

quantities, termed d_1 and γ_1 in previous papers (Williams *et al.*, 1979; Fisher *et al.*, 1979), correspond to b and the angle between the diacetylene axis and the b axis in BBS. The b axis in BBS is 5.028 Å and the estimated range of angles between the diacetylene units and the b axis for reactivity is 40 to 49°. The actual value of the angle is 65.6° which is clearly outside this range, in contrast to the reactive ditosylate (TS) derivative.

This work was supported by grants from the SERC and The Royal Society. One of us (RLW) thanks the SERC for a studentship.

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Acta Cryst. (1982). **B38**, 2080–2082

Structure of 4-Ethoxyindeno[1,2-*d*]azepine

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(Received 8 January 1981; accepted 23 February 1982)

Abstract. C₁₅H₁₃NO, m.p. 388–390 K, monoclinic, $P2_1/a$, $a = 23.752$ (4), $b = 5.834$ (1), $c = 8.485$ (2) Å, $\beta = 92.22$ (2)°, $V = 1174.8$ (4) Å³, $D_m = 1.268$, $D_x = 1.262$ Mg m⁻³, $Z = 4$. Final $R = 0.044$ for 1650 non-zero reflexions. The indenoazepine ring is planar within 0.102 (2) Å, the azepine ring taking a twist-boat conformation. The bond alternation in the azaazulene ring is more remarkable than in the azulene ring. The observed bond lengths are in agreement with those calculated by the LCAO–SCF–MO method.

Introduction. 4-Ethoxyindeno[1,2-*d*]azepine (1) is a novel non-benzenoid aromatic compound, whose NMR and electronic spectra suggest the presence of a fully conjugated 14 π ring system (Kimura, Satake & Morosawa, 1979). The present study has been undertaken in order to determine the precise molecular

structure of (1), which has an electron-withdrawing >C=N– bond in the seven-membered ring.

Crystals were grown from an acetone solution by slow evaporation as purplish-blue plates with developed faces {100}. The intensity data were collected with a specimen of 0.15 × 0.25 × 0.13 mm on a Rigaku four-circle diffractometer. The intensities were measured up to $2\theta = 120^\circ$ with the ω – 2θ scan method (scan speed 4° min⁻¹ in 2θ ; scan range in 2θ : 1.2 + 0.15 tan θ) using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at 40 kV and 200 mA. Background was measured for 4 s on either side of the peak. In total 1754 reflexions were collected, of which 1650 non-zero reflexions were used in the refinement. The intensities were corrected for Lorentz and polarization factors, but not for absorption [$\mu(\text{Cu } K\alpha) = 0.59$ mm⁻¹].

The structure was solved by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by a block-diagonal least-squares method

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Table 1. Final atomic parameters (positional $\times 10^4$, for H $\times 10^3$) with e.s.d.'s in parentheses
$$B_{eq} = \frac{4}{3} (\sum_i \beta_{ii}/a_i^2).$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B_{iso} (\AA^2)
C(1)	7271.7 (7)	3973 (3)	8686 (2)	4.17 (8)
C(2)	6723.3 (8)	3540 (4)	9104 (2)	4.75 (9)
C(3)	6453.5 (8)	1527 (4)	8620 (2)	5.08 (9)
C(4)	6716.6 (8)	-90 (4)	7713 (2)	4.89 (9)
C(5)	7654.5 (8)	-1004 (3)	6381 (2)	4.45 (9)
C(6)	8633.0 (9)	-540 (3)	5444 (2)	4.78 (9)
C(7)	9133.9 (9)	526 (4)	5379 (2)	5.19 (10)
N(8)	9359.2 (6)	2427 (3)	6141 (2)	5.02 (8)
C(9)	9094.5 (7)	3783 (3)	7049 (2)	4.21 (8)
C(10)	8514.0 (7)	3868 (3)	7512 (2)	4.07 (8)
C(11)	7268.7 (7)	324 (3)	7291 (2)	4.05 (8)
C(12)	8154.5 (8)	126 (3)	6306 (2)	4.00 (8)
C(13)	8112.8 (7)	2288 (3)	7210 (2)	3.62 (7)
C(14)	7541.5 (7)	2359 (3)	7784 (2)	3.70 (7)
O(15)	9380.4 (5)	5541 (2)	7766 (2)	4.89 (6)
C(16)	9965.7 (8)	5850 (4)	7406 (3)	5.62 (11)
C(17)	10180.3 (9)	7759 (4)	8437 (3)	6.23 (12)
H(1)	747.5 (7)	541 (3)	898 (2)	2.4 (4)
H(2)	652.2 (7)	470 (3)	975 (2)	3.0 (4)
H(3)	606.9 (8)	128 (3)	892 (2)	3.2 (4)
H(4)	651.4 (8)	-155 (4)	739 (2)	3.7 (5)
H(5)	757.6 (8)	-250 (4)	590 (2)	3.5 (5)
H(6)	860.7 (8)	-205 (3)	477 (2)	3.0 (4)
H(7)	943.0 (9)	-30 (4)	468 (3)	5.1 (6)
H(10)	842.3 (7)	525 (3)	815 (2)	2.2 (4)
H(16A)	997.8 (9)	616 (4)	627 (2)	4.1 (5)
H(16B)	1017.5 (9)	434 (4)	757 (3)	4.7 (5)
H(17A)	996.0 (9)	916 (4)	822 (3)	4.9 (5)
H(17B)	1057.6 (10)	815 (4)	814 (3)	5.5 (6)
H(17C)	1017.1 (11)	733 (5)	954 (3)	6.9 (7)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

The observed bond lengths are compared with the theoretical values derived from the LCAO-SCF-MO method.

C(14)-C(1)	1.386 (3)	1.40	C(12)-C(6)	1.429 (3)	1.45
C(1)-C(2)	1.386 (3)	1.39	C(6)-C(7)	1.345 (3)	1.36
C(2)-C(3)	1.392 (3)	1.40	C(7)-N(8)	1.381 (3)	1.38
C(3)-C(4)	1.382 (3)	1.39	N(8)-C(9)	1.285 (3)	1.30
C(4)-C(11)	1.394 (3)	1.41	C(9)-C(10)	1.449 (3)	1.45
C(11)-C(14)	1.408 (3)	1.41	C(10)-C(13)	1.343 (3)	1.36
C(11)-C(5)	1.446 (3)	1.45	C(9)-O(15)	1.361 (2)	1.34
C(5)-C(12)	1.362 (3)	1.37	O(15)-C(16)	1.446 (2)	-
C(12)-C(13)	1.482 (3)	1.47	C(16)-C(17)	1.494 (4)	-
C(13)-C(14)	1.460 (3)	1.46			
C(14)-C(1)-C(2)	118.5 (2)		C(7)-N(8)-C(9)	125.8 (2)	
C(1)-C(2)-C(3)	120.3 (2)		N(8)-C(9)-C(10)	132.5 (2)	
C(2)-C(3)-C(4)	121.8 (2)		C(9)-C(10)-C(13)	126.9 (2)	
C(3)-C(4)-C(11)	118.4 (2)		C(10)-C(13)-C(12)	128.5 (2)	
C(4)-C(11)-C(14)	119.8 (2)		C(13)-C(12)-C(6)	124.5 (2)	
C(11)-C(14)-C(1)	121.3 (2)		C(1)-C(14)-C(13)	131.2 (2)	
C(11)-C(5)-C(12)	109.7 (2)		C(4)-C(11)-C(5)	131.8 (2)	
C(5)-C(12)-C(13)	108.2 (2)		C(5)-C(12)-C(6)	127.2 (2)	
C(12)-C(13)-C(14)	106.2 (2)		C(10)-C(13)-C(14)	125.4 (2)	
C(13)-C(14)-C(11)	107.5 (2)		N(8)-C(9)-O(15)	119.0 (2)	
C(14)-C(11)-C(5)	108.5 (2)		C(10)-C(9)-O(15)	108.5 (2)	
C(12)-C(6)-C(7)	128.1 (2)		C(9)-O(15)-C(16)	117.8 (1)	
C(6)-C(7)-N(8)	132.8 (2)		O(15)-C(16)-C(17)	106.2 (2)	

Table 3. The least-squares planes and displacements (\AA) of the atoms from the planes

$$X = ax + cz \cos \beta, Y = by, Z = cz \sin \beta.$$

(A) Six-membered ring

$$0.311X - 0.458Y + 0.833Z - 10.353 = 0$$

C(14)*	0.001 (2)	C(4)*	-0.003 (3)
C(1)*	-0.002 (3)	C(11)*	0.001 (3)
C(2)*	0.000 (2)	C(5)	0.007 (3)
C(3)*	0.002 (2)	C(13)	0.043 (3)

(B) Five-membered ring

$$0.296X - 0.464Y + 0.835Z - 10.099 = 0$$

C(11)*	0.006 (3)	C(1)	-0.006 (4)
C(5)*	0.001 (3)	C(4)	0.025 (4)
C(12)*	-0.007 (3)	C(6)	-0.092 (4)
C(13)*	0.010 (3)	C(10)	0.074 (4)
C(14)*	-0.010 (3)		

(C) Seven-membered ring

$$0.273X - 0.526Y + 0.805Z - 9.447 = 0$$

C(12)*	0.058 (2)	C(10)*	-0.045 (2)
C(6)*	-0.007 (2)	C(13)*	-0.024 (2)
C(7)*	-0.053 (2)	C(5)	0.131 (3)
N(8)*	0.023 (2)	C(14)	-0.030 (3)
C(9)*	0.047 (2)	O(15)	0.176 (2)

Dihedral angles ($^\circ$) between the planes

(A) and (B)	0.95 (12)	(B) and (C)	4.14 (7)
(A) and (C)	4.72 (6)		

* Atoms used for the calculation of the planes.

(Ashida, 1979). Including all the H atoms, found on a difference Fourier map, the refinements gave a final *R* of 0.044 for 1650 non-zero reflexions. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1.0$ for $0 < |F_o| \leq 15.0$ and $(15.0/|F_o|)^2$ for $|F_o| > 15.0$.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Computations were carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

The final atomic parameters are listed in Table 1.* A projection of the crystal structure viewed along **b** and numbering of the atoms are shown in Fig. 1. Bond lengths and angles are given in Table 2, and the displacements of atoms from the least-squares planes in Table 3.

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36754 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

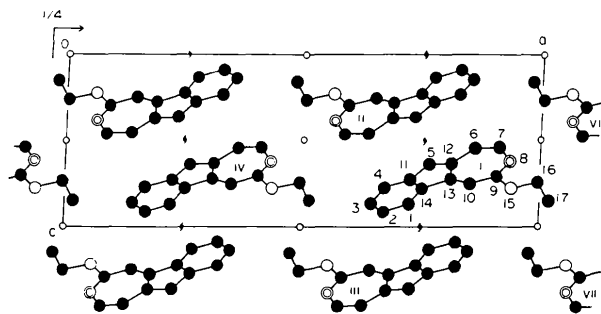


Fig. 1. Projection of the crystal structure along b , and numbering of the atoms (O: O, \odot : N, \bullet : C). The H atoms are omitted. Symmetry code: (i) x, y, z ; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} + y, 2 - z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (v) $x, 1 + y, z$; (vi) $2 - x, 1 - y, 1 - z$; (vii) $2 - x, 1 - y, 2 - z$.

Discussion. The endocyclic bond lengths are in agreement with those from the LCAO-SCF-MO calculation (Table 2). The bond alternation in the azaazulene ring is more remarkable than that in azulene derivatives (Fallon & Ammon, 1974; Ammon & Sundaralingam, 1966) and 6-dimethylamino-5-azaazulene (Lindner, 1969). The seven-membered ring takes a twist-boat conformation (Table 4), whose characteristic feature has been described in terms of the endocyclic torsion angles for cycloheptane (Hendrickson, 1961). The N(8), C(9) and C(12) atoms deviate upward from the ring plane. The torsion angles around the shorter bonds are smaller than those around the longer bonds. The C(12)-C(13) length corresponds to that for a $C(sp^2)-C(sp^2)$ single bond. The C(9)-C(10) and C(6)-C(12) lengths are shorter than that, but longer than the others. The five-membered ring has a slight but significant puckering to take a half-chair (C_2) conformation, the twofold axis passing through C(5) and the midpoint of C(13) and C(14). The six-membered ring is planar within the experimental error. The C(11)-C(14) bond is significantly longer than the C(3)-C(4) bond. On the basis of these structural aspects, the indenoazepine ring is better described as a resonance hybrid of the fully conjugated 14π ring structures (I), (II) and (III) (Kimura *et al.*, 1979). The ring system is planar within $0.102(2)$ Å as a whole.

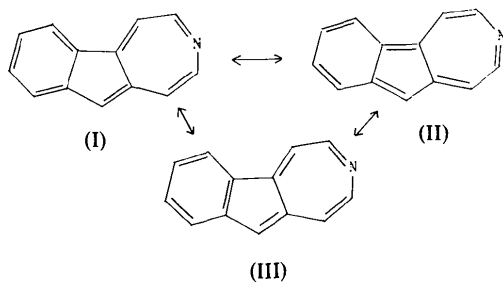


Table 4. The endocyclic torsion angles ($^\circ$) in the seven-membered ring

C(12)-C(6)-C(7)-N(8)	4.3 (4)	C(9)-C(10)-C(13)-C(12)	-1.9 (4)
C(6)-C(7)-N(8)-C(9)	-6.6 (4)	C(10)-C(13)-C(12)-C(6)	-6.7 (3)
C(7)-N(8)-C(9)-C(10)	-2.7 (4)	C(13)-C(12)-C(6)-C(7)	5.2 (3)
N(8)-C(9)-C(10)-C(13)	8.6 (4)		

The inner angles at C(1) and C(4) are smaller than the sp^2 angle as commonly observed in a benzene ring fused with a five-membered ring (Ito, Moriya, Kashino & Haisa, 1975). With respect to the conformation of the ethoxy group $\tau[N(8)-C(9)-O(15)-C(16)] = 2.8(3)^\circ$ and $\tau[C(9)-O(15)-C(16)-C(17)] = -175.8(2)^\circ$. There are no significant differences in the O-C lengths and C-O-C angle from those observed in aromatic ethers (Haisa & Kashino, 1977).

In the crystal the molecules related by a 2_1 axis are arranged in an alternate hexagonal array to form a sheet parallel to (100). The dihedral angle between the indenoazepine rings in the sheet is $59.25(4)^\circ$. The shortest intermolecular contacts in the sheet are: C(13) \cdots C(5ⁱⁱ) 3.629(3), C(14) \cdots C(1ⁱⁱⁱ) 3.601(3), C(1) \cdots C(5^v) 3.657(3) Å. The sheets are stacked along a by van der Waals interactions. The intermolecular contacts between the sheets are loose, in consistency with the morphology of the crystals: C(3) \cdots C(16^{iv}) 3.897(3), C(17) \cdots C(7^{vi}) 3.814(4), O(15) \cdots H(17C) 3.00(3) Å.

The authors thank Professor Masao Kakudo, Dr Noritake Yasuoka and the staff of the Crystallographic Research Center, Institute for Protein Research, Osaka University, for use of the diffractometer.

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