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Structure of 11,12-Bis(diazo)-11,12-dihydroindeno[2,1-*a*]fluorene

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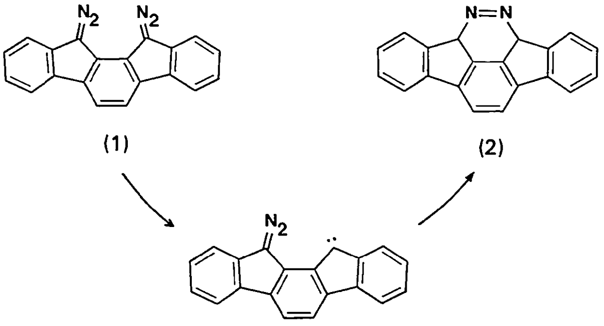
Abstract. $C_{20}H_{10}N_4$, $M_r = 306{\cdot}32$, orthorhombic, *Pbcn*, $a = 14{\cdot}53$ (2), $b = 10{\cdot}007$ (9), $c = 20{\cdot}033$ (4) Å, $V = 2913$ (4) Å^3, $Z = 8$, $D_x = 1{\cdot}397$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}805$ cm^{-1}, $F(000) = 1264$, $T = 290$ K, $R = 0{\cdot}059$ for 1259 observed independent reflections. The indenofluorene ring is planar and considerable distortion of bond angles and bond lengths is observed in the two closely located diazo groups. In the crystal structure, pairs of molecules with antiparallel orientations form a herringbone packing pattern, commonly observed in polycondensed aromatic hydrocarbons.

Introduction. Photochemical or thermal decomposition of 11,12-bis(diazo)-11,12-dihydroindeno[2,1-*a*]-fluorene (1) is expected to give two carbene centers which are capable of conjugation. It is interesting to compare the spin multiplicity and electronic structure of the dicarbene to those of *m*-phenylenebis-(phenylmethylene) which has quintet spin multiplicity. The diazo compound (1) was obtained as green needles with the characteristic double absorption maxima at 490 ($\varepsilon = 36$) and 568 nm ($\varepsilon = 16$), suggesting strong through-space interaction between the two diazo chromophores (Sugawara, Bethell & Iwamura, 1984). Ready formation of an aromatic cyclic azine (2) is further evidence for the close proximity of the two diazo groups in (1).

The present paper reports the X-ray crystal structure of the bis(diazo) compound (1), focusing attention on the local environment of the two closely located diazo groups.



Experimental. The title compound (1) was prepared and crystallized by the method reported previously (Bethell, Gallagher & Bott, 1989); dark-green crystal with dimensions 0·70 × 0·20 × 0·20 mm. Data collection: Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; cell parameters refined with 25 strong reflections ($20 < 2\theta < 25°$), ω–2θ scan, scan speed 4° min^{-1}. Three standard reflections (301, $\bar{1}0\bar{5}$ and $19\bar{4}$) showed no significant variations; 3791 reflections ($2 < 2\theta < 45°$; $0 \le h \le 15$, $0 \le k \le 10$, $0 \le l \le 21$) collected, 1259 [$|F_o| > 3\sigma(F_o)$] were used for analysis. Data corrected for Lorentz and polarization effects, no absorption correction applied ($\mu r < 1$). Structure solved by direct methods using *SAPI85* (Fan, 1986), block-diagonal least-squares refinement on *F*, scattering factors from *International Tables for X-ray Crystal-*

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lography (1974, Vol. IV), the positions of the H atoms were obtained from a ΔF map, anisotropic thermal parameters for non-H atoms, isotropic for H atoms, $R = 0\cdot059$, $wR = 0\cdot057$, $w = 0\cdot7$ ($|F_o| < 20\cdot0$), $1\cdot0$ ($20\cdot0 \leq |F_o| < 100\cdot0$), $10000/|F_o|^2$ ($100\cdot0 \leq |F_o|$), max. $|\Delta\rho| = 0\cdot38$ e Å^{-3}, max. $(\Delta/\sigma) = 0\cdot16$. Calculations carried out on a FACOM A-70 with *UNICS*-III (Sakurai & Kobayashi, 1979).

Discussion. The packing of the molecule in the unit cell is shown in Fig. 1. Pairs of molecules with antiparallel orientations form a herringbone packing pattern, which is commonly observed in polycondensed aromatic hydrocarbons (Desiraju & Gavezzotti, 1989).

The final fractional coordinates of the molecular structure with equivalent thermal parameters of the non-H atoms are given in Table 1.* An *ORTEP* (Johnson, 1965) drawing of the molecule with the atom-numbering scheme is shown in Fig. 2. Bond lengths and angles are given in Table 2. The indeno[2,1-*a*]fluorene moiety is planar, judging from the deviations of the atoms from the least-squares

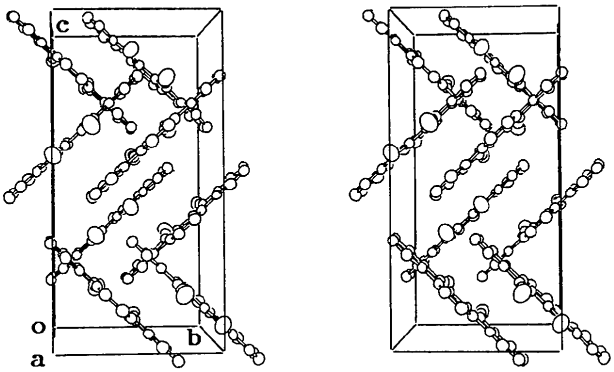

Fig. 1. Stereoview of the packing of the molecules along the *a* axis in the unit cell.

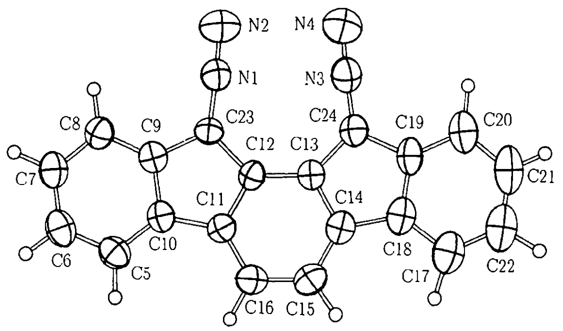

Fig. 2. *ORTEP* drawing showing the thermal ellipsoids at the 50% probability level, with the numbering scheme.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	9105 (2)	−2362 (3)	1788 (2)	4·6 (1)
N(2)	9871 (3)	−2299 (5)	1688 (2)	7·9 (2)
N(3)	8950 (2)	−58 (4)	794 (2)	4·9 (1)
N(4)	9735 (3)	−53 (5)	800 (2)	7·5 (1)
C(5)	6405 (3)	−4242 (4)	2761 (2)	4·4 (1)
C(6)	6857 (3)	−5145 (5)	3171 (2)	4·6 (1)
C(7)	7807 (3)	−5200 (4)	3191 (2)	4·6 (1)
C(8)	8340 (3)	−4376 (4)	2799 (2)	4·1 (1)
C(9)	7887 (3)	−3468 (4)	2390 (2)	3·7 (1)
C(10)	6923 (3)	−3402 (4)	2363 (2)	3·6 (1)
C(11)	6659 (3)	−2368 (4)	1885 (2)	3·6 (1)
C(12)	7471 (3)	−1810 (4)	1604 (2)	3·3 (1)
C(13)	7400 (3)	−783 (4)	1136 (2)	3·4 (1)
C(14)	6517 (3)	−329 (4)	941 (2)	3·9 (1)
C(15)	5728 (3)	−895 (5)	1221 (2)	4·7 (1)
C(16)	5804 (3)	−1910 (4)	1687 (2)	4·2 (1)
C(17)	5988 (4)	1494 (5)	97 (2)	5·7 (2)
C(18)	6630 (3)	710 (4)	445 (2)	4·2 (1)
C(19)	7579 (3)	928 (4)	332 (2)	4·1 (1)
C(20)	7901 (3)	1876 (5)	−118 (2)	5·0 (1)
C(21)	7238 (4)	2616 (5)	−449 (2)	6·3 (2)
C(22)	6316 (4)	2444 (5)	−347 (2)	6·1 (2)
C(23)	8230 (3)	−2496 (4)	1910 (2)	3·4 (1)
C(24)	8059 (3)	3 (4)	766 (2)	3·8 (1)

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

N(1)—N(2)	1·132 (6)	C(12)—C(13)	1·394 (6)
N(1)—C(23)	1·303 (5)	C(12)—C(23)	1·436 (6)
N(3)—N(4)	1·141 (6)	C(13)—C(14)	1·415 (6)
N(3)—C(24)	1·298 (6)	C(13)—C(24)	1·444 (6)
C(5)—C(6)	1·385 (6)	C(14)—C(15)	1·397 (6)
C(5)—C(10)	1·383 (6)	C(14)—C(18)	1·448 (6)
C(6)—C(7)	1·382 (6)	C(15)—C(16)	1·384 (6)
C(7)—C(8)	1·378 (6)	C(17)—C(18)	1·404 (7)
C(8)—C(9)	1·389 (6)	C(17)—C(22)	1·386 (8)
C(9)—C(10)	1·403 (6)	C(18)—C(19)	1·414 (7)
C(9)—C(23)	1·455 (6)	C(19)—C(20)	1·390 (7)
C(10)—C(11)	1·461 (6)	C(19)—C(24)	1·449 (7)
C(11)—C(12)	1·422 (6)	C(20)—C(21)	1·384 (8)
C(11)—C(16)	1·382 (6)	C(21)—C(22)	1·366 (8)
N(2)—N(1)—C(23)	177·2 (5)	C(13)—C(14)—C(15)	120·2 (4)
N(4)—N(3)—C(24)	176·6 (5)	C(13)—C(14)—C(18)	108·5 (4)
C(6)—C(5)—C(10)	118·7 (4)	C(15)—C(14)—C(18)	131·3 (4)
C(5)—C(6)—C(7)	121·1 (4)	C(14)—C(15)—C(16)	120·2 (4)
C(6)—C(7)—C(8)	121·4 (4)	C(11)—C(16)—C(15)	120·6 (4)
C(7)—C(8)—C(9)	117·5 (4)	C(18)—C(17)—C(22)	118·3 (5)
C(8)—C(9)—C(10)	121·8 (4)	C(14)—C(18)—C(17)	131·9 (4)
C(8)—C(9)—C(23)	131·6 (4)	C(14)—C(18)—C(19)	109·3 (4)
C(10)—C(9)—C(23)	106·5 (3)	C(17)—C(18)—C(19)	118·8 (4)
C(5)—C(10)—C(9)	119·5 (4)	C(18)—C(19)—C(20)	122·5 (4)
C(5)—C(10)—C(11)	131·8 (4)	C(18)—C(19)—C(24)	105·9 (4)
C(9)—C(10)—C(11)	108·8 (3)	C(20)—C(19)—C(24)	131·6 (4)
C(10)—C(11)—C(12)	108·6 (3)	C(19)—C(20)—C(21)	116·2 (5)
C(10)—C(11)—C(16)	131·2 (4)	C(20)—C(21)—C(22)	123·0 (5)
C(12)—C(11)—C(16)	120·1 (4)	C(17)—C(22)—C(21)	121·3 (5)
C(11)—C(12)—C(13)	119·6 (4)	N(1)—C(23)—C(9)	121·8 (4)
C(11)—C(12)—C(23)	106·2 (3)	N(1)—C(23)—C(12)	128·3 (4)
C(13)—C(12)—C(23)	134·2 (4)	C(9)—C(23)—C(12)	109·9 (3)
C(12)—C(13)—C(14)	119·3 (4)	N(3)—C(24)—C(13)	127·9 (4)
C(12)—C(13)—C(24)	134·2 (4)	N(3)—C(24)—C(19)	122·4 (4)
C(14)—C(13)—C(24)	106·5 (4)	C(13)—C(24)—C(19)	109·7 (4)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53577 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane [average: 0·007 (4) Å]. The N atoms deviate slightly from this plane [N(2) is 0·165 (4) Å above the plane, N(4) is 0·066(4) Å below the plane], in order to avoid the strain caused by the short contact between N(2) and N(4) [2·873 (7) Å]: this distance is shorter than the sum of the van der Waals radii of nitrogen, 3·0 Å. The N(1)—C(23)—C(12) and N(3)—C(24)—C(13) bond angles are 128·3 (4) and 127·9 (4)°, respectively, which shows that both of the diazo groups extend outwards at the foot of the C(23), C(24) atoms. Closer examination of the diazo groups also shows that the C(23)—N(1)—N(2) and C(24)—N(3)—N(4) bonds are bent outwards slightly at atoms N(1) and N(3). The strain arising from the close location of the diazo groups seems to be reduced by the deformations of these bond angles.

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Structure of 6-*tert*-Butyl-3-cyclohexyl-2-(2,5-dimethylphenoxy)-3,4-dihydro-2*H*-1,3,2-benzoxazaphosphorine 2-Oxide

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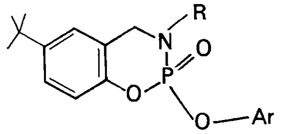
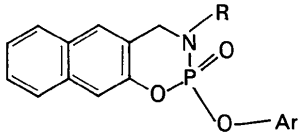
Abstract. $C_{25}H_{34}NO_3P$, $M_r = 427·5$, monoclinic, $P2_1/n$, $a = 13·623$ (3), $b = 11·427$ (2), $c = 15·177$ (3) Å, $\beta = 91·08$ (2)°, $V = 2362·2$ Å^3, $Z = 4$, $D_x = 1·20$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1·3$ cm^{-1}, $F(000) = 920$, $T = 297$ K, $R = 0·04$ for 3378 observed reflections. The oxazaphosphorine ring adopts a sofa conformation. The phosphoryl O atom, O(2), occupies an equatorial position and the O atom, O(3), an axial position, which is in agreement with the anomeric effect. On comparing the geometry of five phosphorus compounds, bond angles around the P atom show no systematic variations, and the only trend in the torsion angles is a change about the O—Ar bond, from synclinal towards coplanar. The molecular packing involves only van der Waals contacts.

Introduction. This type of phosphorus heterocycle has been found to possess significant antitumour activity (Friedman, Papanastassiou & Levi, 1963) and for this reason its X-ray structure is of great interest. The crystal and molecular structures of three derivatives of 1,3,2-benzoxazaphosphorine 2-oxide have been reported by Subramanian, Selladurai & Ponnuswamy (1989), Selladurai, Subramanian & Nagaraju (1989) and Selladurai & Subramanian (1990). We now report the X-ray crystallographic results for a fourth derivative (1*e*).



(1*a*) Ar = 2-chlorophenyl, *R* = cyclohexyl
(1*b*) Ar = 3,5-dimethylphenyl, *R* = cyclohexyl
(1*d*) Ar = 4-methylphenyl, *R* = cyclohexyl
(1*e*) Ar = 2,5-dimethylphenyl, *R* = cyclohexyl



(1*c*) Ar = 3,5-dimethylphenyl, *R* = 4-methylphenyl

Experimental. Transparent, colourless crystals were grown from ethanol solution. Crystal dimensions 0·40 × 0·53 × 0·66 mm. Unit-cell parameters and their e.s.d.'s derived from a least-squares treatment of 25 medium-angle reflections ($25 < 2\theta < 35°$).

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