Table 3. *Important intermolecular distances* (Å) *and angles* (°)

	C⋯O/ O⋯O	H⋯O	C—H⋯O/ O—H⋯O	Symmetry of the last atom
O(7')—H(7')⋯O(4')	2·930 (2)	2·21 (2)	157·6 (12)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
C(2)—H(21)⋯O(3')	3·371 (2)	2·49 (2)	148·5 (15)	$1-x, -y, 1-z$
C(5)—H(5)⋯O(3')	3·387 (2)	2·58 (2)	137·5 (13)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
C(9)—H(93)⋯O(4')	3·498 (3)	2·54 (3)	169·3 (20)	$1+x, y, z$

twisted boat conformation with C(3a) and C(7) 0·316 (1) and 0·402 (1) Å respectively out of the mean plane passing through C(4), C(5), C(6) and C(7a) (within the deviation, ±0·081 Å); O(4), connected to C(4), lies in this plane. The dihedral angle between the planes is 43·2 (2)°. Variations in C—C bond lengths and the distortion in the six-membered ring are indicative of strain. In the furan ring, the O(1)—C(2) and O(1)—C(7a) distances are almost equal. This is in contrast to general observations of benzofuran systems which show differences in C—O lengths (Das, Sinha, Narkhede & Manisekharan, 1990). The methyl groups attached to C(7) have an average C—C distance of 1·538 (2) Å whereas the methyl C(8) is at a distance of 1·491 (3) Å. The

C—H distances are normal [average 0·098 (3) Å] but O(7')—H(7') is 0·76 (2) Å. Important intermolecular distances are listed in Table 3. In the crystal (Fig. 2), the molecules are linked into chains by an inter-molecular O—H⋯O bond; possible C—H⋯O inter-actions are also seen (Taylor & Kennard, 1982).

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Structure of 2-Benzoyl-1-phenylamino-2-(1-pyridinio)ethylene-1-thiolate

By Vladimir N. Nesterov, Valery E. Shklover, Yuri T. Struchkov, Yuli A. Sharanin, Anatoly M. Shestopalov and Andrey S. Demerkov

A. N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov St, Moscow B-334, USSR

Abstract. $C_{20}H_{16}N_2OS$, $M_r = 332$, monoclinic, $C2/c$, $a = 17·7807$ (12), $b = 8·9144$ (5), $c = 21·6994$ (11) Å, $\beta = 100·465$ (5)°, $V = 3382·2$ (3) Å^3, $Z = 8$, $D_m = 1·298$, $D_x = 1·306$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0·71069$ Å, $\mu = 2·004$ cm^{-1}, $F(000) = 1392$, $T = 293$ K, $R = 0·037$, $wR = 0·046$ for 1555 independent reflections. The molecule has a Z configuration relative to the formally double C(1)=C(2) bond. The negative charge is delocalized over the conjugated ylide S⋯C(1)⋯C(2)⋯C(3)⋯O moiety, the positive charge is


⋮
N(1)

localized at the N atom of the pyridinium ring.

Introduction. 2-Benzoyl-1-phenylamino-2-(1-pyridinio)ethylene-1-thiolate (I) has been obtained by interaction of *N*-phenacylpyridinium bromide with phenyl isothiocyanate in the presence of equimolar amounts of triethylamine in methanol at room temperature.

The data from UV, IR and NMR spectroscopy do not allow the unambiguous assignment of configuration (*E* or *Z*) of molecule (I) relative to the formal double C(1)=C(2) bond, so the X-ray structural analysis of the compound (I) was performed.
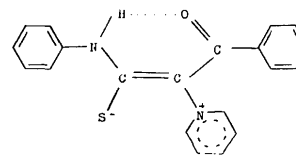
(I)

Experimental. Yellow prismatic crystals were obtained by recrystallization from nitromethane, one of which, with dimensions $0.3 \times 0.3 \times 0.4$ mm, was used for the measurements of unit-cell parameters (12 reflections with $14 < 2\theta < 16°$) and intensities of 1885 reflections ($-18 \le h \le 7$, $0 \le k \le 9$, $0 \le l \le 19$) with a four-circle automatic Hilger & Watts diffractometer (293 K, Mo $K\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 40°$). Density measured by flotation. Control of the quality of the sample was performed by measurements of intensities of two standard reflections ($\bar{8}00$ and 134) after each 100 reflections measured. No absorption or secondary-extinction corrections were applied. The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971), which allowed the location of all non-H atoms, and refined by the full-matrix least-squares technique in the anisotropic approximation for non-H atoms for 1555 independent reflections with $I \ge 2\sigma$. The minimized function was $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma^2(F_o) + |0.03F_o|^2]^{-1}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). H-atom positions were calculated and refined isotropically. The final discrepancy factors were $R = 0.037$, $wR = 0.046$, $S = 3.39$, the final value of the ratio (max. shift)/e.s.d. = 0.5, the max. and min. heights of the peaks of the final zero Fourier synthesis were ± 0.4 e Å^{-3}. All calculations were carried out with an Eclipse S/200 computer using the *INEXTL* program package (Gerr, Yanovsky, Struchkov, 1983).

Discussion. Atomic coordinates and bond angles are given in Tables 1* and 2, respectively. The geometry of (I) with bond lengths is shown in Fig. 1.

It is proved unambiguously by the X-ray structural data that molecule (I) has a Z configuration with an SC(1)C(2)N(2) torsion angle of $5.4 (1)°$. The molecule contains an approximately planar conjugated S⋯C(1)⋯C(2)⋯C(3)⋯O moiety [the devia-

         N(1)

tions of the atoms from the r.m.s. plane do not exceed $0.051 (2)$ Å], in which conjugation results in an elongation of the formally double $C(1)=C(2)$ bond to $1.429 (3)$ Å and a shortening of the formally single $C(2)$—$C(3)$ bond to $1.407 (3)$ Å [the standard values of lengths for $C(sp^2)=C(sp^2)$ double and $C(sp^2)$—$C(sp^2)$ single bonds are 1.331 and 1.478 Å respectively (Allen, Kennard, Watson, Brammer,

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Table 1. *Atomic coordinates ($\times 10^5$ for S, $\times 10^4$ for O, N, C) and equivalent isotropic temperature factors for* (I)

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
S	39437 (4)	−34 (7)	43146 (3)	3.93 (2)
O	3618 (1)	−3764 (2)	5717 (1)	4.4 (1)
N(1)	3976 (1)	−2913 (2)	4665 (1)	3.6 (1)
N(2)	3474 (1)	263 (2)	5572 (1)	2.8 (1)
C(1)	3859 (1)	−1457 (2)	4800 (1)	3.0 (1)
C(2)	3666 (1)	−1254 (2)	5406 (1)	2.8 (1)
C(3)	3584 (1)	−2383 (2)	5841 (1)	3.1 (1)
C(4)	3467 (1)	−1984 (2)	6488 (1)	3.1 (1)
C(5)	3951 (1)	−1012 (3)	6872 (1)	4.2 (1)
C(6)	3832 (2)	−696 (3)	7466 (1)	5.0 (1)
C(7)	3233 (2)	−1337 (3)	7690 (1)	5.5 (1)
C(8)	2764 (2)	−2319 (3)	7323 (1)	5.4 (1)
C(9)	2878 (2)	−2652 (3)	6727 (1)	4.3 (1)
C(10)	4015 (1)	1342 (2)	5687 (1)	3.4 (1)
C(11)	3824 (1)	2739 (2)	5859 (1)	4.0 (1)
C(12)	3089 (2)	3047 (2)	5929 (1)	4.2 (1)
C(13)	2551 (1)	1945 (3)	5810 (1)	4.4 (1)
C(14)	2744 (1)	566 (2)	5622 (1)	3.4 (1)
C(15)	4149 (1)	−3679 (2)	4140 (1)	3.4 (1)
C(16)	4334 (2)	−5178 (3)	4234 (1)	4.2 (1)
C(17)	4477 (2)	−6064 (3)	3747 (1)	5.3 (1)
C(18)	4444 (2)	−5463 (3)	3167 (1)	6.3 (1)
C(19)	4274 (2)	−3990 (4)	3070 (1)	6.1 (1)
C(20)	4125 (2)	−3078 (3)	3553 (3)	4.9 (1)

Table 2. *Bond angles (°) in* (I)

C(1)—N(1)—C(15)	134.7 (2)	C(5)—C(6)—C(7)	120.6 (3)
C(2)—N(2)—C(10)	121.0 (2)	C(6)—C(7)—C(8)	119.5 (3)
C(2)—N(2)—C(14)	118.6 (2)	C(7)—C(8)—C(9)	120.6 (3)
C(10)—N(2)—C(14)	120.4 (2)	C(4)—C(9)—C(8)	120.6 (2)
S—C(1)—N(1)	124.3 (2)	N(2)—C(10)—C(11)	119.8 (2)
S—C(1)—C(2)	122.6 (2)	C(10)—C(11)—C(12)	120.3 (2)
N(1)—C(1)—C(2)	113.1 (2)	C(11)—C(12)—C(13)	119.0 (2)
N(2)—C(2)—C(1)	116.8 (2)	C(12)—C(13)—C(14)	120.2 (2)
N(2)—C(2)—C(3)	116.1 (2)	N(2)—C(14)—C(13)	120.3 (2)
C(1)—C(2)—C(3)	126.8 (2)	N(1)—C(15)—C(16)	115.4 (2)
O—C(3)—C(2)	122.6 (2)	N(1)—C(15)—C(20)	125.8 (2)
O—C(3)—C(4)	116.8 (2)	C(16)—C(15)—C(20)	118.8 (2)
C(2)—C(3)—C(4)	120.6 (2)	C(15)—C(16)—C(17)	120.7 (2)
C(3)—C(4)—C(5)	122.2 (2)	C(16)—C(17)—C(18)	120.1 (3)
C(3)—C(4)—C(9)	119.4 (2)	C(17)—C(18)—C(19)	119.8 (3)
C(5)—C(4)—C(9)	118.3 (2)	C(18)—C(19)—C(20)	121.1 (3)
C(4)—C(5)—C(6)	120.4 (2)	C(15)—C(20)—C(19)	119.5 (3)

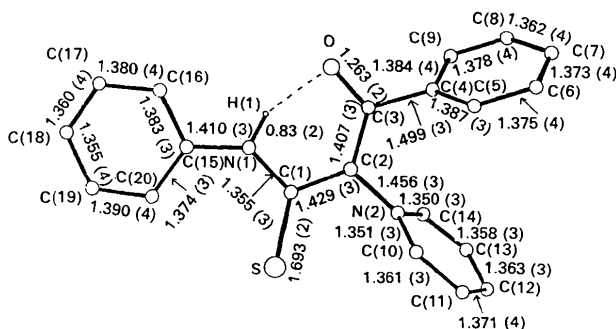

Fig. 1. General view of (I) with the bond lengths (Å). The intramolecular N—H⋯O hydrogen bond is shown by a dashed line.

Orpen & Taylor, 1987)].* The analogous redistri-
bution of the C—C bond lengths has been estab-
lished for the similar conjugated S—C—C—C—O
moieties of the molecules of 2-benzoyl-1-methylthio-
2-(1-pyridinio)ethylene-1-thiolate [(II); 1·397 (8) and
1·413 (9) Å] and 2-benzoyl-1-methylthio-2-(4-phenyl-
1-pyridinio)ethylene-1-thiolate [(III); 1·414 (5) and
1·436 (8) Å] (Alvarez-Builla, Gálvez, Cuadro,
Florencio & Blanco, 1987).

Considerable shortening of the formally single
C(1)—S⁻ bond to 1·693 (2) Å in comparison with
the standard C—S value of 1·751 Å suggests partici-
pation of the S atom in the conjugation. The C(1)≡S
bond length in (I) is comparable with that in ylides
(II) [1·684 (7) Å] and (III) [1·680 (6) Å], as well as in
Z and E isomers, co-existing in the crystal of 1-(2-
amino-1-cyano-2-thioethylene)pyridinium ylide [(IV);
1·712 (7) and 1·704 (6) Å] (Fischer, Knippel, Wollin,
Kálmán & Argay, 1983), but it is somewhat shorter
than, for instance, in the molecule of morpholinium
5-acetyl-3-cyano-1,4-dihydro-6-methyl-4-(2-nitrophe-
nyl)-2-pyridinethiolate [1·725 (3) Å] (Nesterov, Shk-
lover, Struchkov, Sharanin, Shestopalov &
Rodinovskaya, 1985).

Considerable elongation of the C(3)=O bond up
to 1·263 (2) Å [the standard bond length of a
non-conjugated C(sp²)=O bond is 1·199 Å] testifies
to participation of the O atom in the conjugation
system. Bond-length values of the same order were
found in ylides (II) [1·251 (9) Å] and (III)
[1·244 (6) Å]. Elongation of the C(3)=O bond in (I)
may be due also to the sufficiently strong intra-
molecular hydrogen bond N(1)—H(1)···O [N(1)···O
2·593 (3), N(1)—H(1) 0·83 (2), H(1)···O 1·83 (2) Å,
N(1)—H(1)···O 152 (2)°].

Participation of the N(1) atom lone pair in conju-
gation with the formally double C(1)=C(2) bond is
confirmed by its planar configuration (the sum of
bond angles is exactly 360°) and coplanarity of the
coordination plane with the aforementioned conju-
gated fragment (the dihedral angle is 1·9°). Conju-
gation causes considerable shortening of the
N(1)—C(1) bond down to 1·355 (3) Å [the standard
length of a conjugated C(sp²)—N(sp²) bond is
1·336 Å] in comparison with the N(1)—C(15) bond
length of 1·410 (3) Å.

As a whole the conformation of (I) is a result of a
compromise between the tendency to form a
common system of delocalized electrons in the afore-
mentioned planar moiety, existence of a strong intra-
molecular hydrogen bond and a large number of
shortened non-bonded contacts (Table 3). These con-
tacts cause the bending of Py⁺ and two Ph substit-
uents [C(4)···C(9) and C(15)···C(20)] to the
conjugated moiety by 66·1, 54·3 and 13·8°, respec-

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* All standard bond lengths are taken from this paper.

Table 3. *Shortened intramolecular noncovalent con-
tacts (Å) in (I)*

S···N(2)	3·004 (2)	N(2)···C(5)	3·017 (3)
S···C(10)	3·191 (2)	C(1)···C(10)	3·132 (3)
S···C(15)	3·327 (2)	C(1)···C(20)	3·177 (3)
S···C(20)	3·246 (3)	C(2)···C(5)	3·137 (3)
O···C(1)	2·947 (3)	C(3)···C(14)	3·019 (3)
O···C(9)	2·926 (3)	C(4)···C(14)	3·077 (3)
N(1)···C(3)	2·806 (3)	C(5)···C(10)	3·337 (3)
N(2)···C(4)	2·824 (3)		

Note: The sums of the van der Waals radii for the pairs of atoms S
and N, S and C, O and C, and N and C are 3·35, 3·50, 3·22 and
3·25 Å respectively; the double van der Waals radius of C atoms is
3·40 Å (Bondi, 1966).

tively. Considerable bending of the substituents
hinders their participation in conjugation with the
planar conjugated moiety of (I). Indeed, the value of
the C(2)—N(2) bond length of 1·456 (3) Å exceeds
the standard value (1·355 Å) for a conjugated
N(sp²)—C(sp²) bond and is close to the values
obtained for a single N⁺(sp²)—C(sp²) bond [e.g.
1·475 (9) Å in (II), 1·455 (6) Å in (III), 1·447 (8) and
1·448 (7) Å in the Z and E isomers of (IV)].

The shortened non-bonded intramolecular con-
tacts cause considerable increases of the SC(1)N(1),
C(1)C(2)C(3) and N(1)C(15)C(20) bond angles to
124·3 (2), 126·8 (2) and 125·8 (2)°, respectively, while
the N(1)C(1)C(2) [113·1 (2)°], N(2)C(2)C(3)
[116·1 (2)°] and N(1)C(15)C(16) [115·4 (2)°] bond
angles are considerably reduced.

Along with the shortened intramolecular contacts,
somewhat shortened intermolecular contacts O···
C(11') 3·148 (3) and O···C(12') 3·055 (3) Å (between
the carbonyl group and the pyridinium groups of the
molecules related by b translation) are also found.
The aforementioned intra- and intermolecular con-
tacts encourage the electrostatic stabilization of the
observed configuration of (I) in the crystal and con-
tribute to the intermolecular charge transfer.

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