

Acta Cryst. (1972). B28, 367

The Crystal Structure of 9,10-Diazaphenanthrene

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(Received 31 March 1971)

9,10-Diazaphenanthrene, $C_{12}H_8N_2$, forms monoclinic crystals of space group $P2_1/c$ with four molecules in the unit cell of dimensions $a=6.945$, $b=11.938$, $c=11.802$ Å and $\beta=110.84^\circ$. The molecules are arranged in pairs, 3.49 Å apart. They are only approximately planar; two C-C bonds in each benzene ring are shorter than the other four.

Introduction

De Vries Reilingh, Rettschnick & Hoytink (1971) have investigated the fluorescence and fluorescence excitation spectra of 9,10-diazaphenanthrene in solution. From these spectra they deduce the existence of dimers in solution in 3-methylpentane with a stabilization enthalpy of 3.6 kcal. mole⁻¹. A determination of the crystal

structure was undertaken in order to throw additional light on the interpretation of the spectra.

Experimental

Crystals of suitable size and quality were provided by de Vries Reilingh. These crystals were yellow needles along an axis which was subsequently called [100].

Table 1. Coordinates and thermal parameters; *e.s.d.* of positional parameters in parenthesesThe values have been multiplied by 10⁴.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>u</i> (11)	<i>u</i> (22)	<i>u</i> (33)	2 <i>u</i> (12)	2 <i>u</i> (23)	2 <i>u</i> (31)
N(11)	7985 (3)	1046 (2)	1615 (2)	351	684	720	-91	-156	275
N(21)	7158 (3)	1582 (2)	612 (2)	391	638	705	-49	16	461
C(11)	4604 (3)	594 (2)	1725 (2)	428	409	460	-59	-194	331
C(12)	6764 (3)	549 (2)	2191 (2)	418	491	510	-20	-187	167
C(13)	7798 (4)	-29 (3)	3282 (3)	618	745	567	235	-83	40
C(14)	6687 (5)	-554 (3)	3873 (3)	1010	727	498	340	88	278
C(15)	4537 (5)	-524 (2)	3409 (3)	908	618	606	52	127	680
C(16)	3498 (4)	40 (2)	2356 (2)	598	494	562	-39	-15	524
C(21)	3690 (3)	1209 (2)	622 (2)	352	389	463	-62	-149	289
C(22)	5034 (3)	1673 (2)	97 (2)	376	433	548	-84	-127	384
C(23)	4271 (4)	2279 (2)	-997 (2)	593	524	613	-10	80	579
C(24)	2189 (4)	2416 (2)	-1555 (2)	645	543	557	26	117	240
C(25)	847 (4)	1976 (2)	-1033 (2)	434	523	698	43	44	131
C(26)	1557 (3)	1385 (2)	33 (2)	346	498	625	-51	-7	286

Table 1 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso}
H(13)	9400 (44)	-50 (29)	3550 (29)	5.3*
H(14)	7410 (61)	-940 (33)	4570 (36)	6.3*
H(15)	3730 (46)	-920 (24)	3820 (26)	4.0*
H(16)	1900 (39)	40 (24)	2030 (24)	3.1*
H(23)	5270 (41)	2510 (24)	-1350 (27)	3.9*
H(24)	1680 (41)	2830 (25)	-2310 (26)	3.5*
H(25)	-650 (44)	2120 (26)	-1450 (27)	4.7*
H(26)	580 (42)	1140 (22)	420 (25)	3.1*

* These values have not been multiplied by 10⁴.

Weissenberg photographs showed them to be monoclinic with space group $P2_1/c$. Cell constants were obtained from Weissenberg photographs calibrated with Al-powder lines: $a = 6.945 \pm 0.003$, $b = 11.938 \pm 0.002$, $c = 11.802 \pm 0.005$ Å, $\beta = 110.84^\circ \pm 0.03^\circ$. The density determined by flotation was 1.33 g.cm^{-3} ; from a unit cell content of four molecules a calculated density of 1.31 g.cm^{-3} was obtained. For the intensity measurements an approximately isometric block with dimensions of about 0.5 mm was cut and mounted along [100]. With an automatic Nonius diffractometer 1317 non-zero intensities were measured at room temperature. Ni-filtered Cu K radiation was used and the measurements were made with a θ - 2θ scan up to $\theta = 68.5^\circ$. Two reflexions, repeatedly measured, did not vary more than 1.2% in intensity during the data collection. This stability made a decay correction unnecessary. No absorption correction was applied, since $\mu = 6.4 \text{ cm}^{-1}$ was estimated to be low enough to obviate this. A few reflexions suspected to suffer from extinction or measuring errors were removed in the refinement stage.

Solution of the structure

The orientations of the planes of the molecules were easily found in a sharpened three-dimensional Patterson synthesis from the vectors of length 1.4 and 2.4 Å around the origin. The directions of the long axes of the molecules within these planes were derived from a Patterson section through the origin parallel to one of

these planes, leaving two possibilities for the positions of the nitrogen atoms. The position of the molecules with respect to the symmetry elements could be found by considering two molecules related by an inversion centre. The vectors between these two partially centrosymmetric molecules must give rise to a typical planar pattern of high maxima corresponding to sets of parallel interatomic vectors. Since the two molecules must be at least 3.5 Å apart, this pattern should be 3.5 Å or more from the origin. Identification of this pattern and combination with the above information yielded a sufficiently accurate set of coordinates.

The structure was refined by a block-diagonal least-squares program, using the form factors of Moore

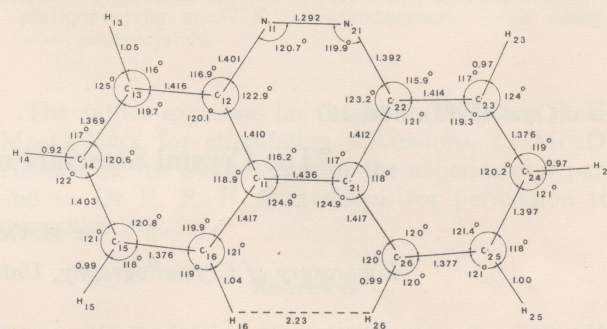


Fig. 1. Intramolecular distances and angles.

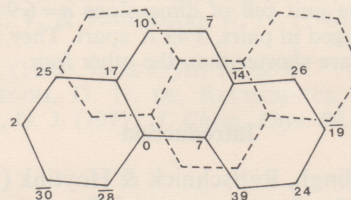


Fig. 2. Projection of molecules related by the centre of symmetry $\frac{1}{2}00$ onto the best plane through the heavy atoms $-0.1582X + 0.8381Y + 0.5220Z - 1.1967 = 0$ the numbers show the distances of the atoms from the plane in units of 0.001 Å.

(1963). The hydrogen atoms were located in a difference density map. The carbon and nitrogen atoms were refined with individual anisotropic temperature parameters and the hydrogen atoms with isotropic ones. With a final R of 0.05 a difference density map contained no features other than a randomly fluctuating background below $0.15 \text{ e.}\text{\AA}^{-3}$. A list of F_o , F_c and ΔF is available on request.

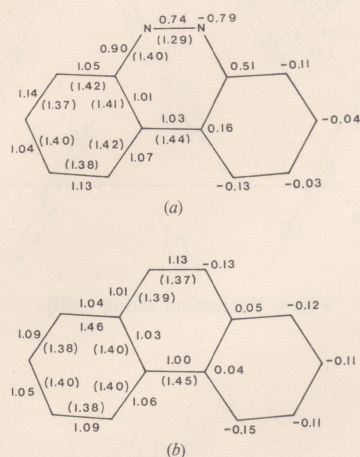


Fig. 3. Overlap populations and net charges from extended-Hückel calculations; (a) diazaphenanthrene, (b) phenanthrene. Bond lengths in parentheses.

Results

The final coordinates together with their e.s.d.'s and the thermal parameters are presented in Table 1. The numbering of the atoms is shown in Fig. 1. In Table 2 the eigenvalues and direction cosines of the libration tensor are given, based on a rigid-body model for the thermal motion (Schomaker & Trueblood, 1968). The r.m.s. deviation between the thermal parameters obtained by the least-squares refinement and those calculated from the rigid-body analysis is 0.0026 \AA^2 .

Table 2. Rigid-body analysis of the thermal motion, eigenvalues and eigenvectors of the libration tensor

Principal axes ($^{\circ}$) ²	Direction cosines with respect to standard axes ($\times 10^3$)		
23.1	137	-821	554
12.8	252	-512	-821
8.5	958	253	137

Table 3 and Fig. 1 list the intramolecular distances and angles, the distances having been corrected for rigid-body motion according to Busing & Levy (1964). In Table 3 the corresponding distances and angles of the two equivalent parts of the molecule have been placed on the same line for comparison. These parts are the same within the limits of accuracy.

Table 3. Distances and angles in the molecule with e.s.d. in parentheses

N(11)–N(21)	1.292 (3) Å	N(21)–C(22)	1.392 (3) Å
C(11)–C(21)	1.436 (3)	C(21)–C(22)	1.412 (4)
N(11)–C(12)	1.401 (4)	C(22)–C(23)	1.414 (3)
C(11)–C(12)	1.410 (3)	C(23)–C(24)	1.376 (3)
C(12)–C(13)	1.416 (3)	C(24)–C(25)	1.397 (4)
C(13)–C(14)	1.369 (5)	C(25)–C(26)	1.377 (3)
C(14)–C(15)	1.403 (5)	C(26)–C(21)	1.417 (3)
C(15)–C(16)	1.376 (3)	C(23)–H(23)	0.97 (3)
C(16)–C(11)	1.417 (4)	C(24)–H(24)	0.97 (3)
C(13)–H(13)	1.05 (3)	C(25)–H(25)	1.00 (3)
C(14)–H(14)	0.92 (4)	C(26)–H(26)	0.99 (3)
C(15)–H(15)	0.99 (4)		
C(16)–H(16)	1.04 (3)		
H(16)–H(26)	2.23 (4)		
C(12)–N(11)–N(12)	120.7 (2) $^{\circ}$	C(22)–N(21)–N(11)	119.9 (2) $^{\circ}$
C(11)–C(12)–N(11)	122.9 (2)	C(21)–C(22)–N(21)	123.2 (2)
C(21)–C(11)–C(12)	116.2 (2)	C(11)–C(21)–C(22)	117.0 (2)
C(16)–C(11)–C(21)	124.9 (2)	C(26)–C(21)–C(11)	124.9 (2)
C(16)–C(11)–C(12)	118.9 (2)	C(26)–C(21)–C(22)	118.0 (2)
C(11)–C(12)–C(13)	120.1 (2)	C(21)–C(22)–C(23)	121.0 (2)
C(12)–C(13)–C(14)	119.7 (3)	C(22)–C(23)–C(24)	119.3 (3)
C(13)–C(14)–C(15)	120.6 (3)	C(23)–C(24)–C(15)	120.2 (2)
C(14)–C(15)–C(16)	120.8 (3)	C(24)–C(25)–C(26)	121.4 (3)
C(15)–C(16)–C(11)	119.9 (2)	C(25)–C(26)–C(21)	120.0 (2)
C(12)–C(13)–H(13)	116 (2)	C(22)–C(23)–H(23)	117 (2)
C(14)–C(13)–H(13)	125 (2)	C(24)–C(23)–H(23)	124 (2)
C(13)–C(14)–H(14)	117 (3)	C(23)–C(24)–H(24)	119 (2)
C(15)–C(14)–H(14)	122 (3)	C(25)–C(24)–H(24)	121 (2)
C(14)–C(15)–H(15)	121 (2)	C(24)–C(25)–H(25)	118 (2)
C(16)–C(15)–H(15)	118 (2)	C(26)–C(25)–H(25)	121 (2)
C(15)–C(16)–H(16)	119 (2)	C(25)–C(26)–H(26)	120 (2)
C(11)–C(16)–H(16)	121 (2)	C(21)–C(26)–H(26)	120 (2)

In Fig. 2 two parallel molecules have been projected onto the best plane through the heavy atoms of one molecule. The deviations of the atoms of this molecule from the plane have been indicated. A χ^2 test on the planarity shows that the molecule as a whole is significantly non-planar (the e.s.d.'s in the position of an atom have been taken as 0.003 Å). The same test shows that of the three rings only C(11)–C(16) and C(21)–C(26) are planar; their normals enclose an angle of 2.5°. From Fig. 2 it can be seen that the molecule shows a torsion around the central bond C(11)–C(21). This torsion can be attributed to steric interaction between H(16) and H(26). The pattern of the angles around atoms C(11), C(12), N(11) and counterparts suggests that the steric interaction between H(16) and H(26) is the dominating effect in determining the shape of the molecule, generating large angles C(16)–C(11)–C(21) and C(26)–C(21)–C(11); this causes smaller angles on the other side of C(11)–C(21) as a result of which the remaining angles in the central ring are increased.

The bonds C(13)–C(14), C(15)–C(16), C(23)–C(24) and C(25)–C(26) are significantly shorter than the other bonds in the benzene rings. This is paralleled in the Mulliken overlap populations (Mulliken, 1955) from an extended-Hückel calculation (Hoffman, 1963) as shown in Fig. 3; in the extended-Hückel calculation *mm*2 symmetry was assumed. In phenanthrene the same behaviour has been found, as can be seen when one compares the overlap populations of Hoffman (1963) with the crystal structure analysis of Trotter (1963). The net charge on atoms C(12) and C(22) is more positive in diazaphenanthrene than in phenanthrene, in accordance with the more electronegative character of nitrogen; the other charges do not differ very much in the two compounds.

Two molecules, related by the inversion centre ($\frac{1}{2}00$) form a pair 3.49 Å apart; their relative positions are shown in Fig. 2. The packing is indicated in Fig. 4, where a projection of the crystal structure along [100] is given. The only short distances involve the hydrogen atoms H(16) and H(26). Apparently the structure can be considered as an assembly of effectively isolated pairs of diazaphenanthrene molecules. The occurrence of these pairs in the crystalline state strongly supports the dimer formation observed by de Vries Reilingh, Rettschnick & Hoytink. The relative positions of the two molecules in a pair as found in the crystal may provide a good model for the dimer in the liquid state, since the fluorescence spectrum of the dimer coincides with the spectrum from microcrystals apart from fine structure in the latter case (see Fig. 5).

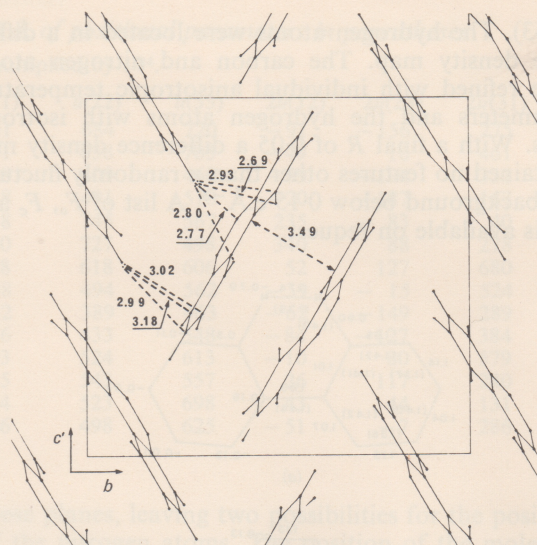


Fig. 4. Projection along [100].

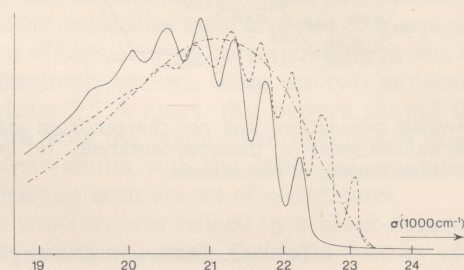


Fig. 5. Fluorescence spectra of 9,10-diazaphenanthrene in 3-methylpentane at 77°K. — monomer; - - - - dimer; ····· microcrystals.

The author expresses his thanks to Professor C. H. MacGillavry for stimulating discussions, to Mr D. Heydenrijk for assistance with the experimental part and to Dr R. P. H. Rettschnick for permission to reproduce Fig. 5.

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