

Supplementary data

Synthesis and X-ray Crystal Structure of New Substituted 3-4'-Bipyrazole Derivatives. Hirshfeld Analysis, DFT and NBO Studies

Ahmed T. A. Boraie ^{1,*}, Matti Haukka ², Ahmed A. M. Sarhan ³, Saied M. Soliman ⁴, Abdullah Mohammed Al-Majid ⁵ and Assem Barakat ^{5,*}

¹ Chemistry Department, Faculty of Science, Suez Canal University, Ismailia 41522, Egypt

² Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland; matti.o.haukka@jyu.fi

³ Chemistry Department, Faculty of Science, Arish University, Al-Arish 45511, Egypt; asarhan@aru.edu.eg

⁴ Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt; saeed.soliman@alexu.edu.eg

⁵ Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Saudi Arabia; amajid@ksu.edu.sa

* Correspondence: ahmed_boraie@science.suez.edu.eg (A.T.A.B.); ambarakat@ksu.edu.sa (A.B.); Tel.: +966-11467-5901 (A.T.A.B.); Fax: +966-11467-5992 (A.B.)

1.1. X-ray Single-Crystal Determination of **2**

The crystal of **2** was immersed in cryo-oil, mounted in a loop, and measured at a temperature of 120 K. The X-ray diffraction data was collected on a Rigaku Oxford Diffraction Supernova diffractometer using Cu K α radiation. The *CrysAlisPro* [1] software package was used for cell refinement and data reduction. A multi-scan absorption correction (*CrysAlisPro* [1]) was applied to the intensities before structure solution. The structure was solved by the intrinsic phasing (*SHELXT*) [2] method. Structural refinement was carried out using *SHELXL* [2] software with the *SHELXLE* [3] graphical user interface. The NH hydrogen atom was located from the difference Fourier map and refined isotropically. All other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95 Å and U_{iso} = 1.2 · U_{eq} (parent atom).

1.2. Hirshfeld Surface Analysis

The topology analyses were performed using the Crystal Explorer 17.5 program [4].

1.3. Computational Methods

The structure of the studied compound was optimized using the B3LYP/6-31G(d,p) method utilizing Gaussian 09 software [5]. Atomic charges were calculated using the NBO 3.1 program [6]. Additionally, the different electron delocalization processes which stabilize the studied system by conjugation effect were calculated using natural bond orbital calculations [7,8].

Table S1. The calculated geometric parameters of **2^a**.

Parameter	Calc	Exp	Parameter	Calc	Exp
R(1-17)	1.223	1.249	A(1-17-2)	125.3	123.2
R(2-3)	1.403	1.377	A(1-17-18)	130.0	131.4
R(2-16)	1.412	1.422	A(3-2-16)	119.4	121.7
R(2-17)	1.412	1.385	A(3-2-17)	109.8	110.0
R(3-19)	1.396	1.360	A(2-3-19)	107.1	107.8
R(4-5)	1.355	1.361	A(2-3-57)	112.1	118.5
R(4-34)	1.337	1.332	A(16-2-17)	128.5	127.1
R(5-31)	1.381	1.370	A(2-16-6)	120.1	119.8
R(5-46)	1.424	1.425	A(2-16-14)	119.8	118.4
R(6-8)	1.394	1.397	A(2-17-18)	104.6	105.3
R(6-16)	1.403	1.391	A(3-19-18)	109.8	109.1
R(8-10)	1.394	1.383	A(3-19-20)	118.0	119.8
R(10-12)	1.396	1.384	A(5-4-34)	105.9	104.6
R(12-14)	1.393	1.391	A(4-5-31)	111.8	112.1
R(14-16)	1.404	1.392	A(4-5-46)	118.5	120.6
R(17-18)	1.471	1.431	A(4-34-32)	110.6	111.6
R(18-19)	1.369	1.384	A(4-34-35)	120.7	121.7
R(18-31)	1.460	1.457	A(31-5-46)	129.6	127.2
R(19-20)	1.467	1.465	A(5-31-18)	125.6	124.1
R(20-21)	1.405	1.398	A(5-31-32)	105.9	106.2
R(20-29)	1.406	1.390	A(5-46-47)	118.9	120.2
R(21-23)	1.392	1.387	A(5-46-55)	120.6	118.8
R(23-25)	1.397	1.382	A(7-6-8)	120.1	120.8
R(25-27)	1.396	1.388	A(7-6-16)	120.1	120.8
R(27-29)	1.393	1.389	A(8-6-16)	119.8	118.4
R(31-32)	1.382	1.371	A(6-8-9)	119.2	119.8
R(32-34)	1.418	1.407	A(6-8-10)	120.6	120.4
R(34-35)	1.472	1.478	A(6-16-14)	120.0	121.7
R(35-36)	1.403	1.394	A(9-8-10)	120.2	119.8
R(35-44)	1.405	1.392	A(8-10-11)	120.4	119.8
R(36-38)	1.394	1.386	A(8-10-12)	119.2	120.4
R(38-40)	1.395	1.385	A(11-10-12)	120.4	119.8
R(40-42)	1.397	1.382	A(10-12-13)	120.0	119.8
R(42-44)	1.392	1.388	A(10-12-14)	121.1	120.4
R(46-47)	1.398	1.385	A(13-12-14)	118.9	119.8
R(46-55)	1.398	1.384	A(12-14-15)	121.3	120.7
R(47-49)	1.393	1.380	A(12-14-16)	119.2	118.6
R(49-51)	1.396	1.383	A(15-14-16)	119.4	120.7
R(51-53)	1.395	1.385	A(17-18-19)	108.0	107.4
R(53-55)	1.395	1.390	A(17-18-31)	121.9	121.4
			A(19-18-31)	130.1	131.0
			A(18-19-20)	132.2	130.9

A(18-31-32)	128.4	129.5
A(19-20-21)	120.6	119.8
A(19-20-29)	120.3	121.0
A(21-20-29)	119.1	119.1
A(20-21-22)	119.6	120.0
A(20-21-23)	120.2	120.1
A(20-29-27)	120.4	120.3
A(20-29-30)	119.4	119.8
A(22-21-23)	120.2	119.9
A(21-23-24)	119.6	119.7
A(21-23-25)	120.3	120.6
A(24-23-25)	120.1	119.7
A(23-25-26)	120.1	120.3
A(23-25-27)	119.8	119.5
A(26-25-27)	120.1	120.2
A(25-27-28)	120.2	119.9
A(25-27-29)	120.1	120.3
A(28-27-29)	119.7	119.8
A(27-29-30)	120.2	119.8
A(31-32-33)	125.3	127.2
A(31-32-34)	105.8	105.5
A(33-32-34)	128.9	127.2
A(32-34-35)	128.7	126.7
A(34-35-36)	121.0	120.0
A(34-35-44)	120.5	121.3
A(36-35-44)	118.6	118.7
A(35-36-37)	119.9	119.7
A(35-36-38)	120.7	120.6
A(35-44-42)	120.6	120.5
A(35-44-45)	118.8	119.8
A(37-36-38)	119.4	119.7
A(36-38-39)	119.6	119.9
A(36-38-40)	120.3	120.1
A(39-38-40)	120.1	119.9
A(38-40-41)	120.3	120.2
A(38-40-42)	119.5	119.7
A(41-40-42)	120.3	120.1
A(40-42-43)	120.0	119.9
A(40-42-44)	120.4	120.3
A(43-42-44)	119.6	119.8
A(42-44-45)	120.6	119.8
A(47-46-55)	120.4	120.9
A(46-47-48)	119.0	120.3
A(46-47-49)	119.6	119.4
A(46-55-53)	119.5	119.0
A(46-55-56)	120.0	120.5

A(48-47-49)	121.4	120.3
A(47-49-50)	119.5	119.7
A(47-49-51)	120.4	120.6
A(50-49-51)	120.1	119.7
A(49-51-52)	120.2	120.2
A(49-51-53)	119.6	119.6
A(52-51-53)	120.2	120.2
A(51-53-54)	120.2	119.8
A(51-53-55)	120.5	120.5

^a Atom numbering refer to **Fig. 4**

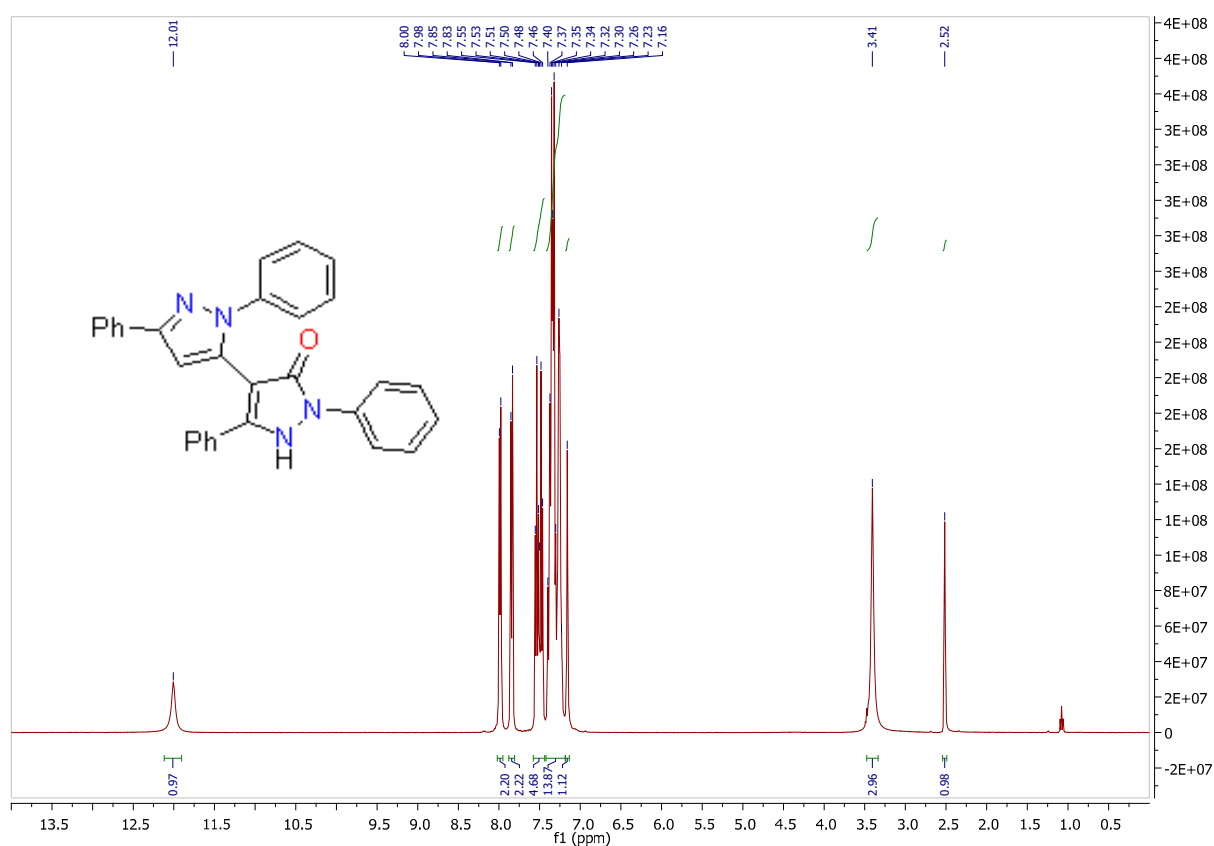
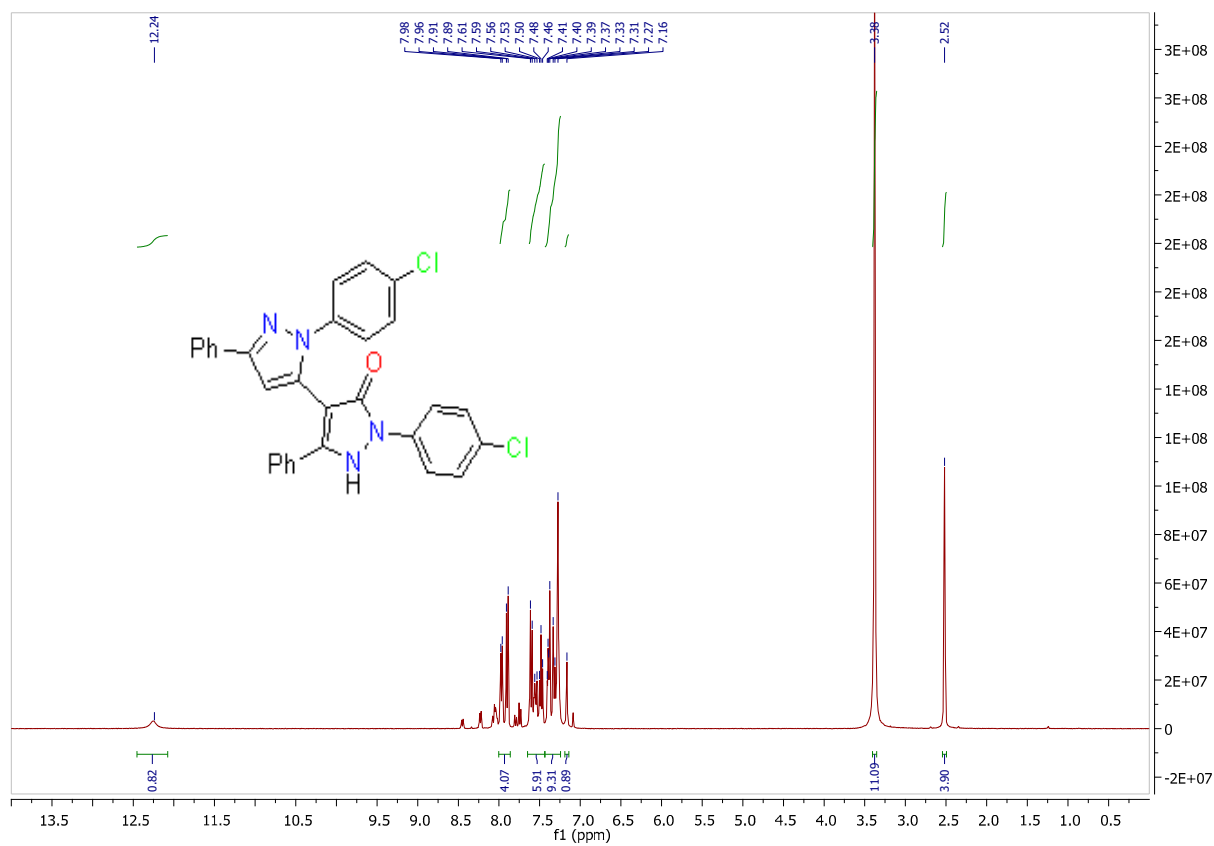
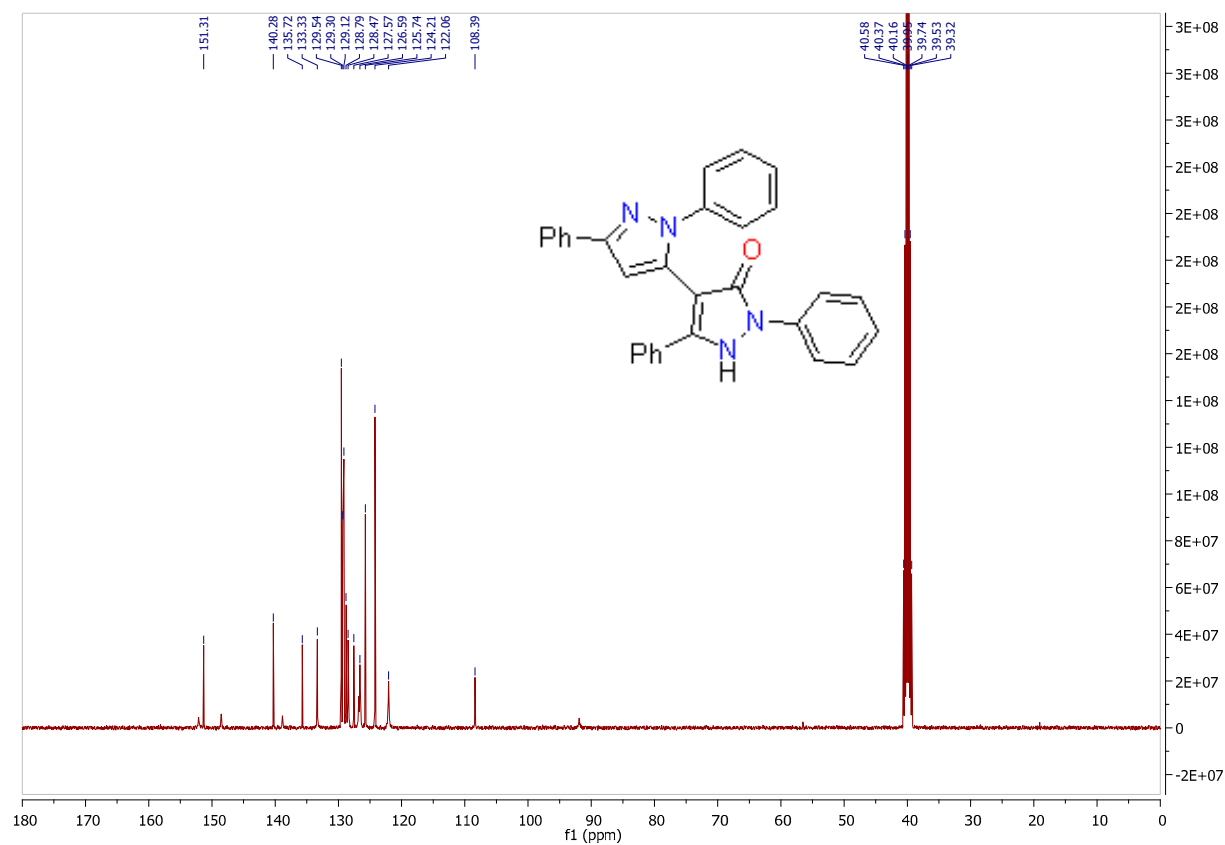


Figure S1. ¹H-NMR 2 in DMSO-*d*₆



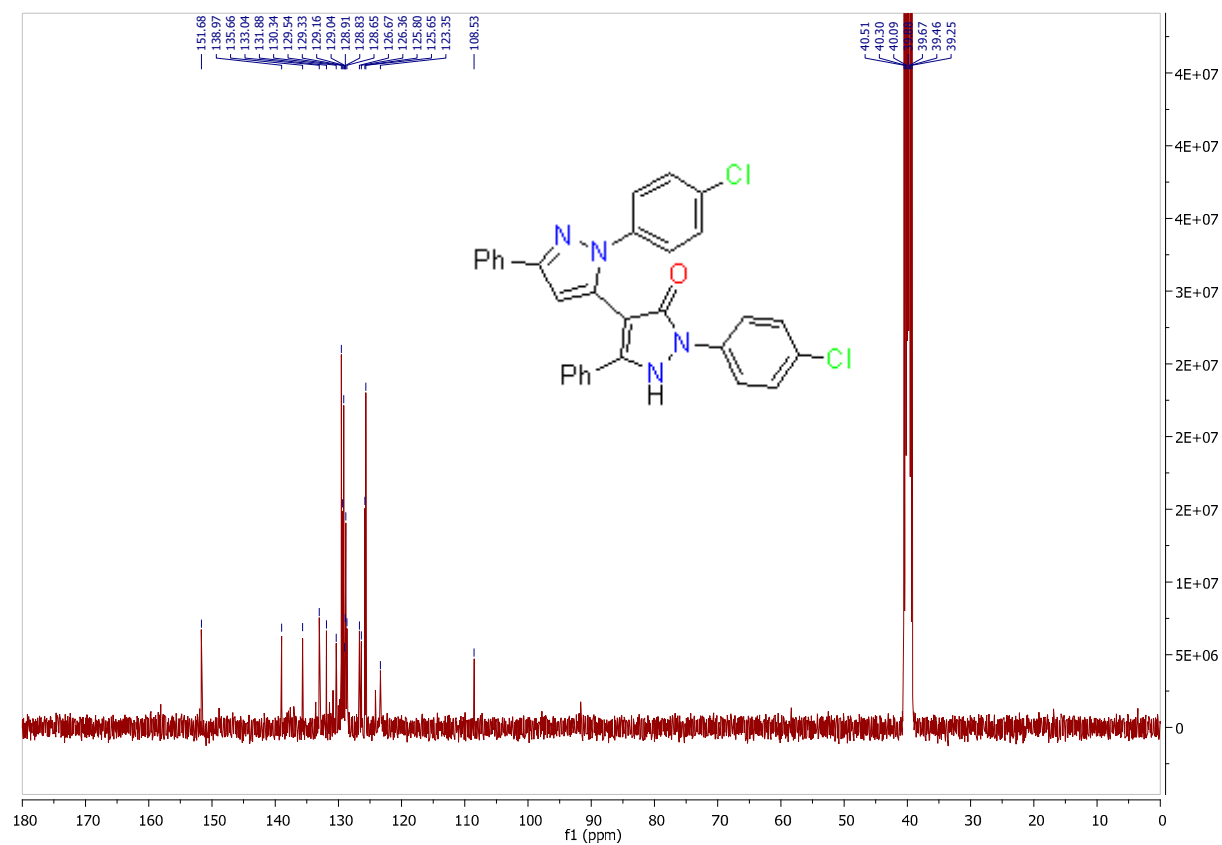


Figure S4. ^{13}C -NMR 3 in $\text{DMSO-}d_6$

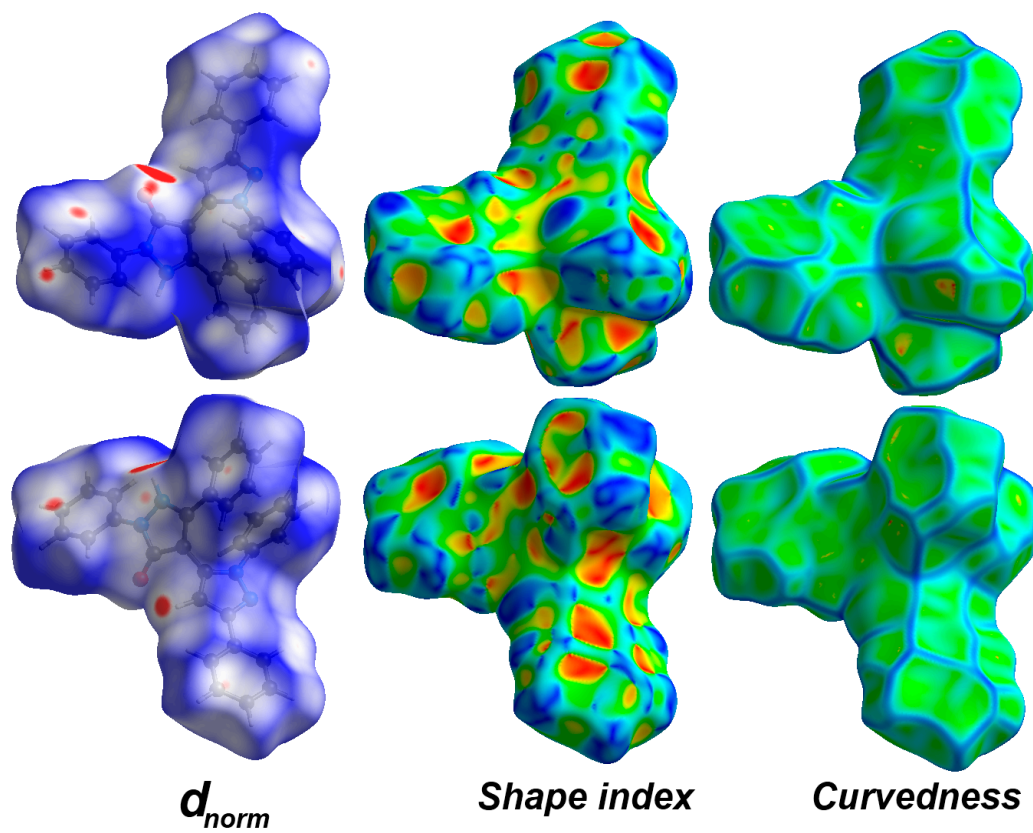


Figure S5. Hirshfeld surfaces for the other molecular unit in the crystal structure of 2.

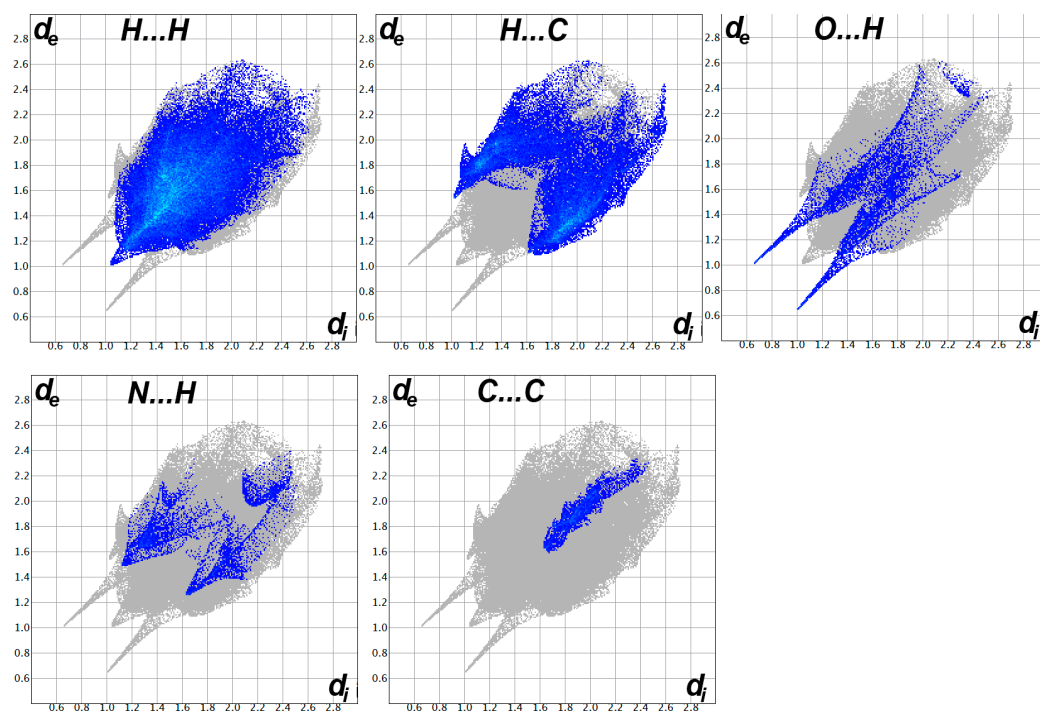


Figure S6. Decomposed fingerprint plots for the other molecular unit the crystal structure of 2.

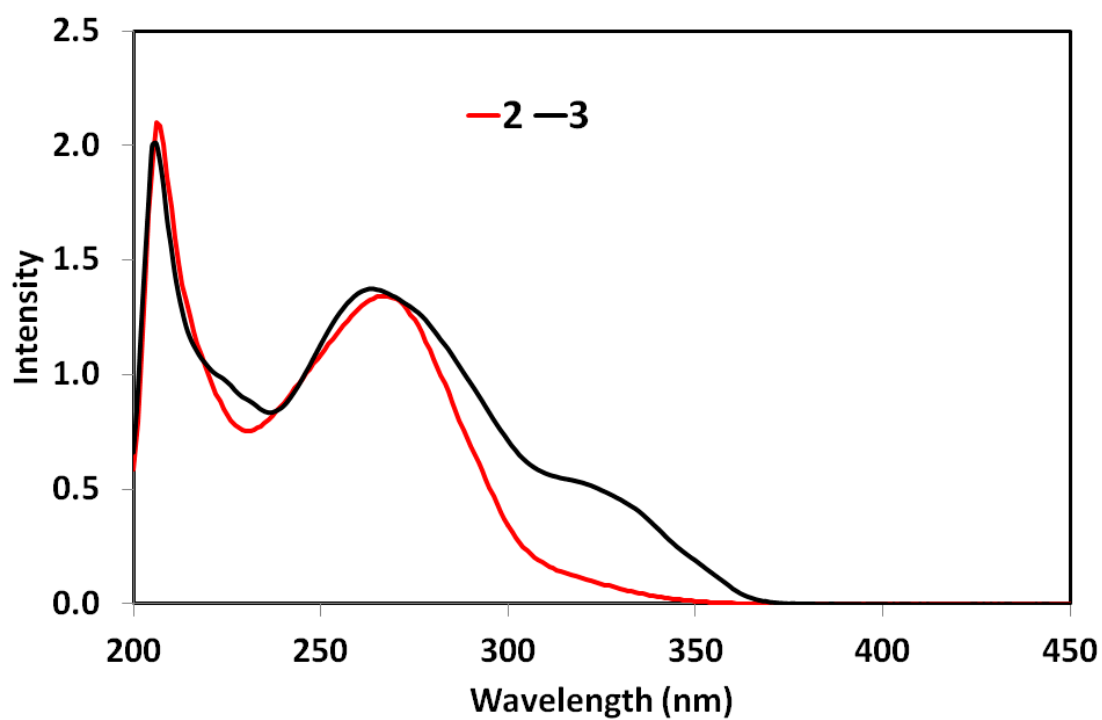


Figure S7. UV-Vis spectra of compounds 2 and 3.

References

1. Rikagu Oxford Diffraction. *CrysAlisPro*; Agilent Technologies inc.: Yarnton, UK, 2018.
2. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3–8.
3. Hübschle, C.B.; Sheldrick, G.M.; Dittrich, B. ShelXle: A Qt graphical user interface for SHELXL. *J. Appl. Cryst.* **2011**, 44, 1281–1284.
4. Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Spackman, P.R.; Jayatilaka, D.; Spackman, M.A. *Crystal Explorer17*; University of Western Australia: Perth, Australia, 2017.
5. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *GAUSSIAN 09*; Revision A02; Gaussian Inc.: Wallingford, CT, USA, 2009; *GaussView*; Version 4.1; Dennington II, R., Keith, T., Millam, J., Eds.; Semichem Inc.: Shawnee Mission, KS, USA, 2007.
6. Reed, A.E.; Curtiss, L.A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, 88, 899–926.
7. Hubert Joe, I.; Kostova, I.; Ravikumar, C.; Amalanathan, M.; Pinzaru, S.C. Theoretical and vibrational spectral investigation of sodium salt of acenocoumarol. *J. Raman Spectrosc.* **2009**, 40, 1033–1038.
8. Sebastian, S.; Sundaraganesan, N. The spectroscopic (FT-IR, FT-IR gas phase, FT-Raman and UV) and NBO analysis of 4-Hydroxypiperidine by density functional method. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2010**, 75, 941–952.