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Key indicators

Single-crystal X-ray study
 $T = 291$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.038
 wR factor = 0.107
Data-to-parameter ratio = 7.0

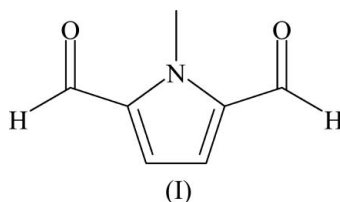
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

1-Methylpyrrole-2,5-dicarbaldehyde

The solid-state structure of the title compound, $\text{C}_7\text{H}_7\text{NO}_2$, is reported. The crystal packing is shaped mainly through carbonyl–carbonyl interactions on the one hand, and $\text{C}-\text{H} \cdots n(\text{O})$ hydrogen bonds and $\pi(\text{CO}) \cdots \pi$ interactions on the other.

Comment

1-Methyl-2,5-pyrroledicarbaldehyde, (I) (Fig. 1), has been a sought-after intermediate, especially for the synthesis of organic semiconductor materials (Berlin *et al.*, 1987; Cadamuro *et al.*, 1993, 1996; Van Der Looy *et al.*, 1997) but also for biologically active compounds and several macrocycles (Cadamuro *et al.*, 1993, 1996).



The structure crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with no mirror symmetry present in the molecule or the structure. As a consequence, the two carbonyl groups have different environments.

The crystal structure can be described as stacks of individual molecules along the $[100]$ direction (Fig. 2) and by planes parallel to (001) consisting of stacked ribbons running along the $[110]$ and $[1\bar{1}0]$ directions (Fig. 3). Between the stacks of individual molecules along the $[100]$ direction, the stabilizing interactions are type II carbonyl–carbonyl interactions, as described by Allen *et al.* (1998). These are situated around the twofold screw axis and involve the carbonyl group $\text{C}6=\text{O}6$:

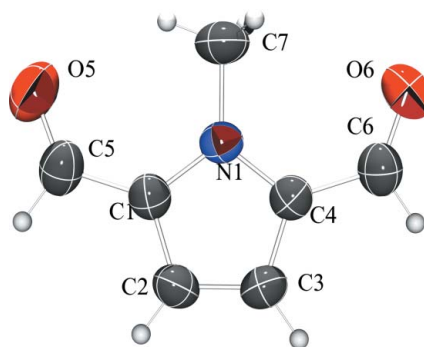


Figure 1
View of (1), including the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

$C6 \cdots O6^i$ 3.318 (3) Å [symmetry code (i) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$] and $O6 \cdots C6^i$ 3.067 (3) Å. They are shown in Fig. 2 by the orange dotted lines. Perpendicular to the direction of these carbonyl–carbonyl contacts, the stacks display a short contact between the C atom of a methyl group and the O atom of a carbonyl group, *viz.* $N1-C7 \cdots O6^{ii}$ 3.157 (3) Å, 179.06 (16)° [symmetry code (ii) $\frac{1}{2} + x, -\frac{1}{2} - y, -z$]. This contact is shown in Fig. 2 by the cyan dotted lines.

The remaining contacts involve the other carbonyl group $C5=O5$ and interact either within the aforementioned ribbons, such as the weak hydrogen bond $C3-H3 \cdots O5^{iii}$ 2.48 (3) Å, $D \cdots A$ 3.417 (3) Å, 170 (2)° [symmetry code (iii) $-1 + x, 1 + y, z$] (cyan dotted lines in Fig. 3), or between the ribbons, such as $C4 \cdots C5^{iv}$ 3.394 (4) Å [symmetry code (iv) $-1 + x, y, z$] (orange dotted lines in Fig. 3), forming the planes mentioned above. The latter contact is the expression of a typical $\pi(CO) \cdots \pi$ contact, in this case given by $CgA \cdots O5^{iv} - C5^{iv}$ 3.598 (2) Å, 3.316 Å perp., 72.26 (17)°, where CgA indicates the centroid of the pyrrole ring and ‘perp.’ indicates the perpendicular distance of $O5$ to the plane of the pyrrole ring.

In conclusion, (I) displays a chiral structure which is completely dominated by interactions concerning the two different carbonyl groups: one of them is involved in carbonyl–carbonyl dipolar interactions, the other in $\pi(CO) \cdots \pi$ contacts and $CH \cdots n(O)$ hydrogen bonds. This is in contrast with the derivative which lacks the *N*-methyl group (Adams *et al.*, 1986), which has an achiral Pn structure in which the crystal symmetry does not coincide with the molecular symmetry. Unsurprisingly, the network in the latter structure consists of hydrogen-bonded layers involving the H atoms of the aldehyde group and the aromatic ring as well as those on the N atom. The O atoms of the carbonyl groups always act as acceptors. In addition, π – π interactions exist between the layers.

Experimental

All starting materials were obtained from Acros and used as received. Benzene was dried over 3 Å molecular sieves prior to use. 1H and ^{13}C NMR spectra were recorded on a Varian Unity-400 apparatus.

N-Methyl-2,5-pyrroledicarbaldehyde (I) was prepared starting from *N*-methyl-2,5-bis(hydroxymethyl)pyrrole (II). For the synthesis of the latter *N*-methylpyrrole (22 ml, 0.255 mol), ground paraformaldehyde (16.1 g, 0.536 mol), potassium carbonate (0.2 g, 0.0015 mol) and water (5 ml) were mixed together and heated under a nitrogen atmosphere to 323–333 K until all the paraformaldehyde had dissolved. The reaction mixture was then cooled in a water bath until completion of the exothermic process (*ca* 30 min.). The mixture was subsequently reheated to 353 K for 3 h. To remove water, *N*-methylpyrrole and *N*-methyl-2-(hydroxymethyl)pyrrole from the resulting crude reaction mixture, it was distilled *in vacuo* (1–2 mmHg/323 K). The remaining impure precipitate was then recrystallized from propanol (10–15 ml) and washed with a small amount of chloroform. Overnight cooling of the filtrate yielded an additional fraction of (II). The yield was 22.7 g (65%) of an off-white powder [m.p. 386–387 K (uncorrected)] in accordance with the literature (Chelintzev & Maksorov, 1916; Severin & Ipach, 1975). (II) should be refrigerated to prevent oxidation. 1H NMR ($CDCl_3$, 400 MHz, TMS): δ 3.71 (*s*, 3H, CH_3), 4.60 (*d*, 4H, $J = 2.6$ Hz, CH_2),

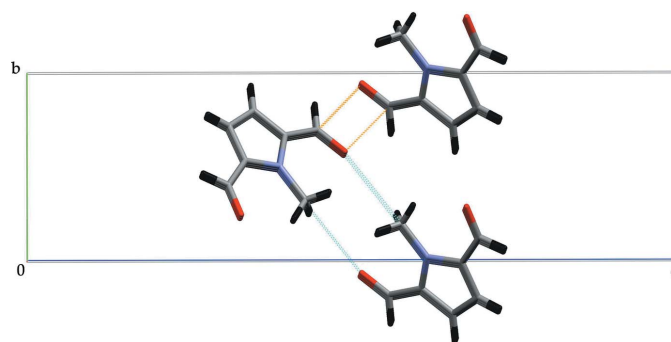


Figure 2
View of the structure projected on to the *bc* plane. For details, see text.

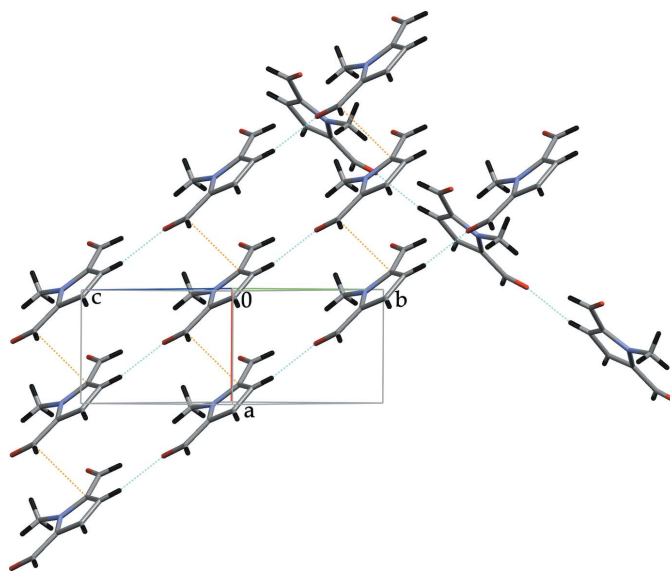


Figure 3
View of the structure along the *bc* cell diagonal. For details, see *Comment*.

6.40 (*s*, 2H, H3 and H4), 7.26 (*s*, 2H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 30.6 (CH_3), 57.1 (CH_2), 132 (C2 and C5), 107.7 (C3 and C4).

N-methyl-2,5-pyrroledicarbaldehyde (I) was prepared by refluxing a mixture consisting of (II) (7.7 g, 0.055 mol), dry benzene (300 ml) and precipitated active manganese dioxide (25.0 g, 0.287 mol) for 6 h and subsequently stirring at room temperature for 24 h. The precipitate was filtered off and washed carefully with 1,4-dioxane or tetrahydrofuran. The impure dark-brown crystals were sublimed under reduced pressure (typically for 6 h at 0.1 mmHg/338 K) (Severin & Ipach, 1975). (I) was collected in a yield of 3.0 g (40%) as light-yellow crystals [m.p. 370 K (uncorrected); lit. 368–369 K (Cresp & Sargent, 1972; Cresp & Sargent, 1973; Severin & Ipach, 1975)]. The NMR data of (I) are identical to those of Loader *et al.* (1982) [1H NMR] and Cadamuro *et al.* (1993) [^{13}C NMR].

Crystal data

$C_7H_7NO_2$
 $M_r = 137.14$
Orthorhombic, $P2_12_12_1$
 $a = 4.650$ (1) Å
 $b = 6.457$ (1) Å
 $c = 22.386$ (4) Å
 $V = 672.1$ (2) Å³
 $Z = 4$
 $D_x = 1.355$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 5.7$ – 19.7°
 $\mu = 0.10$ mm⁻¹
 $T = 291$ (2) K
Prism, light yellow
 $0.4 \times 0.3 \times 0.2$ mm

Data collection

Enraf–Nonius Mach3
diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
1499 measured reflections
766 independent reflections
652 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 25.3^\circ$
 $h = 0 \rightarrow 5$
 $k = 0 \rightarrow 7$
 $l = -26 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 21%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.107$
 $S = 1.00$
766 reflections
109 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.0615P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.14 \text{ e } \text{Å}^{-3}$

The large value for the intensity decay was caused by the volatility of the compound. Sublimation took place during the course of the measurement. All H atoms were located in a difference density map and refined freely [$\text{C}—\text{H} = 0.90(3)–0.99(3) \text{ Å}$], except the methyl H atoms, for which a common distance was refined and the group was rotated so that it coincides with the maxima in the Fourier difference map [$\text{C}—\text{H} = 0.92 \text{ Å}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Bruno *et al.*, 2002) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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References

- Adams, H., Bailey, N. A., Fenton, D. E., Moss, S., Rodriguez de Barbarin, C. O. & Jones, G. (1986). *J. Chem. Soc. Dalton Trans.* pp. 693–699.
- Allen, F. H., Baalham, C. A., Lommerse J. P. M. & Raithby P. R. (1998). *Acta Cryst. B* **54**, 320–329.
- Berlin, A., Bradamante, S., Ferracciolo, R., Pagani, G. A. & Sannicolò, F. (1987). *J. Chem. Soc. Perkin Trans. I*, pp. 2631–2635.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M. K., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst. B* **58**, 389–397.
- Cadamuro, S., Degani, I., Fochi, R., Gatti, A. & Piscopo, L. (1993). *J. Chem. Soc. Perkin Trans. I*, pp. 2939–2944.
- Cadamuro, S., Degani, I., Gatti, A. & Piscopo, L. J. (1996). *J. Chem. Soc. Perkin Trans. I*, pp. 2365–2369.
- Chelintzev, V. V. & Maksorov, B. V. (1916). *J. Russ. Phys. Chem. Soc.* **48**, 748–779.
- Cresp, T. M. & Sargent, M. V. (1972). *J. Chem. Soc. Chem. Comm.* pp. 807–808.
- Cresp, T. M. & Sargent, M. V. (1973). *J. Chem. Soc. Perkin Trans. I*, pp. 2961–2971.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Loader, C. E., Barnett, G. H. & Anderson, H. J. (1982). *Can. J. Chem.* **60**, 383–289.
- Severin, Th. & Ipach, I. (1975). *Chem. Ber.* **108**, 1768–1775.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Van Der Looy, J. F. A., Thys, G. J. H., Dieltiens, P. E. M., De Schrijver, D., Van Alsenoy, C. & Geise, H. J. (1997). *Tetrahedron*, **53**, 15069–15084.