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## Strained Heterocyclic Systems. 18.\* Structure of 1,2,3-Methyldiyne-2,3-dihydro-1H-cyclopenta[b]quinoxaline

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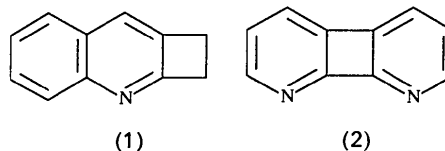
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**Abstract.**  $C_{12}H_8N_2$ ,  $M_r = 180.211$ , monoclinic,  $P2_1/n$ ,  $a = 8.6126$  (8),  $b = 12.5147$  (13),  $c = 8.5484$  (7) Å,  $\beta = 99.663$  (7)°,  $V = 908.31$  (15) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.32$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 5.93$  cm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 291$  K, final  $R = 0.063$  for 1645 unique reflections. This study demonstrates that a fused strained ring system adjacent to the N atom of an azaarene results in an abnormally small C—N—C bond angle.

**Introduction.** In previous papers (Deroski, Markgraf & Ricci, 1983; Deroski, Ricci, MacBride & Mark-

graf, 1984) we reported that 1,2-dihydrocyclobuta[b]quinoline (1) and 1,8-diazabiphenylene (2) contained C—N—C bond angles of 112.5 and 112.9°, respectively.



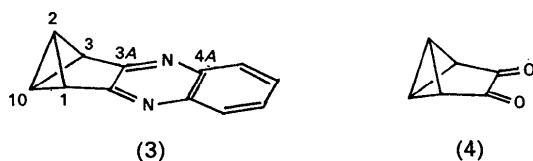
Such abnormally small angles resulting from the fusion of a strained ring adjacent to the N atom cause an increase in the  $s$  character of the non-bonding orbital (Moomaw, Kleier, Markgraf,

\* Part 17: Markgraf, Mueller & Myers (1989).

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Thoman & Ridyard, 1988). The orbital rehybridization induced by such ring deformation has been correlated with decreased basicity in these strained heterocyclic systems (Markgraf & Scott, 1967; Hull, MacBride & Wright, 1984).

That tricyclo[3.1.0.0<sup>2,6</sup>]hexane is a strained molecule is known from NMR coupling constants (Christl & Herzog, 1986) and quantum-chemical studies (Zil'berg, Ioffe & Nefedov, 1983). The incorporation of such a framework into an azaarene should distort the ring geometry. Recently the preparation of 1,2,3-methylidyne-2,3-dihydro-1H-cyclopenta[b]quinoxaline (3) was reported (Christl & Kraft, 1988). The structural analysis presented here was undertaken as part of our continuing study of strain effects on the properties of heterocyclic systems.



**Experimental.** (3) was prepared at room temperature by the dropwise addition of a solution of tricyclo[3.1.0.0<sup>2,6</sup>]hexane-3,4-dione (4) (101 mg, 0.934 mmol) in anhydrous dichloromethane (2 ml) to a stirred solution of 1,2-phenylenediamine (101 mg, 0.934 mmol) in anhydrous dichloromethane (3 ml). After 5 min the pair of triplets of (4) at  $\delta$  3.13 and 3.83 were no longer observed in the NMR spectrum; the triplets of (3) appeared at  $\delta$  2.99 and 4.39. The pale-yellow reaction solution was filtered through basic alumina (activity I), the solvent was removed on a rotary evaporator, and the residue was dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to give 159 mg (95%) of a pale-yellow solid. The analytical sample was prepared by washing three times with 0.5 ml portions of diethyl ether and drying at 293 K/1.33 Pa (m.p. 395–398 K). Elemental analysis for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>: calculated: C = 79.98, H = 4.47, N = 15.55; found: C = 80.26, H = 4.54, N = 15.67%; IR (KBr): ( $\nu$ , cm<sup>-1</sup>) 3120, 3090, 1595, 1455, 1425, 1350, 1300, 1070, 935, 915, 770, 760, 725, 720; MS (70 eV) (relative abundance): 180 (100, M<sup>+</sup>), 179 (53), 153 (13), 76 (26), 75 (14), 63 (12), 52 (14), 51 (18), 50 (40). The transparent pale-brown crystal used in the present study grew from a solution of (3) in a mixture of diethyl ether and dichloromethane by very slow evaporation of the solvents.

A crystal measuring 0.34 × 0.39 × 0.22 mm and of habit {100}, {110}, (111) was mounted on an Enraf-Nonius CAD-4 diffractometer; intensity data were collected with variable scan speeds for a total of 2132 reflections,  $\theta$ -2 $\theta$  scans ( $3 \leq 2\theta \leq 156^\circ$ ), maximum

value of  $(\sin\theta)/\lambda = 0.6344 \text{ \AA}^{-1}$ , graphite-monochromated Cu K $\alpha$  radiation; lattice parameters determined from 25 reflections ( $24 \leq \theta \leq 39^\circ$ ), systematic absences ( $h0l$ ,  $h+l=2n$ ;  $0k0$ ,  $k=2n$ ); monitored reflections (080,  $\bar{3}43$ , 115) showed a nearly linear decay of about 6% over the course of data collection and the individual intensities were scaled to the zero-time monitor reflections; background was measured on one sixth of the total scan width, and normal scans which did not result in sufficiently high precision of net intensity measurements were repeated at a slower scan speed; 1645 unique reflections measured and used in the analysis;  $h$ ,  $k$  and  $l$  range +10, +15,  $\pm 10$ , respectively; Lorentz-polarization correction applied,  $\psi$ -scan empirical absorption correction with *BNLABS*, a local version of *ORABS* (Busing & Levy, 1957); minimum and maximum corrections to  $F_o^2$  of 0.842 and 0.858, respectively; agreement between 120 symmetry-equivalent reflections gave  $R_{\text{int}} = 0.03$ . The structure was solved by direct methods with *MULTAN77* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1977); initial refinement by differential synthesis (McMullan, 1979); H-atom coordinates obtained from difference Fourier synthesis and included along with arbitrary isotropic thermal parameters ( $U = 0.063 \text{ \AA}^2$ ) as fixed contributions in final full-matrix least-squares refinement, parameters refined included scale factor, a type-I isotropic extinction parameter,  $g$  (Becker & Coppens, 1975), positional and anisotropic thermal parameters for all non-H atoms; inclusion of extinction decreased  $R$  (based on  $F$ ) by about 2%, most significant extinction occurs for reflections 121, 131 and 011 with corrections of 0.56, 0.60 and 0.72, respectively;  $R = 0.063$  and  $wR = 0.073$ ,  $S = 1.76$  for 128 variables using all data;  $(\Delta/\sigma)_{\text{max}} = 0.012$ ; largest peak in the final difference Fourier synthesis was  $0.19 \text{ e \AA}^{-3}$  (about 4% the height of a carbon peak);  $w = [\sigma^2(F_o^2)]^{-1} = [\sigma_{\text{count}}^2(F_o^2) + (0.05F_o^2)^2]^{-1}$ . Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1962, Vol. 3, Table 3.3.1A); that for hydrogen was the best spherically averaged value (Stewart, Davidson & Simpson, 1965).

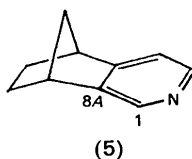
**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters for the refined atoms are given in Table 1.\* Bond distances and angles are listed in Table 2. Fig. 1 shows an *ORTEP* drawing (Johnson, 1976) of molecule (3) with atomic numbering scheme.

\* Lists of structure factors, anisotropic thermal parameters for C and N atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53291 (14 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.			$U_{eq}$
	<i>x</i>	<i>y</i>	<i>z</i>	
N(4)	237 (2)	6727 (1)	569 (2)	50 (1)
N(9)	2714 (2)	5715 (1)	-797 (2)	50 (1)
C(1)	1877 (3)	7088 (2)	-2942 (3)	64 (2)
C(2)	245 (3)	7491 (2)	-3557 (3)	64 (2)
C(3)	-18 (3)	7823 (2)	-1930 (3)	60 (2)
C(3A)	603 (2)	6981 (2)	-793 (3)	45 (1)
C(4A)	1170 (2)	5917 (2)	1344 (2)	43 (1)
C(5)	935 (3)	5616 (2)	2873 (3)	62 (2)
C(6)	1877 (4)	4857 (2)	3714 (3)	74 (2)
C(7)	3062 (4)	4359 (2)	3044 (3)	71 (2)
C(8)	3305 (3)	4635 (2)	1551 (3)	60 (2)
C(8A)	2372 (2)	5421 (2)	689 (2)	44 (1)
C(9A)	1842 (2)	6482 (2)	-1460 (2)	45 (1)
C(10)	1340 (3)	8217 (2)	-2692 (3)	73 (2)

The quinoxaline rings of (3) are planar with a maximum deviation from planarity of 0.009 (2) Å for C(9A). The shortest intermolecular contact is C(2)⋯C(6) at 3.451 (4) Å. A significant feature of (3) is the C(3A)—N(4)—C(4A) bond angle of 113.5 (2)°, a value comparable to those calculated and determined for (1) and (2). Thus (3) represents the third molecule in which an abnormally acute CNC angle adjacent to a fused strained ring has been observed. To our knowledge, the only other molecule containing a bicyclic ring fused to a heterocyclic system for which the molecular structure is known is 5,6,7,8-tetrahydro-5,8-methanoisoquinoline (5) (Tanida, Irie & Hayashi, 1984). The geometries of four derivatives of (5) were determined crystallographically and the range of bond angle N(2)—C(1)—C(8A) was 120.6–122.3° (Shiro, 1988).



A noteworthy aspect of the present study is the C(2)—C(10) distance of 1.424 (3) Å, the shortest such bond reported for the tricyclo[3.1.0.0<sup>2,6</sup>]hexane system. The comparable bonds in (6) and (7) are C(1)—C(6) and C(4)—C(5), respectively, for which values of 1.452 (Suenram & Harmony, 1973) and 1.462 Å (Irrgartinger & Lukas, 1979) have been reported. In (3) the dihedral angle defined by planes C(1)—C(2)—C(3) and C(1)—C(10)—C(3) is 85.9 (2)°. In (6) and (7) the comparable planes are defined by C(2)—C(1)—C(5) and C(2)—C(6)—C(5) and by C(3)—C(4)—C(6) and C(3)—C(5)—C(6), respectively, for which dihedral angles of 83.4 and 88.9° have been reported. All of these values are

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

N(4)—C(3A)	1.296 (3)	C(3)—C(3A)	1.472 (3)
N(4)—C(4A)	1.391 (3)	C(3)—C(10)	1.514 (4)
N(9)—C(8A)	1.400 (3)	C(3A)—C(9A)	1.435 (3)
N(9)—C(9A)	1.291 (3)	C(4A)—C(5)	1.408 (3)
C(1)—C(2)	1.502 (4)	C(4A)—C(8A)	1.402 (3)
C(1)—C(9A)	1.481 (3)	C(5)—C(6)	1.372 (4)
C(1)—C(10)	1.513 (4)	C(6)—C(7)	1.398 (4)
C(2)—C(3)	1.504 (4)	C(7)—C(8)	1.371 (4)
C(2)—C(10)	1.424 (3)	C(8)—C(8A)	1.399 (3)
C(3A)—N(4)—C(4A)	113.5 (2)	C(9A)—C(3A)—N(4)	124.1 (2)
C(8A)—N(9)—C(9A)	113.5 (2)	N(4)—C(4A)—C(8A)	122.6 (2)
C(2)—C(1)—C(9A)	108.6 (2)	C(8A)—C(4A)—C(5)	119.0 (2)
C(2)—C(1)—C(10)	56.4 (2)	C(4A)—C(5)—C(6)	120.4 (2)
C(9A)—C(1)—C(10)	107.9 (2)	C(5)—C(6)—C(7)	120.2 (2)
C(1)—C(2)—C(3)	92.7 (2)	C(6)—C(7)—C(8)	120.3 (2)
C(1)—C(2)—C(10)	62.2 (2)	C(7)—C(8)—C(8A)	120.3 (2)
C(3)—C(2)—C(10)	62.2 (2)	C(8)—C(8A)—C(4A)	119.8 (2)
C(2)—C(3)—C(3A)	108.6 (2)	C(4A)—C(8A)—N(9)	121.9 (2)
C(2)—C(3)—C(10)	56.3 (2)	N(9)—C(9A)—C(3A)	124.5 (2)
C(3A)—C(3)—C(10)	107.2 (2)	C(3A)—C(9A)—C(1)	103.9 (2)
C(3)—C(3A)—C(9A)	105.1 (2)		

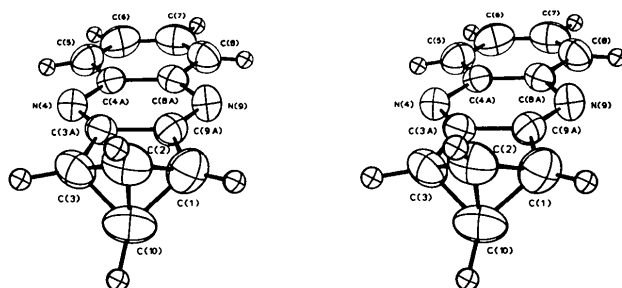
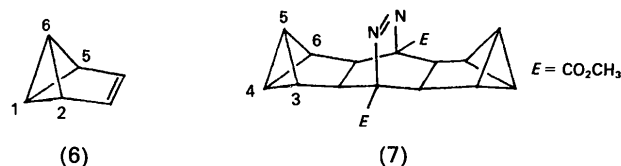


Fig. 1. Perspective view of (3) with thermal ellipsoids of non-H atoms plotted at the 50% probability level. H atoms are included as spheres of arbitrary radius.

considerably smaller than the interflap angles of 123.5 and 125.0° for the four-membered rings of bicyclo[2.1.1]hex-2-ene (Zebelman, Bauer & Chiang, 1972) and bicyclo[2.1.1]hexane (Chiang, 1971), respectively.



Another dihedral angle indicative of ring strain is that of the bicyclo[1.1.0]butane moiety. Previous reports have observed (Irrgartinger & Lukas, 1979) and calculated (Paddon-Row, Houk, Dowd, Garner & Schappert, 1981) the relationship between bond distance and dihedral angle in this simplest bicyclo framework. In (3) the angle defined by planes C(2)—C(1)—C(10) and C(2)—C(3)—C(10) is 109.7 (2)°. In compounds (6) and (7) the analogous angles are 106.0 and 110.6°, determined by microwave spectroscopy

and X-ray structure analysis respectively. These values are all less than the angle of  $121.7^\circ$  reported for bicyclobutane (Cox, Harmony, Nelson & Wiberg, 1969, 1970). Although the C(2)—C(10) bond distance and the above dihedral angle in (3) do not conform to the precise relationship described in the literature, their values are consistent with the highly strained nature of this heterocyclic system.

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## Structure of 2-Phenyl-1,2,3-triazolo[4,5-e][1,2,3,4]tetrazine at 153 K

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**Abstract.**  $C_8H_5N_7$ ,  $M_r = 199.2$ , monoclinic,  $P2_1/n$ ,  $a = 14.780$  (3),  $b = 5.325$  (2),  $c = 10.805$  (3) Å,  $\beta = 95.59$  (2)°,  $U = 846.3$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.563$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha_1) = 1.5405$  Å,  $\mu = 0.927$  mm<sup>-1</sup>,  $F(000) = 408$ ,  $T = 153$  K, final  $R = 0.069$  for 794 observed reflections. The triazolotetrazine ring is planar indicating extensive  $\pi$ -electron delocalization. The C—C bond length in this ring [1.383 (9) Å] indicates a significant deviation from the estimation based on semiempirical MO calculations. The dihedral angle between this ring and the phenyl ring is  $1.4$  (6)°.

**Introduction.** We have previously described the first example of an aromatic 1,2,3,4-tetrazine (Kaihoh, Itoh, Yamaguchi & Ohsawa, 1988). Although pre-

vious analysis established the structure of this compound, crystal instability at room temperature did not provide a satisfactory basis for detailed discussion. The present paper describes an X-ray-diffraction study of the title compound at 153 K and will make a contribution to the theoretical studies of the unknown 1,2,3,4-tetrazine ring system.

**Experimental.** The preparation and physical properties of this compound are given in Kaihoh *et al.* (1988). An explosive reddish plate,  $0.09 \times 0.02 \times 0.38$  mm, by recrystallization from tetrahydrofuran at 253 K. Rigaku AFC5 four-circle diffractometer used with  $\omega$ - $2\theta$  scan method,  $\omega$ -scan width ( $1.3 + 0.41 \tan \theta$ )°, scan speed  $16^\circ \text{ min}^{-1}$ . Lattice parameters obtained from least-squares analysis of 23 reflections