On the incidence of non-covalent intramolecular interligand interactions on the conformation of carbene complexes: a case study

Noël Lugan,[ab*] **Israel Fernández,**[c*] **Rémy Brousses,**[ab] **Dmitry A. Valyaev,**[abd] **Guy Lavigne**[ab] **and N. A. Ustynyuk**[d]

Supplementary Information

Experimental section

X-ray Diffraction Studies. A parallelipedic-shaped yellow crystal of **2** of dimensions 0.40 x 0.40 x 0.35 mm^3 was mounted on a on a Bruker D8 diffractometer equiped with APEX II detector and an Oxford Cryosystem N_2 gas stream low-temperature device. Graphite-monochromatized Mo K_α radiation was used for collecting diffraction data at a temperature of T = 100(±1) K. The frames were reduced using the APEX2 suite of programs.[1S] Semi-empirical absorption corrections using spherical harmonics were applied using the SADABS procedure as implemented in APEX2. The resulting 168793 reflections (<redundancy> = 9) were merged in Laue group *2/m* with the use of the program SORTAV[2S] to give 17253 unique reflections up to a resolution S of 1.21 $Å^{-1}$ (R_{int} = 0.0246) providing 94.6 % of data 2.7° < θ < 68.4°. The multipolar refinement was conducted on a complete data set by limiting the resolution to S = 1.1 $Å^{-1}$. Other crystallographic and data collection details are given in Table 2S.

In a first step, the crystal structure was solved using SIR92,[3S] then refined in a classical manner by full matrix least-squares on F^2 using the SHELX program.[4S] Details of this initial refinement are given in Table 2S. Subsequent multipole refinement was carried out within the Hansen-Coppens formalism[5S] using the MoPro package.[6S] The positions for the hydrogen atoms were allowed to vary in a restrained model as implemented in MoPro [Csp^2−H = 1.083 Å ; Csp^3−H = 1.093 Å], whereas their anisotropic temperature factors were estimated by the method of Madsen[7S] using the SHADE2 web server[8S] and held fixed during the multipolar refinement procedure. An electroneutrality constraint was systematically applied. The multipole expansion was truncated at the hexadecapole level (l_{max} = 4) for Mn and at the octupole level (l_{max} = 3) for C and O atoms. A H−C bond directed dipole (l_{max} = 2) was introduced for the hydrogen atoms. The positions and the thermal parameters for non-hydrogen atoms were first refined using high resolution data only (1.1 > S > 0.7 $Å^{-1}$). Then the valence electron density was fitted using low resolution data only (S < 0.7 $Å^{-1}$) in successive cycles on P_v, κ, $P_{lm\pm}$ and κ' parameters, until convergence was reached. For Mn, the multipoles were allowed to refine assuming $3d^5$ valence configuration, the 4s electrons being set in the core. Two sets of κ/κ' for the two type of chemically different O atoms (Mn−C*O*, *O*Et) and four sets of κ/κ' for the four type of chemically different C atoms (Mn−*C*O, Mn=*C*, C_5H_5, Csp^3) were used and refined. The κ' parameters for the hydrogen atoms were fixed to 1.2. In the final cycles of refinement, all parameters were allowed to vary (within the limits of the above constraints and restraints), with data for which I > 3σ(I), truncated at 1.1 $Å^{-1}$.

The Hirshfeld rigid bond test[9S] is respected for all light atoms-light atoms bonds, all Δ(msda) values being less than 1.0 x 10^{-3} Å^2. The Mn-C bonds, however, do not totally fulfil the Hirshfield criterion. The Δ(msda) for the Mn-$C_{Cp\ ring}$ were actually found in a 1.6-2.0 x 10^{-3} Å^2 range, while for the Mn-Ccarbene bond and the two Mn-CO bonds, values were 1.2 x 10^{-3} Å^2, and 1.0.10-3 10^{-3} Å^2, respectively. Attempts to improve those values by introducing anharmonic thermal parameters for Mn remained inconclusive, so these were not considered further.

Final multipolar parameters for complex **2** are given in Table 5S. The kinetic energy densities values $G(\rho)$ given in that table were estimated using the approximation of Abramov,[10S] while the corresponding potential energy densities values $V(\rho)$ were obtained from the local virial theorem, $V(\rho) = 1/4\ \nabla^2\rho(r) - 2G(\rho)$.

The analysis of the topology of the electron density was carried out using WinXPro program package.[11S] Topological parameters at selected bond critical points in **2** are shown in Table 6S, along with those resulting from the analysis of the theoretical ED distribution.

Computational Details. All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[12S] Dispersion-corrected meta-hybrid M06L functional, which has been recommended to account for weak interactions,[13S] in combination with the triple-ξ quality plus two sets of polarization functions def2-TZVPP[14S] basis set for all atoms have been used. All complexes were characterized by frequency calculations,[15S] and have positive definite Hessian matrices.

Donor-acceptor interactions were computed using the natural bond orbital (NBO)[16S] method. The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi^*} = -n_\phi \frac{\left\langle \phi^* \left| F \right| \phi \right\rangle^2}{\varepsilon_{\phi^*} - \varepsilon_\Phi}$$

where F is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled Natural Bond Orbitals having ε_ϕ y ε_{ϕ^*} and energies, respectively; n_ϕ stands for the occupation number of the filled orbital.

Wavefunctions for AIM calculations for **2** were computed at the M06L/def2-TZVPP level using the gas-phase fully optimized geometry at the M06L/def2-TZVPP level.

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Table 1S. Crystal Data and Details of the Structure Determination for Complex **2**.

Crystal data	
Complex	**2**
Empirical formula	$C_{12}H_{15}MnO_3$
M_r	262.175
T/ K	100
λ /Å	0.71069
Crystal system	monoclinic
Space group (no.)	$P2_1/c$ (#14)
a/ Å	11.1515(2)
b/ Å	7.8616(1)
c/ Å	14.1583(2)
α/ °	90
β/ °	109.389(7)
γ/ °	90
V/ Å^3	1170.84(6)
Z	4
D_c/ g.cm^{-3}	1.486
μ/ mm^{-1}	1.114
F(000)	544
Number of measured reflctns (<redundancy>)	168634 (9)
Number of independant reflctns (R_{int})	17263 (2.46)
SHELX refinment (S < 0.8 Å^{-1})	
$2\theta_{max}$/ °	52.74
Completeness to θ_{max} (%)	0.99
Index range, *hkl*	-13<h<13
	-9<k<9
	-17<l<17
Independent reflections	2385
Parameters	156

Table 1S (continued)

R [I>2σ(I)] (calculated aginst F^2)	0.0209
R_w [I>2σ(I)] (calculated against F^2)	0.0681
R (all data) (calculated against F^2)	0.0211
Rw (all data) (calculated against F^2)	0.0685
$\Delta\rho_{max/min}$/ e.Å^{-3}	0.422/-0.314
MoPro refinment (S < 1.1 Å^{-1})	
θ_{max}/ °	53.2
Completeness to θ_{max} (%)	0.99
Index range, *hkl*	-27<h<27
	-19<k<19
	-34<l<34
Independent reflections (I>3σ(I))	11120
Parameters /restraints	488 / 61
GOF	1.13
R [I>3σ(I)] (calculated against F)	0.0130
R_w [I>3σ(I)] (calculated against F)	0.0176
$\Delta\rho_{max/min}$/ e.Å^{-3}	0.23/-0.25

Table 2S. Bond Distances (Å) for complex **2**.

Mn1-C3	1.9012(2)	C15-H15	1.083
Mn1-C2	1.7798(3)	C16-H16a	1.093
Mn1-C1	1.7835(3)	C16-H16b	1.093
Mn1-C11	2.1815(2)	C16-H16c	1.093
Mn1-C14	2.1596(3)		
Mn1-C13	2.1599(3)		
Mn1-C12	2.1621(2)		
Mn1-C15	2.1734(2)		
C1-O1	1.1609(4)		
C2-O2	1.1635(4)		
C3-O3	1.3338(3)		
C3-C4	1.5163(3)		
C4-H4a	1.093		
C4-H4c	1.093		
C4-H4b	1.093		
C5-O3	1.4416(4)		
C5-C6	1.5079(4)		
C5-H5b	1.093		
C5-H5a	1.093		
C6-H6c	1.093		
C6-H6a	1.093		
C6-H6b	1.093		
C11-C12	1.4237(4)		
C11-C15	1.4298(3)		
C11-C16	1.4984(4)		
C12-C13	1.4265(4)		
C12-H12	1.083		
C13-C14	1.4223(4)		
C13-H13	1.083		
C14-C15	1.4195(4)		
C14-H14	1.083		

Table 3S. Selected bond angles (°) for complex **2**

Mn1-C3-O3	131.32(2)	C2-Mn1-C15	95.16(1)
Mn1-C3-C4	124.68(2)	C3-Mn1-C11	123.53(1)
Mn1-C2-O2	173.99(3)	C3-Mn1-C14	131.14(1)
Mn1-C1-O1	178.00(3)	C3-Mn1-C13	96.911(10)
Mn1-C11-C12	70.13(2)	C3-Mn1-C12	93.390(9)
Mn1-C11-C15	70.53(2)	C3-Mn1-C15	157.276(10)
Mn1-C11-C16	128.20(3)	C3-O3-C5	122.60(3)
Mn1-C14-C15	71.404(10)	C3-C4-H4a	116.2(5)
Mn1-C14-C13	70.79(2)	C3-C4-H4c	105.5(6)
Mn1-C14-H14	122.9(4)	C3-C4-H4b	109.3(6)
Mn1-C13-C14	70.76(2)	C4-C3-O3	103.96(2)
Mn1-C13-C12	70.81(1)	C5-C6-H6c	110.2(6)
Mn1-C13-H13	124.6(5)	C5-C6-H6a	109.1(5)
Mn1-C12-C11	71.61(1)	C5-C6-H6b	109.7(4)
Mn1-C12-C13	70.65(2)	C6-C5-O3	107.75(3)
Mn1-C12-H12	125.5(4)	C6-C5-H5b	110.0(5)
Mn1-C15-C11	71.14(2)	C6-C5-H5a	111.0(4)
Mn1 C15 C14	70.35(2)	C11-Mn1-C14	64.25(1)
Mn1-C15-H15	123.3(4)	C11-Mn1-C13	64.43(1)
C1-Mn1-C3	92.13(1)	C11-Mn1-C12	38.26(1)
C1-Mn1-C2	89.69(1)	C11-Mn1-C15	38.332(9)
C1-Mn1-C11	144.02(1)	C11-C12-13	108.60(2)
C1-Mn1-C14	89.66(1)	C11-C12-H12	124.2(5)
C1-Mn1-C13	110.64(1)	C11-C15-C14	108.24(2)
C1-Mn1-C12	149.15(1)	C11-C15-H15	124.6(4)
C1-Mn1-C15	106.04(1)	C11-C16-H16a	111.9(6)
C2-Mn1-C3	98.55(1)	C11-C16-H16b	110.5(6)
C2-Mn1-C11	89.49(1)	C11-C16-H16c	111.7(4)
C2-Mn1-C14	130.30(2)	C12-Mn1-C14	64.23(1)
C2-Mn1-C13	153.91(1)	C12-Mn1-C13	38.54(1)
C2-Mn1-C12	119.35(1)	C12-Mn1-C15	64.02(1)

Table 3S (continued)

C12-C11-C15	107.31(2)
C12-C11-C16	126.50(4)
C12-C13-C14	107.51(2)
C12-C13-H13	126.2(5)
C13-Mn1-C14	38.45(1)
C13-Mn1-C15	64.24(1)
C13-C14-C15	108.35(3)
C13-C14-H14	126.3(5)
C13-C12-H12	127.1(5)
C14-Mn1-C15	38.25(1)
C14-C15-H15	127.1(4)
C14-C13-H13	126.3(5)
C15-C11-C16	126.03(3)
C15-C14-H14	125.4(5)
O3-C5-H5b	106.2(5)
O3-C5-H5a	110.4(5)
H4a-C4-H4c	107.1(7)
H4a-C4-H4b	112.7(8)
H4b-C4-H4c	105.2(8)
H5a-C5-H5b	111.4(7)
H6a-C6-H6c	109.9(7)
H6a-C6-H6b	108.1(7)
H6b-C6-H6c	109.9(8)
H16a-C16-H16b	108.3(8)
H16a-C16-H16c	107.0(9)

Table 4S. Multipolar parameters for complex **2.**

atom:	**Mn1**
system coord.	D_0 Z Mn1 C3 X
κ, κ'	1.020558 0.959931
Pv	5.9730
P00	0.0000
P1m±	-0.0250 0.0300 -0.0040
P2m±	-0.0060 0.0080 -0.0620 -0.0630 -0.0280
P3m±	0.0030 0.0020 0.0100 -0.0190 -0.0170 0.0260 0.0030
P4m±	0.0050 -0.0160 0.0110 0.0000 0.2390 -0.0010 -0.0060 0.1260 0.0310
atom:	**C1**
system coord.	Mn1 Z C1 O1 X
κ, κ'	1.035549 0.974894
Pv	4.2310
P00	0.0000
P1m±	0.0330 0.0230 0.0150
P2m±	-0.0030 0.0130 0.3840 -0.0140 0.0250
P3m±	-0.0070 -0.0040 -0.0080 -0.0850 0.0170 -0.0230 -0.0020
atom:	**C2**
system coord.	Mn1 Z C2 O2 X
κ, κ'	1.035549 0.974894
Pv	4.2800
P00	0.0000
P1m±	0.0120 0.0390 -0.0640
P2m±	-0.0050 -0.0110 0.3830 -0.0320 0.0540
P3m±	0.0000 -0.0070 -0.0060 -0.1480 0.0100 -0.0230 0.0310
atom:	**C3**
system coord.	C4 X C3 O3 Y
κ, κ'	1.042077 0.754973
Pv	3.8230
P00	0.0000
P1m±	-0.2020 0.0240 -0.1780
P2m±	0.1630 0.0310 -0.3800 0.0240 0.0250
P3m±	-0.1770 -0.0070 -0.0460 0.0330 -0.0820 0.0110 0.4020
atom:	**C4**
system coord.	C3 Z C4 H4a X
κ, κ'	1.006377 0.796315
Pv	4.4030
P00	0.0000
P1m±	0.0160 -0.1450 -0.0500
P2m±	0.0010 -0.0410 -0.0650 -0.0440 -0.0090
P3m±	0.0190 0.0670 -0.0450 0.5350 -0.0420 -0.0640 -0.0800
atom:	**C5**
system coord.	O3 X C5 C6 Y
κ, κ'	1.006377 0.796315
Pv	4.4420
P00	0.0000
P1m±	-0.0710 0.2000 -0.2100
P2m±	0.0650 0.0020 0.1510 -0.0230 -0.1920
P3m±	-0.1570 -0.0080 -0.1690 0.2920 -0.1940 -0.0310 0.3340

Table 4S (continued)

atom:	**C6**
system coord.	C5 Z C6 H6a X
κ, κ'	1.006377 0.796315
Pv	4.4910
P00	0.0000
P1m±	-0.0200 -0.0680 -0.0210
P2m±	-0.0180 -0.0240 -0.0470 0.0540 -0.0420
P3m±	0.0310 0.1000 -0.0300 0.3910 -0.0080 0.0310 0.2640
atom:	**C11**
system coord.	D_0 X C11 Mn1 Z
κ, κ'	1.033709 0.780684
Pv	3.8900
P00	0.0000
P1m±	0.0360 0.0390 0.0240
P2m±	-0.0020 0.0250 -0.2820 0.0400 0.0500
P3m±	0.0220 -0.0100 0.0080 0.0480 0.0490 -0.0180 -0.3990
atom:	**C12**
system coord.	D_0 X C12 Mn1 Z
κ, κ'	1.033709 0.780684
Pv	4.1350
P00	0.0000
P1m±	-0.0710 0.0060 -0.0030
P2m±	-0.0070 0.0140 -0.2950 -0.0710 0.0710
P3m±	0.0110 0.0530 0.0210 0.0270 0.0210 0.0700 -0.4300
atom:	**C13**
system coord.	D_0 X C13 Mn1 Z
κ, κ'	1.033709 0.780684
Pv	4.0430
P00	0.0000
P1m±	-0.0200 -0.0360 0.0260
P2m±	0.0030 -0.0160 -0.3030 -0.0120 0.1380
P3m±	0.0160 -0.0100 0.0070 0.0310 0.0760 -0.0380 -0.4340
atom:	**C14**
system coord.	D_0 X C14 Mn1 Z
κ, κ'	1.033709 0.780684
Pv	4.0020
P00	0.0000
P1m±	0.0710 -0.0400 0.0620
P2m±	0.0510 -0.0200 -0.3490 0.0120 0.0600
P3m±	0.0430 -0.0380 -0.0160 0.0490 0.0240 0.0310 -0.4420
atom:	**C15**
system coord.	D_0 X C15 Mn1 Z
k, k'	1.033709 0.780684
Pv	3.9570
P00	0.0000
P1m±	0.1620 -0.0210 -0.0320
P2m±	0.0360 -0.0460 -0.2950 0.0070 0.0600
P3m±	0.0030 -0.0230 -0.0270 0.0310 0.0600 0.0130 -0.4400
atom:	**C16**
system coord.	C11 Z C16 H6a X
κ, κ'	1.006377 0.796315
Pv	4.1410
P00	0.0000
P1m±	0.0410 -0.0830 0.0100
P2m±	-0.0140 -0.0180 -0.0470 -0.0200 0.0250
P3m±	-0.0530 -0.0280 0.0150 0.3730 0.0140 0.0370 0.2330

Table 4S (continued)

atom:	**O1**
system coord.	C1 Z O1 Mn1 Y
κ, κ'	0.989052 1.004645
Pv	6.5360
P00	0.0000
P1m±	-0.0070 0.0190 -0.0360
P2m±	0.0020 0.0120 0.0570 -0.0140 -0.0290
P3m±	0.0250 -0.0150 0.0190 -0.0110 0.0090 0.0040 0.0330
atom:	**O2**
system coord.	C2 Z O2 Mn1 Y
κ, κ'	0.989052 1.004645
Pv	6.5000
P00	0.0000
P1m±	-0.0410 0.0210 -0.0620
P2m±	0.0180 0.0080 0.0500 0.0060 -0.0320
P3m±	-0.0020 0.0250 0.0300 -0.0170 0.0210 0.0210 0.0500
atom:	**O3**
system coord.	C3 X O3 C5 Y
κ, κ'	0.991614 0.936490
Pv	6.4780
P00	0.0000
P1m±	-0.0930 -0.0330 -0.0320
P2m±	0.0370 0.0010 0.0170 -0.0180 -0.0060
P3m±	0.0200 0.0070 -0.0300 -0.0140 0.0010 -0.0040 0.1040
atom:	**H4a**
system coord.	C4 Z H4a Mn1 X
κ, κ'	1.201352 1.200000
Pv	0.5910
P00	0.0000
P1m±	0.0000 0.1680 0.0000
atom:	**H4b**
system coord.	C4 Z H4b Mn1 X
κ, κ'	1.201352 1.200000
Pv	0.5910
P00	0.0000
P1m±	0.0000 0.1140 0.0000
atom:	**H4c**
system coord.	C4 Z H4c Mn1 X
κ, κ'	1.201352 1.200000
Pv	0.5910
P00	0.0000
P1m±	0.0000 0.1230 0.0000
atom:	**H5a**
system coord.	C5 Z H5a O3 X
κ, κ'	1.201352 1.200000
Pv	0.6930
P00	0.0000
P1m±	0.0000 0.0990 0.0000
atom:	**H5b**
system coord.	C5 Z H5b O3 X
κ, κ'	1.201352 1.200000
Pv	0.8820
P00	0.0000
P1m±	0.0000 0.0920 0.0000

Table 4S (continued)

atom:	**H6a**
system coord.	C6 Z H6a C5 X
κ, κ'	1.201352 1.200000
Pv	0.8280
P00	0.0000
P1m±	0.0000 0.2020 0.0000
atom:	**H6b**
system coord.	C6 Z H6b C5 X
κ, κ'	1.201352 1.200000
Pv	0.8280
P00	0.0000
P1m±	0.0000 0.0990 0.0000
atom:	**H6c**
system coord.	C6 Z H6c C5 X
κ, κ'	1.201352 1.200000
Pv	0.8280
P00	0.0000
P1m±	0.0000 0.1460 0.0000
atom:	**H16a**
system coord.	C16 Z H16a C11 X
κ, κ'	1.201352 1.200000
Pv	0.7920
P00	0.0000
P1m±	0.0000 0.1780 0.0000
atom:	**H16b**
system coord.	C16 Z H16b C11 X
κ, κ'	1.201352 1.200000
Pv	0.7920
P00	0.0000
P1m±	0.0000 0.1880 0.0000
atom:	**H16c**
system coord.	C16 Z H16c C11 X
κ, κ'	1.201352 1.200000
Pv	0.7920
P00	0.0000
P1m±	0.0000 0.1450 0.0000
atom:	**H12a**
system coord.	C12 Z H12a Mn1 X
κ, κ'	1.338664 1.200000
Pv	0.6180
P00	0.0000
P1m±	0.0000 0.1290 0.0000
atom:	**H13a**
system coord.	C13 Z H13a Mn1 X
κ, κ'	1.338664 1.200000
Pv	0.6150
P00	0.0000
P1m±	0.0000 0.1300 0.0000
atom:	**H14a**
system coord.	C14 Z H14a Mn1 X
κ, κ'	1.338664 1.200000
Pv	0.6150
P00	0.0000
P1m±	0.0000 0.1750 0.0000

Table 4S (continued)

atom:	**H15a**
system coord.	C15 Z H15a Mn1 X
κ, κ'	1.338664 1.200000
Pv	0.6180
P00	0.0000
P1	

Table 5S Values of the experimental and theoretical[a] (*italic*) orthodox parameters[b] at the bond critical points in **2**.

	d	**d_1**	**d_2**	***ρ*(r)**	**$\nabla^2\rho(r)$**	**λ_1**	**λ_2**	**λ_3**	**ε**	***G*(r)**	***G*(r)/ρ(r)**	***V*(r)**	**E_{int}**
Interatomic bonds													
Mn1-C1	1.784	0.92	0.87	1.03	14.10	-5.08	-4.82	24.00	0.05	1.50	1.46	-2.02	
	1.781	*0.90*	*0.88*	*1.03*	*13.31*	*-4.07*	*-4.01*	*21.39*	*0.01*	*1.40*	*1.36*	*-1.87*	
Mn1-C2	1.780	0.92	0.86	1.01	14.82	-4.71	-4.67	24.20	0.01	1.51	1.49	-1.99	
	1.776	*0.90*	*0.88*	*1.04*	*13.35*	*-4.33*	*-3.84*	*21.52*	*0.13*	*1.42*	*1.37*	*-1.91*	
Mn1-C3	1.901	0.95	0.95	0.99	7.58	-5.14	-4.44	17.16	0.16	1.15	1.16	-1.76	
	1.900	*0.94*	*0.96*	*0.89*	*8.36*	*-4.07*	*-3.44*	*15.87*	*0.18*	*0.95*	*1.07*	*-1.31*	
Mn1-C11	2.167	1.10	1.08	0.41	5.98	-1.62	-0.21	7.80	6.60	0.46	1.12	-0.50	
	2.169	*1.07*	*1.11*	*0.50*	*5.30*	*-1.55*	*-0.48*	*7.33*	*2.24*	*0.51*	*1.03*	*-0.65*	
Mn1-C12	not detected												
	2.153	*1.06*	*1.10*	*0.50*	*5.80*	*-1.54*	*-0.44*	*7.78*	*2.49*	*0.54*	*1.09*	*-0.68*	
Mn1-C13	2.160	1.10	1.12	0.41	5.85	-1.72	-0.08	7.65	19.64	0.46	1.11	-0.50	
	2.151	*1.05*	*1.11*	*0.49*	*6.05*	*-1.67*	*-0.15*	*7.87*	*10.21*	*0.56*	*1.13*	*-0.69*	
Mn1-C14	2.160	1.10	1.08	0.40	6.08	-1.66	-0.02	7.77	72.65	0.46	1.14	-0.50	
	2.145	*1.06*	*1.09*	*0.52*	*5.35*	*-1.70*	*-0.72*	*7.77*	*1.38*	*0.53*	*1.02*	*-0.68*	
Mn1-C15	not detected												
	2.157	*1.06*	*1.11*	*0.49*	*5.76*	*-1.70*	*-0.14*	*7.60*	*11.35*	*0.54*	*1.09*	*-0.67*	
C1-O1	1.161	0.41	0.75	3.47	-27.58	-34.37	-32.25	39.03	0.07	5.10	1.47	-12.12	
	1.158	*0.39*	*0.77*	*3.09*	*17.90*	*-31.93*	*-31.86*	*81.69*	*0.00*	*6.79*	*2.20*	*-12.34*	
C2-O2	1.164	0.42	0.75	3.49	-33.00	-36.12	-33.01	36.14	0.09	4.91	1.41	-12.14	
	1.160	*0.39*	*0.77*	*3.07*	*17.36*	*-31.64*	*-31.50*	*80.51*	*0.00*	*6.71*	*2.19*	*-12.20*	
C3-C4	1.516	0.76	0.76	1.69	-12.03	-11.94	-11.17	11.08	0.07	1.37	0.81	-3.58	
	1.508	*0.77*	*0.74*	*1.78*	*-17.30*	*-12.82*	*-12.33*	*7.84*	*0.04*	*0.43*	*0.24*	*-2.07*	
C3-O3	1.334	0.51	0.82	2.15	-13.45	-15.65	-15.26	17.46	0.03	2.24	1.05	-5.43	
	1.331	*0.44*	*0.89*	*2.01*	*-3.70*	*-15.85*	*-13.73*	*25.88*	*0.15*	*2.91*	*1.44*	*-6.07*	

C4-H4a	1.093	0.76	0.34	1.61	-15.79	-16.93	-13.19	14.33	0.28	1.04	0.65	-3.19
	1.082	*0.67*	*0.41*	*1.93*	*-24.27*	*-17.97*	*-17.63*	*11.33*	*0.02*	*0.36*	*0.19*	*-2.42*
C4-H4b	1.093	0.77	0.32	1.53	-13.44	-15.90	-12.93	15.39	0.23	1.01	0.66	-2.95
	1.090	*0.68*	*0.41*	*1.89*	*-23.43*	*-17.43*	*-17.21*	*11.21*	*0.01*	*0.35*	*0.19*	*-2.35*
C4-H4c	1.093	0.76	0.33	1.43	-10.59	-14.10	-11.79	15.30	0.20	0.97	0.68	-2.68
	1.094	*0.68*	*0.42*	*1.86*	*-22.78*	*-16.82*	*-16.74*	*10.78*	*0.00*	*0.37*	*0.20*	*-2.33*
C5-C6	1.508	0.77	0.74	1.77	-10.52	-12.09	-10.11	11.68	0.20	1.60	0.90	-3.93
	1.502	*0.77*	*0.73*	*1.78*	*-17.41*	*-12.78*	*-12.30*	*7.66*	*0.04*	*0.43*	*0.24*	*-2.08*
C5-O3	1.442	0.59	0.85	1.64	-4.30	-11.14	-10.04	16.87	0.11	1.62	0.99	-3.55
	1.436	*0.50*	*0.93*	*1.63*	*-10.41*	*-10.64*	*-10.03*	*10.27*	*0.06*	*1.46*	*0.89*	*-3.65*
C5-H5a	1.093	0.77	0.32	1.81	-16.50	-18.25	-15.77	17.52	0.16	1.39	0.77	-3.93
	1.090	*0.68*	*0.40*	*1.96*	*-25.09*	*-19.16*	*-18.33*	*12.40*	*0.05*	*0.31*	*0.16*	*-2.37*
C5-H5b	1.093	0.72	0.38	1.70	-11.37	-14.84	-14.34	17.81	0.04	1.41	0.83	-3.61
	1.089	*0.69*	*0.40*	*1.96*	*-24.99*	*-19.09*	*-18.20*	*12.29*	*0.05*	*0.31*	*0.16*	*-2.37*
C6-H6a	1.093	0.70	0.40	1.83	-15.50	-16.05	-14.92	15.47	0.08	1.48	0.81	-4.04
	1.087	*0.67*	*0.41*	*1.90*	*-23.54*	*-17.36*	*-17.20*	*11.03*	*0.01*	*0.36*	*0.19*	*-2.37*
C6-H6b	1.093	0.73	0.36	1.83	-15.14	-16.59	-15.85	17.30	0.05	1.48	0.81	-4.03
	1.088	*0.67*	*0.41*	*1.90*	*-23.64*	*-17.47*	*-17.30*	*11.13*	*0.01*	*0.36*	*0.19*	*-2.37*
C6-H6c	1.093	0.72	0.38	1.80	-14.38	-15.71	-15.38	16.71	0.02	1.48	0.82	-3.96
	1.088	*0.67*	*0.41*	*1.90*	*-23.67*	*-17.49*	*-17.32*	*11.15*	*0.01*	*0.36*	*0.19*	*-2.37*
C11-C12	1.424	0.70	0.73	2.09	-15.26	-14.79	-12.59	12.11	0.18	2.04	0.97	-5.15
	1.417	*0.71*	*0.71*	*2.01*	*-19.03*	*-14.66*	*-11.73*	*7.35*	*0.25*	*0.71*	*0.36*	*-2.76*
C11-C15	1.430	0.70	0.74	2.07	-15.21	-14.69	-12.40	11.87	0.19	2.00	0.96	-5.06
	1.425	*0.72*	*0.71*	*1.98*	*-18.75*	*-14.41*	*-11.71*	*7.37*	*0.23*	*0.69*	*0.35*	*-2.69*
C11-C16	1.498	0.78	0.72	1.75	-11.29	-11.48	-10.97	11.16	0.05	1.51	0.87	-3.81
	1.487	*0.77*	*0.72*	*1.80*	*-17.64*	*-12.67*	*-12.27*	*7.30*	*0.03*	*0.46*	*0.25*	*-2.15*
C12-C13	1.427	0.71	0.72	2.01	-13.98	-14.44	-11.95	12.40	0.21	1.91	0.95	-4.81
	1.418	*0.71*	*0.71*	*1.99*	*-18.75*	*-14.43*	*-11.57*	*7.25*	*0.25*	*0.71*	*0.36*	*-2.73*
C12-H12a	1.083	0.73	0.36	1.82	-15.95	-17.97	-16.81	18.82	0.07	1.43	0.79	-3.98

	1.078	*0.68*	*0.40*	*1.95*	*-25.10*	*-18.60*	*-18.15*	*11.66*	*0.02*	*0.33*	*0.17*	*-2.42*	
C13-C14	1.422	0.72	0.71	2.00	-14.26	-14.36	-12.03	12.13	0.19	1.88	0.94	-4.76	
	1.417	*0.71*	*1.71*	*2.00*	*-18.95*	*-14.53*	*-11.71*	*7.29*	*0.24*	*0.71*	*0.35*	*-2.74*	
C13-H13a	1.083	0.73	0.35	1.86	-17.37	-18.39	-17.47	18.49	0.05	1.44	0.78	-4.10	
	1.077	*0.68*	*0.40*	*1.95*	*-25.12*	*-18.66*	*-18.11*	*11.65*	*0.03*	*0.33*	*0.17*	*-2.43*	
C14-C15	1.420	0.75	0.67	2.04	-15.59	-14.96	-12.39	11.76	0.21	1.90	0.94	-4.90	
	1.412	*0.71*	*0.70*	*2.02*	*-19.27*	*-14.74*	*-11.79*	*7.26*	*0.25*	*0.73*	*0.36*	*-2.80*	
C14-H14a	1.083	0.71	0.37	1.85	-17.83	-18.12	-17.08	17.36	0.06	1.45	0.79	-4.15	
	1.077	*0.68*	*0.40*	*1.96*	*-25.43*	*-18.82*	*-18.50*	*11.89*	*0.02*	*0.32*	*0.16*	*-2.41*	
C15-H15a	1.083	0.72	0.36	1.87	-17.76	-18.18	-17.27	17.68	0.05	1.39	0.74	-3.86	
	1.078	*0.68*	*0.40*	*1.95*	*-25.11*	*-18.65*	*-18.15*	*11.70*	*0.03*	*0.33*	*0.17*	*-2.41*	
C16-H16a	1.093	0.71	0.39	1.78	-15.37	-15.66	-14.83	15.13	0.06	1.39	0.78	-3.86	
	1.087	*0.67*	*0.41*	*1.90*	*-23.65*	*-17.53*	*-17.29*	*11.18*	*0.01*	*0.36*	*0.19*	*-2.37*	
C16-H16b	1.093	0.70	0.40	1.76	-15.44	-15.38	-14.49	14.43	0.06	1.34	0.76	-3.76	
	1.091	*0.68*	*0.42*	*1.88*	*-23.22*	*-17.25*	*-17.01*	*11.03*	*0.01*	*0.36*	*0.19*	*-2.35*	
C16-H16c	1.093	0.71	0.38	1.74	-14.35	-15.33	-14.49	15.47	0.06	1.35	0.78	-3.70	
	1.088	*0.68*	*0.41*	*1.91*	*-23.73*	*-17.61*	*-17.38*	*11.26*	*0.01*	*0.35*	*0.19*	*-2.37*	
Intramolecular interligand weak interactions													
C1-H5a	2.410	1.43	1.01	0.08	0.97	-0.22	-0.17	1.37	0.28	0.06	0.72	-0.05	2.1
	2.422	*1.44*	*1.03*	*0.08*	*0.95*	*-0.24*	*-0.11*	*1.30*	*1.22*	*0.06*	*0.71*	*-0.05*	*2.2*
C2-H5b	2.530	1.40	1.17	0.09	1.07	-0.21	-0.17	1.45	0.25	0.06	0.71	-0.05	2.5
	2.515	*1.43*	*1.18*	*0.08*	*0.99*	*-0.18*	*-0.05*	*1.23*	*2.38*	*0.06*	*0.74*	*-0.05*	*2.2*
H4a-H12a	2.35	1.27	1.22	0.05	0.64	-0.21	-0.19	1.03	0.11	0.04	0.70	-0.03	1.1
	not detected												
H4a-H13a	2.14	1.05	1.22	0.04	0.65	-0.20	-0.15	1.00	0.27	0.03	0.91	-0.02	1.0
	not detected												
Intermolecular weak interactions													
O1-H4a_4	2.520	1.587	1.087	0.02	0.46	-0.12	-0.07	0.64	0.84	0.02	0.96	-0.01	0.6
O2-H5b_3	2.600	1.526	1.079	0.03	0.64	-0.14	-0.12	0.89	0.19	0.03	0.94	-0.02	1.0

O2-H5a_3	2.515	1.569	1.016	0.02	0.60	-0.12	-0.07	0.78	0.90	0.03	1.21	-0.02	0.8
H4a-O1_4	2.520	1.087	1.587	0.02	0.46	-0.12	-0.07	0.64	0.84	0.02	0.96	-0.01	0.6
H5b-O2_3	2.600	1.079	1.526	0.03	0.64	-0.14	-0.12	0.89	0.19	0.03	0.94	-0.02	1.0
H15a-O2_1	2.515	1.016	1.569	0.02	0.60	-0.12	-0.07	0.78	0.90	0.03	1.21	-0.02	0.8
H4c-H6a_4	2.240	1.133	1.287	0.02	0.39	-0.12	-0.06	0.58	1.03	0.02	0.83	-0.01	0.6
H5a-H12a_4	2.558	1.159	1.553	0.03	0.51	-0.13	-0.03	0.67	2.82	0.03	0.87	-0.02	0.8
H6a-H4c_4	2.240	1.382	1.075	0.01	0.29	-0.08	-0.05	0.43	0.52	0.01	1.07	-0.01	0.4
H6b-H15a_1	2.347	1.176	1.193	0.03	0.41	-0.13	-0.09	0.63	0.49	0.02	0.80	-0.01	0.6
H6c-H13a_3	2.344	1.357	1.122	0.01	0.25	-0.01	0.00	0.27	2.72	0.01	2.05	-0.01	0.3
H16a-H16b_2	2.478	1.198	1.328	0.02	0.30	-0.08	-0.05	0.43	0.57	0.01	0.92	-0.01	0.4
H16b-H16a_2	2.478	1.328	1.198	0.02	0.30	-0.08	-0.05	0.43	0.57	0.01	0.92	-0.01	0.4
H13a-H6c_3	2.344	1.171	1.401	0.01	0.21	-0.01	0.00	0.22	3.48	0.01	1.65	-0.01	0.2
H15a-H6b_1	2.347	1.193	1.176	0.03	0.41	-0.13	-0.09	0.63	0.50	0.02	0.80	-0.01	0.6

[a]ED computation (M06L/def2-TZVPP) based on the gas-phase optimized geometry (M06L/def2-TZVPP); [b]d (Å), d_1 and d_2, $\rho(r)$ (e.Å^{-3}), $\nabla^2\rho(r)$ (e.Å^{-5}), G (hartree.Å^{-3}), V (hartree.Å^{-3}), and E_{int} (kcal.mol^{-1}) are the interatomic distance, the distances from the bcp to the nuclear attractors, the ED, the laplacian of the ED, the ellipticity of the bond, kinetic, potential energies densities, and interaction energy, respectively.

Table 6S. Cartesian coordinates (in Å) and total energies (in a.u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text. All data have been computed at the M06L/def2-TZVPP level.

1-A$_{anti}$: E= -1764.339154

O	2.401560000	1.017160000	-0.154586000
C	1.075989000	1.152262000	-0.102749000
Mn	-0.313745000	-0.133410000	0.017894000
C	0.864376000	2.644444000	-0.132310000
C	0.434156000	-0.871480000	1.455838000
O	0.882642000	-1.360319000	2.404264000
C	0.420213000	-1.364096000	-1.033867000
O	0.800181000	-2.217418000	-1.719767000
C	3.033495000	-0.254248000	-0.232339000
H	1.673960000	3.163857000	0.378417000
H	-0.083417000	2.950547000	0.291910000
H	0.884445000	2.978171000	-1.172243000
H	2.868409000	-0.702661000	-1.208554000
H	4.093236000	-0.063701000	-0.094402000
H	2.678220000	-0.927550000	0.542914000
C	-2.213890000	-0.166549000	1.025148000
C	-2.310048000	-0.934703000	-0.154517000
C	-2.045395000	-0.068909000	-1.250309000
C	-1.804955000	1.227205000	-0.741687000
C	-1.903927000	1.171012000	0.670561000
H	-2.338996000	-0.536484000	2.029277000
H	-2.519859000	-1.988875000	-0.213835000
H	-2.028949000	-0.352593000	-2.289061000
H	-1.578399000	2.098845000	-1.331443000
H	-1.780180000	1.990670000	1.357776000

1-A$_{syn}$: E= -1764.33482

O	2.334019000	-0.122012000	-0.019282000
C	1.240229000	0.657394000	-0.003199000
Mn	-0.458318000	-0.146685000	0.001972000
C	1.557900000	2.121511000	0.009950000
C	0.079393000	-1.287237000	1.259762000
O	0.431726000	-2.024482000	2.076500000
C	0.076699000	-1.318998000	-1.226372000
O	0.422975000	-2.077861000	-2.025781000
C	3.658791000	0.404010000	-0.019204000
H	2.126317000	2.405066000	-0.879491000
H	2.185289000	2.379464000	0.866518000
H	0.668886000	2.736617000	0.047560000
H	3.859780000	0.983930000	0.881125000
H	4.317944000	-0.456778000	-0.044708000
H	3.844445000	1.025494000	-0.894614000
C	-2.212745000	0.381267000	1.125982000
C	-2.609470000	-0.344384000	-0.023275000
C	-2.184925000	0.392056000	-1.156789000
C	-1.542547000	1.571130000	-0.711056000
C	-1.559530000	1.564792000	0.707537000
H	-2.369254000	0.078824000	2.148134000
H	-3.119795000	-1.291994000	-0.033913000
H	-2.316933000	0.099452000	-2.185217000
H	-1.118578000	2.332203000	-1.344338000
H	-1.152683000	2.320452000	1.358146000

1-B_{syn}: E= -1764.337323

O	2.043492000	-1.104875000	0.000281000
C	1.400537000	0.076031000	0.000083000
Mn	-0.479622000	0.101528000	-0.000002000
C	2.309597000	1.263278000	-0.000153000
C	-0.494274000	1.373263000	-1.242265000
O	-0.508588000	2.204945000	-2.047336000
C	-0.494579000	1.373086000	1.242468000
O	-0.509167000	2.204690000	2.047613000
C	3.468486000	-1.192479000	0.000159000
H	2.964768000	1.262069000	-0.874774000
H	2.964742000	1.262508000	0.874483000
H	1.748075000	2.189930000	-0.000395000
H	3.897001000	-0.728850000	0.887766000
H	3.701357000	-2.252060000	0.000199000
H	3.896852000	-0.728944000	-0.887563000
C	-1.807066000	-1.143948000	-1.142481000
C	-2.498303000	-0.667451000	0.000010000
C	-1.806916000	-1.144345000	1.142258000
C	-0.699968000	-1.909498000	0.708671000
C	-0.700057000	-1.909253000	-0.709298000
H	-2.068596000	-0.938848000	-2.167190000
H	-3.378668000	-0.048694000	0.000169000
H	-2.068297000	-0.939562000	2.167068000
H	0.031450000	-2.383175000	1.340240000
H	0.031232000	-2.382769000	-1.341134000

1-C_{anti}: E= -1764.335497

O	2.471567000	0.148228000	-0.695041000
C	1.288938000	0.709191000	-0.497064000
Mn	-0.344816000	-0.009010000	0.167077000
C	-2.415424000	-0.112824000	-0.314124000
C	-1.933583000	-1.416526000	-0.078026000
C	-0.918685000	-1.692715000	-1.040796000
C	-0.793564000	-0.552541000	-1.869454000
C	-1.710764000	0.430291000	-1.429691000
C	1.390624000	2.113812000	-1.005560000
C	-0.595635000	1.458248000	1.153726000
O	-0.783067000	2.418447000	1.771821000
C	0.364790000	-0.930553000	1.517754000
O	0.755495000	-1.572286000	2.401011000
H	2.188239000	2.244608000	-1.735977000
H	1.600981000	2.770985000	-0.159060000
H	0.440285000	2.446174000	-1.414263000
H	-2.264342000	-2.084811000	0.698636000
H	-0.367895000	-2.613317000	-1.135137000
H	-0.102971000	-0.446477000	-2.691028000
H	-1.863161000	1.402778000	-1.865527000
H	-3.183048000	0.389024000	0.249939000
C	2.705182000	-1.208865000	-0.314981000
H	1.864000000	-1.836407000	-0.598073000
H	3.606653000	-1.511816000	-0.837958000
H	2.858443000	-1.275732000	0.758482000

1-D_{anti}: E= -1764.335840

O	-2.471148000	-0.343327000	-0.570151000
C	-1.399760000	0.445604000	-0.568168000

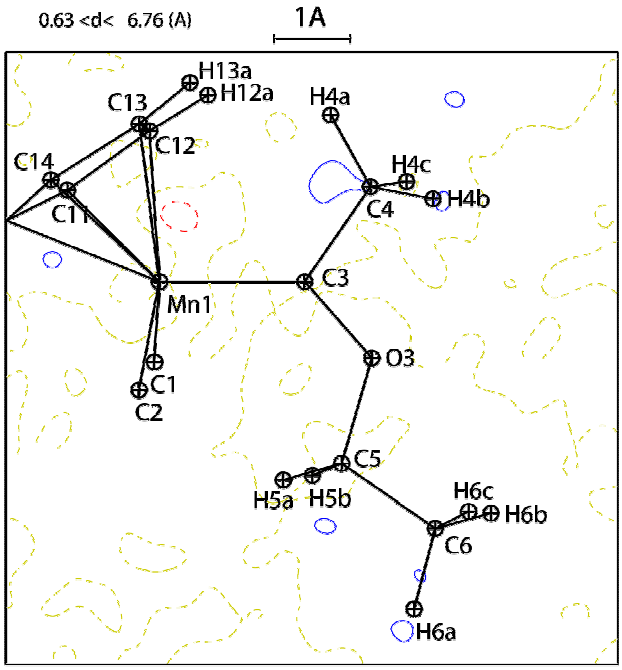
Mn	0.354511000	0.091505000	0.089928000
C	-1.830382000	1.735936000	-1.195011000
C	-0.254750000	0.287230000	1.761840000
O	-0.650013000	0.397621000	2.843832000
C	0.814638000	1.801330000	-0.029062000
O	1.191083000	2.894789000	-0.105753000
C	-2.446880000	-1.623550000	0.052689000
H	-2.847550000	1.703939000	-1.582005000
H	-1.141400000	2.017083000	-1.989263000
H	-1.761313000	2.531397000	-0.452412000
H	-1.969147000	-2.355316000	-0.594965000
H	-1.919311000	-1.580689000	1.002610000
H	-3.485563000	-1.901046000	0.203611000
C	1.868719000	-1.321548000	0.651774000
C	2.378891000	-0.458613000	-0.336980000
C	1.585692000	-0.615433000	-1.510617000
C	0.600278000	-1.594993000	-1.232213000
C	0.765854000	-2.034784000	0.098306000
H	2.241804000	-1.420652000	1.657132000
H	3.209980000	0.216490000	-0.222762000
H	1.722696000	-0.096983000	-2.444041000
H	-0.150637000	-1.933991000	-1.927193000
H	0.184493000	-2.787607000	0.602325000

2: E= -1842.937715

Mn	-0.434217000	-0.049114000	0.275092000
C	0.497353000	-0.017719000	1.793204000
C	0.086305000	1.602909000	-0.115089000
C	0.966919000	-0.977786000	-0.610091000
C	0.805712000	-2.300468000	-1.316734000
C	2.844755000	0.534056000	-0.299059000
C	4.335114000	0.397813000	-0.429015000
C	-2.341955000	0.337484000	-0.677326000
C	-1.970333000	-1.014551000	-0.883686000
C	-1.860356000	-1.656443000	0.375721000
C	-2.162491000	-0.693187000	1.369942000
C	-2.462482000	0.528647000	0.729886000
C	-2.634716000	1.344440000	-1.732115000
O	1.071583000	-0.002264000	2.798423000
O	0.314108000	2.719537000	-0.333368000
O	2.260763000	-0.697103000	-0.750916000
H	-0.069938000	-2.853001000	-1.001527000
H	1.691379000	-2.920964000	-1.184790000
H	0.712404000	-2.114351000	-2.389245000
H	2.543862000	0.723278000	0.729918000
H	2.455871000	1.343528000	-0.915741000
H	4.820918000	1.318449000	-0.114572000
H	4.624617000	0.197400000	-1.458134000
H	4.711448000	-0.411441000	0.192678000
H	-2.043715000	1.168718000	-2.628226000
H	-3.685925000	1.303634000	-2.019621000
H	-2.430662000	2.356696000	-1.390838000
H	-1.804431000	-1.466814000	-1.847677000
H	-1.601546000	-2.686093000	0.554804000
H	-2.148414000	-0.861241000	2.434065000
H	-2.715026000	1.457507000	1.214657000

Figure 1S. Residual electron density maps for **2** after the multipolar refinement (0.1 e.Å^{-3} isocontours; positive: full lines; negative: dashed lines; zero contour: yellow dashed line)

In the carbene plane



In the Cp plane

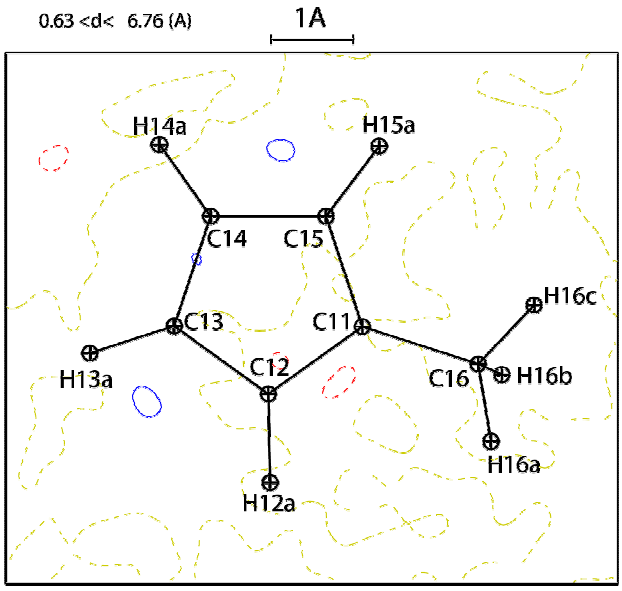
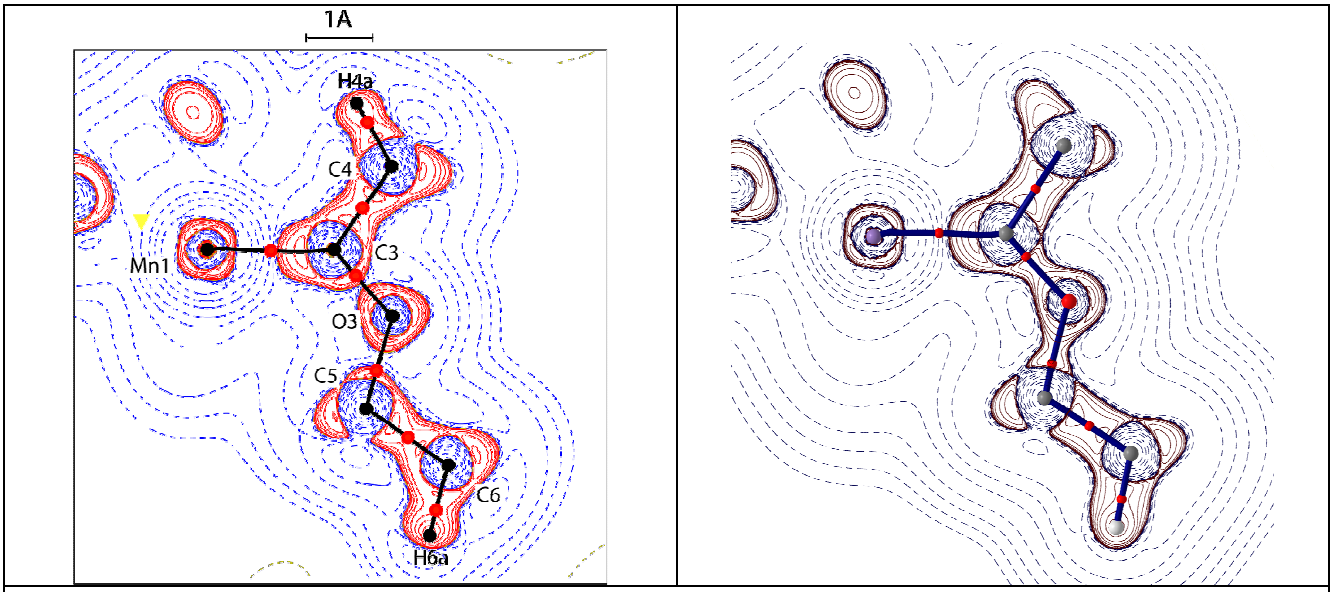
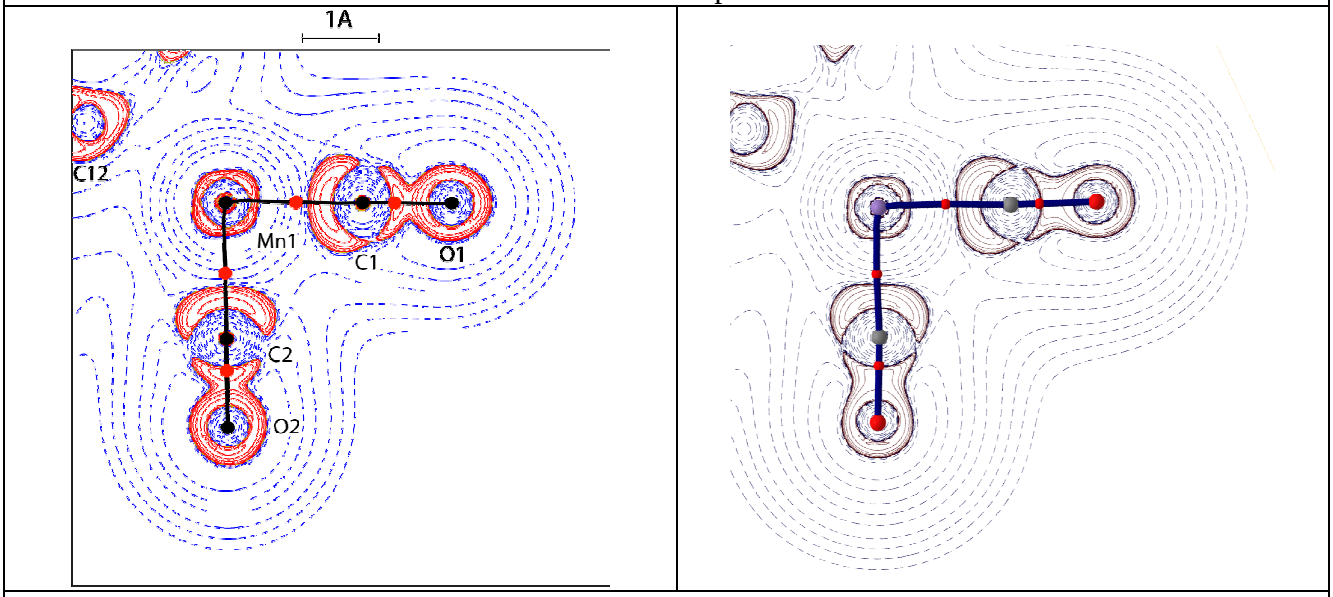


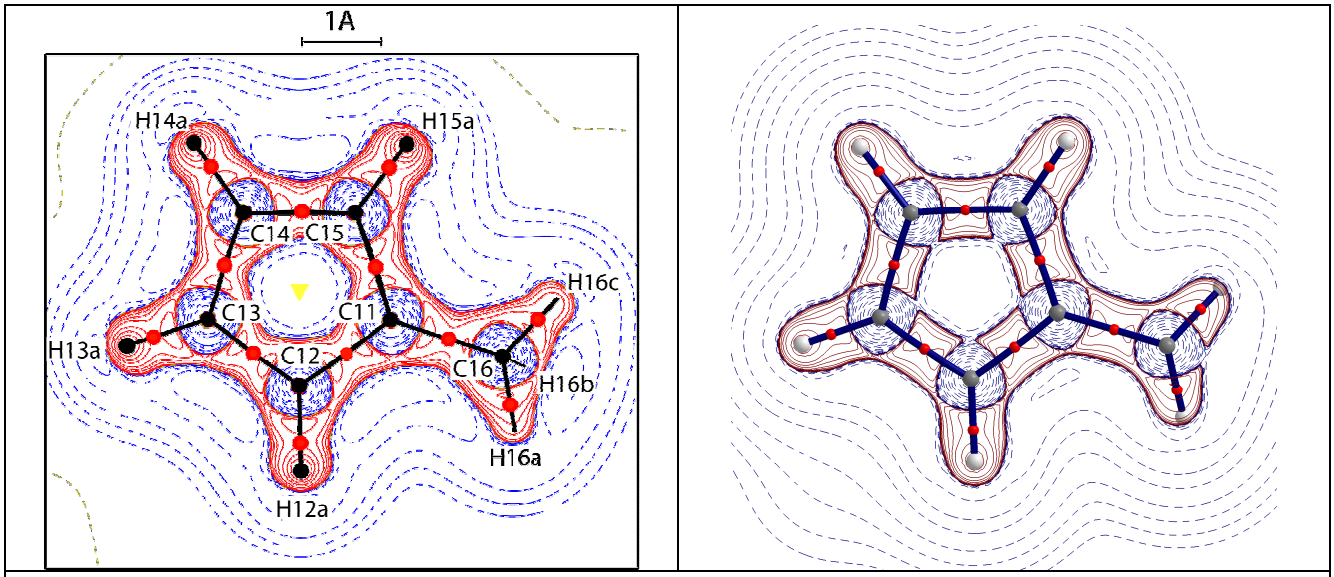
Figure 2S. Laplacian of the experimental (left) and theoretical (right, M06L/def2-TZVPP level) electron density for **2** in various planes. Contours are drawn at 0.000, ±2.0 x 10n, ±4.0 x 10n, ±8.0 x 10n e.Å^{-5} levels, where n = 0, -3, ±2, ±1; positive: solid (red) lines, negative: dashed (blue) lines.



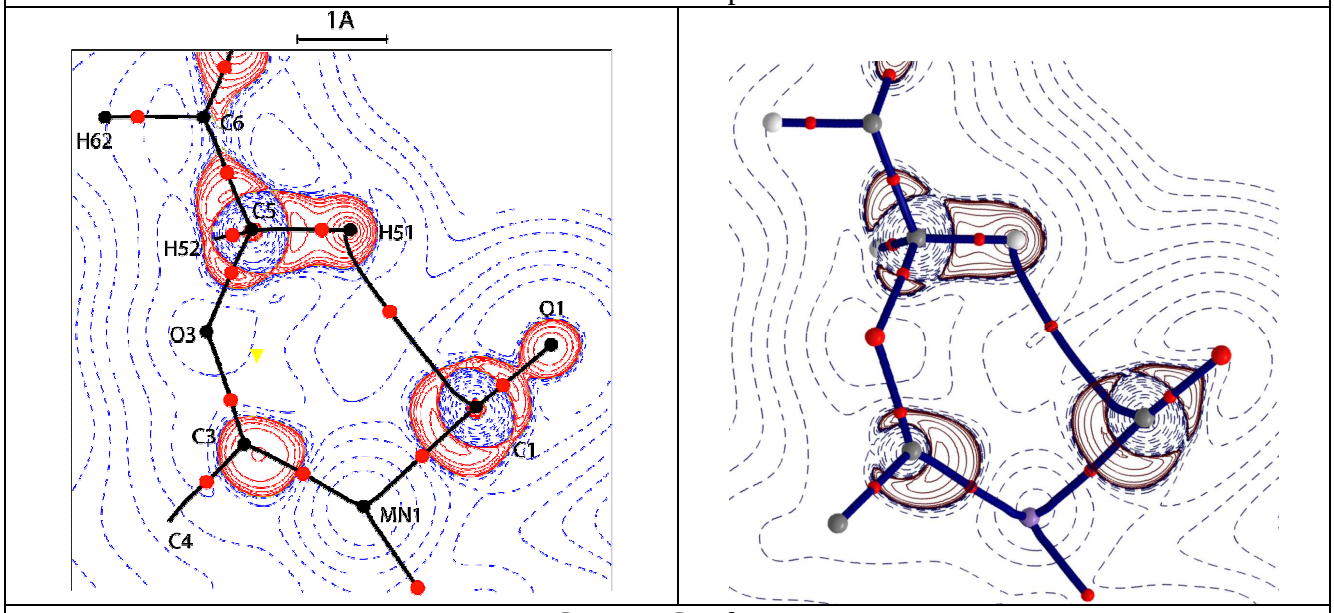
Mn1-C3-O3 plane



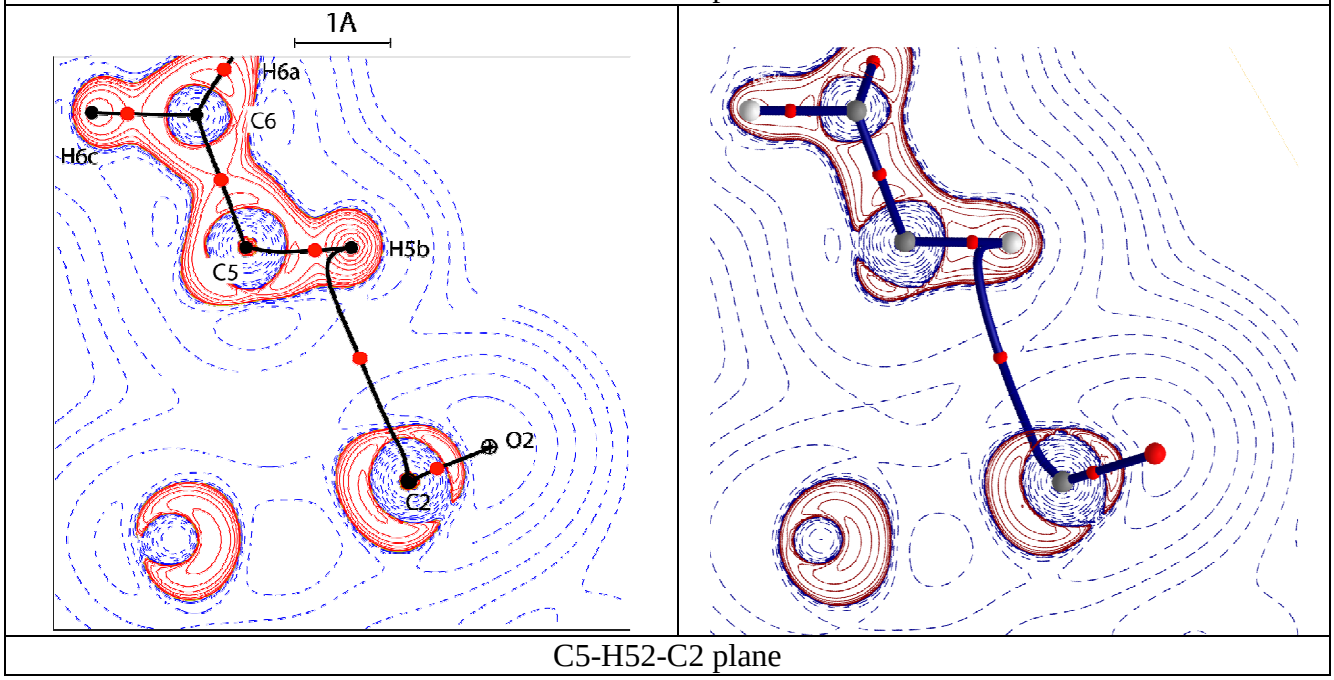
Mn1-C1-C2 plane



C11-C13-C14 plane



C5-H51-C1 plane



C5-H52-C2 plane

Figure 3S. Theoretical molecular graph based on for the gas-phase optimized geometry **(**M06L/def2-TZVPP level).for complex **2 (**M06L/def2-TZVPP level). Small red, yellow, and blue dots are *bcp*'s, *rcp*'s, *ccp*'s, respectively, while blue lines are *bp*'s