

*The role of Aromatic Interactions in the Structure and Energetics of  
Benzyl Ketones*

**(Supplementary Information)**

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**TABLE S1.** Crystal data, data acquisition conditions and refinement parameters for DBK.

<b>Dibenzyl ketone</b>	
empirical formula	C <sub>15</sub> H <sub>14</sub> O
formula weight	$M_r = 210.26 \text{ mol.dm}^{-3}$
temp/K	123 (2) K
$\lambda/\text{\AA}$	0.71073 \AA
crystal system	Monoclinic, P21/c
cell constants	$a = 9.4756(2) \text{ \AA}$ , $b = 5.65970(10) \text{ \AA}$ , $c = 21.2859(3) \text{ \AA}$ , $\beta = 96.4720(10)^\circ$
volume	$V = 1134.27(4) \text{ \AA}^3$
molecules per unit cell, $Z$	4
$D_x$	1.231 Mg m <sup>-3</sup>
$F(000)$	244
crystal size/shape/colour	0.20 × 0.10 × 0.04 mm (Block, yellow)
$\theta$ range for data collection	3.02–30.62°
Cell parameters	from 6687 reflections
Absorption Coefficient	$\mu = 0.075 \text{ mm}^{-1}$
Radiation source:	fine-focus sealed tube
Monochromator:	graphite
$\theta$ range	$\theta_{\min} = 3.1^\circ$ ; $\theta_{\max} = 30.6^\circ$ ; $\omega$ scans
limiting indices	$h = -13 \rightarrow 13$ ; $k = -8 \rightarrow 8$ ; $l = -30 \rightarrow 30$
reflections collected/unique	17359 / 3485; 2653 with $I > 2\sigma(I)$ ; $R_{\text{int}} = 0.033$
Max and Min transmission	$T_{\min} = 0.985$ , $T_{\max} = 0.997$
data/restraints/parameters	3485 / 0 / 145
goodness-off-fit on $F^2$	1.015
final R indices	$R[F^2 > 2\sigma(F^2)] = 0.0432$ ; $wR(F^2) = 0.1067$
final R indices (all data)	$R = 0.0630$ ; $wR(F^2) = 0.1189$
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$	0.32 e \AA <sup>-3</sup> and -0.20 e \AA <sup>-3</sup>
refinement method	full matrix least-squares on $F^2$
CCDC No.	735344

**TABLE S2.** Experimental results<sup>a</sup> for the combustion of DBK, at  $T = 298.15$  K.

	1	2	3	4	5	6	7
$m(\text{cpd.}) / \text{g}$	0.44001	0.46285	0.34269	0.31322	0.46354	0.26343	0.44688
$m'(\text{fuse}) / \text{g}$	0.00249	0.00195	0.00239	0.00264	0.00252	0.00294	0.00259
$T_i / \text{K}$	298.158	298.168	298.154	298.151	298.151	298.189	298.151
$T_f / \text{K}$	299.287	299.351	299.062	298.988	299.337	298.911	299.299
$\Delta T_{\text{ad}} / \text{K}$	1.05220	1.10611	0.82011	0.74970	1.10906	0.63154	1.06944
$\varepsilon_i (\text{cont.}) / (\text{J.K}^{-1})$	14.92	14.95	14.80	14.77	14.95	14.71	14.93
$\varepsilon_f (\text{cont.}) / (\text{J.K}^{-1})$	15.62	15.68	15.34	15.26	15.68	15.12	15.63
$\Delta m(\text{H}_2\text{O}) / \text{g}$	-0.3	-0.3	-0.3	0.0	-1.5	-0.9	-1.9
$-\Delta U(\text{IBP})^a / \text{J}$	16372.91	17211.85	12761.24	11666.55	17252.25	9825.34	16633.99
$\Delta U(\text{HNO}_3) / \text{J}$	0.13	0.17	0.11	0.08	0.33	0.15	0.76
$\Delta U(\text{ignition}) / \text{J}$	1.05	1.07	1.00	1.06	1.10	0.94	1.04
$\Delta U_{\Sigma} / \text{J}$	8.72	9.22	6.64	6.03	9.24	5.01	8.88
$-m' \cdot \Delta_{\text{C}} u^{\circ}(\text{fuse}) / \text{J}$	40.44	31.67	38.81	-42.87	40.92	47.75	42.06
$-\Delta_{\text{C}} u^{\circ}(\text{cpd.}) / \text{J} \cdot \text{g}^{-1}$	37096.22	37096.04	37103.07	37087.28	37107.50	37093.41	37104.31
$-\langle \Delta_{\text{C}} u^{\circ} \rangle^b / \text{J} \cdot \text{g}^{-1} = 37098.26 \pm 2.7$							

<sup>a</sup>  $\Delta U(\text{IBP})$  includes  $\Delta U(\text{ignition})$ ;

$m(\text{cpd.})$  is the mass of compound burnt in each experiment;  $m'(\text{fuse})$  is the mass of the fuse (cotton) used in each experiment;  $T_i$  is the initial temperature rise;  $T_f$  is the final temperature rise;  $\varepsilon_i (\text{cont.})$  is the energy equivalent of the contents in the initial state;  $\varepsilon_f (\text{cont.})$  is the energy equivalent of the contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from 2900.0 g;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ignition})$  is the electric energy for the ignition;  $\Delta U_{\Sigma}$  is the standard state correction;  $\Delta_{\text{C}} u^{\circ}(\text{fuse})$  is the massic energy of combustion of the fuse (cotton) and  $\Delta_{\text{C}} u^{\circ}$  is the standard massic energy of combustion.

<sup>b</sup> Mean value and given error as the standard deviation of the mean.

**TABLE S3.** Experimental results obtained by Calvet microcalorimetry for the sublimation of DBK.

$m_{\text{compound}} /$ mg	$\Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 /$ kJ·mol <sup>-1</sup>	$\langle \Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 \rangle /$ kJ·mol <sup>-1</sup>	$k \cdot \langle \Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 \rangle /$ kJ·mol <sup>-1</sup>	$H_{\text{m}}^0(\text{g}, T) - H_{\text{m}}^0(\text{g}, 298.15 \text{ K}) /$ kJ·mol <sup>-1</sup>
5.26	126.02			
5.66	130.54			
4.61	131.00			
5.61	131.03			
4.80	128.65			
5.12	129.44	128.7 ± 1.3	129.8 ± 2.0	18.2
4.91	130.29			
5.34	126.02			
4.87	125.25			
5.62	128.52			
$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^0 (T = 298.15 \text{ K}) = (111.6 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$				

**TABLE S4.** Experimental results obtained by Calvet microcalorimetry for the vaporization of DBK as a metastable liquid.

$m_{\text{compound}} /$ mg	$\Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 /$ kJ·mol <sup>-1</sup>	$\langle \Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 \rangle /$ kJ·mol <sup>-1</sup>	$k \cdot \langle \Delta_{\text{cr},298.15\text{K}}^{\text{g,T}} H_{\text{m}}^0 \rangle /$ kJ·mol <sup>-1</sup>	$H_{\text{m}}^0(\text{g}, T) - H_{\text{m}}^0(\text{g}, 298.15 \text{ K}) /$ kJ·mol <sup>-1</sup>
5.35	98.53			
5.60	98.54			
5.23	103.95			
5.25	101.85	102.1 ± 1.9	103.0 ± 2.3	18.3
5.16	104.06			
5.34	102.94			
5.90	104.56			
$\Delta_{\text{v}}^{\text{g}} H_{\text{m}}^0 (T = 298.15 \text{ K}) = (84.6 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$				

**TABLE S5.** Calculated energies, in Hartree, for the molecules presented in Scheme 1, at various levels of theory.

	MP2			B3LYP
	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	6-311++G(d,p)
Propanone	-192.577175	-192.616081	-192.774850	-193.218261
Pentan-3-one	-270.941221	-270.992658	-271.220640	-271.867665
Benzyl methyl ketone	-422.914157	-422.988128	-423.324870	-424.323351
Benzyl ethyl ketone	-462.096717	-462.177073	-462.548210	-463.648167
Dibenzyl ketone	-653.255669	-653.370329	-653.880547	-655.428512

**TABLE S6.** Calculated energies, in Hartree, for the PES scan of the benzyl group of DBK (OCCPh dihedral angle), at the MP2/cc-pVDZ level of theory.

$\Phi$ (OCCPh)	$E_{el}$ / Hartree	$\Delta E_{rel}$ / kJ·mol <sup>-1</sup>
0	-653.249687	15.7
20	-653.250569	13.4
40	-653.251675	10.5
60	-653.253747	5.0
70	-653.254535	3.0
80	-653.255445	0.6
90	-653.255649	0.1
92.5	-653.255588	0.2
95	-653.255489	0.5
97.5	-653.255357	0.8
100	-653.255197	1.2
105	-653.254801	2.3
110	-653.255147	1.4
120	-653.255611	0.2
<b>125.323</b>	<b>-653.255669</b>	<b>0.0</b>
140	-653.255324	0.9
160	-653.254177	3.9
180	-653.253185	6.5
200	-653.254177	3.9
220	-653.255324	0.9
<b>234.677</b>	<b>-653.255669</b>	<b>0.0</b>
240	-653.255611	0.2
250	-653.255147	1.4
255	-653.254801	2.3
260	-653.255197	1.2
262.5	-653.255357	0.8
265	-653.255489	0.5
267.5	-653.255588	0.2
270	-653.255649	0.1
280	-653.255445	0.6
290	-653.254535	3.0
300	-653.253747	5.0
320	-653.251675	10.5
340	-653.250569	13.4
360	-653.249687	15.7

**TABLE S7.** Calculated energies, in Hartree, for the PES scan of the benzyl group of BEK (OCCPh dihedral angle), at the MP2/cc-pVDZ level of theory.

$\Phi$ (OCCPh)	$E_{el}$ / Hartree	$\Delta E_{rel}$ / kJ·mol <sup>-1</sup>
0	-462.093779	7.7
5	-462.093968	7.2
10	-462.094167	6.7
20	-462.094468	5.9
25	-462.094555	5.7
35	-462.094634	5.5
40	-462.094661	5.4
50	-462.094791	5.1
55	-462.094929	4.7
65	-462.095386	3.5
70	-462.095683	2.7
80	-462.096277	1.2
90	-462.096277	1.2
<b>95.643</b>	<b>-462.096716</b>	<b>0.0</b>
100	-462.096684	0.1
110	-462.096418	0.8
125	-462.096013	1.8
140	-462.095651	2.8
155	-462.095007	4.5
170	-462.094333	6.3
180	-462.094160	6.7
190	-462.094333	6.3
205	-462.095007	4.5
220	-462.095651	2.8
235	-462.096013	1.8
250	-462.096418	0.8
260	-462.096684	0.1
<b>264.357</b>	<b>-462.096717</b>	<b>0.0</b>
270	-462.096277	1.2
280	-462.096277	1.2
290	-462.095683	2.7
295	-462.095386	3.5
305	-462.094929	4.7
310	-462.094791	5.1
320	-462.094661	5.4
325	-462.094634	5.5
335	-462.094555	5.7
340	-462.094468	5.9
350	-462.094167	6.7
355	-462.093968	7.2
360	-462.093779	7.7

**TABLE S8.** Calculated energies, in Hartree, for the PES scan of the ethyl group of BEK (OCCCH<sub>3</sub> dihedral angle), at the MP2/cc-pVDZ level of theory.

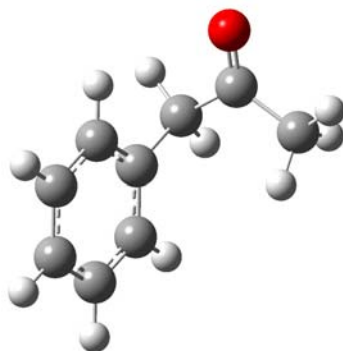
$\Phi$ (OCCCH <sub>3</sub> )	$E_{el}$ / Hartree	$\Delta E_{rel}$ / kJ·mol <sup>-1</sup>
<b>0</b>	<b>-462.096717</b>	<b>0.0</b>
30	-462.095971	2.0
60	-462.094890	4.8
90	-462.093756	7.8
120	-462.093808	7.6
150	-462.092657	10.7
180	-462.091525	13.6
210	-462.093217	9.2
240	-462.093761	7.8
270	-462.094026	7.1
300	-462.093870	7.5
330	-462.095280	3.8
<b>360</b>	<b>-462.096717</b>	<b>0.0</b>

**TABLE S9.** Peak list of <sup>1</sup>H-NMR signals for dibenzyl ketone at various  $T$ .

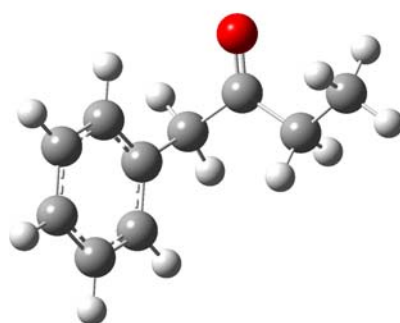
$T$ / K	$\delta_{CH_2}$ / ppm	$\delta_{ortho}$ / ppm	$\delta_{meta}$ / ppm	$\delta_{para}$ / ppm
192.5	3.888	7.188	7.351	7.288
201.3	3.878	7.186	7.346	7.284
211.5	3.868	7.184	7.342	7.280
221.3	3.858	7.181	7.338	7.276
230.7	3.851	7.178	7.335	7.272
241.8	3.842	7.175	7.330	7.268
252.9	3.834	7.172	7.326	7.263
264.3	3.826	7.168	7.321	7.259
275.9	3.819	7.165	7.317	7.255
290.5	3.811	7.161	7.312	7.251
301.0	3.806	7.159	7.309	7.247
307.9	3.802	7.157	7.307	7.245
314.1	3.800	7.156	7.305	7.244
321.3	3.797	7.155	7.303	7.241
327.5	3.794	7.153	7.301	7.240
331.1	3.793	7.153	7.300	7.239

**TABLE S10.** Peak list of <sup>1</sup>H-NMR signals for benzyl ethyl ketone at various  $T$ .

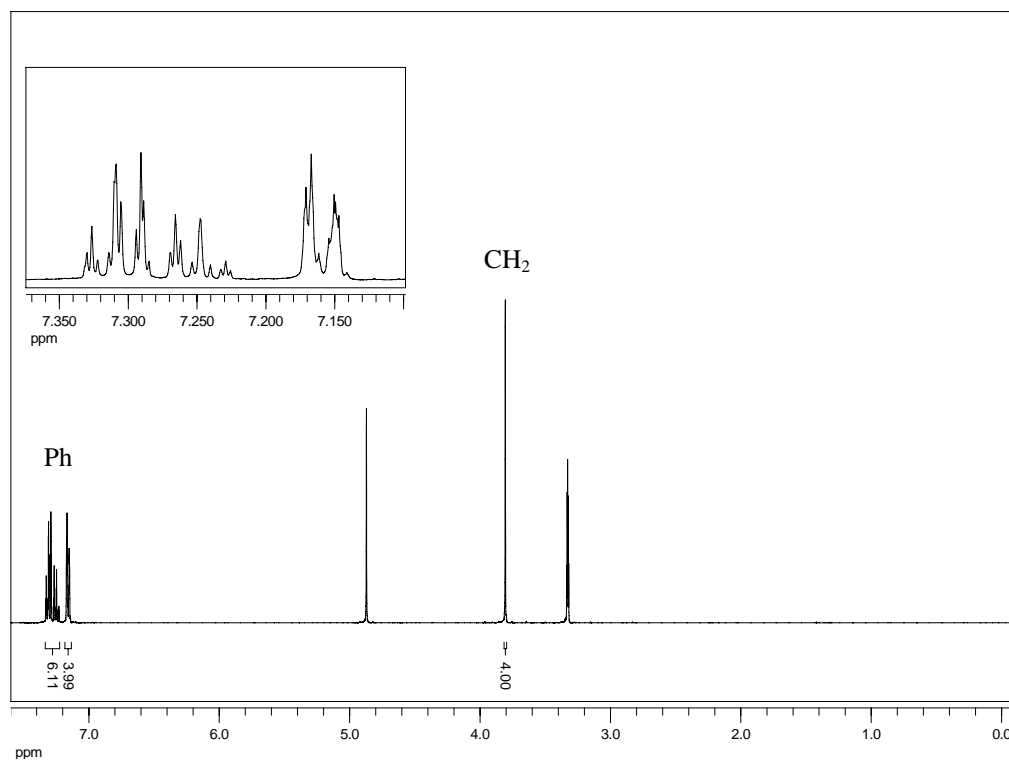
$T$ / K	$\delta_{CH_2}$ / ppm	$\delta_{CH_2(CH_3)}$ / ppm	$\delta_{CH_3}$ / ppm	$\delta_{ortho}$ / ppm	$\delta_{meta}$ / ppm	$\delta_{para}$ / ppm
192.2	3.766	2.594	0.966	7.216	7.347	7.279
202.0	3.762	2.587	0.971	7.218	7.344	7.275
215.5	3.758	2.578	0.976	7.218	7.340	7.270
226.1	3.754	2.571	0.978	7.217	7.336	7.266
241.8	3.750	2.561	0.984	7.217	7.332	7.260
252.9	3.747	2.554	0.987	7.216	7.329	7.257
270.5	3.741	2.543	0.991	7.213	7.324	7.252
282.6	3.738	2.537	0.994	7.212	7.321	7.248
292.1	3.735	2.532	0.997	7.210	7.318	7.246
301.6	3.733	2.527	0.999	7.209	7.316	7.262
314.6	3.730	2.522	1.001	7.207	7.313	7.259
315.6	3.729	2.520	1.001	7.207	7.312	7.258
328.3	3.727	2.516	1.004	7.206	7.311	7.256



**Figure S1.** Optimized geometry of benzyl methyl ketone (BMK) at the MP2/cc-pVDZ.

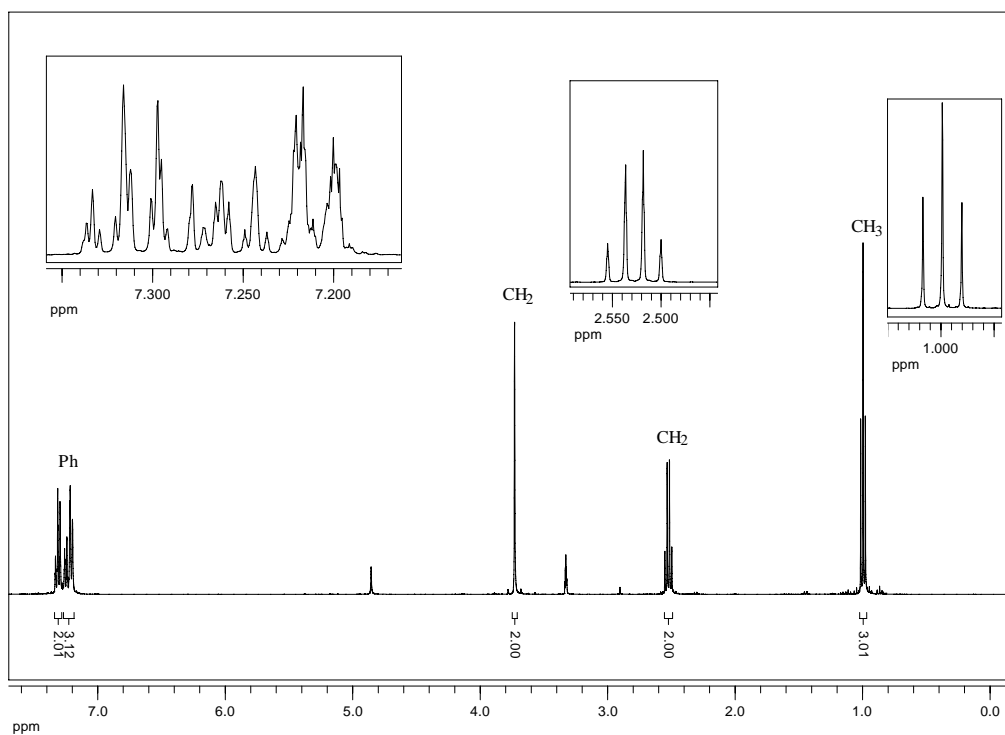


**Figure S2.** Optimized geometry of benzyl ethyl ketone (BEK) at the MP2/cc-pVDZ.



**Figure S3.**  $^1\text{H}$ -NMR spectrum of DBK in  $\text{MeOD-}d_4$  at 298 K.





**Figure S4.**  $^1\text{H-NMR}$  spectrum of BEK in  $\text{MeOD-}d_4$  at 298 K.