SUPPLEMENTAL MATERIAL

Table 1S. Scaled diagonal force constants from MP2/6-31G(d) *ab initio* calculations for dicyclopropyl ketone.

Table 2S. Symmetry coordinates for dicyclopropyl ketone.

Fig. 1S. Asymmetric torsional potential function for dicyclopropyl ketone. Solid curve is the calculated potential function at MP2(full)/6-31G(d) level; dotted curve is calculated at MP2(full)/6-31+G(d) level. Torsional dihedral angle of 0° corresponds to the *cis*-*cis* conformer.

TABLE 1S. Calculated energies (Hartree) and energy differences (cm^{-1}) for the two conformers of dicyclopropyl ketone.

Method / Basis set	*cis-cis*	*cis-trans*	ΔE
RHF/6-31G(d)	-345.706689	-345.702818	850
RHF/6-31+G(d)	-345.713051	-345.709741	726
MP2/6-31G(d)	-346.820603	-346.816696	857
MP2/6-31+G(d)	-346.841661	-346.838581	676
MP2/6-311G(d,p)	-347.140389	-347.137121	717
MP2/6-311+G(d,p)	-347.149730	-347.147381	516
MP2/6-311G(2d,2p)	-347.232147	-347.229067	676
MP2/6-311+G(2d,2p)	-347.239367	-347.237182	480
B3LYP/6-31G(d)	-347.931942	-347.928081	847
B3LYP/6-31+G(d)	-347.945432	-347.942169	716
B3LYP/6-311G(d,p)	-348.025697	-348.021809	853
B3LYP/6-311+G(d,p)	-348.029984	-348.026825	693
B3LYP/6-311G(2d,2p)	-348.038211	-348.034417	833
B3LYP/6-311+G(2d,2p)	-348.042254	-348.039141	683
B3LYP/6-311G(2df,2pd)	-348.049398	-348.045607	832
B3LYP/6-311+G(2df,2pd)	-348.053104	-348.050015	678

TABLE 2S. Scaled[a] diagonal force constants from MP2/6-31G(d) *ab initio* calculations for dicyclopropyl ketone.

Stretches ($mdyn \cdot Å^{-1}$)			Bends ($mdyn \cdot Å \cdot rad^{-2}$)		
Parameter	*cis-cis*	*cis-trans*	Parameter	*cis-cis*	*cis-trans*
C=O	11.012	11.081	OC_1C_3	0.721	0.747
C_1–C_3	4.558	4.425	OC_1C_4	0.721	0.692
C_1–C_4	4.558	4.506	$C_3C_1C_4$	0.595	0.692
C_3–$C_{7,8}$	1.780	1.792	$C_1C_3C_{7,8}$	0.841	0.871
C_7–C_8	2.006	2.000	$C_3C_7C_8$,$C_3C_8C_7$	0.651	0.656
C_4–$C_{9,10}$	1.780	1.769	$C_7C_3C_8$	0.714	0.714
C_9–C_{10}	2.006	1.965	$C_1C_4C_{9,10}$	0.841	0.793
C_3–H_5	5.071	5.098	$C_4C_9C_{10}$, $C_4C_{10}C_9$	0.651	0.645
C_4–H_6	5.071	5.080	$C_9C_4C_{10}$	0.714	0.692
C_7–H_{11}, C_8–H_{13}	5.153	5.157	$C_1C_3H_5$	0.301	0.303
C_7–H_{12}, C_8–H_{14}	5.134	5.130	$C_1C_4H_6$	0.301	0.301
C_9–H_{15} C_{10}–H_{17}	5.153	5.141	$C_{7,8}C_3H_5$	0.647	0.659
C_9–H_{16} C_{10}–H_{18}	5.134	5.133	$C_3C_7H_{11}$, $C_3C_8H_{13}$	0.703	0.704
			$C_3C_7H_{12}$, $C_3C_8H_{14}$	0.650	0.651
			$C_8C_7H_{11}$, $C_7C_8H_{13}$	0.638	0.643
			$C_8C_7H_{12}$, $C_7C_8H_{14}$	0.593	0.597
			$C_{9,10}C_4H_6$	0.647	0.693
			$C_4C_9H_{15}$, $C_4C_{10}H_{17}$	0.703	0.649
			$C_4C_9H_{16}$, $C_4C_{10}H_{18}$	0.650	0.647
			$C_{10}C_9H_{15}$, $C_9C_{10}H_{17}$	0.638	0.603
			$C_{10}C_9H_{16}$, $C_9C_{10}H_{18}$	0.593	0.606
			$H_{11}C_7H_{12}$, $H_{13}C_8H_{14}$	0.242	0.242
			$H_{15}C_9H_{16}$, $H_{17}C_{10}H_{18}$	0.242	0.249
			C=O out-of-plane bend	0.533	0.521
			C_1C_3 torsion	0.002	0.003
			C_1C_4 torsion	0.002	0.006

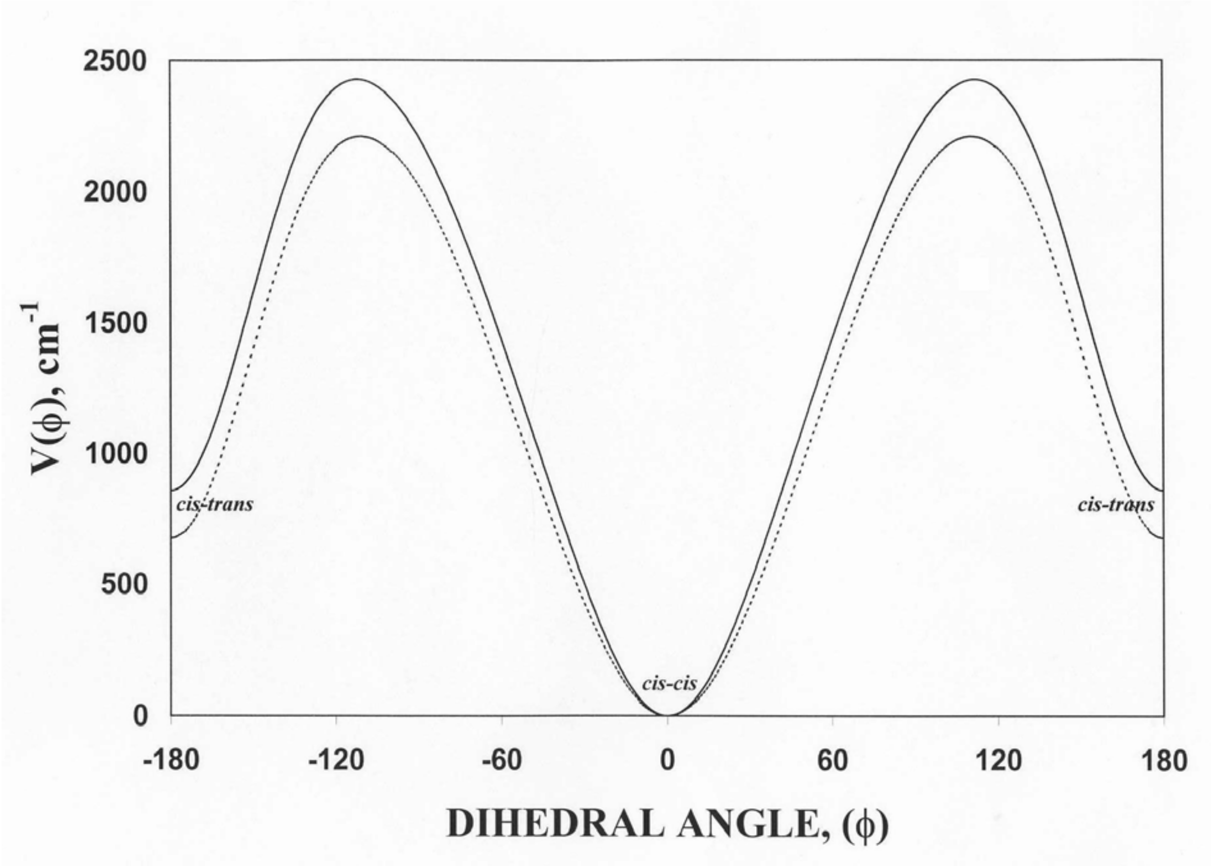
[a] With scaling factors of 0.88 for CH stretches and 0.90 for all other modes.

TABLE 3S. Symmetry coordinates for dicyclopropyl ketone.

cis-*cis* (C_{2v})	*cis*-*trans* (C_s)	Description			Symmetry Coordinate[a]
A_1	A'	CH_2 antisymmetric stretch	S_1	=	$r_3 - r_4 + r_5 - r_6 + r_7 - r_8 + r_9 - r_{10}$
A_1	A'	CH stretch	S_2	=	$r_1 + r_2$
A_1	A'	CH_2 symmetric stretch	S_3	=	$r_3 + r_4 + r_5 + r_6 + r_7 + r_8 + r_9 + r_{10}$
A_1	A'	C=O stretch	S_4	=	R
A_1	A'	CH_2 deformation	S_5	=	$4\varepsilon_1 - \alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 + 4\varepsilon_2 - \beta_1 - \beta_2 - \beta_3 - \beta_4 + 4\varepsilon_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4 + 4\varepsilon_4 - \delta_1 - \delta_2 - \delta_3 - \delta_4$
A_1	A'	CH in-plane bend	S_6	=	$2\xi_1 - \eta_1 - \eta_2 + 2\xi_2 - \theta_1 - \theta_2$
A_1	A'	Ring breathing	S_7	=	$R_3 + R_4 + R_5 + R_6 + R_7 + R_8$
A_1	A'	CC(O)C symmetric stretch	S_8	=	$R_1 + R_2$
A_1	A'	CH_2 wag	S_9	=	$\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \beta_1 + \beta_2 - \beta_3 - \beta_4 + \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 + \delta_1 + \delta_2 - \delta_3 - \delta_4$
A_1	A'	Ring deformation	S_{10}	=	$2R_5 - R_3 - R_4 + 2R_8 - R_6 - R_7$
A_1	A'	CH_2 rock	S_{11}	=	$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \beta_1 - \beta_2 + \beta_3 - \beta_4 + \gamma_1 - \gamma_2 + \gamma_3 - \gamma_4 + \delta_1 - \delta_2 + \delta_3 - \delta_4$
A_1	A'	CH_2 twist	S_{12}	=	$\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \beta_1 - \beta_2 - \beta_3 + \beta_4 + \gamma_1 - \gamma_2 - \gamma_3 + \gamma_4 + \delta_1 - \delta_2 - \delta_3 + \delta_4$
A_1	A'	CC(O)C bend	S_{13}	=	$2\lambda - \kappa_1 - \kappa_2$
A_1	A'	Ring–C in-plane bend	S_{14}	=	$\mu_1 + \mu_2 + \nu_1 + \nu_2$
A_2	A''	CH_2 antisymmetric stretch	S_{15}	=	$r_3 - r_4 - r_5 + r_6 - r_7 + r_8 + r_9 - r_{10}$
A_2	A''	CH_2 symmetric stretch	S_{16}	=	$r_3 + r_4 - r_5 - r_6 - r_7 - r_8 + r_9 + r_{10}$
A_2	A''	CH_2 deformation	S_{17}	=	$4\varepsilon_1 - \alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 - 4\varepsilon_2 + \beta_1 + \beta_2 + \beta_3 + \beta_4 - 4\varepsilon_3 + \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 + 4\varepsilon_4 - \delta_1 - \delta_2 - \delta_3 - \delta_4$
A_2	A''	CH_2 twist	S_{18}	=	$\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 - \beta_1 + \beta_2 + \beta_3 - \beta_4 - \gamma_1 + \gamma_2 + \gamma_3 - \gamma_4 + \delta_1 - \delta_2 - \delta_3 + \delta_4$
A_2	A''	CH out-of-plane bend	S_{19}	=	$\eta_1 - \eta_2 - \theta_1 + \theta_2$
A_2	A''	CH_2 wag	S_{20}	=	$\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 - \beta_1 - \beta_2 + \beta_3 + \beta_4 - \gamma_1 - \gamma_2 + \gamma_3 + \gamma_4 + \delta_1 + \delta_2 - \delta_3 - \delta_4$
A_2	A''	CH_2 rock	S_{21}	=	$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 - \beta_1 + \beta_2 - \beta_3 + \beta_4 - \gamma_1 + \gamma_2 - \gamma_3 + \gamma_4 + \delta_1 - \delta_2 + \delta_3 - \delta_4$
A_2	A''	Ring deformation	S_{22}	=	$R_3 - R_4 - R_6 + R_7$
A_2	A''	Ring–C out-of-plane bend	S_{23}	=	$\mu_1 - \mu_2 - \nu_1 + \nu_2$
A_2	A''	Torsion	S_{24}	=	$\tau_1 + \tau_2$
B_1	A''	CH_2 antisymmetric stretch	S_{25}	=	$r_3 - r_4 - r_5 + r_6 + r_7 - r_8 - r_9 + r_{10}$
B_1	A''	CH_2 symmetric stretch	S_{26}	=	$r_3 + r_4 - r_5 - r_6 + r_7 + r_8 - r_9 - r_{10}$
B_1	A''	CH_2 deformation	S_{27}	=	$4\varepsilon_1 - \alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 - 4\varepsilon_2 + \beta_1 + \beta_2 + \beta_3 + \beta_4 + 4\varepsilon_3 - \gamma_1 - \gamma_2 - \gamma_3 - \gamma_4 - 4\varepsilon_4 + \delta_1 + \delta_2 + \delta_3 + \delta_4$
B_1	A''	CH_2 twist	S_{28}	=	$\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 - \beta_1 + \beta_2 + \beta_3 - \beta_4 + \gamma_1 - \gamma_2 - \gamma_3 + \gamma_4 - \delta_1 + \delta_2 + \delta_3 - \delta_4$

B_1	A″	CH out-of-plane bend	S_{29}	=	$\eta_1 - \eta_2 + \theta_1 - \theta_2$
B_1	A″	CH_2 wag	S_{30}	=	$\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 - \beta_1 - \beta_2 + \beta_3 + \beta_4 + \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 - \delta_1 - \delta_2 + \delta_3 + \delta_4$
B_1	A″	CH_2 rock	S_{31}	=	$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 - \beta_1 + \beta_2 - \beta_3 + \beta_4 + \gamma_1 - \gamma_2 + \gamma_3 - \gamma_4 - \delta_1 + \delta_2 - \delta_3 + \delta_4$
B_1	A″	Ring deformation	S_{32}	=	$R_3 - R_4 + R_6 - R_7$
B_1	A″	C=O out-of-plane bend	S_{33}	=	ω
B_1	A″	Ring–C out-of-plane bend	S_{34}	=	$\mu_1 - \mu_2 + \nu_1 - \nu_2$
B_1	A″	Torsion	S_{35}	=	$\tau_1 - \tau_2$
B_2	A′	CH_2 antisymmetric stretch	S_{36}	=	$r_3 - r_4 + r_5 - r_6 - r_7 + r_8 - r_9 + r_{10}$
B_2	A′	CH_2 symmetric stretch	S_{37}	=	$r_3 + r_4 + r_5 + r_6 - r_7 - r_8 - r_9 - r_{10}$
B_2	A′	CH stretch	S_{38}	=	$r_1 - r_2$
B_2	A′	CH_2 deformation	S_{39}	=	$4\varepsilon_1 - \alpha_1 - \alpha_2 - \alpha_3 - \alpha_4 + 4\varepsilon_2 - \beta_1 - \beta_2 - \beta_3 - \beta_4 - 4\varepsilon_3 + \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 - 4\varepsilon_4 + \delta_1 + \delta_2 + \delta_3 + \delta_4$
B_2	A′	CH in-plane bend	S_{40}	=	$2\xi_1 - \eta_1 - \eta_2 - 2\xi_2 + \theta_1 + \theta_2$
B_2	A′	Ring breathing	S_{41}	=	$R_3 + R_4 + R_5 - R_6 - R_7 - R_8$
B_2	A′	CC(O)C antisymmetric stretch	S_{42}	=	$R_1 - R_2$
B_2	A′	CH_2 twist	S_{43}	=	$\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \beta_1 - \beta_2 - \beta_3 + \beta_4 - \gamma_1 + \gamma_2 + \gamma_3 - \gamma_4 - \delta_1 + \delta_2 + \delta_3 - \delta_4$
B_2	A′	CH_2 wag	S_{44}	=	$\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \beta_1 + \beta_2 - \beta_3 - \beta_4 - \gamma_1 - \gamma_2 + \gamma_3 + \gamma_4 - \delta_1 - \delta_2 + \delta_3 + \delta_4$
B_2	A′	Ring deformation	S_{45}	=	$2R_5 - R_3 - R_4 - 2R_8 + R_6 + R_7$
B_2	A′	CH_2 rock	S_{46}	=	$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \beta_1 - \beta_2 + \beta_3 - \beta_4 - \gamma_1 + \gamma_2 - \gamma_3 + \gamma_4 - \delta_1 + \delta_2 - \delta_3 + \delta_4$
B_2	A′	C=O in-plane bend	S_{47}	=	$\kappa_1 - \kappa_2$
B_2	A′	Ring–C in-plane bend	S_{48}	=	$\mu_1 + \mu_2 - \nu_1 - \nu_2$

[a] Not normalized.



2500
2000
1500
1000
500
0
V(ϕ), cm^{-1}
-180
-120
-60
0
60
120
180
DIHEDRAL ANGLE, (ϕ)
cis-trans
cis-cis
cis-trans

Fig. 1S