calculated by PARST (Nardelli, 1983) are given in Tables 1 and 2.* The molecular structure and labelling scheme is shown in Fig. 1, and the conformation of the dimer in Fig. 2. Distortions in the benzenoid ring systems have been analysed by calculating best planes, cf. Table 3.

Related literature. 2,11-Dithia[3.3]metacyclophanes are a convenient source for preparation of [2.2]metacyclophanes by elimination of sulfur. They have been synthesized with a variety of substituents (Vögtle, 1990). The hydrocarbon [3.3]metacyclophane (Semmelhack, Harrisson, Young, Guiterrez, Shakin & Clardy, 1985) and the unsubstituated 2,11-dithia[3.3]metacyclophane (Anker, Bushnell & Mitchell, 1979) display the *syn* conformation of the two benzene rings in the solid state and in solution, while intra-annular substituents might lead to the *anti* conformation as in 9-methyl- or 9-amino-2,11-dithia[3.3]metacyclophane (Vögtle & Neumann, 1970).

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* Lists of structure factors, anisotropic thermal parameters, complete bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55281 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Deviations (Å) from least-squares planes of the benzoic systems*

Plane 1		Plane 2	
C(1)	0.029 (2)	C(3)	−0.095 (2)
C(12)	0.087 (3)	C(4)	0.021 (3)
C(13)	−0.010 (2)	C(5)	−0.036 (3)
C(14)	−0.008 (3)	C(6)	0.075 (3)
C(15)	0.008 (3)	C(7)	0.041 (3)
C(16)	0.021 (3)	C(8)	−0.034 (3)
C(17)	−0.011 (2)	C(9)	0.026 (2)
C(18)	−0.050 (2)	C(10)	−0.204 (3)
		C(19)	0.096 (2)

Equation of plane 1: $-0.364x + 0.442y - 0.820z = -8.786$ Å; $\chi^2 = 2167$.
Equation of plane 2: $-0.530x + 0.226y - 0.817z = -6.562$ Å; $\chi^2 = 13302$.

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Structure of Phenylazocarboxamide

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Abstract. Phenylazocarboxamide, $C_7H_7N_3O$, $M_r = 149.15$, monoclinic, $P2_1/c$, $a = 5.187\,(3)$, $b = 14.362\,(5)$, $c = 19.845\,(4)$ Å, $\beta = 93.42\,(4)°$, $V = 1476\,(1)$ Å^3, $Z = 8$, $D_m = 1.341\,(2)$, $D_x = 1.342$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 7.51$ cm^{-1}, $F(000) = 624$, $T = 296$ K, final $R = 0.045$ for 1448 reflections [$I > 3\sigma(I)$]. Two conformers are present. Their structures resemble each other. Each conformer has a fully extended *trans* configuration about the azo double bond. The intermolecular hydrogen bonds are formed between the N and O atoms of the carboxamide groups.

Experimental. Crystals of phenylazocarboxamide were obtained from 50% ethanol as needles, 0.10 ×

0.1 × 0.5 mm. Data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters were determined by least-squares fit to 2θ values of 25 reflections ($57.2 < 2\theta < 74.3°$). Intensity data were collected up to $2\theta = 120.0°$ using ω–2θ scans with scan speed $32.0°\,(\omega)\,\text{min}^{-1}$ and scan width $(1.78 + 0.30\tan\theta)°$. The ratio of peak counting time to background counting time was 2:1 at 50 kV and 180 mA. Over h 0–5, k 0–13, l −15–15, 2581 reflections were measured of which 1448 with $I > 3\sigma(I)$ were used for the analysis. Three reference reflections monitored at 100 reflection intervals showed no crystal deterioration. Lorentz, polarization and absorption corrections (maximum and

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta).$$

	x	y	z	B_{eq}
O(1)	0.6614 (4)	−0.0181 (2)	0.5787 (1)	4.1 (1)
O(1')	0.8515 (4)	0.1753 (2)	0.4760 (1)	5.2 (2)
N(1)	0.6221 (4)	0.1162 (2)	0.6664 (1)	3.4 (1)
N(1')	0.9297 (5)	0.3250 (2)	0.5496 (1)	3.5 (1)
N(2)	0.8390 (4)	0.1063 (2)	0.6443 (1)	3.4 (1)
N(2')	0.7030 (4)	0.3116 (2)	0.5280 (1)	3.7 (1)
N(3)	1.0945 (4)	0.0032 (2)	0.5913 (1)	4.0 (1)
N(3')	0.4272 (4)	0.1934 (2)	0.4937 (1)	4.1 (1)
C(1)	0.6000 (5)	0.1961 (2)	0.7088 (2)	3.2 (1)
C(1')	0.9738 (6)	0.4145 (2)	0.5797 (2)	3.2 (1)
C(2)	0.7709 (6)	0.2704 (3)	0.7099 (2)	3.8 (2)
C(2')	0.8112 (6)	0.4900 (3)	0.5677 (2)	4.1 (2)
C(3)	0.7363 (6)	0.3437 (3)	0.7530 (2)	4.8 (2)
C(3')	0.8754 (7)	0.5742 (3)	0.5976 (2)	4.8 (2)
C(4)	0.5379 (7)	0.3428 (3)	0.7963 (2)	4.9 (2)
C(4')	1.0934 (7)	0.5823 (3)	0.6405 (2)	5.0 (2)
C(5)	0.3661 (6)	0.2690 (3)	0.7952 (2)	4.5 (2)
C(5')	1.2517 (6)	0.5069 (3)	0.6532 (2)	5.1 (2)
C(6)	0.3934 (6)	0.1961 (3)	0.7502 (2)	4.0 (2)
C(6')	1.1955 (6)	0.4228 (3)	0.6216 (2)	4.3 (2)
C(7)	0.8520 (6)	0.0235 (2)	0.6010 (2)	3.1 (1)
C(7')	0.6734 (6)	0.2194 (2)	0.4964 (2)	3.6 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *between non-*H *atoms, and hydrogen bonds* (Å)

O(1)—C(7)	1.216 (3)	C(1)—C(6)	1.388 (4)
O(1')—C(7')	1.210 (4)	C(1')—C(2')	1.386 (5)
N(1)—N(2)	1.240 (3)	C(1')—C(6')	1.384 (4)
N(1)—C(1)	1.431 (4)	C(2)—C(3)	1.373 (5)
N(1')—N(2')	1.243 (3)	C(2')—C(3')	1.379 (5)
N(1')—C(1')	1.430 (4)	C(3)—C(4)	1.380 (5)
N(2)—C(7)	1.471 (4)	C(3')—C(4')	1.379 (5)
N(2')—C(7')	1.470 (4)	C(4)—C(5)	1.383 (5)
N(3)—C(7)	1.317 (4)	C(4')—C(5')	1.373 (5)
N(3')—C(7')	1.328 (4)	C(5)—C(6)	1.389 (5)
C(1)—C(2)	1.388 (4)	C(5')—C(6')	1.384 (5)

N(2)—N(1)—C(1)	114.0 (3)	C(2')—C(3')—C(4')	120.5 (3)
N(2')—N(1')—C(1')	114.1 (3)	C(3)—C(4)—C(5)	120.1 (3)
N(1)—N(2)—C(7)	111.9 (2)	C(3')—C(4')—C(5')	120.4 (4)
N(1')—N(2')—C(7')	111.1 (3)	C(4)—C(5)—C(6)	119.8 (3)
N(1)—C(1)—C(2)	123.5 (3)	C(4')—C(5')—C(6')	119.8 (3)
N(1)—C(1)—C(6)	116.1 (3)	C(1)—C(6)—C(5)	119.5 (3)
C(2)—C(1)—C(6)	120.4 (3)	C(1')—C(6')—C(5')	119.5 (3)
N(1')—C(1')—C(2')	123.5 (3)	O(1)—C(7)—N(2)	123.1 (3)
N(1')—C(1')—C(6')	115.8 (3)	O(1)—C(7)—N(3)	126.9 (3)
C(2')—C(1')—C(6')	120.7 (3)	N(2)—C(7)—N(3)	110.0 (3)
C(1)—C(2)—C(3)	119.5 (3)	O(1')—C(7')—N(2')	123.5 (3)
C(1')—C(2')—C(3')	118.9 (3)	O(1')—C(7')—N(3')	126.3 (3)
C(2)—C(3)—C(4)	120.7 (3)	N(2')—C(7')—N(3')	110.2 (3)

D (at x, y, z)	A		$D \cdots A$
N(3)	O(1)	(i)	2.982 (4)
N(3)	O(1')	(ii)	2.911 (4)
N(3')	O(1)	(iii)	2.922 (4)
N(3')	O(1')	(iv)	2.997 (4)

Symmetry code: (i) $1 + x, y, z$; (ii) $2 - x, -y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $-1 + x, y, z$.

minimum transmission factors 0.98 and 1.00) were applied. The structure was solved by direct methods using *MITHRILL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984), and refined by least squares with anisotropic thermal parameters for all non-H atoms. H atoms were located from difference Fourier maps, and included in the refinement with isotropic thermal parameters. $\sum w(|F_o| - |F_c|)^2$ was minimized [$w = 4F_o^2/\sigma^2(F_o^2)$] in the refinement of 199 parameters. Final $R = 0.045$, $wR = 0.054$; $(\Delta/\sigma)_{max} = 0.01$; $S = 1.66$. The maximum and minimum peaks in the final difference Fourier map were 0.15 and −0.25 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). All numerical calculations were performed using the *TEXSAN* crystallographic software package of Molecular Structure Corporation (1985). Final atomic parameters of the non-H atoms of conformers (I) and (II) are listed in Table 1.* Selected bond lengths, bond angles and hydrogen bonds are listed in Table 2. A perspective view of phenylazocarboxamide is shown in Fig. 1 with the atomic numbering scheme.

Related literature. Phenylazocarboxamide is the oxidized form of 2-phenylhydrazinecarboxamide which is known as cryogenin having anti-inflammatory activity (Kaplan, Wolke & Malone, 1967).
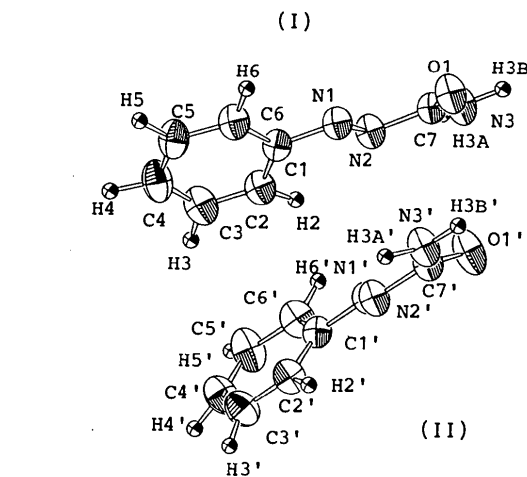
(I)

Fig. 1. Perspective view of phenylazocarboxamide with the atomic numbering used.

DNA-damaging activity *in vivo* of 2-phenylhydrazinecarboxamide, as well as other hydrazine derivatives, has been examined by Parodi, Flora, Cavanna, Pino, Robbiano, Bennicelli & Brambilla (1981). It is also used as a basic compound to synthesize a number of novel and stable cyclic bi-coordinated phosphorus compounds (Rodi, Lopez, Malavaud, Boisdon & Barrans, 1991).

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Structure of the Cation Radical Salt 3,8-Dimethoxy-1,6-dithiapyrenium Hexafluorophosphate

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Abstract. $C_{16}H_{12}O_2S_2^+.PF_6^-$, $M_r = 445.35$, orthorhombic, Cmca, $a = 6.628$ (4), $b = 21.495$ (6), $c = 23.526$ (6) Å, $V = 3352$ (2) Å^3, $Z = 8$, $D_x = 1.765$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 4.70$ cm^{-1}, $F(000) = 1800$, $T = 294$ K, $R = 0.065$ for 629 observed reflections. The structure consists of segregated stacks along the a axis of flat organic cations spaced by $\frac{1}{2}a = 3.314$ Å. A short S⋯S distance of 3.348 (2) Å is found within the organic stack. The surrounding anions have disordered F atoms.

Experimental. Small needle-shaped crystals of the title compound were grown by electrochemical oxidation of 3,8-dimethoxy-1,6-dithiapyrene in CH_2Cl_2 containing $(n\text{-Bu})_4NPF_6$. A single crystal with dimensions $0.30 \times 0.09 \times 0.03$ mm was selected for study on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator. The unit cell was derived from settings of 22 reflections having $4.5 < \theta < 9.5°$. Intensity data were collected in ω-scan mode with $\Delta\omega = (0.80 + 0.35\tan\theta)°$ within the range $0 < \theta < 20°$, $-6 \leq h \leq 6$, $-20 \leq k \leq 20$, $0 \leq l \leq 22$ (the low cut-off angle was used because of weak scattering at higher θ). No significant decay was observed for the three intensity control reflections. Corrections for Lorentz, polarization and absorption (Gaussian integration, transmission 0.96–0.99) effects were applied. A total of 3177 reflections were measured, and after removal of systematic absences these were merged to 880 unique reflections, $R_{int}(F) = 0.026$. The systematic absences were consistent with space groups Cmca and Aba2. The structure was solved in the former space group by direct methods using SHELXS86 (Sheldrick, 1990). 629 reflections having $I > 2\sigma(I)$ were included in the least-squares refinement of the structure (on F) using SHELX76 (Sheldrick, 1976). Complex atomic scattering factors were taken from International Tables for X-ray Crystallography (1974, Vol. IV). All atoms of the organic cation except two methyl H atoms were located and kept fixed on the mirror plane perpendicular to the a axis. The P atom of the PF_6^- cation was also restricted to the mirror plane. Four F atoms were fairly close to this plane, but their displacement parameters became physically unreasonable if the atoms were constrained to the mirror plane. Therefore, a disordered model for PF_6^- with split F-atom positions was introduced. One set of F-atom positions is related to the other set by the mirror plane operation, and the two sets of positions are equally occupied. Removal of the mirror plane and refinement in the non-centrosymmetric space group Aba2 was also attempted, but the deviations of the resultant positions from the 'in-plane' positions were small and the associated e.s.d.'s quite large. In addition, the latter refinement involved severe correlations and the resultant thermal parameters of F atoms were still unreasonable. Therefore,