Supplementary materials

Charge density analysis using a multipolar atoms and a spherical charges model: 2-methyl-1,3-cyclopentanedione, a compound displaying a resonance-assisted-hydrogen-bond.

Ayoub Nassour, Maciej Kubicki, Jonathan Wright, Teresa Borowiak, Grzegorz Dutkiewicz, Claude Lecomte and Christian Jelsch.

Table S1.

Summary of the electron density models and crystallographic refinements. *SCA*, *XYZ*, *UIJ* refer to scale factor, atomic coordinates and thermal displacement parameters respectively. H and Q refer to hydrogen and virtual atoms respectively. Diffraction data are obtained experimentally (EXP) or by theoretical calculations (THEO).

Model name	Refinement	hkl data	Restraints and constraints
EXP_MUL[a]	*SCA XYZ UIJ* refined except for H.	EXP	Stereochemical and thermal constraints on H atoms.
EXP_VIR[b]	*SCA XYZ UIJ* refined except for H and Q atoms.	EXP	Stereochemical constraints on H. Thermal constraints on H and Q.
THEO_MUL[c]	- Geometry fixed. - P_{val}, P_{lm}, k, k' refined	THEO	k of H atoms restrained.
THEO_VIR[d]	- Geometry fixed - *XYZ* of Q atoms, P_{val} and k of all atoms refined	THEO	k of H atoms restrained.

[a]Multipolar model vs. experimental structure factors.

[b]Virtual spherical charges model vs. experimental structure factors.

[c]Multipolar model vs. theoretical structure factors.

[d]Virtual spherical charges model vs. theoretical structure factors.

Table S2. Net atomic charges derived from the AIM analysis Q_Ω in the MCPD molecule for the multipolar models. The refined electron populations P_{val}/P_{vir} of the models for the virtual atoms models are also given. O1 6.26543

Atom	EXP_MUL Q_Ω	THEO_MUL Q_Ω	EXP_VIR P_{val}/P_{vir}	THEO_VIR P_{val}/P_{vir}
C1	+0.87	+0.86	3.43	2.75
O1	-1.09	-1.14	5.81	6.24
C2	+0.10	-0.03	4.63	3.43
C21	-0.23	+0.14	2.97	3.09
C3	+0.67	*+0.53*	3.10	3.09
O3	-1.26	*-1.21*	6.16	6.43
C4	-0.19	*+0.09*	4.10	2.74
C5	-0.11	*+0.036*	3.43	3.04
H3	+0.66	*+0.65*	0.28	0.31
H4	+0.08	+0.02	0.77	0.44
H5	+0.07	+0.01	0.66	0.44
H21A	+0.10	+0.04	0.64	0.30
H21B	+0.10	-0.018	0.64	0.44
qC1C2	/	/	0.51	0.59
qC2C21			0.22	0.47
qC2C3			0.44	0.62
qC3C4			0.30	0.58
qC4C5			0.22	0.62
qC5C1			0.40	0.56
qC1O1			0.30	0.31
qC3O3			0.16	0.10
qO3H3			0.25	0.30
qCH21A			0.60	0.87
qCH21B			0.62	0.74
qC4H4			0.23	0.80
qC5H5			0.45	0.74
LPO1a			0.18	0.14
LPO1b			0.14	0.13
LPO3			0.06	0.04

Table S3. Bond peak heights in the deformation electron density maps in the plane of the MCPD pentacycle (Fig. 3) in e. $Å^{-3}$.

Bond \ model	EXP_MUL	THEO_MUL	EXP_VIR	THEO_VIR
C1-C2	0.95	0.65	0.85	0.70
C2=C3	0.80	0.75	0.75	0.75
C3-C4	0.70	0.55	0.60	0.50
C4-C5	0.55	0.45	0.75	0.45
C5-C1	0.55	0.55	0.55	0.60
C2-C21	0.50	0.45	0.65	0.45

Figure S1. Residual electron density map in the plane *y*=0 of the molecule.

(a) experimental multipolar. (b) experimental virtual.

Contour level: ±0.05e·Å^{-3}. Positive: solid blue lines; negative: dashed red lines; dashed yellow lines.

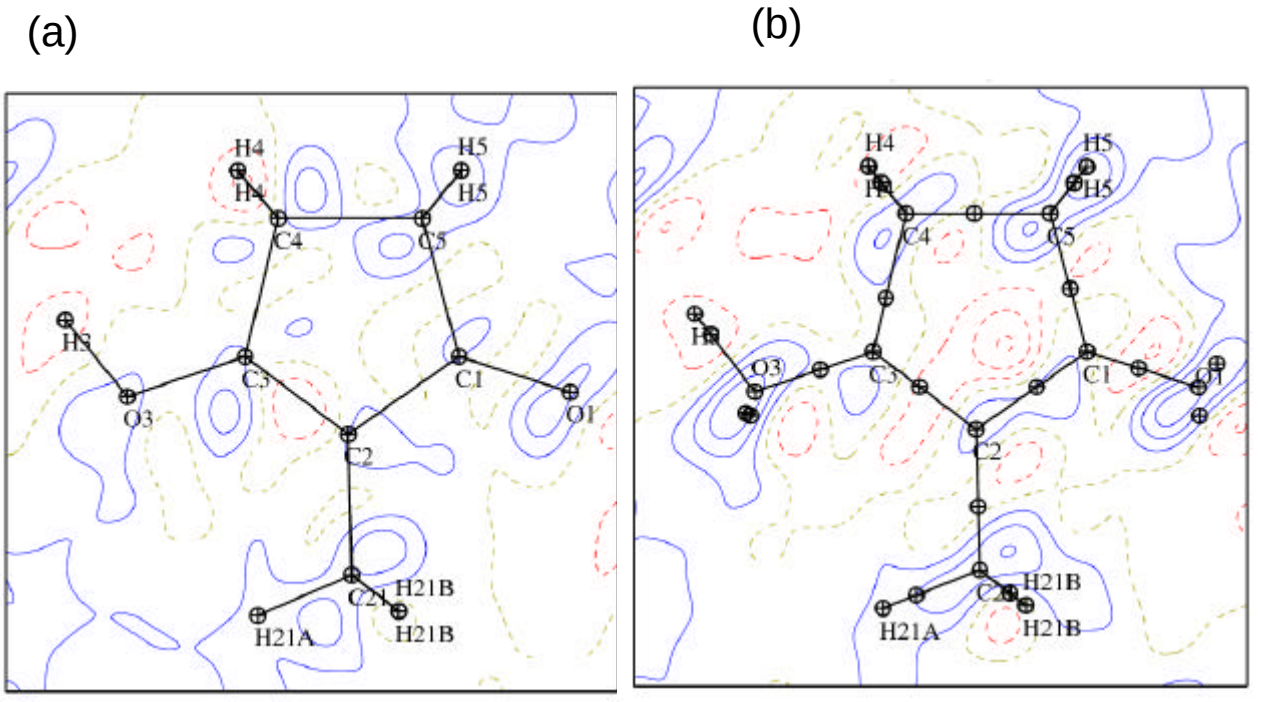
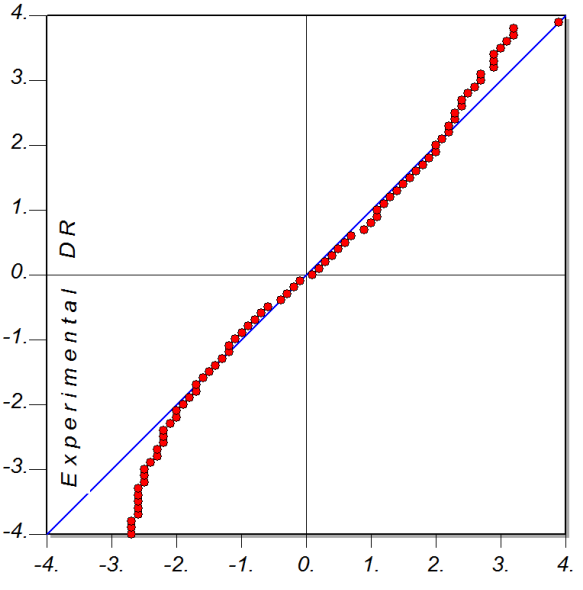
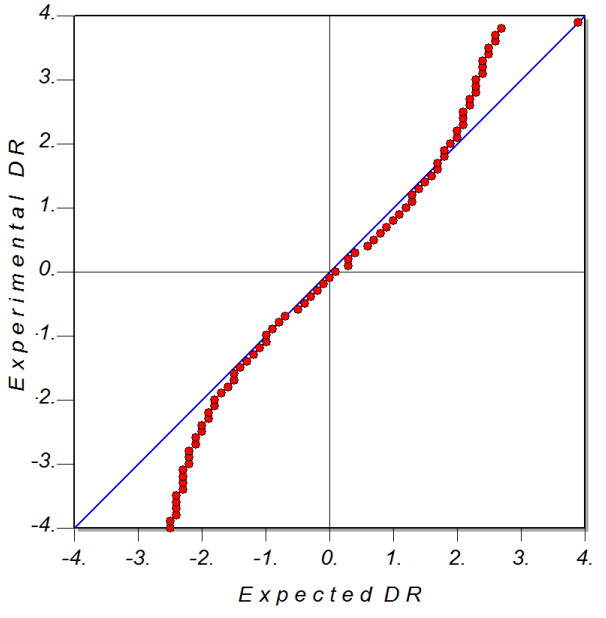


Figure S2 . Expected vs. Experimental delta(RHO) for:
(a) EXP_MUL, (b) EXP_VIR and (c) EXP_IAM spherical refinements.

Zhurov *et al*., (2008) J. Appl. Cryst. **41**, 340-349.



(a)



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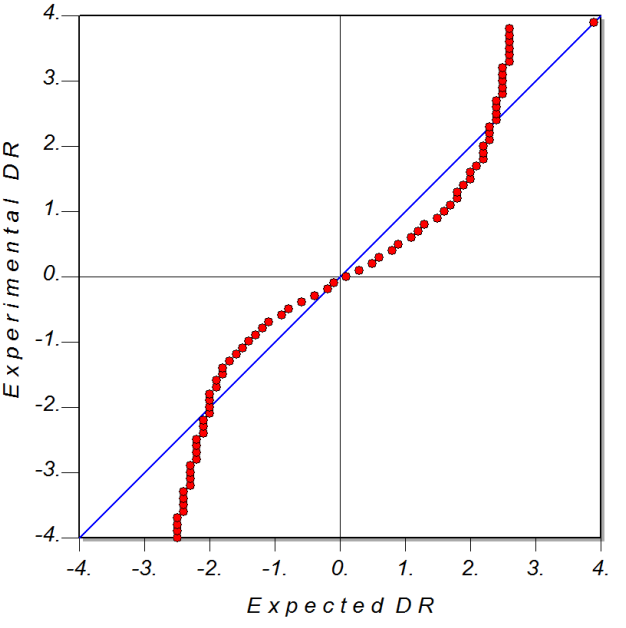
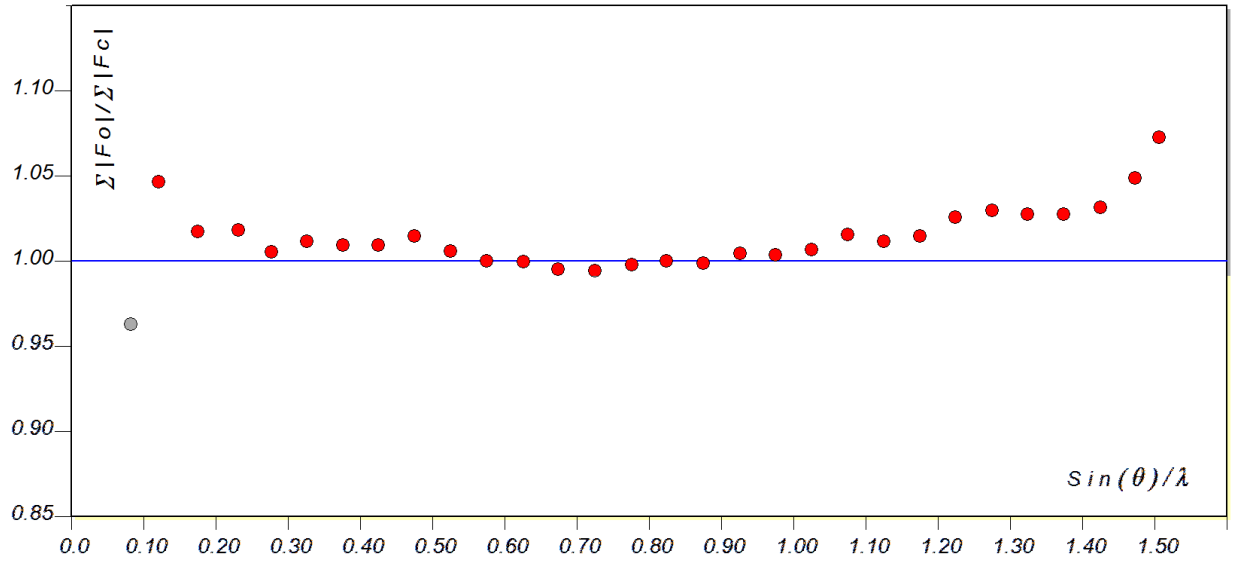
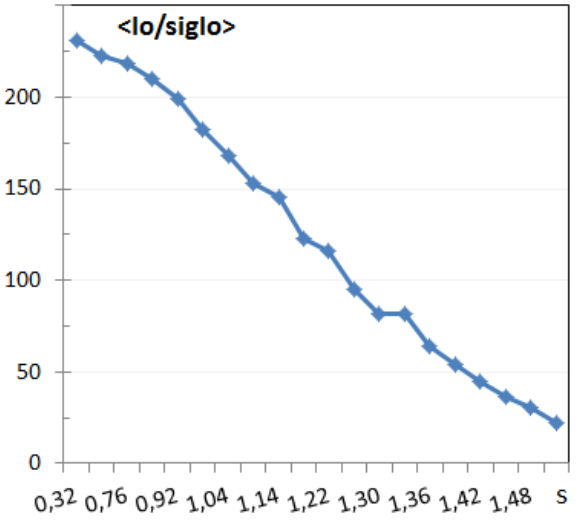


(c)

Figure S3. Average F_{calc}/ Average F_{obs} as a function of sin$q$ / l





Average
I_{obs} / sigma(I_{obs})
as a function of sin$q$ / l
in bins of equal number
of reflections.

Figure S4

Electrostatic potential map of the interacting assemble of three molecules, showing the good shape complementarity.

Top: experimental multipolar. Bottom: experimental virtual.

Contour ±0.05e/Å. Positive: solid blue; negative: red dashed lines; zero: yellow dashed lines.

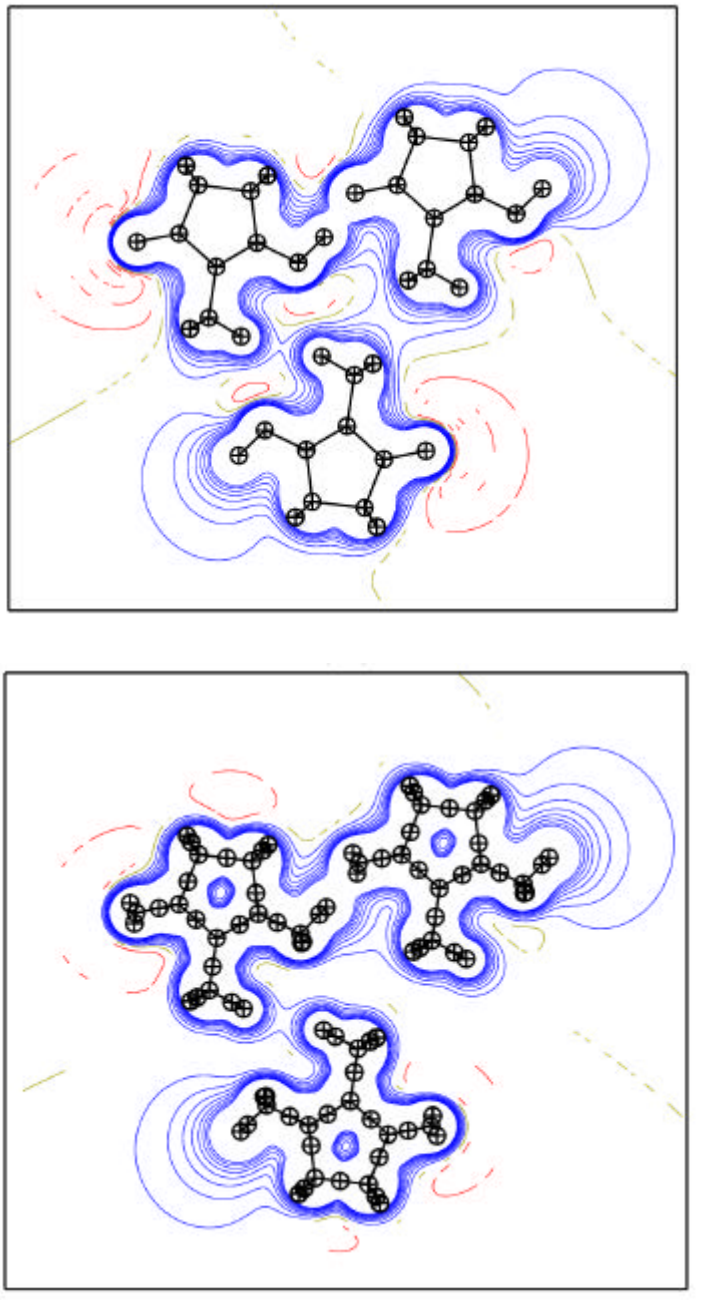


Figure S5

Deformation electron density in the lone pairs plane of the hydroxyl oxygen atom O3.
Left : theoretical models, Right: experimental models.
Top: residual density using a spherical atom model. Fourier synthesis truncated at *d*>0.5Å.
Bottom: static electron density of the virtual atom models..
Contour level: ±0.05e·Å-3. Positive: solid blue lines; negative: dashed red lines;
dashed yellow lines.

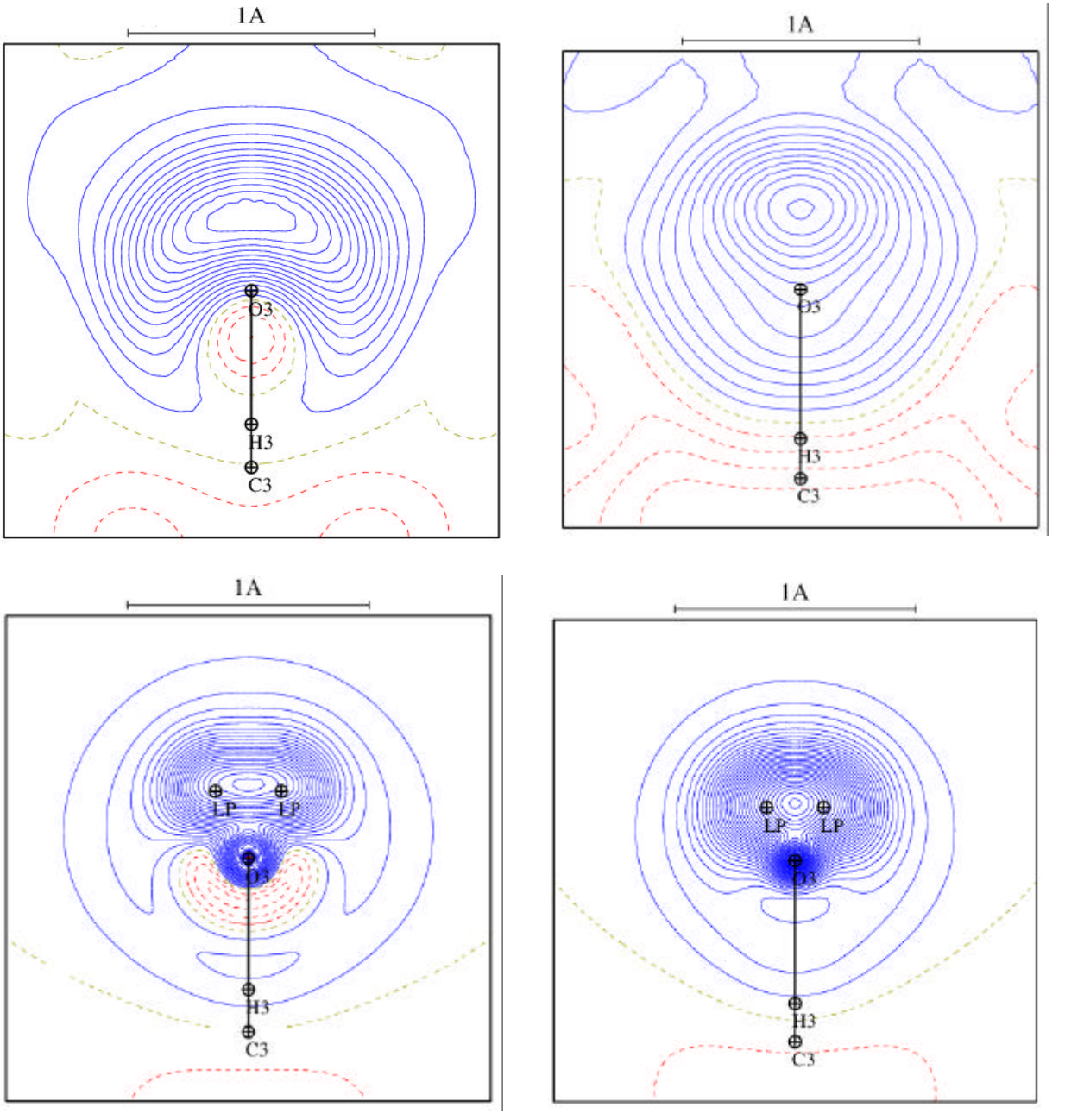


Figure S6.

Difference between the B3LYP electron density and that of the THEO_MUL (top) and THEO_VIR (bottom) models. Contours as in Fig. Sup5.