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Supramolecular Ribbons. Crystal Structure and Spectroscopic Properties of 2,2′-Bipyrroyl

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Summary. A crystal structure determination of 2,2′-bipyrroyl (**1**; 2,2′-dipyrryl-diketone, *bis* (2-pyrrolyl)ethanedione) and its spectroscopic properties in solution are reported. In the crystal, **1** self-assembles *via* hydrogen bonding into supramolecular ribbons that extend indefinitely through the crystal lattice. The observed molecular conformation is one where each pyrrole ring and adjacent carbonyl group are co-planar (torsion angle ~0.9°), with the N-H pointing in the same direction as the C=O. The two carbonyls have a transoid but not co-planar geometry with a torsion angle of ~128°. Adjacent molecules in the crystal are linked by pairs of intermolecular hydrogen bonds, pyrrole NH to carbonyl oxygen, to form a matrix of polymeric chains that lie like neatly stacked, parallel streams of ribbons. Molecular mechanics calculations on the monomer indicate an intramolecularly hydrogen bonded planar conformation (*sp*, *ap*, *sp*) at the global energy minimum. In $CHCl_3$, **1** is monomeric according to vapor pressure osmometry ($MW_{obs} = 179 \pm 10\ vs \cdot MW_{calc} = 188$). In *THF*, the measured molecular weight is 340±15, which corresponds best to one molecule of **1** solvated by two *THF* molecules ($MW = 322$ for $C_{10}H_8N_2O_4 \cdot 2\ C_4H_8O$) rather than to a dimer.

Keywords. Pyrrole; α-Diketone; Hydrogen bonding; Conformational analysis.

Introduction

2,2′-Bipyrroyl (**1**) [1] is an α-diketone and the pyrrole analog of benzil (**2**) (Fig. 1). Unlike **1**, the structure of **2** has been investigated intensively over many years. Benzil crystallizers in two solid phases, a low temperature phase (<84 K) of monoclinic symmetry $P2_1$ and a high temperature phase (84 K < T < 368 K) of trigonal symmetry $P3_121$, where molecules lie in helical chains around a 3-fold axis [2]. It is known to adopt a helical conformation with a 2-fold axis of molecular symmetry at room temperature in the crystal: each benzene ring lies nearly co-planar with its adjacent carbonyl (*sp*, ~9°), and the α-diketone core is twisted transoid (*ac*, ~107°) [2, 3, 4]. Benzil thus adopts a chiral conformation in the crystal, and individual crystals contain only left-handed helices (or right-handed helices). Left- and right-handed crystals can be separated, and single crystals were found to exhibit circular dichroism [5]. Benzil has been studied extensively since it was first reported in 1836 [6] in chemical reactions, photophysically (especially as

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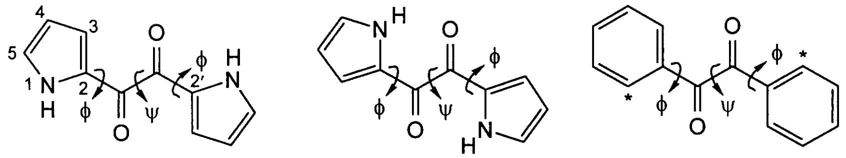


1a **1b** **2**

Fig. 1. Constitutional structures of 2,2′-dipyrrylethanedione (**1**, 2,2′-bipyrroyl) and benzil (**2**) with designated torsion angles (ψ,ϕ) about the carbon-carbon single bonds that govern their confirmations

a triplet sensitizer), and spectroscopically [4, 7], and it has recently been used as a blockade of the antigen-antibody reaction of some proteins and peptides [8].

In startling contrast, bipyrroyl **1** has scarcely been studied, with only three citations in *Chemical Abstracts* since the synthesis of the compound was first reported by *Oddo* in 1911 [1]. None of the three references offers information on structure. Rather, they are concerned with a new synthesis [9], with no spectroscopic properties being reported; an ESR analysis of the radical ion [10] on material obtained from Ref. [4]; and thermal deprotection of the *t-BOC* derivative of **1** and other pyrroles and indoles [11].

Our interests in hydrogen bonding of pyrrole compounds and their stereochemistry prompted us to examine **1**. In particular, we wished to learn whether an intermolecularly hydrogen-bonded array or an intramolecularly hydrogen-bonded conformation would be favored [12]. In the present communication we describe the stereochemistry of **1** in the crystal and report on its spectroscopic properties and its self-association in solution. These studies support extensive intermolecular hydrogen bonding in the crystal and the absence of self-association in *THF* and $CHCl_3$.

Results and Discussion

Configuration and overall conformation

An examination of the structural drawing (Fig. 2A) of the X-ray structure of **1** shows that, like benzil [2], it adopts a conformation in the crystal where each ring is co-planar with its adjoining carbonyl group, and the α-diketone is twisted transoid. The O=C–C=O torsion angle of **1** is somewhat larger (*ap*, ~128°) than that of **2** (*ac*, ~111°) [2–4], and whereas individual crystals of **1** contain equal numbers of molecules with left- and right-handed helicities, crystals of **2** contain all left-handed or all right-handed molecules, as in crystals of 2,2′-dipyrryl ketone (**3**) [12]. Most interesting is that **1** is intermolecularly hydrogen bonded in the crystal, fitting into a polymeric motif (Fig. 2B) akin to that seen in crystals of a symmetric acetylenic *bis*-pyridone [14]. In the crystal of **1**, parallel ribbons of alternately left- and right-handed helical intermolecularly hydrogen bonded molecules lie neatly layered, with molecular units falling into stacked columns (Fig. 3). The layered molecules of **1** lie about 3.887 Å apart in the stack.

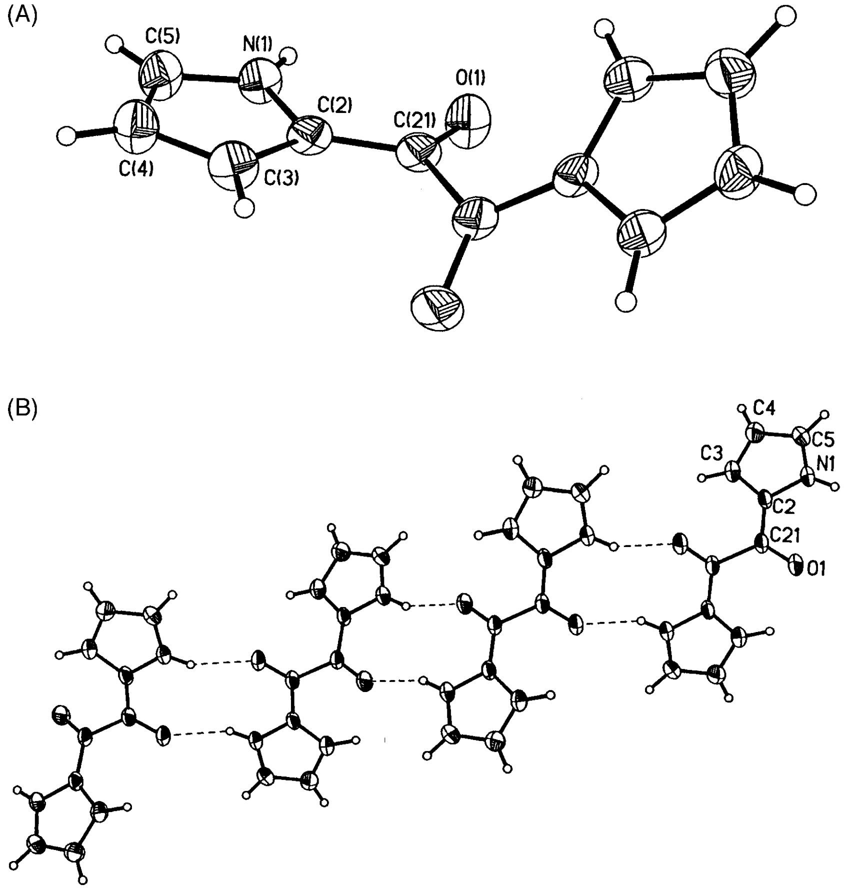


Fig. 2. (A) Structural drawing of **1** showing the atom numbering scheme (50% probability ellipsoids) as observed in its crystal structure and with hydrogens located; hydrogen atoms have an arbitrary radius of 0.1 Å. (B) Segment of a polymeric chain of intermolecularly hydrogen bonded molecules of **1** characteristic of its crystal structure

Although **1** possesses a high degree of encoded molecular recognition functionality that expresses itself in the crystal by an impressive matrix of intermolecular hydrogen bonds (non-bonded N to O in the NH···O triad is 2.853 Å), the diketone bond lengths and bond angles are rather like those found in benzil [2]. Thus, the α-dicarbonyl C(21)-C(21)#1 sp^2C-sp^3C bond length (1.532 Å) in **1** is comparably long to that of benzil (1.523 Å). Other bond lengths and angles in **1** (Fig. 4) in and around the α-diketone core match up nicely with those of benzil. The C=O distance is slightly longer in **1** than in **2**, perhaps as a consequence of hydrogen bonding in **1**. The (O)C–C=O angle is larger in **1** by ~3°, but the C–C(O)–C angle is smaller in **1** by ~3°. The pyrrole ring bond lengths and bond angles match up well with those (Fig. 4) found in the crystal structure of the dipyrrylmethane, 5,5′-diethoxycarbonyl-3,3′,4,4′-tetraethyldipyrrol-2-ylmethane [15].

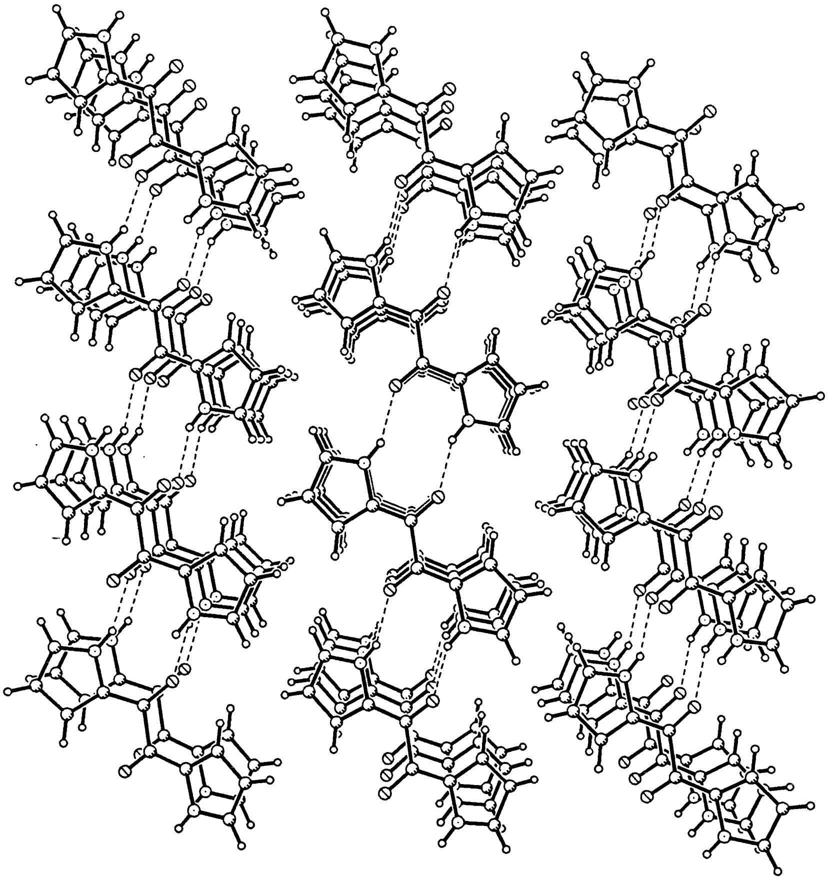
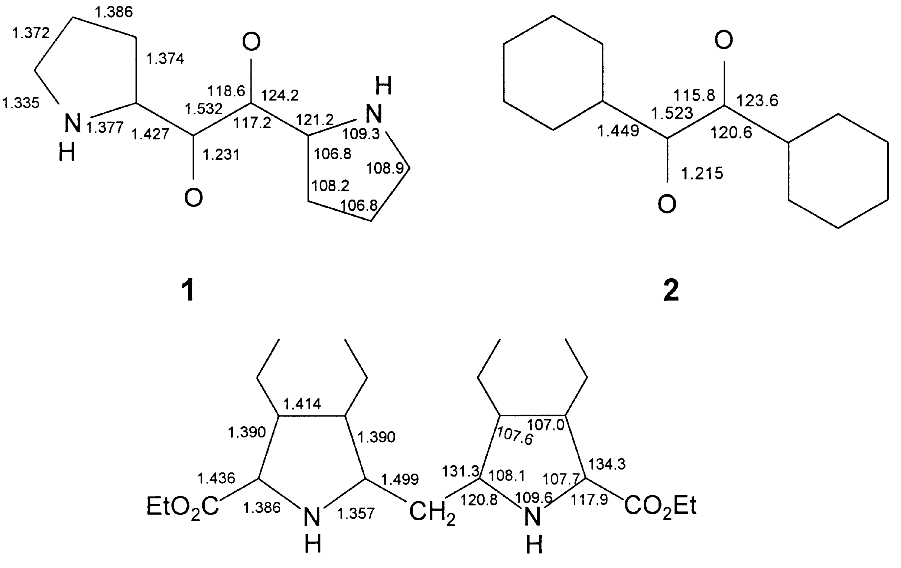


Fig. 3. View down the *b* axis in the crystal structure of **1**; parallel chains of intermolecularly hydrogen bonded molecules of **1** lie superimposed in stacked ribbons; hydrogen bonds are indicated by dashed lines; the N to O nonbonded distance of the N–H···O=C array is 2.853 Å, well below the sum (3.10 Å) of the *van der Waal* radii of N and O

Comparison of conformation from molecular mechanics and X-ray analysis

Insight into the preferred conformation of **1** in solution may be obtained from molecular mechanics calculations [16] as well as by crystallography. Given planar pyrrole rings, the conformation of **1** is largely determined by the various torsion angles associated with the α-diketone single bond (ψ) and with the single bond connecting carbonyl group and ring (ϕ) (Fig. 1). The two ϕ values for **1** in the crystal (Table 1) indicate that the pyrrole ring and the attached carbonyl are co-planar, whereas in benzil (**2**) the phenyl moiety and attached carbonyl are twisted out of co-planarity by only $\sim 10°$. Thus, most of the deformation from planarity in **1** and **2** comes from rotation within the α-diketone moiety according to the large ψ angles (Table 1). The overall shapes of **1** and **2** in the crystal are similar, with **1** having a somewhat larger ψ angle – possibly due to the extensive intermolecular hydrogen bonding in crystals of **1**.

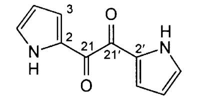


1 **2**

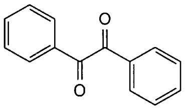
3

Fig. 4. Bond lengths (Å) and angles (°) in **1** compared with the diketone unit of **2** and the pyrroles of dipyrrylmethane **3**; e.s.d.s for bonds and angles in 1 are 0.003 Å and 0.2°, respectively; in **2** they are 0.06 Å and 0.4° for the room temperature phase of **2** [2]; **3**: e.s.d.s. for bonds are 0.004–0.005 Å and for angles 0.3° [15]

Table 1. Comparison of conformation determining torsion angles in **1**[a] and **2**(°)



1



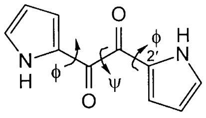
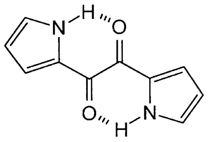
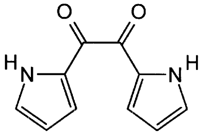
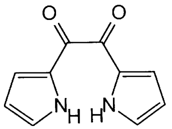
2

	crystal	crystal[b]	gas[c]
ψ(O(1)-C(21)-C(21′)-O(1′))	128	107	117
ψ'(C(2)-C(21)-C(21′)-C(2′))		116	116
ψ''(O(1)-C(21)-C(21′)-C(2′))		−68.5	63.6
ϕ'(C(3)-C(2)-C(21)-C(21′))	0.9	−9.7	−9.9
ϕ(O(1)-C(21)-C(2)-N(1))	−1.7		

[a] The primed atoms of this table correspond to those atoms labelled with # in tables of atomic coordinates, *e.g.* C(21′) corresponds to C(21)#1, and C(2′) corresponds to C(2)#1; [b] data from room temperature from (trigonal form) [4]; [c] analysis of gas phase vibrations [4]

In contrast to the conformation of **1** found in the crystal, molecular mechanics calculations predict a planar, intramolecularly hydrogen bonded conformation (*ap*, *ap*, *ap*) at the global energy minimum (Table 2). This conformer is slightly lower in energy than a non-hydrogen bonded conformation (*sp*, *ap*, *sp*) whose shape is similar to that found in the crystal, albeit with larger diketone torsion angle (ψ) and twist angles (ϕ) between a pyrrole ring and its adjacent carbonyl. Other

Table 2. Conformation determining torsion angles in **1** from molecular mechanics calculations[a]

Compound	(ϕ,ψ,ϕ)	Torsion angles (°)				Total steric energy (kcal/mole)
		ψ(O=C–C=O)	ψ'(C–C(O)–C(O)–C)	ϕ(N–C–C=O)	ϕ(C–C–C=O)	
	*sp*, *ap*, *sp*	151	154	−24.3	−27.6	57.2
	*ap*, *ap*, *ap*	178	179	176.9	176.8	55.5
	*sp*, *sp*, *sp*	30.3	30.1	30.7	32.4	59.5
	*ap*, *sp*, *ap*	9.1	10.6	128.5	51.8	60.1

[a] From PCMODEL [16]

conformations (*sp*, *sp*, *sp* and *ap*, *sp*, *ap*) are higher in energy. On the other hand, an *sp*, *ap*, *sp* conformer self-associated using intermolecular hydrogen bonds, as in the crystal, might lie at the global energy minimum. Whether a monomer, dimer or higher aggregate are present in solution seemed testable using vapor pressure osmometry (VPO) measurements.

State of aggregation and hydrogen bonding in solution

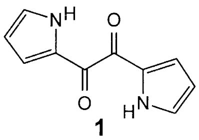
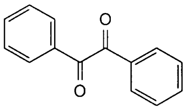
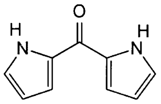
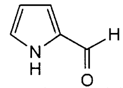
^{1}H NMR spectroscopic analyses have proven useful in assessing the ability of dipyrrinones and linear tetrapyrroles in forming intermolecularly hydrogen bonded dimers [17–20]. Vapor phase osmometry (VPO) measurements of molecular weights in solution has lent strong evidence in support of intermolecularly hydrogen bonded dimers in bilirubin dimethyl ester, other bilirubin analogs not possessing carboxylic acid groups, and dipyrrinones [20, 21]. In our studies, summarized in Table 3, benzil (**2**, $MW_{\mathrm{calc}} = 210$) was used as a calibration standard from which we measured $MW_{\mathrm{obs}} = 220$ and 221 in $CHCl_3$ and *THF*, respectively (Table 3). We then measured the molecular weights of **1** in $CHCl_3$ and *THF*, as well as those of several related pyrrole α-carbonyl compounds in $CHCl_3$. Bipyrroyl (**1**), pyrrole-α-adhehyde, and dipyrrylketone (**3**) (Table 3) all showed molecular weights corresponding to the monomer in $CHCl_3$. Although **1** showed $MW_{\mathrm{obs}} = 340\pm15$ in *THF*, we surmise that this corresponds to a monomer that is hydrogen bonded to two *THF* molecules (calcd. for $C_{10}H_8N_2O_4 \cdot 2C_4H_8O$: 332, $MW_{\mathrm{dimer}} = 376$). Alternatively, partial self-association might lead to a molecular weight lying between that of the monomer and the dimer of **1**. A similar situation arises for 2,2′-dipyrrylketone (**3**) (Table 3). In $CHCl_3$ it is monomeric; in *THF* the observed molecular weight (292±20) corresponds to the monomer that is hydrogen bonded to two *THF* molecules ($MW_{\mathrm{calc}} = 304$).

Conformation in solution

Given that **1** is monomeric in solution, we examined its ^{1}H NMR spectrum to attempt to distinguish among various possible conformations, *e.g*. those given in Table 2. In earlier work [17–21], pyrrole and lactam chemical shifts of dipyrrinones and bilirubins proved to be especially useful in sorting out intra- and intermolecular hydrogen bonding. For comparison with **1** we examined the concentration dependence of the NH chemical shift of a simple model for one-half of **1**, pyrrole-α-aldehyde, and 2,2′-dipyrrylketone (**3**) (Table 3). **1** shows very little concentration dependence of its pyrrole NH chemical shift in the range 10^{-2} to 10^{-4} M, as might be characteristic of solutions that are largely monomeric (cf. VPO results, Table 3). The NH chemical shifts of **1** are shielded by ~0.2–0.4 ppm relative to those of pyrrole-α-aldehyde and 2,2′-dipyrrylketone which are also monomeric in $CHCl_3$ solution (Table 3). The difference in chemical shifts between **1** and the other two compounds might be attributed to intramolecular hydrogen bonding in **1** (of the short shown in Table 2), or simply to small differences in the α-substituents.

Additional evidence on possible intramolecular hydrogen bonding in **1** comes from IR studies of the N-H stretching vibration. For 10^{-2} *M* pyrrole-α-aldehyde

Table 3. Molecular weights of **1**, related pyrroles, and benzil (**2**) in chloroform solution at 45°C

	Calculated *MW*/g	Observed *MW*/g	Conc. Range (mol/kg)
 **1**	188	179±10 340±15[a]	$3.3–10.7\times10^{-3}$
 **2**	210	220±15 221±15[a]	$39–17.7\times10^{-3}$
 **3**	160	164±10 292±20[a]	$4.1–13.2\times10^{-3}$
 Pyrrole-α-aldehyde	95	89±10	$1.1–3.2\times10^{-3}$

[a] Determined in *THF* at 45°C

Table 4. Concentration dependence of the NH ^{1}H NMR chemical shifts of **1** and related pyrroles in $CDCl_3$ at 25°C

Concentration (*M*)	Pyrrole NH Chemical Shift (δ ppm)[a]		
	Bipyrroyl (**1**)	Dipyrrylketone (**3**)	Pyrrole-α-aldehyde
0.01	9.33	9.50	9.64
0.001	9.20	9.43	9.58
0.0001	9.17	9.40	9.55

[a] Chemical shift downfield from *TMS* at 500 MHz

and 2,2′-dipyrryl ketone (**3**) in $CHCl_3$, one sees a single N-H stretching band at 3453 and 3452 cm^{-1}, respectively. In contrast, **1** shows two N-H stretchings, a more intense band at 3447 cm^{-1} and a second band at 3415 cm^{-1}. Consistent with previously reported N-H stretchings from dipyrrylmethanes, which show $\nu_{N\text{-}H}$ values of ~3460 cm^{-1} for a non-hydrogen bonded NH and $\nu_{N\text{-}H} = 3361–3397\ cm^{-1}$ for an intramolecularly hydrogen bonded NH [20, 22], for **1**, **3**, and pyrrole-α-aldehyde we would assign the higher wavenumber NH stretch (~3450 cm^{-1}) to a non-hydrogen bonded N-H and the lower wavenumber stretch (~3415 cm^{-1}) to an intramolecularly hydrogen bonded N-H. Thus, we find no evidence for hydrogen bonding in **3** or pyrrole-α-aldehyde in $CHCl_3$ solutions at $10^{-2}–10^{-4}$ *M*, whereas in **1** we find evidence for intramolecular hydrogen bonding, possibly of the sort shown in Table 2.

Our findings from the crystal structure of **1** reveal a supramolecular topology with considerably self-assembly *via* intramolecular hydrogen bonding, in layers of ribbons of **1** extending indefinitely through the crystal lattice. In contrast **1** is monomeric in $CHCl_3$ solution and probably intramolecularly hydrogen bonded.

Experimental

All nuclear magnetic resonance spectra were determined on a GE QE-300 or a Varian Unity Plus 500 MHz spectrometer. Chemical shifts are reported in δ (ppm) downfield from *TMS*. Infrared spectra were measured on a Perkin Elmer 1600 FT spectrophotometer, and UV spectra were determined on a Perkin-Elmer λ-12 spectrophotometer. Vapor pressure osmometry measurements were performed on a Gonotec Osmomat 070 osometer calibrated with benzil in $CHCl_3$ and *THF* (both at 45°C). Sample concentrations were 1.1 to 11.7×10^{-3} mol/kg; in this range, only small changes in MW_{obs} were found.

Table 5. Crystallographic data for 2,2′-Bipyrroyl (**1**)

Formula weight	188.2
Crystallized from	Methanol
Temperature (K)	298
Crystal size (mm)	$0.12\times0.62\times0.38$
Formula	$C_{10}H_8N_2O_2$
Space group	$C2/c$
Z	4
Cell dimensions	$a = 21.423(5)$ Å
	$b = 3.8872(9)$ Å
	$c = 13.060(3)$ Å
	$\alpha = 90°$
	$\beta = 125.119(11)°$
	$\gamma = 90°$
	$V = 878.5(4)$ Å
Nr / ν range of Refs. used for cell refinement	35 / $7.26 < \theta < 12.46°$
Calc. density d_x (g/cm^3)	1.423
Data collection range	$3.5 < 2\theta < 50°$
Scan type / scan range	ω / 1.2°
Nr. of total data recorded	1081
Nr. of unique data	767
Weighting scheme[a]	$a = 0.1019$, $b = 0.2779$
No. Obs. / no. parameters	733 / 64
R_1^{b}, $wR_2^{\text{c}}(I > 2\sigma(I))$	$R_1 = 0.053$, $wR_2 = 0.1509$
e.s.d. of C–C bond length	0.003
Highest peak in final ΔF map (e · Å^{-3})	0.221
Anisotropic non-H atoms	all
Isotropic non-H atoms	none
$\mu(\text{Mo}K_\alpha)$ (mm^{-1})	0.102
Radiation (λ(Å))	0.71073
Transm. factors	0.9669-0.8463

[a] $w^{-1} = (\sigma^2(F_o^2) + (aP)^2 + bP)$ where $P = (F_o^2 + 2F_c^2)/3$; Goodness of Fit (GOOF): $(\Sigma(w(F_o^2 - F_c^2)^2)/(M - N)^{0.5}$ where M is the number of reflections and N is the number of parameters refined; [b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [c] $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\sigma(w(F_o^2)^2))^{0.5}$.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**

	x	y	z	U_{eq}^{a}
O(1)	427(1)	−11(5)	1768(2)	55(1)
N(1)	−963(1)	2737(5)	−387(2)	44(1)
C(2)	−789(1)	2599(6)	809(2)	37(1)
C(21)	−72(1)	1211(6)	1852(2)	39(1)
C(3)	−1402(1)	4040(7)	727(2)	46(1)
C(4)	−1951(1)	5004(7)	−520(2)	51(1)
C(5)	−1659(1)	4161(7)	−1182(2)	49(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor U_{eq}

2,2′-Dipyrryldiketone (**1**; $C_{10}H_8N_2O_2$, 188 amu)

2,2′-Bipyrroyl was prepared as described previously from pyrrylmagnesium bromide and oxalyl chloride [1]. After flash chromatography using CH_2Cl_2 as eluent and crystallization from H_2O, pure **1** was obtained.

M.p.: 200.5–201.5°C (Ref. [1]: m.p.: 199.5–200°C, Ref. [9]: m.p.: 203–205°C); IR: $\nu = 3300$ (NH), 1630 (C=O) cm^{-1}; UV/Vis: $\varepsilon_{323}^{\max} = 20000$, $\varepsilon_{252}^{\max} = 8300$ (H_2O); $\varepsilon_{320}^{\max} = 17000$, $\varepsilon_{307}^{\max} = 15400$, $\varepsilon_{248}^{\max} = 7300$, $\varepsilon_{230}^{\max} = 4600$, ($CH_3OH$); $\varepsilon_{317}^{\max} = 16400$, $\varepsilon_{308}^{\max} = 15900$, $\varepsilon_{243}^{\max} = 8000$, $\varepsilon_{230}^{\max} = 6300$ (CH_3CN); ^{1}H NMR ($CDCl_3$, δ, 500 MHZ): 6.27 (ddd, $^3J = 4.0$, $^3J = 2.5$, $^4J = 2.5$ Hz, 2H), 7.04 (ddd, $^3J = 2.5$, $^3J = 1.5$, $^4J = 1.5$ Hz, 2H), 7.27 (ddd, $^3J = 4.0$, $^4J = 1.5$, $^4J = 1.0$ Hz, 2H), 11.17 (br s, 2H) ppm; ^{13}C NMR ($(CD_3)_2SO$, δ, 125.7 MHz): 124.6, 134.5, 142.0, 142.4 (C(2)), 195.0 (C=O)ppm.

X-Ray structure and solution

Crystals of **1** were grown in methanol by slow evaporation of the solvent. Suitable crystals were coated with epoxy cement, mounted on a glass fiber, and placed on a Siemens P4 diffractometer at room temperature. Unit cell parameters were determined by least squares analysis of 35 reflections with $7.26 < \theta < 12.46°$ using graphite monochromatized MoK_α radiation (0.71073 Å). 1081 reflections were collected in the range $3.5 < 2\theta < 50°$ yielding 767 unique reflections ($R_{\text{int}} = 0.0977$). The data were corrected for *Lorentz* and polarization effects. Crystal data are given in Table 5. Scattering factors and corrections for anomalous dispersion were taken from a standard source [13]. Atomic coordinates, bond lengths, bond angles, and related structural data for **1** have been deposited at the Cambridge Structural Data File (CDC No. 136801).

Calculations were performed using a Siemens SHELXTL PLUS, version 5.03, system of programs refining on F^2. The structure was solved by direct methods in the space group C_2/c. The molecule is positioned on a crystallographic 2-fold rotational axis bisecting the carbonyl carbons C(21)-(C21)#1.

All non-hydrogen atoms (Table 6) were refined with anisotropic thermal parameters. The data were corrected using an empirical model derived from psi scans. Hydrogen atom positions were calculated using a riding model with a C-H distance fixed at 0.96 Å and a thermal parameter 1.2 times that of the host carbon atom. The largest peak in the final difference map corresponded to 0.221 $e^-/\text{Å}^3$ and was located 0.951 Å from the C2 carbon. Figure 2 provides bond lengths and angles.

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