Crystal and molecular structure of phenanthridine. By P. ROYCHOWDHURY, *X-ray Laboratory, Presidency College, Calcutta, India*

Phenanthridine, $C_{13}H_9N$, has space group $P2_12_12_1$ with $a = 11·72$, $b = 16·41$, $c = 4·97$ Å with four molecules per unit cell. $R = 7·8\%$.

Phenanthridine, $C_{13}H_9N$ (Fig. 1), forms orthorhombic crystals with four molecules in a unit cell of dimensions $a = 11·72$, $b = 16·41$ and $c = 4·97$ Å, space group $P2_12_12_1$. Approximate positional parameters were obtained by a combination of a weighted reciprocal-lattice plot for the $hk0$ reflexions (Figs. 2 and 3) and the trial-and error method. Least-squares refinement, using 491 reflexion intensities obtained photographically with Cu $K\alpha$ radiation and estimated visually, and using the computer program *ORFLS* by Busing, Martin & Levy (1962), led to the solution of the structure with a final residual value of 7·8%. In the final cycles of refinement the positional and anisotropic thermal parameters were included for all atoms except hydrogen. The contributions of these atoms were included in the structure-factor calculations keeping the atoms fixed in their calculated positions with their temperature factors equal to those of the atoms to which they were covalently bonded. These factors were obtained from the earlier cycles of refinement. Electron-density sections, and difference syntheses for confirmation of hydrogen-atom positions were com-
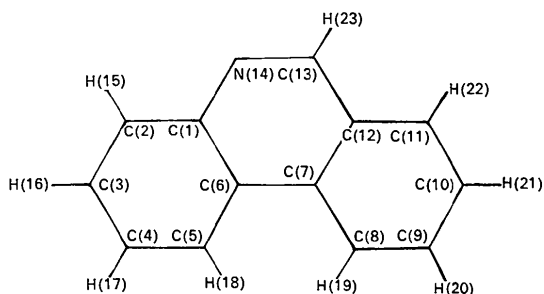

Fig. 1. Conventional structural formula of phenanthridine and the numbering of the different atoms.
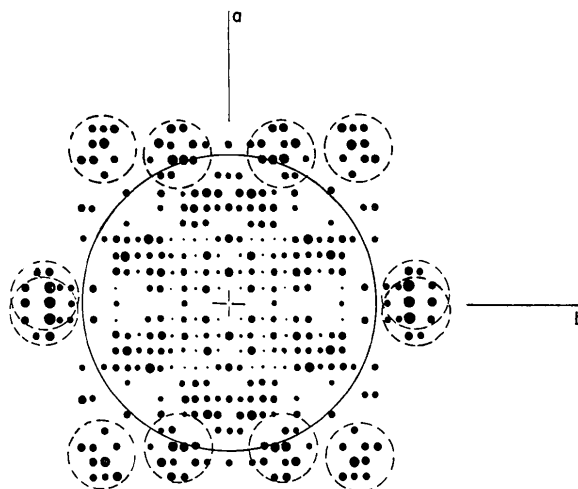

Fig. 2. *hk*O weighted reciprocal lattice of phenanthridine (weights proportional to the unitary structure factors).

Table 1. *Positional parameter of non-hydrogen atoms and their estimated standard deviations*

	$x/a(\times 10^4)$	$y/b(\times 10^4)$	$z/c(\times 10^4)$
C(1)	6045 (9)	3259 (7)	2697 (26)
C(2)	6358 (10)	2689 (8)	758 (25)
C(3)	5637 (10)	2021 (7)	224 (28)
C(4)	4593 (11)	1935 (8)	1648 (24)
C(5)	4282 (9)	2519 (7)	3524 (28)
C(6)	5003 (9)	3193 (7)	4131 (25)
C(7)	4663 (9)	3820 (7)	6103 (24)
C(8)	3661 (9)	3808 (7)	7698(26)
C(9)	3428 (10)	4425 (8)	9415 (25)
C(10)	4180 (11)	5077 (8)	7 (29)
C(11)	5228 (11)	5091 (7)	8493 (27)
C(12)	5456 (10)	4458 (7)	6652 (28)
C(13)	6527 (9)	4437 (7)	5053 (30)
N(14)	6802 (6)	3883 (5)	3325 (19)

Table 2. *Thermal parameters of non-hydrogen atoms with their estimated standard deviations* (*values* $\times 10^4$)

The thermal parameters are given by the expression $\exp(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	49 (10)	34 (5)	240 (84)	−9 (6)	9 (23)	−8 (15)
C(2)	70 (10)	47 (6)	254 (96)	11 (7)	12 (25)	6 (18)
C(3)	96 (11)	31 (5)	373(92)	14 (7)	−7 (28)	1 (19)
C(4)	99 (13)	46 (6)	160 (86)	5 (8)	−23 (24)	11 (18)
C(5)	70 (11)	35 (5)	398 (94)	−13 (7)	−32 (26)	14 (19)
C(6)	63 (10)	31 (5)	226 (85)	2 (6)	−30 (22)	9 (16)
C(7)	65 (11)	33 (5)	158 (86)	7 (7)	−26 (22)	8 (16)
C(8)	71 (10)	43 (6)	163 (88)	−1 (7)	−7 (26)	13 (18)
C(9)	86 (11)	46 (6)	140 (99)	5 (7)	−5 (24)	10 (18)
C(10)	89 (11)	46 (7)	287 (96)	3 (7)	38 (28)	−11 (20)
C(11)	97 (14)	33 (6)	290 (94)	−7 (7)	−46 (27)	−8 (18)
C(12)	74 (11)	36 (4)	293 (88)	0 (7)	−32 (24)	−18 (17)
C(13)	56 (10)	40 (6)	485 (90)	−11 (7)	9 (29)	15 (19)
N(14)	54 (7)	35 (3)	354 (58)	−10 (4)	29 (16)	3 (12)

puted. The conventional structural formula is shown in Fig. 1. The final values of the atomic parameters are given in Tables 1, 2, 3 and 4. Bond lengths and angles are given in Tables 5 and 6. The remarkable feature of the structure is the hypershortening of the C(13)–N(14) and the lengthening of the C(6)–C(7) and C(12)–C(13) bond distances. Theoretical calculations of the bond lengths on the basis of SCF MO were carried out and the C(13)–N(14) bond distance was found to be the shortest, having a theoretical bond distance of 1·295 Å. C(12)–C(13) was found to be the longest bond, having a value of 1·455 Å, and C(6)–C(7) was calculated to be 1·4520 Å. Even though the experimental and theoretical values differ qualitatively by a maximum amount

Table 3. *Unrefined positional parameters of hydrogen atoms* ($\times 10^4$)

	x/a	y/b	z/c
H(15)	7167	2742	−382
H(16)	5900	1569	−1294
H(17)	4034	1414	1207
H(18)	3457	2441	4668
H(19)	3038	3315	7324
H(20)	2619	4436	644
H(21)	4010	5567	1479
H(22)	5822	5584	8934
H(23)	7090	4933	5477

Table 4. *Thermal parameters of hydrogen atoms* ($\times 10^4$)

	β_{11}	β_{22}	β_{33}
H(15)	76	39	425
H(16)	83	42	462
H(17)	82	42	455
H(18)	80	41	447
H(19)	70	36	386
H(20)	68	35	380
H(21)	80	41	442
H(22)	82	42	455
H(23)	80	41	445

Table 5. *Bond lengths*

C(1)—C(2)	1·392 Å
C(2)—C(3)	1·409
C(3)—C(4)	1·420
C(4)—C(5)	1·387
C(5)—C(6)	1·424
C(6)—C(1)	1·419
C(1)—N(14)	1·391
N(14)–C(13)	1·291
C(13)–C(12)	1·486
C(12)–C(7)	1·426
C(7)—C(6)	1·475
C(7)—C(8)	1·417
C(8)—C(9)	1·352
C(9)—C(10)	1·417
C(10)–C(11)	1·437
C(11)–C(12)	1·410
C(2)—H(15)	1·109
C(3)—H(16)	1·101
C(4)—H(17)	1·196
C(5)—H(18)	1·130
C(8)—H(19)	1·106
C(9)—H(20)	1·179
C(10)–H(21)	1·105
C(11)–H(22)	1·089
C(13)–H(23)	1·069

Table 6. *Bond angles*

C(2)—C(1)—C(6)	121·58°
C(2)—C(1)—N(14)	118·87
C(6)—C(1)—N(14)	119·48
C(1)—C(2)—C(3)	119·67
C(2)—C(3)—C(4)	120·03
C(5)—C(4)—C(3)	119·48
C(4)—C(5)—C(6)	121·63
C(5)—C(6)—C(1)	117·58
C(5)—C(6)—C(7)	121·49
C(1)—C(6)—C(7)	120·89
C(12)-C(7)—C(8)	116·27
C(12)-C(7)—C(6)	117·59
C(8)—C(7)—C(6)	125·87
C(9)—C(8)—C(7)	120·72
C(8)—C(9)—C(10)	124·77
C(9)—C(10)–C(11)	115·78
C(12)-C(11)–C(10)	119·25
C(7)—C(12)–C(13)	115·57
C(11)-C(12)–C(7)	122·85
C(11)-C(12)–C(13)	121·52
N(14)-C(13)–C(12)	125·59
C(1)—N(14)–C(13)	120·61
H(15)-C(2)—C(1)	121·52
H(15)-C(2)—C(3)	118·55
H(16)-C(3)—C(2)	119·07
H(16)-C(3)—C(4)	121·10
H(17)-C(4)—C(3)	112·75
H(17)-C(4)—C(5)	113·93
H(18)-C(5)—C(4)	118·90
H(18)-C(5)—C(6)	119·30
H(19)-C(8)—C(9)	121·38
H(19)-C(8)—C(7)	117·62
H(20)-C(9)—C(8)	117·60
H(20)-C(9)—C(10)	110·23
H(21)-C(10)–C(9)	125·08
H(21)-C(10)–C(11)	119·50
H(22)-C(11)–C(12)	123·83
H(22)-C(11)–C(10)	117·10
H(23)-C(13)–N(14)	120·95
H(23)-C(13)–C(12)	113·50

Table 7. *Some of the molecular approach distances*

The symbols I, II, III, IV indicate the symmetry positions as listed in *International Tables for X-ray Crystallography* (1969)

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C(2,I)—C(8,III)	3·729 Å
C(2,I)—C(5,III)	4·048
C(3,I)—C(9,III)	4·044
C(3,I)—C(8,III)	3·934
C(3,I)—C(10,IV)	3·980
C(3,I)—C(11,IV)	3·804
C(4,I)—C(10,IV)	3·759
C(4,I)—C(11,IV)	3·877
C(5,I)—N(14,III)	4·023
C(5,I)—C(2,III)	4·048
C(8,I)—C(2,III)	3·729
C(8,I)—C(3,III)	3·934
C(8,I)—C(10,II)	4·027
C(8,I)—C(9,II)	4·130
C(9,I)—C(10,II)	3·848
C(9,I)—C(9,II)	3·804
C(10,I)–C(9,II)	3·848
C(10,I)–C(3,IV)	3·980
C(11,I)–C(4,IV)	3·877
C(11,I)–C(3,IV)	3·804
C(11,I)–N(14,II)	3·868
C(13,I)–N(14,II)	3·753
C(13,I)–C(13,II)	3·846
N(14,I)–C(13,II)	3·753
N(14,I)–C(5,III)	4·023
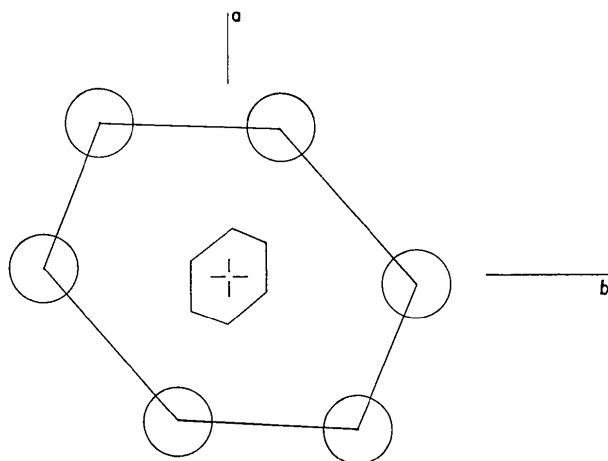
Fig. 3. Projected benzene ring of phenanthridine from weighted reciprocal-lattice section $hk0$.

of 0·03 Å there is a close resemblance between the trends of the bond lengths. Theoretical calculations by Dewar & Gleicher (1966) indicate an identical trend. The C(6)–C(7) bond is a 'contact bond' linking the two benzenoid rings, and is longer than the normal aromatic C–C distance (1·396 Å), a characteristic feature of aromatic molecules containing a phenanthrenoid arrangement of rings.

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DEWAR, M. J. S. & GLEICHER, G. J. (1966). *J. Chem. Phys.* **44**, 759–773.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England).

International Union of Crystallography
Tenth General Assembly and International Congress of Crystallography. Preliminary Announcement

At the invitation of the Stichting voor Fundamenteel Onderzoek der Materie met Röntgen- en Elektronenstralen the Tenth General Assembly and International Congress of Crystallography of the International Union of Crystallography will be held at the R.A.I. Congress Centre, Amsterdam, The Netherlands, 7–15 August 1975.

The first formal announcement will appear in *Acta Crystallographica* at the end of 1973 or early in 1974 and will give the address from which copies of the *First Circular* can be obtained. In addition, copies of this *First Circular* will be sent to all National Committees for Crystallography.

Inter Congress Symposium on Intra- and Intermolecular Forces
Pennsylvania State University, U.S.A.
14–16 August 1974

An Inter-Congress Symposium on Intra- and Intermolecular Forces, sponsored by the International Union of Crystallography, will be held immediately before the meeting of the American Crystallographic Association at the Pennsylvania State University, University Park, Pennsylvania, on 19–24 August 1974. The topics of the symposium are (i) theoretical and experimental determination of nonbonded interactions, (ii) models for calculation of molecular conformation, (iii) molecular and ionic packing in crystals, (iv) vibrational and spectroscopic analyses, (v) nonbonded interactions in polymers and (vi) conformational calculations for proteins and other biological macromolecules. It is intended that the programme will appeal to non-crystallographers with an interest in intra- and intermolecular forces, as well as to crystallographers. Copies of the *First Circular* and further information may be obtained from Professor D. E. Williams, Chemistry Department, University of Louisville, Louisville, Kentucky 40208, U.S.A.

Conference on Applications of X-ray Analysis
Denver, 22–24 August 1973

The 22nd Annual Denver Conference on Applications of X-ray Analysis will be held on 22, 23 and 24 August 1973 at the Brown Palace Hotel, Denver, Colorado, U.S.A. Further information may be obtained from the Program Chairman, Dr C. O. Ruud, Metallurgy and Materials Science Division, University of Denver, Denver, Colorado 80210, U.S.A.