

## ESI

### Fast degenerate double proton transfer in the solid state between two indazolinone tautomers

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#### 1S. X-Ray data collection and structure refinement

Prismatic colorless single crystals of **6** (C<sub>7</sub>H<sub>4</sub>F<sub>2</sub>N<sub>2</sub>O) suitable for X-ray diffraction experiments were obtained by crystallization from methanol. Data collection were carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) operating at 50 kV and 30 mA. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 30s covered 0.3 in  $\omega$ . The first 100 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable drop in the intensities of standard reflections was observed. The cell parameter were determined and refined by a least-squares fit of all reflections.

A summary of the fundamental crystal and refinement data is given in Table 1. Full-matrix least-squares refinements were carried out, minimizing  $\omega(F_o^2 - F_c^2)^2$ .  $R_w$  and goodness-of-fit are based on  $F^2$ . Most of the calculations were carried out with the Smart software for data collection and reduction and SHELXTL-97 (G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Gottingen, Germany, 1997) for structure solution and refinement. Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms bonded to the nitrogen and oxygen atoms have been located in a Fourier synthesis, included and refined their coordinates and fixed the thermal parameters (H2a y H2b at 50%). The remaining hydrogen atoms were included in calculated positions and refined as riding on their respective carbon atoms. Final R( $R_w$ ) values were 0.0363(0.0825).

The supplementary crystallographic data have been passed to the Cambridge Crystallographic Data Centre (CCDC deposition number .....).

Table 1. Crystal and refinement data for **6**

Compound	<b>6</b>
Empirical formula	C <sub>7</sub> H <sub>4</sub> F <sub>2</sub> N <sub>2</sub> O
Formula weight	170.12
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	9.0766 (7)
<i>b</i> (Å)	11.6167 (9)
<i>c</i> (Å)	12.4603 (10)
$\beta$ (°)	103.471 (2)
<i>V</i> (Å <sup>3</sup> )	1277.67 (17)
<i>Z</i>	8
<i>T</i> (K)	296(2)
<i>F</i> (000)	688
$\rho_{\text{calc.}}$ (g cm <sup>-3</sup> )	1.769
$\mu$ (mm <sup>-1</sup> )	0,161
Scan technique	$\omega$ and $\varphi$
Data collected	(-10,-13,-14) to (10,12,14)
$\theta$ range (°)	2.90 – 25.00
Reflections collected	4493
Independent reflections	1083 ( $R_{\text{int}} = 0.0380$ )
Completeness to maximum $\theta$	96.1%
Data/restraints/parameters	1083 / 0 / 115
GOF ( $F^2$ )	1.071
$R^a$ [ $I > 2\sigma(I)$ ]	0.0315
$Rw_F^b$ (all data)	0.0825
Largest residual peak and hole (e Å <sup>-3</sup> )	0.155 / -0.225

<sup>a</sup> $\Sigma[|F_o| - |F_c|] / \Sigma|F_o|.$

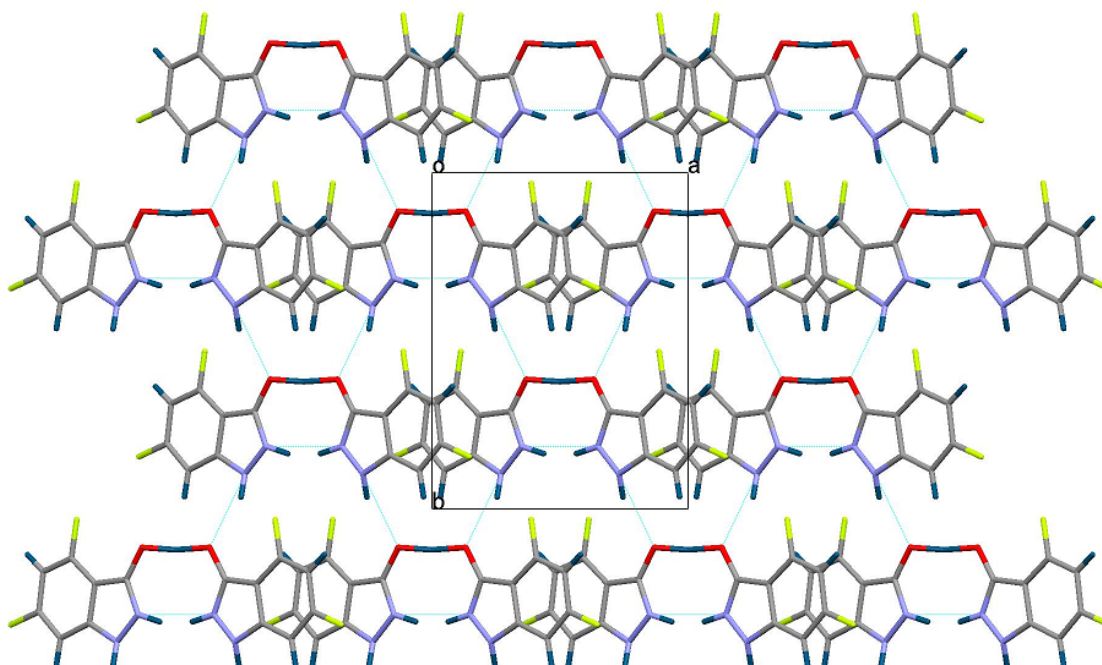
<sup>b</sup> $\{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Hydrogen bonds in the crystal structure of **6** (distances in Å, angles in °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H2B...O1 <sup>a</sup>	1.292(2)	1.292(2)	2.579(2)	173(3)
N2-H2A...N2 <sup>a</sup>	0.91(2)	2.04(2)	2.888(3)	155(4)
N1-H1...O1 <sup>b</sup>	0.89(4)	2.10(2)	2.936(18)	157(2)

<sup>a</sup>(-x+1, y, -z+1/2), <sup>b</sup>(-x+1/2, y+1/2, -z+1/2)

Hydrogen bonding between dimers of **6** through N1-H1...O1 (-x+1/2, y+1/2, -z+1/2) are responsible of the formation of layers parallel to [110]. See Figure 1S.



**Fig. 1S** Packing along c axis in dimeric units of **6**

## 2S. NMR spectroscopy.

2.1. Solution NMR spectra were recorded on a Bruker DRX 400 (9.4 Tesla, 400.13 MHz for  $^1\text{H}$ , 100.62 MHz for  $^{13}\text{C}$  and 40.56 MHz for  $^{15}\text{N}$ ) spectrometer with a 5-mm inverse-detection H-X probehead equipped with a z-gradient coil, at the temperatures indicated in each case. Chemical shifts ( $\delta$  in ppm) are given from internal solvent, DMSO- $d_6$  2.49 for  $^1\text{H}$  and 39.5 for  $^{13}\text{C}$ , THF- $d_8$ , 3.58 for  $^1\text{H}$  and 67.4 for  $^{13}\text{C}$ ; for  $^{15}\text{N}$  NMR nitromethane (0.00) was used as external standard. Typical resolution for  $^1\text{H}$  NMR spectra is 0.15-0.25 Hz per point and for  $^{13}\text{C}$  NMR spectra 0.6 Hz per point.

2D inverse proton detected heteronuclear shift correlation spectra, ( $^1\text{H}$ - $^{13}\text{C}$ ) gs-HMQC, ( $^1\text{H}$ - $^{13}\text{C}$ ) gs-HMBC and ( $^1\text{H}$ - $^{15}\text{N}$ ) gs-HMBC, were acquired and processed using standard Bruker NMR software and in non-phase-sensitive mode. Gradient selection was achieved through a 5% sine truncated shaped pulse gradient of 1 ms. Variable temperature experiments were recorded on the same spectrometer. A Bruker BVT300 temperature unit was used to control the temperature of the cooling gas stream and an exchanger to achieve low temperatures.

2.2. Solid state  $^{13}\text{C}$  (100.73 MHz) and  $^{15}\text{N}$  (40.60 MHz) CPMAS NMR spectra have been obtained on a Bruker WB 400 spectrometer at 300 K using a 4 mm DVT probehead and a 4-mm diameter cylindrical zirconia rotor with Kel-F end-caps. The non-quaternary suppression (NQS) technique to observe only the quaternary carbon atoms was employed.  $^{13}\text{C}$  spectra were originally referenced to a glycine sample and then the chemical shifts were recalculated to the  $\text{Me}_4\text{Si}$  (for the carbonyl atom  $\delta$  (glycine) = 176.1 ppm) and  $^{15}\text{N}$  spectra to  $^{15}\text{NH}_4\text{Cl}$  and then converted to nitromethane scale using the relationship:  $\delta^{15}\text{N}(\text{nitromethane}) = \delta^{15}\text{N}(\text{ammonium chloride}) - 338.1$  ppm. A Bruker BVT3000 temperature unit was used to control the temperature of the cooling gas stream an a exchanger to achieve low temperatures. To avoid problems at low temperatures caused by air moisture, pure nitrogen was used as bearing, driving and cooling gas. The rotational frequencies were of about 6 kHz and we used boron nitride caps.

### 3S. Spectral data of 6 recorded on a Bruker DRX 400

#### <sup>1</sup>H NMR ( $\delta$ in ppm, $J$ in Hz)

Solvent	NH	OH	H5	H7
DMSO- <i>d</i> <sub>6</sub>	11.8 (br s)	10.9 (br s)	6.71 (ddd)	6.92 (dd)
300 K			<sup>4</sup> $J_{H7}$ =1.9 <sup>3</sup> $J_{F4}$ = <sup>3</sup> $J_{F6}$ =10.3	<sup>4</sup> $J_{H5}$ =1.9 <sup>3</sup> $J_{F6}$ =9.5

#### <sup>13</sup>C NMR ( $\delta$ in ppm, $J$ in Hz)

Conditions	C3	C3a	C4	C5	C6	C7	C7a
DMSO- <i>d</i> <sub>6</sub>	153.6 (s)	98.9 (d)	155.7 (dd)	94.4 (dd)	161.8 (dd)	92.0 (dd)	143.6 (dd)
300 K		<sup>2</sup> $J_{F4}$ =20.2	<sup>1</sup> $J_{F4}$ =253.3 <sup>3</sup> $J_{F6}$ =16.7	<sup>2</sup> $J_{F4}$ =30.5 <sup>2</sup> $J_{F6}$ =23.3	<sup>1</sup> $J_{F6}$ =242.7 <sup>3</sup> $J_{F4}$ =11.7	<sup>2</sup> $J_{F6}$ =26.1 <sup>4</sup> $J_{F4}$ =4.7	<sup>3</sup> $J_{F4}$ =15.1 <sup>3</sup> $J_{F6}$ =10.3
CPMAS	157.5	99.1	157.5	94.6	163 (br s)	94.6	145.9
300 K							

#### <sup>15</sup>N NMR ( $\delta$ in ppm, $J$ in Hz)

Conditions	N1	N2
THF- <i>d</i> <sub>8</sub>	-224.1 (d)	-117,9
207 K	<sup>1</sup> $J_{H1}$ =107.1	
CPMAS	-240.9	-169 (br s)
300 K		

#### 4S. Spectral data of 6-<sup>15</sup>N<sub>2</sub> recorded on a Bruker DRX 400

##### <sup>1</sup>H NMR ( $\delta$ in ppm, $J$ in Hz)

Solvent	NH	OH	H5	H7
DMSO- <i>d</i> <sub>6</sub> 300 K	11.8 (d) <sup>1</sup> <i>J</i> <sub>N1</sub> =99	10.9 (s)	6.70 (ddd) <sup>4</sup> <i>J</i> <sub>H7</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F4</sub> = <sup>3</sup> <i>J</i> <sub>F6</sub> =10.3	6.91 (ddd) <sup>4</sup> <i>J</i> <sub>H5</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F6</sub> =9.4 <sup>3</sup> <i>J</i> <sub>N1</sub> =1.0
THF- <i>d</i> <sub>8</sub> 300K	11.1 (br s)	10.8 (br s)	6.48 (ddd) <sup>4</sup> <i>J</i> <sub>H7</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F4</sub> = <sup>3</sup> <i>J</i> <sub>F6</sub> =10.0	6.76 (ddd) <sup>4</sup> <i>J</i> <sub>H5</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F6</sub> =9.3 <sup>3</sup> <i>J</i> <sub>N1</sub> =1.2
THF- <i>d</i> <sub>8</sub> 193K	11.6 (ddd) <sup>1</sup> <i>J</i> <sub>N1</sub> =108 <sup>2</sup> <i>J</i> <sub>N2</sub> =8.3 <sup>5</sup> <i>J</i> <sub>F4</sub> =1.9	10.8 (s)	6.77 (ddd) <sup>4</sup> <i>J</i> <sub>H7</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F4</sub> = <sup>3</sup> <i>J</i> <sub>F6</sub> =10.1	7.01 (ddd) <sup>4</sup> <i>J</i> <sub>H5</sub> =1.9 <sup>3</sup> <i>J</i> <sub>F6</sub> =9.3 <sup>3</sup> <i>J</i> <sub>N1</sub> =1.1

##### <sup>13</sup>C NMR ( $\delta$ in ppm, $J$ in Hz)

Solvent	C3	C3a	C4	C5	C6	C7	C7a
DMSO- <i>d</i> <sub>6</sub> 300 K	153.6 (s)	99.0 (dd) <sup>2</sup> <i>J</i> <sub>F4</sub> =20.2 <sup>2</sup> <i>J</i> <sub>N1</sub> =3.6	155.6 (dd) <sup>1</sup> <i>J</i> <sub>F4</sub> =253.4 <sup>3</sup> <i>J</i> <sub>F6</sub> =16.5	94.4 (dd) <sup>2</sup> <i>J</i> <sub>F4</sub> =30.3 <sup>2</sup> <i>J</i> <sub>F6</sub> =22.9	161.9 (ddd) <sup>1</sup> <i>J</i> <sub>F6</sub> =242.6 <sup>3</sup> <i>J</i> <sub>F4</sub> =11.6 <sup>3</sup> <i>J</i> <sub>N1</sub> =2.6	92.2 (dd) <sup>2</sup> <i>J</i> <sub>F6</sub> =26.1 <sup>4</sup> <i>J</i> <sub>F4</sub> =4.3	143.6 (m)
THF- <i>d</i> <sub>8</sub> 193 K	154.7 (s)	99.5 (dd) <sup>2</sup> <i>J</i> <sub>F4</sub> =20.9 <sup>2</sup> <i>J</i> <sub>N1</sub> =3.4	157.0 (dd) <sup>1</sup> <i>J</i> <sub>F4</sub> =253.9 <sup>3</sup> <i>J</i> <sub>F6</sub> =16.0	95.3 (dd) <sup>2</sup> <i>J</i> <sub>F4</sub> =30.6 <sup>2</sup> <i>J</i> <sub>F6</sub> =23.1	163.5 (ddd) <sup>1</sup> <i>J</i> <sub>F6</sub> =245.8 <sup>3</sup> <i>J</i> <sub>F4</sub> =11.0 <sup>3</sup> <i>J</i> <sub>N1</sub> =2.6	92.7 (dd) <sup>2</sup> <i>J</i> <sub>F6</sub> =26.3 <sup>4</sup> <i>J</i> <sub>F4</sub> =3.5	144.5 (m)

##### <sup>15</sup>N NMR ( $\delta$ in ppm, $J$ in Hz)

Conditions	N1	N2
DMSO- <i>d</i> <sub>6</sub> 300 K	-224.1 (d) <sup>1</sup> <i>J</i> <sub>N2</sub> =10.9	-121.8
THF- <i>d</i> <sub>8</sub> 300 K	-229.5 (dd) <sup>1</sup> <i>J</i> <sub>N2</sub> =12.1	-118.3 (d) <sup>1</sup> <i>J</i> <sub>N1</sub> =12.1
THF- <i>d</i> <sub>8</sub> 193 K	-227.6 (d) <sup>1</sup> <i>J</i> <sub>N2</sub> =10.6	-119.3 (d) <sup>1</sup> <i>J</i> <sub>N1</sub> =10.6
CPMAS 300K	-241.2	-168.6
CPMAS 173 K	-241.8	-169.4

## 5S. Spectral data of 6- <sup>15</sup>N<sub>2</sub> recorded on a Bruker 600 MHz instrument

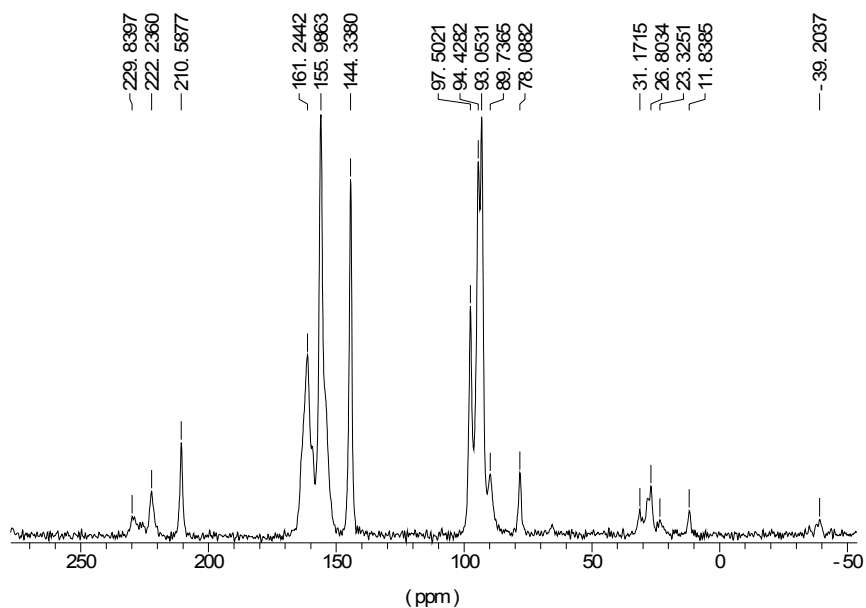
### <sup>13</sup>C CPMAS NMR chemical shifts at 300 K (10 kHz)

Peak Picking region:

Start(ppm)	Start(Hz)	End(ppm)	End(Hz)	MI(%)	MAXI(%)
277.40	41862.2	-53.84	-8125.6	-2.39	100.50

Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	588	34684.47	229.8397	11237517	3.9
2	682	33537.01	222.2360	28293396	9.9
3	826	31779.20	210.5877	61687496	21.5
4	1436	24332.91	161.2442	121734656	42.5
5	1501	23539.45	155.9863	286299936	100.0
6	1645	21781.64	144.3380	241848192	84.5
7	2224	14713.77	97.5021	154952768	54.1
8	2262	14249.90	94.4282	254037056	88.7
9	2279	14042.38	93.0531	284723680	99.4
10	2320	13541.89	89.7365	40217648	14.0
11	2464	11784.08	78.0882	41075864	14.3
12	3044	4704.00	31.1715	16056978	5.6
13	3098	4044.82	26.8034	31868780	11.1
14	3141	3519.92	23.3251	8967616	3.1
15	3283	1786.52	11.8385	15176869	5.3
16	3914	-5916.11	-39.2037	9195823	3.2



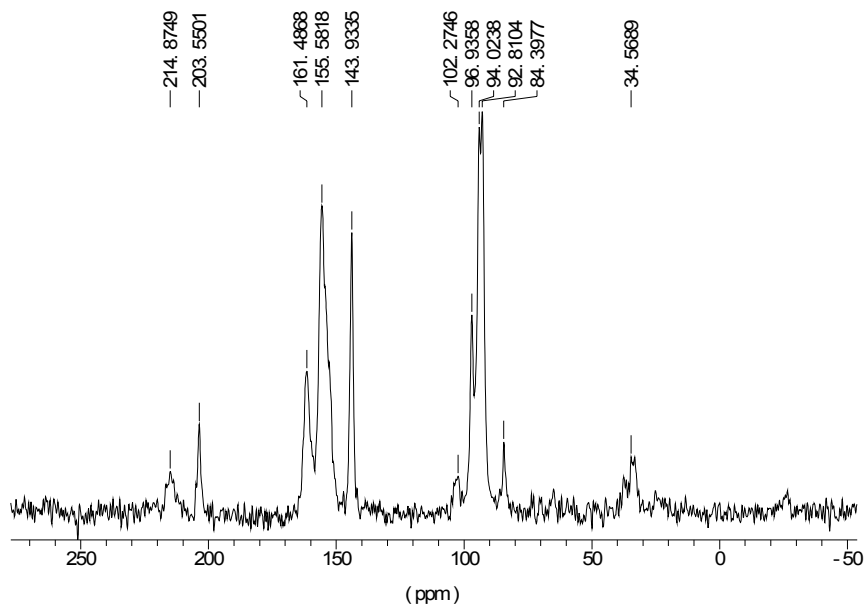
### <sup>13</sup>C CPMAS NMR chemical shifts at 173 K (9 kHz)

Peak Picking region:

Start(ppm)	Start(Hz)	End(ppm)	End(Hz)	MI(%)	MAXI(%)
277.40	41862.2	-53.84	-8125.6	-7.73	100.50

Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	773	32426.17	214.8749	44316092	9.5
2	913	30717.19	203.5501	100023744	21.4
3	1433	24369.53	161.4868	162202176	34.7
4	1506	23478.42	155.5818	356660640	76.3
5	1650	21720.60	143.9335	325195200	69.5
6	2165	15433.98	102.2746	38695616	8.3
7	2231	14628.32	96.9358	228235600	48.8
8	2267	14188.87	94.0238	449153376	96.0
9	2282	14005.76	92.8104	467660512	100.0
10	2386	12736.23	84.3977	78863488	16.9
11	3002	5216.70	34.5689	61615960	13.2





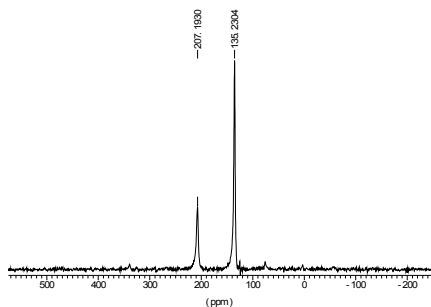
### <sup>15</sup>N CPMAS NMR chemical shifts at 300 K (8 kHz)

Peak Picking region:

Start(ppm)	Start(Hz)	End(ppm)	End(Hz)	MI(%)	MAXI(%)
574.63	34944.9	-247.47	-15049.0	-1.15	100.50

Peak Picking results:

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	3661	12599.91	207.1930	100447680	29.8
2	4378	8223.69	135.2304	337391904	100.0



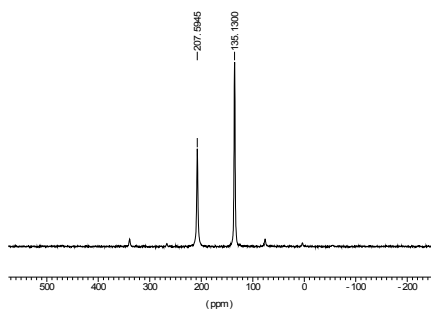
### <sup>15</sup>N CPMAS NMR chemical shifts at 173 K (8 kHz)

Peak Picking region:

Start(ppm)	Start(Hz)	End(ppm)	End(Hz)	MI(%)	MAXI(%)
574.63	34944.9	-247.47	-15049.0	-0.65	100.50

Peak Picking results:

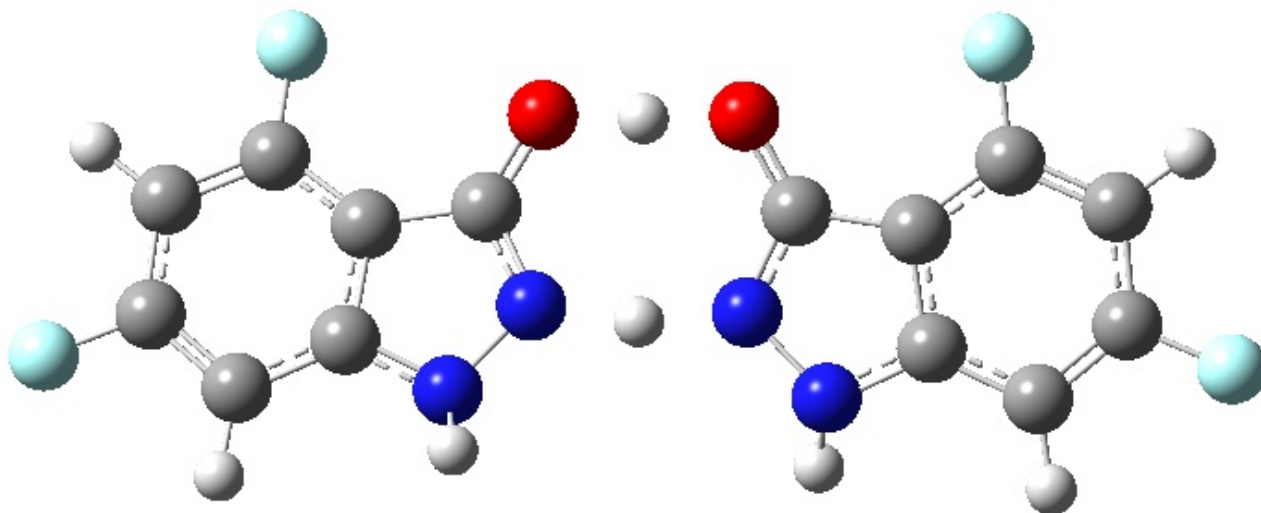
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	3657	12624.32	207.5945	212633984	45.8
2	4379	8217.59	135.1300	464364672	100.0



## 6S. Theoretical calculations.

### Energetic results at the B3LYP/6-311++G(d,p) computational level

	E <sub>total</sub> (hartree)	E <sub>total</sub> +ZPE hartree	E <sub>rel</sub> (kJ/mol)	E <sub>rel</sub> +ZPE (kJ/mol)	EI (kJ/mol)
oxo-tautomer <b>6a</b>	-653.726099	-653.619955			
hydroxy-tautomer <b>6b</b>	-653.726718	-653.621398	-1.63	-3.79	
dimer <b>6a/6b</b>	-1307.47553	-1307.2624			-59.64
dimer_TS	-1307.46013	-1307.25492	40.43	19.64	



Absolute shieldings (ppm)

	<p>oxo-tautomer <b>6a</b></p> <p>1 C 14.4514                  2 C 13.3504                  3 C 80.0168                  4 H 25.3856                  5 C 7.0017                  6 C 84.4028                  7 H 25.4401                  8 C 72.9720                  9 C 21.6841                  10 F 276.8538                  11 F 273.8978                  12 N 131.7179                  13 N 92.0022                  14 O -54.8605                  15 H 25.9930                  16 H 26.6444</p>
	<p>hydroxy-tautomer <b>6b</b></p> <p>1 C 23.6347                  2 C 17.2677                  3 C 83.2252                  4 H 25.3401                  5 C 10.7380                  6 C 89.4299                  7 H 25.3714                  8 C 79.7269                  9 C 33.8518                  10 F 283.0987                  11 F 283.1574                  12 N 87.7298                  13 N -32.8737                  14 O 228.9042                  15 H 26.9591                  16 H 24.0414</p>

	Dimer <b>6a/6b</b>
	1 C 17.6218
	2 C 15.8284
	3 C 82.6569
	4 H 25.3464
	5 C 9.1057
	6 C 89.4796
	7 H 25.4084
	8 C 76.8015
	9 C 32.4983
	10 F 280.3728
	11 F 281.7233
	12 N 95.4011
	13 H 19.5937
	14 H 24.6439
	15 C 12.2213
	16 C 13.4622
	17 C 79.8905
	18 H 25.3213
	19 C 7.0949
	20 C 84.5578
	21 H 25.3044
	22 C 72.8092
	23 C 23.7121
	24 F 276.0448
	25 F 274.2303
	26 N 128.2617
	27 N 79.3486
	28 O 16.6191
	29 H 19.5949
	30 H 26.2599
	31 N -13.6376
32 O 203.2939	

These shieldings can be transformed into chemical shifts using the following equations:

$\delta^1\text{H} = 31.0 - 0.97 \sigma^1\text{H}$  (A. M. S. Silva, R. M. S. Sousa, M. L. Jimeno, F. Blanco, I. Alkorta, J. Elguero, *Magn. Reson. Chem.* 2008, **46**, 859).

$\delta^{13}\text{C} = 175.7 - 0.963 \sigma^{13}\text{C}$  (F. Blanco, I. Alkorta, J. Elguero, *Magn. Reson. Chem.* 2007, **45**, 797).

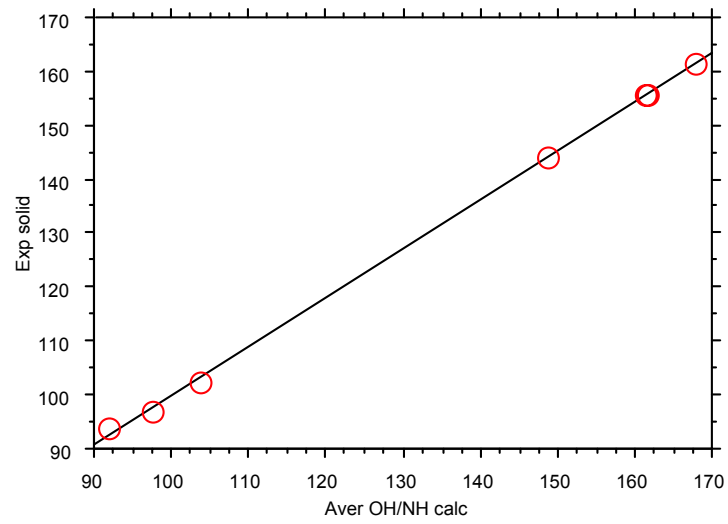
The  $^1\text{H}$  chemical shifts are almost useless since these molecules have only two CHs. The calculated  $^{13}\text{C}$  chemical shifts correspond to those of the hydroxy tautomer **6b** in solution:

DMSO:  $\delta^{13}\text{C}_{\text{exp}} = (0.993 \pm 0.006) \delta^{13}\text{C}_{\text{calc}}$ , n = 7,  $R^2 = 1.000$

THF:  $\delta^{13}\text{C}_{\text{exp}} = (1.001 \pm 0.006) \delta^{13}\text{C}_{\text{calc}}$ , n = 7,  $R^2 = 1.000$

The  $^{13}\text{C}$  NMR data of  $6\text{-}^{15}\text{N}_2$  in the solid state from the spectra reproduced in Section **5S** are: 161.5 (C6), 155.6 (C3,C4), 144.0 (C7a), 102.3 (C3a), 96.9 (C5) and 94.0 ppm (C7).

These chemical shifts agree very well with the calculated ones (averaged) for **6a/6b**:



The trendline corresponds to  $\delta^{13}\text{C}_{\text{exp}} = (9.4 \pm 1.4) + (0.905 \pm 0.010) \delta^{13}\text{C}_{\text{calc}}$ ,  $n = 7$ ,  $R^2 = 0.999$ .