Equilibrium Structures and Vibrational Assignments for Isoamyl Alcohol and *tert*-Amyl Alcohol: A Density Functional Study

Wolfgang Förner and Hassan M. Badawi

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Supporting Information

Table S1. Internal coordinate definitions of isoamyl alcohol and *tert*-amyl alcohol (for atom numbering see Figure 1).

Table S2. Group coordinates (not normalized, all are of a species in *gauche* conformers) for isoamyl and *tert*-amyl alcohol (both molecules must have (3 × 18 – 6) = 48 coordinates).

Table S3. Calculated (DFT and MP2) structural parameters, dipole moments and rotational constants for *gauche-trans* isoamyl alcohol and *gauche-gauche tert*-amyl alcohol (for atom numbering see Figure 1).

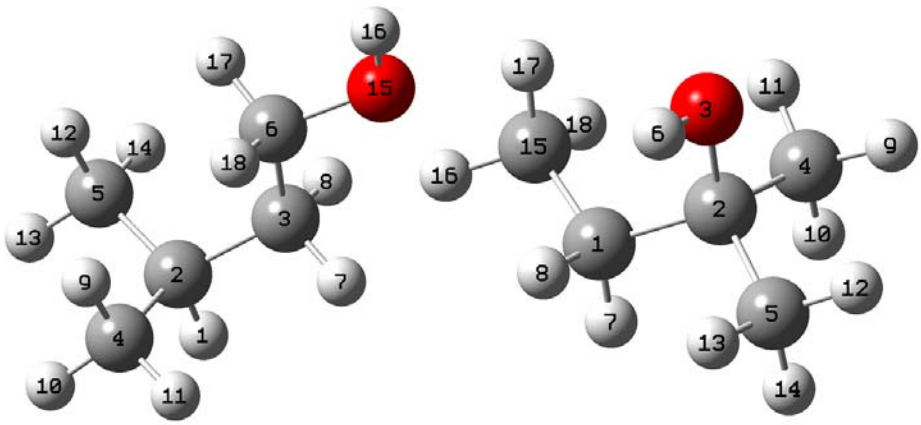

Figure 1. Atom numbering of the *trans-trans* structure of isoamyl alcohol (left) and the *gauche-gauche* structure of *tert*-amyl alcohol (right).

Table S1: Internal coordinate definitions of isoamyl alcohol and *tert*-amyl alcohol (for atom numbering see Figure 1).

No.	Coordinate		Definition
Internal coordinates for the methyl 1 ($C_4H_9H_{10}H_{11}$) and methyl 2 ($C_5H_{12}H_{13}H_{14}$) groups subsystems (common in both molecules)			
1	C_4H_9	stretch	Q_4
2	C_4H_{10}	stretch	Q_5
3	C_4H_{11}	stretch	Q_6
4	$C_2C_4H_9$	bend	α_4
5	$C_2C_4H_{10}$	bend	α_5
6	$C_2C_4H_{11}$	bend	α_6
7	$H_9C_4H_{10}$	bend	β_4
8	$H_9C_4H_{11}$	bend	β_5
9	$H_{10}C_4H_{11}$	bend	β_6
10	$H_9C_4C_2C_1 + H_{10}C_4C_2C_1 + H_{11}C_4C_2C_1$	CH_3 torsion	τ_4
11	C_5H_{12}	stretch	Q_7
12	C_5H_{13}	stretch	Q_8
13	C_5H_{14}	stretch	Q_9
14	$C_2C_5H_{12}$	bend	α_7
15	$C_2C_5H_{13}$	bend	α_8
16	$C_2C_5H_{14}$	bend	α_9
17	$H_{12}C_5H_{13}$	bend	β_7
18	$H_{12}C_5H_{14}$	bend	β_8
19	$H_{13}C_5H_{14}$	bend	β_9
20	$H_{12}C_5C_2C_1 + H_{13}C_5C_2C_1 + H_{14}C_5C_2C_1$	CH_3 torsion	τ_5
Internal coordinates for the C_2–C_4C_5 subgroup ($X=H_1$, $Y=C_3$ in isoamyl alcohol and $X=O_3$, $Y=C_1$ in *tert*-amyl alcohol), in both molecules			
21	C_2C_4	stretch	A_3
22	C_2C_5	stretch	A_4
23	YC_2X	bend	ε_3
24	$C_4C_2C_5$	bend	δ_3
25	YC_2C_4	bend	σ_5
26	YC_2C_5	bend	σ_6
27	XC_2C_4	bend	γ_5
28	XC_2C_5	bend	γ_6

to be continued on next page

Table S1: continued from previous page

No.	Coordinate		Definition
Internal coordinates for the hydroxy ethyl and *tert*-CH subunits in isoamyl alcohol			
29	C_3C_2	stretch	R_1
30	C_3C_6	stretch	R_2
31	C_6O_{15}	stretch	S
32	$O_{15}H_{16}$	stretch	P
33	C_6H_{17}	stretch	D_1
34	C_6H_{18}	stretch	D_2
35	C_3H_7	stretch	A_1
36	C_3H_8	stretch	A_2
37	$C_2C_3C_6$	bend	ε_2
38	$C_3C_6O_{15}$	bend	θ
39	$C_6O_{15}H_{16}$	bend	φ
40	$H_{17}C_6C_3$	bend	ω_1
41	$H_{18}C_6C_3$	bend	ω_2
42	$H_{17}C_6O_{15}$	bend	χ_1
43	$H_{18}C_6O_{15}$	bend	χ_2
44	$H_{17}C_6H_{18}$	bend	Ω
45	$C_2C_3H_7$	bend	σ_3
46	$C_2C_3H_8$	bend	σ_4
47	$C_6C_3H_7$	bend	γ_3
48	$C_6C_3H_8$	bend	γ_4
49	$H_7C_3H_8$	bend	δ_2
50	$H_{16}O_{15}C_6C_3$	OH torsion	τ_2
51	$C_2C_3C_6O_{15}$	CO torsion	τ_3
52	C_2H_1	stretch	T_1
Internal coordinates for the ethyl and *tert*-OH subunits in *tert*-amyl alcohol			
29	C_1C_{15}	stretch	R_1
30	C_1C_2	stretch	R_2
31	$C_{15}H_{16}$	stretch	Q_1

to be continued on next page

Table S1: continued from previous page

No.	Coordinate		Definition
32	$C_{15}H_{17}$	stretch	Q_2
33	$C_{15}H_{18}$	stretch	Q_3
34	C_1H_7	stretch	A_1
35	C_1H_8	stretch	A_2
36	$C_{15}C_1C_2$	bend	ε_1
37	$C_{15}C_1H_7$	bend	σ_1
38	$C_{15}C_1H_8$	bend	σ_2
39	$C_2C_1H_7$	bend	γ_1
40	$C_2C_1H_8$	bend	γ_2
41	$H_7C_1H_8$	bend	δ_1
42	$C_1C_{15}H_{16}$	bend	α_1
43	$C_1C_{15}H_{17}$	bend	α_2
44	$C_1C_{15}H_{18}$	bend	α_3
45	$H_{18}C_{15}H_{17}$	bend	β_1
46	$H_{18}C_{15}H_{16}$	bend	β_2
47	$H_{17}C_{15}H_{16}$	bend	β_3
48	$H_{16}C_{15}C_1C_2 + H_{17}C_{15}C_1C_2 + H_{18}C_{15}C_1C_2$	CH_3 torsion	τ_1
49	C_2O_3	stretch	T_2
50	O_3H_6	stretch	T_3
51	$C_2O_3H_6$	bend	κ
52	$H_6O_3C_2C_1$	OH torsion	η_1
isopropyl subgroup torsion in isoamyl alcolhol			
53	$H_1C_2C_3C_6 + C_4C_2C_3C_6 + C_5C_2C_3C_6$	isopropyl torsion	η_2
hydroxy isopropyl subgroup torsion in *tert*-amyl alcolhol			
53	$O_3C_2C_1C_{15} + C_4C_2C_1C_{15} + C_5C_2C_1C_{15}$	hydroxy isopropyl torsion	η_3

Table S2: Group coordinates (not normalized, all are of a species in *gauche* conformers) for isoamyl and *tert*-amyl alcohol (both molecules must have (3 × 18 – 6) = 48 coordinates).

Description	group coordinate
Partial group coordinates for the methyl 1 ($C_4H_9H_{10}H_{11}$) and methyl 2 ($C_5H_{12}H_{13}H_{14}$) group subsystems (common in both molecules)	
CH_3 symmetric stretch	$T_1 = Q_4 + Q_5 + Q_6$
CH_3 antisymmetric stretch	$T_2 = 2\,Q_4 - Q_5 - Q_6$
CH_3 antisymmetric stretch	$T_3 = Q_5 - Q_6$
CH_3 symmetric deformation	$T_4 = \beta_4 + \beta_5 + \beta_6 - \alpha_4 - \alpha_5 - \alpha_6$
CH_3 antisymmetric deformation	$T_5 = \beta_4 + \beta_5 - 2\,\beta_6$
CH_3 rock	$T_6 = 2\,\alpha_4 - \alpha_5 - \alpha_6$
CH_3 antisymmetric deformation	$T_7 = \beta_4 - \beta_5$
CH_3 rock	$T_8 = \alpha_5 - \alpha_6$
CH_3 torsion	$T_9 = \tau_4$
CH_3 symmetric stretch	$T_{10} = Q_7 + Q_8 + Q_9$
CH_3 antisymmetric stretch	$T_{11} = 2\,Q_7 - Q_8 - Q_9$
CH_3 antisymmetric stretch	$T_{12} = Q_8 - Q_9$
CH_3 symmetric deformation	$T_{13} = \beta_7 + \beta_8 + \beta_9 - \alpha_7 - \alpha_8 - \alpha_9$
CH_3 antisymmetric deformation	$T_{14} = \beta_7 + \beta_8 - 2\,\beta_9$
CH_3 rock	$T_{15} = 2\,\alpha_7 - \alpha_8 - \alpha_9$
CH_3 antisymmetric deformation	$T_{16} = \beta_7 - \beta_8$
CH_3 rock	$T_{17} = \alpha_8 - \alpha_9$
CH_3 torsion	$T_{18} = \tau_5$

from the above given partial coordinates, the complete group coordinates are obtained as the in phase (iph) combinations, $S_i = T_i + T_{i+9}$, i = 1,9, and as the out of phase (oph) combinations, $S_{i+9} = T_i - T_{i+9}$, i = 1,9.

to be continued on next page

Table S2: continued from previous page

note that all the following symmetry labels are for the *trans-trans* conformer of isoamyl alcohol only which has C_s symmetry (27 A' + 21 A"). In the above part all coordinates S_1 – S_8 and S_{18} are A', while S_9 – S_{17} are A".

Description	**group coordinate**
group coordinates for the C_2–C_4C_5 subgroup (common in both molecules)	
A' CC_2 symmetric stretch	$S_{19} = A_3 + A_4$
A" CC_2 antisymmetric stretch	$S_{20} = A_3 - A_4$
A' CC_2 scissor	$S_{21} = [\sqrt{6} + 2]\,\delta_3 - [\sqrt{6} - 2]\,\varepsilon_3 - \sigma_5 - \sigma_6 - \gamma_5 - \gamma_6$
A' CCC bend	$S_{22} = [\sqrt{6} - 2]\,\delta_3 - [\sqrt{6} + 2]\,\varepsilon_3 + \sigma_5 + \sigma_6 + \gamma_5 + \gamma_6$
A' CC_2 wag	$S_{23} = \sigma_5 + \sigma_6 - \gamma_5 - \gamma_6$
A" CC_2 twist	$S_{24} = \sigma_5 - \sigma_6 - \gamma_5 + \gamma_6$
A" CC_2 rock	$S_{25} = \sigma_5 - \sigma_6 + \gamma_5 - \gamma_6$
group coordinates for the hydroxy ethyl and *tert*-CH subunits in isoamyl alcohol	
A' CH_2 symmetric stretch	$S_{26} = A_1 + A_2$
A' CH_2 symmetric stretch	$S_{27} = D_1 + D_2$
A' OH stretch	$S_{28} = P$
A' CO stretch	$S_{29} = S$
A' CH_2 scissor	$S_{30} = [\sqrt{6} + 2]\,\delta_2 - [\sqrt{6} - 2]\,\varepsilon_2 - \sigma_3 - \sigma_4 - \gamma_3 - \gamma_4$
A' CH_2 scissor	$S_{31} = [\sqrt{6} + 2]\,\Omega - [\sqrt{6} - 2]\,\theta - \omega_1 - \omega_2 - \chi_1 - \chi_2$
A' CH_2 wag	$S_{32} = \sigma_3 + \sigma_4 - \gamma_3 - \gamma_4$
A' CH_2 wag	$S_{33} = \omega_1 + \omega_2 - \chi_1 - \chi_2$

to be continued on next page

Table S2: continued from previous page

Description	group coordinate
A' C-OH ipl bend	$S_{34} = \varphi$
A' CCC antisymmetric stretch	$S_{35} = R_1 - R_2$
A' CCC symmetric stretch	$S_{36} = R_1 + R_2$
A' CCO ipl bend	$S_{37} = [\sqrt{6} - 2\,]\,\Omega - [\sqrt{6} + 2]\,\theta + \omega_1 + \omega_2 + \chi_1 + \chi_2$
A' CCC ipl bend	$S_{38} = [\sqrt{6} - 2\,]\,\delta_2 - [\sqrt{6} + 2]\,\varepsilon_2 + \sigma_3 + \sigma_4 + \gamma_3 + \gamma_4$
A" CH_2 antisymmetric stretch	$S_{39} = A_1 - A_2$
A" CH_2 antisymmetric stretch	$S_{40} = D_1 - D_2$
A" CH_2 twist	$S_{41} = \sigma_3 - \sigma_4 - \gamma_3 + \gamma_4$
A" CH_2 twist	$S_{42} = \omega_1 - \omega_2 - \chi_1 + \chi_2$
A" OH torsion	$S_{43} = \tau_2$
A" CH_2 rock	$S_{44} = \sigma_3 - \sigma_4 + \gamma_3 - \gamma_4$
A" CH_2 rock	$S_{45} = \omega_1 - \omega_2 + \chi_1 - \chi_2$
A" CO torsion	$S_{46} = \tau_3$
A' *tert*-CH stretch	$S_{47} = T_1$
isopropyl subunit torsion	
A" isopropyl torsion	$S_{48} = \eta_2$
group coordinates for the ethyl and *tert*-OH subunits in *tert*-amyl alcohol (all are A in the *gauche-gauche* conformer)	
CH_2 symmetric stretch	$S_{26} = A_1 + A_2$
CH_2 scissor	$S_{27} = [\sqrt{6} + 2\,]\,\delta_1 - [\sqrt{6} - 2]\,\varepsilon_1 - \sigma_1 - \sigma_2 - \gamma_1 - \gamma_2$
CH_2 wag	$S_{28} = \sigma_1 + \sigma_2 - \gamma_1 - \gamma_2$

to be continued on next page

Table S2: continued from previous page

Description	group coordinate
CH_3 symmetric stretch	$S_{29} = Q_1 + Q_2 + Q_3$
CH_3 antisymmetric stretch	$S_{30} = 2\,Q_1 - Q_2 - Q_3$
CCC symmetric stretch	$S_{31} = R_1 + R_2$
CCC antisymmetric stretch	$S_{32} = R_1 - R_2$
CH_3 symmetric deformation	$S_{33} = \beta_1 + \beta_2 + \beta_3 - \alpha_1 - \alpha_2 - \alpha_3$
CH_3 antisymmetric deformation	$S_{34} = \beta_1 + \beta_2 - 2\,\beta_3$
CH_3 rock	$S_{35} = 2\,\alpha_1 - \alpha_2 - \alpha_3$
CCC ipl bend	$S_{36} = [\sqrt{6} - 2\,]\,\delta_1 - [\sqrt{6} + 2]\,\varepsilon_1 + \sigma_1 + \sigma_2 + \gamma_1 + \gamma_2$
CH_2 antisymmetric stretch	$S_{37} = A_1 - A_2$
CH_3 antisymmetric stretch	$S_{38} = Q_2 - Q_3$
CH_2 twist	$S_{39} = \sigma_1 - \sigma_2 - \gamma_1 + \gamma_2$
CH_2 rock	$S_{40} = \sigma_1 - \sigma_2 + \gamma_1 - \gamma_2$
CH_3 antisymmetric deformation	$S_{41} = \beta_1 - \beta_2$
CH_3 rock	$S_{42} = \alpha_2 - \alpha_3$
CH_3 torsion	$S_{43} = \tau_1$
tert-CO stretch	$S_{44} = T_2$
tert-OH stretch	$S_{45} = T_3$
tert-COH bend	$S_{46} = \kappa$
tert-OH torsion	$S_{47} = \eta_1$
hydroxy isopropyl subgroup torsion	
hydroxy isopropyl torsion	$S_{48} = \eta_3$

Table S3: Calculated (DFT and MP2) structural parameters, dipole moments and rotational constants for *gauche-trans* isoamyl alcohol and *gauche-gauche tert*-amyl alcohol (for atom numbering see Figure 1).

	Isoamyl alcohol		*tert*-amyl alcohol		
	DFT	MP2		DFT	MP2
bond lengths (Å)					
C_5C_2	1.536	1.531	C_5C_2	1.535	1.528
C_4C_2	1.537	1.532	C_4C_2	1.529	1.523
C_2C_3	1.547	1.540	C_2C_1	1.546	1.536
C_3C_6	1.524	1.520	C_1C_{15}	1.531	1.529
C_6O_{15}	1.433	1.429	C_2O_3	1.444	1.438
C_5H_{12}	1.094	1.095	C_5H_{12}	1.093	1.094
C_5H_{13}	1.094	1.095	C_5H_{13}	1.096	1.097
C_5H_{14}	1.095	1.096	C_5H_{14}	1.094	1.095
C_4H_9	1.091	1.092	C_4H_9	1.092	1.094
C_4H_{10}	1.095	1.096	C_4H_{10}	1.093	1.095
C_4C_{11}	1.094	1.095	C_4H_{11}	1.091	1.092
C_2H_1	1.098	1.099	C_1H_7	1.096	1.098
C_3H_7	1.096	1.097	C_1H_8	1.098	1.100
C_3H_8	1.098	1.099	$C_{15}H_{16}$	1.093	1.094
C_6H_{17}	1.098	1.099	$C_{15}H_{17}$	1.092	1.093
C_6H_{18}	1.098	1.098	$C_{15}H_{18}$	1.093	1.093
$O_{15}H_{16}$	0.962	0.961	O_3H_6	0.964	0.964
Bond angles (deg)					
$C_5C_2C_4$	111.1	110.7	$C_5C_2C_4$	110.5	110.5
$C_5C_2C_3$	112.6	112.1	$C_5C_2C_1$	109.8	109.1
$C_4C_2C_3$	113.4	113.1	$C_4C_2C_1$	112.4	112.1
$C_2C_3C_6$	118.0	116.6	$C_2C_1C_{15}$	115.6	114.7
$C_3C_6O_{15}$	110.0	109.4	$C_1C_2O_3$	109.9	109.8
$C_6O_{15}H_{16}$	108.7	107.3	$C_1C_{15}H_{17}$	111.0	110.6
$H_{17}C_6H_{18}$	107.5	107.9	$H_{16}C_{15}H_{17}$	108.1	108.4
$C_3C_6H_{17}$	108.5	108.6	$H_{16}C_{15}H_{18}$	107.3	107.6
$H_7C_3H_8$	106.4	106.9	$H_{17}C_{15}H_{18}$	107.9	108.3
$C_2C_3H_7$	109.2	109.4	$H_7C_1H_8$	105.8	106.3
$C_2C_5H_{13}$	111.5	110.8	$C_2C_1H_7$	108.5	108.5
$H_{12}C_5H_{13}$	107.2	107.6	$C_2C_5H_{13}$	110.9	110.5
$H_{13}C_5H_{14}$	107.7	107.9	$H_{12}C_5H_{13}$	108.3	108.5

to be continued on next page

Table S3: continued from previous page

$H_{14}C_5H_{12}$	108.0	108.4	$H_{13}C_5H_{14}$	107.6	108.0
$C_2C_4H_{10}$	110.4	110.1	$H_{14}C_5H_{12}$	108.5	108.9
$H_9C_4H_{11}$	107.4	108.0	$C_2C_4H_{10}$	110.8	110.4
$H_9C_4H_{10}$	108.6	108.8	$H_9C_4H_{11}$	107.9	108.2
$H_{10}C_4H_{11}$	107.8	108.0	$H_9C_4H_{10}$	108.6	108.9
$C_5C_2H_1$	107.0	107.5	$H_{10}C_4H_{11}$	108.7	109.0
$C_3C_2H_1$	105.2	105.8	$C_5C_2O_3$	109.3	109.4
			$C_4C_2O_3$	104.9	105.0
			$C_2O_3H_6$	108.4	107.0
Dihedral angles (deg)[a]					
$H_{10}C_4C_2H_9$	+120.7	+120.5	$H_{10}C_4C_2O_3$	–177.0	–175.0
$H_{13}C_5C_2H_{12}$	–119.2	–119.1	$H_6O_3C_2C_5$	–56.2	–56.6
$C_4C_2C_3H_1$	+116.5	+117.0	$H_{13}C_5C_2O_3$	+63.5	+64.5
$H_1C_2C_3C_6$	+170.3	+164.3	$C_4C_2C_1H_7$	+66.1	+68.4
$C_2C_3C_6O_{15}$	+67.5	+61.9	$C_4C_2C_1C_{15}$	–57.8	–55.2
$H_{16}O_{15}C_6C_3$	+177.3	+175.8	$H_{16}C_{15}C_1C_2$	–172.8	–171.0
$H_{18}C_6C_3O_{15}$	–122.0	–121.6	$H_{17}C_{15}C_1C_2$	–52.9	–51.1
Dipole moments (Debye)					
	1.6578	1.8841		1.6747	1.8035
Rotational constants (GHz)					
A	4.6237	4.5343		4.5027	4.5433
B	2.4162	2.5100		2.5737	2.6093
C	2.0949	2.2329		2.5056	2.5418

[a] A dihedral angle ABCD is defined as the smaller one of the two possible angles between the projections of the bond AB and the bond CD into a plane perpendicular to the bond BC. When looking along the bond BC into B to C direction, then the dihedral angle is positive when the move from A to D through the dihedral angle is clockwise.