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2-[3-(Pyrrolidin-1-yl)cyclohex-2-en-1-ylidene]propanedinitrile

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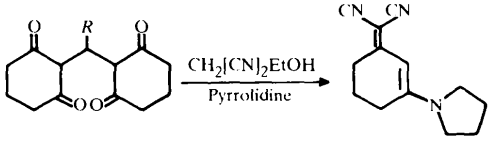
Abstract

In the title compound, $C_{13}H_{15}N_3$, the cyclohexene ring adopts a conformation intermediate between sofa and half-chair, and the substituted pyrrolidine ring assumes a conformation intermediate between envelope and half-chair. The dihedral angle between the pyrrolidine and cyclohexene rings is 7.2 (1)°. The propanedinitrile group occupies the equatorial position with respect to the cyclohexene ring.

Comment

Applications of malononitrile in organic chemistry comprise the synthesis of unique heterocyclic systems, pharmaceuticals, pesticides, fungicides and solvato-chromic dyes (Fatiadi, 1978). The pyrrolidine part of the title compound has useful medicinal properties. Pyrrolidine derivatives inhibit the production of prostaglandin E2 and intracellular phospholipase A2, and are useful for prevention and treatment of rheumatoid arthritis, asthma, allergies, rhinitis and related diseases (Mitsuaki *et al.*, 1997). Some of the aminopyrrolidine products are used as pharmaceutical and agrochemical intermediates (Fumiaki & Shozo, 1997). The pyrrolidine–cyclohexyl compounds act as highly-lipophilic chemically-novel potent selective kappa opioid agonists (Sabin *et al.*, 1997) and were found to be preferential dopamine autoreceptor antagonists (Haekan *et al.*, 1997). Some of the arylpyrrolidine derivatives are used as insecticides, acaricides and herbicides (Santel *et al.*, 1997). In view of the above medicinal significance, the title compound was investigated to define the conformation of the cyclohexene ring with respect to the pyrrolidine ring of the molecule.



(1) $R = H$
(2) $R = CH_3$
(3)

An *ORTEP* drawing (Zsolnai, 1997) of the molecule with atomic numbering scheme is shown in Fig. 1. Cremer & Pople (1975) puckering parameters show that the cyclohexene ring is in a half-chair conformation, distorted towards a half-boat [Q = 0.461 (2) Å, θ = 56.0 (2)° and φ = −111.8 (3)°] (Duax & Norton, 1975; Caracelli *et al.*, 1997). The conformation of the pyrrolidine ring assumes an intermediate between an envelope and a half-chair conformation as seen by the ring puckering parameters [Q = 0.129 (4) Å and φ = 52.1 (1)°] (Zukerman-Schpector *et al.*, 1984). C11 and C12 in the pyrrolidine ring have high anisotropic dis-

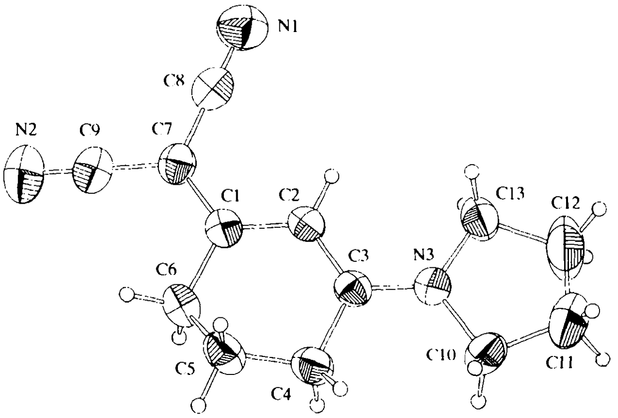


Fig. 1. Molecular structure of the title compound with 50% probability displacement ellipsoids. H atoms have been assigned as circles of an arbitrary radius.

placement parameters. This indicates disorder resulting from some ring motion. As a consequence the C—C distances observed in the pyrrolidine ring are scarcely reliable, but appear shorter than standard values for Csp^3—Csp^3 single-bond distances. The sum of angles at N3, 359.7 (1)°, indicates sp^2 hybridization.

The deviations of C11 and C12 from the plane defined by N3, C10 and C13 are 0.1035 (4) and 0.0907 (4) Å, respectively. The best plane through the pyrrolidine ring makes an angle of 7.2 (1)° with the cyclohexene ring. The propanedinitrile group bonded to C1 is in an equatorial position, while the substituent at C3 is in an axial position. The bond lengths of the triple bonds agree well with reported values [N1≡C8 = 1.146 (3) and N2≡C9 = 1.147 (3) Å], which is found in 3,3-dimethylgutaronitrile and also in 2-anilino-4,6-dimethylpyridine-3-carbonitrile structures (Heroux & Brisse, 1996; Mefetah *et al.*, 1997). The C—N distances [N3—C13 = 1.469 (2) and 1.475 (2) Å] in the pyrrolidine ring agree with literature values of those found in clemizole (Parvez & Sabir, 1996).

The orientation of the pyrrolidine and propanedinitrile group substitutions are described by the torsion angles C2—C3—N3—C10 = −178.7 (2), C4—C3—N3—C13 = 173.3 (2), C1—C7—C8—N1 = −25.7 (7) and C1—C7—C9—N2 = −145.5 (2)° with respect to the cyclohexene ring. The structures are held together by C—H···N-type hydrogen bonds.

Experimental

2,2′-Methylenebis(cyclohexane-1,3-dione) or 2,2′-ethylidinebis(cyclohexane-1,3-dione) was refluxed with malononitrile (4 mmol) in ethanol in the presence of pyrrolidine for 15 h. During the reaction, cyclohexane-1,3-dione probably was generated from (1) and (2) (see scheme) and reacted with pyrrolidine and malononitrile. The product (3) was obtained on concentration of the reaction mixture. Yield 80%, m.p. 498 K. IR (KBr): 2940, 2200, 1540, 1300 cm^{-1}. MS *m/z* 213, 186, 185, 172, 143, 116, 80, 70. The IR spectrum shows the presence of the CN group at 2200 cm^{-1}. The ^{1}H NMR spectrum showed the following signals at δ 1.9 (*m* 6H, C5—CH_2, and C3′ and C4′—CH_2), 2.4-2.6 (*m*, 4H, C4— and C6—CH_2), 3.4 and 3.6 (2*t*, 4H, N—CH_2), 5.5 (*s*, C2—C5) (Murugan & Ramakrishnan, 1998).

Crystal data

$C_{13}H_{15}N_3$
$M_r = 213.28$
Monoclinic
$P2_1/n$
$a = 7.118 (1)$ Å
$b = 20.894 (1)$ Å
$c = 7.768 (2)$ Å
$\beta = 92.20 (3)°$
$V = 1154.4 (3)$ Å^3
$Z = 4$
$D_x = 1.227$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 5–11°$
$\mu = 0.588$ mm^{-1}
$T = 293 (2)$ K
Parallelepiped
0.51 × 0.44 × 0.42 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2507 measured reflections
2341 independent reflections
2193 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$

$\theta_{max} = 75.53°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 26$
$l = -9 \rightarrow 8$
3 standard reflections every 100 reflections frequency: 60 min intensity decay: <0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.188$
$S = 0.994$
2330 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.4176P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.256$ e Å^{-3}
$\Delta\rho_{min} = -0.388$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0258 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C8	1.146 (3)	C3—C4	1.501 (2)
N2—C9	1.147 (3)	C4—C5	1.517 (3)
N3—C13	1.469 (2)	C5—C6	1.513 (2)
N3—C10	1.475 (2)	C7—C9	1.417 (2)
C1—C2	1.390 (2)	C7—C8	1.426 (3)
C1—C7	1.401 (2)	C10—C11	1.495 (3)
C1—C6	1.501 (2)	C11—C12	1.399 (4)
C2—C3	1.394 (2)	C12—C13	1.493 (3)
C3—N3—C13	123.57 (14)	N1—C8—C7	179.3 (2)
C3—N3—C10	125.03 (15)	N2—C9—C7	179.4 (2)
C13—N3—C10	111.11 (14)	N3—C10—C11	103.6 (2)
N3—C3—C2	121.88 (14)	N3—C13—C12	104.2 (2)
N3—C3—C4	117.97 (14)		
C10—N3—C3—C2	−178.7 (2)	C2—C1—C7—C8	−1.8 (2)
C13—N3—C3—C4	173.3 (2)	C6—C1—C7—C8	179.9 (15)
C1—C2—C3—N3	174.04 (15)	C1—C7—C8—N1	−25.7 (17)
N3—C3—C4—C5	160.57 (15)	C1—C7—C9—N2	−145.5 (2)
C2—C1—C7—C9	177.1 (2)	C10—C11—C12—C13	14.9 (5)
C6—C1—C7—C9	−1.1 (2)		

H atoms were refined with fixed geometry (C—H 0.93–0.97 Å), each riding on a carrier atom, with fixed isotropic displacement parameters 1.2 (for all H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they were attached.

Data collection: *SDP* (Frenz, 1989). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ZORTEP*. Software used to prepare material for publication: *SHELXL*93, *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1029). Services for accessing these data are described at the back of the journal.

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A mesogenic alkenyl compound

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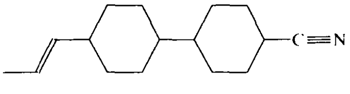
Abstract

In the title compound, 4′-propen-1-ylbicyclohexane-4-carbonitrile, $C_{16}H_{25}N$, both cyclohexane rings adopt chair conformations. The dihedral angle between the rings is 105.90 (5)°. The normals to the least-squares mean planes through the propenyl chain and the adjacent cyclohexane ring make an angle of 97.95 (15)°. Molecules of the compound are packed along the *c* axis. The molecular arrangement is a precursor of a nematic phase.

Comment

The title compound has been reported as a new type of liquid-crystal compound (Schadt *et al.*, 1989). The introduction of a double bond at specific side-chain positions markedly affects the properties of liquid crystals. Different experimental techniques have been applied to these compounds (Schadt *et al.*, 1989; Nath *et al.*, 1995). Upon heating it adopts a nematic liquid-crystal phase from 64.9° until it becomes isotropic at 99.7°. As part of our program to solve the structures of the homologous series of cyanoalkenyl compounds (Gupta *et al.*, 1994), and in order to clarify the precise relationship between nematic structure and the molecular interactions, we have studied the title compound (designated as 1d1CC).



1d1CC

The compound can be considered in three parts, namely the alkenyl chain, the central core and the cyano group (Fig. 1). Both cyclohexane rings adopt chair conformations. The dihedral angle between the rings is 105.90 (5)°. The normals to the least-squares mean planes through the propenyl chain and the adjacent cyclohexane ring make an angle of 97.95 (15)°. Atom C16 of the cyano group is displaced slightly upwards from the plane of the cyclohexane ring *B* (C10–C15) whereas C7 is displaced slightly downwards. The alkenyl-group atom C3 is displaced downwards and C10 is displaced upwards from the plane of the cyclohexane ring *A* (C4–C9). The puckering parameters of the six-

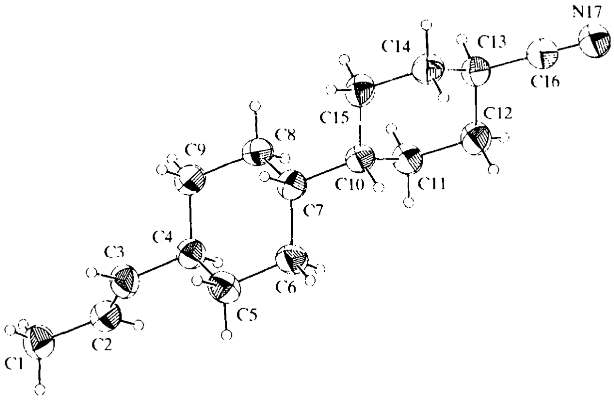


Fig. 1. Perspective drawing (*ZORTEP*; Zsolnai & Huttner, 1994) of the title compound showing the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have an arbitrary radius.