Supplementary Material

Four-directional synthesis of adamantane derivatives

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Appendix 1: X-ray Crystal Structure Determination of Tetra-(Z)-allylic Alcohol 21

![Crystal Structure Diagram]

Figure 3. The crystal structure of tetra-(Z)-allylic alcohol 21 (50% probability ellipsoids).

Crystal data for tetra-(Z)-allylic alcohol 21: C_{22}H_{32}O_{4}, M = 360.47, monoclinic, P2_1 (no. 4), a = 7.2942(7), b = 11.5286(12), c = 11.5044(10) Å, β = 92.841(8)°, V = 966.24(16) Å^3, Z = 2, D_c = 1.239 g cm^-3, μ(Cu-Kα) = 0.665 mm^-1, T = 173 K, colorless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3465 independent measured reflections (R_{int} = 0.0378), F^2 refinement, R_1(obs) = 0.0334, wR_2(all) = 0.0826, 2910 independent observed absorption-corrected reflections ([F_o] > 4σ(|F_o|), completeness to θ_{full}(67.7°) = 99.7%), 252 parameters. The absolute structure of 21 could not be unambiguously determined [Flack parameter x^+ = –0.01(17)]. CCDC 1982520.

The hydrogen atoms of the O14-, O18-, O22- and O26-based OH groups in the structure of tetra-(Z)-allylic alcohol 21 were all located from ΔF maps and refined freely subject to O–H distance constraints of 0.90 Å.

Appendix 2: X-ray Crystal Structure Determination of Tetra-syn-Cyclopropyl Alcohol 35
Figure 4. The crystal structure of tetra-syn-cyclopropyl alcohol 35 showing the major (ca. 64%) occupancy orientation of the C9-bound cyclopropyl alcohol moiety, isomer A (25% probability ellipsoids).

Figure 5. The crystal structure of tetra-syn-cyclopropyl alcohol 35 showing the minor (ca. 36%) occupancy orientation of the C9-bound cyclopropyl alcohol moiety, isomer B (25% probability ellipsoids).
Figure 6. The crystal structure of tetra-syn-cyclopropyl alcohol 35 showing an overlay of both the major and minor occupancy orientations of the C9-bound cyclopropyl alcohol moiety. The major (ca. 64%) occupancy orientation (isomer A) has been drawn with dark bonds, whilst the minor (ca. 36%) occupancy orientation (isomer B) has been drawn with open bonds.

**Crystal data for tetra-syn-cyclopropyl alcohol 35**: C_{26}H_{40}O_{4}, \( M = 416.58 \), monoclinic, \( C2 \) (no. 5), \( a = 22.471(3) \), \( b = 10.5857(11) \), \( c = 9.5321(12) \) Å, \( \beta = 96.404(11) \)°, \( V = 2253.3(5) \) Å³, \( Z = 4 \), \( D_c = 1.228 \) g cm⁻³, \( \mu(Mo-K\alpha) = 0.081 \) mm⁻¹, \( T = 173 \) K, colorless plates, Oxford Diffraction Xcalibur 3 diffractometer; 6184 independent measured reflections (\( R_{int} = 0.0833 \)), \( F^2 \) refinement, \( R_1(\text{obs}) = 0.0905 \), \( wR_2(\text{all}) = 0.2903 \), 2785 independent observed absorption-corrected reflections \( [|F_o| > 4\sigma(|F_o|)] \), completeness to \( \theta_{\text{full}}(25.2^\circ) = 99.4\% \), 294 parameters. The absolute structure of tetra-syn-cyclopropyl alcohol 35 could not be determined from the diffraction data [Flack parameter \( \chi = 10.0(10) \)] and so was set by internal reference based on the known stereochemistries of the four cyclopropyl alcohol groups. CCDC 1982521.

The C26-based cyclopropyl sidearm in the structure of tetra-syn-cyclopropyl alcohol 35 was found to be disordered. Two orientations were identified of ca. 64 and 36% occupancy (corresponding to inverted stereochemistries at C26 and C28), their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The hydrogen atoms of the O15-, O20-, O25- and O30/O30'-based OH groups could not be reliably located from \( \Delta F \) maps, and adding them in idealized positions with free rotation about the C–O vector to find the best fit with the observed electron density (the SHELX HFIX/AFIX 147 command) gave positions that clashed with adjacent molecules. So, they were added in somewhat arbitrary positions that should be treated with caution.
References

51  SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.
Appendix 3: $^1$H and $^{13}$C spectra of dimer 63.

$^1$H NMR of dimer 63 in C$_6$D$_6$ (500 MHz).
$^{13}$C NMR of dimer 63 in C$_6$D$_6$ (100 MHz).
$^{13}$C DEPT of dimer 63 in C$_6$D$_6$ (125 MHz).
\(^{13}\text{C}\) DEPT of dimer 63 in C_{6}D_{6} (125 MHz).
$^1$H and $^{13}$C correlation spectrum of dimer 63 in C$_6$D$_6$. 
\(^1\)H and \(^{13}\)C correlation spectrum of dimer 63 in C\(_6\)D\(_6\).
$^1$H and $^{13}$C correlation spectrum of dimer 63 in C$_6$D$_6$.
$^1$H and $^{13}$C correlation spectrum of dimer 63 in C$_6$D$_6$. 
$^1$H and $^{13}$C correlation spectrum of dimer 63 in C$_6$D$_6$. 

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'H and $^{13}$C correlation spectrum of dimer 63 in C$_6$D$_6$. 
$^1$H COSY spectrum of dimer 63 in C$_6$D$_6$. 
\(^1\)H COSY spectrum of dimer 63 in C\(_6\)D\(_6\).
$^1$H COSY spectrum of dimer 63 in C$_6$D$_6$. 
\(^1\)H COSY spectrum of dimer 63 in C\(_6\)D\(_6\).
$^1$H COSY spectrum of dimer 63 in CdD$_6$. 
\(^1\)H COSY spectrum of dimer 63 in C\(_6\)D\(_6\).
$^1$H COSY spectrum of dimer 63 in C$_6$D$_6$. 
$^1$H COSY spectrum of dimer 63 in C$_6$D$_6$. 
checkCIF (basic structural check) running

Checking for embedded cif data in CIF ...
Found embedded cif data in CIF. Extracting cif data from uploaded CIF, please wait......

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) 21, 35

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Structure factor report

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Click on the hyperlinks for more details of the test.

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Wavelength given = 1.54168

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PLAT595_ALERT_2_C No Peak in Check Donor : Low Friedel Pair Coverage 88 %

PLAT595_ALERT_2_C No Peak in Check Donor : Low Friedel Pair Coverage 88 %

**Alert level G**

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PLAT183_ALERT_1_G No Info/Value for _atom_site_solution_primary._Please Do!
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PLAT961_ALERT_5_G Datasets contain no Negative Intensities.

0 ALERT level A = Most likely a serious problem — resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
6 ALERT level G = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

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The following ALERTS were generated. Each ALERT has the format

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*Alert level C*

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0.29% Report

PLAT241_ALERT_3_C High MainH Value as Compared to Neighbors of...

C12 Check

PLAT340_ALERT_3_C Low Bond Precision in C-C Bonds...

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PLAT906_ALERT_3_C Large K Value in the Analysis of Variance...

3.70 K Check

PLAT907_ALERT_3_C Lack > 0.5, Structure Needs to be Inverted...

10.00 Check

PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage...

52 %

*Alert level G*

PLAT902_ALERT_2_G Number of Distance or Angle Restraints on MissSite.

11 Note

PLAT903_ALERT_2_G Number of Uiso or Uj Restricted non-H Atoms...

10 Report

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