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*Supplementary Information*

Conformational Isomers of *Trans*-Urocanic Acid  
Observed by Rotational Spectroscopy

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**Table S1.** DFT atomic coordinates for Conformer A of *trans*-UCA.

Atom	$a / \text{Å}$	$b / \text{Å}$	$c / \text{Å}$
N(1)	-3.366637	-0.373920	0.000003
H(1)	-4.307693	-0.726318	-0.000018
C(2)	-2.990454	0.942393	-0.000066
H(2)	-3.707630	1.745894	-0.000098
N(3)	-1.692591	1.069217	0.000071
C(4)	-1.182327	-0.218582	-0.000001
C(5)	-2.221062	-1.124337	0.000043
H(5)	-2.233104	-2.199000	0.000065
C(6)	0.224966	-0.519132	-0.000023
H(6)	0.501601	-1.567122	-0.000014
C(7)	1.206202	0.391232	-0.000039
H(7)	0.993972	1.449669	-0.000038
C(8)	2.608478	-0.035753	-0.000053
O(9)	3.017950	-1.175394	0.000003
O(10)	3.454745	1.029614	0.000038
H(10)	4.352182	0.667419	0.000083

**Table S2.** DFT atomic coordinates for Conformer B of *trans*-UCA.

Atom	$a / \text{Å}$	$b / \text{Å}$	$c / \text{Å}$
N(1)	-3.350900	-0.398648	-0.000022
H(1)	-4.286395	-0.765551	-0.000054
C(2)	-2.995101	0.923096	-0.000004
H(2)	-3.724341	1.715683	-0.000006
N(3)	-1.699388	1.069679	0.000030
C(4)	-1.169232	-0.209708	0.000001
C(5)	-2.193628	-1.131385	-0.000002
H(5)	-2.189903	-2.206161	-0.000006
C(6)	0.244730	-0.486392	0.000000
H(6)	0.529170	-1.530798	-0.000009
C(7)	1.202850	0.450011	0.000019
H(7)	0.954854	1.500838	0.000029
C(8)	2.633993	0.149340	0.000011
O(9)	3.510131	0.984655	-0.000035
O(10)	2.923314	-1.183679	0.000013
H(10)	3.888217	-1.246872	-0.000022

**Table S3.** DFT atomic coordinates for Conformer C of *trans*-UCA.

Atom	$a / \text{Å}$	$b / \text{Å}$	$c / \text{Å}$
N(1)	-3.153656	0.815973	0.000024
H(1)	-3.896915	1.492761	0.000072
C(2)	-3.293843	-0.545035	0.000202
H(2)	-4.256910	-1.026433	0.000300

N(3)	-2.132358	-1.140303	-0.000216
C(4)	-1.181310	-0.132896	0.000000
C(5)	-1.814424	1.092911	-0.000056
H(5)	-1.438737	2.099458	-0.000074
C(6)	0.224539	-0.450991	0.000019
H(6)	0.459310	-1.508488	0.000039
C(7)	1.237777	0.424789	-0.000042
H(7)	1.081980	1.494428	-0.000097
C(8)	2.627873	-0.039625	-0.000053
O(9)	3.009695	-1.186865	0.000068
O(10)	3.498948	1.008631	0.000026
H(10)	4.387856	0.626033	0.000101

**Table S4.** DFT atomic coordinates for Conformer D of *trans*-UCA.

Atom	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å
N(1)	-3.156861	0.792256	-0.000026
H(1)	-3.912047	1.455730	-0.000024
C(2)	-3.272855	-0.570708	0.000130
H(2)	-4.227097	-1.069343	0.000195
N(3)	-2.100591	-1.145158	-0.000101
C(4)	-1.168130	-0.120697	0.000014
C(5)	-1.822726	1.093450	-0.000065
H(5)	-1.465250	2.106596	-0.000102
C(6)	0.244134	-0.414908	0.000050
H(6)	0.486398	-1.469355	0.000106
C(7)	1.236224	0.485889	-0.000002
H(7)	1.047865	1.550411	-0.000074
C(8)	2.657812	0.143277	0.000072
O(9)	3.553548	0.958997	0.000013
O(10)	2.908448	-1.193455	-0.000054
H(10)	3.870882	-1.287875	-0.000066

All atomic coordinates taken from Gaussian 09 output files from ground-state optimisation calculations at the B3LYP-D3BJ/aug-cc-pVTZ level of theory. Atoms are numbered as indicated in Figure 1 in the paper; hydrogen atoms are numbered based on the heavy atom to which they are attached.

**Table S5a.** Comparison of experimentally-determined and DFT-calculated parameters for conformers A-C of *trans*-UCA.

Parameter	Conformer A		Conformer B		Conformer C	
	Experiment <sup>a</sup>	DFT	Experiment <sup>a</sup>	DFT	Experiment <sup>a</sup>	DFT
$A_0$ / MHz	4920.844(15)	4953.435	4899.57069(52)	4931.61873	4932.59263(97)	4966.4367
$B_0$ / MHz	576.93690(17)	576.69335	582.26973(17)	582.00863	568.35033(18)	568.86484
$C_0$ / MHz	516.64802(18)	516.55456	520.69877(14)	520.57284	510.02466(13)	510.40240
$\Delta_J$ / kHz	0.00819(26)	0.00924	0.00882(39)	0.00925	0.00822(32)	0.00821
$\Delta_{JK}$ / kHz	0.0183(12)	0.0159	0.0298(24)	0.0235	0.0164(80)	0.0275
$\chi_{aa}$ (N1) / MHz	1.321(14)	1.370	1.316(16)	1.374	1.303(36)	1.272
$[\chi_{bb}$ (N1)– $\chi_{cc}$ (N1)] / MHz	4.03(26)	3.72	3.707(18)	3.725	3.499(34)	3.575
$\chi_{ab}$ (N1) / MHz	[0.032] <sup>b</sup>	0.032 <sup>b</sup>	[0.031] <sup>c</sup>	0.031 <sup>b</sup>	[–0.096] <sup>c</sup>	–0.096 <sup>b</sup>
$\chi_{aa}$ (N3) / MHz	–0.134(33)	–0.105	[–0.014] <sup>c</sup>	–0.014	1.341(35)	1.497
$[\chi_{bb}$ (N3)– $\chi_{cc}$ (N3)] / MHz	–4.72(36)	–4.77	–4.275(18)	–4.857	–6.000(33)	–6.586
$\chi_{ab}$ (N3) / MHz	[–2.934] <sup>c</sup>	–2.934 <sup>b</sup>	[–2.906] <sup>c</sup>	–2.906 <sup>b</sup>	[1.422] <sup>c</sup>	1.422 <sup>b</sup>
$N^d$	190	-	303	-	139	-
$\sigma_{r.m.s.}$ / kHz <sup>e</sup>	10.0	-	16.6	-	20.5	-

<sup>a</sup> Fit performed using Watson's A reduced Hamiltonian.

<sup>b</sup> Values of  $\chi_{ab}$  calculated using DFT at the B3LYP-D3BJ/aug-cc-pVTZ level and used to determine angle between inertial axis and the principal nuclear axis frame of reference (see Table S6).

<sup>c</sup> Value fixed at result calculated by DFT at the B3LYP-D3BJ/aug-cc-pVTZ level.

<sup>d</sup> Number of transitions included in fit.

<sup>e</sup> Root mean square deviation of fit.

**Table S5b.** Comparison of experimentally-determined and DFT-calculated parameters for conformer D of *trans*-UCA.

Parameter	Conformer D	
	Experiment <sup>a</sup>	DFT
$A_0$ / MHz	4907.69(10)	4942.49
$B_0$ / MHz	574.28994(27)	574.77390
$C_0$ / MHz	514.53661(29)	514.89554
$\Delta_J$ / kHz	0.00782(43)	0.00843
$\Delta_{JK}$ / kHz	0.0508(45)	0.0793
$\chi_{aa}$ (N1) / MHz	[1.273] <sup>c</sup>	1.273
$[\chi_{bb}$ (N1)– $\chi_{cc}$ (N1)] / MHz	[3.570] <sup>c</sup>	3.570
$\chi_{ab}$ (N1) / MHz	[–0.090] <sup>c</sup>	–0.090
$\chi_{aa}$ (N3) / MHz	[1.448] <sup>c</sup>	1.448
$[\chi_{bb}$ (N3)– $\chi_{cc}$ (N3)] / MHz	[–6.499] <sup>c</sup>	–6.4989
$\chi_{ab}$ (N3) / MHz	[1.517] <sup>c</sup>	1.517
$N^d$	83	–
$\sigma_{r.m.s.}$ / kHz <sup>e</sup>	12.2	–

<sup>a</sup> Fit performed using Watson's A reduced Hamiltonian

<sup>b</sup> Values of  $\chi_{ab}$  calculated using DFT at the B3LYP-D3BJ/aug-cc-pVTZ level and used to determine angle between inertial axis and the principal nuclear axis frame of reference (see Table S6).

<sup>c</sup> Value fixed at result calculated by DFT at the B3LYP-D3BJ/aug-cc-pVTZ level.

<sup>d</sup> Number of transitions included in fit.

<sup>e</sup> Root mean square deviation of fit.

**Table S6.** Diagonalization of nuclear quadrupole coupling tensors to determine  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$ .

$\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$  represent projections of the nuclear quadrupole coupling tensor onto principal axes located on each individual nucleus. Determination of  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$  from the experimentally-determined values of  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  respectively was performed using Kisiel's QDIAG available from the PROSPE<sup>S1</sup> website. Values of  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  were not determined experimentally for conformer D and therefore  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$  are not calculated for this conformer. The off-diagonal term,  $\chi_{ab}$ , was calculated for each conformer using DFT at the B3LYP-D3BJ/aug-cc-pVTZ level. Noting the level of agreement between DFT-calculated and experimentally-determined values of  $\chi_{aa}$  (N1) and  $[\chi_{bb}(\text{N1}) - \chi_{cc}(\text{N1})]$  in Table S5, an uncertainty of 25% of the value of the parameter was assumed in  $\chi_{ab}$  when obtaining the results shown below.

The  $a$ - and  $b$ -axes are rotated through an angle,  $\varphi(X)$ , where  $X$  is the nucleus on which the axes are centred. The labelling system used for the nitrogen atoms was chosen to be consistent with that used by Christen et al. in their study of imidazole<sup>S2</sup>. For the pyrrolic nitrogen atom (N1), the  $z$ -axis is out of the molecular plane and  $\varphi$  is the angle between the  $a$  and  $y$ -axes. For the pyridinic nitrogen (N3), the  $y$ -axis is perpendicular to the plane of the molecule, and  $\varphi$  is the angle between the  $a$  and  $x$ -axes. The signs of  $\varphi(\text{N1})$  and  $\varphi(\text{N3})$  are not available from the experimental results but were deduced by comparison with the DFT-calculated molecular geometries illustrated in Figure 3. A positive sign of  $\varphi$  indicates anticlockwise rotation of the inertial axes into the principal nuclear axes when the conformer is drawn as shown in Figure 3, a negative sign of  $\varphi$  indicates the opposite. The results allow direct comparisons with  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$  provided in other works. All values of  $\chi_{xx}$ ,  $\chi_{yy}$  and  $\chi_{zz}$  are close to those determined for the isolated imidazole molecule. The results are empirical evidence in support of the assignments of all conformers to the observed spectra.

$\chi$	Conformer A	Conformer B	Conformer C	Imidazole <sup>a</sup>	4-Iodoimidazole <sup>b</sup>	2-Iodoimidazole <sup>b</sup>
$\chi_{xx}$ (N1) / MHz	1.36(13) <sup>c</sup>	1.188(12)	1.060(28)	0.890(52)	1.136(21)	0.98(26)
$\chi_{yy}$ (N1) / MHz	1.321(14) <sup>c</sup>	1.324(16)	1.341(36)	1.633(58)	1.386(23)	1.77(26)
$\chi_{zz}$ (N1) / MHz	-2.68(13) <sup>c</sup>	-2.511(12)	-2.401(25)	-2.524(12)	-2.5223(86)	-2.7561(47)
$\eta$ (N1) / (MHz) <sup>d</sup>	-0.015(8)	0.054(8)	0.12(2)	0.294(45)	0.098(12)	0.28(13)
$\varphi$ (N1) / °	0 <sup>c</sup>	13.6(36)	-21.5(47)	-43.7	-14.4(81)	41.3(25)
$\chi_{xx}$ (N3) / MHz	1.91(69)	2.02(69)	1.72(18)	1.835(23)	1.75(23)	2.17(14)
$\chi_{yy}$ (N3) / MHz	2.43(18)	2.1444(94)	2.330(24)	2.278(24)	2.0051(86)	2.0097(47)
$\chi_{zz}$ (N3) / MHz	-4.34(70)	-4.16(69)	-4.05(18)	-4.113(34)	-3.76(23)	-4.18(14)
$\eta$ (N3) / MHz <sup>d</sup>	0.12(16)	0.03(16)	0.15(4)	0.108(13)	0.07(6)	-0.039(34)
$\varphi$ (N3) / °	-34.9(24)	-35.0(23)	14.8(31)	-9.4	19.2(30)	-18.2(17)

<sup>a</sup> Results from reference S2. The values quoted for imidazole use the alternative definition applied in reference S2 that  $\varphi$ (N1) is the angle between the *a* inertial axis and the *x* axis; and  $\varphi$ (N3) is the angle between the *a* inertial axis and the *z* axis.

<sup>b</sup> Results from reference S3.

<sup>c</sup> The standard deviations of  $\chi_{aa}$ (N1) and [ $\chi_{bb}$ (N1)- $\chi_{cc}$ (N1)] for conformer A, and the very small value calculated for  $\chi_{ab}$ (N1), imply that the value of  $\varphi$ (N1) is indistinguishable from zero at the precision of the experiment. The values given for  $\chi_{xx}$ (N1),  $\chi_{yy}$ (N1) and  $\chi_{zz}$ (N1) are therefore set equal to those of  $\chi_{bb}$ (N1),  $\chi_{aa}$ (N1) and  $\chi_{cc}$ (N1) respectively.

$$\text{d where } \eta(\text{N1}) = \frac{\chi_{xx}(\text{N1}) - \chi_{yy}(\text{N1})}{\chi_{zz}(\text{N1})} \quad \text{and } \eta(\text{N3}) = \frac{\chi_{xx}(\text{N3}) - \chi_{yy}(\text{N3})}{\chi_{zz}(\text{N3})} .$$

## Supplementary References

- S1 Z. Kisiel, PROSPE - Programs for ROtational SPEctroscopy, <http://www.ifpan.edu.pl/~kisiel/prospe.htm>.
- S2 D. Christen, J. H. Griffiths and J. Sheridan, *Zeitschrift fur Naturforsch. - Sect. A J. Phys. Sci.*, 1981, 36, 1378–1385.
- S3 G. A. Cooper, C. J. Anderson, C. Medcraft and N. R. Walker, *J. Mol. Spectrosc.*, 2018, 354, 15-23.