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Supplementary Material

Probe Intramolecular Hydrogen Bonding of Stereoisomers Using Computational Spectroscopy

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Table S1 Comparative performance evaluation of quantum mechanical methods for geometric (Å) and energy (kcal·mol^{-1}) properties of in Fc comformers.

Model	Fe-Cp (Δ)*	Fe-C (Δ)*	C-C (Δ)*	C-H (Δ)*	ΔE[a]
B3LYP[b]	1.670 (0.010)	2.065 (0.001)	1.428 (0.012)	1.082 (0.022)	0.58 (35.5)
HF[b]	1.852 (0.192)	2.206 (0.142)	1.41 (0.030)	1.072 (0.027)	-0.01 (101.1)
MP2[b]	1.484 (0.176)	1.924 (0.140)	1.441 (0.001)	1.084 (0.020)	2.40 (166.7)
MP2(Full)[b]	1.457 (0.203)	1.905 (0.159)	1.443 (0.003)	1.084 (0.020)	1.11 (23.3)
M06-2X[b]	1.734 (0.074)	2.113 (0.049)	1.420 (0.020)	1.081 (0.023)	0.08 (91.1)
CAM-B3LYP[b]	1.656 (0.004)	2.051 (0.013)	1.422 (0.018)	1.081 (0.023)	0.60 (33.3)
HF[c][66]	1.865 (0.205)	2.219 (0.155)	1.413 (0.027)	1.074 (0.030)	0.10 (88.9)
MP2[d][23]	1.465 (0.195)	1.91 (0.154)	1.441 (0.001)	1.076 (0.028)	4.58 (408.9)
CCSD(T)[d] [23]	1.655 (0.005)	2.056 (0.008)	1.433 (0.007)	1.077 (0.027)	1.15 (27.8)
Exp[67]	1.660	2.064±0.003	1.440±0.002	1.104±0.006	0.9 ±0.3

*The values within parenthesis indicate the absolute deviation from experimental valuees for bond lengths, or percentage (%) deviation for ΔE.

[a] ΔE = Etot(D5d) - Etot (D5h) in kcal·mol^{-1}.

[b]m6-31G(d); [c]DZP; [d]TZV2P+f basic set.

Table S2 Density functional effects with dispersion correction in energy differences ($\Delta(\Delta E_{e\text{-}s})$)* of gas and solution phase of Fc (kcal·mol^{-1}).

Model[a]	gas	CCl_4
B3LYP	-0.58	-0.54
B3LYP-D3	-0.10	-0.50
CAM-B3LYP	-0.60	-0.52
CAM-B3LYP-D3	-0.58	-0.53

* Energy difference, $\Delta(\Delta E_{e\text{-}s}) = \Delta(\Delta E(D_{5h} - D_{5d}))$.
[a] Using m6-31G(d) basic set. PCM solvation model.

Table S3 Comparison of selected calculated properties of eclipsed and staggered Fc conformers using PCM in different solvents.[a]

Fc (D_{5h})	Fe-C_5 (Å)	Fe-C (Å)	C-C (Å)	C-H (Å)	C_5-H (°)	ΔE(s-g)[b]	ν_1 (cm^{-1})	α[c]
ACN	1.670	2.066	1.429	1.083	0.70	-2.34	-12.7	148.41
DCM	1.670	2.066	1.429	1.083	0.70	-1.93	-12.5	141.71
THF	1.670	2.066	1.429	1.083	0.69	-1.83	-11.6	140.11
CCl_4	1.670	2.066	1.429	1.082	0.68	-0.87	16.1	123.73
DOX	1.670	2.066	1.429	1.082	0.68	-0.86	16.2	123.59
HEX	1.670	2.065	1.428	1.082	0.66	-0.69	-15.9	120.53
Gas[7]	1.670	2.065	1.428	1.082	0.66	-	17.3	107.90
Fc (D_{5d})	Fe-C_5 (Å)	Fe-C (Å)	C-C (Å)	C-H (Å)	C_5-H (°)	ΔE(s-g)[b]	ν_1(cm^{-1})	α[c]
ACN	1.675	2.070	1.429	1.083	0.98	-2.25	-14.3	148.76
DCM	1.675	2.070	1.429	1.083	0.97	-1.90	-13.0	142.05
THF	1.675	2.070	1.429	1.083	0.97	-1.81	-12.9	140.44
CCl_4	1.674	2.068	1.429	1.083	0.95	-0.91	-26.0	123.85
DOX	1.674	2.068	1.429	1.083	0.95	-0.90	-26.0	123.71
HEX	1.674	2.068	1.428	1.083	0.95	-0.74	-26.6	120.74
Gas[7]	1.674	2.068	1.428	1.082	0.92	-	-29.9	108.04

[a]This work. Basis sets, m6-31G(d) for Fe, 6-31G(d) for others using PCM model**.**

[b]$\Delta E(s\text{-}g) = E_{tot}(sol) - E_{tot}(gas)$ in $kcal \cdot mol^{-1}$.

[c]Polarizability.

Table S4 Comparison of measured and calculated IR frequencies of Fc conformers in CCl_4 solution and the assignment in the entire IR region up to 3300 cm^{-1}.*

D_{5h} (gas)		D_{5h} (CCl_4)	D_{5d} (gas)		D_{5d} (CCl_4)	Fc (CCl_4)	Assig.
Mode No	υ(I)[8],$ Sym.	υ(I) $ Sym.	Mode No	υ(I)[8],$ Sym.	υ(I) $ Sym.	Exp[34],e	
2,3	166 (0.63), e_1'	164 (1.33), ?a	2,3	156 (0.45), e_{1u}	155 (0.82), a_{2u}	170 (m)	FeCp bending
7	471 (17.75), a_2''	469 (23.15), a_2''	7,8[g]	459 (25.54), e_{1u}	458[g] (33.28), ?b	478 (s)	ν FeCp
8,9	488 (22.30), e_1'	487 (28.01), e_1'	9[h]	461 (17.39), a_{2u}	460[h] (22.73), ?b	492 (s)	ηFeCp
18	844(60.31), a_2''	844(76.59), ?b	18	848 (60.85), a_{2u}	848 (76.99), ?d	811 (s)	ωCH
22,23	870 (1.58), e_1'	869 (1.39), ?c	22,23	871 (1.92), e_{1u}	869 (1.68), ?d	834 (w)	asym. ωCH
30,31	1035 (17.04), e_1'	1032 (23.21), e_1'	30,31	1035 (16.29), e_{1u}	1034 (22.52), e_{1u}	1002 (s)	βCCH
37	1141(20.23), a_2''	1137(27.52), a_2''	36	1139 (20.46), a_{2u}	1138 (27.70), a_{2u}	1108 (s)	δCp
46,47	1470 (1.55), e_1'	1467 (1.62), e_1'	44,45	1469 (1.37), e_{1u}	1468 (1.41), e_{1u}	1411 (s)	βCCH, νCC
54,55	3257 (23.63), e_1'	3257 (28.94), ?c	54,55	3256 (23.88), e_{1u}	3256 (29.90), ?f	3085 (s)	νCH
56	3268 (2.75), a_2''	3268 (3.50), a_2''	57	3267 (2.54), a_{2u}	3267 (3.27), ?f		νCH

*ν= stretch; δ=breathing; γ= asym. stretch; β=in plane bending; ω=out of plane bending; η=MCp tilting; The question marks ? refer to certain distortions without being assigned to a particular symmetry. The PCM solvent model is employed in the simulation.

$ υ(cm^{-1}) (I($km \cdot mol^{-1}$))

e w = weak, m = medium, s = strong.

g Assignment differs from D_{5h} and is ν FeCp here.

h Assignment differs from D_{5h} and is ring tilt here.

Cartesian Coordinates (in Å) for the compounds in this article (global minimum structures unless stated):

Ferrocene (Fc, gas phase)

Fc Eclipsed conformer (D5h Opt B3LYP/m6-31G(d))

Fe	0.00000000	0.00000000	0.00000000
C	0.00000000	1.21485700	1.66956500
C	-0.71407500	-0.98284000	1.66956500
C	0.71407500	-0.98284000	1.66956500
C	1.15539800	0.37541100	1.66956500
C	-1.15539800	0.37541100	1.66956500
C	0.00000000	1.21485700	-1.66956500
C	-0.71407500	-0.98284000	-1.66956500
C	0.71407500	-0.98284000	-1.66956500
C	1.15539800	0.37541100	-1.66956500
C	-1.15539800	0.37541100	-1.66956500
H	0.00000000	2.29720800	1.65953100
H	-1.35026500	-1.85848000	1.65953100
H	1.35026500	-1.85848000	1.65953100
H	2.18477500	0.70987600	1.65953100
H	-2.18477500	0.70987600	1.65953100
H	0.00000000	2.29720800	-1.65953100
H	-1.35026500	-1.85848000	-1.65953100
H	1.35026500	-1.85848000	-1.65953100
H	2.18477500	0.70987600	-1.65953100
H	-2.18477500	0.70987600	-1.65953100

Fc Staggered conformer (D5d Opt B3LYP/m6-31G(d))

Fe	0.00000000	0.00000000	0.00000000
C	-0.71407200	-0.98283600	1.67361400
C	0.71407200	0.98283600	-1.67361400
C	0.00000000	1.21485200	1.67361400
C	-1.15539300	0.37541000	1.67361400
C	1.15539300	0.37541000	1.67361400
C	0.71407200	-0.98283600	1.67361400
C	1.15539300	-0.37541000	-1.67361400
C	0.00000000	-1.21485200	-1.67361400
C	-1.15539300	-0.37541000	-1.67361400
C	-0.71407200	0.98283600	-1.67361400
H	0.00000000	2.29721300	1.65952200
H	-2.18477900	0.70987800	1.65952200
H	2.18477900	0.70987800	1.65952200
H	-1.35026800	-1.85848400	1.65952200
H	1.35026800	-1.85848400	1.65952200
H	2.18477900	-0.70987800	-1.65952200
H	0.00000000	-2.29721300	-1.65952200
H	1.35026800	1.85848400	-1.65952200
H	-2.18477900	-0.70987800	-1.65952200
H	-1.35026800	1.85848400	-1.65952200

GUA (2-MP) (AS, B3LYP/6-311++G(d,p), gas phase)

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z

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1 6 0 0.168543 2.845857 0.000000

2 8 0 -0.630480 1.668360 0.000000
3 6 0 0.000000 0.446701 0.000000
4 6 0 1.373869 0.235572 0.000000
5 6 0 -0.884084 -0.648333 0.000000
6 6 0 1.873227 -1.071832 0.000000
7 6 0 0.999798 -2.152940 0.000000
8 6 0 -0.380814 -1.941256 0.000000
9 8 0 -2.231636 -0.440200 0.000000
10 1 0 -0.528609 3.682044 0.000000
11 1 0 0.797420 2.894807 0.894794
12 1 0 0.797420 2.894807 -0.894794
13 1 0 2.059650 1.072753 0.000000
14 1 0 2.944882 -1.231496 0.000000
15 1 0 1.384891 -3.165869 0.000000
16 1 0 -1.079275 -2.769620 0.000000
17 1 0 -2.382680 0.514686 0.000000

Mequinol (4-MP) (AS, B3LYP/6-311++G(d,p), gas phase)

Center Atomic Atomic Coordinates (Angstroms)
Number Number Type X Y Z
---

1 6 0 -0.004455 0.018012 0.000956
2 8 0 0.000049 0.024295 1.419590
3 6 0 1.207965 0.002015 2.065303
4 6 0 1.153690 -0.003371 3.464467
5 6 0 2.448986 -0.021527 1.430945
6 6 0 2.317975 -0.019682 4.215842
7 6 0 3.621715 -0.050881 2.193849
8 6 0 3.564085 -0.023738 3.582472
9 8 0 4.682463 -0.108973 4.380743
10 1 0 0.467425 -0.887267 -0.398097
11 1 0 0.501796 0.900822 -0.406340
12 1 0 -1.052194 0.036996 -0.295211
13 1 0 0.183177 0.007333 3.945709
14 1 0 2.527259 -0.029907 0.352217
15 1 0 2.279133 -0.024421 5.298429
16 1 0 4.582680 -0.092584 1.689863
17 1 0 5.437415 0.272878 3.921116

Furfural (B3LYP/6-311++G(d,p), gas phase)

O -0.63351 -1.10871 0.00015

O 2.59441 0.35923 -0.00007
C 0.27738 -0.07934 0.00013
C -0.38534 1.12027 0.00021
C -1.77385 0.81473 -0.00025
C -1.86202 -0.54866 0.00004
C 1.68562 -0.44574 -0.00014
H 0.08353 2.09113 0.00046
H -2.60028 1.50734 -0.00044
H -2.69449 -1.23276 -0.00034
H 1.87326 -1.5375 -0.00026