

(E)-1,2-Bis(1,2-dimethyl-3-indoliziny)etheneWei-Wei Liu,^a Yi-Zhi Li,^b Ou Song^a and Hong-Wen Hu^{a*†}^aDepartment of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and ^bCoordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.050

wR factor = 0.106

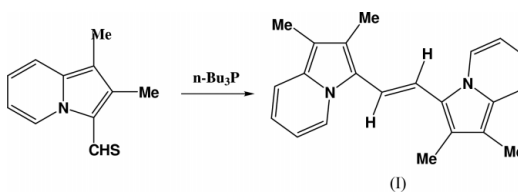
Data-to-parameter ratio = 15.5

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

The molecule of the title compound, $\text{C}_{22}\text{H}_{22}\text{N}_2$, has a center of symmetry, and two bulky indoliziny groups are situated on opposite sides of the $\text{C}=\text{C}$ double bond, resulting in an *E* configuration. The two indoliziny groups and the $\text{C}=\text{C}$ double bond are in the same plane, forming a fully extended conjugated system. There are $\pi-\pi$ stacking interactions between neighboring molecules related by a center of symmetry.

Comment

Thiocarbonyl compounds are much more reactive than the corresponding carbonyl compounds because of the lower electronegativity and the special electronic structure of the S atom as compared with the O atom. Thiocarbonyl compounds can take part in diverse chemical reactions. As a result, they have found wide-ranging applications in the synthesis of cyclic compounds (Vedejs *et al.*, 1998), natural products (Vedejs *et al.*, 1998), organic conductors and superconductors (Parg *et al.*, 1994). Many practical applications of thiocarbonyl compounds have also been reported (Mastalerz *et al.*, 2001). The majority of thiocarbonyl chemistry is based on investigations with thioketones as substrate, because simple thioaldehydes are unstable. However, resonance-stabilized thioaldehydes, such as 1,2-dimethyl-3-thioformylindolizine, are quite stable, even on prolonged standing. We have investigated the reactions of this indolizine thioaldehyde with tributylphosphine, and found that the conversion of the indolizine thioaldehyde into the title compound, (I), is stereoselective (see Scheme). The structure of (I) is similar to that of *trans*-stilbene. It is expected that (I) may have great potential as an antitumor agent.



The title molecule is centrosymmetric (Fig. 1 and Table 1). The two bulky indoliziny groups are situated on opposite sides of the $\text{C}=\text{C}$ double bond, resulting in an *E* configuration. The indolizine rings are coplanar with the $\text{C}=\text{C}$ double bond, forming a fully extended conjugated system. In the crystal structure, two neighboring molecules related by a center of symmetry show a $\pi-\pi$ stacking interaction, with a perpendicular distance of $3.269(6) \text{ \AA}$ between the six-membered rings.

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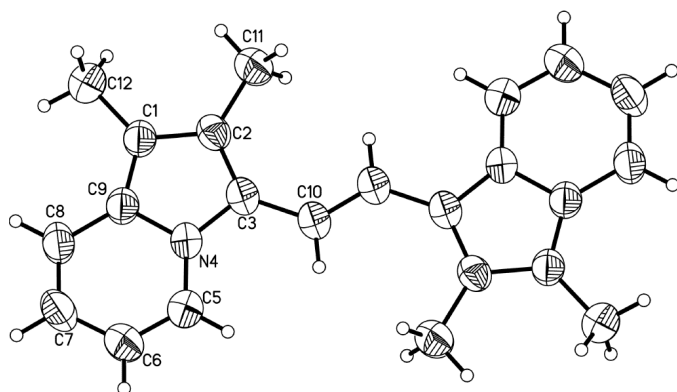


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids.

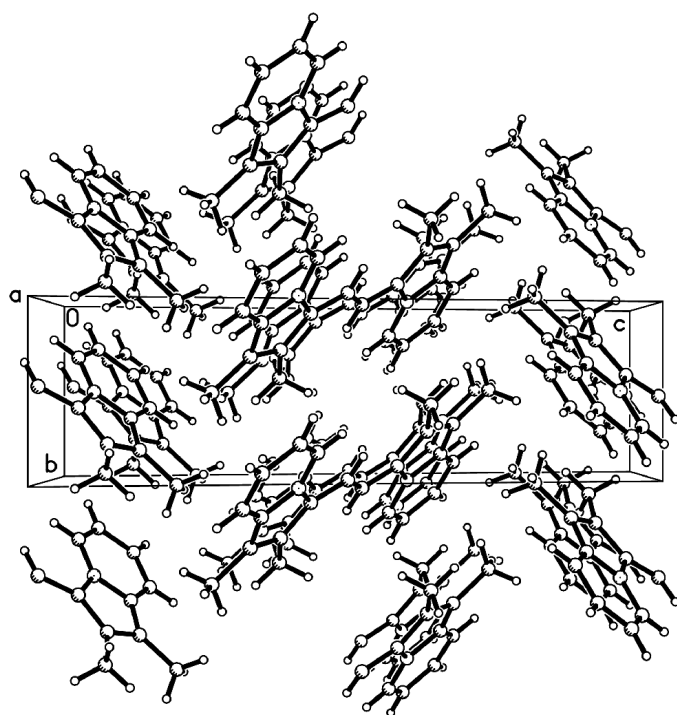


Figure 2
The packing of (I), viewed down the *a* axis.

Experimental

A solution of 1,2-dimethyl-3-thioformylindolizine (0.28 g, 1.5 mmol) in anhydrous THF (8 ml) was stirred at room temperature and, after the air had been replaced by N₂ gas, tributylphosphine (1.1 g, 5.4 mmol) was added. The reaction mixture was maintained under reflux for 14 h until all the 1,2-dimethyl-3-thioformylindolizine disappeared (monitored by TLC). The solvent was removed *in vacuo*, the mixture was cooled and the title compound, (I), was collected by filtration and washed with petroleum ether. Yellow single crystals of (I) suitable for X-ray crystallographic analysis were obtained by recrystallization from petroleum ether.

Crystal data

C₂₂H₂₂N₂
M_r = 314.42
Monoclinic, P2₁/c
a = 8.253 (2) Å
b = 5.435 (1) Å
c = 19.056 (4) Å
β = 102.51 (1)°
V = 834.5 (3) Å³
Z = 2

D_x = 1.251 Mg m⁻³
Mo Kα radiation
Cell parameters from 1482 reflections
θ = 2.5–24.4°
μ = 0.07 mm⁻¹
T = 293 (2) K
Block, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Bruker Smart APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
4170 measured reflections
1530 independent reflections

1105 reflections with I > 2σ(I)
R_{int} = 0.060
θ_{max} = 25.5°
h = -8 → 10
k = -6 → 6
l = -23 → 20

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.050
wR(F²) = 0.106
S = 1.02
1530 reflections
99 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.02P)² + 0.25P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.27 e Å⁻³
Δρ_{min} = -0.31 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C3–C10	1.438 (2)	C10–C10 ⁱ	1.315 (3)
C10 ⁱ –C10–C3	128.2 (3)		
C2–C3–C10–C10 ⁱ	1.2 (4)		

Symmetry code: (i) -x, -y, 1 - z.

All H atoms were positioned geometrically and refined as riding, with isotropic displacement parameters 1.2 to 1.5 times U_{eq} of the parent atom. The distances to H atoms were in the range 0.93–0.96 Å.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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