Electronic supplementary information for

Structures of the Conformational Isomers and Polymorph Modifications of N-substituted 2,6-(E,E)-bis(ferrocenylidene)piperid-4-ones: photo- and electrochemically induced E/Z isomerization

Alexander S. Romanov,[a,b]* Alexey V. Shapovalov,[a] Gary F. Angles,[b] Tatiana V. Timofeeva,[b] Maddalena Corsini,[c] Stefania Fusi,[c] and Fabrizia Fabrizi de Biani [c,]*

[a]Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation,
[b]Department of Natural Sciences, New Mexico Highlands University, Las Vegas, New Mexico 87701,
[c] Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, 53100 Siena, Italy

Table S1. ^{1}H NMR data of the compounds **1**–**4** (300 MHz, CD_2Cl_2, δ in ppm) and their protonated forms (300 MHz, CD_2Cl_2, δ in ppm)

Compound	C_5H_5	C_5H_4	CH_2	CH	NR (R = H, Me, Et, CH_2Ph)
1	4.17 s (10H)	4.50 br t (4H), J = 1.2 Hz 4.54 br t (4H), J = 1.2 Hz	3.94 br s (4H)	7.52 s (2H)	1.97 br s (1H, NH)
2	4.22 s (10H)	4.55 br s (4H) 4.51 br s (4H)	3.68 br s (4H)	7.60 s (2H)	2.56 br s (3H, NMe)
3	4.18 s (10H)	4.51 t (4H), J = 1.8 Hz 4.45 t (4H), J = 1.8 Hz	3.61 br d (4H), J = 1.5 Hz	7.52 s (2H)	2.66 quad (2H, $NC\underline{H}_2$), J = 6.9 Hz 1.18 t (3H, $NCH_2C\underline{H}_3$), J = 6.9 Hz

4	4.05 s (10H)	4.42-4.40 overlapping m (8H)	3.63 br d (4H), J = 1.5 Hz	7.50 s (2H)	3.78 s (2H, NC<u>H</u>$_2$Ph), 7.45-7.42 m (2H, NCH$_2$Ph, meta) 7.38-7.33 m (2H, NCH$_2$Ph, ortho) 7.30-7.24 m (1H, NCH$_2$Ph, para)
2·HBF$_4$	4.85 s (10H)	5.72 br s (4H) 5.25 br s (4H)	4.46 br s (4H)	8.24 s (2H)	7.68 (br s, NH), 3.15 br s (3H, NMe)
3·HBF$_4$	4.30 s (10H)	4.66 br s (4H) 4.46 br s (4H)	4.73 br s (2H) 4.57 br s (2H)	7.97 s (2H)	8.56 (br s, NH), 3.21 br s (2H, NC<u>H</u>$_2$), 1.30 br s (3H, NCH$_2$C<u>H</u>$_3$)
4·HBF$_4$	4.98 s (10H)	5.84 br s (4H) 5.31 br s (4H)	4.71 br s (2H) 4.51 br s (2H)	7.96 s (2H)	7.73 (br s, NH), 4.32 s (2H, NC<u>H</u>$_2$Ph), 7.56 br s m (5H, NCH$_2$Ph)

Table S2. ^{13}C NMR data of the compounds **1**, **2**, **3**, and **4** (75 MHz, CD_2Cl_2, δ in ppm)

Compound	**1**	**2**	**3**	**4**
C_5H_5	69.83	69.83	69.68	69.80
C_5H_4	71.54 71.38	71.52 71.42	71.36 71.19	71.48 71.28
C_{ipso}Fc	79.13	78.75	78.87	78.78
CH=	135.76	137.02	136.06	136.22
CH_2	48.11	56.53	54.42	55.09
C	132.07	129.43	130.40	138.62
NR	–	45.38 (R = Me)	51.77 (R = N<u>C</u>H$_2$CH$_3$)	62.85 (R = <u>C</u>H$_2$Ph)

			12.61 (R = $NCH_2\underline{C}H_3$)	130.67, 129.43, 128.79, 127.70 (R = $CH_2\underline{Ph}$)
C=O	185.68	184.36	185.14	185.19

Table S3. Crystal data, data collection and structure refinement parameters for **2**, **3** and salts **2**·HBF_4 and **4**·HBF_4.

	2	**3**	**2**·HBF_4 (Triclinic)	**2**·HBF_4 (Monoclinic)	**4**·HBF_4
Empirical formula	$C_{28}H_{27}Fe_2NO$	$C_{29}H_{29}Fe_2NO$	$C_{28}H_{28}BF4Fe_2NO$	$C_{28}H_{28}BF4Fe_2NO$	$C_{34}H_{32}BF_4Fe_2NO$
Molecular weight	505.21	519.23	593.02	593.02	669.12
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*$P2_1$*	*$P2_1$*	*P-1*	*$P2_1/c$*	*C2/c*
Crystal color, habit	red, plate	red, plate	black, plate	black, prism	black, plate
Crystal size (mm)	0.29 × 0.23 × 0.06	0.17 × 0.11 × 0.05	0.21 × 0.26 × 0.42	0.29 × 0.31 × 0.49	0.09 × 0.15 × 0.20
a (Å)	5.9820(7)	6.012(3)	12.7933(6)	15.2280(8)	29.902(4)
b (Å)	12.7479(15)	12.956(6)	13.4321(7)	14.2504(8)	7.6059(11)
c (Å)	14.4154(17)	14.400(7)	15.0676(8)	11.8362(6)	28.606(5)
α (°)	90	90	107.1180(10)	90	90

β (°)	95.467(3)	94.957(8)	91.0530(9)	110.2650(10)	110.776(3)
γ (°)	90	90	93.3580(10)	90	90
V (Å^3)	1094.3(2)	1117.6(9)	2468.6(2)	2409.5(2)	6082.7(15)
Z	2	2	4	4	8
D_{calc} (g cm^{-3})	1.533	1.543	1.596	1.635	1.461
$2\theta_{max}$ (°)	28.00	26.00	28.00	26.00	26.00
Abs. coeff., μ(Mo-Kα) (cm^{-1})	1.347	1.321	1.229	1.259	1.007
Absorption correction			SADABS		
T_{max}/T_{min}	0.9235/0.6960	0.9369/0.8066	0.7824/0.6263	0.7116/0.5774	0.9148/0.8240
Number of collected reflections	16333	10471	28268	22825	5979
Number of independent reflections	5221	4391	11899	4739	5810
Number of observed reflections (I > 2σ(I))	4956	3235	9556	4128	3572
R_{int}	0.0250	0.0866	0.0258	0.0262	N/A
Number of parameters	289	292	705	326	361

R_1 (on F for observed reflexions)[a]	0.0389	0.0556	0.0620	0.0355	0.0663
wR_2 (on F^2 for all reflexions)[b]	0.1016	0.1331	0.1694	0.0980	0.1765
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$				
A	0.05	0.54	0.08	0.05	0.085
B	2.2	0.01	8.1	3.5	15.0
F(000)	524	540	1216	1216	2752
GOF	1.002	1.012	1.021	1.050	1.099
$\Delta\rho_{max}/\Delta\rho_{max}$ (e Å^{-3})	1.388/–0.584	1.091/–0.884	1.678/–1.420	1.202/–0.558	1.044/–1.431

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma(F_o)$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

Table S4. Intermolecular and intramolecular hydrogen bonds (Å, °) found for **2**, **3** and salts **2**·HBF_4 and **4**·HBF_4.

Compound	D–H···A	d(D–H)	d(H···A)	d(D···A)	DHA
2	C27A–H27A[a]···O1	1.00	2.34	3.237(4)	149.3(2)
3	C27A–H27A[a]···O1	1.00	2.40	3.279(8)	145.9(5)
	C7B–H7B[b]···O1	1.00	2.70	3.603(8)	156.4(5)
	C14C–H14C[c]···N1	1.00	2.60	3.562(7)	162.0(5)
2·HBF_4 (Monoclinic)	N1A–H1A[d]···O1	0.98(5)	1.88(5)	2.837(5)	163.0(3)

	C3–H3A···F1	1.00	2.42	3.279(5)	145.3(4)
	C3–H3A···F4	1.00	2.66	3.405(6)	132.4(4)
	C6A–H6A[e]···F3	1.00	2.40	3.335(6)	168.2(5)
	C17–H17A···F3	1.00	2.39	3.293(6)	149.2(5)
	C26–H26A···F4	1.00	2.51	3.452(6)	156.4(5)
2·HBF_4 (Triclinic)	N1A–H1A···F5	0.93(7)	1.88(7)	2.808(7)	176.1(6)
	C3A–H3AB···F2	1.00	2.41	3.261(7)	143.1(6)
	C3A–H3AB···F4	1.00	2.43	3.333(7)	150.7(6)
	C4–H4AA···F4	1.00	2.46	3.354(8)	149.7(6)
	C15A–H15A···F8	1.00	2.62	3.298(5)	125.2(5)
	C25A–H25B···F5	1.00	2.62	3.563(5)	156.8(5)
	N1B–H1B···O1AB[f]	0.92(7)	2.01(7)	2.706(5)	130.5(6)
	N1B–H1B···F8A[f]	0.92(7)	2.36(7)	2.960(5)	122.7(6)
	C3B–H3BB···F1[f]	1.00	2.34	3.244(6)	150.9(6)
	C4B–H4BA···F8[f]	1.00	2.40	2.987(6)	117.4(6)
	C7B–C7BA···F6	1.00	2.24	3.160(6)	155.9(6)
	C18B–H18B···F1	1.00	2.43	3.120(7)	125.4(6)
4·HBF_4	N1–H1A···F4A[g]	0.93(5)	1.55(5)	2.466(9)	167.2(7)
	C28–H28A···F4[g]	1.00	2.45	3.375(10)	148.4(7)
	C7–H7A···F1	1.00	2.17	2.913(11)	130.7(7)
	C3–H3A···F3	1.00	2.06	2.941(9)	147.4(7)

Symmetry transformations used to generate equivalent atoms: [a] = 1 + x, y, z; [b] = 2 – x, –1/2 + y, – z; [c] = 2 – x,1/2 + y, – z; [d] = – x,1 – y, 1 – z; [e] = x, 3/2 – y, 1/2 + z; [f] = x, 1 + y, z; [g] = x, –1 + y, z.