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Redetermination of the Structure of Phenanthridine

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Abstract. $C_{13}H_9N$, $M_r = 179.22$, orthorhombic, $P2_12_12_1$, $a = 4.872\ (2)$, $b = 11.526\ (4)$, $c = 15.811\ (4)$ Å, $V = 887.7\ (5)$ Å^3, $Z = 4$, $D_x = 1.341$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 376$, $T = 110$ K, final $R = 0.045$ for 1713 observed reflections. Phenanthridine was found to be planar in the solid state with a mean deviation of 0.002 Å from the mean plane of the C and N atoms. The geometries of the benzene fragments in the molecule are rather similar and in the central pyridine moiety the C—N bond lengths are typical of C—N single and double bonds. In the crystal the molecules are stacked according to the screw axes. Comparison with a previous structure determination of phenanthridine reveals great differences in bond lengths and angles.

Introduction. Polycyclic compounds can be divided into four groups depending on the combination of the individual rings (Rademacher, 1987). The rings can be connected by a single bond as in bicyclopropyl, by a common C atom as in spiropentane, by bridging as in bicyclo[1.1.1]pentane or by a common bond (annelation) as in bicyclobutane. The annelation of aromatic and/or heteroaromatic rings leads to polycyclic aromatic hydrocarbons (PAHs) or polycyclic heteroaromatic hydrocarbons (PHHs). In the course of our studies on polycyclic heteroaromatic compounds we have reinvestigated the structure of phenanthridine by X-ray diffraction.

This compound can be regarded as the combination of two benzene molecules with a pyridine ring. The main questions in this structural investigation are how the geometries of the molecular benzene and pyridine subunits are affected by the annelation and how the geometry – relative to phenanthrene (Kay, Okaya & Cox, 1971) – is changed by the introduction of the heteroatom.

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

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

	x	y	z	U_{eq}
C(1)	3640 (5)	10228 (2)	4918 (1)	250 (6)
C(2)	5062 (5)	9192 (2)	4925 (1)	263 (6)
C(3)	4537 (5)	8381 (2)	5567 (1)	257 (6)
C(4)	2625 (5)	8596 (2)	6186 (1)	234 (6)
C(5)	−1551 (5)	9233 (2)	7522 (1)	245 (6)
C(6)	−3569 (5)	9553 (2)	8085 (1)	276 (6)
C(7)	−4981 (5)	10603 (2)	7983 (1)	277 (6)
C(8)	−4321 (5)	11328 (2)	7325 (1)	262 (6)
N(9)	−1674 (4)	11816 (2)	6100 (1)	265 (5)
C(10)	183 (5)	11534 (2)	5550 (1)	243 (5)
C(11)	1680 (4)	10465 (2)	5548 (1)	203 (5)
C(12)	1158 (4)	9648 (2)	6197 (1)	193 (5)
C(13)	−870 (4)	9949 (2)	6828 (1)	185 (5)
C(14)	−2255 (4)	11025 (2)	6744 (1)	229 (6)

Experimental. Phenanthridine was obtained from Aldrich and crystals were grown from a solution in carbon tetrachloride. Crystal size: 0.2 × 0.2 × 0.3 mm, Nicolet *R*3*m*/*V* four-circle diffractometer, Wyckoff scan, scan width 1.0°, lattice parameters determined with 49 reflections ($15 \leq 2\theta \leq 25°$), no absorption correction applied, maximum value of $(\sin\theta)/\lambda = 0.70$ Å^{-1}, *hkl* range $-6 \leq h \leq 24$, $0 \leq k \leq 5$, $0 \leq l \leq 22$, two standard reflections (*hkl* = 012 and $1\bar{1}2$) with no significant variation during the experiment, 2220 measured intensities, $R_{\rm int} = 0.048$, 2065

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Table 2. *Selected bond lengths* (Å), *angles* (°) *and differences between the two structure determinations for phenanthridine*

	(*a*)	(*b*)	|*Δ*|
C(1)—C(2)	1.381 (3)	1.437	0.056
C(1)—C(11)	1.406 (3)	1.410	0.004
C(2)—C(3)	1.403 (3)	1.417	0.014
C(3)—C(4)	1.374 (3)	1.352	0.022
C(4)—C(12)	1.408 (3)	1.417	0.009
C(5)—C(6)	1.377 (3)	1.387	0.010
C(5)—C(13)	1.411 (3)	1.424	0.013
C(6)—C(7)	1.401 (3)	1.420	0.029
C(7)—C(8)	1.373 (3)	1.409	0.036
C(8)—C(14)	1.406 (3)	1.392	0.014
N(9)—C(10)	1.296 (3)	1.291	0.005
N(9)—C(14)	1.397 (3)	1.391	0.006
C(10)—C(11)	1.432 (3)	1.486	0.054
C(11)—C(12)	1.415 (3)	1.426	0.011
C(12)—C(13)	1.447 (3)	1.475	0.028
C(13)—C(14)	1.418 (3)	1.419	0.001
C(1)—C(2)—C(3)	119.4 (2)	115.78	3.62
C(1)—C(11)—C(12)	120.4 (2)	122.85	2.45
C(2)—C(1)—C(11)	120.1 (2)	119.25	0.85
C(2)—C(3)—C(4)	121.2 (2)	124.77	3.57
C(3)—C(4)—C(12)	120.5 (2)	120.72	0.22
C(4)—C(12)—C(11)	118.2 (2)	116.27	1.93
C(5)—C(6)—C(7)	120.5 (2)	119.48	1.02
C(5)—C(13)—C(14)	118.2 (2)	117.58	0.62
C(6)—C(5)—C(13)	120.9 (2)	121.63	0.73
C(6)—C(7)—C(8)	119.9 (2)	120.03	0.13
C(7)—C(8)—C(14)	120.7 (2)	119.67	1.03
C(8)—C(14)—C(13)	119.8 (2)	121.58	1.78
N(9)—C(10)—C(11)	125.0 (2)	125.59	0.69
N(9)—C(14)—C(13)	122.9 (2)	119.48	3.42
C(10)—N(9)—C(14)	117.8 (2)	120.61	2.81
C(10)—C(11)—C(12)	118.6 (2)	115.57	3.03
C(11)—C(12)—C(13)	117.6 (2)	117.59	0.01
C(12)—C(13)—C(14)	118.0 (2)	120.89	2.89

Notes: (*a*) This work; (*b*) Roychowdhury (1973), no e.s.d.'s are given.

unique reflections, 356 unobserved reflections [$F_o \geq 4\sigma(F_o)$], structure solved by direct methods and full-matrix refinement on F with *SHELXTL-Plus* (Sheldrick, 1988). H atoms located from difference Fourier synthesis and refined with isotropic temperature factors, 163 parameters refined, $R = 0.045$ and $wR = 0.052$ with $w^{-1} = [\sigma^2(F_o) + 0.0027F_o^2]$, $S = 1.011$, $(\Delta/\sigma)_{\max} = 0.002$, maximum and minimum electron densities based on final Fourier synthesis, $(\Delta\rho)_{\max} = 0.33$ and $(\Delta\rho)_{\min} = -0.29$ e Å^{-3}, atomic scattering factors as incorporated in *SHELXTL-Plus* (Sheldrick, 1988) and from Cromer & Mann (1968), f', f'' values from Cromer & Liberman (1970).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Selected bond distances and angles are given in Table 2. The numbering scheme and the geometry of the molecule are shown in Fig. 1. The molecule is planar with a mean deviation of 0.02 Å from the mean plane. The C—C bond lengths in the central pyridine unit are elongated by 0.04–0.07 Å compared with pyridine, as a result of the annelation (Mootz & Wussow, 1981). This effect was also observed in phenanthrene (Kay, Okaya & Cox, 1971) for the central benzene unit (Bacon, Curry & Wilson, 1964). The annelated benzene rings in phenanthridine show bond length differences of 0.01–0.02 Å compared with benzene (Bacon, Curry & Wilson, 1964), but reveal an unchanged geometry compared with phenanthrene (Kay, Okaya & Cox, 1971). The C—N bond lengths are in the normal range of C—N single [C(14)—N(9)] and C=N double bonds [C(10)—N(9)] (Rademacher, 1987). Therefore, phenanthridine can be considered as an imino-bridged biphenyl, similar to phenanthrene. In the crystal the molecules are arranged in stacks along the screw axes (Fig. 2). Non-bonding distances shorter than the sum of the van der Waals radii were not observed.

A previous investigation of the crystal and molecular structure of phenanthridine with an R value of 0.078 was undertaken by Roychowdhury (1973). In contrast to this work we have found bond

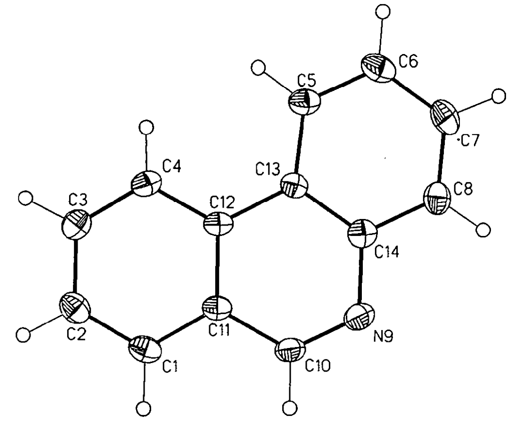

Fig. 1. Perspective view of the molecule showing the atomic labelling. Ellipsoids are drawn to include 50% probability for non-H atoms.

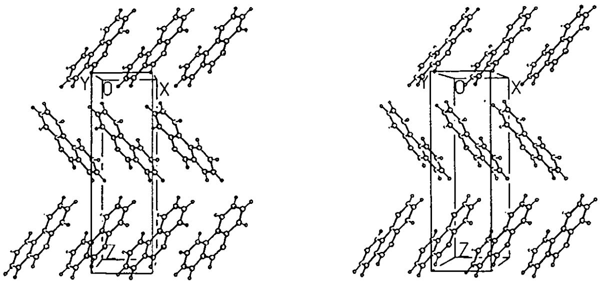

Fig. 2. Stereoview showing the crystal packing along the *y* axis.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71147 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1015]

lengths and angles that differ by up to ~0.06 Å [for C(1)—C(2)] and ~4° [for C(1)—C(2)—C(3) and C(2)—C(3)—C(4)] (Table 1). These discrepancies may be explained by the fact that Roychowdhury obtained the reflections photographically and estimated their intensities visually.

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Structure of 1,3,6,8-Tetrahydrodithieno[3,4-*a*:3′,4′-*c*]benzene

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Abstract. 1,3,6,8-Tetrahydrothieno[3,4-*e*][2]benzothiophene, $C_{10}H_{10}S_2$, $M_r = 194.32$, tetragonal, $I4_1/a$, $a = 22.386$ (4), $c = 13.883$ (7) Å, $V = 6957$ (4) Å^3, $Z = 32$, two independent molecules, $D_x = 1.482$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.52$ mm^{-1}, $F(000) = 3264$, $T = 120$ K, final $R = 0.042$ for 1567 observed reflections. The central ring of the title compound has an almost unchanged benzene geometry and for the annelated 2,5-dihydrothiophene rings typical values of C—S and C—C single and C=C double bonds were observed. While the carbon skeleton of the molecule is planar, the S atoms show deviations of 0.142 [S(1)], 0.082 [S(4)], 0.072 [S(21)] and 0.289 Å [S(24)] from the mean plane. The crystal structure is stabilized by intermolecular S···H hydrogen bonds with S···H distances of 2.90 ± 0.06 Å (mean value) and C—H···S angles of 146 ± 10° (mean value); S···S distances of 3.64 Å were observed also.

Introduction. In cycloalkene-annelated benzenes, ring contraction may introduce strain into the aromatic ring and this could lead to double-bond fixation. The effect of bond fixation in a benzene ring towards one of the Kekulé structures was first proposed by Mills & Nixon (1930) and is known as the Mills–Nixon effect. Much effort was undertaken to prove the existence or non-existence of this effect (Baldridge & Siegel, 1992; Faust, Glendening, Streitwieser & Vollhardt, 1992; Stanger, 1991). To our knowledge little is known about systematic changes of the benzene geometry caused by the annelation of heterocycloalkenes. Here we report the structure of 1,3,6,8-tetrahydrodithieno[3,4-*a*:3′,4′-*c*]benzene, where two 2,5-dihydrothiophenes are annelated to a benzene moiety. The main aim of this study was to investigate the possibility of a heteroatom Mills–Nixon effect.

Experimental. 1,3,6,8-Tetrahydrodithieno[3,4-*a*:3′,4′-*c*]benzene was synthesized from 1,2,3,4-tetramethylbenzene (prehnitene) as described in the literature (Giovannini & Vuilleumier, 1977). Crystal size: 0.10 × 0.12 × 0.25 mm, Nicolet *R*3*m*/*V* four-circle diffractometer, Wyckoff scan, scan width 0.8°, lattice parameters determined with 50 reflections ($15 \le 2\theta \le 25°$), no absorption correction applied, maximum value of $(\sin\theta)/\lambda = 0.54$ Å^{-1}, *hkl* range $-24 \le h \le 24$, $-13 \le k \le 18$, $-18 \le l \le 7$, two standard reflections ($hkl = 224$ and $0\bar{4}0$) with no significant variation during the experiment, 7130 measured intensities, $R_{\rm int} = 0.039$, 2143 unique reflections, 846 unobserved reflections [$F_o \ge 4\sigma(F_o)$], structure solved by direct methods and full-matrix refinement on *F* with *SHELXTL-Plus* (Sheldrick, 1988). H atoms located from difference Fourier synthesis and refined

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