SUPPORTING INFORMATION

The Contribution of Directional Dihydrogen Interactions in the Supramolecular Assembly of Single Crystals: Quantum Chemical and Structural investigation of $C_{17}H_{17}N_3O_2$ Azine

Leonardo R. de Almeida,[§] Paulo S. Carvalho Jr,*[§] Hamilton B. Napolitano,[§] Solemar S. Oliveira,[§] Ademir J. Camargo,[§] Andreza S. Figueredo,[§] Gilberto L. B. de Aquino[§] and Valter H. Carvalho-Silva.*[§]

[§]*Grupo de Química Teórica e Estrutural de Anápolis, Campus de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, Caixa Postal 459, 75001-970, Anápolis, GO, Brazil.*

**E-mail: paulquim@gmail.com, fatioleg@gmail.com.*

Table S1. Crystallographic information of the AZN collected at 120(2) K.

	AZN at 120(2) K
Empirical formula	$C_{17}H_{17}N_3O_2$
Formula weight	295.33 g/mol
Temperature	120(2) K
Wavelength	MoKα 0.71073 Å
Crystal system	Triclinic
Space Group	P-1
Unit cell dimensions	a = 7.074(6) Å b = 8.108(7) Å c = 13.329(8) Å α = 95.469(4)º β = 104.295(4)º γ = 92.864(4)º
Volume	735.46(2) $Å^3$
Z	2
Calculated density (g/cm3)	1.334 g/cm^3
Absorption coefficient	0.090 mm^{-1}
F(000)	312.0
Crystal size	0.347 x 0.276 x 0.046 mm
θ range for data collection	5.062º to 51.612º
Limiting indices	$-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	18895
Reflections unique	2830 [R_{int} = 0.0854, R_{sigma} = 0.0549]
Data / restrictions / parameters	2830 / 0 / 201
Solution / refinement	Direct methods / least-square full matrix
Goodness-of-fit on F^2	1.040
Final *R* indices [I>2σ(I)]	R_1 = 0.0481; wR_2 = 0.1124
R indices (All data)	R_1 = 0.0764, wR_2 = 0.1279
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.34

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for AZN at 120(2) K. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C5	3260(2)	13735(2)	2855.9(12)	16.4(4)
N3	3471.5(19)	15185.7(17)	2307.4(10)	19.4(3)
C9	1872(2)	6627(2)	7085.0(12)	16.4(4)
C7	2896(2)	10817(2)	2839.7(12)	18.3(4)
C2	2833(2)	11016(2)	3882.6(12)	16.7(4)
N1	2094(2)	8053.2(17)	5628.7(11)	19.4(3)
O2	3420.7(18)	14950.8(15)	1375.9(9)	26.3(3)
C8	2099(2)	8123(2)	6593.0(13)	18.4(4)
N2	2371.7(19)	9641.5(17)	5324.0(11)	19.1(3)
O1	3684.9(18)	16569.2(14)	2793.8(9)	26.2(3)
C14	1553(2)	5057(2)	6524.7(12)	18.5(4)
C13	1420(2)	3659(2)	7013.8(12)	18.7(4)
C3	3021(2)	12612(2)	4403.5(13)	18.3(4)
C12	1592(2)	3758(2)	8083.5(12)	16.9(4)
C1	2553(2)	9541(2)	4390.6(12)	18.3(4)
C4	3235(2)	13986(2)	3894.1(12)	17.8(4)
C10	2025(2)	6741(2)	8154.1(13)	20.2(4)
C6	3104(2)	12175(2)	2317.8(12)	18.8(4)
C11	1885(2)	5327(2)	8641.9(13)	20.6(4)
C15	1522(2)	2192(2)	8611.8(13)	20.2(4)
C17	185(3)	2271(2)	9350.2(13)	24.4(4)
C16	3586(3)	1818(2)	9177.7(15)	29.7(5)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for AZN at 120(2) K. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
C5	14.5(8)	17.4(9)	18.3(8)	5.8(7)	5.0(7)	0.8(7)
N3	19.6(8)	19.6(8)	20.5(8)	4.3(6)	6.6(6)	2.8(6)
C9	13.0(8)	17.8(9)	20.3(9)	3.7(7)	6.7(7)	2.4(7)
C7	19.1(9)	15.8(9)	19.5(9)	-0.5(7)	4.9(7)	1.3(7)
C2	12.5(8)	19.1(9)	19.4(9)	4.2(7)	4.5(7)	3.0(7)
N1	20.1(8)	16.5(8)	23.0(8)	6.1(6)	6.9(6)	0.6(6)
O2	37.7(8)	25.9(7)	17.9(7)	6.9(5)	10.4(5)	3.8(6)
C8	18.2(9)	16.8(9)	21.6(9)	1.7(7)	7.8(7)	3.1(7)
N2	19.6(8)	17.0(8)	22.4(8)	5.9(6)	7.2(6)	2.3(6)
O1	36.6(8)	14.7(7)	28.9(7)	1.5(5)	11.8(6)	2.3(5)
C14	19.9(9)	21.7(9)	15.6(8)	1.8(7)	7.6(7)	2.9(7)
C13	19.3(9)	17.2(9)	19.3(9)	-0.4(7)	5.4(7)	1.6(7)
C3	18.7(9)	20.5(9)	16.9(8)	1.9(7)	6.3(7)	3.9(7)
C12	13.5(8)	19.0(9)	19.7(9)	3.4(7)	6.2(7)	3.3(7)
C1	16.2(9)	17.3(9)	21.0(9)	1.4(7)	4.4(7)	1.7(7)
C4	16.0(8)	16.2(9)	20.8(9)	-0.9(7)	4.9(7)	1.9(7)
C10	25.5(9)	15.6(9)	20.4(9)	-1.2(7)	8.3(7)	2.3(7)
C6	20.6(9)	21.6(10)	14.9(8)	2.1(7)	5.4(7)	2.8(7)
C11	27.3(10)	21.2(10)	15.0(8)	2.0(7)	8.3(7)	3.2(7)
C15	24.9(10)	16.4(9)	20.0(9)	3.0(7)	6.5(7)	1.5(7)
C17	29.1(10)	22.1(10)	24.6(10)	8.1(8)	9.7(8)	0.6(8)
C16	30.1(11)	23.1(10)	37.8(11)	11.5(8)	7.7(9)	7.8(8)

Table S4. Bond Lengths for AZN at 120(2) K.

Bond	Length (Å)	Bond	Length (Å)
C5–N3	1.463(2)	N1–C8	1.280(2)
C5–C4	1.384(2)	N1–N2	1.4058(19)
C5–C6	1.379(2)	N2–C1	1.277(2)
N3–O2	1.2295(17)	C14–C13	1.371(2)
N3–O1	1.2239(17)	C13–C12	1.395(2)
C9–C8	1.453(2)	C3–C4	1.379(2)
C9–C14	1.392(2)	C12–C11	1.391(2)
C9–C10	1.396(2)	C12–C15	1.514(2)
C7–C2	1.396(2)	C10–C11	1.382(2)
C7–C6	1.378(2)	C15–C17	1.523(2)
C2–C3	1.393(2)	C15–C16	1.529(2)
C2–C1	1.458(2)		

Table S5. Bond Angles for AZN at 120(2) K.

Bonds	Angle (˚)	Bonds	Angle (˚)
C4–C5–N3	118.66(15)	C1–N2–N1	110.90(14)
C6–C5–N3	118.59(14)	C13–C14–C9	120.79(15)
C6–C5–C4	122.75(15)	C14–C13–C12	121.42(15)
O2–N3–C5	118.10(14)	C4–C3–C2	120.64(15)
O1–N3–C5	118.68(13)	C13–C12–C15	120.38(15)
O1–N3–O2	123.21(14)	C11–C12–C13	117.84(15)
C14–C9–C8	121.85(15)	C11–C12–C15	121.76(15)
C14–C9–C10	118.24(15)	N2–C1–C2	121.83(16)
C10–C9–C8	119.88(15)	C3–C4–C5	118.30(15)
C6–C7–C2	120.89(16)	C11–C10–C9	120.68(15)
C7–C2–C1	118.75(15)	C7–C6–C5	118.16(15)
C3–C2–C7	119.24(15)	C10–C11–C12	121.02(15)
C3–C2–C1	122.00(15)	C12–C15–C17	112.71(14)
C8–N1–N2	111.74(14)	C12–C15–C16	110.28(14)
N1–C8–C9	121.41(16)	C17–C15–C16	110.93(14)

Table S6. Torsion angles for AZN at 120(2) K.

Bonds	Angle (˚)	Bonds	Angle (˚)
N3–C5–C4–C3	179.54(13)	C13–C12–C15–C17	-133.73(16)
N3–C5–C6–C7	-179.69(14)	C13–C12–C15–C16	101.69(18)
C9–C14–C13–C12	0.2(2)	C3–C2–C1–N2	3.4(2)
C9–C10–C11–C12	0.1(3)	C1–C2–C3–C4	-178.34(15)
C7–C2–C3–C4	1.0(2)	C4–C5–N3–O2	-177.41(14)
C7–C2–C1–N2	-175.97(15)	C4–C5–N3–O1	2.4(2)
C2–C7–C6–C5	0.4(2)	C4–C5–C6–C7	0.7(2)
C2–C3–C4–C5	-0.1(2)	C10–C9–C8–N1	175.40(15)
N1–N2–C1–C2	179.24(13)	C10–C9–C14–C13	-0.9(2)
C8–C9–C14–C13	177.43(15)	C6–C5–N3–O2	2.9(2)
C8–C9–C10–C11	-177.62(15)	C6–C5–N3–O1	-177.25(14)
C8–N1–N2–C1	173.70(14)	C6–C5–C4–C3	-0.8(2)
N2–N1–C8–C9	-178.84(13)	C6–C7–C2–C3	-1.2(2)
C14–C9–C8–N1	-2.9(2)	C6–C7–C2–C1	178.21(14)
C14–C9–C10–C11	0.8(2)	C11–C12–C15–C17	48.2(2)
C14–C13–C12–C11	0.6(2)	C11–C12–C15–C16	-76.36(19)
C14–C13–C12–C15	-177.51(14)	C15–C12–C11–C10	177.33(15)
C13–C12–C11–C10	-0.8(2)		

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for AZN at 120(2) K.

Atom	*x*	*y*	*z*	U(eq)
H7	2793	9730	2485	22
H8	2254	9176	6995	22
H14	1425	4953	5795	22
H13	1206	2600	6616	22
H3	3002	12756	5116	22
H1	2503	8475	4017	22
H4	3362	15076	4247	21
H10	2228	7801	8550	24
H6	3139	12040	1607	23
H11	1991	5429	9370	25
H15	985	1252	8055	24
H17A	742	3114	9941	37
H17B	64	1186	9605	37
H17C	-1110	2564	8980	37
H16A	4389	1681	8676	45
H16B	3523	793	9507	45
H16C	4171	2740	9712	45

AZN structure colleted at 298K

In order to verify a possible phase transition, and hence, qualitatively to evaluate the thermal stability of the structure, AZN crystal has also collected at 298K in a Kappa CCD Enraf Nonius FR590 diffractometer. No significant difference is observed between the structures collected in 120K and 298K. Slight differences in geometric parameters can be attributed to the effect of temperature on the molecules of thermal vibration.

Table S8. Crystallographic information of the AZN collected at 298(2) K.

	AZN at 298(2) K
Empirical formula	$C_{17}H_{17}N_3O_2$
Formula weight	295.33 g/mol
Temperature	298(2) K
Wavelength	MoKα 0.71073 Å
Crystal system	Triclinic
Space Group	P-1
Unit cell dimensions	a = 7.195(3) Å b = 8.159(2) Å c = 13.575(4) Å α = 94.960(1)º β = 102.380(1)º γ = 93.741(4)º
Volume	772.65(5) $Å^3$
Z	2
Calculated density (g/cm3)	1.269 g/cm^3
Absorption coefficient	0.085 mm^{-1}
F(000)	312.0
Crystal size	0.1 x 0.1 x 0.1 mm
θ range for data collection	2.977° to 24.996°
Limiting indices	$-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $0 \leq l \leq 16$
Reflections collected	2712
Reflections unique	2712[Rint = 0.015, Rsigma = 0.0337]
Data / restrictions / parameters	2712 / 0 / 202
Solution / refinement	Direct methods / least-square full matrix
Goodness-of-fit on F^2	1.059
Final *R* indices [I>2σ(I)]	$R_1 = 0.0544$; $wR_2 = 0.1474$
R indices (All data)	$R_1 = 0.0733$; $wR_2 = 0.1603$
Largest diff. peak/hole / e $Å^{-3}$	0.26 e -0.19 $e.A^{-3}$

Table S9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for AZN at 298(2) K. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	1736.6(19)	52.6(15)	8554.4(9)	86.7(4)
N1	2873.1(17)	6988.8(14)	4322.1(10)	59.6(4)
O1	1387.0(18)	-1531.8(13)	7172.1(9)	85.7(4)
N3	1636.2(17)	-166.6(15)	7642.6(10)	62.1(4)
N2	2615.3(16)	5403.9(14)	4640.8(9)	59.2(4)
C2	2202.2(17)	4009.2(16)	6067.9(10)	50.5(4)
C5	1822.4(18)	1285.1(17)	7092.2(10)	50.8(4)
C7	2172(2)	4192.8(18)	7091.4(11)	59.2(4)
C4	1817.1(19)	1053.4(18)	6072.9(11)	56.4(4)
C1	2459.6(18)	5482.1(17)	5555.8(11)	55.8(4)
C9	3060.9(18)	8419.0(17)	2880.4(10)	51.6(4)
C3	2005(2)	2430.4(18)	5565.5(11)	57.0(4)
C13	3535(2)	11373.3(17)	2918.5(11)	59.4(4)
C8	2852.0(19)	6933.3(18)	3385.7(11)	56.1(4)
C12	3319(2)	11274.7(17)	1876.1(11)	56.5(4)
C6	1991(2)	2827.8(18)	7610.1(11)	60.5(4)
C14	3416(2)	9981.6(18)	3416.0(11)	58.0(4)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for AZN at 298(2) K. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	120.6(10)	79.5(8)	63.9(8)	23.0(6)	22.2(7)	12.1(7)
N1	64.9(7)	52.0(8)	64.8(8)	14.3(6)	17.3(6)	5.2(5)
O1	119.5(10)	52.6(8)	91.3(9)	11.8(6)	34.4(7)	10.7(6)
N3	65.3(8)	59.0(8)	65.0(9)	16.1(7)	15.3(6)	11.6(6)
N2	66.6(8)	50.3(7)	63.5(8)	12.5(6)	17.2(6)	7.4(5)
C2	46.2(7)	49.7(8)	54.8(9)	6.9(6)	8.7(6)	5.4(6)
C5	48.0(7)	49.4(8)	55.6(9)	11.1(7)	9.7(6)	6.8(6)
C7	70.7(9)	48.2(8)	55.6(9)	0.1(7)	9.6(7)	3.9(7)
C4	61.2(8)	48.7(8)	57.7(9)	1.6(7)	10.8(7)	5.5(6)
C1	57.9(8)	47.9(8)	60.7(10)	5.3(7)	11.5(7)	4.7(6)
C9	49.8(7)	51.4(9)	56.3(9)	8.3(7)	15.7(6)	8.5(6)
C3	65.7(9)	56.7(9)	49.5(8)	5.6(7)	13.6(6)	8.0(7)
C13	69.4(9)	49.4(9)	58.8(9)	-0.5(7)	16.2(7)	3.0(7)
C8	59.1(8)	50.5(8)	62.1(10)	8.6(7)	18.0(7)	10.4(6)
C12	63.2(8)	50.0(8)	58.7(9)	7.7(7)	17.3(6)	6.4(6)
C6	69.7(9)	63.9(10)	47.1(8)	5.5(7)	11.0(6)	6.3(7)
C14	66.2(9)	58.7(9)	50.6(9)	5.5(7)	15.1(7)	8.8(7)
C10	85.7(10)	47.9(9)	60.8(10)	0.1(7)	21.2(8)	4.5(7)
C11	94.2(11)	59.3(10)	50.6(9)	5.8(7)	21.0(8)	4.2(8)
C15	87.3(11)	50.3(9)	64.8(10)	9.2(7)	15.1(8)	6.1(7)
C16	109.1(14)	68.3(11)	85.5(12)	28.2(9)	33.2(10)	2.3(10)
C17	101.8(14)	77.7(13)	124.4(17)	34.4(11)	13.0(11)	21.8(10)

Table S11. Bond Lengths for AZN at 298(2) K.

Bond	Length (Å)	Bond	Length (Å)
O2–N3	1.2211(16)	C4–C3	1.382(2)
N1–N2	1.4120(16)	C9–C8	1.4584(19)
N1–C8	1.2648(18)	C9–C14	1.392(2)
O1–N3	1.2176(15)	C9–C10	1.3847(19)
N3–C5	1.4677(18)	C13–C12	1.3848(19)
N2–C1	1.2674(17)	C13–C14	1.3775(19)
C2–C7	1.3896(19)	C12–C11	1.387(2)
C2–C1	1.4603(19)	C12–C15	1.514(2)
C2–C3	1.388(2)	C10–C11	1.385(2)
C5–C4	1.379(2)	C15–C16	1.520(2)
C5–C6	1.373(2)	C15–C17	1.518(2)
C7–C6	1.382(2)		

Table S12. Bond Angles for AZN at 298(2) K.

Bonds	Angle (°)	Bonds	Angle (°)
C8–N1–N2	112.38(12)	C10–C9–C8	120.34(13)
O2–N3–C5	118.29(13)	C10–C9–C14	117.97(12)
O1–N3–O2	122.96(13)	C4–C3–C2	120.96(13)
O1–N3–C5	118.75(13)	C14–C13–C12	121.64(13)
C1–N2–N1	111.75(12)	N1–C8–C9	122.30(13)
C7–C2–C1	119.00(12)	C13–C12–C11	117.53(13)
C3–C2–C7	119.00(13)	C13–C12–C15	120.67(13)
C3–C2–C1	122.00(13)	C11–C12–C15	121.79(14)
C4–C5–N3	118.95(13)	C5–C6–C7	118.70(14)
C6–C5–N3	118.79(13)	C13–C14–C9	120.71(13)
C6–C5–C4	122.26(13)	C9–C10–C11	120.90(13)
C6–C7–C2	120.72(13)	C10–C11–C12	121.23(14)
C5–C4–C3	118.35(13)	C12–C15–C16	112.47(12)
N2–C1–C2	122.36(13)	C12–C15–C17	110.53(13)
C14–C9–C8	121.68(13)	C17–C15–C16	111.53(15)

Table S13. Torsion Angles for AZN at 298(2) K.

Bonds	Angle (˚)	Bonds	Angle (˚)
O2–N3–C5–C4	176.48(12)	C13–C12–C11–C10	0.7(2)
O2–N3–C5–C6	-3.7(2)	C13–C12–C15–C16	129.16(16)
N1–N2–C1–C2	-179.32(10)	C13–C12–C15–C17	-105.46(17)
O1–N3–C5–C4	-3.60(19)	C8–N1–N2–C1	-173.82(11)
O1–N3–C5–C6	176.23(13)	C8–C9–C14–C13	-177.48(12)
N3–C5–C4–C3	-179.63(10)	C8–C9–C10–C11	177.61(12)
N3–C5–C6–C7	179.82(11)	C12–C13–C14–C9	-0.4(2)
N2–N1–C8–C9	179.02(10)	C6–C5–C4–C3	0.5(2)
C2–C7–C6–C5	-0.7(2)	C14–C9–C8–N1	4.1(2)
C5–C4–C3–C2	0.3(2)	C14–C9–C10–C11	-1.1(2)
C7–C2–C1–N2	175.70(12)	C14–C13–C12–C11	-0.6(2)
C7–C2–C3–C4	-1.3(2)	C14–C13–C12–C15	178.28(12)
C4–C5–C6–C7	-0.4(2)	C10–C9–C8–N1	-174.51(12)
C1–C2–C7–C6	-177.96(11)	C10–C9–C14–C13	1.2(2)
C1–C2–C3–C4	178.14(11)	C11–C12–C15–C16	-52.0(2)
C9–C10–C11–C12	0.1(2)	C11–C12–C15–C17	73.34(19)
C3–C2–C7–C6	1.5(2)	C15–C12–C11–C10	-178.15(13)
C3–C2–C1–N2	-3.7(2)		

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for AZN at 298(2) K.

Atom	*x*	*y*	*z*	U(eq)
H7	2274	5246	7431	71
H4	1690	-3	5736	68
H1	2511	6515	5914	67
H3	1999	2298	4877	68
H13	3766	12405	3292	71
H8	2698	5909	3006	67
H6	1984	2952	8297	73
H14	3574	10087	4117	70
H10	2651	7277	1466	77
H11	2857	9611	646	81
H15	3872	13749	1867	81
H16A	6018	12550	1008	127
H16B	4871	13810	365	127
H16C	4324	11908	94	127
H17A	874	12232	305	152
H17B	1496	14130	447	152
H17C	623	13319	1270	152

142 **Table S15**. Hydrogen-bonds geometry for AZN at 120(2) K and 298(2) K.

AZN at 120(2) K				
Interaction	**D···H**	**D···A**	**H···A**	**D−H···A**
C1−H1···O1$^{(i)}$	0.930(1)	3.323(2)	2.481(2)	150.64(2)
C7−H7···O1$^{(i)}$	0.930(1)	3.514(2)	2.731(2)	142.45(2)
C11−H11···O2$^{(ii)}$	0.930(1)	3.584(2)	2.707(2)	157.68(2)
C16−H16A···O2$^{(ii)}$	0.960(1)	3.506(2)	2.678(2)	144.70(2)
C16−H16C···O2$^{(iii)}$	0.960(1)	3.548(2)	2.637(2)	158.62(2)
C16−H16A···O1$^{(iii)}$	0.960(1)	3.668(2)	2.795(2)	151.48(2)
AZN at 298(2) K				
C1−H1···O1$^{(i)'}$	0.930(1)	3.375(2)	2.530(2)	151.26(1)
C7−H7···O1$^{(i)'}$	0.930(1)	3.566(2)	2.779(2)	142.96(2)
C11−H11···O2$^{(ii)'}$	0.930(1)	3.741(2)	2.842(2)	163.14(2)
C16−H16A···O2$^{(iii)'}$	0.960(1)	3.577(2)	2.780(2)	140.91(2)
C16−H16C···O2$^{(ii)'}$	0.960(1)	3.651(2)	2.746(2)	157.36(2)
C16−H16A···O1$^{(iii)'}$	0.960(1)	3.851(2)	2.977(2)	152.04(2)

Symmetry codes: (i) x,+y-1,+z; (ii) x,+y-1,+z+1; (iii) -x,-y+2,-z+1; (i)' x,+y+1,+z; (ii)' x,+y+1,+z-1; (iii)' -x+1,-y+1,-z+1.

143

144

145

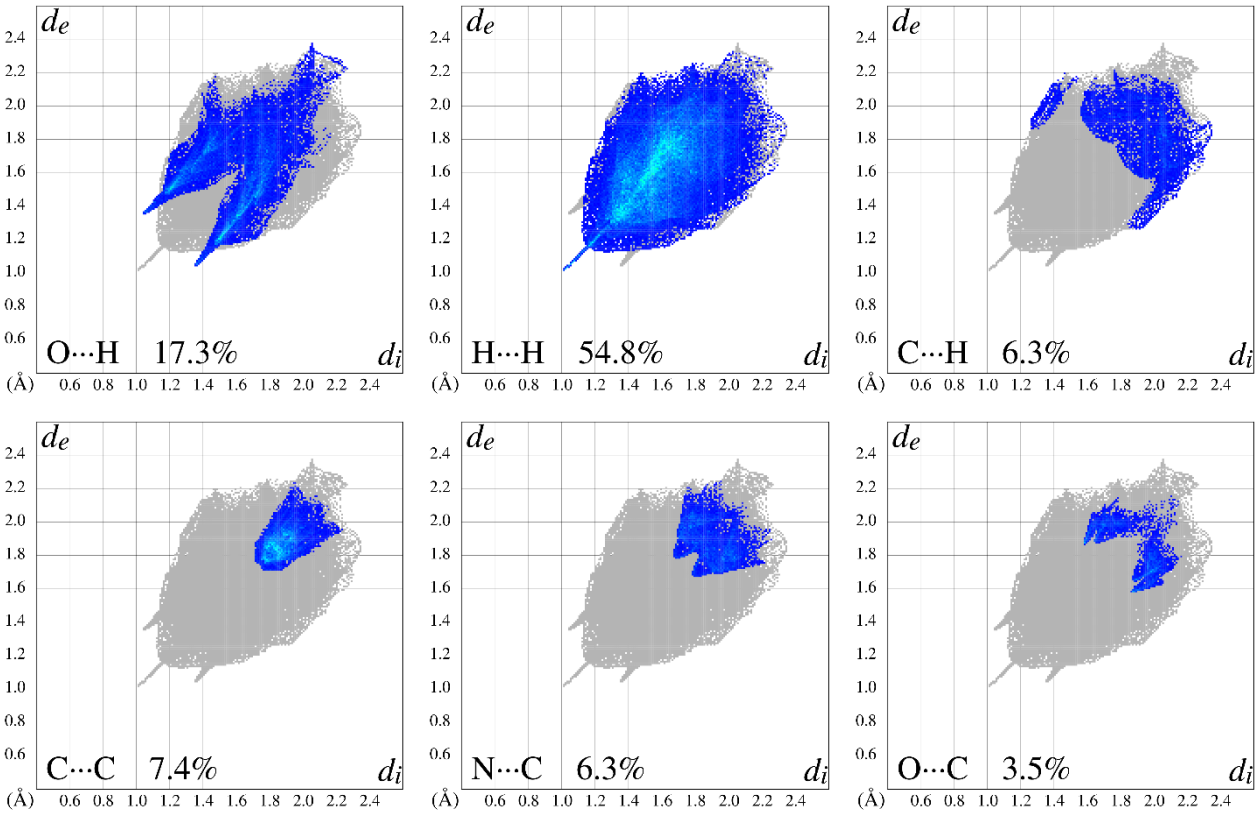
146

147

Hirshfeld Surface and Fingerprint Plots

The remaining percentage of contacts from AZN, which have been performed through analysis of 2D fingerprint plots derived from Hirshfeld Surface (Figure S1) (SPACKMAN; MCKINNON, 2002; SPACKMAN; JAYATILAKA, 2009), summarizes information about the following intermolecular interactions: O···H (17.3%), H···H (54.8%), C···H (6.3%), C···C (7.4%), N···C (6.3%), O···C (3.5%), N···H (3.6%) and N···N (0.7%).

Remaining contacts



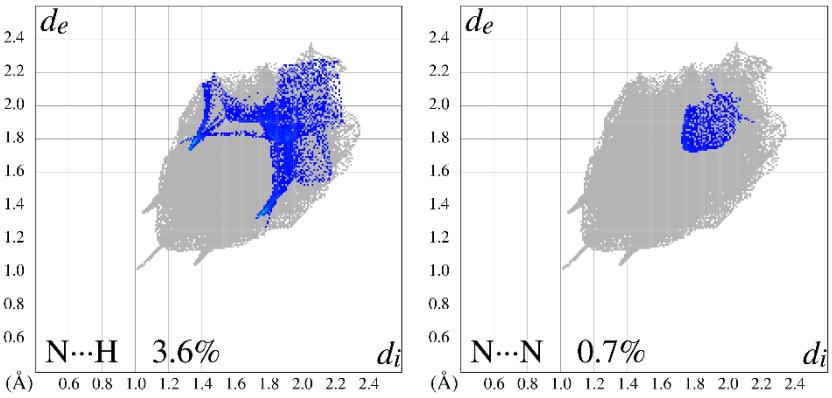


Figure S1. Remaining fingerprint plots of AZN.

The value of 3.5% for C···O contacts, can be resulted from the slippage in molecules, which the nitro group (NO_2) take place in parallel above the aromatic ring B (C9→C15 = Cg2) observed from the dimer, what holds the oxygens and some carbon atoms to be positioned above each other on the surface. While the N···H (3.6 %) and N···N (0.7 %) are mainly because the same idea of slippage but take place around the backbone of azine molecules on the fragment (R_1R_2C=N-N=CR_3R_4), but do not characterize any functional intermolecular interaction previously discussed.

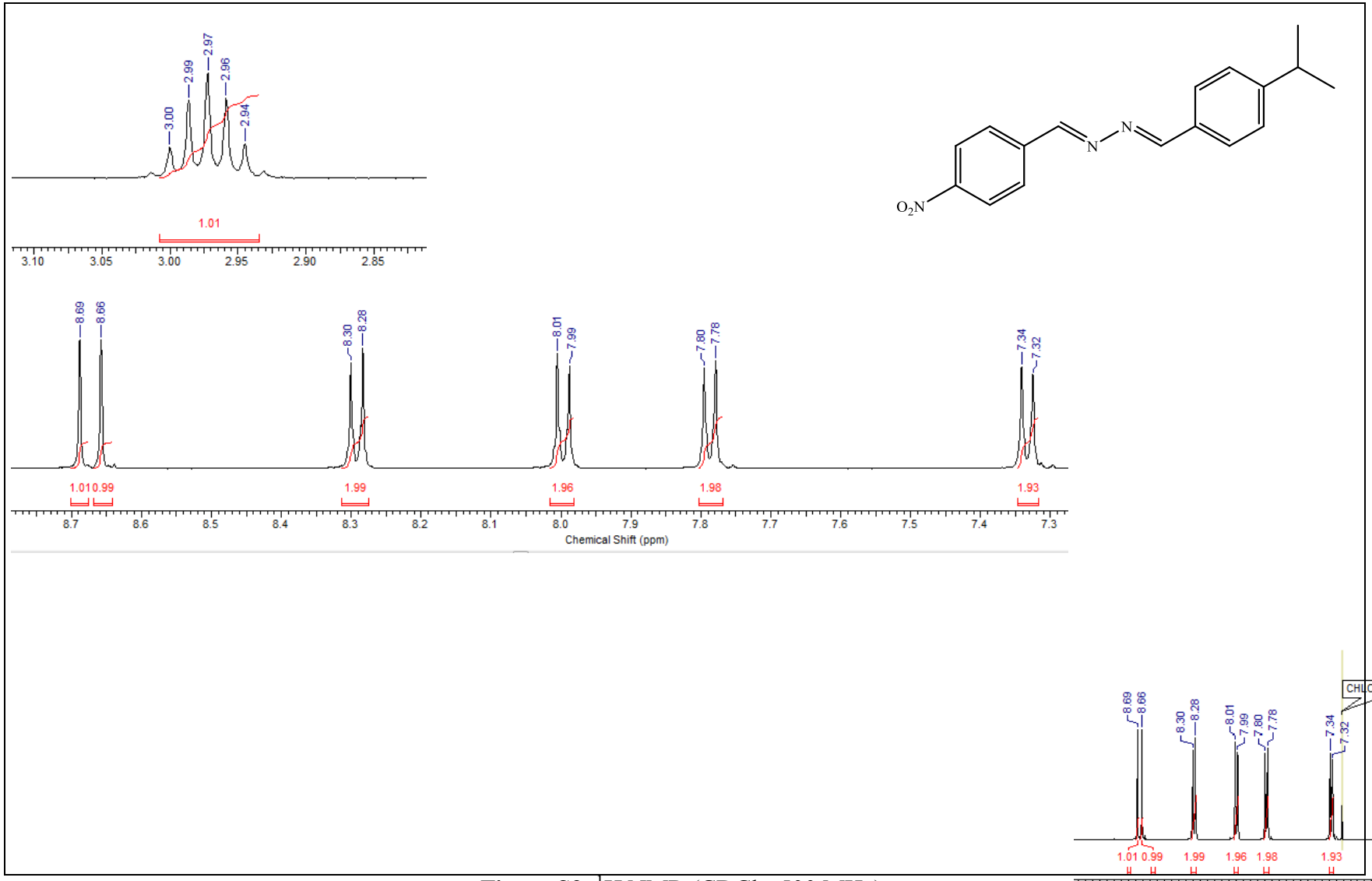
Conventionally, the hydrophobic interactions are marked by contacts between C···C, C···H and H···H, and these are not easily observed or measured, especially the last two. However, with the fingerprint plot, these interactions can be observed through a generic way. The contacts C···H with 6.3% are mainly located at regions near the aromatic rings with the carbon atoms of the system.

Table S16. Topological parameters (in au) of the critical point discriminated in Fig.4 calculated at wB97XD /6-311G(d,p) and APFD /6-311G(d,p) level.

	ρ		$\nabla^2\rho$		G		V		E		ε	
	wB97XD	APFD	wB97XD	APFD	wB97XD	APFD	wB97XD	APFD	wB97XD	APFD	wB97XD	APFD
CP_1	0.008	0.008	0.022	0.005	0.005	0.005	-0.004	-0.004	0.001	0.001	0.009	0.008
CP_2	0.004	0.004	0.013	0.013	0.003	0.003	-0.002	-0.002	0.001	0.001	0.102	0.107
CP_3	0.003	0.003	0.010	0.010	0.002	0.002	-0.001	-0.001	0.001	0.001	0.784	0.799
CP_4	0.004	0.004	0.014	0.014	0.003	0.003	-0.002	-0.002	0.001	0.001	2.255	2.329
CP_5	0.005	0.005	0.016	0.016	0.003	0.003	-0.003	-0.003	0.001	0.001	0.072	0.072
CP_6	0.008	0.008	0.026	0.026	0.006	0.006	-0.005	-0.005	0.001	0.001	0.089	0.088
CP_7	0.007	0.006	0.022	0.022	0.005	0.005	-0.004	-0.004	0.001	0.001	0.104	0.104

Table S17. Interaction energy without (ΔE) and with BSSE correction (ΔE_{BSSE}) for configurations discriminated in Fig.4 calculated at M062X /6-311G(d,p) , wB97XD /6-311G(d,p) and APFD /6-311G(d,p) level.

Configuration	**M062X**		**wB97XD**		**APFD**	
	ΔE	ΔE_{BSSE}	ΔE	ΔE_{BSSE}	ΔE	ΔE_{BSSE}
AB-CD	-0.98	-0.89	-0.75	-0.64	-0.7	-0.58
AB	-47.46	-41.04	-30.5	-24.39	-27.14	-20.67
BF	-1.00	-0.95	-0.70	-0.65	-0.66	-0.59
GH	-7.64	-6.55	-5.27	-4.22	-5.17	-4.00



182 **Figure S2.** ^{1}H NMR ($CDCl_3$, 500 MHz).

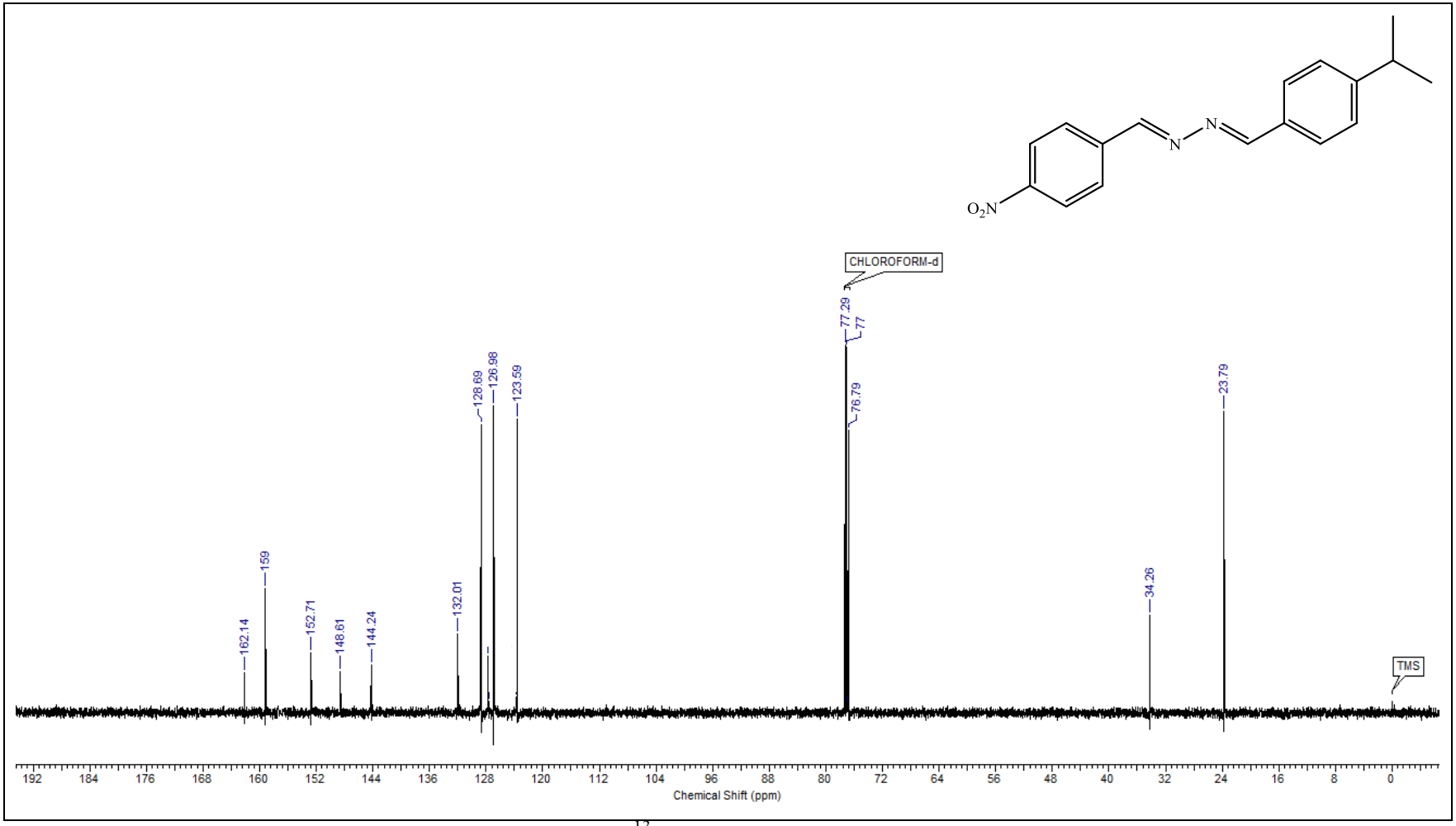
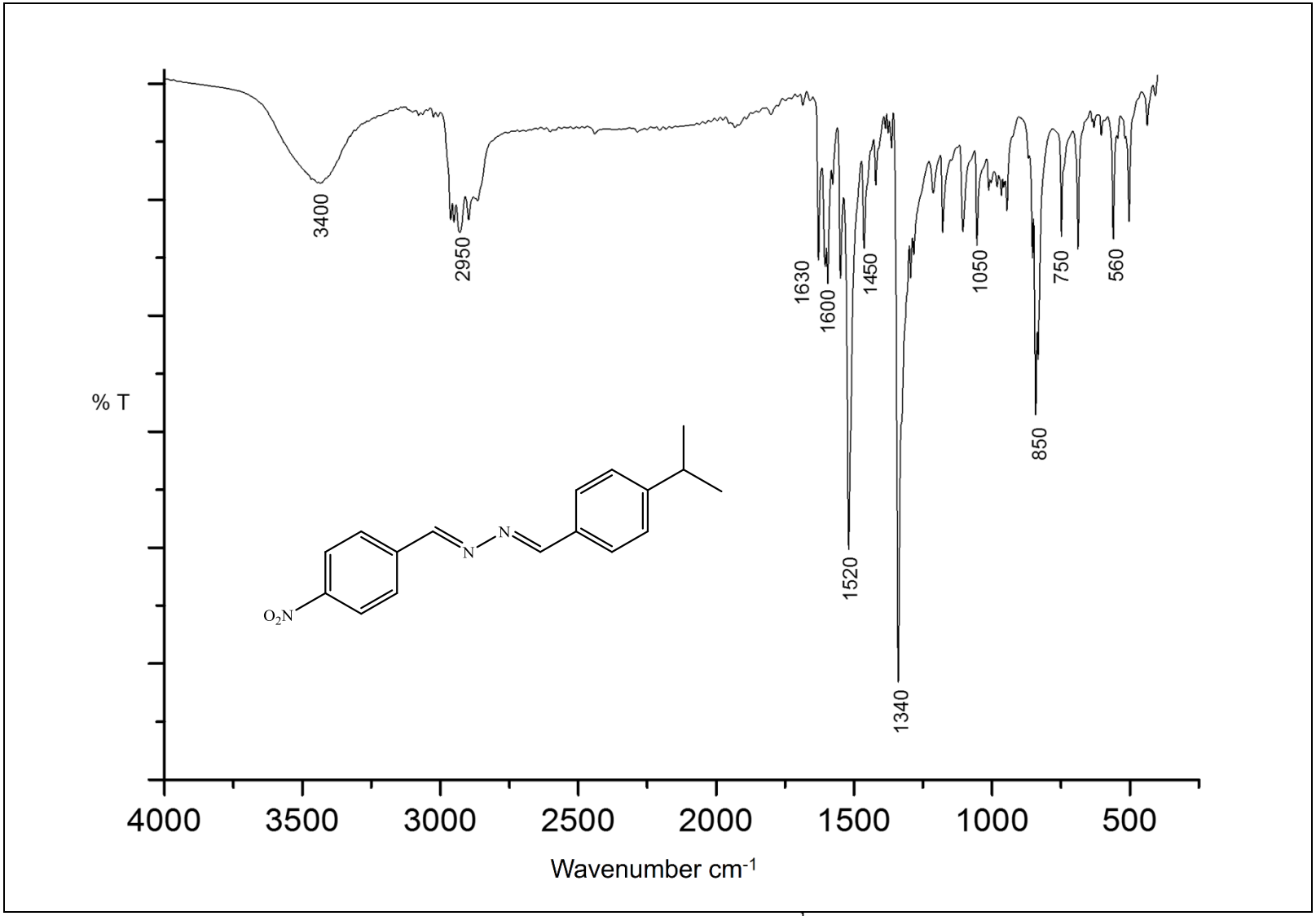


Figure S3. ^{13}C NMR ($CDCl_3$,125 MHz).



186 **Figure S4**. IR (4000-500 cm^{-1}).

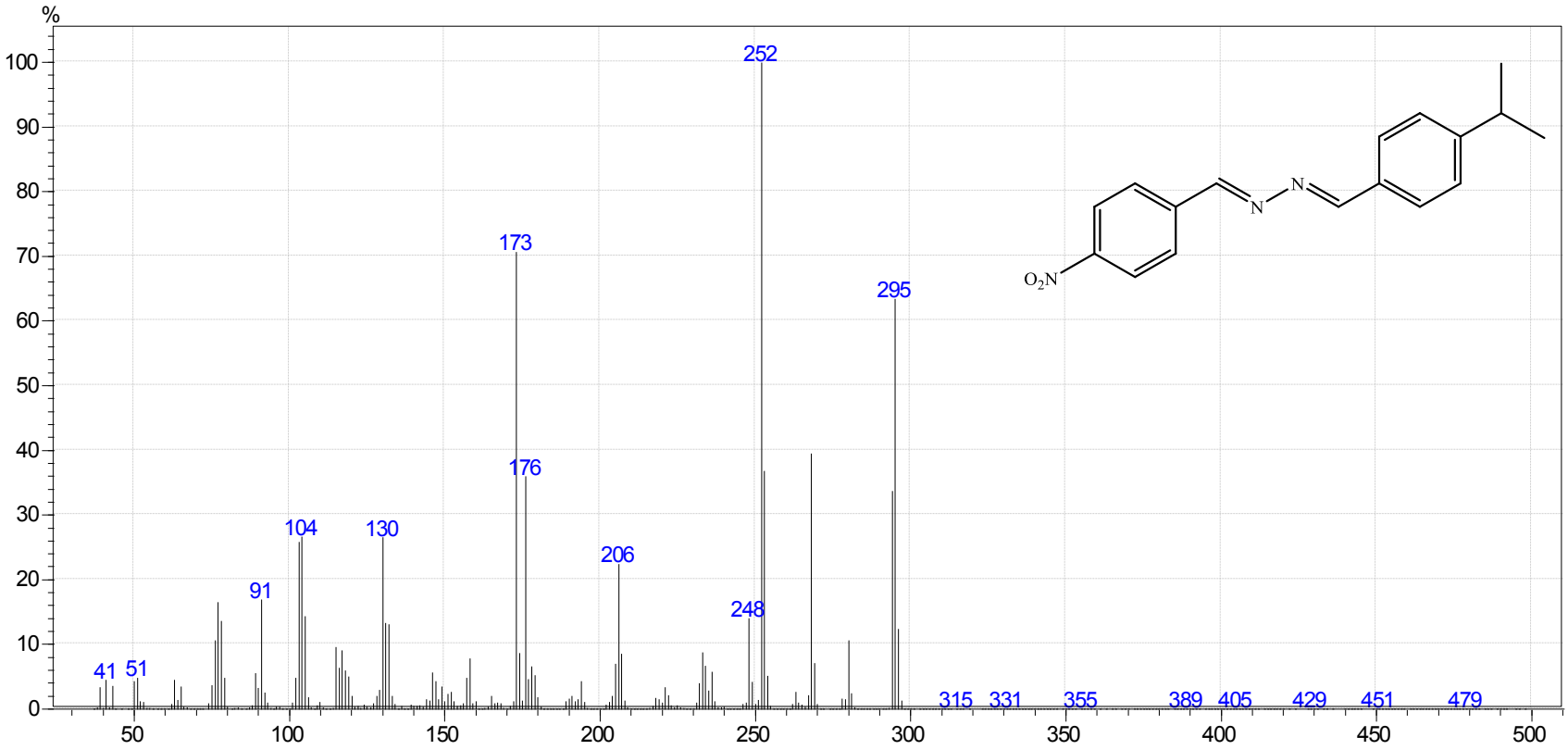


Figure S5. GC-MS-EI.

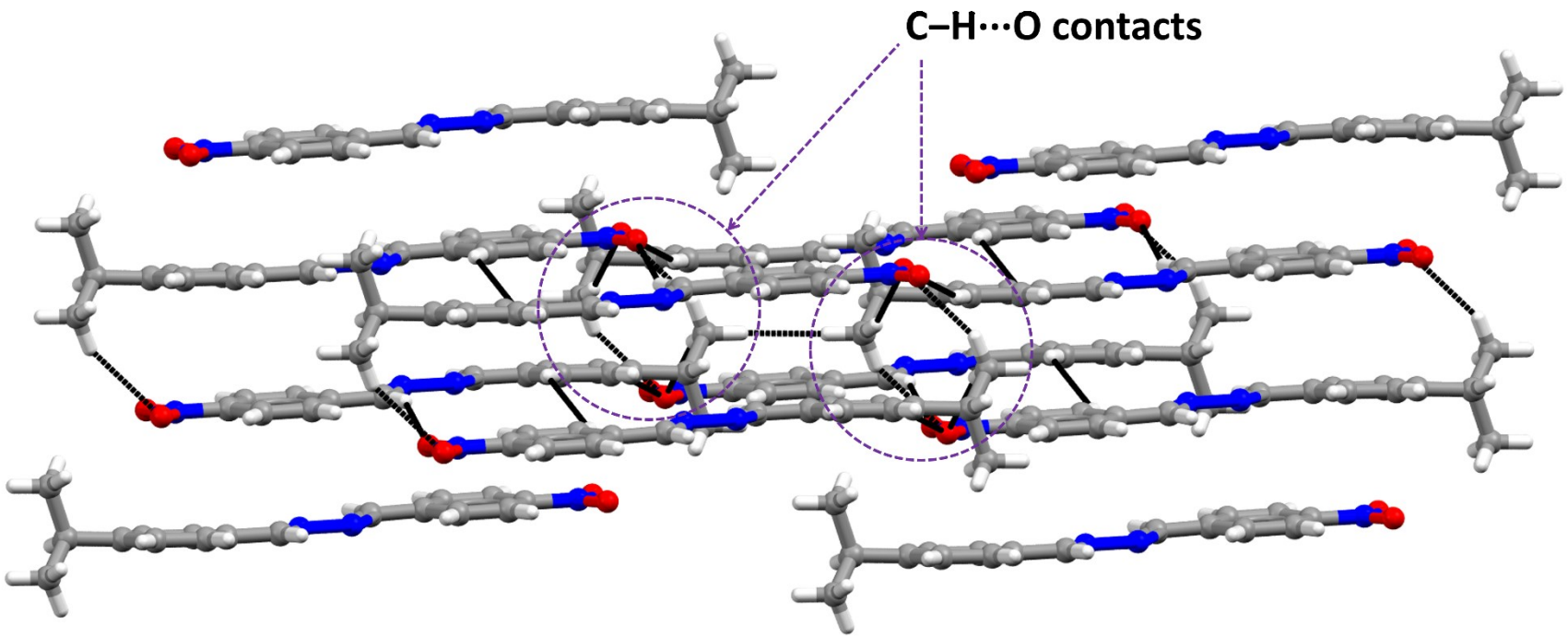


Figure S6. Remaining C–H···O contacts in AZN supramolecular assembly.

Table S18. Bond length of atoms studied in molecular dynamic simulation

Atoms	Bond length (Å)	Standard deviation
$H\alpha_B$-$H\alpha_C$	2.208	0.367
$H\alpha_B$-$C16_B$	1.108	0.039
$C16_B$-$O1_A$	4.065	0.263
$C16_B$-$O2_A$	3.733	0.207
$O1_A$-$N3_A$	1.253	0.025
$O2_A$-$N3_A$	1.249	0.024
$H\alpha_C$-$C16_C$	1.108	0.037
$C16_C$-$O1_D$	4.043	0.224
$C16_C$-$O2_D$	3.712	0.152
$O1_D$-$N3_D$	1.250	0.030
$O2_D$-$N3_D$	1.254	0.031
$H\alpha_B$-$O1_A$	4.737	0.283
$H\alpha_B$-$O2_A$	4.513	0.222
$H\beta_B$-$O1_A$	3.198	0.355
$H\beta_B$-$O2_A$	2.828	0.224
$H\gamma_B$-$O1_A$	4.689	0.404
$H\gamma_B$-$O2_A$	3.870	0.429
$H\alpha_C$-$O1_D$	4.628	0.442
$H\alpha_C$-$O2_D$	4.398	0.429
$H\beta_C$-$O1_D$	3.254	0.451
$H\beta_C$-$O2_D$	2.862	0.310
$H\gamma_C$-$O1_D$	4.661	0.386
$H\gamma_C$-$O2_D$	3.876	0.396

206 **Table S19.** Bond angle of atoms studied in molecular dynamic simulation

Atoms	Bond Angle (°)	Standard deviation
$H\alpha_C$-$H\alpha_B$-$C16_B$	157.0	13.0
$H\alpha_B$-$C16_B$-$O1_A$	122.3	11.5
$H\alpha_B$-$C16_B$-$O2_A$	129.7	8.9
$C16_B$-$O1_A$-$N3_A$	83.3	3.7
$C16_B$-$O2_A$-$N3_A$	98.7	4.9
$H\alpha_B$-$H\alpha_C$-$C16_C$	151.4	26.3
$H\alpha_B$-$C16_C$-$O1_D$	117.1	22.9
$H\alpha_B$-$C16_C$-$O2_D$	123.9	25.0
$C16_C$-$O1_D$-$N3_D$	83.5	3.7
$C16_C$-$O2_D$-$N3_D$	98.8	4.5
$O1_A$-$N3_A$-$O2_A$	124.4	4.0
$O1_D$-$N3_D$-$O2_D$	124.3	3.4
$C16_C$- $H\gamma_C$-$O1_D$	132.7	23.8
$C16_C$- $H\gamma_C$-$O2_D$	137.9	21.7

207

208

209 **Table S20.** Dihedral angle of atoms studied in molecular dynamic simulation

Atoms	Dihedral Angle (°)	Standard deviation
$H\alpha_B$-$C16_B$-$O1_A$-$N3_A$	-137.5	7.8
$H\alpha_B$-$C16_B$-$O2_A$-$N3_A$	111.9	13.6
$H\alpha_C$-$H\alpha_B$-$C16_B$-$O1_A$	-2.6	84.3
$H\alpha_C$-$H\alpha_B$-$C16_B$-$O2_A$	-15.7	88.1
$C16_C$-$H\alpha_C$-$H\alpha_B$-$C16_B$	-1.1	148.3
$H\alpha_C$-$C16_C$-$O1_D$-$N3_D$	133.6	21.3
$H\alpha_C$-$C16_C$-$O2_D$-$N3_D$	-106.4	33.0
$H\alpha_B$-$H\alpha_C$-$C16_C$-$O1_D$	6.7	84.2
$H\alpha_B$-$H\alpha_C$-$C16_C$-$O2_D$	13.6	88.8

210

211