

The molecules form stacks in the crystallographic **b** direction (Figs. 2*a,b*) with an interplanar separation of 3.4 Å.

## References

- SHELDRICK, G. M. (1983). *SHELXTL Users Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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## Structure of 1-Butyl-5-[(4-chlorophenyl)azo]-1,2,5,6-tetrahydro-4-methyl-2,6-dioxo-3-pyridinecarbonitrile

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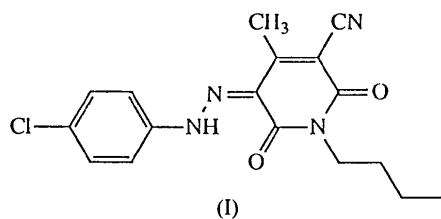
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**Abstract.** C<sub>17</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>2</sub>, *M<sub>r</sub>* = 344.8, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.586 (2), *b* = 11.429 (4), *c* = 19.592 (8) Å, β = 93.52 (3)°, *V* = 1695 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.35 Mg m<sup>-3</sup>, Cu *K*α radiation, λ = 1.54178 Å, μ = 2.19 mm<sup>-1</sup>, *F*(000) = 776, room temperature, *R* = 0.045 for 1499 observed reflections with |*F<sub>o</sub>*| > 3σ(|*F<sub>o</sub>*|). The molecule has an essentially planar and highly conjugated geometry reinforced by an intramolecular NH⋯O hydrogen bond. The molecules form parallel overlapping stacks in the crystal.

**Introduction.** As part of a general study of the crystal chemistry of dyes and to provide templates for molecular-modelling studies, the crystal structure of the yellow dye (I) was determined.



**Experimental.** Orange acicular single crystals, bounded by {011} faces, suitable for X-ray crystallography were grown at room temperature from methyl ethyl ketone. Crystal size 0.09 × 0.01 × 0.50 mm. Refined unit-cell parameters obtained from setting angles of 18 reflections with 9 < θ < 30°. Nicolet *R3m* diffractometer. 2030 measured, 1748 independent (*R<sub>int</sub>* = 0.053) reflections (θ < 50°), Cu *K*α radiation (graphite monochromator), ω scan. 1499 reflections [|*F<sub>o</sub>*| > 3σ(|*F<sub>o</sub>*|)] considered observed, index range *h* -7/7, *k* 0/11, *l* 0/19, two check reflections measured every 50 reflections, no

significant decomposition, 5% variation; data brought to uniform scale, Lorentz and polarization corrections, numerical absorption correction, minimum and maximum transmission factors 0.67 and 0.83. Structure solved by direct methods; non-H atoms refined anisotropically; position of H atom on N(11) and orientation of methyl hydrogens on C(18) determined from a Δ*F* map. H atom on N(11) refined isotropically subject to an N—H distance constraint; remaining H-atom positions calculated (C—H 0.96 Å), assigned isotropic thermal parameters and allowed to ride on their parent C atoms. Methyl groups refined as rigid bodies. An empirical extinction correction was applied [*g* = 0.0036 (7)]. Refinement using *F* magnitudes by block-cascade full-matrix least squares; *R* = 0.045, *wR* = 0.49 [*w*<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.00068*F*<sup>2</sup>]. *S* = 1.56; 228 refined parameters. (Δ/σ)<sub>max</sub> = 0.017 e Å<sup>-3</sup>; residual electron density in difference map within -0.17 and 0.21 e Å<sup>-3</sup>; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

**Discussion.** Table 1\* lists the fractional atomic coordinates of the non-H atoms, Table 2 lists the bond length and angles, and selected torsion angles.

\* Lists of structure factors, anisotropic thermal parameters, torsion angles, bond lengths and bond angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54559 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0027]

Table 1. Atom coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N(1)	9020 (3)	3647 (2)	8575 (1)	43 (1)*
C(2)	8691 (4)	2733 (3)	9015 (1)	46 (1)*
O(2)	9021 (3)	2837 (2)	9635 (1)	60 (1)*
C(3)	7927 (4)	1657 (3)	8717 (1)	42 (1)*
N(3)	7560 (3)	725 (2)	9089 (1)	44 (1)*
C(4)	7536 (3)	1569 (3)	7990 (1)	43 (1)*
C(5)	7902 (4)	2501 (3)	7598 (1)	42 (1)*
C(6)	8698 (4)	3589 (3)	7866 (2)	46 (1)*
O(6)	9042 (3)	4407 (2)	7500 (1)	63 (1)*
C(7)	9748 (4)	4744 (3)	8885 (2)	53 (1)*
C(8)	8340 (4)	5495 (3)	9185 (2)	59 (1)*
C(9)	6992 (4)	6024 (3)	8675 (2)	62 (1)*
C(10)	7709 (5)	7002 (3)	8245 (2)	78 (2)*
N(11)	7874 (3)	720 (2)	9752 (1)	47 (1)*
C(12)	7422 (4)	-280 (3)	10131 (1)	43 (1)*
C(13)	7918 (4)	-296 (3)	10823 (2)	48 (1)*
C(14)	7490 (4)	-1245 (3)	11215 (2)	54 (1)*
C(15)	6563 (4)	-2163 (3)	10911 (2)	50 (1)*
Cl	6016 (1)	-3365 (1)	11407 (1)	76 (1)*
C(16)	6044 (4)	-2144 (3)	10224 (2)	55 (1)*
C(17)	6476 (4)	-1196 (3)	9831 (2)	49 (1)*
C(18)	6732 (4)	464 (3)	7711 (2)	55 (1)*
C(19)	7530 (4)	2494 (3)	6868 (2)	53 (1)*
N(19)	7228 (4)	2493 (3)	6287 (2)	75 (1)*

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U<sub>i</sub>* tensor.

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

N(1)—C(2)	1.387 (4)	N(1)—C(6)	1.397 (4)
N(1)—C(7)	1.485 (4)	C(2)—O(2)	1.230 (3)
C(2)—C(3)	1.466 (4)	C(3)—N(3)	1.329 (4)
C(3)—C(4)	1.441 (4)	N(3)—N(11)	1.308 (3)
C(4)—C(5)	1.351 (4)	C(4)—C(18)	1.492 (4)
C(5)—C(6)	1.466 (4)	C(5)—C(19)	1.442 (4)
C(6)—O(6)	1.217 (4)	C(7)—C(8)	1.516 (5)
C(8)—C(9)	1.512 (4)	C(9)—C(10)	1.520 (5)
N(11)—C(12)	1.415 (4)	C(12)—C(13)	1.386 (4)
C(12)—C(17)	1.379 (4)	C(13)—C(14)	1.378 (5)
C(14)—C(15)	1.378 (4)	C(15)—Cl	1.748 (3)
C(15)—C(16)	1.378 (4)	C(16)—C(17)	1.380 (4)
C(19)—N(19)	1.147 (4)		
C(2)—N(1)—C(6)	123.7 (2)	C(2)—N(1)—C(7)	117.3 (2)
C(6)—N(1)—C(7)	119.0 (2)	N(1)—C(2)—O(2)	120.5 (3)
N(1)—C(2)—C(3)	117.8 (2)	O(2)—C(2)—C(3)	121.7 (3)
C(2)—C(3)—N(3)	123.0 (2)	C(2)—C(3)—C(4)	120.3 (2)
N(3)—C(3)—C(4)	116.6 (2)	C(3)—N(3)—N(11)	121.1 (2)
C(3)—C(4)—C(5)	118.0 (3)	C(3)—C(4)—C(18)	118.4 (3)
C(5)—C(4)—C(18)	123.6 (3)	C(4)—C(5)—C(6)	124.1 (2)
C(4)—C(5)—C(19)	121.7 (3)	C(6)—C(5)—C(19)	114.3 (3)
N(1)—C(6)—C(5)	116.1 (3)	N(1)—C(6)—O(6)	121.3 (3)
C(5)—C(6)—O(6)	122.6 (3)	N(1)—C(7)—C(8)	112.5 (2)
C(7)—C(8)—C(9)	115.7 (3)	C(8)—C(9)—C(10)	114.2 (3)
N(3)—N(11)—C(12)	119.3 (2)	N(11)—C(12)—C(13)	117.6 (3)
N(11)—C(12)—C(17)	121.8 (3)	C(13)—C(12)—C(17)	120.6 (3)
C(12)—C(13)—C(14)	119.8 (3)	C(13)—C(14)—C(15)	119.3 (3)
C(14)—C(15)—Cl	119.4 (2)	C(14)—C(15)—C(16)	121.1 (3)
Cl—C(15)—C(16)	119.5 (2)	C(15)—C(16)—C(17)	119.6 (3)
C(12)—C(17)—C(16)	119.6 (3)	C(5)—C(19)—N(19)	179.7 (3)
C(2)—N(1)—C(7)—C(8)	-79.6 (3)		
N(1)—C(2)—C(3)—N(3)	179.8 (2)		
C(2)—C(3)—N(3)—N(11)	-0.2 (4)		
N(3)—C(3)—C(4)—C(5)	-179.7 (3)		
C(3)—N(3)—N(11)—C(12)	178.4 (2)		
C(18)—C(4)—C(5)—C(19)	0.2 (4)		
C(4)—C(5)—C(6)—O(6)	178.7 (3)		
N(3)—N(11)—C(12)—C(17)	-7.6 (4)		
C(2)—N(1)—C(6)—O(6)	-178.5 (3)		

Table 2 (cont.)

C(6)—N(1)—C(7)—C(8)	100.1 (3)
C(4)—C(3)—N(3)—N(11)	179.8 (2)
N(1)—C(7)—C(8)—C(9)	-67.5 (3)
N(3)—N(11)—C(12)—C(13)	174.3 (3)

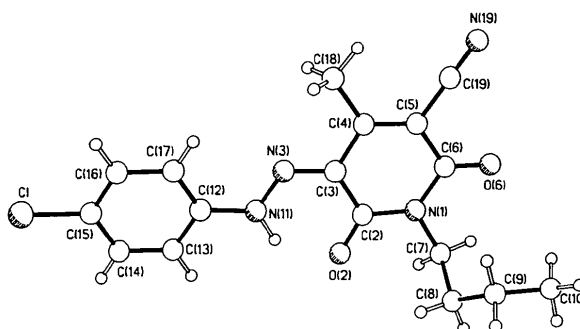


Fig. 1. Ball and stick representation of the structure of (I) showing atom-numbering scheme.

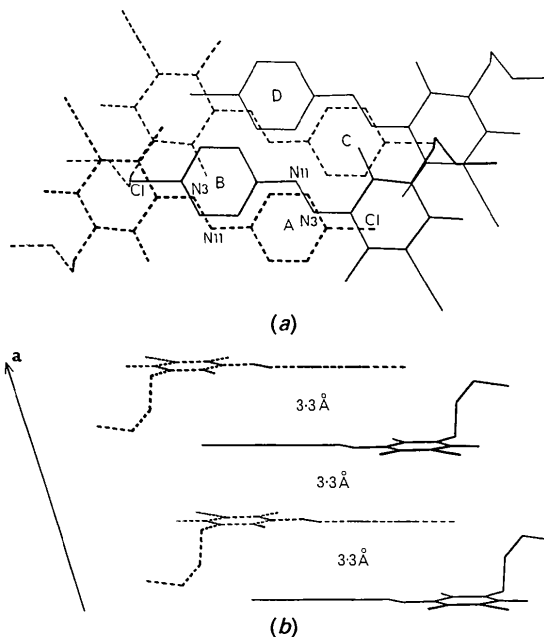


Fig. 2. (a) Plan and (b) elevation of the stacking of the molecules in the crystals. The sequence within the stack is A, B, C, D.

The structure of (I) is illustrated in Fig. 1 which includes the atom-numbering scheme. With the exception of the *n*-butyl substituent, the molecule is essentially planar, there being a small rotation of  $8^\circ$  between the planes of pyridone and chlorophenyl rings. This is almost entirely due to a torsional rotation (*ca*  $7^\circ$ ) about the N(11)—C(12) bond. The N(3)—N(11) bond is held coplanar with the pyridone ring by the formation of an intramolecular N—H...O hydrogen bond between N(11) and the ring carbonyl oxygen atom O(2) [N(11)...O(2) 2.59,

H(11)···O(2) 1.79 Å, N—H···O angle 136°. There is a noticeable degree of bond ordering in the pyridone ring and adjacent azo group. A clear pattern of delocalization is apparent extending from O(2) through N(1) to O(6). C(2)—C(3), C(3)—C(4) and C(5)—C(6) have predominantly single-bond character with C(4)—C(5) displaying partial double-bond character. Both C(3)—N(3) [1.329 (4) Å] and N(3)—N(11) [1.308 (3) Å] clearly have appreciable double-bond character, giving rise to the requirement for a formal positive charge associated with N(11), and a consequent negative charge on C(3). The N(11)—C(12) bond length [1.415 (4) Å] is as expected for a nitrogen—phenyl single bond.

The molecules lie with their principal molecular axis along the  $\langle 011 \rangle$  directions, and with the mean

plane of the molecule approximately perpendicular to [100]. They pack to form partially overlapping stacks in the crystallographic  $a$  direction (Figs. 2*a,b*) with interplanar separations of 3.3 Å. Within each stack there is staggering of adjacent overlapping pairs of molecules (Fig. 2*a*) along  $\langle 01\bar{1} \rangle$ . Overlap within these pairs is consistent with a degree of weak intermolecular electrostatic interaction, and with the N(3)—N(11) bond lying almost directly above, over and parallel to the C(15)—C(16) bond in the chlorophenyl ring (and the converse).

#### References

- SHELDRICK, G. M. (1983). *SHELXTL*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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## Structures of Two 4,5-Dihydro-3*H*-pyrroles (1-Pyrrolines)

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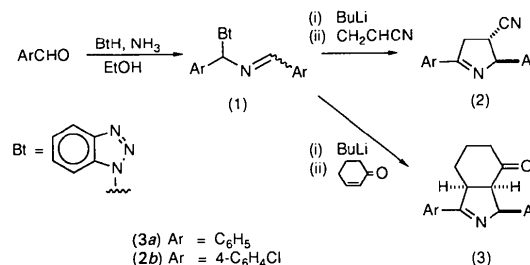
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**Abstract.** (2*b*) *trans*-2,5-Bis(4-chlorophenyl)-4,5-dihydro-3*H*-pyrrole-4-carbonitrile, C<sub>17</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>,  $M_r = 315.2$ , monoclinic,  $P2_1/n$ ,  $a = 9.780$  (4),  $b = 5.841$  (3),  $c = 26.112$  (10) Å,  $\beta = 93.02$  (3)°,  $V = 1490$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.405$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.43$  mm<sup>-1</sup>,  $F(000) = 648$ ,  $T = 175$  K,  $R = 0.036$  for 1524 independent observed reflections. (3*a*) *cis*-3,3*a-cis*-3*a,7a*-1,3-Diphenyl-3*a,4,5,6,7,7a*-hexahydro-3*H*-isoindol-4-one, C<sub>20</sub>H<sub>19</sub>NO,  $M_r = 289.4$ , monoclinic,  $P2_1/n$ ,  $a = 12.061$  (4),  $b = 7.666$  (3),  $c = 17.206$  (6) Å,  $\beta = 105.51$  (3)°,  $V = 1533$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.254$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.07$  mm<sup>-1</sup>,  $F(000) = 616$ ,  $T = 175$  K,  $R = 0.038$  for 1683 independent observed reflections. The pyrroline ring of (2*b*) exists in an envelope conformation with C(4) deviating from the plane of the other four ring atoms by 0.423 Å, while the pyrroline ring of (3*a*) exists in a twisted envelope conformation with C(3*a*) lying 0.353 Å from the plane of the other ring atoms.

**Introduction.** We recently described a procedure for the preparation of 4,5-dihydro-3*H*-pyrroles from

aromatic aldehydes and various dipolarophiles as outlined in the scheme below (Katritzky, Hitchings & Zhao, 1991). The ylides produced by deprotonation of the intermediate imines (1) undergo regio-specific and stereoselective 1,3-dipolar cycloaddition reactions. For example, reactions with acrylonitrile and cyclohexenone gave good yields of single products, the full structures of which could not be unambiguously determined by spectroscopic methods. We herein describe single-crystal X-ray structure determinations of these products which are identified as (2*b*) and (3*a*), respectively.



**Experimental.** Colourless crystals of dimensions 0.55 × 0.14 × 0.08 mm for (2*b*) and 0.46 × 0.35 ×

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