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Crystalline adducts of the Lawsone molecule (2-hydroxy-1,4-naphthaquinone): optical properties and computational modelling†

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Four new crystalline adducts of the Lawsone molecule (2-hydroxy-1,4-naphthaquinone) with 4,4′-bipyridine, 4-(2-pyridine-4-ethyl)pyridine, 1,3-di(4-pyridyl)propane and 2-hydroxy pyridine are reported. Adduct formation leads to colour shifts, which are characterised by UV/visible spectroscopy. Complementary quantum-chemical calculations are used to study the energetics of the adduct formation, and to gain insight into the origin of the observed colour changes.

They also observed intrinsic radical formation in both polymorphs, arising from electron-density percolation through intermolecular hydrogen bonds, using electron paramagnetic resonance (EPR) spectroscopy. In contrast, recently-reported cocrystals of Lawsone with tris(hydroxymethyl)aminomethane were found to be EPR inactive.9

Due to its C==O and O–H functional groups, Lawsone readily forms Michael-addition products and Mannich bases,10 some of which have antimalarial properties.11,12 These functional groups also make the molecule an ideal candidate for forming cocrystals though molecular recognition mediated by H-bonding interactions.

Cocrystallisation reactions are known for their simplicity and versatility.13–15 They have found applications in various fields to modify phase-transition temperatures,16 to improve solubility,17–22 to enhance fluorescence,23–29 and to alter melting points.19,30 These reactions also find application in the pharmaceutical industry, e.g. for improving the tableting properties,31,32 dissolution rates33–35 and stability36,37 of pharmaceutical compounds. They can also be used to improve the elastic properties of materials.38

Recently, it has been demonstrated that cocrystallisation can also be used for colour tuning. Yan et al. used cocrystallisation to tune the colour and fluorescence properties of the well-known fluorescent whitener 1,4-bis-p-cyano-styrlybenzene.24 Research by Bučar et al. similarly demonstrated that the colours of pigments can be drastically changed using cocrystallization.26 Jones et al. studied the role of proton transfer and disorder in the formation of coloured adducts,39 and in their systems found that disorder favoured the formation of coloured adducts, whereas proton transfer disfavoured it. MacGillivray et al. reported a coloured cocrystal between acetaminophen and 2,4-pyridinedicarboxylic acid,40 both of which are themselves colourless.

Introduction

The naturally-occurring compound Lawsone (2-hydroxy-1,4-naphthaquinone) has been in use for the past 5000 years for utilities ranging from traditional tattoo ink (henna) to medicinal remedies. Since it is an abundant naturally-occurring dye, it is used as artificial-tanning and hair colourants. Its UV-absorbing properties also make it a good anti-tanning agent.1,2 Lawsone has also been identified as having anti-fungal,3 anti-corrosion4 and even anti-cancer properties,5 and has been intercalated into Zn hydroxides to act as a drug-delivery system.6 It reacts with primary amino acids to form photoluminescent products, which can be used to detect fingerprints.7

In 2005, Todkary et al. reported the existence of two polymorphic forms of Lawsone, formed through solvent interactions.8

† Electronic supplementary information (ESI) available: Contains additional tables and figures to support the discussion in the text. The structures of the reported crystalline adducts 1a–1d are available free of charge from the CCDC under the codes 1418634–1418637 from www.ccdc.cam.ac.uk/getstructures. The PBE0sol-optimised gas-phase structures of 1, coformers a–d, the d, dimer, and 1a–1d, as well as the optimised crystal structures of 1a–1d, are available online under the DOI 10.15125/BATH-00137 (http://dx.doi.org/10.15125/BATH-00137). All other experimental characterisation and simulation results are presented in the manuscript and supporting information, with raw data available from the authors on request. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ce01644d
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In this paper, we report four crystalline adducts of Lawsone (\(1; 1\text{a}–1\text{d}\)) with aza-donors, viz. 4,4’-bipyridine (a), 4-(2-pyridine-4-ethyl)pyridine (b), 1,3-di(4-pyridyl)propane (c) and 2-hydroxy pyridine (d; Chart 1). The solid-state structures of the adducts are obtained from single-crystal X-ray diffraction (XRD), and the crystals are further characterised by optical microscopy, thermal analysis, near-infrared (NIR) spectroscopy and UV/visible reflectance. All four crystalline adducts exhibit changes in colour with respect to neat Lawsone.

We have also carried out complementary density-functional theory calculations to model the energetics of the adduct formation, and to investigate the origin of the colour changes in terms of the electronic structure.

**Experimental**

**Synthesis**

Lawsone (2-hydroxy-1,4-naphthoquinone), 4,4’-bipyridine, 4-(2-pyridine-4-ethyl)pyridine, 1,3-di(4-pyridyl)propane and 2-hydroxy pyridine were purchased from Sigma Aldrich and used without further purification. Crystalline adducts 1a–1c were formed by dissolving Lawsone and the coformer in methanol in a 2:1 molar ratio and allowing them to crystallise. Owing to its higher solubility, 1c tended to crystallise only at low temperatures (usually below 4 °C), and typically re-dissolved if left standing at room temperature for too long. 1d was obtained by dissolving Lawsone and 2-hydroxy pyridine in dichloromethane in a 1:1 molar ratio, with toluene being added to the mixture to reduce the rate of evaporation.

**Spectroscopy**

UV-visible absorption spectra were recorded in a 2:1 mixture of acetonitrile and methanol (to keep the hydrogen-bonded species associated) using a Cary 60 Spectrophotometer (Agilent). Reflectance spectra of the crystals were recorded using a home-built spectrometer on loan from Mobile Labs (CHARISMA initiative) with a resolution of 8 nm. NIR and MIR spectra of the crystalline adducts were recorded using, respectively, a Perkin Elmer Spectra One NIR spectrometer (4000–10 000 cm\(^{-1}\) spectral range, 4 cm\(^{-1}\) resolution, 30 scans) and a Perkin Elmer Spectrum MIR spectrometer (600–3200 cm\(^{-1}\) range, 4 cm\(^{-1}\) resolution, 30 scans).

**Thermal analysis**

Differential-scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a Rheometric instrument in simultaneous thermal-analysis mode with a 10 °C min\(^{-1}\) heating rate.

**Crystallography**

Single-crystal diffraction data for 1a–1c was obtained using an Oxford Xcalibur diffractometer with a Mo (Kα) source (wavelength 0.71073 Å) at 180 K. The structures were solved using SHELX-97.41 The diffraction pattern of 1d was collected on a similar instrument at 150 K, solved using SHELXT,42 and refined using the OSCAIL software.43 A comparison between powder patterns obtained from the filtrate and powder patterns simulated from the crystal structures showed a good match, suggesting that the products obtained from solution crystallisation do not contain residual starting materials (see Fig. S1–S4†).

**Computational modelling**

Computational modelling was carried out within the Kohn-Sham density-functional theory framework,44,45 as implemented in the Vienna Ab Initio Simulation Package (VASP) code.46

Initial models of the crystal structures of 1a–1d were built from the X-ray structures. Additional gas-phase models of Lawsone, coformers a–d, the d\(_2\) dimer and the H-bonded species 1a–1d were created by extracting the atomic coordinates of each species from the crystal structures and placing them in a simulation cell with an initial 10 Å vacuum gap between the closest atoms in adjacent periodic images.

Geometry optimisations and initial total-energy calculations were carried out with the PBEsol functional with projector augmented-wave (PAW) pseudopotentials and a plane-wave kinetic-energy cutoff of 850 eV. In the calculations on the crystalline models, the Brillouin zone was sampled with \(\Gamma\)-centred Monkhorst-Pack \(k\)-point meshes with \(1 \times 3 \times 1\), \(3 \times 1 \times 1\), \(1 \times 1 \times 3\) and \(1 \times 3 \times 1\) subdivisions for 1a, 1b, 1c and 1d, respectively. This corresponds to two irreducible \(k\)-points in each structure. In the gas-phase calculations, the electronic wavefunctions were evaluated at the \(\Gamma\) point. These convergence parameters were sufficient to converge the absolute total energies to within 1 meV atom\(^{-1}\), and the pressure to well within 1 kbar (0.1 GPa). The electronic wavefunctions were optimised to a tolerance of \(10^{-6}\) eV, and the positions of
the ions, and also the cell shape/volume in the case of the crystalline models, were optimised until the magnitude of the forces on the ions was less than $10^{-2}$ eV Å$^{-1}$.

Electronic-structure calculations, including the evaluation of energy gaps, the orbital analyses, and the computation of absorption spectra, were performed using the PBE0 hybrid functional$^{31}$ using the PBEsol-optimised structures as input. The absorption spectra were computed using the linear-optics routines in VASP$^{32}$ and the number of electronic bands was increased to 3× the default value in these calculations in order to ensure the convergence of the sum over empty states.

We note that, due to the size of the unit cell of the 1c crystal (536 atoms), we had to reduce the plane-wave cutoff to 550 eV for the PBE0 calculations on this system. This is still above 1.3× the default cutoff recommended for the pseudopotentials we used, and so we expect it should give reasonable absorption spectra and charge/orbital densities; however, the total energies cannot be compared with those calculated using higher cutoffs, and so we did not include PBE0 formation energies for this compound in Table 1 (see discussion below).

### Results and discussion

Fig. 1 shows the supramolecular organisation of the component molecules in 1a–1d. The crystal-structure parameters from the single-crystal X-ray diffraction are reported in Table S1$^\dagger$ and the structures are available from the CCDC under the codes 1418634–1418637. While 1a, 1b and 1d crystallised in the monoclinic space group $P_{2_1}/n$, 1c adopted the orthorhombic space group $Fdd2$. In 1a–1c, the coformers act as spacers, joining two molecules of 1 and forming discrete 3-membered supramolecular assemblies (Fig. 1a–c).

The Lawsone molecules and coformer are almost coplanar in 1a and 1b, whereas the Lawsone molecules are significantly tilted with respect to each other in 1c. In 1d, 2-hydroxy pyridine exists in its tautomeric form (2-pyridone), and two molecules of 2-pyridone interact to form dimers, which then act as spacers joining two molecules of 1 as in 1a–1c (Fig. 1d). In 1d, a dimer of d (d$_3$) thus plays an equivalent role to coformers a–c in adducts 1a–1c.

This gives rise to different Lawsone:coformer ratios in the crystalline adducts, viz. 2 : 1 and 1 : 1 stoichiometries in 1a–1c and 1d, respectively.

In 1a, 1c and 1d, 1 interacts with the coformers through neutral O–H⋯N hydrogen bonds, whereas in 1b cations of b interact with anions of 1 by two N–H⋯O and N–H⋯O hydrogen bonds. This is supported by NIR spectra (Fig. S5$^\dagger$), in which O–H combination bands are seen in 1a and 1c, but not in 1b (we also recorded standard IR spectra, which may be found in Fig. S6$^\dagger$). In general, proton transfer in cocrystallisation reactions is typically considered to be a function of $\Delta\mu^\text{w}$.$^{53-57}$ As a point of terminology, the proton transfer exhibited by 1b in the solid state means this is a salt, whereas a cocrystal is typically taken to be formed through (formally) neutral intermolecular interactions. We therefore refer to the solid forms of 1a–1d as “crystalline adducts” in the following discussion.

In 1d, the NIR combination bands observed are of amide III groups.$^{56}$ This system is peculiar, in that d undergoes tautomerisation to give 2-pyridone, as observed elsewhere in

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**Table 1** Calculated formation energies ($E_f$) of the gas-phase H-bonded species and corresponding crystals of 1a–1d, plus the gas-phase homodimer of d (d$_2$). Two sets of energies are given: the first were obtained from models fully relaxed with the PBEsol functional, while the second were obtained from single-point calculations on these models with the PBE0 hybrid functional (denoted “PBE0@PBEsol”). In each set, the left-hand column gives the formation energies, while the right-hand one gives the (per H-bonded unit) differences between the crystals and gas-phase species. We note that PBE0@PBEsol values for the crystal of 1c are missing, as the size of the unit cell made it impractical to perform these calculations at the same level of accuracy as used in the calculations on the others.

| Species          | [kJ mol$^{-1}$ Adduct$^{-1}$] | PBEsol $E_f$ | $\Delta E$ | PBE0@PBEsol $E_f$ | $\Delta E$ |
|------------------|--------------------------------|--------------|------------|------------------|------------|
| d homodimer      |                                |              |            |                  |            |
| Gas phase 1a     | $-104.17$                      | $-78.39$     |            |                  |            |
| Gas phase 1b     | $-87.19$                       | $-46.74$     |            |                  |            |
| Gas phase 1c     | $-89.25$                       | $-47.61$     |            |                  |            |
| Gas phase 1d     | $-92.28$                       | $-50.71$     |            |                  |            |
| Crystal 1a       | $-187.18$                      | $-130.16$    |            |                  |            |
| Crystal 1b       | $-187.18$                      | $-130.16$    |            |                  |            |
| Crystal 1c       | $-161.35$                      | $-96.87$     | $-50.13$   |                  |            |
| Crystal 1d       | $-185.46$                      | $-110.47$    | $-62.87$   |                  |            |
| Crystal 1d       | $-176.64$                      | $-84.36$     |            |                  |            |
| Crystal 1c       | $-176.64$                      | $-84.36$     |            |                  |            |
| Crystal 1d       | $-234.21$                      | $-154.16$    | $-24.00$   |                  |            |

**Fig. 1** Crystal packing in 1a (a), 1b (b), 1c (c) and 1d (d).
the literature.\textsuperscript{57} The formation of a zwitterion can be ruled out, since the C–O bond distance of 1.26 Å is suggestive of a double bond, and the melting point determined by DSC was much lower than that of the salt 1b (see Fig. S7\textsuperscript{†}). A similar bond length has been observed in other literature studies.\textsuperscript{58} A six-membered ring is formed through intermolecular hydrogen bonding between the two 2-pyridone molecules, and the carbonyl oxygen of 2-pyridone also forms intermolecular hydrogen bonds with the hydroxyl group of Lawsone. Such homodimer formation has also been observed in co-crystals of carbamazipine, where the homosynthon formed by the amide hydrogen bonding forms 1D H-bonds with the coformer.\textsuperscript{59} From here on, d, the d\textsubscript{3} dimer and 1d will refer to 2-pyridone, its dimer, and its adduct with Lawsone, respectively, where appropriate, rather than to species derived from the initial 2-hydroxy pyridine.

Coformers b and d are both known to undergo photodimerisation reactions.\textsuperscript{58,60} However, in 1b the distances between the C–C bonds in b in adjacent layers is 3.816 Å, while the distance between molecules of d in 1d is 5.153 Å. These distances are both longer than the ideal C–C distance for photodimerisation (1.727–3.324(4) Å), and hence we do not expect to see this phenomenon in our systems.\textsuperscript{58}

To study the crystal morphologies, we recorded bright-field microscope images of the four crystalline adducts (Fig. 2). 1a formed block crystals, while 1b formed bladed crystals and 1c and 1d both formed needle-like crystals. We further characterised 1a–1d by differential-scanning calorimetry (DSC; see Fig. S7\textsuperscript{†}). The DSC traces show 1b to have the highest melting point of 210.10 °C, compared to 183.96 and 155.80 °C for 1a and 1c, respectively. This is naturally accounted for by the stronger ionic hydrogen bonds in 1b. The melting point of 1d was recorded to be 147.90 °C.

Adduct formation also led to clear differences in colour with respect to neat Lawsone (Fig. 3). While the crystalline adducts of 1 with a and d displayed hypsochromic shifts in colour, bathochromic colour shifts were observed in 1b and 1c. Differences in the colour of neat Lawsone and 1a–1d are clearly evident in the UV-visible reflectance spectra of the crystals (Fig. 4a). We also recorded solution spectra (Fig. 4b) in a 2:1 mixture of acetonitrile and methanol, to retain the H-bonded species. These spectra show small shoulder-like features in the visible region in the case of 1b and 1c, but these were weak in comparison to the absorption in the UV. These features were not as prominent in the spectra of 1a and 1d as in the spectra of the other two adducts.

To better understand the energetics of the adduct formation and the origin of the colour changes, we carried out complementary theoretical modelling within the density-functional theory (DFT) formalism.

As a starting point, we first fully relaxed the crystal structures of 1a–1d with the PBEsol functional,\textsuperscript{47} optimising both the positions of the atoms and the unit-cell shapes/volumes. We also relaxed gas-phase models of Lawsone and the four coformers a–d, the d\textsubscript{3} homodimer, and the H-bonded species 1a–1d, all of which were made by extracting the relevant species from the collected crystal structures. Finally, to obtain more accurate energetics and electronic structures, and to calculate the optical-absorption spectra of the solid-state species, we performed single-point calculations on the PBEsol-optimised models using the PBE0 hybrid functional.\textsuperscript{51}

The calculated unit-cell parameters are compared to the experimental structures in Table S2.\textsuperscript{†} We found that PBEsol seemed to give a fairly good reproduction of the structures,
with a tendency to overestimate the cell volume but with
<5% variation in most parameters. Without measuring the
thermal expansion of the crystals, to check how steeply
the lattice parameters change with temperature, we would not
expect a perfect match between the calculations and the
experimental structures, since the DFT optimisation is
"athermal", i.e. is performed at 0 K and in the absence of
lattice-dynamical effects such as the vibrational zero-point
energy, while the crystal structures were collected at finite
temperature. However, the discrepancy in the cell volume in
1a–1c was found to be mostly due to a consistent over-
estimate of the length of the short lattice vectors, which is
most likely an indicator that PBEsol is not able to describe
fully the attractive part of the dispersive interaction between
molecules along the stacking direction. In support of this, the
single-point PBE0 calculations predicted negative cell pres-
ures, implying that a more accurate functional would indeed
lead to a reduction in the cell volume, although we note that
PBE0 would also not necessarily describe the dispersion in-
teractions correctly. While internal relaxation of the atomic coor-
dinates occurred during the optimisation of 1d, the calcula-
tions predicted no change to the cell shape or volume.

After optimising the H-bonded species in the gas phase,
we found they generally retained a structure similar to that in
the solid form, with the exception of the proton transfer in
1b. In both the experimental and the PBEsol-optimised crys-
tal structures, the proton appears to be shared equally
between the coformer N and the Lawsone O. After optimisa-
tion of the gas-phase adduct, however, it appears to be
mainly associated with the latter, as is the case in the other
crystalline adducts. Images of the optimised gas-phase
adduct and crystal structure of 1b are given in Fig. S9† for
comparison. This observation suggests that the proton trans-
fer is a consequence of the crystal packing, and the resultant
intermolecular interactions, in the solid form.

To investigate the energetics of the adduct formation, we
calculated the formation energies ($E_f$) of the gas-phase
H-bonded species and crystals of 1a–1d (Table 1). To a first
approximation, the formation energies of the gas-phase spe-
cies correspond to the energies of the H-bonding interac-
tions, while the (per-unit) differences in $E_f$ between the gas-
phase species and crystals gives an indication of the strength
of the interactions between the constituent components in
the solid state.

For 1a–1c, the PBEsol and PBE0 calculations predict the
energy of each Lawsone-coformer H bond to be on the order
of 45 and 25 kJ mol$^{-1}$, respectively, increasing in the order
c > b > a. In adduct 1d, there are two types of H bond, viz.
those between the two 2-pyridone molecules, and those
between the d$_2$ dimer and Lawsone; for the present discus-
sion, we estimate the two contributions from the difference
in the formation energies of the d$_2$ dimer and the gas-phase
1d adduct. The d–d interaction is stronger than the bond
between the dimer and Lawsone at ~50/40, and 40/25 kJ
mol$^{-1}$ per bond with PBEsol and PBE0, respectively. Interest-
ingly, PBEsol predicts the bond between the d$_2$ dimer and
Lawsone to be the weaker of the four, whereas PBE0 predicts
it to be the strongest. Nonetheless, the range in the calcu-
lated bond strengths between Lawsone and a–e/d$_2$ is fairly
small at <5 (PBEsol) and <2.5 (PBE0) kJ mol$^{-1}$.

For 1a–1c, the per-unit energy gain due to the inter-
molecular interactions in the crystal is of a similar magni-
tude to the H-bonding in the gas phase, being around 85 and
55 kJ mol$^{-1}$ with PBEsol and PBE0, respectively, for 1a–1c. 1d
behaves a little differently in this respect, with the energy dif-
fERENCE between the gas phase and solid forms being around
half that between the gas-phase adduct and the isolated
Lawsone and d$_2$ species. The reasons for this are not clear,
but this analysis nonetheless provides some interesting
insight into the relative energetic stabilisation provided by
H-bonding and dispersive interactions.

Next, we used the PBE0 calculations to investigate the
electronic structures of the molecules, gas-phase H-bonded
species and crystals. Fig. 5 shows the simulated absorption
spectra of crystals 1a–1d. The four spectra are qualitatively
similar in form, with a handful of features between 300–400
nm, a steep rise below approx. 250 nm, and a smooth tail off
above 400 nm. The spectra in Fig. 4(b) were recorded only to
narrower than the HOMO-LUMO gap of its dimer, which are fairly similar, and around 400 meV.

Taking the gas-phase energy gap of Lawsone as a reference, the gaps of the component species, with the exception being the gaps of 1a and 1d at the zone centre (Γ), which show a relatively small widening of 20 and 40 meV, respectively.

By analysing orbital-density plots obtained from the PBE0 calculations, we found that the forms of the HOMOs and LUMOs of the H-bonded species could be qualitatively well understood in terms of the frontier orbitals of the component molecules. In 1a and 1c, the HOMO and LUMO are both linear combinations of the corresponding Lawsone orbitals. In 1b, the HOMO is on the Lawsone molecules, whereas the LUMO resides on the coformer, and the reverse occurs in 1d. There is little evidence of electronic delocalisation between the Lawsone and coformer molecules in the H-bonded species, nor, by extension, between the Lawsone molecules across the bridging coformers. In all four systems, the HOMO and LUMOs of the gas-phase species match up very well with the HOCOs and LUCOs of the crystals, respectively, with the orbital densities at both k-points being visually near identical. An example orbital-density analysis for 1a is illustrated in Fig. 6, and similar analyses for 1b–1d may be found in Fig. S10.

In 1a and 1c, the HOMO and LUMO in the adducts are both on Lawsone, so it is reasonable to suggest that the narrowing of the gap is due to the frontier orbitals on Lawsone being perturbed by the H-bonding interaction with the coformer. In 1b and 1d, the coformer provides a lower-energy LUMO and higher-energy HOMO, respectively, and so the narrowing of the gap with respect to neat Lawsone cannot be attributed solely to the H-bonding interaction in this way. It is worth noting, however, that this may account for why the

| Species | $E_{g,1}$ (eV) | $\Delta E_1$ (meV) | $E_{g,2}$ (eV) | $\Delta E_2$ (meV) |
|---------|---------------|------------------|---------------|------------------|
| Lawsone (1) | 4.121 (301) | — | 4.121 (301) | — |
| Coformer a | 5.544 (224) | — | 5.544 (224) | — |
| Coformer b | 4.508 (275) | — | 4.508 (275) | — |
| Coformer c | 6.357 (195) | — | 6.357 (195) | — |
| Coformer d | 5.105 (243) | — | 5.105 (243) | — |
| d homodimer | 5.141 (241) | — | 5.141 (241) | — |
| Gas-phase 1a | 3.907 (317) | —214 | 3.907 (317) | —214 |
| Gas-phase 1b | 3.767 (329) | —355 | 3.767 (329) | —355 |
| Gas-phase 1c | 3.887 (319) | —234 | 3.887 (319) | —234 |
| Gas-phase 1d | 3.732 (332) | —389 | 3.732 (332) | —389 |
| Crystal 1a | 3.927 (316) | —195 | 3.622 (342) | —500 |
| Crystal 1b | 3.579 (346) | —543 | 3.277 (378) | —844 |
| Crystal 1c | 3.685 (336) | —436 | 3.400 (365) | —722 |
| Crystal 1d | 3.774 (329) | —348 | 3.396 (365) | —726 |
The gap of these species undergoes a larger shift with respect to Lawsone than those of 1a and 1c.

To explore this further, and to investigate how reliably the frontier orbitals of the isolated component molecules might be used to predict those of the H-bonded species (and hence the crystals), we constructed orbital-alignment diagrams matching up the HOMOs and LUMOs of Lawsone and the coformers with the four highest-occupied and lowest-unoccupied orbitals of the corresponding gas-phase adducts (Fig. 7). The reason for our considering four orbitals is that the molecular orbitals from the two Lawsone molecules in the H-bonded species generally formed (near-) degenerate pairs, presumably corresponding to in-phase and antiphase combinations. When performing the alignment, the orbital energies were adjusted to the electrostatic potential in the vacuum region of the cells. We note that this procedure cannot be applied to bulk materials (at least not those without a sufficiently large internal pore), and so we were unable to include the crystals in our alignment.

The analysis in Fig. 7 shows that, in general, the frontier orbitals of Lawsone and the coformer are significantly perturbed on forming the H-bonded complexes. The H bonding appears to cause the Lawsone orbitals to shift to higher energies, while those of the coformer are lowered with respect to the isolated molecule.

In the case of 1a and 1c, for which the HOMO and LUMO are both Lawsone-based, the HOMO of the coformer is below that of Lawsone, and thus the stabilisation due to the H bonding serves to push it further below the Lawsone orbitals. Although the coformer LUMO is lowered in energy, this is insufficient to bring it below the Lawsone-based LUMO observed in these species, although the alignment diagram for 1a shows that they are close in energy in this system. In both species, the primary origin of the colour shift in the gas phase can thus be ascribed to a slight difference in the relative destabilisation of the Lawsone HOMO and LUMO, which serves overall to narrow the energy gap.

Considering the other two species, in 1b the destabilisation of the Lawsone-based LUMO and stabilisation...
of the coformer orbitals is sufficient to push the LUMO onto the coformer. In 1d, the HOMO on the coformer is above that of Lawsone, and in this case the rearrangement of the orbital energies is insufficient to swap the order, leading to a coformer-based HOMO in this species, although as for the LUMOs in 1a the two HOMOs are close in energy.

The energy shifts make it somewhat difficult to predict a priori the relationship between the frontier orbitals in Lawsone and the coformers and those in the corresponding H-bonded species. However, given that the direction of the shift appears to be a consistent trend, we can extract two general observations: (1) if the HOMO on the coformer is below or similar in energy to that on Lawsone, the Lawsone orbitals will likely become the HOMO in the adduct, and (2) if the LUMOs on the two components are similar in energy, or if the orbital on the coformer is below the Lawsone LUMO, the LUMO of the adduct will likely be coformer based. Using these principles, it may be possible to assess qualitatively how other potential coformers may shift the colour of neat Lawsone using relatively cheap gas-phase calculations.

Conclusions

Four crystalline adducts of the Lawsone molecule with bipyrindine, ethylenebipyridine, propylenebipyridine and 2-hydroxy pyridine were synthesised and characterised using single-crystal X-ray diffraction, thermal analysis, and UV/visible and IR spectroscopy. Three of the coformers yielded crystals based around three-membered complexes consisting of one conformer and two Lawsone molecules, while the fourth gave a 1:1 complex with a similar structure based around a H-bonded dimer of the coformer. Whereas Lawsone and the coformer in the bipyrindine (1a) and propylenebipyridine (1c) adducts interact through neutral H bonds, the ethylenebipyridine (1b) system shows a solid-state proton transfer, which is also clearly evident from its IR spectrum. 2-hydroxy pyridine undergoes tautomerisation and forms homodimers that then hydrogen bond with the Lawsone molecules. The crystalline adducts were all found to exhibit visible shifts in colour with respect to neat Lawsone.

The hierarchy of interactions in the adduct formation, viz. H-bonding between Lawsone and the coformers and dispersive interactions in the solid state, allowed us to use computational modelling to study the contributions of the various effects to the energetics and colour shift. Both interactions lead to roughly equal energetic gains on adduct formation, and the typical strength of H-bonding interactions between Lawsone and one of the coformers was calculated to be on the order of 25 kJ mol⁻¹ from single-point PBE0 calculations on PBEsol-optimised structures. It was also noted that the proton transfer in 1b was not observed in the gas-phase adduct, suggesting that this is a product of the inter-molecular interactions in the solid state. The long-wavelength absorption features in the spectra of the crystalline adducts were found to be relatable to the size of the HOCO-LUCO gap, which could be rationalised in terms of the frontier orbitals of Lawsone and the coformer. From our electronic-structure analyses, the H-bonding appears to raise and lower the energies of the Lawsone and coformer orbitals, respectively, ultimately leading to the energy gaps of the H-bonded gas-phase species being 200–400 meV lower than those of a gas-phase Lawsone molecule. The intermolecular interactions between units in the crystal lead to a further narrowing of the gap of a similar magnitude.

In summary, the combined experimental and theoretical approach taken in this study has allowed us to gain some interesting insight into the energetics of the adduct formation and origin of the colour shift in crystalline adducts of the Lawsone molecule, which we hope will contribute to future crystal-engineering studies on this and related systems.

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