Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

N(1)—C(31)	1·392 (6)	C(1)—O(1)	1·217 (7)
N(1)—C(21)	1·441 (7)	C(1)—C(3)	1·471 (9)
N(1)—C(11)	1·439 (6)	C(3)—C(2)	1·329 (9)
C(11)—C(12)	1·390 (7)	C(2)—C(22)	1·453 (8)
C(12)—C(13)	1·384 (7)	C(21)—C(22)	1·401 (7)
C(13)—C(14)	1·371 (8)	C(22)—C(23)	1·408 (8)
C(14)—C(15)	1·390 (9)	C(23)—C(24)	1·367 (9)
C(15)—C(16)	1·388 (8)	C(24)—C(25)	1·375 (8)
C(16)—C(11)	1·377 (7)	C(25)—C(26)	1·387 (8)
C(12)—C(1)	1·499 (8)	C(26)—C(21)	1·379 (8)
N(1)—C(31)—C(32)	119·2 (2)	C(15)—C(16)—C(11)	119·6 (6)
N(1)—C(31)—C(36)	120·7 (2)	C(12)—C(1)—O(1)	118·1 (6)
C(31)—N(1)—C(21)	123·7 (4)	C(12)—C(1)—C(3)	122·7 (6)
C(31)—N(1)—C(11)	123·0 (4)	O(1)—C(1)—C(3)	118·8 (6)
C(11)—N(1)—C(21)	112·2 (5)	C(1)—C(3)—C(2)	135·7 (6)
N(1)—C(11)—C(16)	121·0 (5)	C(3)—C(2)—C(22)	136·1 (6)
N(1)—C(11)—C(12)	118·4 (5)	C(2)—C(22)—C(21)	125·1 (6)
C(12)—C(11)—C(16)	120·7 (5)	C(2)—C(22)—C(23)	118·5 (6)
C(11)—C(12)—C(13)	119·3 (5)	C(21)—C(22)—C(23)	116·2 (6)
C(11)—C(12)—C(1)	121·6 (5)	C(22)—C(23)—C(24)	122·1 (6)
C(1)—C(12)—C(13)	119·1 (5)	C(23)—C(24)—C(25)	120·3 (7)
C(12)—C(13)—C(14)	120·3 (6)	C(24)—C(25)—C(26)	119·7 (6)
C(13)—C(14)—C(15)	120·4 (6)	C(25)—C(26)—C(21)	119·8 (6)
C(14)—C(15)—C(16)	119·6 (6)	C(26)—C(21)—C(22)	121·9 (6)

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Structure of *syn*-1,6:8,13-Bismethano-2-aza[14]annulene,* C₁₅H₁₃N

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Abstract. $M_r = 207·28$, monoclinic, $P2_1/c$, $a = 9·473$ (2), $b = 8·959$ (3), $c = 13·617$ (4) Å, $\beta = 109·34$ (2)°, $V = 1090·4$ (6) Å³, $Z = 4$, $D_m = 1·26$ (by flotation in dilute K₂HgI₄), $D_x = 1·262$ Mg m⁻³, $F(000) = 440$, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·038$ mm⁻¹, room temperature, $R = 0·043$ for 1269 independent observed reflections. There are no unusual geometrical features.

Introduction. In recent years 1,6-methano-2-aza[10]annulene, the first example of an aza derivative of bridged annulenes, was synthesized (Schäefer-Ridder, Wagner, Schwanborn, Schreiner, Devrout & Vogel, 1978) and the molecular geometry of a bromo derivative has been determined by X-ray diffraction (Destro, Simonetta & Vogel, 1981). One homolog of this compound, namely *syn*-1,6:8,13-bismethano-2-aza[14]annulene (I), has now become available (Vogel, 1983) and the results of the study of its crystal structure are presented here.

* IUPAC name: 4-azatricyclo[8.4.1.1³,⁸]hexadeca-2,4,6,8,10,12-14-heptaene.

(I)   (II)
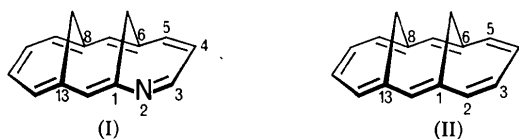
Experimental. Crystals of the title compound were obtained from ethyl acetate/hexane; single crystal (yellow-orange prism) $0·3 \times 0·5 \times 0·3$ mm, Enraf–Nonius CAD-4 diffractometer, 2681 independent reflexions measured, $\theta \le 30°$, 1269 considered observed ($I \ge 2·5\sigma_I$) and used in crystal analysis; each reflection was assigned a variance $\sigma(I) = |\sigma(I_{raw})^2 + (pI_{raw})^2|^{1/2}/Lp$ with $\sigma(I_{raw})$ based on counting statistics and $p = 0·011$; intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption. Structure solved by direct methods and refined by least squares using the program *SHELX* (Sheldrick, 1976), non-H atoms anisotropic and H atoms isotropic; scattering factors for C and N atoms from Cromer & Mann (1968), those of Stewart, Davidson & Simpson (1965) used for H; refinement based on minimization of $\sum w(|F| - k|F_c|)^2$ with

$w = |\sigma^2(F) + 0.00017F^2|^{-1}$; H-atom positions derived from difference maps and refined isotropically together with C and N atoms; final $R = 0.043$ and $R_w = 0.038$; ratio of maximum least-squares shifts to error in final refinement cycle 0.060; maximum and minimum heights in final difference Fourier synthesis 0.18 and -0.16 e Å^{-3}.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

The atom numbering is shown in Fig. 1; bond distances and angles are given in Fig. 1(a), dihedral angles in Fig. 1(b) and torsional angles along the ring in Fig. 1(c). Standard deviations in bond lengths and angles are 0.003 Å and 0.2° (not involving H atoms); standard deviations for dihedral and torsion angles are 0.1 and 0.3° respectively.

The geometry of the title compound can be compared with that of the corresponding hydrocarbon, syn-1,6:8,13-bismethano[14]annulene (II) (Destro, Pilati & Simonetta, 1977). Substitution of an N atom in the ring does not alter the aromatic character, as can be seen by examination of the usual indices $\bar{r} = <r_i>$, and $\bar{\tau} = <|\tau_i|>$. In fact, we have $\bar{r} = 1.392$ (6) Å and $\bar{\tau} = 22$ (2)° for (I), to be compared with the corresponding values of 1.395 (4) and 22 (3)° for (II).

C—N bonds are 0.058 (6) Å shorter on average than the corresponding C—C bonds in hydrocarbon (II); this value is in line with the average shortening measured on going from anthracene (Mason, 1964) to acridine (Phillips, 1965): 0.057 (9) Å.

The stiffness of the annulene ring seems to be practically unaffected: compare the value of the dihedral angle between the planes of the CH$_2$ bridges, 26.6 (9)° in (II), 26.1 (9)° in (I), and the non-bonded
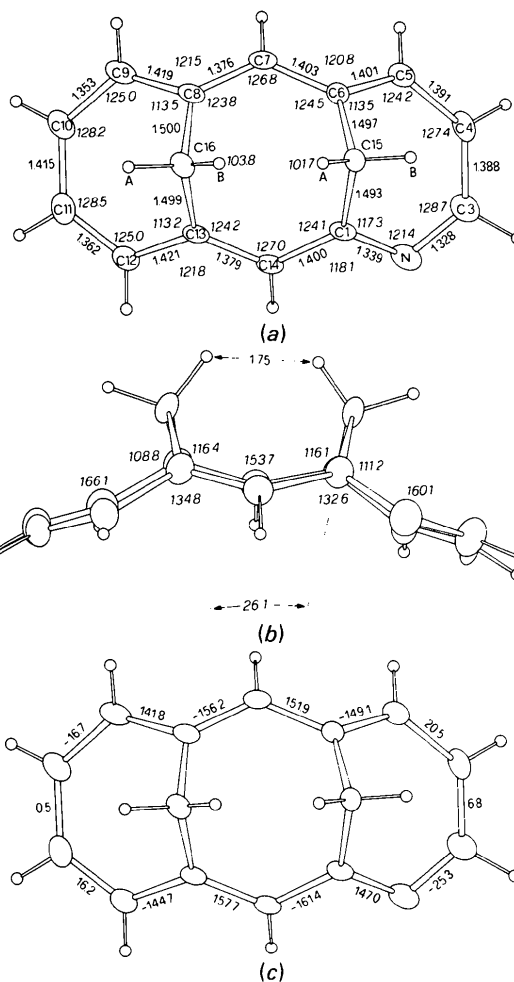
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* Lists of structure factors, coordinates of hydrogen atoms and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38398 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} matrix.

	x	y	z	U_{eq}
C(1)	0.49251 (26)	0.32692 (24)	0.32563 (15)	432
N	0.57808 (24)	0.44692 (22)	0.32846 (15)	616
C(3)	0.70148 (31)	0.47239 (29)	0.40851 (22)	639
C(4)	0.73689 (30	0.42475 (32)	0.51081 (23)	611
C(5)	0.65612 (29)	0.32647 (31)	0.55085 (20)	559
C(6)	0.55075 (24)	0.22437 (23)	0.49063 (15)	388
C(7)	0.42703 (26)	0.18233 (24)	0.51920 (17)	429
C(8)	0.28953 (27)	0.13629 (22)	0.45361 (16)	421
C(9)	0.15877 (30)	0.14950 (27)	0.48196 (21)	549
C(10)	0.02169 (31)	0.18725 (30)	0.41634 (22)	622
C(11)	−0.01540 (32)	0.25491 (30)	0.31710 (20)	582
C(12)	0.07780 (29)	0.29669 (31)	0.26437 (19)	522
C(13)	0.22813 (25)	0.24793 (24)	0.28773 (14)	408
C(14)	0.33794 (27)	0.34042 (27)	0.27617 (15)	439
C(15)	0.56657 (26)	0.19338 (26)	0.38675 (17)	419
C(16)	0.25770 (30)	0.09904 (25)	0.34094 (17)	447

Fig. 1.(a) Atomic numbering, bond lengths (Å) and angles (°), (b) dihedral angles (°) and (c) torsional angles (°) along the ring in title compound.

distances between internal H atoms of the bridges, 1.78 (2) Å in (II), 1.75 (3) Å in (I). C(1)···C(6) [2.319 (2) Å] and C(8)···C(13) [2.360 (2) Å] are typical of a 14-membered annulene ring without internal bonding. In summary, the title compound shows all the geometrical features that might be expected as a consequence of aza substitution in (II).

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