Ritter Reactions. Part 4.[1] Rearrangement of 3,3,7,7-Tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane and Crystal Structure of 1-Acetamido-2,2,5,6,6-pentamethyladamantane

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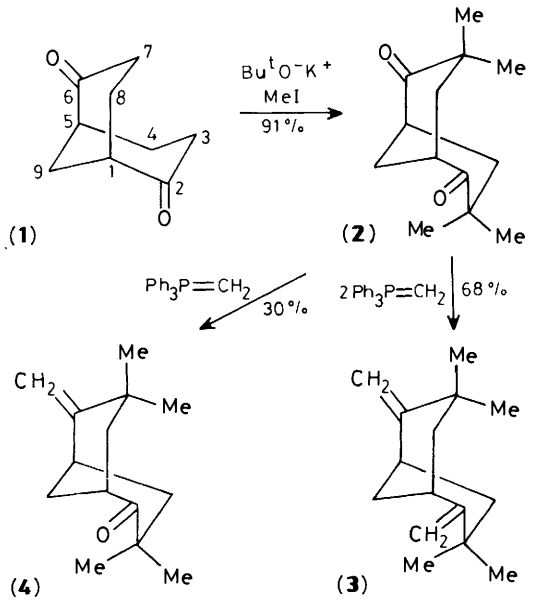
3,3,7,7-Tetramethyl-2,6-dimethylenebicyclo[3.3.1]nonane (**3**) was prepared by methylation of bicyclo[3.3.1]nonane-2,6-dione (**1**) followed by Wittig reaction. When the diene (**3**) was subjected to typical Ritter reaction conditions a 70% yield was obtained of a single compound whose structure was determined to be 1-acetamido-3,4,4,8,8-pentamethyladamantane (**5**) using *X*-ray diffraction methods. The crystal structure [$P2_1/c$, a = 7.091 (1), b = 23.398 (1), c = 9.651 (1), β = 95.79 (1), Z = 4] was shown to be disordered with a 4:1 ratio of enantiomers on the same site. Constrained refinement produced a final R = 0.054. A mechanistic pathway is proposed for this complex rearrangement involving the isolated intermediate 3,4,4,7,8,8-hexamethylbicyclo[3.3.1]nona-2,6-diene (**8**).

Simple derivatives of bicyclo[3.3.1]nonane, unsubstituted at C-3 and C-7 generally adopt the twin-chair conformation.[2] As part of an investigation into other conformations of this ring system and their potential involvement in intramolecular cyclisations we have elected to study 3,3,7,7-tetramethyl derivatives where the twin-chair is ruled out through steric crowding of the *endo*-3 and *endo*-7 methyl groups.

Marvell *et al.*[3] have shown that alkylation of bicyclo-[3.3.1]nonan-2-one using iodomethane and potassium t-butoxide affords solely the 3,3-dimethyl derivative, with no methylation taking place at the bridgehead site C-1. Using similar conditions we were able to convert bicyclo[3.3.1]nonane-2,6-dione (**1**)[4] into its 3,3,7,7-tetramethyl derivative (**2**) in 91% yield with no indication of further alkylated material being produced.



The methylated diketone (**2**) had dramatically altered properties compared to (**1**). It exhibited two carbonyl vibrations (at 1 705 and 1 690 cm^{-1}) in its i.r. spectrum (mull) and was soluble in petroleum whereas, in contrast, the starting material (**1**) is almost completely insoluble in diethyl ether. In addition the tetramethyl derivative (**2**) had a considerably shorter g.l.c. retention time than the unsubstituted compound. The tetramethyl diketone readily underwent Wittig reaction to afford the diolefin (**3**) and the corresponding keto olefin (**4**).

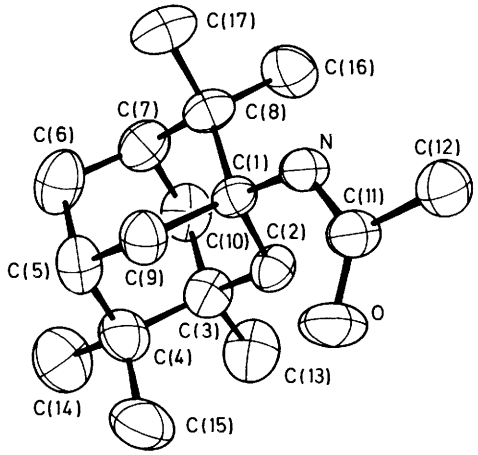
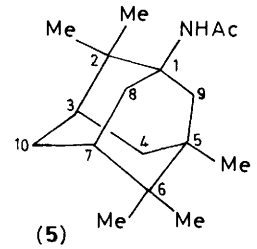


Figure. Crystallographic numbering system used for (**5**)

When a solution of the diolefin (**3**) in acetic acid and acetonitrile was treated with concentrated sulphuric acid (typical Ritter reaction conditions[5]) a single product, m.p. 181.5—182 °C, was obtained in 70% yield after work-up of the reaction.

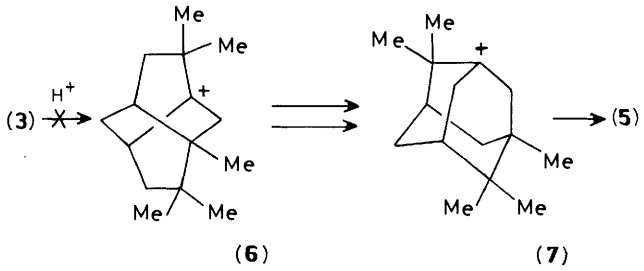
Analytical data and the absence of all olefinic signals (see Experimental section) demonstrated that this compound was the result of an intramolecular cyclisation and the formal addition of acetamide. Examination of its spectral properties showed it to be an *N*-alkylacetamide and the alkyl group to be a tricyclic structure linked to the nitrogen at a quaternary bridgehead site. Use of both off-resonance decoupling and INEPT[6] ^{13}C n.m.r. methods revealed that this tricyclic system comprised five CH_3, four CH_2, two CH, and four C groupings. The information available at this stage was not adequate to distinguish between various isomeric structures and, since a rearrangement reaction was suspected, an unambiguous structure determination was carried out by *X*-ray diffraction (see Experimental section). This revealed that the product was 1-acetamido-2,2,5,6,6-pentamethyladamantane (**5**). The structure of the molecule and the crystallographic numbering system used are shown in the Figure.

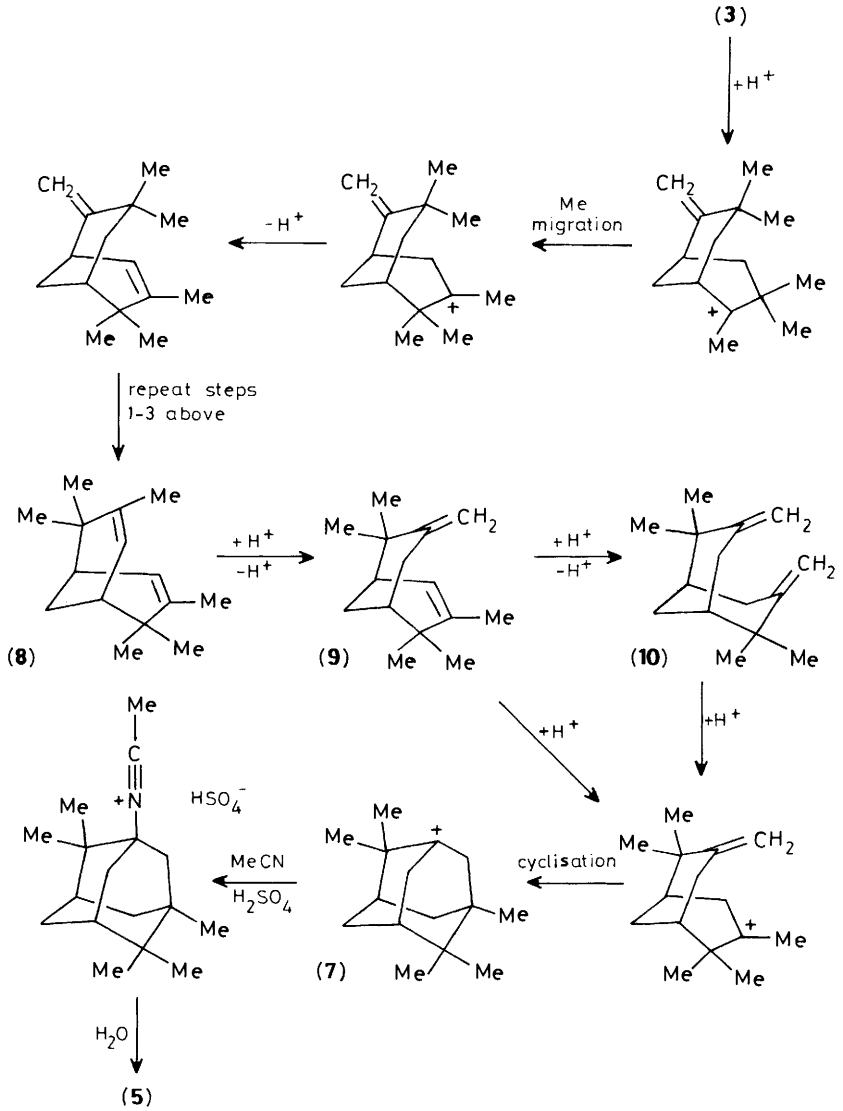


(5)

Additional supporting evidence for the structure (**5**) is available from the mass spectral fragmentation pattern. It is known[7,8] that the molecular radical ion of 1-acetamidoadamantane (m/z = 193) first undergoes α-cleavage followed by elimination of $C_4H_9^{\bullet}$ (mass 57) producing a base peak ion with m/z = 136. The pentamethyl analogue (**5**) behaves in the same manner except that due to the reduced symmetry three α-cleavage pathways are now available. One of these paths should produce a prominent ion with m/z = 164. The other two pathways both lead to an ion with m/z = 178. Since one of the latter processes involves α-cleavage generating a tertiary radical, while the other two involve primary radicals, the base peak would be expected to be m/z = 178 and this is borne out in practice.

The conversion of (**3**) into (**5**) is noteworthy for proceeding so cleanly in high yield (70%), and for the complex nature of the rearrangement which must be involved. In earlier work we have discussed a number of reactions which combine intramolecular cyclisation with Ritter reaction.[9] It is therefore conceivable that protonation of the diolefin (**3**) could result in intramolecular cyclisation to the pentamethyltwistyl ion (**6**). Whitlock and Siefken[10] have shown that twistyl ions rearrange to the thermodynamically more favourable 1-adamantyl ion in high yield under equilibrating conditions and therefore in this present case (**6**) could be expected to rearrange to (**7**) which is the obvious immediate precursor of (**5**). However it is not





Schematic sequence for the rearrangement of (**3**) to (**8**) and the subsequent formation of (**5**)

certain whether the diolefin (**3**) would exist in the twin twist-boat conformation[2] necessary for such a transannular formation of (**6**) to occur.

When the diolefin (**3**) was subjected to less vigorous Ritter conditions it proved possible to isolate a rearranged isomeric diolefin (**8**) in 75% yield. Subjection of (**8**) to the original Ritter conditions gave an 84% yield of the amide (**5**). This interception of an intermediate makes it possible to propose the alternative pathway from (**3**) to (**5**) shown in the Scheme. It is proposed that each olefinic system in (**3**) undergoes sequential protonation, methyl migration, and deprotonation yielding the intermediate (**8**). This sequence of events will be especially favourable since the generation of planar carbons at C-3 and C-7 removes the severe steric crowding originally present between the *endo*-3 and *endo*-7 methyl groups of (**3**). Further protonation and deprotonation would yield the diolefins (**9**) or (**10**) which on protonation would be expected[9,11] to undergo intramolecular cyclisation to the pentamethyl-1-adamantyl ion (**7**). This particularly stable ion would then undergo Ritter reaction to produce the amide product (**5**).

Experimental

^1H (100 MHz) and ^{13}C (25.1 MHz) N.m.r. spectra were recorded in $CDCl_3$ on a JEOL JNM-FX100 spectrometer, and are reported as chemical shifts (δ) relative to internal $SiMe_4$. The substitution of carbon atoms was determined by off-resonance decoupling, except where stated otherwise for (**5**). Mass spectra were recorded using an A.E.I. MS9 spectrometer.

3,3,7,7-*Tetramethylbicyclo*[3.3.1]*nonane*-2,6-*dione* (**2**).—A solution of potassium t-butoxide (33.0 g, 0.29 mol) in t-butyl alcohol (350 ml) was stirred vigorously under dry nitrogen at room temperature and bicyclo[3.3.1]nonane-2,6-dione (**1**)[4] (7.90 g, 0.052 mol) added. After 20 min iodomethane (82.5 g, 0.58 mol) was added. Precipitation of potassium iodide commenced almost at once and the reaction warmed up considerably. After 5 h, water (200 ml) was added, the t-butyl alcohol evaporated under reduced pressure, the residue acidified with 2.5M hydrochloric acid and thoroughly extracted with dichloromethane. The combined extracts were washed (saturated $NaHCO_3$, then water), dried (Na_2SO_4), and evaporated to give a pale yellow oil which was distilled to give the *dione* (**2**) (9.82 g, 91%), b.p. 280—285 °C. This material was recently briefly described in a communication [lit.,[12] b.p. 130—132 °C (7 mmHg), lit.,[12] yield 70%]. Crystallisation from pentane at low temperature gave (**2**) as a white solid, m.p. 46.5—47.5 °C (Found: C, 75.3; H, 10.0. $C_{13}H_{20}O_2$ requires C, 75.0; H, 9.7%); g.l.c. relative retention times (5% LAC-2-R-446 on Chromosorb W, 180 °C) (**2**):(**1**) = 1.00:1.69; $\nu_{max.}$(Nujol) 1 705s, 1 690s, 1 090m, 1 070w, 1 050m, 1 020w, 980m, 920m, 885w, 845w, and 805w cm^{-1}; δ_H 1.07 (6 H, s), 1.22 (6 H, s), 2.02—2.08 (4 H, m), 2.32—2.37 (2 H, t), and 2.81 (2 H, br m); δ_C 27.4(t), 28.4(q), 30.1(q), 41.2(t), 42.2(d), 43.1(s), and 218.1(s).

3,3,7,7-*Tetramethyl*-2,6-*dimethylenebicyclo*[3.3.1]*nonane* (**3**).—A solution of methyltriphenylphosphonium bromide (24.99 g, 0.07 mol) in dry dimethyl sulphoxide (DMSO) (75 ml) was stirred under a nitrogen atmosphere and a solution of sodium methylsulphinyl methylide (0.07 mol) in DMSO added by syringe. After 10 min, 3,3,7,7-tetramethylbicyclo[3.3.1]-nonane-2,6-dione (**2**) (6.24 g, 0.03 mol) was added in dry DMSO (20 ml). After the reaction mixture had been stirred for 10 min it was heated at 80—90 °C for 2 h and then cooled and worked up with water and pentane in the usual manner.[13] The combined pentane extracts were dried (Na_2CO_3) and distilled down to a volume of *ca.* 10 ml. This concentrated solution was eluted through a column of activated neutral alumina with pentane (500 ml) and distilled to give the *diene* (**3**) as an oil, b.p. 245—250 °C (4.18 g, 68%) (Found: C, 88.1; H, 11.85. $C_{15}H_{24}$ requires C, 88.2; H, 11.8%); $\nu_{max.}$(film) 3 085w, 1 630m, and 875s cm^{-1}; δ_H 1.12 (6 H, s), 1.14 (6 H, s), 1.50—1.91 (6 H, m), 2.6—2.9 (2 H, m), and 4.76 and 4.81 (4 H, d); δ_C 29.0(t), 32.4(q), 34.8(s), 35.3(q), 36.2(d), 45.6(t), 106.8(t), and 161.4(s). Further elution of the column with light petroleum—diethyl ether (1:1) gave a small amount of the *keto olefin* (**4**).

3,3,7,7-*Tetramethyl*-6-*methylenebicyclo*[3.3.1]*nonan*-2-*one* (**4**).—A similar procedure to that described above was used but employing equimolar quantities of Wittig reagent and (**2**) (4.18 g, 0.02 mol). The products were separated as above to give the *keto olefin* (**4**) as an oil, b.p. 260—265 °C (1.25 g, 30%) (Found: C, 81.7; H, 10.6. $C_{14}H_{22}O$ requires C, 81.5; H, 10.75%); $\nu_{max.}$(film) 3 080m, 1 710s, 1 635m, 1 470m, 1 380m, 1 355m, 1 085m, 1 065m, 1 020m, 985m, and 885s cm^{-1}; δ_H 0.96 (3 H, s), 1.12 (3 H, s), 1.14 (3 H, s), 1.24 (3 H, s), 1.4—3.0 (8 H, m), and 4.78 (2 H, s); δ_C 28.0(q), 29.4(t), 31.3(q), 32.2(q), 32.7(q), 35.2(s), 37.2(d), 42.2(d), 42.5(t), 43.1(s), 45.0(t), 108.1(t), 160.2(s), and 220.7(s).

1-*Acetamido*-2,2,5,6,6-*pentamethyladamantane* (**5**).—*From the diolefin* (**3**). A mixture of diolefin (**3**) (1.02 g, 5.0 mmol), acetonitrile (8 ml), and acetic acid (7 ml) was stirred in a flask fitted with a condenser and drying tube. Concentrated sulphuric acid (4 ml) was added cautiously in portions *via* the condenser causing the solution to warm up considerably and turn light red. After 45 min the reaction mixture had cooled and water (40 ml) was added, quenching the colour and precipitating a white solid. The reaction was extracted several times with chloroform, and the combined extracts were washed (aq. $NaHCO_3$, then H_2O) and dried (Na_2SO_4). Evaporation of solvent from the filtrate gave an off-white solid which was triturated with a little light petroleum (b.p. 40—60 °C) and filtered to give the *amide* (**5**) (0.92 g, 70%) which after recrystallisation from a large volume of light petroleum (b.p. 40—60 °C) gave m.p. 181.5—182 °C (Found: C, 77.65; H, 10.7; N, 5.8. $C_{17}H_{29}NO$ requires C, 77.5; H, 11.1; N, 5.3%); $\nu_{max.}$(Nujol) 3 350s, 1 650s, and 1 535 cm^{-1}; δ_H 0.74 (3 H, s), 0.96 (3 H, s), 1.04 (6 H, s), 1.07 (3 H, s), 1.2—2.7 (10 H, m), 1.92 (3 H, s, CH_3CO), and 4.97 (1 H, br s, NH); δ_C 22.9, 23.0, 23.2, 23.6, and 23.7 (all CH_3), 25.0(q), 27.7(t), 31.5(t), 35.2(t), 36.4(s), 37.1(s), 38.7(t), 39.0(s), 41.4(d), 41.5(d), 58.0(s), and 169.4(s). The first five ^{13}C peaks listed were too close in chemical shift to allow determination of their substitution by off-resonance decoupling. Their identity as CH_3 groups was revealed using proton decoupled INEPT spectra[6] with delay periods of 0.75 J and 0.5 J. This procedure also confirmed the substitution of the other carbon atoms; *m/z* (≥5% of base peak) 264 (6%), 263 (M^+, 31), 248 (19), 220 (10), 204 (6), 192 (5), 189 (8), 179 (17), 178 (100, base peak), 164 (11), 161 (8), 151 (5), 150 (20), 137 (6), 136 (19), 135 (8), 134 (6), 133 (8), 122 (8), 121 (11), 120 (10), 119 (12), 109 (6), 108 (12), 107 (11), 106 (5), 105 (13), 96 (6), 95 (7), 94 (5), 93 (9), 91 (10), 83 (6), 81 (6), 79 (8), 77 (6), 69 (8), 67 (9), 57 (6), 55 (14), 44 (9), 43 (24), 42 (8), 41 (33), 40 (33), and 39 (6). Needle-shaped crystals for *X*-ray diffraction were grown by evaporation of a chloroform solution.

From the diolefin (**8**). Concentrated sulphuric acid (3 ml) was added to a stirred mixture of 3,4,4,7,8,8-hexamethylbicyclo-[3.3.1]nona-2,6-diene (**8**) (0.57 g, 2.79 mmol), acetonitrile (5 ml), and acetic acid (4 ml) following the procedure described above. The reaction warmed up considerably and turned pale reddish-yellow and after 1 h was worked up as above. Evaporation of the chloroform gave the amide (**5**) as a white solid (0.62 g, 84%). This material was identical to that prepared from the diolefin (**3**).

3,4,4,7,8,8-*Hexamethylbicyclo*[3.3.1]*nona*-2,6-*diene* (**8**).—A mixture of the diolefin (**3**) (1.02 g, 5.0 mmol) and acetonitrile (5

Table 1. Crystallographic details for (**5**)

Formula	$C_{17}H_{29}NO$
Formula mass	263.4
Crystal description	{010}{100}{001}
Space group	$P2_1/c$
a/Å	7.091 (1)
b/Å	23.398 (1)
c/Å	9.651 (1)
β/°	95.79 (1)
V/Å^3	1 593.0 (2)
T/°C	21 (1)
Z	4
D_{obs}/g cm^{-3}	1.08
D_c/g cm^{-3}	1.10
Radiation, λ/Å	Cu-K_α, 1.541 8
μ/cm^{-1}	4.79
Crystal dimensions/mm	0.27 × 0.24 × 0.37
Scan mode	θ/2θ
$2\theta_{max.}$/°	140
ω scan angle/°	0.80 + 0.15 tan θ
Aperture width/°	1.00 + 0.50 tan θ
No. of intensity measurements	3 296
Criterion for observed reflection	$I/\sigma(I) > 3$
No. of independent observed reflections	2 555
No. of reflections (m), variables (n) in final refinement	2 555, 188
$R = \Sigma^m\|\Delta F\|/\Sigma^m\|F_o\|$	0.054
$R_w = [\Sigma^m\omega\|\Delta F\|^2/\Sigma^m\omega\|F_o\|^2]^{\frac{1}{2}}$	0.089
$s = [\Sigma^m\omega\|\Delta F\|^2/(m-n)]^{\frac{1}{2}}$	3.20
Crystal decay	None
Max., mean, min. transmission coefficients	0.90, 0.88, 0.85
Range of indices	$-8 \leqslant h \leqslant 8$
	$0 \leqslant k \leqslant 28$
	$0 \leqslant l \leqslant 11$

ml) was added to a stirred solution of acetic acid (5 ml), acetonitrile (5 ml), and concentrated sulphuric acid (0.5 ml) in a flask fitted with a condenser and drying tube. The reaction mixture turned yellowish, only warmed up moderately, and after 1.5 h was diluted with water (20 ml). The solution was made basic (3M NaOH) and extracted with ethyl acetate. The combined extracts were washed (H_2O), and dried (Na_2SO_4), and evaporated to give a mushy solid which was triturated with light petroleum (b.p. 60—80 °C) and filtered to give the amide (**5**) (0.16 g, 12%). The filtrate was evaporated and the oil eluted through a short column of alumina using pentane. Evaporation of the solvent gave the rearranged *diolefin* (**8**) as a mobile liquid (0.76 g, 74.5%) (Found: M^+, 204.1884. $C_{15}H_{24}$ requires M^+, 204.1878); $\nu_{max.}$(film) 2 990s, 1 630m, 1 470s, 1 355s, 1 145s, 1 085m, 1 025s, 990s, 970s, 915m, 890m, 850s, 830s, and 785m cm^{-1}; δ_H 0.96 (6 H, s), 1.07 (6 H, s), 1.09—1.25 (2 H, m, CH_2), 1.58 (6 H, t, =C–CH_3), 1.61—1.77 (2 H, m, CH), and 5.34 and 5.39 (2 H, d, =CH–); δ_C 18.7(q), 23.8(t), 25.6(q), 27.4(q), 39.5(s), 42.0(d), 124.3(d), and 139.2(s).

Data Collection and Processing.—Diffraction studies were carried out using an Enraf Nonius CAD4 *X*-ray diffractometer and Cu-K_α radiation. Numerical details pertaining to the crystal lattice, and intensity collection are given in Table 1. Data collection, reduction and absorption corrections were performed as previously described [14] using the scan range and aperature given in Table 1. Weights $\omega = 1/\sigma^2(F_o)$ were assigned to reflections, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$.

Structure analysis and refinement. Direct methods [15] and Fourier syntheses were used to locate all the non-hydrogen atoms. Hydrogen atoms were included to agree with geometric requirements and given the same thermal parameters as the atoms to which they were attached. Least-squares refinement using anisotropic thermal parameters reduced R to 0.130. Difference maps then revealed that a disorder existed which could be explained by having a minor component of the other enantiomer at the same location as the reference molecule. Refinement then proceeded using the constrained least-squares refinement program RAELS.[16] Parameters were defined relative to local orthogonal axial systems [17] so that a simple coupling together of parameters could be used to reduce the number of independent variables and hence eliminate covariance problems that arise between parameters describing atoms that overlap as a result of disorder. Two refinable axial systems were established [18] and all positional and thermal parameters of the major component [occupancy 0.790(1)] were referenced to one axial system while those of the minor component [occupancy 0.210(1)] were referenced to the other. A single variable was used to describe occupancy. A common set of refinable local co-ordinates was used to describe atoms of both components, except that atoms of the NHAc group had different local co-ordinates for each enantiomer. Slack constraints were used to control this side chain so that differences between internal geometries within the two models approached zero and the side chains approached planarity. The C(1)–N–C(11) angles and the C(8)–C(1)–N–C(11) torsional angles were unconstrained. Individual atom anisotropic thermal parameters were defined relative to the relevant local axial system and were coupled together so that each non hydrogen atom and its associated H atoms had the same local parameters for both enantiomers. A final value of $R = 0.054$ was obtained for the 2 555 out of 3 018 independent data with $F > 3\sigma(F)$ used in refinement.

Table 2. Fractional co-ordinates for the non-hydrogen atoms of the major component of structure (**5**)

	x	y	z
O	0.535 6(3)	0.250 4(1)	0.255 6(2)
N	0.471 8(4)	0.211 3(1)	0.041 0(2)
C(1)	0.338 6(3)	0.165 7(1)	0.076 1(2)
C(2)	0.440 3(3)	0.126 3(1)	0.187 9(2)
C(3)	0.309 4(3)	0.078 5(1)	0.232 0(3)
C(4)	0.133 2(3)	0.106 5(1)	0.292 2(3)
C(5)	0.031 8(3)	0.144 1(1)	0.175 8(3)
C(6)	−0.031 0(4)	0.108 6(1)	0.047 4(3)
C(7)	0.142 6(4)	0.083 1(1)	−0.011 2(2)
C(8)	0.276 2(4)	0.130 4(1)	−0.058 0(2)
C(9)	0.164 8(3)	0.191 5(1)	0.134 0(2)
C(10)	0.244 9(4)	0.044 6(1)	0.098 9(3)
C(11)	0.561 6(3)	0.248 3(1)	0.132 0(2)
C(12)	0.699 6(6)	0.288 0(2)	0.072 7(3)
C(13)	0.423 0(4)	0.039 7(1)	0.335 9(3)
C(14)	−0.004 7(5)	0.061 1(2)	0.339 2(4)
C(15)	0.189 7(5)	0.143 2(1)	0.422 1(3)
C(16)	0.445 6(4)	0.104 0(1)	−0.123 6(3)
C(17)	0.169 5(4)	0.166 5(1)	−0.174 3(3)

Description of the structure (**5**). The crystallographic numbering system used is shown in the Figure. There is only a limited departure from mirror symmetry in the adamantane framework across a plane defined by atoms C(1), C(4), and C(8). The C(8)–C(1)–N–C(11) torsional angle is not constrained to 180° and the methyl group attached to C(3) is mirror related to a hydrogen attached to C(5). The NHAc functional group is involved in hydrogen bonding. Chains parallel to c are formed by hydrogen bonding the O atoms to N atoms in molecules related by the c-glide. The observed disorder leaves the NHAc groups approximately coincident but accommodates the minor component enantiomer by changing the C(8)–C(1)–N–C(11) torsional angle by 10° from −176.6(2)° to +172.7(7)°.

Table 3. Bond lengths and bond angles for the structure (**5**)

Bond lengths

O–C(11)	1.227(2)	N–C(1)	1.488(2)	N–C(11)	1.346(2)	C(1)–C(2)	1.542(2)
C(1)–C(9)	1.528(3)	C(1)–C(8)	1.562(2)	C(2)–C(3)	1.540(3)	C(3)–C(10)	1.540(4)
C(3)–C(4)	1.573(3)	C(3)–C(13)	1.523(3)	C(10)–C(7)	1.520(4)	C(7)–C(6)	1.528(4)
C(7)–C(8)	1.553(3)	C(6)–C(5)	1.520(4)	C(5)–C(9)	1.536(3)	C(5)–C(4)	1.546(3)
C(4)–C(14)	1.543(3)	C(4)–C(15)	1.539(4)	C(8)–C(16)	1.542(4)	C(8)–C(17)	1.541(3)
C(11)–C(12)	1.504(2)	O–N[a]	2.974(2)	O–HN[a]	2.011(2)	O–N[b,a]	3.066(5)
O[b]–N[a]	3.102(8)	O[b]–N[b,a]	3.195(7)				

Bond angles

C(1)–N–C(11)	125.6(1)	N–C(1)–C(2)	109.0(1)	N–C(1)–C(9)	110.7(2)
N–C(1)–C(8)	108.9(1)	C(2)–C(1)–C(9)	108.5(1)	C(2)–C(1)–C(8)	109.7(2)
C(9)–C(1)–C(8)	109.9(2)	C(1)–C(2)–C(3)	112.0(2)	C(2)–C(3)–C(10)	106.3(2)
C(2)–C(3)–C(4)	108.9(2)	C(2)–C(3)–C(13)	108.8(2)	C(10)–C(3)–C(4)	110.0(2)
C(10)–C(3)–C(13)	109.5(2)	C(4)–C(3)–C(13)	113.1(2)	C(3)–C(10)–C(7)	111.0(2)
C(10)–C(7)–C(6)	108.6(2)	C(10)–C(7)–C(8)	111.3(2)	C(6)–C(7)–C(8)	111.5(2)
C(7)–C(6)–C(5)	109.5(2)	C(6)–C(5)–C(9)	108.5(2)	C(6)–C(5)–C(4)	111.0(2)
C(9)–C(5)–C(4)	110.4(2)	C(1)–C(9)–C(5)	110.5(2)	C(3)–C(4)–C(5)	107.3(2)
C(3)–C(4)–C(14)	111.9(2)	C(3)–C(4)–C(15)	112.5(2)	C(5)–C(4)–C(14)	110.1(2)
C(5)–C(4)–C(15)	109.8(2)	C(14)–C(4)–C(15)	105.4(2)	C(1)–C(8)–C(7)	105.4(1)
C(1)–C(8)–C(16)	112.6(2)	C(1)–C(8)–C(17)	113.0(2)	C(7)–C(8)–C(16)	111.0(2)
C(7)–C(8)–C(17)	109.5(2)	C(16)–C(8)–C(17)	105.4(2)	O–C(11)–N	123.5(2)
O–C(11)–C(12)	120.9(2)	N–C(11)–C(12)	115.6(1)	C(1)[b]–N[b]–C(11)[b]	126.8(3)

Torsional angles

C(8)[b]–C(1)[b]–N[b]–C(11)[b]	172.7(7)	C(8)–C(1)–N–C(11)	−176.6(2)

Equivalent position indicators: [a] $x, \frac{1}{2} - y, \frac{1}{2} + z$. [b] Denotes molecule of lesser (0.2) occupancy.

Fractional co-ordinates for the non-hydrogen atoms of the major component are given in Table 2. Bond lengths and angles are given in Table 3. Complete listings of positional and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

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* For details see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 1*, 1989, Issue 1.

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