Electronic Supplementary Material (ESI) for CrystEngComm.

Experimental electron densities of neutral and zwitterionic forms of piroxicam drug

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SUPPORTING INFORMATION

Text TS1. Additionnal information on Scheme 2. 4
Scheme S1. Possible tautomers of piroxicam: nPX1 (N2H-O3H); nPX2 (N2H-O4H); nPX3 (N3H-O3H); nPX4 (N3H-O4H) and nPX5 (O3H-O4H) respectively. 6
Scheme S2. Possible resonance structure of zwitterionic form. 6
Scheme S3. Cationic form and 3 different conformations (EZE, ZZZ and ZZE) of anionic form found in crystal structures respectively. 6
Scheme S4. Structure formula based on statistic study for zwitterionic form (a) and ZZE anionic form (b). 6
Figure S1. Bond distance in Å for all 20 structures of neutral piroxicam studied in crystal forms. (a) C-O bond distance; (b) C-C bond distance; (c) C-N bond distance. Each radius presents one structure, of which the upward vertical radius is from the structure. 7
Figure S2. Bond distance in Å for all 20 structures of neutral piroxicam and 27 structures of zwitterionic piroxicam studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure, of which the upward vertical radius is from the structure studied in this paper. 8
Figure S3. Bond distance in Å for all 20 structures of neutral piroxicam and 5 structures of cationic piroxicam studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line f or C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure. 9
Figure S4. Bond distance in Å for all 20 structures of neutral piroxicam and 9 structures of anionic piroxicam in salt studied in crystal forms. One anionic structure has disorder at N3 and C11, thus for C-O and C-C, it is counted twice in the figure. (a) C-O bon d distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure. 10
Figure S5. Bond distance in Å for all 27 structures of zwitterionic piroxicam and 9 structures of anionic piroxicam in salt studied in crystal forms. One anionic structure has disorder at N3 and C11, thus for C-O and C-C, it is counted twice in the figure. (a) C- O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure. 11
Figure S6. Bond distance in Å for all 20 structures of neutral piroxicam and 4 structures of neutral piroxicam in complex studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure. 12
Figure S7. Bond distance in Å for all 27 structures of zwitterionic piroxicam and 7 structures of *EZE* conformation anionic piroxicam in complex studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, do tted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure. 13
Figure S8. Residual density map at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. All data included. 14

Figure S9. Residual density map at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. All data included. 15
Figure S10. Static deformation density map at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.05 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. 16
Figure S11. Static deformation density map at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.05 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. 17
Figure S12. 2D laplacian map of total electron density at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. Contour intervals are +/- 2, 4, $8*10^n$ $eÅ^{-5}$ (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines. 18
Figure S13. 2D laplacian map of total electron density at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. Contour intervals are +/- 2, 4, $8*10^n$ $eÅ^{-5}$ (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines. 19
Figure S14. Residual density map at the phenyl and pyridine plan for nPX, zPXL, zPXR respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. 20
Figure S15. Static deformation density map at the phenyl and pyridine plan for nPX, zPXL, zPXR respectively. The contour intervals are 0.05 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes.....21
Figure S16. 2D laplacian map of total electron density at phenyl and pyridine plan for nPX, zPXL, zPXR respectively. Contour intervals are +/- 2, 4, $8*10^n$ $eÅ^{-5}$ (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines. 22
Figure S17. Electrostatic potential generated at the molecular surface (total electron density equals 0.001eBohr^{-3} i.e. 0.0067e$Å^{-3}$) for nPX, zPXL and zPXR molecule respectively. 23
Table S1. Crystallization situations of piroxicam in polymorphs, hydrates, co-crystals, salts and complexes as retrieved from the CSD database. 24
Table S2. Data Collection and Refinement Details of form III and IV of sulfathiazole 28
Table S3. Estimate of average error on the electron density map. σ(Δρ)=2/V*[Σ(k.Fo-Fc)^2]^(1/2) (Rees, B. Acta Cryst. 1976, A32, 483-488).....29
Table S4. Topology of the experimental electron density of piroxicam (nPX, zPXL and zPXR) for covalent bonds not listed in the paper.....30
Table S5 Selected bond lengths and angles. Standard deviations are in parentheses. For hydrogen bonds, D is the donor and A, the acceptor……..31

Supplementary Materiel Text TS1.

Additionnal information on Scheme 2.

Different piroxicam (PX) drug: neutral, zwitterionic, anionic and cationic forms.

Tautomerization is an intramolecular isomerization that involves breaking or making bonds. In the case of PX, this prototropic tautomerism results in the proton transfer accompanied by electron delocalization. Five possible tautomers are shown in Scheme S1. The different conformations depend on which of the C-O bond is a double bond and on whether the nitrogen of the pyridine ring is free (nPX1, nPX2), implied in an intramolecular hydrogen bond (nPX5) or is linked to a proton (nPX3, nPX4).

The switch of covalent bond properties C-O (C2-O3 and C10-O4) and C-N (N2-C11 and N3-C11) can be determined *via* bond distances values. We have thus measured the corresponding C-O and C-N bonds in published crystal structure extracted from CSD[1], where PX keeps the neutral form. Figure S1 shows, for all studied structures, larger distance between O3 and C2 than that between O4 and C10, the difference is around 0.1Å. In Figure S1b, a difference of 0.1Å exists in the neighbour bonds C1-C2 and C1-C10. We conclude that in solid state C10-O4 and C1-C2 bonds are more likely double bonds and the hydrogen atom may not be attached to O4. The nPX2, nPX4 and nPX5 tautomers should be excluded. Figure S1c shows the C-N bond; N3-C11 is statistically shorter than N2-C11 bond with a difference of 0.05Å, which is consistent with properties of the pyridine ring. nPX3 tautomer is excluded. Therefore PX crystallizes in neutral form only in the nPX1 (N2H, O3H) EZE conformation.

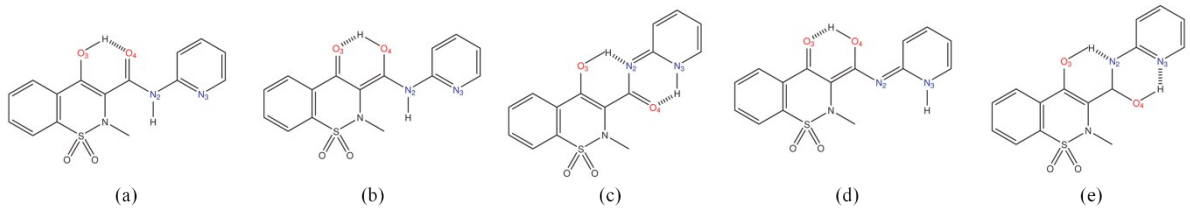
PX may also present in crystal structures charged forms such as zwitterionic, cationic and anionic form. Table S1 summarizes the different structures extracted from CSD.[1] Neutral form exists in 3 polymorphs, 16 co-crystals and 3 complexes; zwitterionic form exists in monohydrate and 20 co-crystals; cationic form exists in 5 salts; anionic form exists in 6 salts and 9 complexes among which one anionic form complex has ZZZ conformation and another presents ZZE conformation (Scheme S3).

The four resonance structures of the zwitterionic form (Scheme S2) show its possible extreme configuration. In crystallographic studies, the refined structure is usually more like a resonance hybrid. Bond distances of neutral and zwitterionic form are shown in Figure S2. Considering only the orange lines, one can observe that N2-C11 and N3-C11 have similar values and C10-O4 is shorter than C2-O3. Compared to neutral form, C2-O3 and N2-C11 simple bonds are shortened towards C10-O4 and N3-C11 respectively whereas C1-C2 double bond is extended towards C1-C10 simple bond(Figure S2a and S2b). These observations indicate the existence of an electron delocalization along the chain (O3, C2, C1, C10, N2, C11) in zwitterionic form. The representation in Scheme S4a is the closest representation to the crystal structures observations. However, the distance between N3 and C11 remains the same, which signifies that the proton transfer does not much influence on the pyridyl ring (Figure S2c).

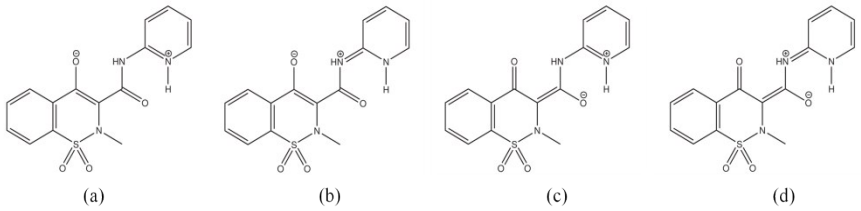
Cationic form has the same configuration as the neutral form, and these 6 distances are rather similar except the N2-C11 bond which is slightly shortened due to the proton capture at N3 (Figure S3).
Anionic form in salts all crystallizes in EZZ conformation. Compared to neutral form, the C-N bonds are similar; compared to zwitterionic form, the C-O and C-C bonds share similar statistic results (Figures S4 and S5) as well as electron delocalization along part of the main chain (Scheme S4b). Participation of metal atoms has various influences on chemical conditions of ligands, thus the similar configuration does not always result in comparable bond distances (Figures S6 and S7). The two complexes, in which PX presents unique conformation, are not reported in these figures.

References

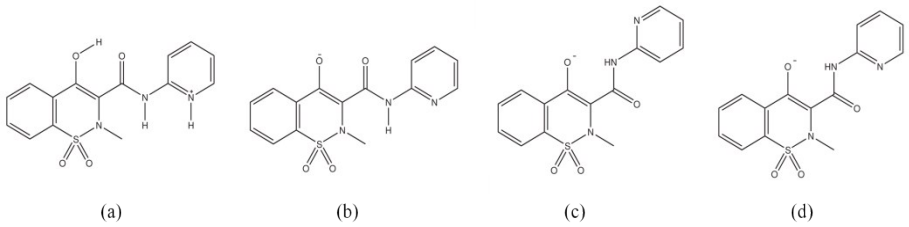
1 The Cambridge Structural Database: A quarter of a million crystal structures and rising. F.H. Allen, Acta Crystallogr., 2002, B58, 380.



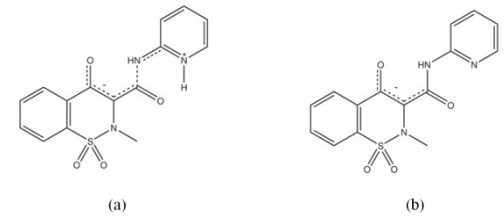
Scheme S1. Possible tautomers of piroxicam: nPX1 (N2H-O3H); nPX2 (N2H-O4H); nPX3 (N3H-O3H); nPX4 (N3H-O4H) and nPX5 (O3H-O4H) respectively.



Scheme S2. Possible resonance structure of zwitterionic form.



Scheme S3. Cationic form and 3 different conformations (EZE, ZZZ and ZZE) of anionic form found in crystal structures respectively.



Scheme S4. Structure formula based on statistic study for zwitterionic form (a) and ZZE anionic form (b).

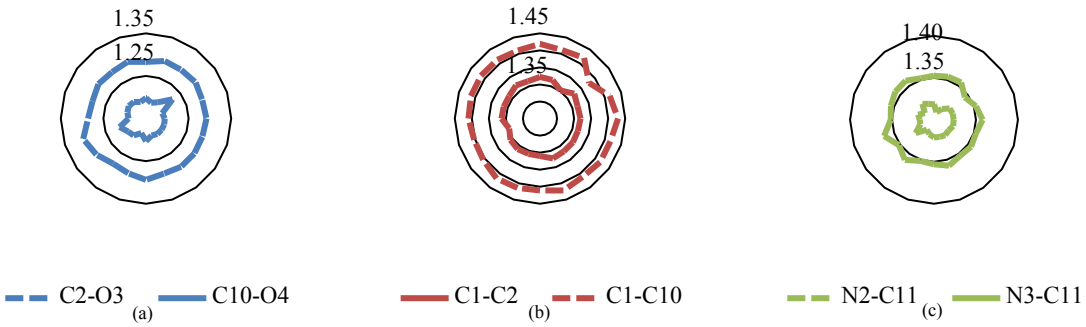
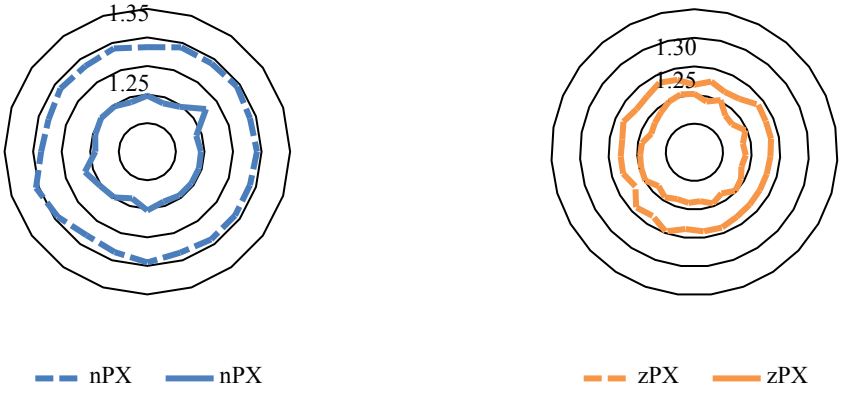


Figure S1. Bond distance in Å for all 20 structures of neutral piroxicam studied in crystal forms. (a) C-O bond distance; (b) C-C bond distance; (c) C-N bond distance. Each radius presents one structure, of which the upward vertical radius is from the structure.



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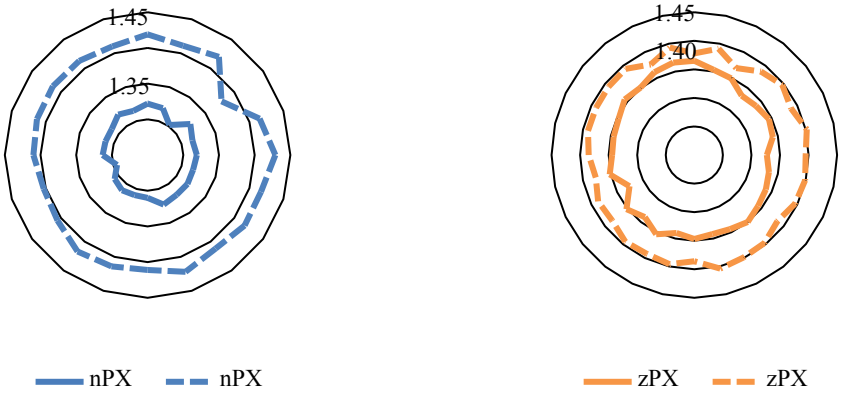

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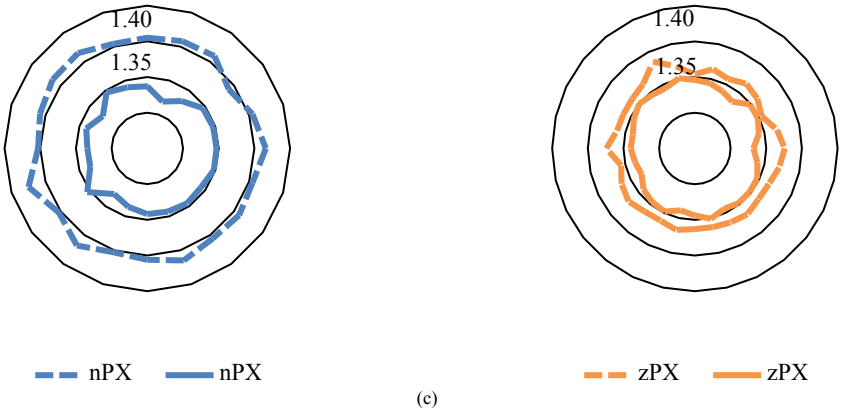
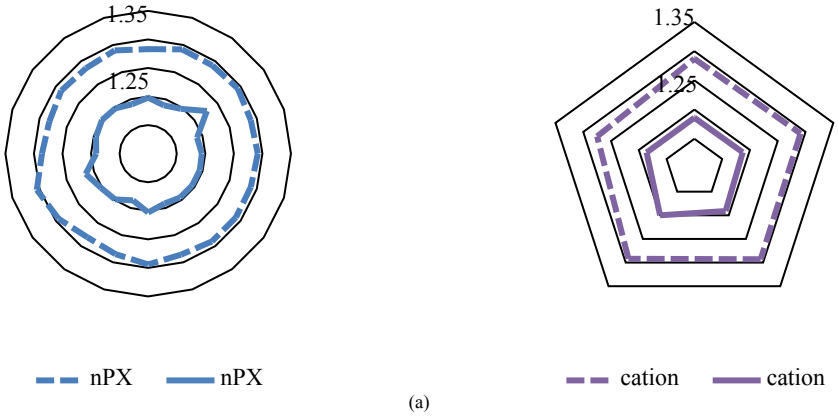


(c)

Figure S2. Bond distance in Å for all 20 structures of neutral piroxicam and 27 structures of zwitterionic piroxicam studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure, of which the upward vertical radius is from the structure studied in this paper.



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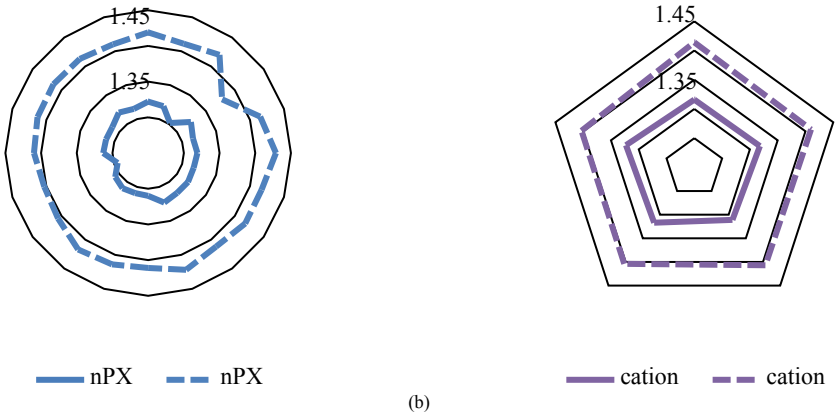

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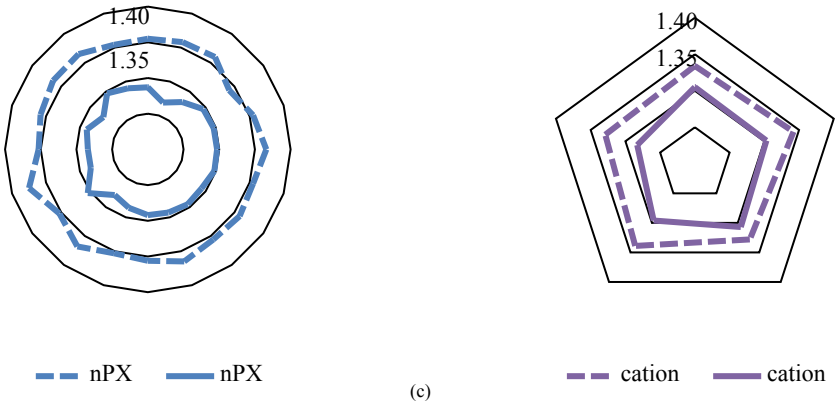
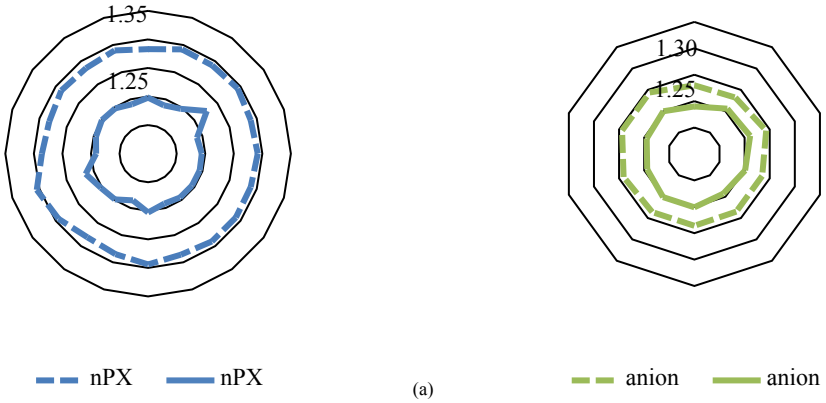


(c)

Figure S3. Bond distance in Å for all 20 structures of neutral piroxicam and 5 structures of cationic piroxicam studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line f or C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure.



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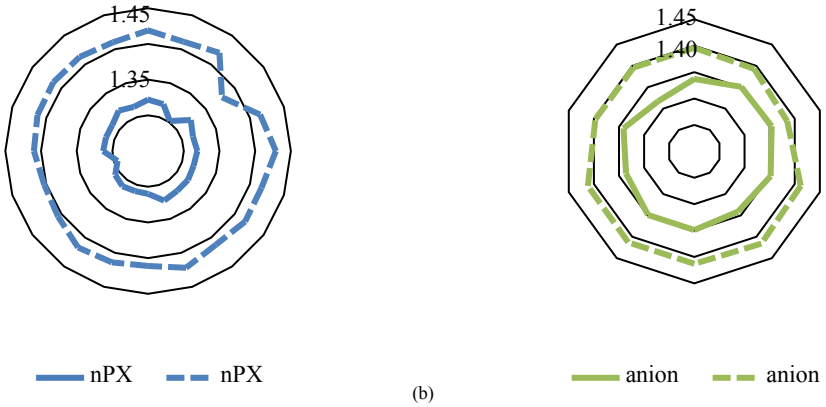

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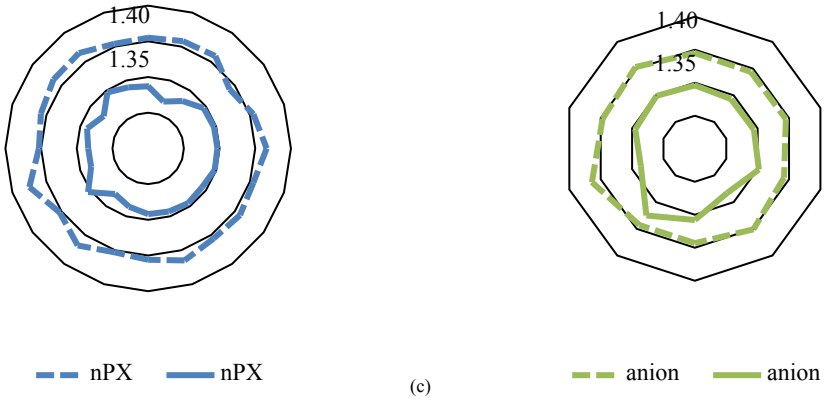
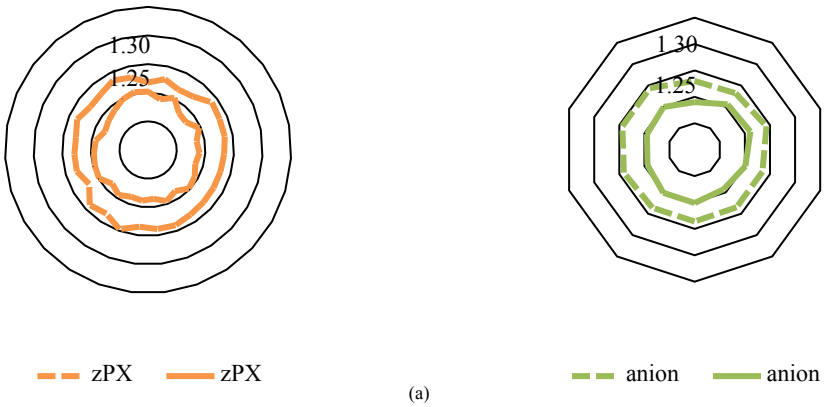


(c)

Figure S4. Bond distance in Å for all 20 structures of neutral piroxicam and 9 structures of anionic piroxicam in salt studied in crystal forms. One anionic structure has disorder at N3 and C11, thus for C-O and C-C, it is counted twice in the figure. (a) C-O bon d distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure.



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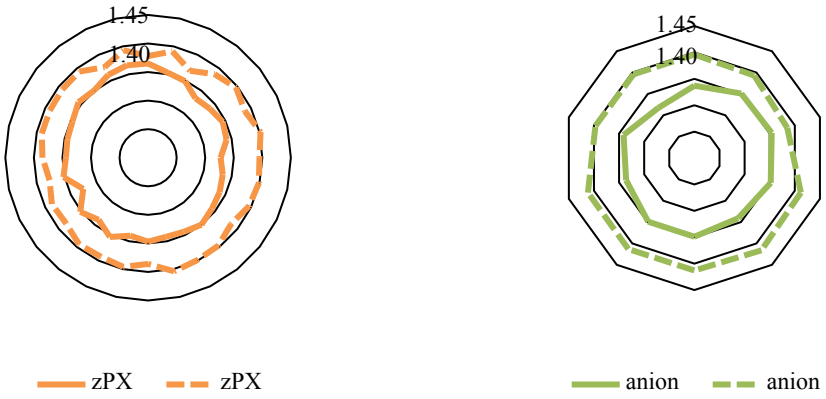

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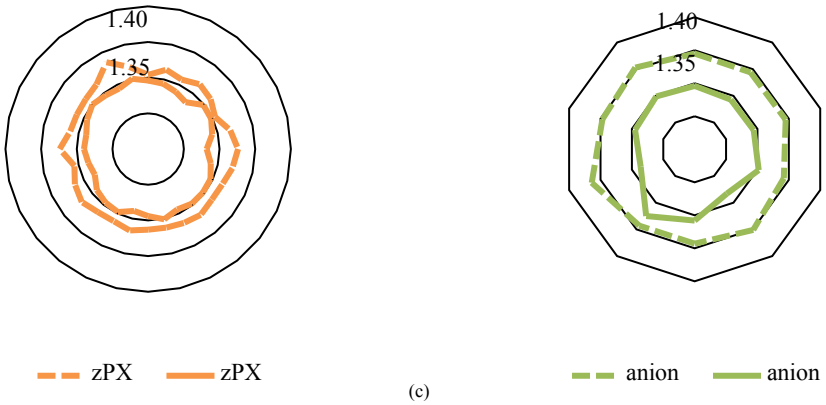

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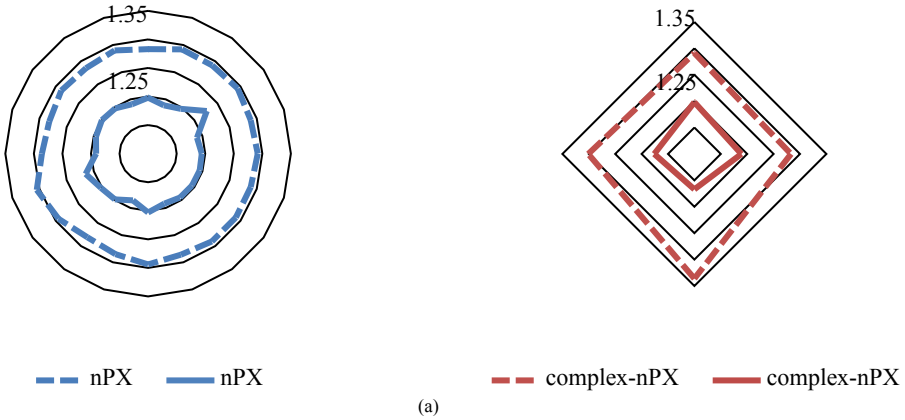
Figure S5. Bond distance in Å for all 27 structures of zwitterionic piroxicam and 9 structures of anionic piroxicam in salt studied in crystal forms. One anionic structure has disorder at N3 and C11, thus for C-O and C-C, it is counted twice in the figure. (a) C- O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure.



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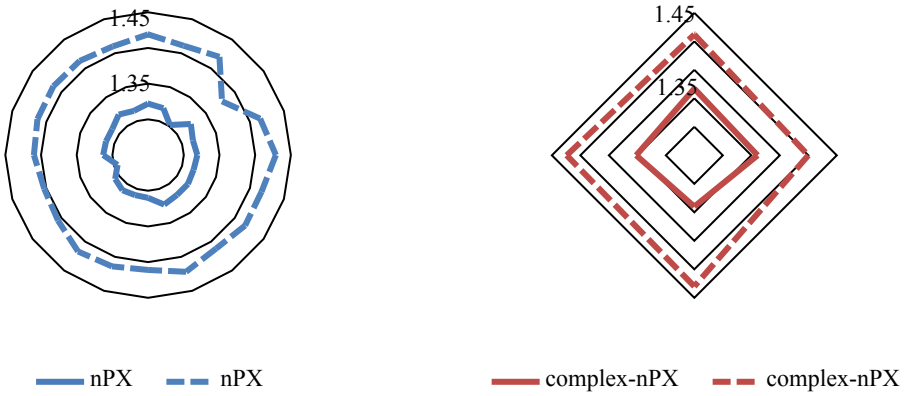

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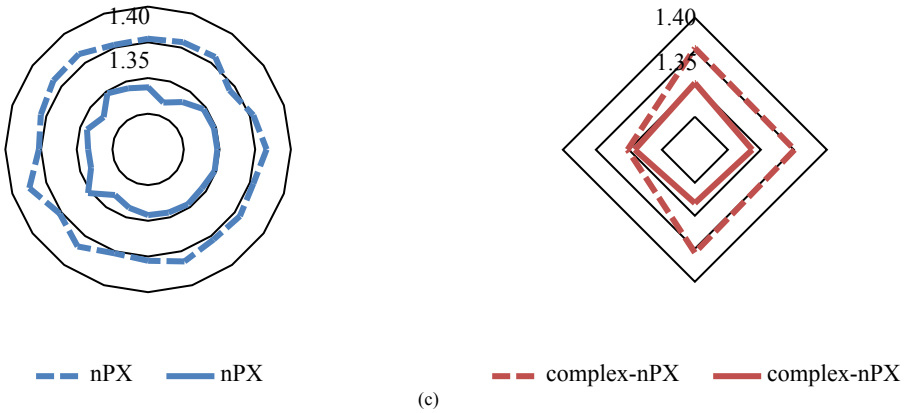

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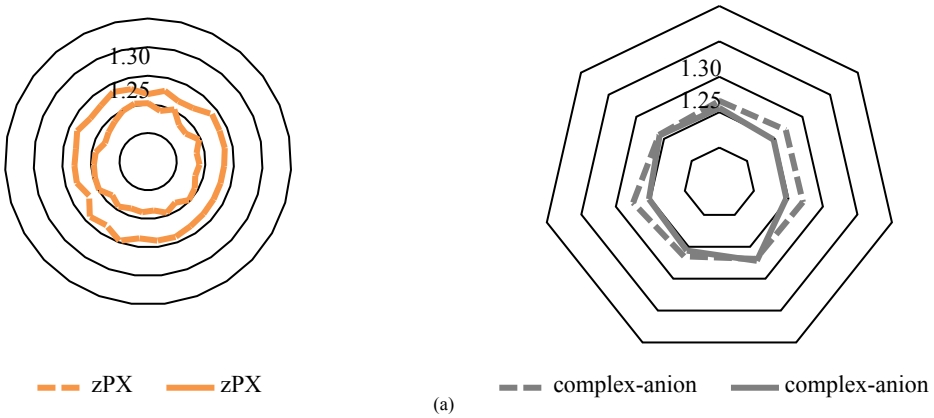
Figure S6. Bond distance in Å for all 20 structures of neutral piroxicam and 4 structures of neutral piroxicam in complex studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, dotted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure.



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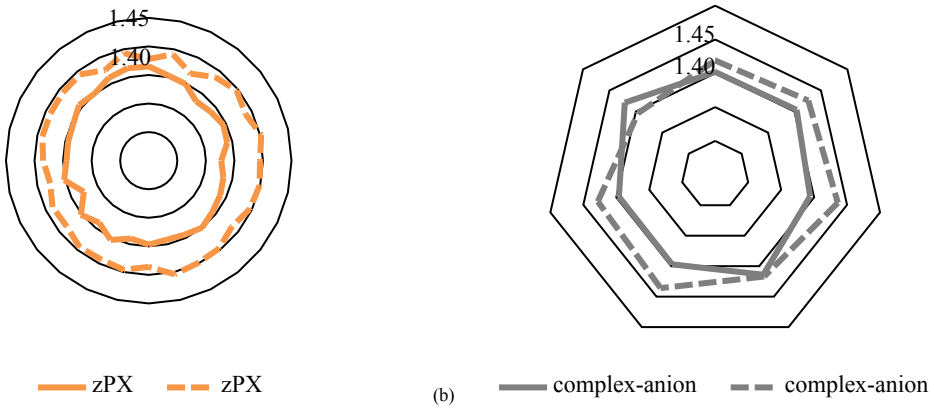

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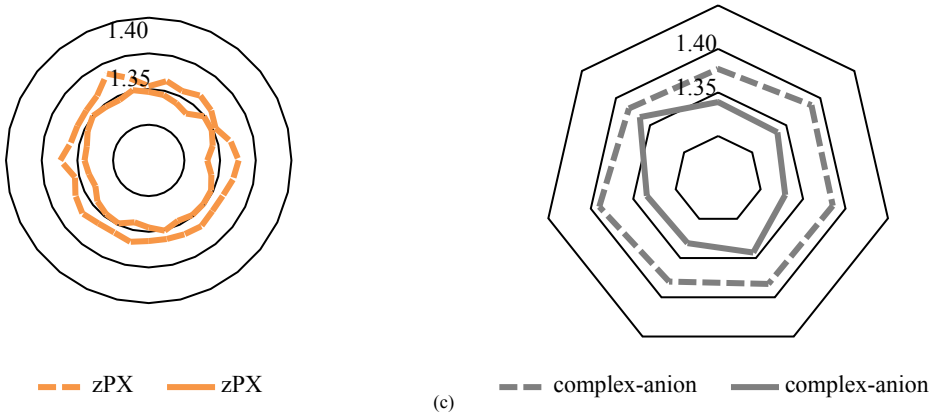

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Figure S7. Bond distance in Å for all 27 structures of zwitterionic piroxicam and 7 structures of *EZE* conformation anionic piroxicam in complex studied in crystal forms. (a) C-O bond distance, dotted line for C2-O3, full line for C10-O4; (b) C-C bond distance, do tted line for C1-C10, full line for C1-C2; (c) C-N bond distance, dotted line for N2-C11, full line for N3-C11. Each radius presents one structure.

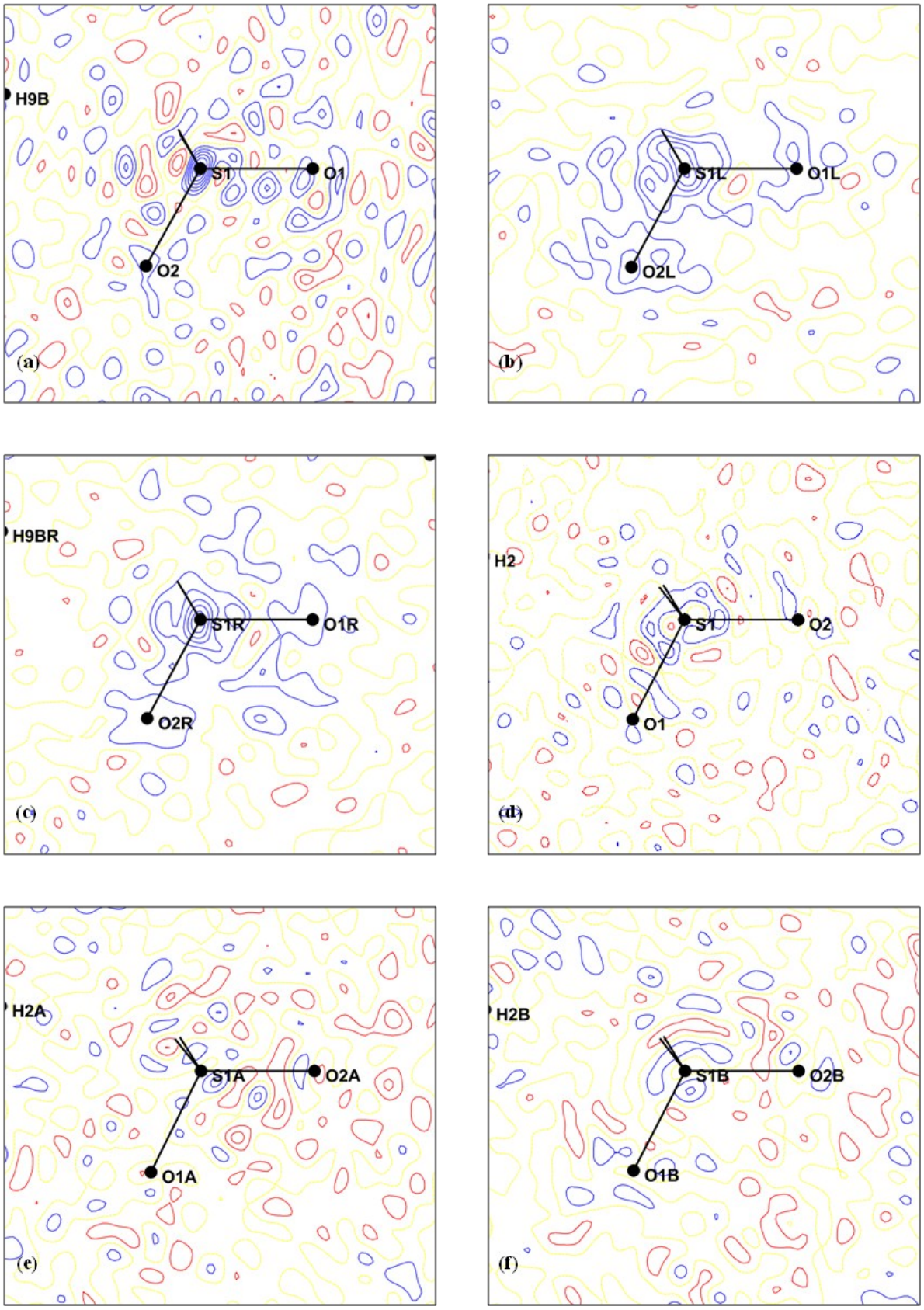

Figure S8. Residual density map at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. All data included.

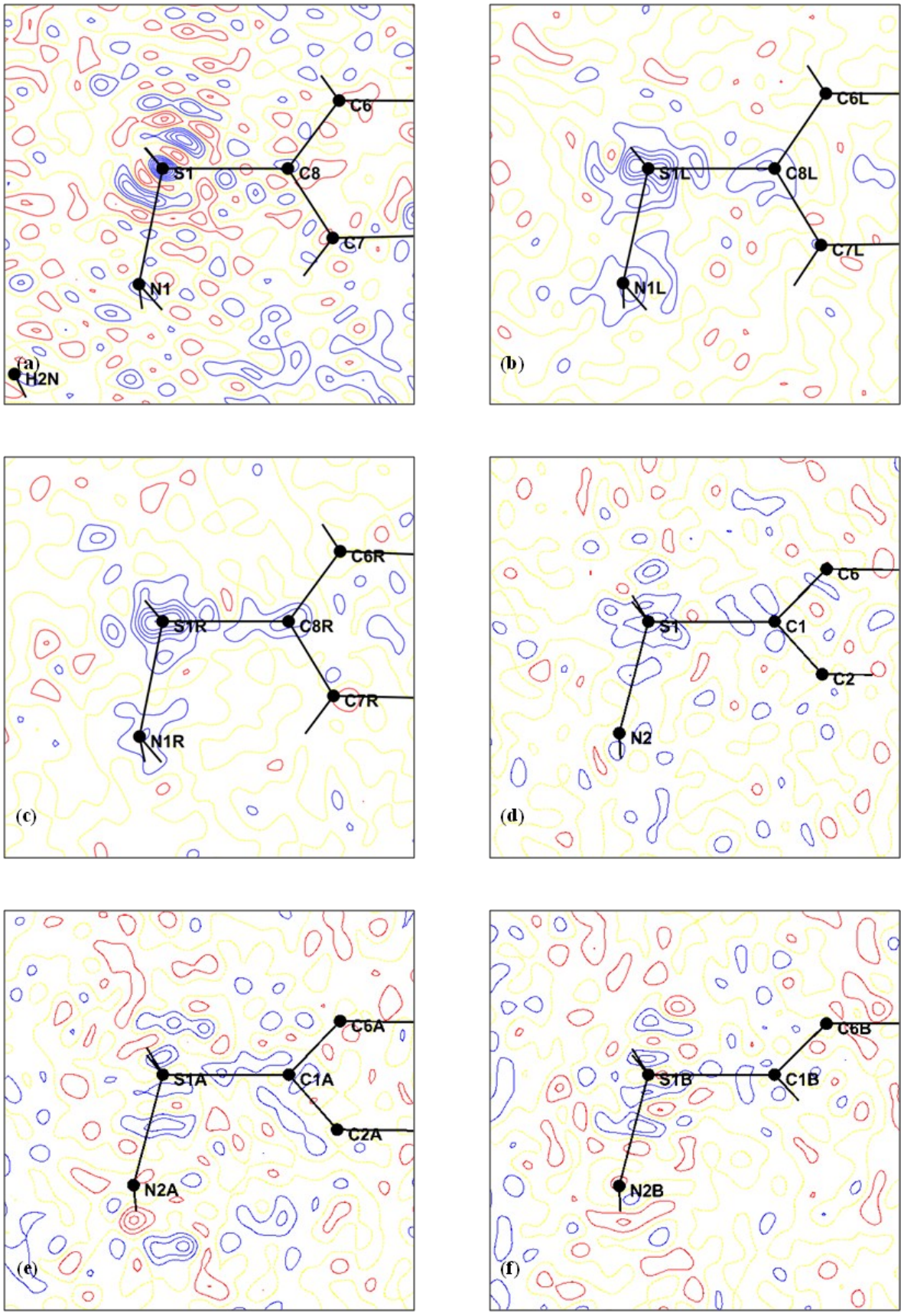

Figure S9. Residual density map at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes. All data included.

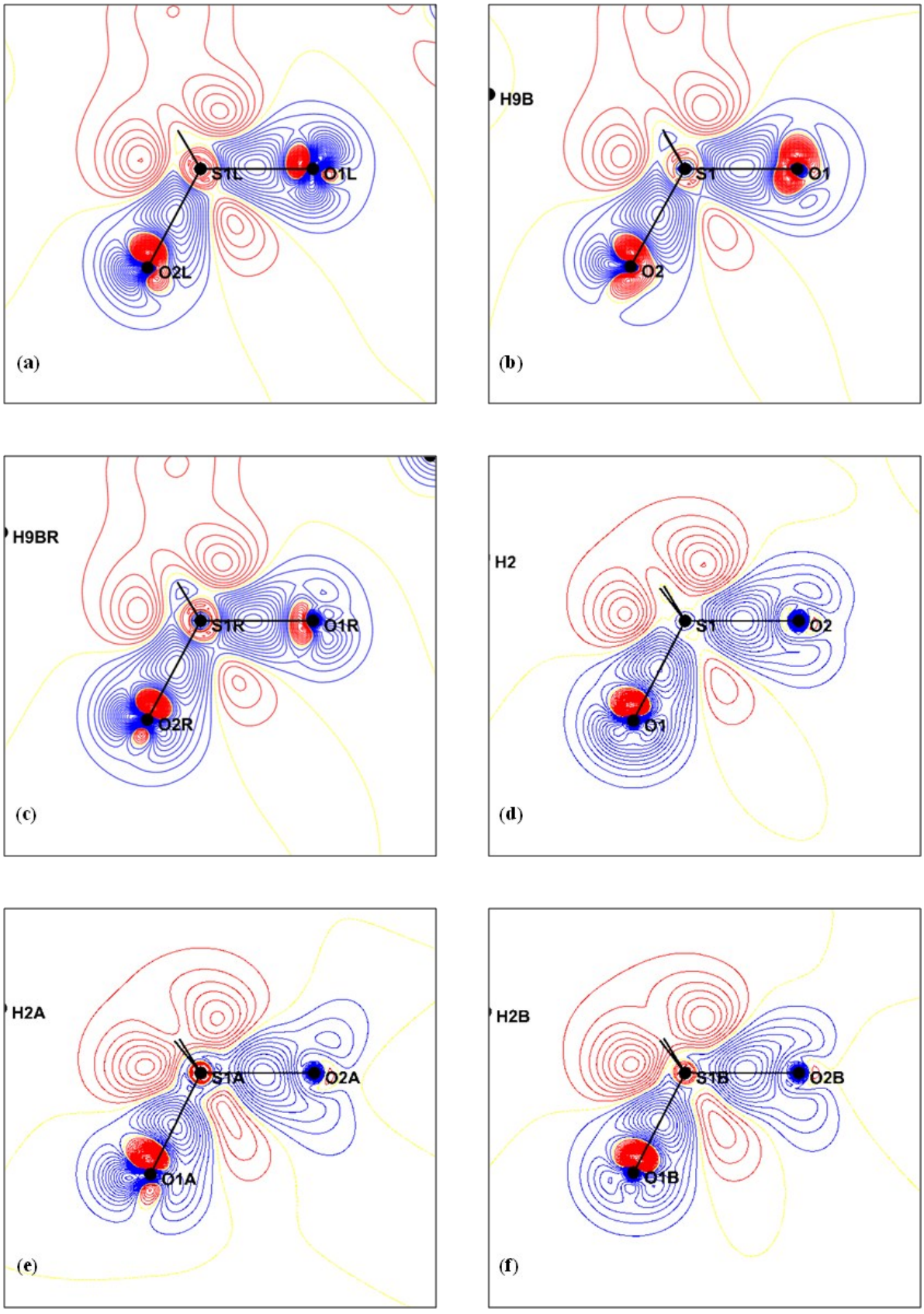

Figure S10. Static deformation density map at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.05 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes.

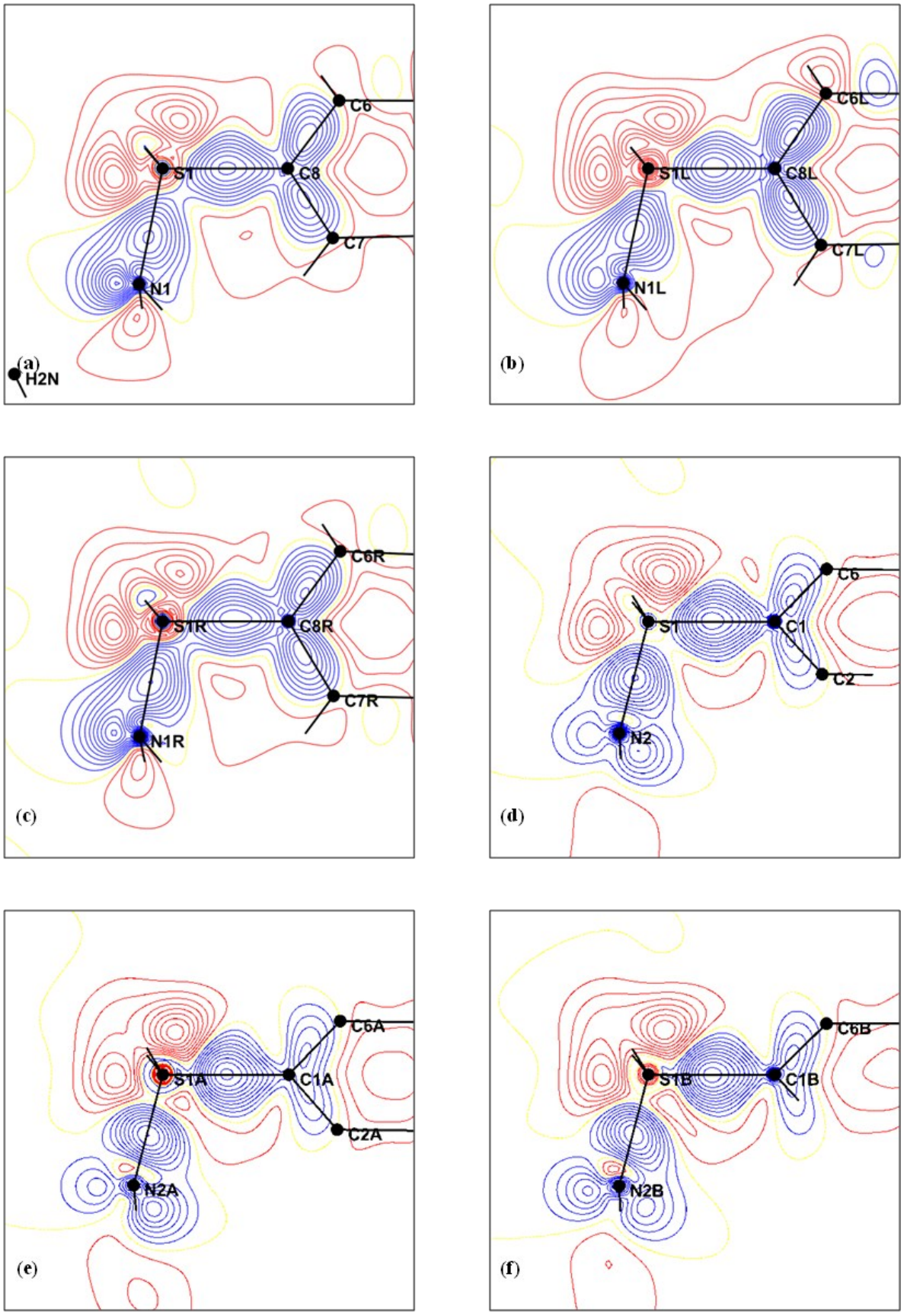

Figure S11. Static deformation density map at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. The contour intervals are 0.05 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes.

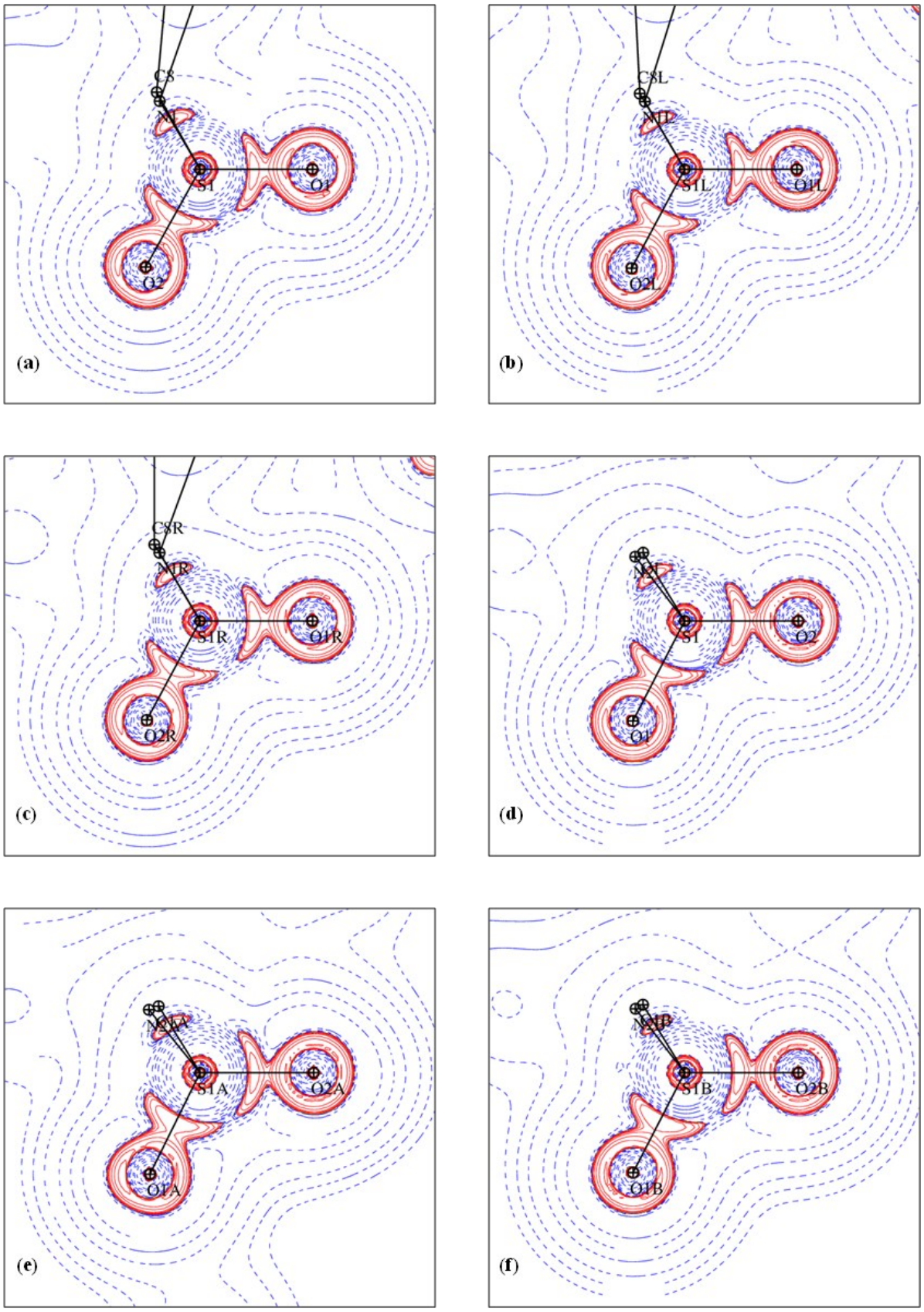

Figure S12. 2D laplacian map of total electron density at the plan S-O-O for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. Contour intervals are +/- 2, 4, $8*10^{n}$ $eÅ^{-5}$ (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines.

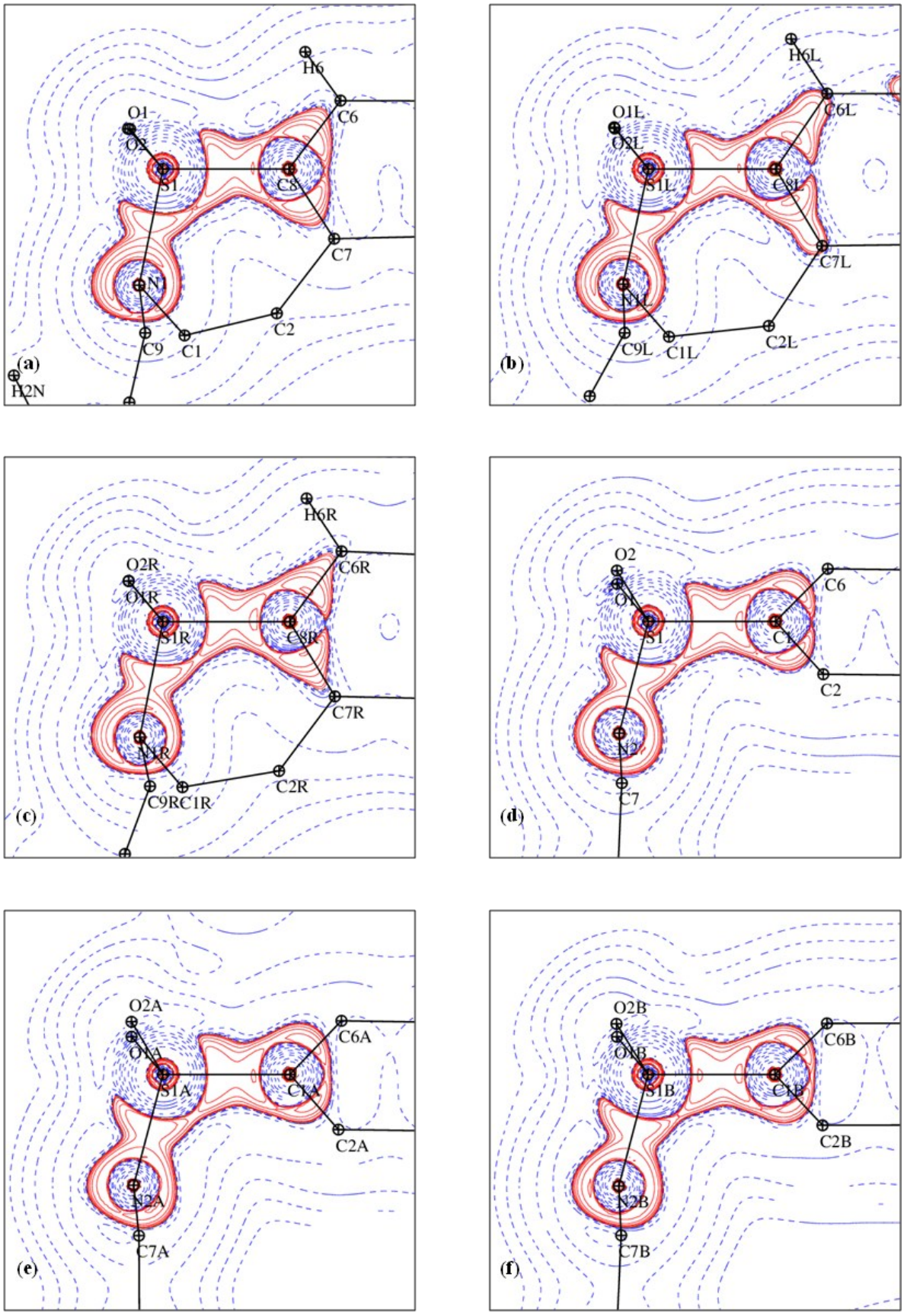

Figure S13. 2D laplacian map of total electron density at the plan S-C-N for nPX, zPXL, zPXR, sulfathiazole IV, III-A and III-B respectively. Contour intervals are +/- 2, 4, $8*10^{n}$ eÅ^{-5} (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines.

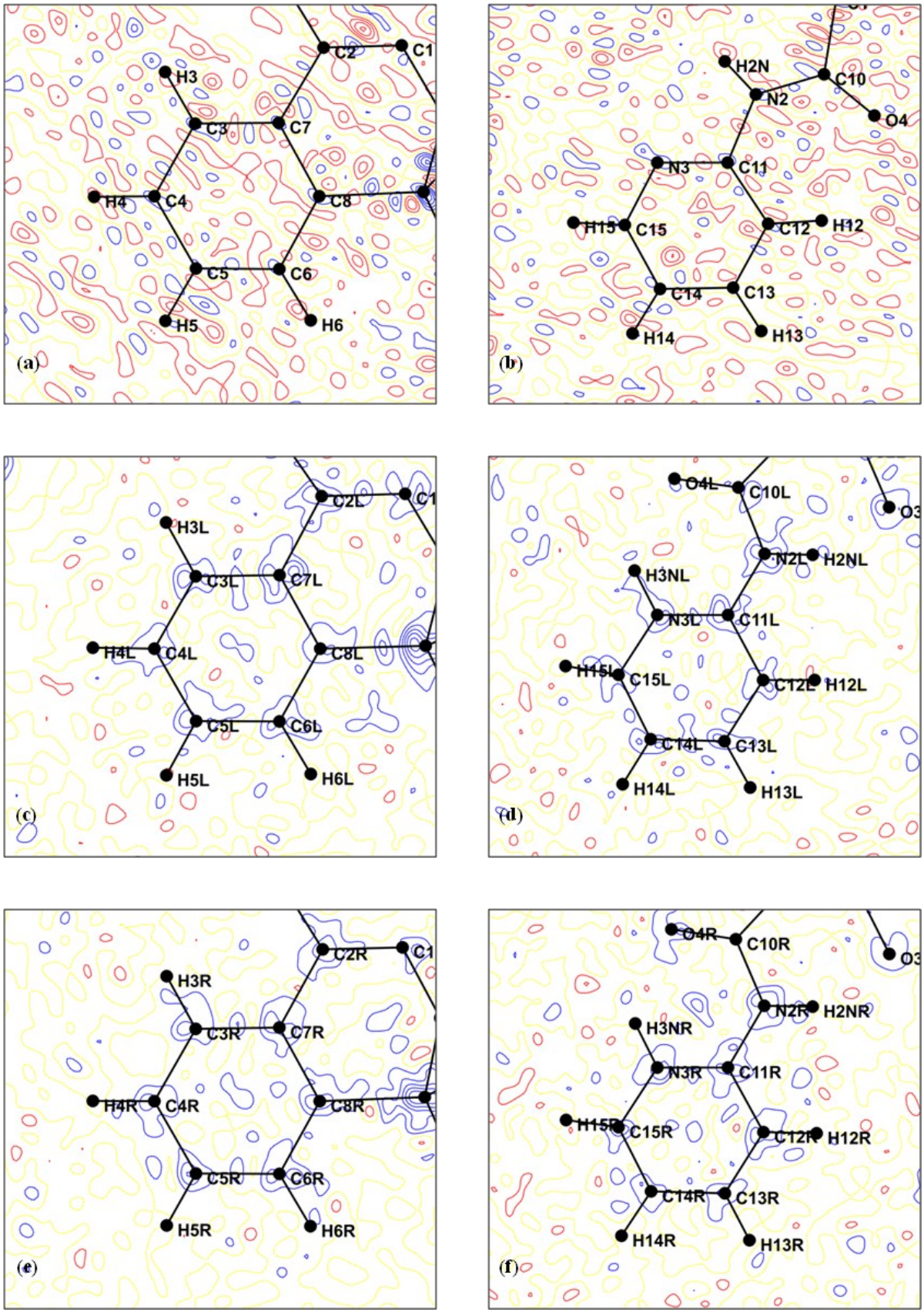

Figure S14. Residual density map at the phenyl and pyridine plan for nPX, zPXL, zPXR respectively. The contour intervals are 0.1 e $Å^{-3}$; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes.

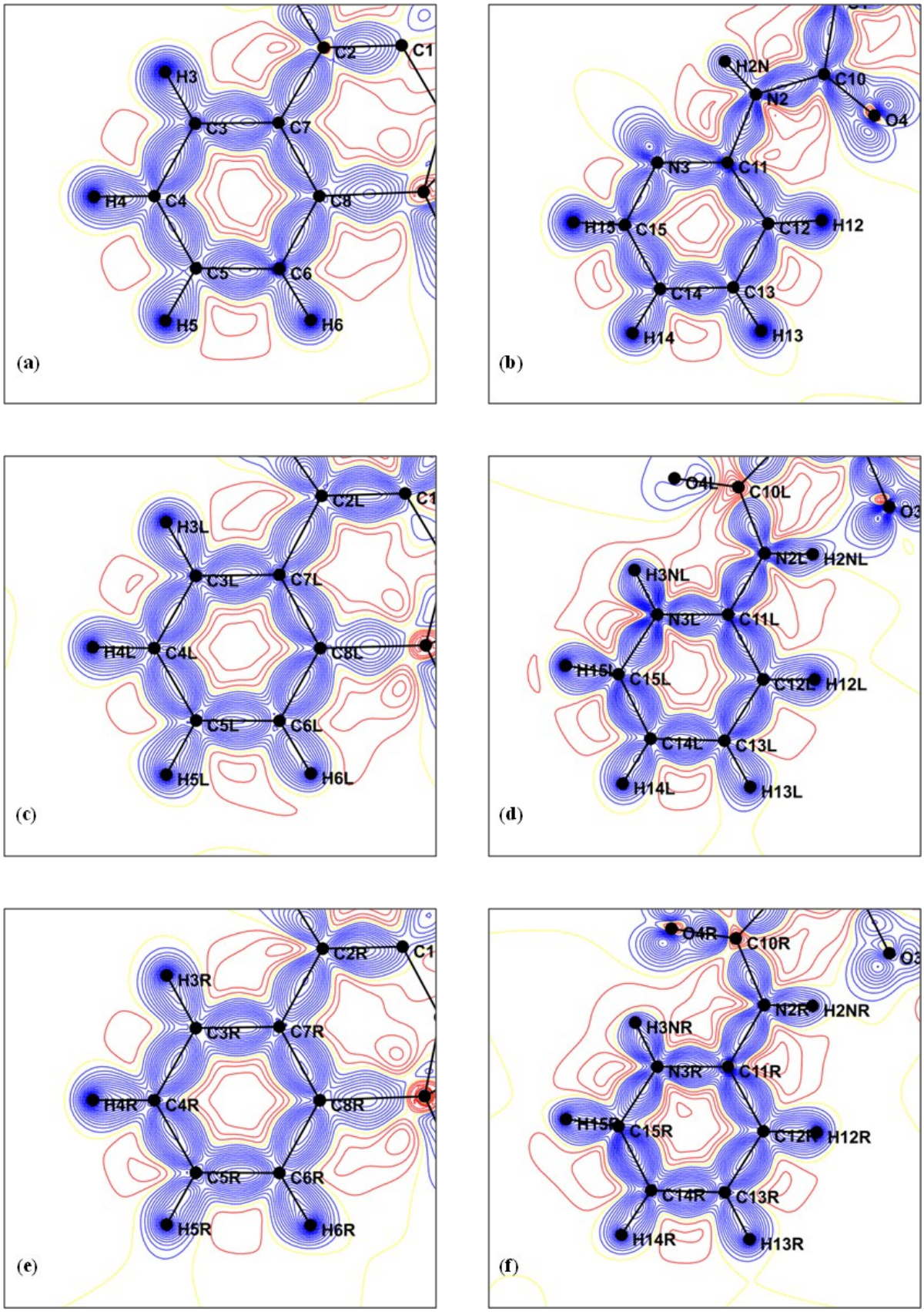

Figure S15. Static deformation density map at the phenyl and pyridine plan for nPX, zPXL, zPXR respectively. The contour intervals are 0.05 e Å^{-3}; positive contours are shown with blue solid lines, negative contours with red lines, and the zero contours with pale yellow dashes.

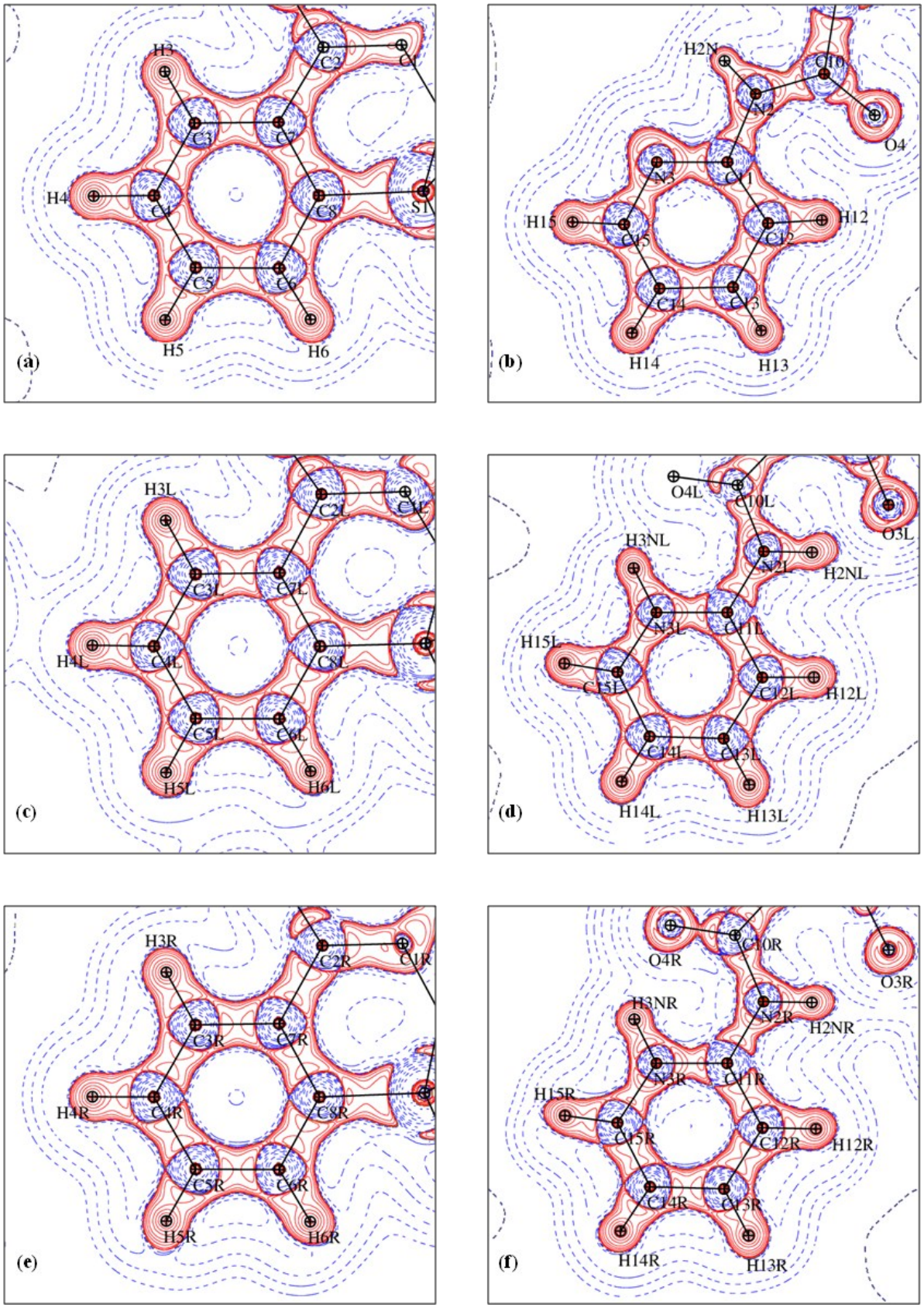

Figure S16. 2D laplacian map of total electron density at phenyl and pyridine plan for nPX, zPXL, zPXR respectively. Contour intervals are +/- 2, 4, $8*10^{n}$ $eÅ^{-5}$ (n=-1, 0, 1, 2); positive contours are shown with blue dashed lines, negative contours with red solid lines.

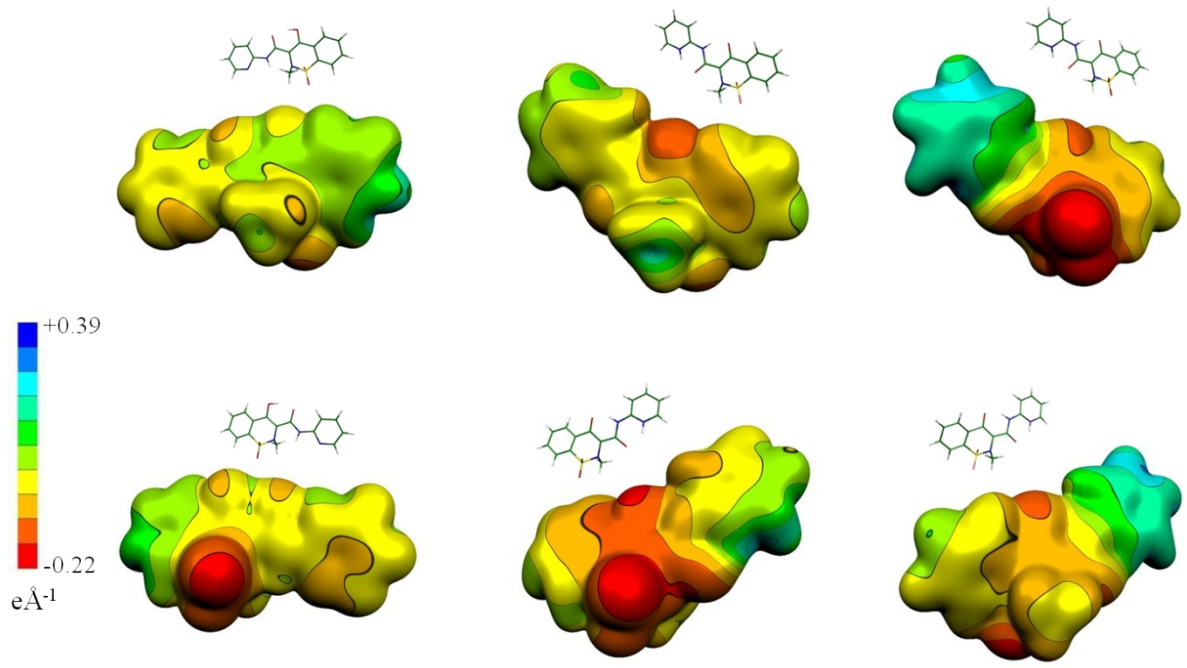

Figure S17. Electrostatic potential generated at the molecular surface (total electron density equals 0.001eBohr^{-3} i.e. 0.0067eÅ^{-3}) for nPX, zPXL and zPXR molecule respectively.

Table S1. Crystallization situations of piroxicam in polymorphs, hydrates, co-crystals, salts and complexes as retrieved from the CSD database.

Type		REFCODE	Neutral	Zwitterion	Charged		Configuration	References
				zwitternionic	anionic	cationic		
Polymorph	Form 1(needle, b)	nPX	•				*EZE*	This work
	Form 1(needle, b)	BIYSEH, BIYSEH01	•				*EZE*	Kojic-Prodic, B.; Ruzic-Toros, Z. *Acta Crystallogr. Sect.**B**:Struct.Crystallogr.Cryst.Chem.* , **1982**, *38*, 2948. Suh, I.-H.; Kim, K.-J.; Ko, T.-S.; Kim, B.-H. *Chung.Kwa.Yong.(Kor.)(Chungnam J.Sci)* **1989**, *16*, 30.
	Form 2 (cubic, a)	BIYSEH06	•				*EZE*	Vrecer, F; Vrbine, M.; Meden, A. *Int.J.Pharm*. **2003**, *256*, 3.
	Form 3	BIYSEH07	•				*EZE*	Naelapaa, K.; Van de Streek, J.; Rantanen, J.; Bond, A.D. *J.Pharm.Sci.* **2012**, *101*, 4214.
Hydrate	mono	zPX		•			*ZZZ*	This work
	mono	CIDYAP CIDYAP01		•			*ZZZ*	Bordner, J.; Richards, J.A.; Weeks, P.; Whipple, E.B. *Acta Crystallogr., Sect.C: Cryst.Struct.Commun.* **1984**, *40*, 989. Reck, G.; Dietz, G.; Laban, G.; Gunther, W.; Bannier, G.; Hohne, E. *Pharmazie* ,**1988**, *43*, 477.
Co-crystal	saccharine	YANNEH		•			*ZZZ*	Bhatt, P.M.; Ravindra, N.V.; Banerjee, R.; Desirajum G.R. *Chem.Commun.* **2005**, 1073.
	2-fluorobenzoic acid	CEKLAH	•				*EZE*	Wales, C.; Thomas, L.H.; Wilson, C.C. *Cryst Eng Comm,* **2012**, *14*, 7264.
	2-methylbenzoic acid	CEKLEL	•				*EZE*	
	3-bromobenzoic acid	CEKLIP	•				*EZE*	
	3-chlorobenzoic acid	CEKLOV	•				*EZE*	
	3-fluorobenzoic acid	CEKLUB	•				*EZE*	
	3-nitrobenzoic acid	CEKMAI	•				*EZE*	
	4-fluorobenzoic acid	CEKMEM	•				*EZE*	
	2-aminobenzoic acid	CEKMIQ		•			*ZZZ*	

(continued)

Co-crystal	2-bromobenzoic acid	CEKMOW		•			*ZZZ*	Wales, C.; Thomas, L.H.; Wilson, C.C. *Cryst Eng Comm,* **2012**, *14*, 7264.
	2-chlorobenzoic acid	CEKMUC		•			*ZZZ*	
	2-fluorobenzoic acid	CEKNAJ		•			*ZZZ*	
	salicylic acid	CEKNEN		•			*ZZZ*	
	2-nitrobenzoic acid	CEKNIR		•			*ZZZ*	
	3-fluorobenzoic acid	CEKNOX		•			*ZZZ*	
	3-hydroxybenzoic acid monohydrate	CEKNUD		•			*ZZZ*	
	3-methylbenzoic acid acetonitrile	CEKPAL		•			*ZZZ*	
	3-methylbenzoic acid	CEKPEP		•			*ZZZ*	
	4-fluorobenzoic acid	CEKPIT		•			*ZZZ*	
	4-methylbenzoic acid	CEKPOZ		•			*ZZZ*	
	succinic acid	DIKCIK	•				*EZE*	Childs, S.L.; Hardcastle, K.I. *Cryst.Growth Des.***2007**, *7*, 1291.
	1-hydroxy-2-naphthoic acid	DIKCOQ	•				*EZE*	
	caprylic acid	DIKCUW	•				*EZE*	
	malonic acid	DIKDAD	•				*EZE*	
	4-hydroxybenzoic acid	DIKDEH	•				*EZE*	
	fumaric acid	DIKDIL	•	•			*EZE* *ZZZ*	
	benzoic acid	DIKDOR		•			*ZZZ*	
	p-dioxane	DIRDUX		•			*ZZZ*	
	4-hydroxybenzoic acid	NIFKIX		•			*ZZZ*	

(continued)

Co-crystal	acetate	TIGNEE	•				*EZE*	Mishnev, A.; Kiselovs, G. (2013) *Z.Naturforsch.,B:Chem.Sci*. **2013**, *68*,168.
	furosemide acetone	XIFRAH	•				*EZE*	
	isobutyric acid	XIFREL	•				*EZE*	
	Triazole(0.5)	SOHWUJ		•			*ZZZ*	Thomas, L.H.; Klapwijk, A.R.; Wales, C.; Wilson, C.C. *CrystEngComm* **2014**, *16*, 5924.
	Benzotriazole	SOHXAQ		•			*ZZZ*	
	Hemipyrazine	SOHXEU		•			*ZZZ*	
Salt	ethaloamine	SECDAF			•		*ZZE*	Bordner, J.; Hammen, P.D.; Whipple E.B. *J. Am. Chem. Soc*. **1989**, *111*, 6572.
	bromanilic acid	SOHVOC				•	*EZE*	Thomas, L.H.; Klapwijk, A.R.; Wales, C.; Wilson, C.C. *CrystEngComm* **2014**, *16*, 5924.
	imidazole hemihydrate	SOHVUI			•		*ZZE*	
	imidazole acetonitrile	SOHWAP			•		*ZZE*	
	imidazole acetonitrile(0.25)	SOHWET			•		*ZZE*	
	2-methylimidazole	SOHWIX			•		*ZZE*	
	Benzimidazole	SOHWOD			•		*ZZE*	
	chloranilic acid	SOHXIY				•	*EZE*	
		SOHXIY01				•	*EZE*	
	chloranilic acid(0.5) acetonitrile	SOHXUK				•	*EZE*	
	hydrochloride	TIGNAA				•	*EZE*	Mishnev, A.; Kiselovs, G. *Z.Naturforsch.,B:Chem.Sci*. **2013**, *68*, 168.
Complex	Cu	AGIHII			•		*ZZZ*	Tamasi, G.; Serinelli, F.; Consumi, M.; Magnani, A.; Casolaro, M.; Cini, R. *J.Inorg.Biochem.***2008**,*102*,1862.
	Sn	JOQQUB			•		*ZZE*	Hadjikakou, S.; Demertzis, M.A.; Miller, J.R.; Kovala-Demertzi, D. *J.Chem.Soc.,Dalton Trans.* **1999**,

								663.

(continued)

Complex	Pt, Cl	NUSHOY	•				*EZE*	Di Leo, D.; Berrettini, F.; Cini, R. *J.Chem.Soc.,Dalton Trans.* **1998**, 1993.
	Pt,Cl	ZOJJUD	•				*EZE*	Cini, R. *J.Chem.Soc.,Dalton Trans*. **1996**, 111.
	Sn	RAFRIA			•		*EZE*	Kovala-Demertzi, D.; Koutsodimou, A.; Galani, A.; Hadjikakou, S.K.; Demertzis, M.A.; Xanthopoulou, M.; Miller, J.R.; Frampton, C.S. *Appl.Organomet.Chem.* 2**004**, *18*, 501.
	Ru,Cl	BINNAP	•				*EZE*	Raja, M.U.; Tauchman, J.; Therrien, B.; Suss-Fink, G.; Riedel, T.; Dyson, P.J. *Inorg.Chim.Acta* **2014**, *409*, 479.
	Co	BIPDEL			•		*ZZZ*	Darabi, F.; Ebrahimi, M.; Hadadzadeh, H.; Khayamian, T.; Rudbari, H.A. *Inorg.Chim.Acta* **2013**, *409*, 379.
	Ru	DOBPER			•		*ZZZ*	Jannesari, Z.; Hadadzadeh, H.; Khayamian, T.; Maleki, B.; Rudbari, H.A. *J.Med.Chem.* **2013**, *69*, 577.
	Mn	HOCDUA			•		*ZZZ*	Tamasi, G.; Corsini, M. ; Cini, R *Z.Anorg.Allg.Chem*. **2014**, *640*, 952.
	Cu	NEDFIN			•		*ZZZ*	Hadadzadeh, H.; Salimi, M.; Weil, M.; Jannesari, Z.; Darabi, F.; Abdi, K.; Khalaji, A.D.; Sardari, S.; Ahangari, R. *J.Mol.Struct.* **2012**, *1022*, 172.
	Cd	VIKMOR			•		*ZZZ*	Cini, R.; Giorgi, G.; Cinquantini, A.; Rossi, C.; Sabat, M. *Inorg.Chem.* **1990**, *29*, 5197
	Cu	VIKMUX			•		*ZZZ*	

Table S2. Data Collection and Refinement Details of form III and IV of sulfathiazole

Compound formula	$C_9H_9N_3S_2O_2$	$C_9H_9N_3S_2O_2$
Polymorph form	III	IV
formula weight	254.30	254.30
crystal system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
a (Å)	17.3862(5)	10.7689(3)
b (Å)	8.4812(2)	8.4602(3)
c (Å)	15.4873(4)	11.3733(3)
β (°)	112.7460(10)	91.6270(10)
V (Å^{-3})	2106.09(10)	1035.77(5)
Z	8	4
D_{calc} (g cm-3)	1.57	1.631
λ (Å)	0.71069	0.71069
μ (mm^{-1})	0.493	0.501
temperature/K	100(2)	100(2)
crystal size		
θ range/deg	2.79 to 62.84	3.00 to 45.58
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.25	1.00
average redundancy		
Completeness	99.6%	99.9%
reflections collected	349008	116151
independent reflections	33493	8792
hkl range	$-43 \le h \le 43$	$-21 \le h \le 21$
	$-21 \le k \le 21$	$-16 \le k \le 17$
	$-38 \le l \le 38$	$-22 \le l \le 22$
R_{int}	0.0729	0.0318
Spherical atom refinement:		
no. of data in refinement	33493	8792
no. of refined parameters	296	151
no. of reflect. used [I > 2σ(I)]	20160	7541
R(F)/wR(F)	0.0483/0.1469	0.0278/0.1077
goodness of fit	1.027	0.977
Multipole refinement:		
no. of reflection used	13979	9115
no. of refined parameters	451	172
R(F)/wR(F)	0.021/0.017	0.019/0.016
goodness of fit	0.490	0.539

Table S3. Estimate of average error on the electron density map. σ (Δ ρ)=2/V*[Σ (k.Fo-Fc)^2]^(1/2) (Rees, B. Acta Cryst. 1976, A32, 483-488)

Experiment	*σ(Δρ)/e.Å^{-3}*
Piroxicam form I (nPX)	0.0789
Hydrated piroxicam (zPXL; zPXR)	0.0756
Sulfathiazole form III	0.0741
Sulfathiazole form IV	0.0588

Table S4. Topology of the experimental electron density of piroxicam (nPX, zPXL and zPXR) for covalent bonds not listed in the paper.

Bond A-B	d(CP-A) (Å)	d(CP-B) (Å)	$\rho(\mathbf{r}_{cp})$ (eÅ^{-3})	$\nabla^2\rho(\mathbf{r}_{cp})$ (eÅ^{-5})	ε
C2-C7	0.724	0.744	1.88	-14.6	0.21
	0.747	0.747	1.80	-13.2	0.19
	0.763	0.732	1.80	-13.6	0.21
C3-C7	0.725	0.672	2.12	-17.9	0.15
	0.709	0.690	2.12	-18.7	0.19
	0.684	0.714	2.12	-18.4	0.22
C3-C4	0.720	0.673	2.14	-18. 5	0.15
	0.686	0.706	2.19	-19.7	0.24
	0.705	0.689	2.16	-19.3	0.19
C4-C5	0.713	0.682	2.14	-18.8	0.14
	0.698	0.698	2.16	-19. 2	0.19
	0.709	0.688	2.15	-18.5	0.22
C5-C6	0.679	0.714	2.14	-19.1	0.18
	0.702	0.691	2.11	-17.6	0.21
	0.692	0.703	2.13	-18.1	0.19
C6-C8	0.683	0.706	2.12	-18.7	0.23
	0.697	0.695	2.17	-19.0	0.19
	0.684	0.706	2.12	-18.8	0.21
C7-C8	0.690	0.715	2.08	-17.6	0.20
	0.689	0.715	2.08	-16.8	0.26
	0.696	0.708	2.11	-17.8	0.23
C11-C12	0.710	0.688	2.13	-18.5	0.20
	0.740	0.666	2.16	-19.6	0.18
	0.720	0.684	2.12	-18.8	0.23
C12-C13	0.688	0.700	2.19	-19.5	0.21
	0.681	0.695	2.28	-21.3	0.23
	0.692	0.685	2.22	-20.4	0.22
C13-C14	0.680	0.712	2.15	-18.7	0.19
	0.688	0.717	2.11	-18.7	0.18
	0.708	0.697	2.08	-17.9	0.16
C14-C15	0.749	0.642	2.14	-18.8	0.20
	0.651	0.717	2.29	-22.6	0.25
	0.638	0.732	2.28	-21.9	0.27

Table S5 Selected bond lengths and angles. Standard deviations are in parentheses. For hydrogen bonds, D is the donor and A, the acceptor.

Distances	**nPX**	**zPXL**	**zPXR**
S1-O1	1.4354(7)	1.4332(2)	1.4346(1)
S1-O2	1.4310(5)	1.4347(1)	1.4366(1)
S1-N1	1.6442(12)	1.6331(1)	1.6309(2)
S1-C8	1.7464(6)	1.7628(1)	1.7556(1)
O3-C2	1.3327(5)	1.2676(1)	1.2768(1)
O4-C10	1.2479(5)	1.2516(1)	1.2412(1)
N1-C1	1.4334(5)	1.4417(1)	1.4413(1)
N1-C9	1.4858(8)	1.4769(2)	1.4771(1)
N2-C10	1.3557(6)	1.3917(1)	1.3881(1)
N2-C11	1.4055(7)	1.3536(1)	1.3637(1)
C7-C3	1.3975(5)	1.3994(1)	1.3978(1)
C4-C3	1.3932(7)	1.3926(1)	1.3935(1)
C4-C5	1.3945(6)	1.3959(2)	1.3962(2)
C5-C6	1.3933(5)	1.3927(1)	1.3949(1)
C8-C6	1.3888(7)	1.3923(1)	1.3908(1)
C8-C7	1.4048(6)	1.4037(1)	1.4046(2)
C7-C2	1.4677(8)	1.4942(1)	1.4954(1)
C1-C2	1.3720(6)	1.4152(1)	1.4031(1)
C1-C10	1.4692(8)	1.4284(1)	1.4406(1)
C11-C12	1.3983(6)	1.4062(1)	1.4037(1)
C12-C13	1.3881(7)	1.3761(1)	1.3773(1)
C14-C13	1.3918(6)	1.4053(1)	1.4046(1)
C14-C15	1.3916(6)	1.3687(2)	1.3699(1)
N3-C11	1.3368(5)	1.3462(1)	1.3444(1)
N3-C15	1.3397(7)	1.3554(1)	1.3552(1)
Angles			
O2-S1-O1	119.05(3)	118.13(2)	118.28(1)
N1-S1-C8	101.58(3)	102.39(1)	101.37(1)
S1-C8-C7	116.46(4)	117.45(2)	116.51(2)
S1-N1-C1	112.82(3)	113.57(2)	112.87(2)
N1-C1-C10	118.11 (4)	115.88(2)	114.73(2)
C10-C1-C2	120.70(5)	123.16(2)	124.53(2)
C10-N2-C11	128.86(5)	126.56(2)	126.34(2)
O4-C10-C1	120.51(4)	125.15(2)	123.95(2)
O3-C2-C1	122.54(5)	124.44(2)	123.98(2)
Dihedral angles			
O4-C10-C1-N1	174.37(2)	-2.32(2)	-0.22(2)
N3-C11-N2-C10	-176.78(3)	-14.74(1)	-6.55(1)
C1-C10-N2-C11	-176.71(3)	-175.93(2)	-170.08(2)
H-bonds **nPX**	*symmetry*	H…A	D…A
O3-H3O...O4	*x, y, z*	1.730(2)	2.561(1)
N2-H2N...O2	*2-x, -y, -z*	2.301(2)	2.999(2)
H-bonds **zPX**			
N2L-H2NL...O3L	*x, y, z*	1.713(2)	2.5300(1)
N2R-H2NR...O3R	*x, y, z*	1.780(2)	2.5873(1)
N3L-H3NL...O4L	*x, y, z*	1.987(2)	2.6732(2)
N3R-H3NR...O1L	*x, y, z*	2.561(1)	2.9396(2)
N3R-H3NR...O4R	*x, y, z*	1.924(2)	2.6501(2)
O5B-H5OB...O3R	*x, y, z*	1.838(2)	2.7522(1)
O5B -H6OB...O4L	*x, y, 1+z*	1.882(1)	2.8075(2)
O5A -H5OA...O5B	*1-x, 1-y, 1-z*	1.982(1)	2.9134(2)
N3L -H3NL...O4R	*2-x, 1-y, -z*	2.052(1)	2.7824(1)
N3R -H3NR...O4L	*2-x, 1-y, -z*	2.207(1)	2.8857(1)