organic compounds

6-Amino-5,5,7-tricyano-3,3a,4,5-tetrahydro-2*H*-indene-4-spirocyclopentane

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The positions of the C=C double bonds in the title compound, $C_{16}H_{16}N_4$, the subject of some dispute in the literature, have been clearly identified. The cyclohexene ring has a distorted half-chair conformation and the cyclopentene and cyclopentane rings adopt envelope conformations. The dihedral angles between planar fragments of the cyclohexene and cyclopentene rings and of the cyclohexene and cyclopentane rings are 7.5 (1) and 86.98 (9)°, respectively. In the crystal, intermolecular N—H···N hydrogen bonds link the molecules into infinite chains running in the [$\bar{1}$10] direction.

Comment

The large number of publications concerned with dimerization of carbo- and heterocyclic ilidenmalononitriles indicates a consistent interest in this type of compound (Prout, 1953; Weir & Hyne, 1963, 1964, 1965; Mirek *et al.*, 1980; Baty *et al.*, 1969; Mirek & Milart, 1986; Sofan *et al.*, 1989). This interest arises from the properties of the compounds, such as light sensitivity and polymerization under UV radiation (Tafeenko *et al.*, 1994). In spite of the published information on the synthesis and spectroscopic studies of the title compound there are differing opinions about its structure: the assignment by Baty *et al.* (1969) and Mirek & Milart (1986), (I), differs from that proposed by Dyachenko & Litvinov (1997), (II), in the position of double bonds.
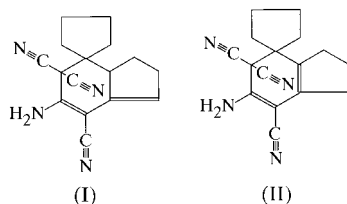
In order to clarify this matter, a crystal structure analysis was undertaken and showed (Fig. 1, Table 1) that the molecule has the structure represented by (I) with the double bonds
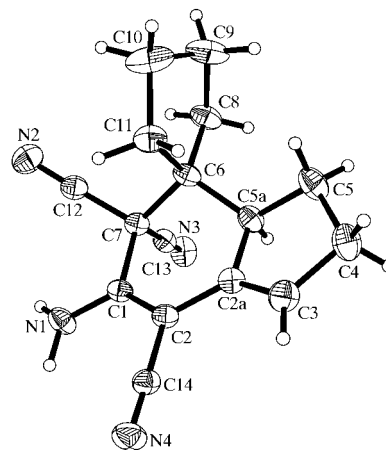

Figure 1
A view of (I) with the atom-numbering scheme. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary small radii for clarity.

identified between C1 and C2 [1.370 (2) Å], and between C2a and C3 [1.341 (2) Å] rather than between C2a and C5a [1.503 (2) Å].

The substituted cyclohexene ring has a distorted half-chair conformation, with C5a and C6 displaced by 0.193 (3) and −0.579 (3) Å, respectively, from the least-squares mean plane [r.m.s. deviation 0.007 (7) Å] defined by C2a, C2, C1 and C7. The cyclopentene ring has an envelope conformation with C5 displaced by −0.346 (3) Å from the least-squares mean plane defined by C4, C3, C2a and C5a [this plane also has an r.m.s. deviation of 0.007 (7) Å]. The dihedral angle between these planes is 7.5 (1)°, so that these two fragments are nearly coplanar. The spiro-linked cyclopentane ring adopts an
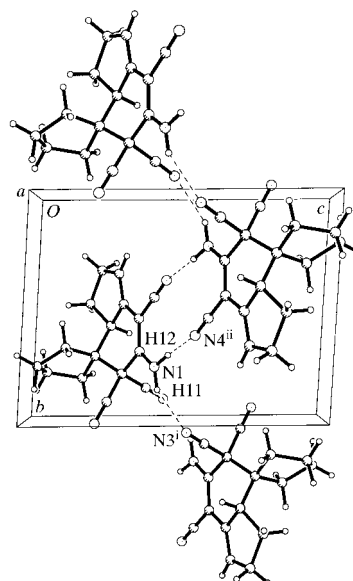

Figure 2
A projection onto the *bc* plane showing the hydrogen-bonding scheme. [Symmetry codes: (i) −*x*, 2 − *y*, 1 − *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*.]

envelope conformation, with C9 located 0.535 (4) Å out of the plane of the other atoms of the ring [this plane has an r.m.s. deviation of 0.005 (8) Å]. The dihedral angle between the cyclopentane ring and the planar region of the cyclohexene ring is 86.98 (9)°. Steric overload in the cyclohexene ring causes increases in the bond lengths C1—C7 and C6—C7 to 1.540 (2) and 1.576 (2) Å, respectively, compared to expected bond lengths of 1.507 for Csp^2—Csp^3 and 1.540 Å for Csp^3—Csp^3 (Allen *et al.*, 1987). It is probable that the electron-acceptor cyano groups on C7 (Fig. 1) also exert an influence on the bond lengths. We have previously observed similar increases in bond lengths (Nesterov, Struchkov *et al.*, 1989; Nesterov, Shklover *et al.*, 1989) as have other authors (Tafeenko *et al.*, 1994) in related compounds.

The intermolecular hydrogen bonding described in Table 2 comprises pairs of pairwise N—H···N interactions [graph-set notation $R_2^2(12)$] which link molecules into infinite chains along [$\bar{1}$10], as shown in Fig. 2.

Experimental

The title compound, (I), was obtained as described by Mirek & Milart (1986). Colourless crystals were obtained by isothermal evaporation from an ethanolic solution of (I).

Crystal data

$C_{16}H_{16}N_4$	$Z = 2$
$M_r = 264.33$	$D_x = 1.286$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.417$ (3) Å	Cell parameters from 24
$b = 8.963$ (4) Å	reflections
$c = 11.902$ (6) Å	$\theta = 11$–12°
$\alpha = 93.35$ (4)°	$\mu = 0.080$ mm^{-1}
$\beta = 90.89$ (4)°	$T = 193$ (2) K
$\gamma = 92.88$ (4)°	Parallelepiped prism, colourless
$V = 682.4$ (6) Å^3	$0.50 \times 0.35 \times 0.25$ mm

Data collection

Siemens *P3*/PC diffractometer	$h = -8 \rightarrow 8$
$\theta/2\theta$ scans	$k = -11 \rightarrow 11$
3498 measured reflections	$l = -15 \rightarrow 15$
3216 independent reflections	3 standard reflections
2400 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{int} = 0.029$	intensity decay: 5%
$\theta_{max} = 28.06°$	

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.20P]$
$wR(F^2) = 0.122$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.024$	$(\Delta/\sigma)_{max} = 0.004$
3216 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
245 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···N3^i	0.93 (2)	2.22 (2)	3.052 (2)	148 (2)
N1—H12···N4^{ii}	0.93 (2)	2.12 (2)	3.038 (2)	166 (2)

Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

The refined C—H distances are in the range 0.94 (2)–1.07 (3) Å.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.338 (2)	C2—C2a	1.441 (2)
N2—C12	1.133 (2)	C2a—C3	1.341 (2)
N3—C13	1.139 (2)	C2a—C5a	1.503 (2)
N4—C14	1.142 (2)	C5a—C6	1.545 (2)
C1—C2	1.370 (2)	C6—C7	1.576 (2)
C1—C7	1.540 (2)	C7—C13	1.485 (2)
C2—C14	1.428 (2)	C7—C12	1.491 (2)
N1—C1—C2	124.95 (13)	C2a—C3—C4	111.59 (15)
N1—C1—C7	116.14 (12)	C2a—C5a—C5	102.55 (13)
C2—C1—C7	118.88 (13)	C2a—C5a—C6	111.08 (12)
C1—C2—C14	117.97 (13)	C5—C5a—C6	118.01 (14)
C1—C2—C2a	123.08 (13)	C5a—C6—C7	105.94 (12)
C14—C2—C2a	118.95 (13)	C1—C7—C6	113.88 (11)
C3—C2a—C2	129.63 (14)	N2—C12—C7	178.54 (17)
C3—C2a—C5a	112.07 (14)	N3—C13—C7	178.55 (16)
C2—C2a—C5a	118.29 (12)	N4—C14—C2	178.71 (17)
C7—C1—C2—C2a	−2.1 (2)	C2—C2a—C5a—C6	39.34 (18)
C1—C2—C2a—C3	174.53 (16)	C4—C5—C5a—C2a	21.11 (17)
C1—C2—C2a—C5a	−6.6 (2)	C2a—C5a—C6—C7	−59.31 (14)
C2a—C3—C4—C5	12.0 (2)	C2—C1—C7—C6	−22.16 (18)
C3—C4—C5—C5a	−20.37 (18)	C5a—C6—C7—C1	51.53 (15)
C3—C2a—C5a—C5	−14.64 (18)		

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