Supplementary Material: 1-hydroxy-2-naphthaldehyde (1H2N)

S1. S₀ and S₁ geometries of 1H2N (*ab initio* calculations)



Figure S1: Gaussian calculation co-ordinate scheme. The orientations of the axes A, B, C (corresponding to the principle moments of inertia I_A , I_B , I_C) are also shown. The *z* co-ordinate corresponds exactly with C. The *y* and *x* axes correspond approximately (~ 99% correspondence) with B and A, respectively.

Table S1: (A) 1H2N DFT B3LYP/6-31G** optimised geometry. (B) Atom co-ordinates and bond lengths.

(A)	(A)									
Atom	x	У	Z							
C ₁	0	0	0							
C ₂	1.378591	0	0							
C ₃	2.093455	1.222762	0							
C ₄	1.384457	2.464589	0							
C ₅	-0.03198	2.425264	0							
C ₆	-0.70817	1.222743	0							
H ₇	-0.54483	-0.93897	0							
H ₈	1.938394	-0.92841	0							
C ₉	3.524826	1.248751	0							
C ₁₀	2.105835	3.699386	0							
H ₁₁	-0.57995	3.363428	0							
H_{12}	-1.79431	1.213761	0							
C ₁₃	3.471935	3.699052	0							
C ₁₄	4.210356	2.478545	0							
H_{15}	1.549248	4.631449	0							
H_{16}	4.025132	4.635084	0							
O ₁₇	4.178143	0.085973	0							
H ₁₈	5.151074	0.307196	0.000062							
C ₁₉	5.656264	2.481906	0							
H ₂₀	6.146187	3.474108	-0.00018							
O ₂₁	6.357388	1.459556	-0.00024							

(B)

Bond Lengths [Å]							
O ₁₇ -H ₁₈	0.997765						
C ₉ -O ₁₇	1.333745						
C ₉ -C ₁₄	1.407958						
C ₁₄ -C ₁₉	1.445912						
O ₂₁ -C ₁₉	1.239667						
O ₂₁ H ₁₈	1.668271						
O ₁₇ O ₂₁	2.576012						

Table S2: Change in 1H2N geometry upon $S_0 \rightarrow S_1$ excitation. S_0 state calculations were performed at the DFT B3LYP/6-31G level. S_1 excited state calculations were performed at the CIS/6-31G level. Δz is the change in the *z* co-ordinate which occurs upon excitation for each atom. 1H2N is more planar in the excited state (S₁) than in the ground state (S₀).

	S (DF	o co-ordinate T B3LYP/6-3	es 1G)	S ₁			
Atom	X _o	Уo	Z ₀	X 1	y 1	Z ₁	$\Delta z = z_1 - z_0$
C ₁	0	0	0	0	0	0	0
C ₂	1.382569	0	0	1.390566	0	0	0
C ₃	2.097476	1.226033	0	2.111169	1.212895	0	0
C ₄	1.384436	2.470238	0	1.360192	2.450272	0	0
C ₅	-0.03475	2.43162	0	-0.03743	2.40567	0	0
C ₆	-0.71185	1.224759	0	-0.7259	1.192789	0	0
H ₇	-0.54447	-0.9383	0	-0.52015	-0.93806	0	0
H ₈	1.94522	-0.92562	0	1.9331	-0.92291	0	0
C ₉	3.526029	1.257154	0	3.502938	1.254865	0	0
C ₁₀	2.110026	3.706232	0	2.082614	3.663476	0	0
H ₁₁	-0.58255	3.36912	0	-0.58528	3.329272	0	0
H ₁₂	-1.7972	1.213254	0	-1.79693	1.177868	0	0
C ₁₃	3.479942	3.707427	0	3.472577	3.685143	0	0
C ₁₄	4.220382	2.484033	0	4.233697	2.518921	0	0
H ₁₅	1.554148	4.638053	0	1.543982	4.591643	0	0
H ₁₆	4.03265	4.642795	0	3.977967	4.632529	0	0
O ₁₇	4.184174	0.066878	-0.000067	4.180143	0.097902	0	0.000067
H ₁₈	5.175405	0.235953	-0.000219	5.144527	0.222648	-0.000058	0.000161
C ₁₉	5.662577	2.492257	0.0001	5.657239	2.542966	0	-0.0001
H ₂₀	6.159931	3.473331	-0.00069	6.134897	3.513924	0	0.00069
O ₂₁	6.375201	1.445634	-0.000762	6.37155	1.510316	0	0.000762

Table S3: 1H2N bond length alterations upon $S_0 \rightarrow S_1$ excitation. S_0 state calculations performed at the DFT B3LYP/6-31G level. S_1 excited state calculations performed at the CIS/6-31G level. The average change in bond length upon excitation is ~ 1.5%.

S₀Bond Bond Length (L₀) [Å]		S ₁ Bond Length (L ₁) [Å]	$\Delta = (L_1 - L_0)$ [Å]	% Δ = 100(L ₁ -L ₀)/L ₀	
C ₂ -C ₁	1.382569	1.390566	0.007997	0.58	
C ₃ -C ₂	C ₃ -C ₂ 1.419243		-0.008434	-0.59	
C ₄ -C ₃	1.434041	1.447435	0.013394	0.93	
C ₅ -C ₄	1.419708	1.398332	-0.021376	-1.51	
C ₆ -C ₅	1.383827	1.394657	0.010830	0.78	
H ₇ -C ₁	1.084828	1.072617	-0.012211	-1.13	
H ₈ -C ₂	1.083213	1.070566	-0.012647	-1.17	
C ₉ -C ₃	1.428892	1.392402	-0.036490	-2.55	
C ₁₀ -C ₄	1.433235	1.412005	-0.021230	-1.48	
H ₁₁ -C ₅	1.085815	1.073862	-0.011953	-1.10	
H_{12} - C_6	1.085419	1.071132	-0.014287	-1.32	
C ₁₃ -C ₁₀	1.369917	1.390132	0.020215	1.48	
C ₁₄ -C ₉	1.409737	1.4600843 0.050347		3.57	
H ₁₅ -C ₁₀	1.08503	1.073135	-0.011895	-1.10	
H ₁₆ -C ₁₃	1.086461	1.073759	-0.012702	-1.17	
O ₁₇ -C ₉	1.360115	1.340586	-0.019529	-1.44	
H ₁₈ -O ₁₇	1.005547	0.972419	-0.033128	-3.29	
C ₁₉ -C ₁₄	1.442218	1.423745	-0.018473	-1.28	
H ₂₀ -C ₁₉	1.09994	1.082089	-0.017851	-1.62	
O ₂₁ -C ₁₉	1.266197	1.25563	-0.010567	-0.83	
C ₁ -C ₆	1.41660	1.3963066	-0.020294	-1.43	
C ₁₃ -C ₁₄	1.430015	1.3926153	-0.037400	-2.62	
Avera	$\frac{1}{2}$ ge of absolute Δ	values [Å] :	0.01923869		
Av	verage of absolu	ıte % <u>Δ</u> :	1.49860549		

Distance	S₀ Distance (L₀) [Å]	S ₁ Distance (L ₁) [Å]	$\Delta = (L_1 - L_0)$ [Å]	% $\Delta = 100(L_1-L_0)/L_0$	
O ₂₁ H ₁₈	1.703772	1.7786721	0.074900	4.40	
O ₁₇ O ₂₁	2.588739	2.6071398	0.018401	0.71	

Table S4: Alteration in 1H2N geometry upon $S_0 \rightarrow S_1$ excitation. S_0 co-ordinates (x_0, y_0, z_0) and S_1 co-ordinates (x_1, y_1, z_1) are taken from Table S2. The co-ordinates (x'_1, y'_1, z'_1) are calculated from the equations: $x_1 = x_0 + n(x_1 - x_0); \quad y_1 = y_0 + n(y_1 - y_0); \quad z_1 = z_0 + n(z_1 - z_0), \text{ where } \mathbf{n} = 7$. The molecular geometry formed by these co-ordinates is shown in Fig. S2 below. It is an 'exaggerated' S_1 geometry formed by increasing the changes in atomic co-ordinates by a factor of 7, in order to better visualise the geometry change.

Atom	$x_1 - x_0$	$x_1 - x_0$ $y_1 - y_0$ $z_1 - z_0$		x'_1	y'_1	z ₁
C ₁	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
C ₂	0.007997	0.000000	0.000000	1.438548	0.000000	0.000000
C ₃	0.013693	-0.013138	0.000000	2.193327	1.134067	0.000000
C ₄	-0.024244	-0.019966	0.000000	1.214728	2.330476	0.000000
C ₅	-0.002683	-0.025950	0.000000	-0.053527	2.249970	0.000000
C ₆	-0.014052	-0.031970	0.000000	-0.810209	1.000969	0.000000
H ₇	0.024312	0.000245	0.000000	-0.374281	-0.936586	0.000000
H ₈	-0.012120	0.002708	0.000000	1.860380	-0.906665	0.000000
C ₉	-0.023091	-0.002289	0.000000	3.364392	1.241131	0.000000
C ₁₀	-0.027412	-0.042756	0.000000	1.918142	3.406940	0.000000
H ₁₁	-0.002728	-0.039848	0.000000	-0.601646	3.090184	0.000000
H ₁₂	0.000278	-0.035386	0.000000	-1.795258	0.965552	0.000000
C ₁₃	-0.007365	-0.022284	0.000000	3.428387	3.551439	0.000000
C ₁₄	0.013315	0.034888	0.000000	4.313587	2.728249	0.000000
H ₁₅	-0.010166	-0.046410	0.000000	1.482986	4.313183	0.000000
H ₁₆	-0.054683	-0.010266	0.000000	3.649869	4.570933	0.000000
O ₁₇	-0.004031	0.031024	0.000067	4.155957	0.284046	0.000402
H ₁₈	-0.030878	-0.013305	0.000161	4.959259	0.142818	0.000908
C ₁₉	-0.005338	0.050709	-0.000100	5.625211	2.847220	-0.000600
H ₂₀	-0.025034	0.040593	0.000690	5.984693	3.757482	0.004140
0 ₂₁	-0.003651	0.064682	0.000762	6.349644	1.898408	0.004572



Figure S2: 1H2N (a) DFT B3LYP/6-31G optimised ground state (S_0) geometry. (b) 'Exaggerated' CIS/6-31G optimised S_1 geometry. The molecular geometry change has been exaggerated to highlight the effect of the geometry change (see also caption of Table S4).

Bond	B3LYP 6-31g** (L _*) [Å]	B3LYP 6-31G (L) [Å]	∆ = (L − L∗) [Å]	% ∆ = 100(L-L∗)/L∗	
O ₁₇ -H ₁₈	0.997765	1.005547	0.007782	0.77994317	
C ₉ -O ₁₇	1.333745	1.360115	0.02637	1.97713956	
C ₉ -C ₁₄	1.407958	1.409737	0.001779	0.1263532	
C ₁₄ -C ₁₉	1.445912	1.442218	-0.00369	-0.25547889	
O ₂₁ -C ₁₉	1.239667	1.266197	0.02653	2.14009085	
O ₂₁ H ₁₈	1.668271	1.703772	0.035501	2.12801158	
0 ₁₇ 0 ₂₁	2.576012	2.588739	0.012727	0.49405826	

 Table S5:
 Comparison of 1H2N geometries calculated using DFT B3LYP 6-31G and DFT B3LYP 6-31G**.

S2. Molecular orbitals of 1H2N (*ab initio* calculations)



Figure S3: Molecular orbitals (DFT B3LYP/6-31G**) involved in the $S_0 \rightarrow S_1$ electronic transition of 1H2N.

S3. Excited singlet states in 1H2N (*ab initio* calculations)

The CIS/6-31G, CIS/6-31G** and CIS/6-31G+ energies of the first four excited singlet states of 1H2N were calculated and are listed in Table S6 together with the computed oscillator strengths of the corresponding transitions from the ground state. Tobita et al.²¹ and Singh et al.³⁷ have assigned the $S_0 \rightarrow S_1$ transition to be of (π, π^*) type on the basis of the high molar extinction coefficient (5690 M⁻¹ cm⁻¹).²¹ The calculated oscillator strength of ~0.23 (average of CIS/6-31G, CIS/6-31G** and CIS/6-31G+ computed oscillator strengths of $S_0 \rightarrow S_1$ transition) is consistent with this observation. Inspection of the HOMO and LUMO orbitals (Fig. S3) shows that the transition occurs mainly in the region of C_{14} - C_9 naphthalene ring π bond and the aldehyde group.

The CIS method of calculation is expected to be 'qualitatively accurate if not always highly quantitatively predictive.⁶⁴ Comparing the theoretical results with the experimentally measured absorption spectra of 1H2N,^{21,37} the absolute error in the CIS calculation of the singlet energies is very large (~10000 cm⁻¹). However, the CIS singlet energies do appear to bear a qualitative resemblance to the experimentally measured absorption maxima. In cyclohexane solution, absorption maxima are observed at 27173, 32440, 33690 and 38182 cm^{-1,21} Assigning these maxima to S_1 , S_2 , S_3 and S_4 , the energy separations of these absorption maxima ($\Delta S_1...S_2$ = 5267 cm⁻¹, $\Delta S_1...S_3$ = 6517 cm⁻¹ and $\Delta S_1...S_4$ = 11009 cm⁻¹)²¹ approximately follow the computed energy separations of the CIS 6-31G** singlet states $(\Delta S_1...S_2 = 3356 \text{ cm}^{-1}, \Delta S_1...S_3 = 3999 \text{ cm}^{-1} \text{ and } \Delta S_1...S_4 = 12050 \text{ cm}^{-1})$. It should be noted, however, that the absorption bands which have been assigned as S₂ and S₃ in Table S6, exhibit significant intensity in cyclohexane solution.²¹ This is not consistent with the low computed oscillator strengths ($f \sim 0.002$ and $f \sim 0.0004$ (CIS 6-31G**)) of S₂ and S₃. In Table S6(b), the theoretical and experimental relative singlet energies are calculated ($\Delta E_{(6-1)}$ $_{31g^{**}}, \Delta E_{(6-31g)}, \Delta E_{(6-31g+)}$ and $\Delta E_{\rm E}$). The calculated relative singlet energies differ, on average, from the experimental values by 2277 cm⁻¹ (i.e. average of absolute values of $\Delta E_{(6-31g^{**})}$ – $\Delta E_{\rm E}$, $\Delta E_{\rm (6-31g)} - \Delta E_{\rm E}$, and $\Delta E_{\rm (6-31g+)} - \Delta E_{\rm E}$).

	CI	CIS 6-31G**			CIS 6-31G			CIS 6-31G+		Experi	Experimental ²¹	
(a)	Ener [cm	Energy f [cm ⁻¹]			Energy [cm ⁻¹]	5y <i>f</i>		Energy [cm ⁻¹]	f	Abs max. [cm ⁻¹]	€ [M⁻¹ cm⁻¹]	
S_1	383	94	0.214	.9	38325	0.239	7	37556	0.2412	27173	5690	
S ₂	417	50	0.0022		39155	0.0005		39216	0.0006	32440	2600	
S ₃	423	93	3 0.0004		42384	0.0009		41570	0.0001	33690	7000	
S 4	50444 0.8117		7	50616	0.8254		49302	0.8578	38182	36000		
											24	
			CIS 6-	31G	3** CIS 6-3			1G	CIS	5-31G+	Exp. ²¹	
((b)		b)		$\Delta E \qquad \Delta E_{(6-31G^{**})} \qquad \Delta E$		Δ	E _(6-31G)	ΔΕ	Δ <i>E</i> _(6-31G+)	۸ <i>६</i>	
		(6-31G**)		-	$\Delta E_{\rm E}$	(6-31G)		- Δ <i>E</i> _E	(6-31G+)	- Δ <i>Ε</i> _Ε	ΔLE	
ΔS	L	3	356	-:	1911	830	-	-4437	1660	-3607	5267	
ΔS	LS₃	(1)	3999	-2	2518	4059	-	-2458	4014	-2503	6517	
ΔS	L	1	2050	1	1041	12291		1282	11746	737	11009	

Table S6: (a) Gaussian CIS calculation of energies of excited singlet states (S_n) and oscillator strengths (*f*) for $S_1 \rightarrow S_n$ transitions of 1H2N using different basis sets: 6-31G**, 6-31G and 6-31G+. Also stated are the absorption maxima of 1H2N in cyclohexane.²¹ (b) Experimental (ΔE_E), CIS 6-31G** ($\Delta E_{(6-31G^*)}$), CIS 6-31G ($\Delta E_{(6-31G^*)}$) and CIS 6-31G+ ($\Delta E_{(6-31G^*)}$) relative singlet energies, computed from the values in (a).





Figure S4: Rotational envelopes of selected features. Energies relative to the origin (25484 cm⁻¹): (a) 0 cm⁻¹ (Origin), (b) 352 cm⁻¹ (v'₇), (c) 481 cm⁻¹ (v'₁₀), (d) 538 cm⁻¹ (v"₁₄), (e) 742 cm⁻¹ (v"₂₀), (f) 697 cm⁻¹. Features (a) – (c) exhibit type AB character (*xy* polarisation of the transition moment; A' symmetry). Features (d) and (e) appear to contain more C type character (*z* polarisation of the transition moment; A" symmetry). The feature at

excess energy 700 cm^{-1} (g) contains two features exhibiting type AB character and one which exhibits more type C character.

S4.1 Errors in γ_n values

The *ab initio* values calculated for the rotational constants (A, B, C, A', B', C') influence the shape of the rotational envelope. An approximate 5% error in the computed bond lengths would result in an approximate uncertainty of 10% of the moments of inertia and hence of the rotational constants. Varying the rotational constant A' by 10%, for the 591 cm⁻¹ feature increases the natural line width of the best fit by only 0.02 cm⁻¹. Since a typical uncertainty of typical bond lengths is only of the order of ca. 0.5% (~0.009 Å ⁶⁵) the errors in rotational constants may be 1%. Thus the error in the rotational constants is in first approximation negligible.

The choice of bandshape mixing parameters (in the present case the ratio of *a* to *b*; *c* = 0) influences the band shape of the envelope. Small variations in the *a/b* ratio change the band shape significantly, however not the natural line width, γ_n . Since an acceptable choice of *a/b* is limited in terms of the best fit a significant error in γ_n is therefore not expected. The variation in fit quality, from line to line, has been accounted for by the (somewhat arbitrary) assumption that a poor choice of *a/b* would increase the error by a maximum of 50% (see below).

The largest sources of error in the fitting procedure are hence (i) the estimate of the Doppler width, γ_d , and (ii) the estimate of the rotational temperature, T_{rot} .

(i) Error based on γ_d : The Doppler shift (~0.09 cm⁻¹) was estimated using a beam angle of 80°. A maximum variation of this angle to 60° corresponds to a Doppler shift of $\gamma_d \sim 0.06 \text{ cm}^{-1}$. Hence, an error of $\pm 0.03 \text{ cm}^{-1}$ in γ_d has been assumed.

(ii) Error based on T_{rot} : A variation of 0.5 K (from 13 K) results in a 0.01 cm⁻¹ change in γ_n . The rotational temperature was estimated as $T_{\text{rot}} = (13.0 \pm 0.3)$ K. Hence, the maximum error in γ_n resulting from the choice of T_{rot} is estimated as ~0.01 cm⁻¹.

In order to account for an uncertainty in the choice of the a/b ratio the combined error in γ_n arising from the error in γ_d and T_{rot} (*i.e.* $\Delta \gamma_n \approx 0.04 \text{ cm}^{-1}$) was weighted by the χ^2 value of each fit, such that the γ_n with the minimum χ^2 value obtained (*i.e.* $\chi^2_{min} = 0.090870$ at an excess energy of 381 cm⁻¹) has an error of 0.04 cm⁻¹, while the γ_n with the maximum χ^2 value obtained (*i.e.* $\chi^2_{max} = 0.670714$ at an excess energy of 481 cm⁻¹) has an error of (1.5 × 0.04 cm⁻¹) = 0.06 cm⁻¹; in other words the errors are χ^2 -weighted between 0.04 and 0.06 cm⁻¹ by,

$$\Delta \gamma_{\rm n} = 0.04 \times \left[1 + 0.5 \left(\frac{\chi^2 - \chi^2_{\rm min}}{\chi^2_{\rm max} - \chi^2_{\rm min}} \right) \right] \tag{1}$$

where the factor 0.5 in equation (1) accounts for the error of 50% in band shape fit quality. In Table 3 in the main text the lifetimes of the rotational states corresponding to the fitted natural linewidths are calculated using $\tau = (4\pi c \gamma_n)^{-1}$. Within error margins, the resultant values for τ lie in the ~(7 – 16) ps range.

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