,5*R*,7*R*)-2,8,8-Trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one (2.5 g, 14 mmol) was dissolved in THF (40 cm<sup>3</sup>) and benzenesulfonohydrazide (2.4 g, 14 mmol) added. The solution was stirred overnight and the THF evaporated. Recrystallisation from diethyl ether yielded (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one benzenesulfonylhydrazone (3.03 g, 65%), mp 105–107 °C (Found: C, 65.25; H, 7.5; N, 8.55. C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 65.05; H, 7.25; N, 8.45%);  $\nu_{\text{max}}$ (liquid film)/cm<sup>-1</sup> 3191 (N–H), 1678w (C=N), 1592w (N–H);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.73 (1H, d, *J* 11, C9-H<sub>a</sub>), 0.86 (3H, s, Me), 1.19 (3H, s, Me), 1.26 (3H, s, Me), 1.72 (1H, br m), 1.80 (1, t), 1.90–2.02 (3H, br m, includes one C6-H and C9-H<sub>b</sub>), 2.25 (1H, d, *J* 16, C4-H), 2.58 (1H, dd, *J* 16, 4, C4-H), 2.86 (1H, m, C5-H), 7.34 (1H, br s, N–H), 7.51 (2H, tm, <sup>3</sup>*J* ~ <sup>3</sup>*J'* ~ 7, *m*-H of Ph), 7.60 (2H, tm, <sup>3</sup>*J* ~ <sup>3</sup>*J'* ~ 7, *p*-H of Ph), 7.96 (2H, br d, <sup>3</sup>*J* ~ 7, *o*-H of Ph);  $\delta_{\text{C}}$ (68 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 23.4, 26.0, 27.3, 30.9, 37.7, 39.3, 40.7, 42.3, 46.0, 49.5, 127.9, 129.0, 133.1, 138.4, 165.0.

**Spiro[cyclobutane-1,1'-cyclohexan]-2-one toluene-*p*-sulfonylhydrazone.** Spiro[cyclobutane-1,1'-cyclohexan]-2-one (2.67 g, 19 mmol) was dissolved in ethanol (60 cm<sup>3</sup>) containing a few drops of concentrated hydrochloric acid. Toluene-*p*-sulfonohydrazide (3.6 g, 19 mmol) was added and the suspension heated to effect dissolution. After 18 h the volume of the solvent was reduced to 30 cm<sup>3</sup> and the suspension cooled to –28 °C. The precipitate was subsequently filtered and dried under vacuum to give spiro[cyclobutanone-1,1'-cyclohexan]-2-one toluene-*p*-



sulfonylhydrazone (4.57 g, 77%), decomp. >110 °C (Found: C, 62.55; H, 7.5; N, 9.3. C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 62.7; H, 7.2; N, 9.15%);  $\nu_{\max}$ (nujol mull)/cm<sup>-1</sup> 3209 (N–H), 1687w (C=N), 1595w (N–H);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.25–1.8 (10H, m), 1.67 (2H, t, *J* 8, C4-H), 2.41 (3H, s, Ph-CH<sub>3</sub>), 2.61 (2H, t, *J* 8, C3-H), 7.28 (2H, d, *J* 8, Ph), 7.5 (1H, br s, NH), 7.80 (2H, d, *J* 8, Ph);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 21.5, 22.0, 25.2, 26.3, 27.8, 34.2, 52.6, 128.0, 129.3, 135.2, 145.3, 168.2.

**4'-tert-Butylspiro[cyclobutane-1,1'-cyclohexan]-2-one toluene-*p*-sulfonylhydrazone.** 4'-tert-Butylspiro[cyclobutane-1,1'-cyclohexan]-2-one (1.22 g, 6.3 mmol) was dissolved in ethanol (25 cm<sup>3</sup>) containing a drop of concentrated hydrochloric acid. Toluene-*p*-sulfonylhydrazide (1.16 g, 6.3 mmol) was added and the suspension heated to effect dissolution. After 8 h a precipitate had formed which was insoluble in the solvent even on heating. The suspension was cooled to 0 °C and the precipitate was filtered and dried under vacuum to give 4'-tert-butylspiro[cyclobutane-1,1'-cyclohexan]-2-one toluene-*p*-sulfonylhydrazone (1.98 g, 87%), mp 108 °C (decomp.) (Found: C, 66.7; H, 8.4; N, 7.6. C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 66.3; H, 8.3; N, 7.7%);  $\nu_{\max}$ (nujol mull)/cm<sup>-1</sup> 3207 (N–H), 1685w (C=N), 1593w (N–H);  $\delta_{\text{H}}$ [400 MHz; (CD<sub>3</sub>)<sub>2</sub>SO] 0.77 [9H, s, C4'-C(CH<sub>3</sub>)<sub>3</sub>], 0.85–0.95 (3H, m), 1.2–1.3 (2H, m), 1.5–1.65 (4H, m), 1.65 (2H, t, *J* 8), 2.36 (3H, Ph-CH<sub>3</sub>), 2.70 (2H, t, *J* 8), 7.38 (2H, d, *J* 8, Ph), 7.68 (2H, d, *J* 8, Ph), 11.3 (1H, br s, NH);  $\delta_{\text{C}}$ [100 MHz; (CD<sub>3</sub>)<sub>2</sub>SO] 22.8, 24.5, 27.6, 29.0, 29.5, 33.9, 35.9, 48.4, 53.8, 128.9, 131.0, 138.3, 144.6, 168.9.

**Spiro[cyclobutane-1,9'-9*H*-thioxanthen]-2-one toluene-*p*-sulfonylhydrazone.** Toluene-*p*-sulfonylhydrazide (1.48 g, 7.9 mmol) was added to a stirred solution of spiro[cyclobutane-1,9'-9*H*-thioxanthen]-2-one (2 g, 7.9 mmol) in ethanol (30 cm<sup>3</sup>). After 24 h the resultant suspension was cooled to 0 °C and the precipitated spiro[cyclobutane-1,9'-9*H*-thioxanthen]-2-one toluene-*p*-sulfonylhydrazone was filtered (2.1 g, 62%). An analytically pure sample was prepared by recrystallisation from THF, decomp. >200 °C (Found: C, 65.8; H, 4.9; N, 6.7. C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires C, 65.7; H, 4.8; N, 6.7%);  $\nu_{\max}$ (nujol mull)/cm<sup>-1</sup> 3183 (N–H), 1677w (C=N), 1596w (N–H);  $\delta_{\text{H}}$ [400 MHz; (CD<sub>3</sub>)<sub>2</sub>SO] 2.06 (2H, t, *J* 8.2, C4-H), 2.55 (3H, s, Ph-CH<sub>3</sub>), 3.02 (2H, t, *J* 8.2, C3-H), 7.09–7.15 (4H, m, Ar-H), 7.21–7.28 (2H, m, Ar-H), 7.44–7.60 (4H, m, Ar-H), 7.87 (2H, d, *J* 8.0, Ph), 11.28 (1H, s, NH);  $\delta_{\text{C}}$ [100 MHz; (CD<sub>3</sub>)<sub>2</sub>SO] 22.8, 29.9, 33.5, 61.3, 125.9, 128.1, 128.5, 129.1, 129.5, 131.4, 133.1, 138.0, 140.8, 145.3, 159.9.

### 3,3-Dialkylcyclobutenes

**3,3-Diethylcyclobutene, 1a.** (a) *Using lithium 2,2,6,6-tetramethylpiperidide.*—A solution of the base lithium 2,2,6,6-tetramethylpiperidide was made by the slow addition of methyl-lithium (1.4 M solution in diethyl ether, 30 cm<sup>3</sup>) to the amine (8.9 cm<sup>3</sup>, 52.8 mmol). When the vigorous bubbling had ceased, dry, degassed THF (5 cm<sup>3</sup>) was added to dissolve any precipitate. The base solution was added dropwise to a solution of the hydrazone (3.24 g, 11 mmol) in dry, degassed THF (20 cm<sup>3</sup>) at –78 °C. The resulting orange solution was stirred for a further 10 min then allowed to warm to room temperature. Stirring was continued overnight. The reaction mixture was cooled to –78 °C and water (20 cm<sup>3</sup>) was added dropwise, upon which the solution turned yellow. It was diluted with pentane (50 cm<sup>3</sup>), washed with water (3 × 20 cm<sup>3</sup>) and dilute HCl solution (20 cm<sup>3</sup>), neutralised with saturated sodium bicarbonate solution (20 cm<sup>3</sup>), washed with brine and dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure with a 20 cm Vigreux column to minimise losses. Distillation in a short-path distillation apparatus (80 mbar, 80 °C) (lit.<sup>65</sup> bp 107.6 °C) and filtration through a plug of alumina (neutral, Brockmann grade I) yielded 3,3-diethylcyclobutene **1a** as a colourless liquid (142 mg, 12%);  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 3045 and 1565 (cyclobutene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 6.14 (1H, d, *J* 2.8), 6.06–6.08 (1H, m), 2.135 (2H, d, *J* 0.9), 1.49 (4H, q, *J* 7.3) and 0.84 (6H, t,

*J* 7.4);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 144.05, 133.55, 52.15, 40.34, 28.69 and 9.49.

(b) *Using lithium diisopropylamide.*—The above procedure was repeated using hydrazone (5.18 g, 17.62 mmol), methyl-lithium (1.4 M solution in diethyl ether, 46 cm<sup>3</sup>) THF (10 cm<sup>3</sup>) and diisopropylamine (8.54 g, 84.4 mmol). After work up 3,3-diethylcyclobutene **1a** (0.55 g, 28%) was isolated.

**3,3-Dipropylcyclobutene, 1b.** The procedure described above using lithium 2,2,6,6-tetramethylpiperidide, applied to 3,3-dipropylcyclobutanone toluene-*p*-sulfonylhydrazone, yielded a crude product which was distilled in a short-path distillation apparatus (100 °C, 50 mbar) to give 3,3-dipropylcyclobutene **1b** as a colourless liquid (60% yield); HRMS: found for M<sup>+</sup>: 138.140 274, calculated for C<sub>10</sub>H<sub>18</sub> 138.140 843;  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 3045 and 1566 (cyclobutene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 6.14 (1H, d, *J* 2.8), 6.03–6.04 (1H, m), 2.16 (2H, d, *J* 0.9), 1.40–1.47 (4H, m), 1.20–1.38 (4H, m) and 0.90 (6H, t, *J* 7.2);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 144.77, 133.14, 51.46, 41.47, 39.27, 18.65 and 14.67; *m/z* 138.2 (M<sup>+</sup>, 31%), 123.1 (8), 109.1 (12), 95.1 (100), 81.2 (31.66), 67.0 (81), 54.9 (35) and 40.8 (35).

**3,3-Dibutylcyclobutene, 1c.** The procedure described above using lithium 2,2,6,6-tetramethylpiperidide, applied to 3,3-dibutylcyclobutanone toluene-*p*-sulfonylhydrazone, yielded a crude product which was distilled in a short-path distillation apparatus (130 °C, 40 mbar) to give 3,3-dibutylcyclobutene **1c** as a colourless liquid (36% yield); HRMS: found for M<sup>+</sup>: 166.170 914, calculated for C<sub>12</sub>H<sub>22</sub> 166.172 141;  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 3045 and 1565 (cyclobutene ring);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 6.14 (1H, d, *J* 2.8), 6.02–6.04 (1H, m), 2.15 (2H, d, *J* 0.9), 1.42–1.48 (4H, m), 1.16–1.37 (8H, m) and 0.90 (6H, t, *J* 6.9);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 144.77, 133.17, 51.33, 41.58, 36.54, 27.69, 23.45 and 14.16. Satisfactory elemental analysis results could not be obtained for this compound.

**3,3-Di(2-phenylethyl)cyclobutene, 1d.** The procedure described above using lithium 2,2,6,6-tetramethylpiperidide, applied to 3,3-di(2-phenylethyl)cyclobutanone toluene-*p*-sulfonylhydrazone, yielded a crude product which was washed through a plug of alumina with pentane and the solvent removed under reduced pressure to give 3,3-di(2-phenylethyl)cyclobutene **1d** as a colourless oil (34% yield). HRMS: found for M<sup>+</sup>: 262.171 074, calculated for C<sub>20</sub>H<sub>22</sub>: 262.172 151;  $\nu_{\max}$ (liquid film)/cm<sup>-1</sup> 3082, 3024, 2917, 2853, 1602, 1495, 1452, 1029, 749, 719, 697 and 665;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.15–7.31 (10H, m), 6.15 (1H, d, *J* 2.9), 6.11 (1H, d, *J* 2.8), 2.60–2.66 (4H, m), 2.30 (2H, s) and 1.85–1.91 (4H, m);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 143.83, 142.98, 133.88, 128.32 (double intensity), 125.63, 51.23, 41.24, 38.92 and 31.95; *m/z* 262 (M<sup>+</sup>, 3%), 234 (3), 157 (15), 171 (5) and 91 (100).

**Spiro[adamantane-2,1'-cyclobut-2'-ene], 3.** Methyl-lithium [41.5 cm<sup>3</sup>, 58 mmol (1.4 M in diethyl ether)] was added slowly to 2,2,6,6-tetramethylpiperidine (10.2 g, 73 mmol). After hydrogen evolution had ceased the lithium salt was dissolved in THF (50 cm<sup>3</sup>) and added dropwise to a solution of spiro[adamantane-2,1'-cyclobutan]-3'-one toluene-*p*-sulfonylhydrazone (5 g, 14 mmol) in THF (100 cm<sup>3</sup>) at –78 °C. The reaction was subsequently allowed to warm to room temperature and after 18 h the reaction mixture was added to water and extracted with hexane. The extract was washed with hydrochloric acid (1 M), saturated sodium hydrogen carbonate, dried with magnesium sulfate and evaporated to dryness. Distillation (80 °C, 0.1 mbar) yielded pure spiro[adamantane-2,1'-cyclobut-2'-ene] **3** (2.14 g, 85%), mp 66–67 °C (Found: C, 89.3; H, 10.3. C<sub>13</sub>H<sub>18</sub> requires C, 89.65; H, 10.3%);  $\nu_{\max}$ (nujol mull)/cm<sup>-1</sup> 1563w (C=C);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.55–1.95 (14H, m), 2.23 (2H, d, *J* 1.1, C4-H), 6.15 (1H, dt, *J* 3, 0.9, C3-H), 6.47 (1H, d, *J* 3, C2-H);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 26.8, 27.5, 34.5, 34.8, 36.9, 37.3, 42.4, 55.6, 134.5, 144.8.

### (1*R*,2*R*,5*R*,7*R*)-2,8,8-Trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene,

**4.** The same basic procedure was employed as for spiro[adamantane-2,1'-cyclobut-2'-ene] described earlier but using:

2,2,6,6-tetramethylpiperidine (7.6 cm<sup>3</sup>, 45 mmol), methyl-lithium [25.8 cm<sup>3</sup>, 36 mmol (1.4 M in diethyl ether)] and (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]nonan-3-one benzenesulfonylhydrazone (3 g, 9 mmol). Short-path distillation (55 °C, 0.2 mbar) on a Kugelrohr apparatus yielded (1*R*,2*R*,5*R*,7*R*)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene **4** (1.02 g, 70%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.93 (3H, s), 1.27 (3H, s), 1.29 (3H, s), 1.70 (1H, d, *J* 10, C9-H<sub>a</sub>), 1.74–1.87 (4H, m, C1-H, 2 × C6-H and C7-H), 1.99 (1H, dddd, *J* ~ 12, 6, 6, 2, C9-H<sub>b</sub>), 2.53 (1H, dm, C5-H), 5.80 (1H, d, *J* 3, C3-H), 6.22 (1H, dd, *J* 3, 0.9, C4-H);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 23.0, 23.9, 26.8, 28.0, 38.9, 43.8, 44.8, 46.8, 52.4, 139.9, 143.2; *m/z* (CI) 161.1332 ([M – 1]<sup>+</sup>, 63%), calc. mass for C<sub>12</sub>H<sub>17</sub>: 161.1330 (–1.1 ppm).

**Spiro[cyclobut-2-ene-1,1'-cyclohexane], 5a.** To diisopropylamine (9.8 cm<sup>3</sup>, 75 mmol), methyl-lithium [43 cm<sup>3</sup>, 60 mmol (1.4 M in diethyl ether)] was added slowly. After hydrogen evolution had ceased the lithium salt formed was dissolved in THF (5 cm<sup>3</sup>) and added dropwise to a solution of spiro[cyclobutane-1,1'-cyclohexan]-2-one toluene-*p*-sulfonylhydrazone (4.61 g, 15 mmol) in THF (40 cm<sup>3</sup>) at –78 °C. The reaction was then allowed to warm to room temperature and after 24 h the reaction mixture was added to water and extracted with pentane (100 cm<sup>3</sup>). The organic layer was washed with hydrochloric acid (1 M), saturated aqueous sodium hydrogen carbonate and dried with magnesium sulfate. The first 90 cm<sup>3</sup> of solvent was removed by distillation through a 15 cm Vigreux column. The remaining solvent (mainly THF) was subsequently removed through a 7 cm Vigreux column using reduced pressure (400 mbar). The vacuum was gradually altered to 80 mbar at which point spiro[cyclobut-2-ene-1,1'-cyclohexane] **5a** distilled (65 °C) (0.47 g, 25%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 1.2–1.6 (10H, m), 2.18 (2H, s, C4-H), 6.06 (1H, d, *J* 2, C3-H), 6.22 (1H, d, *J* 2, C2-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 24.5, 25.9, 36.3, 42.5, 49.6, 133.7, 145.4; *m/z* (CI) 123.1171 ([M + 1]<sup>+</sup>, 13%), calc. mass for C<sub>9</sub>H<sub>15</sub>: 123.1174 (+2.3 ppm).

**4'-tert-Butylspiro[cyclobut-2-ene-1,1'-cyclohexane], 5b.** The same basic procedure was employed as for spiro[adamantane-2,1'-cyclobut-2'-ene] described earlier but using: diisopropylamine (3.9 cm<sup>3</sup>, 30 mmol), methyl-lithium [17 cm<sup>3</sup>, 24 mmol (1.4 M in diethyl ether)], 4'-tert-butylspiro[cyclobutane-1,1'-cyclohexan]-2-one toluene-*p*-sulfonylhydrazone (1.98 g, 5.5 mmol) and THF (total 40 cm<sup>3</sup>). Purification was effected using dry-flash column chromatography using alumina (Brockman Grade 1) with benzene–hexane (1:49) as the eluent yielding 4'-tert-butylspiro[cyclobut-2-ene-1,1'-cyclohexane] **5b** (0.29 g, 30%);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 0.84 (9H, s, Me), 0.85–1.05 (3H, m), 1.35–1.5 (2H, m), 1.55–1.75 (4H, m), 2.16 (2H, s, C4-H), 6.06 (1H, d, *J* 3, C3-H), 6.08 (1H, d, *J* 3, C2-H);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 25.3, 27.6, 32.4, 36.5, 41.7, 47.5, 49.4, 133.5, 146.1; *m/z* (CI) 177.1645 ([M – 1]<sup>+</sup>, 28%), calc. mass for C<sub>13</sub>H<sub>21</sub>: 177.1643 (–1.1 ppm).

**Spiro[cyclobut-2-ene-1,9'-9*H*-thioxanthene], 2a.** The same basic procedure was employed as for spiro[adamantane-2,1'-cyclobut-2'-ene] described earlier but using: diisopropylamine (1.4 cm<sup>3</sup>, 8.4 mmol), methyl-lithium [5.8 cm<sup>3</sup>, 8.1 mmol (1.4 M in diethyl ether)] and spiro[cyclobutane-1,9'-9*H*-thioxanthene]-2-one toluene-*p*-sulfonylhydrazone (0.84 g, 2 mmol) in THF (85 cm<sup>3</sup>). Purification was effected using dry-flash column chromatography using alumina (Brockman Grade 1) with benzene–hexane (1:49) as the eluent yielding spiro[cyclobut-2-ene-1,9'-9*H*-thioxanthene] **2a** (0.31 g, 65%). An analytically pure sample was prepared by recrystallisation from ethanol, mp 81–82 °C (Found: C, 81.5; H, 5.3. C<sub>16</sub>H<sub>12</sub>S requires C, 81.3; H, 5.1%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 2.61 (2H, s, C4-H), 6.46 (1H, d, *J* 3, C3-H), 6.85 (1H, d, *J* 3, C2-H), 7.1–7.25 (4H, m, Ar-H), 7.43 (4H, m, Ar-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 48.9, 56.5, 125.8, 127.4, 127.4, 127.8, 134.2, 137.4, 138.4, 142.2.

#### Ring opening metathesis polymerisations

**Poly[1,1-diethylbut-2-ene-1,4-diyl].** In a glove box under

nitrogen, half of a solution of (2,6-diisopropylphenylimido)-(neophylidene)bis(*tert*-butoxide)molybdenum (24.3 mg, 0.05 mmol) in dry, deoxygenated dichloromethane (8 cm<sup>3</sup>) was added to a stirred solution of 3,3-diethylcyclobutene **1a** (0.62 g, 5.63 mmol) in dry, deoxygenated dichloromethane (20 cm<sup>3</sup>). The reaction mixture was stirred for 5 min before the rest of the initiator solution was added, then stirring was continued for a further 19 h. The reaction was terminated by the addition of a 10-fold excess of dry, distilled benzaldehyde. Removal of the solvent under reduced pressure yielded a green polymeric material which was washed with methanol, then dissolved in *n*-hexane (20 cm<sup>3</sup>) and added dropwise to vigorously stirred methanol (100 cm<sup>3</sup>). Poly[1,1-diethylbut-2-ene-1,4-diyl] precipitated out as a white solid which was subsequently dried under vacuum at 50 °C overnight;  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 5.19 (br s), 2.01 (br s), 1.28 (br q), 0.73 (br t);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 140.05, 124.44, 41.91, 39.45, 29.18, 7.93.

**trans-Poly[1,1-dipropylbut-2-ene-1,4-diyl].** The same basic procedure was employed as for poly[1,1-diethylbut-2-ene-1,4-diyl] above, but using: (2,6-diisopropylphenylimido)(neophylidene)bis(*tert*-butoxide)molybdenum (48.5 mg, 0.1 mmol) and 3,3-dipropylcyclobutene **1b** (1.32 g, 9.55 mmol) to give poly[1,1-dipropylbut-2-ene-1,4-diyl] (1.29 g, 93%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 5.21 (br s), 2.02 (br s), 1.20 (br s), 0.85 (br s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 140.93, 123.73, 41.82, 40.25, 40.02, 16.77, 14.88.

**cis-Poly[1,1-dipropylbut-2-ene-1,4-diyl].** In a glove box, under nitrogen, 3,3-di-*n*-propylcyclobutene **1b** (0.063 g, 0.456 mmol) in dry, deoxygenated CDCl<sub>3</sub> (0.45 cm<sup>3</sup>) was added to a solution of (2,6-diisopropylphenylimido)(neophylidene)bis(hexafluoro-*tert*-butoxide)molybdenum<sup>46</sup> (9.9 mg, 0.013 mmol) in 0.45 dry, deoxygenated CDCl<sub>3</sub>. The reaction mixture was allowed to stir for 10 min, then transferred to an NMR tube which was subsequently sealed under vacuum at liquid nitrogen temperatures, allowed to warm to room temperature, then, after 2.5 h, analysed by NMR spectroscopy;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 5.35 (s), 5.21 (br s), 5.08 (s), 2.01 (br s), 1.20 (br m), 0.86 (br m);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 135.62, 127.17, 41.56, 39.66, 35.00, 16.87, 14.99.

**Poly[1,1-dibutylbut-2-ene-1,4-diyl].** In a glove box, under nitrogen, 3,3-di-*n*-butylcyclobutene **1c** (0.805 g, 4.84 mmol) in dry, deoxygenated dichloromethane (2 cm<sup>3</sup>) was added to a solution of the (2,6-diisopropylphenylimido)(neophylidene)-bis(*tert*-butoxide)molybdenum (17 mg, 0.031 mmol) in 2 cm<sup>3</sup> dry, deoxygenated dichloromethane over a period of 20 min. The reaction mixture was then allowed to stir for 10 h. The reaction was terminated by the addition of a 10-fold excess of benzaldehyde (dry, distilled). The polymer produced was precipitated by the addition of the reaction mixture to a large amount of methanol, then filtered and dried in a vacuum oven at 40 °C for 10 h to give poly[1,1-dibutylbut-2-ene-1,4-diyl] (4.4 g).  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 5.22 (br s), 2.01 (br s), 1.21 (br m), 0.88 (br t);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 140.83, 123.75, 41.55, 39.84, 37.67, 25.87, 23.59, 14.20.

**Poly[1,1-di(2-phenylethyl)but-2-ene-1,4-diyl].** The same basic procedure was employed as for poly[1,1-diethylbut-2-ene-1,4-diyl] described earlier, but using (2,6-diisopropylphenylimido)-(neophylidene)bis(*tert*-butoxide)molybdenum (32.4 mg, 0.066 mmol) and 3,3-di(2-phenylethyl)cyclobutene **1d** (0.80 g, 3.05 mmol) to give poly[1,1-di(2-phenylethyl)but-2-ene-1,4-diyl];  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.12–7.00 (br m), 5.45 (br m), 2.51 (br m), 2.24 (br m), 1.66 (br m);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 142.71, 140.36, 128.34, 128.23 (double intensity), 125.61, 124.61, 42.15, 39.64 (double intensity), 30.334.

**Polymerisation of spiro[cyclobut-2-ene-1,1'-cyclohexane].** In three portions over 20 min a solution of spiro[cyclobut-2-ene-1,1'-cyclohexane] **5a** (450 mg, 3.7 mmol) in dichloromethane (5 cm<sup>3</sup>) was added to a solution of (2,6-diisopropylphenylimido)-(neophylidene)bis(*tert*-butoxide)molybdenum (40 mg, 0.074 mmol) in dichloromethane (4 cm<sup>3</sup>). After 24 h a 10-fold excess of benzaldehyde was added and the polymer precipitated from

methanol (100 cm<sup>3</sup>). The polymer was redissolved in chloroform (15 cm<sup>3</sup>) and reprecipitated from methanol (100 cm<sup>3</sup>). Residual methanol was removed by heating under reduced pressure (45 °C, 0.5 mbar) for 8 h yielding unsaturated polymer (416 mg);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 1.1–1.6 (10H, br m), 1.98 (2H, d, *J* 5, C3'-H), 5.18 (1H, d, *J* 13, C1'-H), 5.25 (1H, dt, *J* 13, 5, C2'-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 22.2, 26.6, 36.1, 39.4, 46.1, 124.5, 140.3.

**Polymerisation of 4'-tert-butylspiro[cyclobut-2-ene-1,1'-cyclohexane].** The same basic procedure was employed as for polymerising **5a** described earlier but using: (2,6-diisopropylphenylimido)(neophylidene)bis(*tert*-butoxide)molybdenum (16 mg, 0.030 mmol) and 4'-*tert*-butylspiro[cyclobut-2-ene-1,1'-cyclohexane] **5b** (270 mg, 1.5 mmol) to give unsaturated polymer (228 mg);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 0.92 (9H, s, Me), 0.96 (1H, br s, C4-H), 1.18 (4H, br s), 1.45–1.65 (4H, br m), 2.05 (2H, d, *J* 7, C3'-H), 5.20 (1H, dt, *J* 16, 7, C2'-H), 5.36 (1H, d, *J* 16, C1'-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 22.3, 27.6, 32.4, 35.6, 37.9, 38.3, 48.0, 122.1, 142.9.

**Polymerisation of (1R,2R,5R,7R)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene.** The same basic procedure was employed as for polymerising **5a** described earlier but using: (2,6-diisopropylphenylimido)(neophylidene)bis(*tert*-butoxide)molybdenum (28.4 mg, 0.058 mmol) and (1R,2R,5R,7R)-2,8,8-trimethyltricyclo[5.1.1.0<sup>2,5</sup>]non-3-ene **4** (471 mg, 2.9 mmol) to give unsaturated polymer (429 mg),  $\nu_{\text{max}}$ (nujol mull)/cm<sup>-1</sup> 1644w, 981;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 1.06 (3H, s, Me), 1.14 (3H, s, Me), ~1.20 (1H, d, *J* ~11, C7-H<sub>a</sub>), 1.23 (3H, s, Me), 1.49 (1H, q, C4-H<sub>c</sub> or C4-H<sub>d</sub>), 1.83 (2H, br d, C1-H, C5-H), 2.03 (1H, br t, C4-H<sub>c</sub> or C4-H<sub>d</sub>), 2.20 (1H, br m, C7-H<sub>b</sub>), 2.46 (1H, q, C3-H), 4.89 (1H, dd, *J* 9, 15, C2'-H), 5.39 (1H, d, *J* 15, C1'-H);  $\delta_{\text{C}}$ (100 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 24.2, 28.5, 28.9, 32.1, 36.2, 39.6, 40.8, 44.7, 45.1, 53.2, 131.2, 137.7.

#### Hydrogenation of polymers

**Poly[1,1-diethylbutane-1,4-diyl].** Toluene-*p*-sulfonohydrazide (2 g, 10.76 mmol) was added to a solution of poly[1,1-diethylbut-2-ene-1,4-diyl] (0.30 g) in xylene (20 cm<sup>3</sup>) and the mixture was heated at 110 °C for 5 days during which time a further 14 g (75 mmol) of the hydrazide was added in 2 g portions at regularly spaced intervals. The reaction mixture was allowed to cool, filtered and the solvent removed under reduced pressure. The residue was redissolved in dichloromethane (10 cm<sup>3</sup>) and added dropwise to a large amount of vigorously stirred methanol to precipitate the polymer which was then dried under vacuum at 50 °C overnight to give poly[1,1-diethylbutane-1,4-diyl] (0.122 g, 41%);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.1–1.3 (4H, br m), 0.8–1.2 (6H, br m), 0.5–0.8 (6H, br m). Satisfactory <sup>13</sup>C NMR data could not be obtained for this polymer due to insolubility.

**Poly[1,1-dipropylbutane-1,4-diyl].** The same basic procedure was employed as for poly[1,1-diethylbutane-1,4-diyl] described earlier but using poly[1,1-dipropylbut-2-ene-1,4-diyl] (0.50 g) to give poly[1,1-dipropylbutane-1,4-diyl] (0.20 g, 40%);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 1.11 (br s), 1.04 (br s), 0.85 (br s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 39.42, 37.88, 37.51, 16.37 (double intensity), 15.14.

**Poly[1,1-dibutylbutane-1,4-diyl].** The same basic procedure was employed as for poly[1,1-diethylbutane-1,4-diyl] described earlier but using poly[1,1-dibutylbut-2-ene-1,4-diyl] (0.2 g) to give poly[1,1-dibutylbutane-1,4-diyl] (0.08 g, 40%);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.17 (br m), 1.05 (br s), 0.97 (br s), 0.82 (br t);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 37.81, 37.25, 36.47, 25.41, 23.68, 16.41, 14.19.

**Poly[1,1-di(2-phenylethyl)butane-1,4-diyl].** The same basic procedure was employed as for poly[1,1-diethylbutane-1,4-diyl] described earlier but using poly[1,1-di(2-phenylethyl)but-2-ene-1,4-diyl] (0.3 g) to give poly[1,1-di(2-phenylethyl)butane-1,4-diyl] (0.1 g, 33%);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 7.13 (br m), 2.50 (br m), 1.56 (br m), 1.34 (br m);  $\delta_{\text{C}}$ (68 MHz; CDCl<sub>3</sub>) 142.95, 128.39, 128.24 (double intensity), 125.66, 39.15, 37.96, 37.64, 30.09, 16.66.

**Diimide reduction of the unsaturated polymer with cyclohexyl side chains.** The unsaturated polymer with cyclohexyl side chains (300 mg) was dissolved in xylene (40 cm<sup>3</sup>). Over 4 days 10 portions of toluene-*p*-sulfonohydrazide (9 g in total) were added to the stirred solution which was heated at 110 °C throughout. After this time the xylene was evaporated and the mixture partially redissolved in chloroform (40 cm<sup>3</sup>) prior to addition to methanol (200 cm<sup>3</sup>). Subsequent filtration yielded crude polymer. The crude material was added to methanol (30 cm<sup>3</sup>) and the suspension heated to reflux for 1 h. On cooling the solution was filtered and the polymer dried by heating under reduced pressure (50 °C, 0.5 mbar) for 8 h. This yielded fully saturated polymer (243 mg);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>, 52 °C) 1.0–1.5 (14H, br m), 1.55 (2H, br s);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>, 52 °C) 16.2, 21.9, 26.8, 35.2, 36.1, 38.7.

**Diimide reduction of the unsaturated polymer with 4'-tert-butylcyclohexyl side chains.** The same basic procedure was employed but using: polymer with 4'-*tert*-butylcyclohexyl side chains (170 mg), xylene (25 cm<sup>3</sup>) and toluene-*p*-sulfonohydrazide (5 g in total) to give fully saturated polymer (138 mg),  $\delta_{\text{H}}$ (270 MHz; C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 130 °C) 0.90 (9H, s, Me), 0.95–1.40 (11H, br m), 1.50–1.70 (4H, m).

**Diimide reduction of the unsaturated polymer with pinene side chains.** The same basic procedure was employed but using: unsaturated polymer with pinene side chains (150 mg), xylene (30 cm<sup>3</sup>) and toluene-*p*-sulfonohydrazide (6 g in total) to give fully saturated polymer (104 mg);  $\delta_{\text{H}}$ (400 MHz; C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 120 °C) 3 singlets (1.28, 1.34, 1.43) visible above broad peak (1.2–1.8). Also broad peaks at 2.15, 2.32.

#### Syntheses of precursors to ketal polymers

**9H-Fluorene-9,9-diethanol, 8.** In a two-necked flask fitted with a dry ice–acetone filled condenser, *n*-butyllithium [64 cm<sup>3</sup>, 0.16 mol (2.5 M in hexane)] was added to a stirred solution of fluorene (26.5 g 0.16 mol) in THF (300 cm<sup>3</sup>) at –28 °C. After 10 min ethylene oxide (8 cm<sup>3</sup>, 0.16 mol) was added. After a further hour a second portion of *n*-butyllithium was added resulting in a bright red sticky sludge precipitating. After 10 min the reaction flask was transferred to a sonicator bath where the water temperature was maintained below 5 °C. A second portion of ethylene oxide was added and the mixture was sonicated for 1 h. Water was cautiously added to the reaction mixture which was then extracted with dichloromethane. Evaporation of the solvent followed by two recrystallisations from toluene yielded 9H-fluorene-9,9-diethanol **8** (29 g, 72%), mp 133–134 °C (Found: C, 80.7; H, 7.1. C<sub>17</sub>H<sub>18</sub>O<sub>2</sub> requires C, 80.3; H, 7.1%);  $\nu_{\text{max}}$ (nujol mull)/cm<sup>-1</sup> 3328s (OH), 1030s;  $\delta_{\text{H}}$ (400 MHz; (CD<sub>3</sub>)<sub>2</sub>SO) 2.32 (4H, t, *J* 8, CH<sub>2</sub>CH<sub>2</sub>OH), 2.85 (4H, dt, *J* 5, 8, CH<sub>2</sub>OH), 4.11 (2H, t, *J* 5, OH), 7.46 (4H, m, Ar-H), 7.64 (2H, m, Ar-H), 7.89 (2H, m, Ar-H);  $\delta_{\text{C}}$ (100 MHz; (CD<sub>3</sub>)<sub>2</sub>SO) 44.0, 53.0, 58.6, 121.6, 124.8, 128.8, 128.9, 141.6, 151.3.

**Dispiro[1,3-dioxacyclooctane-2,2'-adamantane-6,9'-9H-fluorene], 19.** 9H-Fluorene-9,9-diethanol **8** (1 g, 3.9 mmol) and adamantanone (0.59 g, 3.9 mmol) were suspended in benzene (50 cm<sup>3</sup>) and toluene-*p*-sulfonic acid was monohydrate (0.007 g, 0.03 mmol) added. The suspension was refluxed on a Dean-Stark apparatus for 24 h. Triethylamine (10 cm<sup>3</sup>) was added and the solvent evaporated. Recrystallisation from toluene yielded dispiro[1,3-dioxacyclooctane-2,2'-adamantane-6,9'-9H-fluorene] **19** (0.97 g, 64%), decomp. >180 °C;  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 1.65–1.75 (6H, m), 1.84 (2H, br s), 1.95–2.14 (8H, m), 2.28 (2H, br s), 3.91 (4H, br s, -CH<sub>2</sub>O-), 7.34 (4H, m, Ar-H), 7.72 (2H, m, Ar-H), 7.80 (2H, m, Ar-H);  $\delta_{\text{C}}$ (100 MHz; CDCl<sub>3</sub>) 27.2, 30.9, 34.1, 37.5, 38.8, 52.7, 59.2, 103.2, 119.8, 125.1, 126.8, 127.2, 139.2, 152.5; molecular weight as determined by vapour pressure osmometry 391 (+1.3%). Crystals suitable for X-ray analysis were prepared by slow diffusion of methanol into a toluene solution.

**Dispiro[1,3-dioxacyclooctane-2,1'-cyclohexane-6,9'-9H-fluorene].** 9H-Fluorene-9,9-diethanol **8** (3 g, 11.8 mmol) was

suspended in benzene (150 cm<sup>3</sup>) and cyclohexanone (1.16 g, 11.8 mmol) and toluene-*p*-sulfonic acid monohydrate (0.013 g, 0.07 mmol) added. The suspension was refluxed on a Dean-Stark apparatus for 24 h. Triethylamine (30 cm<sup>3</sup>) was added and the solvent was evaporated. The crude product was added to toluene (50 cm<sup>3</sup>), stirred rapidly for 10 min and then filtered to remove the remaining diol. The toluene was then evaporated and the product was recrystallised twice by adding ethanol to the toluene solution to yield dispiro[1,3-dioxacyclooctane-2,1'-cyclohexane-6,9'-9*H*-fluorene] (1.89 g, 48%), mp 126–127 °C (Found: C, 82.8; H, 7.75. C<sub>23</sub>H<sub>26</sub>O<sub>2</sub> requires C, 82.6; H, 7.8%); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 1.48 (2H, br s), 1.58 (4H, br s), 1.81 (4H, br s), 1.92–2.11 (4H, br s, -CH<sub>2</sub>CH<sub>2</sub>O-), 3.95 (4H, br s, -CH<sub>2</sub>O-), 7.25–7.40 (4H, m, Ar-H), 7.71 (2H, m, Ar-H), 7.81 (2H, m, Ar-H); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 23.1, 25.6, 33.8, 38.7, 52.6, 60.0, 101.2, 119.9, 124.8, 126.9, 127.2, 139.2, 152.3; molecular weight as determined by vapour pressure osmometry 322 (C<sub>23</sub>H<sub>26</sub>O<sub>2</sub> requires 334).

**Polymerisation of dispiro[1,3-dioxacyclooctane-2,1'-cyclohexane-6,9'-9*H*-fluorene].** Dispiro[1,3-dioxacyclooctane-2,1'-cyclohexane-6,9'-9*H*-fluorene] (0.4 g, 1.19 mmol) was dissolved in benzene (1 cm<sup>3</sup>) and toluene-*p*-sulfonic acid monohydrate (0.0023 g, 0.012 mmol) added. After 24 h stirring triethylamine (0.1 cm<sup>3</sup>) was added and the solvent was evaporated. The polymer was dried by heating under reduced pressure (40 °C, 0.5 mbar) for 8 h. δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 1.0–1.1 (10H, br s), 1.91 (4H, t, *J* 8.2, -CH<sub>2</sub>CH<sub>2</sub>O-), 2.52 (4H, t, *J* 8.3, -CH<sub>2</sub>O-), 7.06 (2H, m, Ar-H), 7.18 (2H, m, Ar-H), 7.29 (2H, m, Ar-H), 7.67 (2H, m, Ar-H); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 22.6, 25.4, 33.2, 39.8, 51.1, 55.2, 99.6, 119.8, 122.7, 127.2, 128.3, 140.4, 149.1; molecular weight as determined by vapour pressure osmometry 3850.

**Spiro[1,3-dioxo-6,6-dimethylcyclooctane-2,2'-adamantane].** 3,3-Dimethylpentane-1,5-diol (prepared by the method of Bloomquist *et al.*<sup>66</sup>) (1.95 g, 15 mmol) was suspended in benzene (150 cm<sup>3</sup>) and adamantanone (2.21 g, 15 mmol) and toluene-*p*-sulfonic acid monohydrate (0.014 g, 0.07 mmol) added. The suspension was refluxed on a Dean-Stark apparatus for 24 h. Triethylamine (20 cm<sup>3</sup>) was added and the solvent evaporated. Column chromatography using silica gel with toluene-petroleum spirit (bp 40–60 °C) (1:5) as the eluent yielded spiro[1,3-dioxo-6,6-dimethylcyclooctane-2,2'-adamantane] as a clear oil (2.8 g, 71%); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 1.01 (6H, s, C6-Me), 1.50–1.66 (10H, m), 1.75 (2H, br s), 1.83–1.92 (4H, m), 2.07 (2H, br s), 3.69 (4H, t, *J* 6, -CH<sub>2</sub>O-); δ<sub>H</sub>(100 MHz; CDCl<sub>3</sub>) 27.2, 29.4, 32.1, 33.6, 33.7, 34.3, 37.5, 42.4, 58.1, 102.2; molecular weight as determined by vapour pressure osmometry 250 (calculated for C<sub>17</sub>H<sub>28</sub>O<sub>2</sub> 264). A satisfactory elemental analysis could not be obtained for this compound.

**Dispiro[1,3,9,11-tetraoxa-6,6,14,14-tetramethylhexadecane-2,2',10,2'-bisadamantane].** Spiro[1,3-dioxo-6,6-dimethylcyclooctane-2,2'-adamantane] (0.5 g, 1.9 mmol) was dissolved in benzene (1 cm<sup>3</sup>) and toluene-*p*-sulfonic acid monohydrate (0.003 g, 0.02 mmol) added. After 24 h stirring triethylamine (0.1 cm<sup>3</sup>) was added and the solvent evaporated. The dimeric ketal dispiro[1,3,9,11-tetraoxa-6,6,14,14-tetramethylhexadecane-2,2',10,2'-bisadamantane] was obtained by crystallisation from ethanol (0.13 g, 26%), decomp. >110 °C (Found: C, 77.7; H, 10.9. C<sub>34</sub>H<sub>56</sub>O<sub>4</sub> requires C, 77.3; H, 10.6%); δ<sub>H</sub>(400 MHz; CDCl<sub>3</sub>) 0.94 (12H, s, C6-Me, C14-Me), 1.51–1.66 (20H, m), 1.78 (4H, m), 1.83–1.91 (8H, m), 2.02–2.15 (4H, m), 3.34 (8H, t, *J* 8, -CH<sub>2</sub>O-); δ<sub>C</sub>(100 MHz; CDCl<sub>3</sub>) 27.2, 29.8, 30.9, 33.4, 33.7, 37.4, 39.1, 55.1, 101.6; molecular weight as determined by vapour pressure osmometry 539 (C<sub>34</sub>H<sub>56</sub>O<sub>4</sub> requires 529).

**Ethyl (2-vinyltricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate.** Triethyl orthoacetate (250 cm<sup>3</sup>), propionic acid (0.3 cm<sup>3</sup>, 4.0 mmol) and 2-(tricyclo[3.3.1.1<sup>3,7</sup>]decanylidenyl)ethanol<sup>67</sup> (12.0 g, 67.3 mmol) were heated at 138 °C for 18 h. The ethanol evolved was collected by distillation during the course of the reaction. The

volatile components were removed by rotary evaporation under high vacuum, giving crude ethyl (2-vinyltricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate as a pale yellow oil (15.6 g). This material was not purified further.

**Hydroboration with borane dimethyl sulfide complex: 2,2-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate, 7.** A 500 cm<sup>3</sup> three-necked round bottom flask was fitted with a 35 cm Vigreux column, on top of which was a still head and a reflux condenser. The receiver of the still head was fitted with a 100 cm<sup>3</sup> round bottom flask and a thermometer. Of the two remaining necks one was fitted with a glass stopper and the other with a rubber septum. The flask was charged with crude ethyl (2-vinyltricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate (7.1 g, 28.6 mmol) and dry THF (17.5 cm<sup>3</sup>). Borane dimethyl sulfide complex (14.75 g, 156 mmol) was then added dropwise from a syringe, *via* the septum, to the stirred solution (**CAUTION: large exotherm!**). The Vigreux column was then lagged with aluminium foil and the mixture heated in an oil bath held at 120 °C for 22 h. After allowing to cool, water (20 cm<sup>3</sup>), 3 M aqueous sodium hydroxide (100 cm<sup>3</sup>) and 30% aqueous hydrogen peroxide (100 cm<sup>3</sup>) were added carefully in succession and the stirred mixture heated at 50 °C for 1 h. After cooling, diethyl ether (100 cm<sup>3</sup>) was added and the mixture filtered. The aqueous phase was extracted with diethyl ether (2 × 100 cm<sup>3</sup>) and the combined ethereal phase dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave a colourless oil which solidified after a prolonged time at high vacuum. Recrystallisation from toluene gave 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate as a white crystalline solid contaminated with a small amount of 2-(1-hydroxyethyl)-2-(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate (2.65 g). The mother liquors were concentrated and purified by column chromatography [silica; ethyl acetate] giving 2-(1-hydroxyethyl)-2-(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate as white crystals (576 mg) and 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate also as white crystals (736 mg). The 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate isolated by recrystallisation and chromatography was combined and recrystallised from toluene giving pure 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate 7 as white crystals [2.29 g, 33% from 2-(tricyclo[3.3.1.1<sup>3,7</sup>]decanylidenyl)ethanol] mp 129–131 °C (Found: C, 74.8; H, 10.7. C<sub>14</sub>H<sub>24</sub>O<sub>2</sub> requires C, 74.95; H, 10.8%); δ<sub>H</sub>([<sup>2</sup>H<sub>6</sub>]DMSO) 4.24 (2H, t, *J* 5.1, OH), 3.39–3.43 (4H, m, CH<sub>2</sub>OH), 1.45–2.08 (18H, m, 5 × CH<sub>2</sub>, 4 × CH, 2 × CH<sub>2</sub>CH<sub>2</sub>OH); δ<sub>C</sub>([<sup>2</sup>H<sub>6</sub>]DMSO) 56.4, 38.7, 37.8, 35.9, 33.6, 32.3, 27.4. An analytical sample of 2-(1-hydroxyethyl)-2-(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate was obtained by recrystallisation from toluene, mp 171–172 °C (Found: C, 75.2; H, 11.2. C<sub>14</sub>H<sub>24</sub>O<sub>2</sub> requires C, 74.95; H, 10.8%); δ<sub>H</sub>([<sup>2</sup>H<sub>6</sub>]DMSO) 4.65 (1H, d, *J* 5.9, CHOH), 4.58 (1H, t, *J* 5.0, CH<sub>2</sub>OH), 4.33 (1H, p, *J* 6.2, CHOH), 3.56–3.66 (1H, m, CH<sub>2</sub>OH), 3.30–3.43 (1H, m, CH<sub>2</sub>OH), 1.29–2.13 (16H, m, 5 × CH<sub>2</sub>, 4 × CH, CH<sub>2</sub>CH<sub>2</sub>OH), 1.00 (3H, d, *J* 6.4, CH<sub>3</sub>); δ<sub>C</sub>([<sup>2</sup>H<sub>6</sub>]DMSO) 66.3, 56.7, 42.5, 39.5, 33.4, 33.2, 33.0, 32.5, 32.5, 31.8, 27.3, 27.1, 24.4, 17.1.

**Catalytic hydroboration: Tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-3'-δ-valerolactone.**† Crude ethyl (2-vinyltricyclo[3.3.1.1<sup>3,7</sup>]decan-2-yl)acetate (1.24 g) and tris(triphenylphosphine)rhodium(I) chloride (231 mg, 0.25 mmol) were dissolved in dry THF (10 cm<sup>3</sup>). To this stirred solution was added a solution of catechol borane (1.21 g, 10 mmol) in dry THF (5 cm<sup>3</sup>). Stirring was continued for 3 days. A mixture of ethanol-THF 1:1 v/v (10 cm<sup>3</sup>), 2 M aqueous sodium hydroxide (10 cm<sup>3</sup>) and 30% aqueous hydrogen peroxide (10 cm<sup>3</sup>) were added carefully in succession and the mixture stirred for 4 h. Diethyl ether (40 cm<sup>3</sup>) and 3 M aqueous sodium hydroxide (25 cm<sup>3</sup>) were added and the aqueous phase extracted with diethyl ether (40 cm<sup>3</sup>). The combined organic phases were extracted with 3 M aqueous sodium hydrox-

† δ-Valerolactone is tetrahydro-2*H*-pyran-2-one.

ide ( $3 \times 25 \text{ cm}^3$ ) and water ( $2 \times 25 \text{ cm}^3$ ) and dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave crude tricyclo[3.3.1.1<sup>3,7</sup>]decane-2-spiro-3'- $\delta$ -valerolactone as a brown oil (781 mg), which was not further purified.

**2,2-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane, 7.** A solution of tricyclo[3.3.1.1<sup>3,7</sup>]decane-2-spiro-3'- $\delta$ -valerolactone (781 mg) in dry diethyl ether ( $10 \text{ cm}^3$ ) was added dropwise to a stirred suspension of lithium aluminium hydride (190 mg, 5.0 mmol) in dry diethyl ether ( $10 \text{ cm}^3$ ), at such a rate that a gentle reflux was maintained. After stirring for 1 h water ( $0.2 \text{ cm}^3$ ), 3 M aqueous sodium hydroxide ( $0.2 \text{ cm}^3$ ) and water ( $0.6 \text{ cm}^3$ ) were added carefully in succession. The mixture was filtered and the solid material washed with diethyl ether ( $15 \text{ cm}^3$ ). The combined organic phases were dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave a beige semi-solid material. Recrystallisation from toluene gave 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane as a white solid (81 mg). The inorganic solids from the reaction were stirred for 16 h in THF ( $50 \text{ cm}^3$ ). Filtration of these solids followed by solvent removal from the filtrate gave 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane as a white solid (220 mg). These two samples were combined [301 mg, 27% from 2-(tricyclo[3.3.1.1<sup>3,7</sup>]decanylidene)ethanol].

**2,2-Bis(2-trimethylsilyloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane.** 2,2-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane **7** (224 mg, 1.0 mmol) was stirred in dry dichloromethane ( $3 \text{ cm}^3$ ). Bis(trimethylsilyl)acetamide ( $1.0 \text{ cm}^3$ , 4.0 mmol) was added and stirring continued for 30 min. The solvent was removed by rotary evaporation and the volatile materials removed by Kugelrohr distillation. This left 2,2-bis(2-trimethylsilyloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decane as a clear colourless oil (357 mg, 97%).

**Ethyl [2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]acetate.** Sodium hydride, 60% dispersion in mineral oil ( $3.24 \text{ g}$ ,  $\sim 72 \text{ mmol}$ ) was washed with *n*-pentane ( $3 \times 20 \text{ cm}^3$ ). Dry diethyl ether ( $55 \text{ cm}^3$ ) was added and to this stirred suspension was added dropwise a solution of triethyl phosphonoacetate ( $16.15 \text{ g}$ ,  $72 \text{ mmol}$ ) in dry diethyl ether ( $90 \text{ cm}^3$ ). After stirring for 1 h a solution of tricyclo[3.3.1.1<sup>3,7</sup>]decane-2,6-dione monoethylene ketal<sup>55</sup> ( $12.0 \text{ g}$ ,  $57.6 \text{ mmol}$ ) in dry diethyl ether ( $90 \text{ cm}^3$ ) was added. Stirring was continued for a further 2 h. Ethanol ( $6 \text{ cm}^3$ ) was added followed by the careful addition of water ( $175 \text{ cm}^3$ ). The organic phase was washed with water ( $115 \text{ cm}^3$ ) and dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave ethyl [2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]acetate as a white solid ( $15.7 \text{ g}$ , 98%). An analytical sample was obtained by recrystallisation from *n*-pentane at  $-20^\circ\text{C}$ , mp  $67\text{--}69^\circ\text{C}$  (Found: C, 69.0; H, 8.0.  $\text{C}_{16}\text{H}_{22}\text{O}_4$  requires C, 69.0; H, 8.0%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.57 (1H, s, =CH), 4.14 (2H, q,  $J$  7.2,  $\text{OCH}_2\text{CH}_3$ ), 3.96 (4H, s,  $\text{OCH}_2\text{CH}_2$ ), 2.35 (1H, s,  $\text{CHC}=\text{CHC}=\text{O}$ ), 1.62–2.20 (11H, m,  $4 \times \text{CH}_2$  and  $3 \times \text{CH}$ ), 1.28 (3H, t,  $J$  7.2,  $\text{OCH}_2\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  170.4, 166.9, 110.3, 108.9, 64.4, 64.4 (one coincident pair of lines), 59.5, 39.7, 36.8, 36.3, 36.0, 31.2, 14.3.

**2-[2,2-(Ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]ethanol.** A solution of ethyl [2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]acetate ( $15.3 \text{ g}$ , 55 mmol) in dry diethyl ether ( $85 \text{ cm}^3$ ) was added dropwise to a stirred suspension of lithium aluminium hydride ( $2.09 \text{ g}$ , 55 mmol) in dry diethyl ether ( $75 \text{ cm}^3$ ), at such a rate that a gentle reflux was maintained. After stirring for 1 h the mixture was cooled with a water bath and water ( $2.1 \text{ cm}^3$ ), 15% w/v aqueous sodium hydroxide ( $2.1 \text{ cm}^3$ ) and water ( $6.3 \text{ cm}^3$ ) were added carefully in succession. The mixture was then filtered and the solid material washed with diethyl ether ( $4 \times 30 \text{ cm}^3$ ). The organic phases were combined and dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave 2-[2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]ethanol as a white solid ( $12.8 \text{ g}$ , 99%). An analytical sample was obtained by recrystallisation from *n*-pentane at  $-20^\circ\text{C}$ , mp  $91\text{--}93^\circ\text{C}$  (Found: C, 70.8; H, 8.8.  $\text{C}_{14}\text{H}_{20}\text{O}_3$  requires C, 71.2; H, 8.5%);  $\delta_{\text{H}}(\text{CDCl}_3)$  5.33 (1H,

t,  $J$  7.1, =CH), 4.14 (2H, d,  $J$  7.1, =CHCH<sub>2</sub>O), 3.97 (4H, s,  $\text{OCH}_2\text{CH}_2$ ), 2.79 (1H, s,  $\text{CHC}=\text{CHCH}_2\text{O}$ ), 2.30 (1H, s,  $\text{CHC}=\text{CHCH}_2\text{O}$ ), 1.56–2.17 (10H, m,  $4 \times \text{CH}_2$  and  $2 \times \text{CH}$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  151.1, 115.9, 110.6, 64.2, 58.0, 38.7, 36.7, 36.6, 36.1, 36.1 (one coincident pair of lines), 30.8.

**Ethyl [6-vinyl-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-yl]acetate.** Triethyl orthoacetate ( $180 \text{ cm}^3$ ), propionic acid ( $0.2 \text{ cm}^3$ , 2.7 mmol) and 2-[2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]ethanol ( $11.5 \text{ g}$ , 48.7 mmol) were heated at  $138^\circ\text{C}$  for 18 h. The ethanol evolved was collected by distillation during the course of the reaction. The volatile components were removed by rotary evaporation under high vacuum, giving crude ethyl [6-vinyl-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-yl]acetate as a pale yellow oil ( $14.2 \text{ g}$ ), which was not further purified.

**2,2-(Ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-spiro-3'- $\delta$ -valerolactone.** Crude ethyl [6-vinyl-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-yl]acetate ( $5.9 \text{ g}$ ) and tris(triphenylphosphine)rhodium(i) chloride ( $890 \text{ mg}$ , 0.96 mmol) were dissolved in dry THF ( $40 \text{ cm}^3$ ). To this stirred solution was added a solution of catecholborane ( $4.62 \text{ g}$ , 38.5 mmol) in dry THF ( $20 \text{ cm}^3$ ). Stirring was continued for 4 days. A mixture of ethanol-THF 1:1 v/v ( $38 \text{ cm}^3$ ), 2 M aqueous sodium hydroxide ( $38 \text{ cm}^3$ ) and 30% aqueous hydrogen peroxide ( $38 \text{ cm}^3$ ) were added carefully in succession and the mixture stirred for 4 h. Diethyl ether ( $150 \text{ cm}^3$ ) and 3 M aqueous sodium hydroxide ( $100 \text{ cm}^3$ ) were added and the aqueous phase extracted with diethyl ether ( $150 \text{ cm}^3$ ). The combined organic phases were extracted with 3 M aqueous sodium hydroxide ( $3 \times 100 \text{ cm}^3$ ) and water ( $2 \times 100 \text{ cm}^3$ ) and dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave 2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-spiro-3'- $\delta$ -valerolactone as a brown oil ( $4.3 \text{ g}$ ), which was not further purified.

**6,6-Bis(2-hydroxyethyl)-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decane.** A solution of crude 2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-spiro-3'- $\delta$ -valerolactone ( $4.3 \text{ g}$ ) in dry diethyl ether ( $35 \text{ cm}^3$ ) was added dropwise to a stirred suspension of lithium aluminium hydride ( $732 \text{ mg}$ , 19.3 mmol) in dry diethyl ether ( $35 \text{ cm}^3$ ), at such a rate that a gentle reflux was maintained. After stirring for 1 h water ( $0.75 \text{ cm}^3$ ), 3 M aqueous sodium hydroxide ( $0.75 \text{ cm}^3$ ) and water ( $2.25 \text{ cm}^3$ ) were added carefully in succession. The mixture was filtered and the solid material washed with diethyl ether. The combined organic phases were dried over magnesium sulfate. Removal of the solvent by rotary evaporation gave a beige semi-solid material. Recrystallisation from toluene gave 6,6-bis(2-hydroxyethyl)-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decane as a white solid ( $178 \text{ mg}$ ). The inorganic solids from the reaction were stirred for 16 h in THF ( $200 \text{ cm}^3$ ). Filtration of these solids followed by solvent removal from the filtrate gave 6,6-bis(2-hydroxyethyl)-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decane as a white solid ( $910 \text{ mg}$ ). These two samples were combined ( $1.09 \text{ g}$ , 14% from 2-[2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6-ylidene]ethanol). An analytical sample was obtained by recrystallisation from toluene, mp  $197\text{--}198^\circ\text{C}$  (Found: C, 68.2; H, 9.2.  $\text{C}_{16}\text{H}_{26}\text{O}_4$  requires C, 68.1; H, 9.3%);  $\delta_{\text{H}}([\text{H}_6]\text{DMSO})$  4.32 (2H, t,  $J$  5.2, OH), 3.90 (4H, s,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.42–3.49 (4H, m,  $\text{CH}_2\text{OH}$ ), 2.00–2.04 (4H, m), 1.69–1.74 (10H, m), 1.41 (2H, s);  $\delta_{\text{C}}([\text{H}_6]\text{DMSO})$  109.8, 63.6, 56.5, 36.8, 35.5, 35.3, 32.5, 28.9.

**6,6-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one, 6.** 6,6-Bis(2-hydroxyethyl)-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decane ( $282 \text{ mg}$ , 1.0 mmol) was dissolved in a mixture of 25% v/v aqueous hydrochloric acid ( $5 \text{ cm}^3$ ) and acetone ( $5 \text{ cm}^3$ ) and the solution stirred for 2 h. The aqueous phase was extracted with dichloromethane ( $8 \times 20 \text{ cm}^3$ ) and the combined organic phase dried over magnesium sulfate. Solvent removed by rotary evaporation gave 6,6-bis(2-hydroxyethyl)-2,2-(ethylenedioxy)tricyclo[3.3.1.1<sup>3,7</sup>]decane **6** as a slightly off-white solid which was washed with toluene and dried under reduced pressure ( $200 \text{ mg}$ , 84%). A crystal suitable for X-ray diffraction studies was

obtained by the slow evaporation of a THF solution, mp 163–164 °C;  $\delta_{\text{H}}$  ( $^2\text{H}_6$ ) DMSO) 4.41 (2H, t,  $J$  5.1, OH), 3.50–3.57 (4H, m,  $\text{CH}_2\text{OH}$ ), 2.43 (4H, d,  $J$  12.3,  $\text{CH}_2$ ), 2.41 (2H, s,  $\text{CHC}=\text{O}$ ), 1.86 (4H, t,  $J$  7.7,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 1.68 (4H, d,  $J$  12.9,  $\text{CH}_2$ ), 1.66 (2H, s, CH);  $\delta_{\text{C}}$  ( $^2\text{H}_6$ ) DMSO) 215.6, 56.4, 45.6, 37.0, 35.4, 33.0, 33.0 (one coincident pair of lines).

**6,6-Bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one.**

6,6-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one **6** (95 mg, 0.4 mmol) was added to dry dichloromethane (1.2 cm<sup>3</sup>) followed by bis(trimethylsilyl)acetamide (0.4 cm<sup>3</sup>, 1.6 mmol). The solid material dissolved and the mixture was stirred for 30 min. The solvent was removed by rotary evaporation and the various acetamide derivatives were removed by Kugelrohr distillation. 6,6-Bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one was left as a clear colourless oil (142 mg, 93%);  $\delta_{\text{H}}$  ( $\text{C}_6\text{D}_6$ ) 3.77 (4H, t,  $J$  7.5,  $\text{CH}_2\text{OTMS}$ ), 2.62 (2H, s,  $\text{CHC}=\text{O}$ ), 2.23 (4H, d,  $J$  12.1,  $\text{CH}_2$ ), 2.00 (4H, t,  $J$  7.5,  $\text{CH}_2\text{CH}_2\text{OTMS}$ ), 1.61 (4H, d,  $J$  13.0,  $\text{CH}_2$ ), 1.43 (2H, s, CH), 0.36 [18H, s, Si( $\text{CH}_3$ )<sub>3</sub>];  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ ) 214.3, 58.75, 46.7, 38.1, 36.2, 34.1, 33.9, 0.0.

**Reaction of 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 with adamantanone**

2,2-Bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 (112 mg, 0.5 mmol), tricyclo[3.3.1.1<sup>3,7</sup>]decanone (75 mg, 0.5 mmol) and a 0.025 M solution of toluene-*p*-sulfonic acid monohydrate in diethyl ether were added to benzene. The mixture was refluxed for 16 h, the water being removed by a Dean-Stark trap. After allowing to cool dry triethylamine (0.5 cm<sup>3</sup>) was added and the volatile components removed by rotary evaporation. The product was a mixture of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-4'-tetrahydropyran and tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 and were separated by column chromatography [alumina Brockman I; *n*-hexane–diethyl ether 10:1].

**Tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6.** Mp 200–201 °C (Found: C, 8.7; H, 10.5.  $\text{C}_{24}\text{H}_{36}\text{O}_2$  requires C, 80.85; H, 10.2%);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 3.75 (4H, dd,  $J$  5.7 and 5.7,  $\text{CH}_2\text{O}$ ), 1.54–2.07 (32H, m,  $10 \times \text{CH}_2$ ,  $8 \times \text{CH}$ ,  $2 \times \text{CH}_2\text{CH}_2\text{O}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 57.3, 39.8, 39.1, 37.5, 37.3, 34.1, 33.9, 33.9 (one coincident pair of lines), 33.1, 27.9, 27.2.

**Tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-4'-tetrahydropyran.** Mp 45 °C (Found: C, 81.4; H, 11.0.  $\text{C}_{14}\text{H}_{22}\text{O}$  requires C, 81.5, H, 10.75%);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 3.66 (4H, dd,  $J$  5.3 and 5.5,  $\text{CH}_2\text{O}$ ), 1.53–2.04 (18H, m,  $5 \times \text{CH}_2$ ,  $4 \times \text{CH}$ ,  $2 \times \text{CH}_2\text{CH}_2\text{O}$ );  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 63.3, 39.5, 35.4, 34.9, 34.15, 32.2, 28.2.

The results of a series of experiments with varying ratios of reactants are shown in Table 4. In general it was found that increasing the acid–diol ratio led to increasing amounts of THP derivative, while increased concentration of diol led to increased polymeric material.

**Ring opening of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 and reaction of polymeric material with trimethylsilyltrifluoromethane sulfonate**

Acetal (79 mg, 0.22 mmol) was added to dry dichloromethane (1.0 cm<sup>3</sup>). Trimethylsilyltrifluoromethane sulfonate (0.006 cm<sup>3</sup>, 33  $\mu\text{mol}$ ) was added and the mixture shaken. After 16 h triethylamine (0.2 cm<sup>3</sup>) was added and the volatile material removed. In both cases the <sup>1</sup>H NMR spectrum showed a 1:1 mixture of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-4'-tetrahydropyran and tricyclo[3.3.1.1<sup>3,7</sup>]decanone. In the case of the polymeric material this had dissolved after 1 h. With tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 a white precipitate formed immediately and this had dissolved after 1 h. Quenching the reaction of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 after 5 min showed a ratio of ~3:1 tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-4'-tetrahydropyran:

**Table 4** Product ratios from reaction of 2,2-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 with adamantane

Acid: diol ratio	[Diol]/ 10 <sup>-3</sup> M	Ratio ketal: THP derivative
1:200	33	93:7
1:100	33	64:36
1:50	33	48:52
1:25	33	10:90
1:200	16.5	95:5
1:200 <sup>a</sup>	100	80:20
1:250 <sup>a</sup>	100	98:2

<sup>a</sup> Significant amounts of a white polymeric material were also formed. It was insoluble in all common organic solvents.

tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6. When the reactions were run by adding a 0.01 M solution of trimethylsilyltrifluoromethane sulfonate in dry dichloromethane (0.111 cm<sup>3</sup>, 1  $\mu\text{mol}$ ) to the acetal mixture, again the <sup>1</sup>H NMR spectra showed a 1:1 mixture of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-4'-tetrahydropyran and tricyclo[3.3.1.1<sup>3,7</sup>]decanone in both cases. The polymeric material had dissolved after 4.5 h. In the case of tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-spiro-2'-(1,3-dioxacyclooctane)-5'-spiro-2''-tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 again a white precipitate formed immediately and had redissolved after 4.5 h.

**Polymerisation of 2,2-bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6**

2,2-Bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-6 (123 mg, 0.33 mmol) in dry dichloromethane (0.4 cm<sup>3</sup>) was cooled to –78 °C and added to trimethylsilyltrifluoromethane sulfonate (0.006 cm<sup>3</sup>, 33  $\mu\text{mol}$ ) at –78 °C. Tricyclo[3.3.1.1<sup>3,7</sup>]decanone (50 mg, 0.33 mmol) was added and the reaction vessel sealed and shaken. A white precipitate formed immediately. The mixture was maintained at –78 °C for 3 h. Dry triethylamine (0.117 cm<sup>3</sup>, 8.4 mmol) was added and the mixture allowed to warm up to room temperature. The solid was filtered off, washed with dichloromethane and dried in air giving a white powder (86 mg, 73%) which was insoluble in pyridine, toluene, ethyl acetate, THF, dichloromethane and ethanol. Infra-red spectroscopy showed no significant absorptions corresponding to siloxy, OH or C=O groups.

**Polymerisation of 6,6-bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one**

6,6-Bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one (85 mg, 222  $\mu\text{mol}$ ) was dissolved in dry dichloromethane (0.075 cm<sup>3</sup>) and cooled to –78 °C. Trimethylsilyltrifluoromethane sulfonate (0.006 cm<sup>3</sup>, 33  $\mu\text{mol}$ ) was added and the vessel sealed and shaken vigorously. After 1 h a further portion of dry dichloromethane (0.10 cm<sup>3</sup>) was added, the mixture shaken again and the vessel kept at –78 °C for 3 days. The reaction mixture had gelled after the first day. Dry triethylamine (0.2 cm<sup>3</sup>) was added and the mixture allowed to warm up to room temperature and stand for 8 h. Dry dichloromethane (0.5 cm<sup>3</sup>) was added and the mixture allowed to stand for 3 days. The pale brown, transparent solid was removed in one piece, stored in dichloromethane overnight and then transferred to a fresh portion of dichloromethane. A small sample was removed and the solvent allowed to evaporate in air. Infra-red spectroscopy showed no significant absorptions corresponding to siloxy groups, and only minor OH and C=O absorption, but X-ray diffraction suggested that the material was amorphous.

**Tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one-6-spiro-4'-tetrahydropyran**

6,6-Bis(2-trimethylsiloxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one (130 mg, 0.34 mmol) was dissolved in dry dichloromethane (0.050 cm<sup>3</sup>) and cooled to –78 °C. Trimethylsilyltrifluoromethane sulfonate (0.006 cm<sup>3</sup>, 33  $\mu\text{mol}$ ) was added and the

vessel sealed and shaken vigorously. The vessel was kept at  $-78\text{ }^{\circ}\text{C}$  for 3 h and room temperature for 3 days. Solid material was formed during the first 3 h but this had redissolved after 3 days. Dry triethylamine ( $0.2\text{ cm}^3$ ) was added and the volatile materials evaporated, leaving tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one-6-spiro-4'-tetrahydropyran as a white solid.  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$  3.42 (4H, t,  $J$  7.5,  $\text{CH}_2\text{O}$ ), 2.27 (2H, s,  $\text{CHC}=\text{O}$ ), 1.88 (4H, d,  $J$  12.1,  $\text{CH}_2$ ), 1.64 (4H, t,  $J$  7.5,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.25 (4H, d,  $J$  13.0,  $\text{CH}_2$ ), 1.07 (2H, s,  $\text{CH}$ );  $\delta_{\text{C}}(\text{C}_6\text{D}_6)$  58.75, 46.7, 38.1, 36.2, 34.1, 33.9 (CI Found:  $M + 1$ , 221.154 16.  $\text{C}_{14}\text{H}_{20}\text{O}_2$  requires  $M + 1$ , 221.154 16).

### Molecular mechanics calculations

Molecular mechanics calculations were carried out using the MM2 force field as implemented in MacroModel V2.5.<sup>68</sup> MM3 calculations were carried out using the 1989 release.<sup>30</sup> Energy-minimisations were carried out using block-diagonal Newton–Raphson algorithm followed by full-matrix Newton–Raphson using standard default convergence factors. The starting models were built using idealised geometries of the conformers for input into the conformational searching procedure. No solvent effects or other corrections were applied. A Monte-Carlo, usage-directed search procedure was used to search conformational space, as contained within the BATCHMIN<sup>69</sup> conformational search program. Typically between 200–1000 conformations were generated by random variations of a set of key dihedral angles, each being fully minimised to a convergence factor of  $0.01\text{ kJ } \text{Å}^{-1}\text{ mol}^{-1}$ . The dihedral driving experiments were initially calculated using  $10^{\circ}$  steps, each point on the potential energy surface being fully minimised except the torsion angle being driven. This was constrained using the standard forcing potential and a force constant of  $200\text{ kJ mol}^{-1}$ . The stationary point on the surface were more accurately located by further calculations with steps of  $2^{\circ}$  being taken.

### Databases studies

Crystal structures containing the cations  $\text{R}_4\text{N}^+$  ( $\text{R} = \text{Et, Pr, Bu}^n$ ) were located from the Cambridge Structural Database (CSD) using the QUEST program.<sup>27</sup> Data for these crystal structures were retrieved from the January 1990 version of the CSD in which the master data file contained 78 641 entries. The data files retrieved were screened manually and automatically and only structures which fulfilled all of the following criteria were retained for further analysis: (i) atomic coordinates included in the CSD, (ii) no disorder within the fragment, (iii) the  $R$ -factor had been reported. Further tests were then applied to ensure that only high quality structures were used. Structures used either had  $R$ -factor  $\leq 0.05$  or (b)  $R$ -factor  $\leq 0.07$  and mean e.s.d. of C–C bond lengths  $< 0.030\text{ Å}$ . The final data files contained 208 ions from 361 structures for  $\text{Et}_4\text{N}^+$ , 35 ions from 41 structures for  $\text{Pr}_4\text{N}^+$ , and 176 ions from 184 structures for  $\text{Bu}_4\text{N}^+$ . The program GEOSTAT<sup>70</sup> was subsequently used to calculate the internal coordinates and the values of the torsion angles ( $\omega_i$ ,  $i = 1-4$ ;  $\omega_{\text{ai}}$ ,  $i = 1-4$ ;  $\omega_{\text{bi}}$ ,  $i = 1-4$ ; see Fig. 17) and the improper torsion angles [ $\tau(6-7-8-9)$ ;  $\varphi(2-3-4-5)$ ; see Fig. 17] for each fragment. The fragments were all referred to a common handedness at the  $\text{N}^+$  centre so that the improper torsion angle  $\tau$  is negative. The conformation of the fragments can be described by the sets of torsion angles  $\omega_i$ ;  $\omega_i$  and  $\omega_{\text{ai}}$ ;  $\omega_i$ ,  $\omega_{\text{ai}}$  and  $\omega_{\text{bi}}$  for  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$  and  $\text{Bu}_4\text{N}^+$  respectively [the conformation about the quaternary centre itself are determined by the C–N<sup>+</sup>–C–C torsion angles ( $\omega_i$ )].

The local  $T_d$  frame symmetry of the  $\text{C}_4\text{N}^+$  unit results in 24 symmetry equivalent isometric conformations<sup>71</sup> that can be generated from each individual fragment with permuted  $\omega_i$  values (see Table 5). This implies three equivalent  $D_{2d}$  symmetry conformers and six  $S_4$  conformers (Table 6).

It was found that the fragments could be conveniently sorted into the various conformational groups by considering  $\tau$ . Fragments with the conformation about the quaternary centre

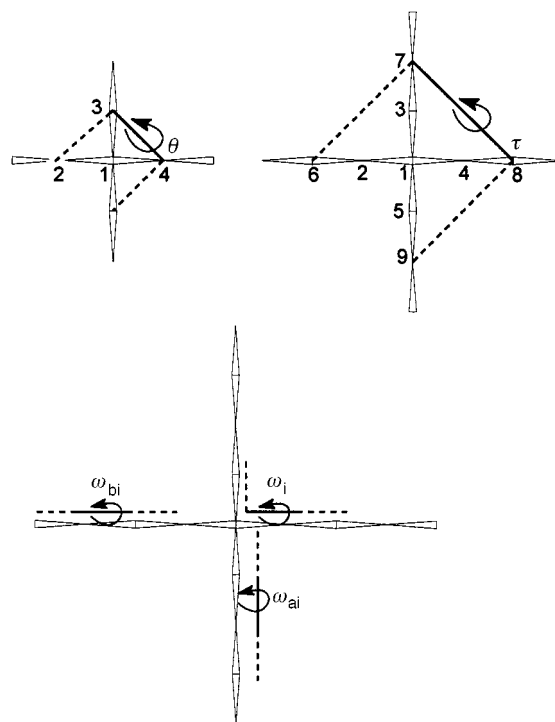


Fig. 17 Definition of torsion angles  $\theta$ ,  $\tau$ , and  $\omega_i$ ,  $\omega_{\text{ai}}$  and  $\omega_{\text{bi}}$  for database studies on  $\text{R}_4\text{N}^+$  ions

being similar to the idealised  $D_{2d}$  conformation have  $\tau \approx 0^{\circ}$  or  $-180^{\circ}$ , for the  $S_4$  conformation  $\tau \approx -80^{\circ}$  and for the higher energy conformers (c) and (d),  $\tau \approx -30^{\circ}$ . Hence the conformers were divided into three groups (a)–(c) (see below) corresponding to  $S_4$ ,  $D_{2d}$  and other conformers respectively.

- (a)  $-90 \leq \tau \leq -48$
- (b)  $-25 \leq \tau \leq 0$  or  $-180 \leq \tau \leq -144$
- (c)  $-48 \leq \tau \leq -25$ .

### 2,2,6,6,10,10-Hexamethyl-2,6,10-triazoniaundecane iodide di(tetraphenylborate)

Crystals of this mixed salt were obtained during attempts to grow crystals of the tri(tetraphenylborate) of the trication, itself prepared by literature methods<sup>72</sup> was mounted in a thin-walled glass capillary under nitrogen.

**Crystal data.**  $\text{C}_{62}\text{H}_{76}\text{N}_3\text{B}_2\text{I}$ ,  $M$  1011.8, monoclinic,  $a$  10.670(2),  $b$  15.063(4),  $c$  34.157(7) Å,  $\beta$  98.05(2),  $V$  5436(2) Å<sup>3</sup> (by least squares refinement of 27 centred reflections),  $\lambda$  0.710 73 Å,  $T$  298 K, space group  $P2_1/n$  (No. 14),  $Z$  4,  $D_x$  1.236 g cm<sup>-3</sup>, colourless rhombic block  $0.50 \times 0.37 \times 0.37$  mm,  $\mu(\text{Mo-K}\alpha)$  0.630 mm<sup>-1</sup>.

**Data collection and processing.** Nicolet P2<sub>1</sub> diffractometer, graphite-monochromated Mo-K $\alpha$  X-radiation,  $\omega - 2\theta$  scans, 11 247 reflections measured ( $4.0 < 2\theta < 50.0^{\circ}$ , for  $2\theta > 40^{\circ}$  only reflections with count rates  $> 10\text{ s}^{-1}$  were recorded. Check reflections, remeasured every 50 ordinary data, showed a variation of  $\pm 1.5\%$  over the period of data collection), 9614 unique reflections with 4576 having  $F^2 \geq 2\sigma(F^2)$  being retained in all calculations. An absorption correction was applied on the basis of azimuthal scan data, maximum and minimum transmission coefficients being 0.93 and 0.73 respectively. Lorentz and polarisation corrections were applied.

### Structure solution and refinement

The structure was solved by heavy atom (Patterson and Fourier) methods. Full matrix least-squares refinement were performed on  $F^2$  with all non-H atoms anisotropic. Hydrogen atoms and phenyl rings in the anions were constrained to idealised geometries. The weighting scheme, calc.  $w = [\sigma_c^2(F_o) + gF_o^2]$  where  $\sigma_c^2(F_o)$  is the variance in  $F_o$  due to counting

**Table 5** Torsion-angle transformations corresponding to the twenty-four frame symmetry operations of  $R_4N^+$  where  $t = 2\pi/3$ 

Torsion-angle coordinates			
$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$
$Q_1$	$Q_2$	$Q_3$	$Q_4$
$Q_2$	$Q_1$	$Q_4$	$Q_3$
$Q_3$	$Q_4$	$Q_1$	$Q_2$
$Q_4$	$Q_3$	$Q_2$	$Q_1$
$-Q_3$	$-Q_2$	$-Q_1$	$-Q_4$
$-Q_1$	$-Q_4$	$-Q_3$	$-Q_2$
$-Q_2 + t$	$-Q_1 + t$	$-Q_3 + t$	$-Q_4 + t$
$-Q_4 - t$	$-Q_2 - t$	$-Q_3 - t$	$-Q_1 - t$
$-Q_1 - t$	$-Q_3 - t$	$-Q_2 - t$	$-Q_4 - t$
$-Q_1 + t$	$-Q_2 + t$	$-Q_4 + t$	$-Q_3 + t$
$Q_1 + t$	$Q_4 + t$	$Q_2 + t$	$Q_3 + t$
$Q_1 - t$	$Q_3 - t$	$Q_4 - t$	$Q_2 - t$
$Q_4 - t$	$Q_2 - t$	$Q_1 - t$	$Q_3 - t$
$Q_3 + t$	$Q_2 + t$	$Q_4 + t$	$Q_1 + t$
$Q_4 + t$	$Q_1 + t$	$Q_3 + t$	$Q_2 + t$
$Q_2 - t$	$Q_4 - t$	$Q_3 - t$	$Q_1 - t$
$Q_3 - t$	$Q_1 - t$	$Q_2 - t$	$Q_4 - t$
$Q_2 + t$	$Q_3 + t$	$Q_1 + t$	$Q_4 + t$
$-Q_4$	$-Q_1$	$-Q_2$	$-Q_3$
$-Q_2$	$-Q_3$	$-Q_4$	$-Q_1$
$-Q_3 - t$	$-Q_1 - t$	$-Q_4 - t$	$-Q_2 - t$
$-Q_2 - t$	$-Q_4 - t$	$-Q_1 - t$	$-Q_3 - t$
$-Q_4 + t$	$-Q_3 + t$	$-Q_1 + t$	$-Q_2 + t$
$-Q_3 + t$	$-Q_4 + t$	$-Q_2 + t$	$-Q_1 + t$

**Table 6** Symmetry related sets of torsion angles for idealised geometries of  $D_{2d}$  and  $S_4$  conformers

Conformer	Torsion angle			
	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$
$D_{2d}$	-60	60	-60	60
	180	-60	180	-60
$S_4$	60	180	60	180
	-60	-60	180	60
	180	60	-60	-60
	180	180	180	180
	60	180	60	60
	-60	60	60	180

statistics and  $g = 0.00040$ , gave satisfactory agreement analyses. Final  $R$  values [ $F^2 \geq 2\sigma(F^2)$ ]  $R_1$  0.0608,  $R'$  0.0611 (all data)  $S(F^2)$  1.58 and 517 refined parameters. Final  $\Delta F$  synthesis showed a largest difference peak of  $0.47 \text{ \AA}^{-3}$  and deepest hole of  $-0.44 \text{ e \AA}^{-3}$ . Calculations were carried out on a Nicolet structure determination system using programs of the SHELXTL PLUS package.<sup>73</sup>

#### Crystal data for dispiro[1,3-dioxacyclooctane-2,2'-adamantane-6,9'-9H-fluorene]

$C_{27}H_{30}O_2$ ,  $M$  386.51, Monoclinic,  $a$  13.633(3),  $b$  10.388(2),  $c$  15.127(4)  $\text{\AA}$ ,  $\beta$  106.95(2),  $V$  2049.1(8)  $\text{\AA}^3$  (by least squares refinement of 16 centred reflections),  $\lambda$  0.71073  $\text{\AA}$ ,  $T$  293 K, space group  $P2_1/n$  (No. 14),  $Z$  4,  $D_x$  1.253  $\text{g cm}^{-3}$ ,  $0.50 \times 0.45 \times 0.25 \text{ mm}$ ,  $\mu(\text{Mo-K}\alpha)$  0.077  $\text{mm}^{-1}$ .

**Data collection and processing.** Siemens P3m diffractometer, graphite-monochromated Mo-K $\alpha$  X-radiation,  $\omega$  Wyckoff scans, 4006 reflections measured ( $3.0 < 2\theta < 50.0$ ). Check reflections, remeasured every 150 ordinary data, showed no significant decomposition of the crystal over the period of data collection, 3612 unique reflections ( $R_{\text{int}}$  0.018) with 2520 having  $F^2 \geq 2\sigma(F^2)$  being retained in all calculations. No corrections for absorption were required. Lorentz and polarisation corrections were applied.

**Structure solution and refinement.** The structure was solved by direct and Fourier methods. Full matrix least-squares

refinement were performed on  $F^2$  with all non-H atoms anisotropic. All the hydrogen atoms were assigned isotropic displacement factors 1.2 times the  $U_{\text{iso}}$  of their attached carbon atoms. The weighting scheme, calc.  $w = [\sigma_c^2(F_o^2) + (gP)^2]^{-1}$  where  $\sigma_c^2(F_o)$  is the variance in  $F_o$  due to counting statistics and  $P = [\max(F_o^2, 0) + 2F_c^2]/3$  and  $a = 0.05$ , gave satisfactory agreement analyses. Final  $R$  values [ $F^2 \geq 2\sigma(F^2)$ ]  $R_1$  0.0456,  $wR_2$  0.1018 (all data),  $R_1$  0.0751,  $wR_2$  0.1142,  $S(F^2)$  1.190 and 263 refined parameters. Final  $\Delta F$  synthesis showed a largest difference peak of  $0.158 \text{ \AA}^{-3}$  and deepest hold of  $-0.128 \text{ e \AA}^{-3}$ . All calculations were carried out using programs of the SHELXTL package.<sup>74</sup>

#### Crystal data for 6,6-bis(2-hydroxyethyl)tricyclo[3.3.1.1<sup>3,7</sup>]decan-2-one

$C_{14}H_{22}O_2$ ,  $M$  238.32, monoclinic,  $a$  6.9967(2),  $b$  11.3050(3),  $c$  7.7197(1)  $\text{\AA}$ ,  $\beta$  92.871(1),  $V$  609.84(3)  $\text{\AA}^3$  (by least squares refinement of 125 reflections),  $\lambda$  0.71073  $\text{\AA}$ ,  $T$  173 K, space group  $P2_1$  (No. 4),  $Z$  2,  $D_x$  1.298  $\text{g cm}^{-3}$ , colourless irregular block  $0.60 \times 0.58 \times 0.26 \text{ mm}$ ,  $\mu(\text{Mo-K}\alpha)$  0.089  $\text{mm}^{-1}$ .

**Data collection and processing.** Siemens SMART diffractometer, graphite-monochromated Mo-K $\alpha$  radiation,  $\omega$  rotation with narrow frames (0.3° steps), 3763 reflections measured ( $2.64 < 2\theta < 27.50^\circ$ ), 2349 unique reflections [ $R_{\text{int}} = 0.0240$ ] giving 2307 with  $F^2 \geq 2\sigma(F^2)$  and 2349 retained in all calculations. No corrections for absorption were required.

**Structure solution and refinement.** The structure was solved by automatic direct methods (all non-H atoms). Full matrix least-squares refinement were performed on  $F^2$  with all non-H atoms anisotropic. Hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement factors 1.5 times  $U_{\text{iso}}$  of their attached atoms for hydroxy groups and 1.2 times  $U_{\text{iso}}$  for all others. The weighting scheme, calc.  $w = 1/[\sigma^2(F_o^2) + (0.0500P)^2 + 0.1136P]$  where  $P = (F_o^2 + 2F_c^2)/3$ , gave satisfactory agreement analyses. Final  $R$  values [ $F^2 \geq 2\sigma(F^2)$ ]  $R_1$  0.0317,  $wR_2$  0.0860 (all data),  $R_1$  0.0323,  $wR_2$  0.0872,  $S(F^2)$  1.063 for 156 refined parameters. Final  $\Delta F$  synthesis showed a largest difference peak of  $0.252 \text{ \AA}^{-3}$  and deepest hole of  $-0.166 \text{ e \AA}^{-3}$ . Calculations were performed and diagrams produced using the SHELX software.<sup>74</sup>

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