Fig. 2. Numbering scheme and thermal ellipsoids (enclosing 50% probability) of nalidixic acid.

With increased precision, both pyridine rings show significant deviations from planarity: the more-substituted ring toward a twist-boat shape, and the other ring toward a boat shape. Equations of mean planes and deviations from them are given in Table 2.

As shown in Fig. 2, the plane of the N-ethyl group is approximately perpendicular to the naphthyridine ring system; the C(1)—C(2)—N(3)—C(4) torsion angle is $-99.0°$.

Programs used in the analysis were from the NRC crystallographic program set (Ahmed, Hall, Pippy & Huber, 1973) and the IISc crystallographic programs (Shiono & Reddy, 1968).

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Methyl Phenyl[*syn*-α-(tosylhydrazono)benzyl]phosphinate – A Short Intramolecular N—H⋯O Hydrogen Bond

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Abstract. $C_{21}H_{21}N_2O_4PS$, $M_r = 428.43$, triclinic, $P\bar{1}$, $a = 11.877$ (8), $b = 10.234$ (7), $c = 10.000$ (7) Å, $\alpha = 107.30$ (2), $\beta = 109.52$ (2), $\gamma = 70.54$ (2)°, $V = 1009$ Å^3, $Z = 2$, $D_c = 1.410$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.271 mm^{-1}. The *syn* configuration around the C=N double bond supports the formation of an intramolecular N—H⋯O hydrogen bond which closes a part of the molecule to a six-membered ring: N—H⋯O 2.660 (7), O⋯H 1.70 (9) Å, ∠N—H⋯O 143 (9)°.

Introduction. The title compound (I) was obtained by benzophenone-sensitized irradiation of the known *anti*

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isomer (II) (Felcht & Regitz, 1975) [Philips HPK 125 high-pressure mercury lamp, 3 h, separation of the photoequilibrium mixture by column chromatography over silica gel, m.p. of (I) 413 K].
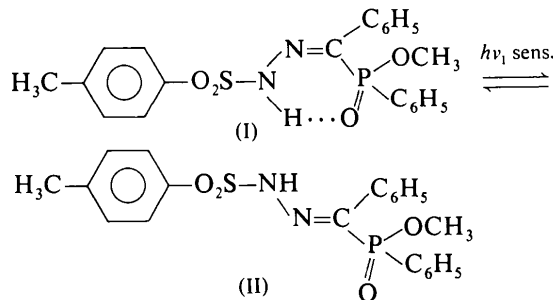
Suitable crystals were obtained from ether. A crystal 0·12 × 0·12 × 0·12 mm was used for data collection on a Philips PW 1100 four-circle diffractometer (Zr-filtered Mo $K\alpha$ radiation, $\theta/2\theta$ scan, scan speed 0·025° s^{-1}). 1151 reflections up to sin $\theta/\lambda = 0.5040$ Å^{-1} were measured. Three reference reflections, monitored every hour, revealed no systematic changes in intensity. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The centrosymmetric space group was confirmed by E distribution tests. The structure was solved by *MULTAN* 74 (Main,

Table 1. *Coordinates* (×10^4) *of the non-hydrogen atoms*

E.s.d.'s are in parentheses.

	x	y	z
P	7831 (2)	1490 (2)	6017 (2)
S	5535 (2)	1768 (2)	8911 (2)
O(1)	7807 (4)	212 (4)	6404 (5)
O(2)	7661 (4)	1362 (4)	4360 (4)
O(3)	5579 (4)	342 (4)	8834 (5)
O(4)	4457 (4)	2876 (5)	9070 (5)
N(1)	5882 (4)	2988 (5)	7267 (5)
N(2)	5820 (4)	1695 (5)	7373 (5)
C(1)	6577 (6)	942 (8)	3301 (7)
C(2)	9234 (5)	2027 (6)	6864 (6)
C(3)	9515 (6)	2497 (7)	8364 (7)
C(4)	10616 (6)	2872 (8)	9096 (8)
C(5)	11442 (6)	2762 (7)	8304 (8)
C(6)	11149 (6)	2302 (8)	6841 (8)
C(7)	10042 (6)	1931 (7)	6095 (7)
C(8)	6640 (5)	3013 (6)	6600 (6)
C(9)	6631 (5)	4462 (6)	6559 (6)
C(10)	6766 (6)	4735 (7)	5348 (7)
C(11)	6764 (6)	6095 (7)	5347 (8)
C(12)	6631 (6)	7160 (7)	6537 (8)
C(13)	6503 (6)	6914 (7)	7754 (8)
C(14)	6488 (5)	5568 (6)	7758 (7)
C(15)	6819 (5)	2223 (6)	10245 (6)
C(16)	6768 (6)	3620 (6)	10932 (7)
C(17)	7835 (6)	3959 (7)	11876 (7)
C(18)	8934 (6)	2954 (7)	12149 (7)
C(19)	8972 (6)	1562 (7)	11488 (7)
C(20)	7922 (6)	1178 (7)	10524 (7)
C(21)	10120 (7)	3356 (9)	13158 (8)

Table 2. *Final coordinates* (×10^3) *of the H atoms*

	x	y	z
H(N2)	657 (6)	76 (8)	711 (8)
H(1.1)	686 (8)	32 (9)	246 (9)
H(1.2)	632 (7)	25 (9)	378 (9)
H(1.3)	604 (9)	178 (10)	302 (10)
H(3)	886 (7)	262 (8)	888 (8)
H(4)	1081 (8)	324 (9)	1017 (9)
H(5)	1154 (9)	308 (11)	884 (11)
H(6)	1169 (7)	226 (8)	612 (8)
H(7)	981 (5)	161 (6)	501 (6)
H(10)	688 (6)	392 (7)	440 (7)
H(11)	685 (6)	620 (7)	438 (7)
H(12)	664 (6)	818 (6)	651 (7)
H(13)	643 (6)	769 (8)	864 (8)
H(14)	641 (6)	533 (8)	874 (7)
H(16)	583 (6)	437 (7)	1073 (7)
H(17)	775 (6)	494 (7)	1241 (7)
H(19)	976 (8)	77 (9)	1149 (9)
H(20)	787 (6)	13 (7)	1000 (7)
H(21.1)	79 (8)	252 (9)	1314 (10)
H(21.2)	30 (7)	398 (9)	275 (9)
H(21.3)	−10 (7)	404 (8)	405 (8)

Woolfson, Lessinger, Germain & Declercq, 1974) with 240 E's ≥ 1·51. Refinement of the structure was by block-diagonal least squares (Bartlett, 1972), iso-tropically and anisotropically with 1134 reflections [F_o > 3σ(F_o)] and unit weights. H atoms were located in a difference map. With the heavy atoms treated aniso-tropically, and H atoms isotropically with the fixed B value of their bonding neighbour, refinement con-verged to $R = 0.037$. Final coordinates are given in Tables 1 and 2, and details of the molecular geometry in Table 3.*

Discussion. From ^{1}H NMR spectra, the existence of an intramolecular NH···O hydrogen bond with the phosphoryl O atom as hydrogen acceptor was known, because the NH proton resonance is independent of concentration; this fact does not hold, on the other hand, for the NH resonance of the *anti* isomer (II). The structure analysis of (I) was carried out to gain information about the geometry of this intramolecular hydrogen bond. The molecular structure is shown in Fig. 1. As the NH···O bond closes part of the molecule to a six-membered ring, no linear arrange-ment of the hydrogen bond was to be expected. In fact (Fig. 2), N(2)−H···O(1) is found to be 143 (9)°. The short distances N(2)···O(1) [2·660 (7) Å] and O(1)···H [1·70 (9) Å] seem to be typical for intra-molecular N−H···O hydrogen bonds, although ex-

Table 3. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

O(2)—C(1)	1·466 (9)	P—C(2)	1·786 (7)	C(8)—C(9)	1·492 (11)	S—C(15)	1·751 (7)
P—O(1)	1·482 (6)	C(2)—C(3)	1·391 (9)	C(9)—C(10)	1·390 (13)	C(15)—C(16)	1·381 (9)
P—O(2)	1·571 (5)	C(3)—C(4)	1·386 (12)	C(10)—C(11)	1·391 (13)	C(16)—C(17)	1·384 (11)
P—C(8)	1·820 (6)	C(4)—C(5)	1·412 (15)	C(11)—C(12)	1·367 (11)	C(17)—C(18)	1·368 (10)
C(8)—N(1)	1·298 (11)	C(5)—C(6)	1·358 (10)	C(12)—C(13)	1·378 (15)	C(18)—C(21)	1·536 (12)
N(2)—N(1)	1·386 (10)	C(6)—C(7)	1·392 (11)	C(13)—C(14)	1·385 (12)	C(18)—C(19)	1·373 (11)
S—N(2)	1·658 (7)	C(7)—C(2)	1·381 (13)	C(14)—C(9)	1·397 (9)	C(19)—C(20)	1·392 (11)
S—O(3)	1·422 (6)					C(20)—C(15)	1·392 (9)
S—O(4)	1·419 (5)						

O(1)—P—O(2)	115·3 (3)	P—C(2)—C(3)	116·8 (7)	C(8)—C(9)—C(10)	121·3 (10)	S—C(15)—C(16)	120·4 (5)
O(1)—P—C(2)	114·8 (3)	P—C(2)—C(7)	122·4 (5)	C(8)—C(9)—C(14)	119·6 (7)	S—C(15)—C(20)	119·3 (5)
O(1)—P—C(8)	110·3 (4)	C(3)—C(2)—C(7)	120·7 (7)	C(10)—C(9)—C(14)	119·1 (7)	C(16)—C(15)—C(20)	120·2 (6)
O(2)—P—C(2)	103·1 (4)	C(2)—C(7)—C(6)	119·1 (7)	C(9)—C(14)—C(13)	120·5 (8)	C(15)—C(20)—C(19)	119·2 (6)
O(2)—P—C(8)	108·0 (3)	C(7)—C(6)—C(5)	121·2 (10)	C(14)—C(13)—C(12)	119·3 (7)	C(20)—C(19)—C(18)	120·9 (6)
C(8)—P—C(2)	104·5 (3)	C(6)—C(5)—C(4)	119·9 (8)	C(13)—C(12)—C(11)	121·1 (8)	C(19)—C(18)—C(17)	118·8 (7)
P—O(2)—C(1)	119·1 (6)	C(5)—C(4)—C(3)	119·3 (7)	C(12)—C(11)—C(10)	120·0 (10)	C(18)—C(17)—C(16)	122·1 (7)
P—C(8)—C(9)	119·6 (6)	C(4)—C(3)—C(2)	119·7 (9)	C(11)—C(10)—C(9)	119·9 (7)	C(17)—C(16)—C(15)	118·8 (6)
P—C(8)—N(1)	124·9 (5)					C(19)—C(18)—C(21)	119·8 (6)
C(9)—C(8)—N(1)	114·6 (5)					C(17)—C(18)—C(21)	121·4 (7)
C(8)—N(1)—N(2)	119·3 (5)						
N(1)—N(2)—S	112·8 (4)						
N(2)—S—O(3)	103·6 (3)						
N(2)—S—O(4)	108·8 (3)						
N(2)—S—C(15)	103·5 (4)						
O(3)—S—O(4)	120·8 (4)						
O(3)—S—C(15)	109·5 (3)						
O(4)—S—C(15)	109·2 (3)						

Hydrogen bond

D H A	D···A	D—H	H···A	∠DHA
N(2)—H(N2)···O(1)	2·660 (7)	1·10 (8)	1·70 (9)	143 (9)
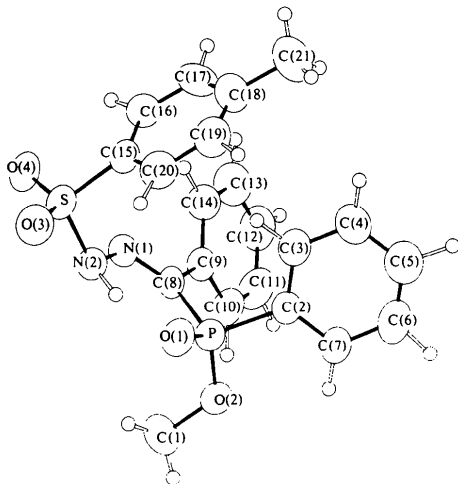
Fig. 1. ORTEP plot (Johnson, 1965) of methyl phenyl[syn-α-(tosylhydrazono)benzyl]phosphinate. Thermal ellipsoids are at the 50% probability level.

Fig. 2. Geometry of the six-membered ring formed by the intramolecular N—H···O hydrogen bond (distances in Å, angles in deg).

perience on this subject is rather limited (Olovsson & Jönsson, 1976). We have found a similar geometry in 3-diazo-2,3-dihydrophenalene-1,2-dione 1-[(4-bromophenyl)sulphonylhydrazone], where N—H···O = 2·56 (1), H···O = 1·94 (13) Å and ∠N—H···O = 113 (9)°. As can be seen from the torsion angles (Table 4), the six-membered ring is not quite planar. Deviations come from N(2) and, to a minor extent, from the H atom; distances of these two atoms from a least-squares plane through the other ring atoms are —0·21 and —0·14 Å respectively.

Table 4. Torsion angles (°) and a least-squares plane in the six-membered ring containing the N—H···O hydrogen bond

Torsion angles

H(N2)—N(2)—N(1)—C(8)	13·7 (4·2)	C(8)—P—O(1)—H(N2)	4·6 (2·6)
N(2)—N(1)—C(8)—P	—10·2 (8)	P—O(1)—H(N2)—N(2)	—1 (10)
N(1)—C(8)—P—O(1)	0·4 (6)	O(1)—H(N2)—N(2)—N(1)	—9 (11)

Least-squares plane defined by N(1)—C(8)—P—O(1)

$$5·6091x + 1·8802y + 6·4865z = 8·5737$$

Deviations (Å)

N(1)	0·001 (2)	C(8)	—0·002 (2)	P	0·001 (2)
O(1)	—0·001 (2)	N(2)	—0·21 (5)	H(N2)	—0·14 (8)

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N-Acetylanthranilic Acid (o-Acetamidobenzoic Acid), a Strongly Triboluminescent Material

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Abstract. $C_9H_9NO_3$, orthorhombic, $Fdd2$, $a = 10.845$ (9), $b = 30.204$ (7), $c = 10.575$ (4) Å, $V = 3464$ Å^3, $D_x = 1.378$, $D_m = 1.36$ Mg m^{-3} (by flotation), $Z = 16$. The final $R = 0.064$ for 799 reflexions and 118 variables. The molecules are inter-bonded by hydrogen bonds through the O(1) of the carboxyl group and O(3^i) of the acetamide group forming chains on alternating planes approximately parallel to (301) and (30̄1).

Introduction. The strong triboluminescence (TL) of N-acetylanthranilic acid and of many other compounds was observed by Zink, Hardy & Sutton (1976). From their experience they suggest that the presence or absence of TL is probably a function of the crystal structure. The crystal structure determination of the title compound was undertaken to provide the necessary information needed to test such a possibility.

N-Acetylanthranilic acid was obtained by refluxing anthranilic acid and acetic anhydride with subsequent hydrolysis. Colorless platelets of single crystals with melting point 461–462 K were obtained by recrystallization from a solution of acetic acid and water. The b direction is perpendicular and the a and c directions are parallel to the flat surface of the platelets. The optical study was carried out on a polarizing microscope and the refractive indices, determined by the immersion method, are:

$n_\alpha = 1.449$ $2V = 30°$
$n_\beta = 1.726$ optical character = biaxial (−)
$n_\gamma = 1.775$ birefringency $= \alpha - \gamma = 0.32$,

where the α, β and γ directions correspond respectively to the crystal b, a and c directions. Intensities were measured at room temperature on an Enraf–Nonius CAD-4 diffractometer with the θ–2θ scan technique up to $\theta = 75°$, using graphite-monochromatized Cu $K\alpha$ radiation and a scintillation counter. Systematic absences were found when the following conditions were not obeyed: hkl: $h + k$, $k + l$, $(l + h) =$ even; $0kl$: $k + l = 4n$ $(k,l = 2n)$; $h0l$: $l + h = 4n$ $(l,h = 2n)$; $hk0$: $h,k = 2n$; $h00$: $h = 4n$; $0k0$: $k = 4n$; $00l$: $l = 4n$, from which the space group $Fdd2$ was inferred. Of the 866 measured independent reflections, 799 with $I > 3\sigma(I)$ were considered as observed, where $\sigma(I)$ is the standard deviation of the intensity on the basis of counting statistics. As the crystal used was a triangular platelet with a largest dimension of 0.3 mm, $\mu = 0.888$ mm^{-1}, no absorption or extinction correction was made. The structure was solved with MULTAN (Germain, Main & Woolfson, 1971). Scattering factors were from Cromer & Waber (1974) for C, O, N and H. The coordinates of all atoms, except hydrogens, and the respective anisotropic temperature factors were refined by full-matrix least-squares minimization of

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