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2,7-Diamino-9-fluorenone

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Abstract. $C_{13}H_{10}N_2O$, orthorhombic, $P2_12_12_1$, a = 15·33 (1), b = 13·23 (1), c = 4·898 (3) Å, Z = 4, d_m = 1·42, d_x = 1·405 g cm^{-3}. The fluorene nucleus is planar and bond lengths indicate that there is little interaction between the benzene rings or between the rings and the carbonyl group of the central ring.

Introduction. The stereochemistry of fluorene (Cook & Iball, 1936) and its derivatives has been discussed since Kuhn & Jacob (1925) revised earlier work on 9-aminofluorene by Wegerhoff (1889), but very few substituted fluorenes or fluorenones have been studied by X-ray crystallography.

Crystals in the form of dark-purple laths were kindly supplied by Dr C. W. Gray of the University of Hull. Cell dimensions were determined from Weissenberg photographs and confirmed by measurements on a Hilger & Watts linear diffractometer. Intensities were recorded on Weissenberg photographs (Cu $K\alpha$) by the equi-inclination technique for three crystals mounted about **a**, **b** and **c**. Layers $0kl$ to $10kl$, $h0l$ and $h1l$, and $hk0$ to $hk3$ were collected. The intensities were measured on the SRC scanning densitometer at the Atlas Computing Laboratory. Absorption corrections were not applied ($\mu_{\text{Cu}\,K\alpha}$ = 6·46 cm^{-1}).

The structure was determined with *SHELX* (Sheldrick, 1975) from 225 reflexions with E > 1·20. The phases of the solution with the lowest RA value [RA is a combination of R(Karle) and $\varphi(0)$] were used to calculate an E map which showed the 16 highest peaks in chemically sensible positions (R = 0·27).

Refinement was by full-matrix least squares, initially with individual isotropic, and later anisotropic temperature parameters for non-hydrogen atoms. Calculated H atom parameters were included in the structure factor calculations, but were not refined. Scattering factors were from *International Tables for X-ray Crystallography* (1974) and the weighting

Table 1. *Atomic coordinates* (× 10^4; *for* H × 10^3)

Estimated standard deviations are in parentheses. For H atoms, a fixed isotropic U of 0·05 Å^2 was used.

	x	y	z
C(1)	929 (3)	2356 (3)	9390 (10)
C(2)	1822 (3)	2506 (4)	10021 (9)
C(3)	2275 (3)	3271 (4)	8660 (11)
C(4)	1902 (3)	3883 (4)	6657 (11)
C(5)	556 (3)	4976 (3)	2172 (10)
C(6)	−138 (3)	5266 (4)	503 (11)
C(7)	−957 (3)	4800 (3)	656 (10)
C(8)	−1084 (3)	4022 (4)	2548 (11)
C(9)	−345 (3)	2941 (3)	6315 (10)
C(10)	554 (3)	2965 (3)	7389 (11)
C(11)	1018 (3)	3723 (3)	6013 (10)
C(12)	434 (2)	4208 (3)	4003 (11)
C(13)	−389 (2)	3743 (3)	4222 (10)
N(1)	2236 (2)	1898 (3)	11906 (9)
N(2)	−1653 (2)	5135 (3)	−993 (10)
O(1)	−932 (2)	2364 (3)	7023 (7)
H(1)	55	179	1043
H(3)	295	340	919
H(4)	228	446	563
H(5)	118	535	202
H(6)	−4	587	−95
H(8)	−171	364	271
H(1)N(1)	219	200	1409
H(2)N(1)	247	114	1147
H(1)N(2)	−203	581	−58
H(2)N(2)	−175	491	−309

Table 2. *Bond lengths* (Å) *and angles* (°)

Estimated standard deviations are in parentheses.

C(1)–C(2)	1·417 (5)	C(9)–O(1)	1·230 (5)
C(1)–C(10)	1·393 (7)	C(9)–C(13)	1·476 (7)
C(2)–C(3)	1·398 (7)	C(13)–C(12)	1·407 (5)
C(2)–N(1)	1·379 (6)	C(13)–C(8)	1·394 (6)
C(3)–C(4)	1·394 (7)	C(8)–C(7)	1·399 (7)
C(4)–C(11)	1·406 (6)	C(7)–C(6)	1·401 (6)
C(11)–C(10)	1·402 (6)	C(7)–N(2)	1·410 (6)
C(11)–C(12)	1·477 (6)	C(6)–C(5)	1·396 (6)
C(10)–C(9)	1·476 (6)	C(12)–C(5)	1·369 (7)
C(1)–C(2)–C(3)	118·6 (4)	C(10)–C(9)–C(13)	105·9 (3)
C(1)–C(2)–N(1)	120·6 (4)	C(10)–C(9)–O(1)	126·6 (4)
C(1)–C(10)–C(11)	122·9 (4)	C(10)–C(11)–C(12)	108·8 (4)
C(1)–C(10)–C(9)	128·6 (4)	C(9)–C(13)–C(12)	109·0 (4)
C(2)–C(1)–C(10)	118·0 (4)	C(9)–C(13)–C(8)	129·3 (4)
C(2)–C(3)–C(4)	123·5 (4)	C(13)–C(9)–O(1)	127·5 (4)
C(3)–C(4)–C(11)	117·8 (4)	C(13)–C(12)–C(5)	119·8 (4)
C(3)–C(2)–N(1)	120·8 (4)	C(13)–C(8)–C(7)	118·6 (4)
C(4)–C(11)–C(10)	119·2 (4)	C(8)–C(7)–N(2)	120·4 (4)
C(4)–C(11)–C(12)	131·9 (4)	C(8)–C(7)–C(6)	118·9 (4)
C(11)–C(10)–C(9)	108·5 (4)	C(8)–C(13)–C(12)	121·6 (5)
C(11)–C(12)–C(13)	107·6 (4)	C(7)–C(6)–C(5)	122·1 (4)
C(11)–C(12)–C(5)	132·5 (7)	C(6)–C(5)–C(12)	118·9 (4)
		C(6)–C(7)–N(2)	120·7 (4)

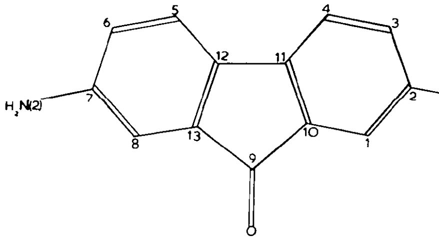

Fig. 1. Atom numbering.

Table 3. *Intramolecular distances* (Å) *less than* 3·5 Å

C(9^{i})···C(7^{ii})	3·384	N(1^{i})···N(2^{iv})	3·202
C(11^{i})···C(6^{ii})	3·485	O(1^{i})···C(6^{iv})	3·453
C(1^{i})···C(12^{ii})	3·418	N(1^{i})···N(2^{v})	3·215
N(1^{i})···O(1^{iii})	3·019		

Symmetry code

(i)	x,	y,	z	(iv)	$-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$
(ii)	x,	y,	$1+z$	(v)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
(iii)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-1-z$				

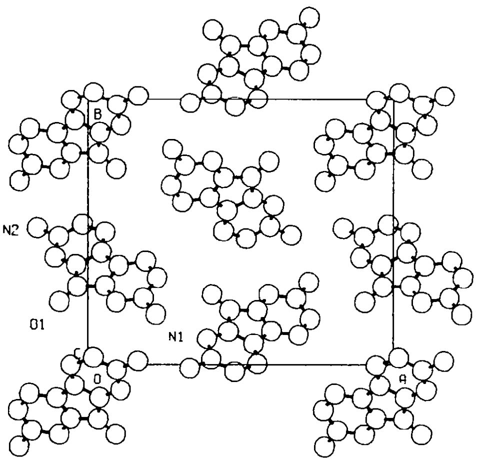

Fig. 2. The structure projected along **c**.

scheme was $w = 1/[\sigma^2(F) + 0{\cdot}019717F^2]$. The final R was 0·064 for 1199 observed reflexions. All calculations were performed on the IBM computer at Cambridge.

Discussion. The final atomic parameters are given in Table 1[*] and bond lengths and angles in Table 2. Atomic numbering is in Fig. 1. The molecule is essentially planar and the equation of the mean plane is $-0{\cdot}27364X + 0{\cdot}66217Y + 0{\cdot}69760Z = 4{\cdot}8624$. The maximum deviation is for N(1), −0·07 Å. The angle between the planes of the two benzene rings is 1·65° while those between the benzene rings and the five-membered ring are 0·90 and 0·75°.

Bond lengths in the molecule compare well with those of fluorene (Burns & Iball, 1954, 1955), 9-fluorenone (Luss & Smith, 1972) and 2,4,7-trinitro-9-fluorenone (Dorset, Hybl & Ammon, 1972). The mean C—C distance in the benzene rings is 1·398 Å, close to the accepted value of 1·394 Å (Sutton, 1965) while in the five-membered ring C(9)–C(10), C(9)–C(13) and C(11)–C(12) all have values close to 1·48 Å, the accepted value for a single bond between sp^2 C atoms (Lide, 1962). This suggests there is little interaction between the benzene rings or between either of these rings and the carbonyl group. Bond angles at the points of fusion of the benzene rings to the five-membered ring are all greater than 120° while the angles adjacent to these in the benzene rings are less than 120°. This has been observed in other fluorenes and also in molecules where four- or five-membered rings are fused to benzene rings, *e.g.* benzo[1,2:4,5]dicyclobutene (Lawrence & MacDonald, 1969). The carbonyl distance, 1·230 (5) Å, compares well with those reported for 9-fluorenone, 1·220 (4) Å, and 2,4,7-trinitro-9-fluorenone, 1·209 (7) Å. The C—N distances, 1·410 (6) and 1·379 (6) Å, are in agreement with those reported for other aminobenzene molecules, *e.g.* 1·420 Å in *N*-(diphenylmethylene)aniline (Tucker, Hoekstra, ten Cate & Vos, 1975).

Intermolecular distances less than 3·5 Å are given in Table 3. The shortest is 3·019 Å between N(1) at x,y,z and O(1) at $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-1-z$, The molecular packing is shown in Fig. 2.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32585 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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P-Methyl-*P*-phenylpropylphosphine Selenide

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Abstract. $C_{10}H_{15}PSe$, $M_r = 245{\cdot}15$; orthorhombic, space group $P2_12_12_1$, $a = 9{\cdot}26\ (1)$, $b = 10{\cdot}94\ (1)$, $c = 11{\cdot}47\ (1)$ Å; $V = 1162$ Å^3; $Z = 4$. $D_m = 1{\cdot}38$ g cm^{-3} (by flotation in KI solution), $D_x = 1{\cdot}40$ g cm^{-3}, $F(000) = 496$; $\mu = 57{\cdot}5$ cm^{-1} (Cu $K\alpha$). The structure was determined by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final R of 0·048 for 969 independent reflexions (Weissenberg camera, Cu $K\alpha$ radiation). The spontaneous resolution of the racemic compound during crystallization has been observed. The mean P–C bond length and C–P–C and Se=P–C angles are 1·83 Å, 106 and 112·5° respectively, while a P=Se distance of 2·12 Å has been found.

Introduction. A few years ago the synthesis and absolute-configuration assignment of the first optically active phosphine selenide (Stec, Okruszek & Michalski, 1971) was reported. The determination of the absolute configuration was based on the knowledge of the configuration of optically active *P*-methyl-*P*-phenylpropylphosphine (Horner, 1964) and the reasonable assumption that the addition of Se to phosphine proceeds with retention of the configuration at the P atom. Since the absolute configurations of optically active phosphines, phosphine oxides, sulphides and selenides have never been determined by X-ray techniques, we thought it worth while to make such a determination. In this paper the preliminary results of our studies on the crystal and molecular structure of the enantiomeric title compound, obtained by spontaneous resolution during crystallization of the racemic compound, are reported. The optical rotation of the enantiomer investigated was not determined, because only very small quantities of separated material were available, but its enantiomeric character is obvious in the light of the crystal parameters (one molecule in the independent part of the unit cell, in a non-centrosymmetric space group).

Crystals in the form of rose-coloured plates elongated along [101], were obtained by slow evaporation of a saturated solution in toluene. The cell-dimensions were calculated from Weissenberg photographs.

Intensities of 969 independent reflexions (70% of total) were collected on a Weissenberg camera (equi-inclination, multiple-film technique) with filtered Cu radiation, and estimated visually by comparison with standard strips. To obtain the best results possible very careful estimation of one half of each of eight photographs from each layer was made. In our opinion, proper scale factors between films of the same layer are the most important factor in increasing accuracy, apart from the estimation of blackening. The reflexions were collected with a spherical crystal, about [100] up to the fifth layer. Interlevel scale factors were initially calculated from $hk0$ reflexions and refined during least-squares calculations. The intensities were corrected for absorption (*International Tables for X-ray Crystallography*, 1959). These data were processed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The scattering factors for Se, P and C were those given by Doyle & Turner (1968) and those from *International Tables for X-ray Crystallography* (1962) were used for H. The illustrations were prepared with *ORTEP* (Johnson, 1965).

The approximate position of the Se atom was found from a three-dimensional Patterson map ($R = 0{\cdot}37$). Successive use of Fourier and difference Fourier