The project has been supported by the A. Messer Foundation, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fonds der Chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-(4aα,4bβ,10bβ,12aβ)-9-Bromo-2-methyl-1,2,3,4,4a,4b,5,6,10b,11,12,12a-dodecahydronaphtho[2,1-*f*]isoquinoline Formed from the Acid-Catalyzed Cyclization of 5-[2-(4-Bromophenyl)ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline

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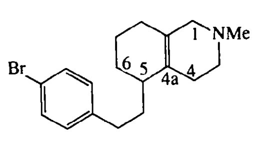
Abstract

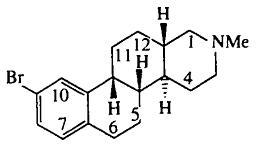
The title compound, $C_{18}H_{24}BrN$, was produced by treating 5-[2-(4-bromophenyl)ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline with 48% hydrobromic acid. Cyclization took place between position 2 of the aromatic ring and position 6 of the octahydroisoquinoline ring, following acid-catalyzed isomerization of the double bond.

Comment

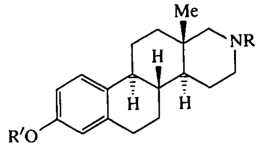
The acid-catalyzed cyclization of 5-[2-(4-bromophenyl)ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline, (1), could potentially give a variety of cyclized products. NMR studies ruled out cyclization at position 4a of the octahydroisoquinoline ring system since there was no aliphatic quaternary signal present in the ^{13}C NMR spectrum. Further studies involving 2D-COSY and HETCOR spectral techniques suggested that the cyclized product was (±)-(4aα,4bβ,10bβ,12aβ)-9-bromo-2-methyl-1,2,3,4,4a,4*b*,5,6,10*b*,11,12,12a-dodecahydronaphtho[2,1-*f*]isoquinoline, (2), and this was confirmed by the X-ray crystallographic analysis described in this paper.



(1)



(2)



(3)

The tetracyclic structure (2) was formed as a result of cyclization between the 2 position of the aromatic ring and the 6 position of the octahydroisoquinoline ring system. This is made possible by an acid-catalyzed isomerization of the double bond from the $\Delta^{4a,8a}$ to the

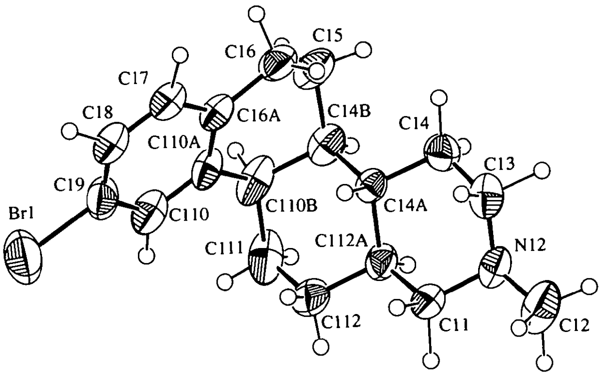


Fig. 1. A view of one of the independent molecules showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

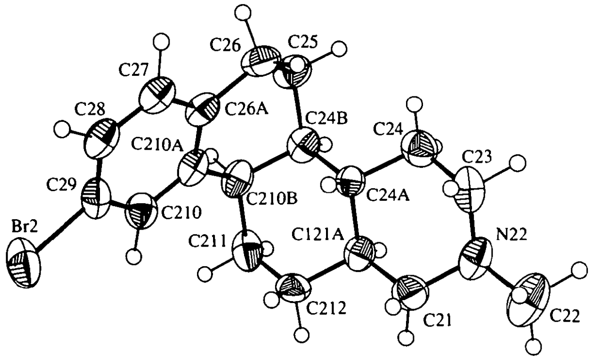


Fig. 2. A view of the second independent molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii.

$\Delta^{5,6}$ position. The structure obtained is a configurational isomer of the known 17-aza-D-homo-1,3,5(10)-triene ring system (3) (Matkovics, Tarodi & Belaspira, 1974). Displacement ellipsoid plots of the two independent molecules are shown in Figs. 1 and 2.

Some concern was expressed by a referee as to whether there might be some missing symmetry element relating the two independent molecules, as there appears to be a glide relationship between them as seen in Fig. 3. To address this possibility, we first checked the cell itself by mounting another crystal of the same compound on a Philips PW1100/20 diffractometer, locating 25 reflections and indexing the cell using Philips PW1100/20 software. This new cell matched the original. *CREDUC* (Le Page, 1982), with the slightly different cell dimensions, again did not reveal any cell of higher symmetry. Secondly, we used the program *MISSYM* (Le Page, 1987) within *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) to search for missing symmetry or pseudosymmetry elements between the atoms within the unit cell, but none were found.

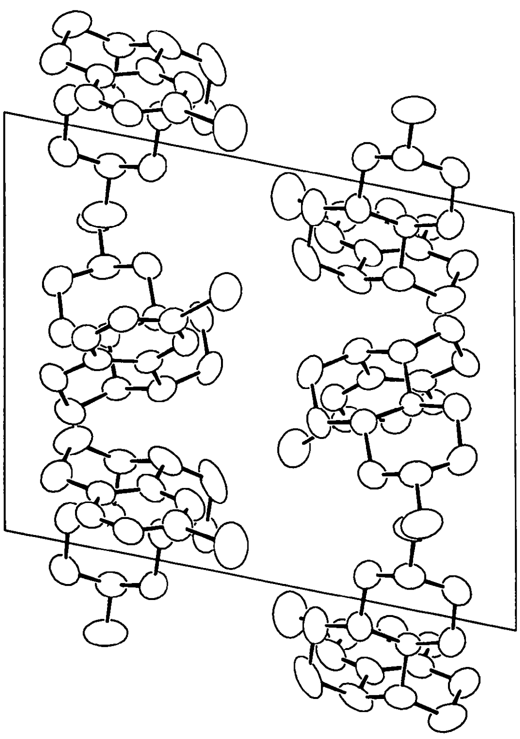


Fig. 3. Packing diagram showing the contents of one unit cell of the title compound. The origin is in the lower-left-hand corner, **a** is directed into the page, **b** vertically upwards and **c** horizontally.

Experimental

The title compound was prepared from 5-[2-(4-bromophenyl)-ethyl]-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline by treatment with 48% HBr. The product was crystallized from petroleum ether (333–353 K).

Crystal data

$C_{18}H_{24}BrN$
$M_r = 334.30$
Triclinic
$P\bar{1}$
$a = 10.848\,(1)$ Å
$b = 10.974\,(1)$ Å
$c = 14.109\,(2)$ Å
$\alpha = 100.93\,(1)^\circ$
$\beta = 104.05\,(1)^\circ$
$\gamma = 90.05\,(1)^\circ$
$V = 1597.9\,(3)$ Å^3
$Z = 4$
$D_x = 1.389$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 12 reflections
$\theta = 16.5–20^\circ$
$\mu = 2.54$ mm^{-1}
$T = 298$ K
Block
$0.26 \times 0.24 \times 0.13$ mm
Colourless

Data collection

Picker FACS-I diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.543$, $T_{\max} = 0.739$
4167 measured reflections
4167 independent reflections

2732 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 22.5^\circ$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 100 reflections intensity decay: 2%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.048$
$S = 1.56$
2732 reflections
361 parameters
H atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.16$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br(1)	0.67192 (6)	0.93167 (8)	0.55781 (5)	0.1012 (5)
C(11)	0.0254 (4)	1.0635 (5)	0.7102 (4)	0.052 (3)
N(12)	−0.0355 (4)	1.0805 (4)	0.7924 (3)	0.052 (2)
C(12)	−0.0949 (5)	1.1996 (5)	0.8042 (5)	0.081 (4)
C(13)	0.0541 (5)	1.0677 (5)	0.8842 (4)	0.059 (3)
C(14)	0.1110 (5)	0.9414 (5)	0.8753 (4)	0.055 (3)
C(14*A*)	0.1743 (4)	0.9152 (4)	0.7893 (3)	0.039 (2)
C(14*B*)	0.2263 (4)	0.7848 (4)	0.7743 (4)	0.053 (3)
C(15)	0.3212 (5)	0.7575 (5)	0.8666 (5)	0.069 (3)
C(16)	0.4354 (4)	0.8485 (5)	0.8988 (4)	0.060 (3)
C(16*A*)	0.4877 (4)	0.8681 (4)	0.8122 (4)	0.047 (3)
C(17)	0.6109 (4)	0.9245 (4)	0.8332 (4)	0.051 (3)
C(18)	0.6655 (4)	0.9446 (5)	0.7590 (4)	0.053 (3)
C(19)	0.5968 (5)	0.9085 (5)	0.6629 (4)	0.060 (3)
C(110)	0.4749 (5)	0.8533 (5)	0.6383 (4)	0.061 (3)
C(110*A*)	0.4196 (4)	0.8327 (4)	0.7136 (4)	0.048 (3)
C(110*B*)	0.2897 (4)	0.7624 (5)	0.6862 (4)	0.061 (3)
C(111)	0.1971 (5)	0.7883 (6)	0.5929 (4)	0.077 (3)
C(112)	0.1448 (5)	0.9170 (5)	0.6079 (4)	0.065 (3)
C(112*A*)	0.0804 (4)	0.9357 (4)	0.6942 (4)	0.048 (3)
Br(2)	−0.15480 (5)	0.67152 (6)	0.43278 (5)	0.0754 (4)
C(21)	0.4784 (5)	0.6969 (5)	0.2789 (4)	0.054 (3)
N(22)	0.5352 (4)	0.6747 (4)	0.1946 (3)	0.055 (2)
C(22)	0.5936 (5)	0.7890 (5)	0.1835 (5)	0.080 (4)
C(23)	0.4406 (5)	0.6194 (5)	0.1042 (4)	0.059 (3)
C(24)	0.3873 (5)	0.4972 (5)	0.1137 (4)	0.054 (3)
C(24*A*)	0.3268 (4)	0.5109 (4)	0.2017 (3)	0.038 (2)
C(24*B*)	0.2770 (4)	0.3878 (4)	0.2187 (4)	0.046 (3)
C(25)	0.1825 (4)	0.3112 (5)	0.1277 (4)	0.056 (3)
C(26)	0.0662 (5)	0.3848 (4)	0.0959 (4)	0.055 (3)
C(26*A*)	0.0142 (4)	0.4495 (4)	0.1815 (4)	0.045 (3)
C(27)	−0.1065 (4)	0.4955 (4)	0.1594 (4)	0.049 (3)
C(28)	−0.1594 (4)	0.5580 (5)	0.2325 (4)	0.051 (3)
C(29)	−0.0878 (5)	0.5775 (4)	0.3298 (4)	0.049 (3)
C(210)	0.0326 (4)	0.5320 (4)	0.3544 (4)	0.047 (3)
C(210*A*)	0.0848 (4)	0.4673 (4)	0.2813 (4)	0.043 (2)
C(210*B*)	0.2158 (4)	0.4082 (4)	0.3077 (4)	0.049 (3)
C(211)	0.3106 (4)	0.4807 (5)	0.4011 (4)	0.056 (3)
C(212)	0.3642 (4)	0.5994 (5)	0.3843 (4)	0.051 (3)
C(212*A*)	0.4244 (4)	0.5767 (4)	0.2960 (4)	0.044 (2)

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—C(19)	1.912 (7)	C(11)—N(12)	1.452 (7)
C(11)—C(112*A*)	1.523 (7)	N(12)—C(12)	1.456 (7)
N(12)—C(13)	1.449 (7)	C(13)—C(14)	1.514 (7)
C(14)—C(14*A*)	1.517 (8)	C(14*A*)—C(14*B*)	1.535 (6)
C(14*A*)—C(112*A*)	1.530 (6)	C(14*B*)—C(15)	1.531 (8)
C(14*B*)—C(110*B*)	1.543 (9)	C(15)—C(16)	1.513 (7)
C(16)—C(16*A*)	1.515 (9)	C(16*A*)—C(17)	1.412 (7)
C(16*A*)—C(110*A*)	1.389 (7)	C(17)—C(18)	1.373 (9)
C(18)—C(19)	1.362 (7)	C(19)—C(110)	1.390 (7)
C(110)—C(110*A*)	1.392 (9)	C(110*A*)—C(110*B*)	1.533 (7)
C(110*B*)—C(111)	1.523 (8)	C(111)—C(112)	1.519 (9)
C(112)—C(112*A*)	1.527 (8)	Br(2)—C(29)	1.911 (5)
C(21)—N(22)	1.450 (8)	C(21)—C(212*A*)	1.526 (7)
N(22)—C(22)	1.457 (8)	N(22)—C(23)	1.455 (6)
C(23)—C(24)	1.501 (8)	C(24)—C(24*A*)	1.523 (7)
C(24*A*)—C(24*B*)	1.536 (7)	C(24*A*)—C(212*A*)	1.537 (5)
C(24*B*)—C(25)	1.535 (6)	C(24*B*)—C(210*B*)	1.539 (8)
C(25)—C(26)	1.520 (7)	C(26)—C(26*A*)	1.513 (7)
C(26*A*)—C(27)	1.389 (7)	C(26*A*)—C(210*A*)	1.407 (7)
C(27)—C(28)	1.373 (8)	C(28)—C(29)	1.379 (7)
C(29)—C(210)	1.386 (7)	C(210)—C(210*A*)	1.376 (7)
C(210*A*)—C(210*B*)	1.554 (6)	C(210*B*)—C(211)	1.540 (6)
C(211)—C(212)	1.507 (8)	C(212)—C(212*A*)	1.522 (7)

N(12)—C(11)—C(112*A*)	111.4 (4)
C(11)—N(12)—C(13)	110.9 (4)
N(12)—C(13)—C(14)	111.6 (4)
C(14)—C(14*A*)—C(14*B*)	113.2 (4)
C(14*B*)—C(14*A*)—C(112*A*)	110.9 (4)
C(11)—N(12)—C(12)	111.7 (5)
C(12)—N(12)—C(13)	110.8 (4)
C(13)—C(14)—C(14*A*)	111.8 (5)
C(14)—C(14*A*)—C(112*A*)	109.3 (4)
C(14*A*)—C(14*B*)—C(15)	113.9 (4)
C(14*A*)—C(14*B*)—C(110*B*)	111.3 (4)
C(14*B*)—C(15)—C(16)	111.3 (5)
C(16)—C(16*A*)—C(17)	118.4 (4)
C(17)—C(16*A*)—C(110*A*)	118.9 (5)
C(17)—C(18)—C(19)	117.9 (5)
Br(1)—C(19)—C(110)	118.8 (4)
C(19)—C(110)—C(110*A*)	119.7 (5)
C(16*A*)—C(110*A*)—C(110*B*)	121.1 (5)
C(14*B*)—C(110*B*)—C(110*A*)	111.3 (4)
C(110*A*)—C(110*B*)—C(111)	115.1 (5)
C(111)—C(112)—C(112*A*)	110.5 (5)
C(11)—C(112*A*)—C(112)	111.7 (5)
N(22)—C(21)—C(212*A*)	111.7 (4)
C(21)—N(22)—C(23)	110.3 (4)
N(22)—C(23)—C(24)	110.9 (5)
C(24)—C(24*A*)—C(24*B*)	114.2 (4)
C(24*B*)—C(24*A*)—C(212*A*)	110.0 (4)
C(24*A*)—C(24*B*)—C(210*B*)	111.6 (4)
C(24*B*)—C(25)—C(26)	110.4 (4)
C(26)—C(26*A*)—C(27)	118.0 (4)
C(27)—C(26*A*)—C(210*A*)	119.5 (5)
C(27)—C(28)—C(29)	118.1 (4)
Br(2)—C(29)—C(210)	119.2 (4)
C(29)—C(210)—C(210*A*)	120.4 (4)
C(26*A*)—C(210*A*)—C(210*B*)	119.9 (4)
C(24*B*)—C(210*B*)—C(210*A*)	111.0 (4)
C(210*A*)—C(210*B*)—C(211)	114.5 (4)
C(211)—C(212)—C(212*A*)	112.0 (4)
C(21)—C(212*A*)—C(212)	112.0 (4)
C(15)—C(14*B*)—C(110*B*)	108.6 (4)
C(15)—C(16)—C(16*A*)	112.6 (4)
C(16)—C(16*A*)—C(110*A*)	122.7 (4)
C(16*A*)—C(17)—C(18)	121.9 (4)
Br(1)—C(19)—C(18)	118.9 (4)
C(18)—C(19)—C(110)	122.4 (6)
C(16*A*)—C(110*A*)—C(110)	119.1 (4)
C(110)—C(110*A*)—C(110*B*)	119.6 (4)
C(14*B*)—C(110*B*)—C(111)	109.8 (4)
C(110*B*)—C(111)—C(112)	113.1 (4)
C(11)—C(112*A*)—C(14*A*)	110.9 (4)
C(14*A*)—C(112*A*)—C(112)	110.1 (4)
C(21)—N(22)—C(22)	110.9 (4)
C(22)—N(22)—C(23)	111.2 (5)
C(23)—C(24)—C(24*A*)	111.8 (4)
C(24)—C(24*A*)—C(212*A*)	108.7 (4)
C(24*A*)—C(24*B*)—C(25)	114.6 (4)
C(25)—C(24*B*)—C(210*B*)	108.8 (4)
C(25)—C(26)—C(26*A*)	113.8 (4)
C(26)—C(26*A*)—C(210*A*)	122.4 (4)
C(26*A*)—C(27)—C(28)	121.7 (5)
Br(2)—C(29)—C(28)	119.3 (4)
C(28)—C(29)—C(210)	121.5 (5)
C(26*A*)—C(210*A*)—C(210)	118.7 (4)
C(210)—C(210*A*)—C(210*B*)	121.3 (4)
C(24*B*)—C(210*B*)—C(211)	109.8 (4)
C(210*B*)—C(211)—C(212)	112.9 (4)
C(21)—C(212*A*)—C(24*A*)	110.6 (4)
C(24*A*)—C(212*A*)—C(212)	110.1 (4)

The cell was identified on the basis of X-ray photographs and transformed into a standard reduced cell with the aid of *CREDUC* (Le Page, 1982) within *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Intensity data were collected with scan widths of (1.6 + 0.692tanθ)° in 2θ, a 2θ scan rate of 2° min^{-1} and background counts of 10 s at each end of every scan. All H atoms were located in the ΔF map and included in structure-factor calculations but not refined. Refinement was by full-matrix least-squares methods.

Data collection: Picker DOS operating system. Cell refinement: Picker DOS operating system. Data reduction:

Xtal2.6 DIFDAT (Hall & Stewart, 1989). Structure solution: *SHELXS86* (Sheldrick, 1985). Structure refinement: *Xtal2.6 CRYLSQ*. Molecular graphics: *Xtal2.6*. Preparation of material for publication: *Xtal2.6 BONDLA*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Dodecylpyridinium Chloride Monohydrate

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Abstract

The molecular and crystal structure of 1-dodecylpyridinium chloride monohydrate, $C_{17}H_{30}N^+.Cl^-.H_2O$, has been determined. It was found that the hydrocarbon chains are arranged in a parallel fashion and that they interlink in a bimolecular layer. The conformation of the hydrocarbon chain is almost completely *trans*-planar with a mean deviation from the plane of 0.005 Å. The pyridine ring also has a mean deviation of 0.005 Å. The angle between the planes of the hydrocarbon chain and the pyridine ring is 79.16°.

Comment

Structural knowledge of molecular aggregation is important for the understanding of chemical and physical properties, as well as other related phenomena. 1-Dodecylpyridinium chloride, (I), is a cationic amphiphilic molecule which possesses a non-polar hydrocarbon chain ending with a methyl group, nitrogen as the element capable of forming an 'onium' structure, and chloride as the counterion. It has a critical micelle concentration (CMC) of 1.5×10^{-2} mol dm^{-3} at 298 K. Furthermore, it can form thin films by solvent evaporation. The present work was aimed at elucidating the molecular aggregation of this compound in the crystalline phase.

(I)

The observed density suggested the presence of one water molecule for each 1-dodecylpyridinium chloride molecule. The molecular structure exhibits normal geometry. The average C—C bond length found in the hydrocarbon chain is 1.529 (7) Å and the average C—C—C bond angle is 111.9 (12)°. These values are close to those found in other long-chain structures, *e.g.* 1.523 (6) Å and 113.8 (3)° for *n*-dodecylammonium bromide (Lundén, 1974), and 1.523 (8) Å and 113.2 (5)° for hexadecyltrimethylammonium bromide (Campanelli & Scaramuzza, 1986).

The torsion angles in the hydrocarbon chain show that the largest deviation from the *trans*-conformation is 179.0 (4)° for N—C6—C7—C8. The molecular packing is governed by coulombic and van der Waals inter-

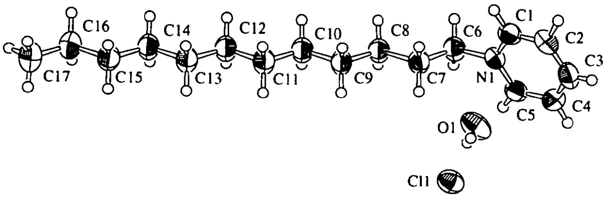

Fig. 1. The molecular structure of 1-dodecylpyridinium chloride monohydrate with the atomic numbering scheme and non-H atoms represented by 50% probability ellipsoids.

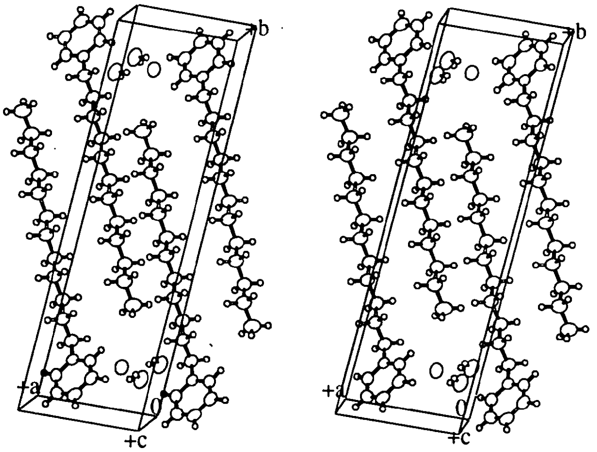

Fig. 2. Stereoview of the crystal structure of the title compound.