β-Carbonylenamines. Crystal and Molecular Structure of *Z*-4-Phenyl-4-piperidino-3-(*p*-tolylsulphonylamino)but-3-en-2-one

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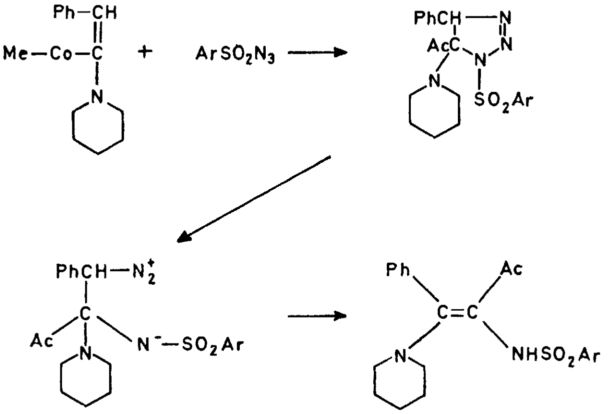
The crystal and molecular structure of the title compound (1) has been determined from *X*-ray three-dimensional diffraction data by direct methods and refined by blocked full-matrix least-squares to *R* 0.043. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.233(1)$, $b = 9.540(1)$, $c = 25.326(6)$ Å, $\beta = 111.42(1)°$. This is the first structural determination of an open-chain enamine with a carbonyl group on β-carbon atom. There is significant π-delocalization involving the piperidine nitrogen and the carbonyl group through the double C=C bond.

IN a previous paper [1] we reported structural evidence for π conjugation involving the sulphonyl group in open-chain β-sulphonylenamines. The most important effects which have been observed concerning the geometry of that functional group were lengthening of the C=C distance, twist deformation around that bond, and significant pyramidal character of the two carbon atoms. The estimated standard deviations for bond lengths involving the sulphonyl group were at the limit of the significance level giving the $C(sp^2)$–S distances only slightly shorter than those observed in alkyl or aryl sulphones. We report now the structure determination of (1), a β-carbonylenamine, *Z*-4-phenyl-4-piperidino-3-(*p*-tolylsulphonylamino)but-3-en-2-one, carried out in order to study π conjugation through the enamine functional group in this class of compounds. The product was synthesized (see Scheme) by reaction between *p*-tolylsulphonyl azide and 4-phenyl-3-piperidinobut-3-en-2-one [2] through a 1,2,3-triazoline intermediate which rapidly rearranged.



SCHEME

EXPERIMENTAL

Crystals were obtained as pale yellow monoclinic prisms from acetonitrile. Preliminary cell dimensions and symmetry information were obtained from rotation and Weissenberg photographs. Lattice parameters were refined by least-squares by use of 22 $(\theta,\chi,\phi)_{hkl}$ measurements on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{22}H_{26}O_3N_2S$, $M = 398.5$, Monoclinic, $a = 9.233(1)$, $b = 9.540(1)$, $c = 25.326(6)$ Å, $\beta = 111.42(1)°$, $Z = 4$, $D_c = 1.276$ g cm^{-3}, $U = 2\,074.2$ Å^3. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; $\mu(\text{Cu-}K_\alpha) = 14.84$ cm^{-1}. Space group $P2_1/c$ from systematic absences.

Intensity data were collected up to θ 70° by use of the ω—2θ scan method and the five-point technique [3] with nickel-filtered Cu-K_α radiation on a Siemens AED single-crystal diffractometer. Of 3 874 independent reflections measured, 582 were not used in the crystal analysis having intensities $\leqslant 2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$ where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal specimen were *ca.* 0.25 × 0.25 × 0.15 mm in the x,y,z directions. No absorption correction was applied.

Structure Analysis and Refinement.—Structure amplitudes were put on an absolute scale by Wilson's [4] statistical method (U 0.035 Å^2) and normalised structure-factor magnitudes E_{hkl} were then derived. The structure was solved by use of 400 reflections with $E \geqslant 1.61$. The E map computed by using the most consistent set of signs, clearly revealed the position of all the non-hydrogen atoms. A structure-factor calculation carried out at this stage gave R 0.29. The structure was refined by blocked full-matrix least-squares cycles, first with isotropic and then with anisotropic thermal

TABLE 1

Fractional co-ordinates (× 10^4) with standard deviations in parentheses

	x	*y*	*z*
S	−643(1)	416(1)	−951(1)
O(1)	−921(2)	−52(2)	−1 521(1)
O(2)	−1 423(2)	−272(2)	−626(1)
O(3)	2 701(3)	2 646(2)	−239(1)
N(1)	1 210(2)	228(2)	−588(1)
N(2)	2 254(2)	−1 500(2)	−1 332(1)
C(1)	−1 139(2)	2 208(2)	−985(1)
C(2)	−1 485(3)	2 947(2)	−1 484(1)
C(3)	−1 935(3)	4 332(2)	−1 580(1)
C(4)	−2 501(3)	5 006(2)	−1 038(1)
C(5)	−1 670(3)	4 247(2)	−534(1)
C(6)	−1 219(3)	2 855(2)	−505(1)
C(7)	−2 578(4)	6 506(3)	−1 066(2)
C(8)	2 327(2)	692(2)	−827(1)
C(9)	2 562(2)	−98(2)	−1 243(1)
C(10)	3 191(2)	579(2)	−1 646(1)
C(11)	4 539(2)	79(2)	−1 709(1)
C(12)	5 160(3)	771(3)	−2 055(1)
C(13)	4 432(3)	1 964(3)	−2 349(1)
C(14)	3 070(3)	2 442(2)	−2 306(1)
C(15)	2 449(2)	1 752(2)	−1 955(1)
C(16)	1 537(3)	−2 070(2)	−1 908(1)
C(17)	2 215(3)	−3 493(2)	−1 958(1)
C(18)	2 090(5)	−4 485(2)	−1 506(1)
C(19)	2 834(4)	−3 837(2)	−922(1)
C(20)	2 110(3)	−2 419(2)	−890(1)
C(21)	3 171(3)	1 976(2)	−563(1)
C(22)	4 663(3)	2 409(3)	−624(1)

parameters; R was reduced to 0.084. In the first block the atoms of the two phenyl rings were refined and in the second block the remaining atoms. A difference-Fourier synthesis was then computed and revealed significant residual peaks of height between 0.9 and 0.7 e$Å^{-3}$ over a background of *ca.* 0.3 $Å^{-3}$, and these were all interpreted as being due to hydrogen atoms. A few least-squares cycles were then carried out including hydrogen atoms with isotropic thermal parameters, and final values of R 0.043 and of R' 0.051 were obtained. The weighting scheme used in the last cycles was $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o)$ were determined from counting statistics. The shifts in parameters in the last cycle where all $<0.3\sigma$.

Positional parameters, together with their standard deviations are given in Tables 1 and 2. Atomic scattering factors were from ref. 5 for non-hydrogen atoms and from ref. 6 for hydrogen. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22477 (13 pp., 1 microfiche).*

TABLE 2

Fractional co-ordinates ($\times 10^3$) for hydrogen atoms

	x	y	z
HN(1)	146(3)	51(3)	−22(1)
HC(2)	−132(3)	253(3)	−187(1)
HC(3)	−225(4)	487(4)	−184(1)
HC(5)	−174(3)	468(3)	−18(1)
HC(6)	−98(4)	235(3)	−18(1)
H1C(7)	−237(4)	706(4)	−133(1)
H2C(7)	−372(5)	656(4)	−129(1)
H3C(7)	−212(5)	688(4)	−76(2)
HC(11)	507(3)	−62(3)	−149(1)
HC(12)	610(3)	39(3)	−210(1)
HC(13)	495(3)	247(3)	−256(1)
HC(14)	252(3)	326(3)	−253(1)
HC(15)	155(3)	205(3)	−189(1)
H1C(16)	37(3)	−215(3)	−197(1)
H2C(16)	169(3)	−145(3)	−219(1)
H1C(17)	337(3)	−337(3)	−193(1)
H2C(17)	164(3)	−383(3)	−240(1)
H1C(18)	98(4)	−469(3)	−160(1)
H2C(18)	263(4)	−523(4)	−148(1)
H1C(19)	413(4)	−371(4)	−81(1)
H2C(19)	280(4)	−433(4)	−66(1)
H1C(20)	275(3)	−194(3)	−50(1)
H2C(20)	90(3)	−253(3)	−99(1)
H1C(22)	450(4)	280(4)	−96(2)
H2C(22)	514(4)	305(3)	−34(1)
H3C(22)	529(4)	161(4)	−58(1)

All the calculations were carried out on a CDC Cyber 76 computer of Consorzio Interuniversitario per la gestione del Centro di Calcolo elettronico per l'Italia Nord-Orientale di Casalecchio, Bologna, with programs written by the authors and with the system SHELX-76 written by George Sheldrick at the University of Cambridge, U.K.

DISCUSSION

Molecular Geometry.—A projection of the structure showing the arbitrary crystallographic atom numbering is shown in Figure 1 and a packing diagram in Figure 2; relevant bond distances and angles are reported in Table 3.

TABLE 3

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond distances

S–O(1)	1.439(2)	C(4)–C(5)	1.395(3)
S–O(2)	1.435(2)	C(5)–C(6)	1.385(3)
S–N(1)	1.630(1)	C(6)–C(1)	1.387(3)
S–C(1)	1.763(2)	C(10)–C(11)	1.396(3)
N(1)–C(8)	1.444(3)	C(10)–C(15)	1.394(3)
C(8)–C(21)	1.474(3)	C(11)–C(12)	1.378(4)
C(8)–C(9)	1.374(3)	C(12)–C(13)	1.391(3)
N(2)–C(9)	1.368(3)	C(13)–C(14)	1.378(4)
C(9)–C(10)	1.492(3)	C(14)–C(15)	1.386(4)
O(3)–C(21)	1.236(4)	N(2)–C(16)	1.469(3)
C(21)–C(22)	1.500(4)	N(2)–C(20)	1.465(3)
C(1)–C(2)	1.378(3)	C(16)–C(17)	1.519(3)
C(2)–C(3)	1.379(3)	C(17)–C(18)	1.521(4)
C(3)–C(4)	1.390(4)	C(18)–C(19)	1.514(4)
C(4)–C(7)	1.505(4)	C(19)–C(20)	1.524(4)

(*b*) Bond angles

O(1)–S–O(2)	119.2(1)	N(1)–C(8)–C(21)	113.9(2)
O(1)–S–N(1)	107.3(1)	C(9)–C(8)–C(21)	126.7(2)
O(1)–S–C(1)	107.7(1)	N(2)–C(9)–C(8)	125.5(2)
O(2)–S–N(1)	105.6(1)	N(2)–C(9)–C(10)	114.9(2)
O(2)–S–C(1)	107.2(1)	C(8)–C(9)–C(10)	119.7(2)
N(1)–S–C(1)	109.6(1)	C(9)–C(10)–C(11)	121.1(2)
S–N(1)–C(8)	119.5(1)	C(9)–C(10)–C(15)	119.8(2)
C(9)–N(2)–C(16)	121.1(2)	C(11)–C(10)–C(15)	119.0(2)
C(9)–N(2)–C(20)	122.1(2)	C(10)–C(11)–C(12)	120.4(2)
C(16)–N(2)–C(20)	113.8(2)	C(11)–C(12)–C(13)	119.9(2)
S(1)–C(1)–C(2)	120.6(2)	C(12)–C(13)–C(14)	120.3(3)
S(1)–C(1)–C(6)	119.0(2)	C(13)–C(14)–C(15)	119.8(2)
C(2)–C(1)–C(6)	120.3(2)	C(10)–C(15)–C(14)	120.5(2)
C(1)–C(2)–C(3)	119.7(2)	N(2)–C(16)–C(17)	111.3(2)
C(2)–C(3)–C(4)	121.4(2)	C(16)–C(17)–C(18)	110.3(3)
C(3)–C(4)–C(5)	118.0(2)	C(17)–C(18)–C(19)	110.3(3)
C(3)–C(4)–C(7)	121.7(3)	C(18)–C(19)–C(20)	111.3(2)
C(5)–C(4)–C(7)	120.3(3)	N(2)–C(20)–C(19)	109.0(2)
C(4)–C(5)–C(6)	121.1(2)	O(3)–C(21)–C(8)	118.3(2)
C(1)–C(6)–C(5)	119.4(2)	O(3)–C(21)–C(22)	119.0(2)
N(1)–C(8)–C(9)	119.3(2)	C(8)–C(21)–C(22)	122.4(2)

(*c*) Carbon–hydrogen bonds

H–N(1)	0.92(3)	H(1)–C(16)	1.03(3)
H–C(2)	1.11(3)	H(2)–C(16)	0.97(3)
H–C(3)	0.92(3)	H(1)–C(17)	1.05(3)
H–C(5)	1.01(3)	H(2)–C(17)	1.10(3)
H–C(6)	0.91(3)	H(1)–C(18)	0.98(4)
H(1)–C(7)	0.92(4)	H(2)–C(18)	0.86(4)
H(2)–C(7)	1.00(4)	H(1)–C(19)	1.10(3)
H(3)–C(7)	0.81(4)	H(2)–C(19)	0.84(4)
H–C(11)	0.90(3)	H(1)–C(20)	1.06(3)
H–C(12)	0.99(3)	H(2)–C(20)	1.05(3)
H–C(13)	0.96(3)	H(1)–C(22)	0.90(4)
H–C(14)	0.99(3)	H(2)–C(22)	0.92(3)
H–C(15)	0.95(3)	H(3)–C(22)	0.94(4)

(*d*) Torsional angles in the piperidine ring

C(16)–N(2)–C(20)–C(19)	−57.4
C(20)–N(2)–C(16)–C(17)	57.2
N(2)–C(16)–C(17)–C(18)	−54.2
C(16)–C(17)–C(18)–C(19)	54.4
C(17)–C(18)–C(19)–C(20)	−56.5
C(18)–C(19)–C(20)–N(2)	56.7

This is the first structural determination of an open-chain enamine bearing on the β-carbon atom a carbonyl and a *p*-tolylsulphonylamino-group and it is quite interesting to analyse in some detail the geometry of this functional group. As already observed in the β-sulphonylenamines we have discussed previously,[1] the substituents involved in π conjugation through the double bond are in a *trans*-configuration and show similar geometrical features. Moreover, in the present case the whole N–C=C–C=O group is in an all-*trans* quasi-planar conformation.

The twist deformation around the C=C double bond [dihedral angle N(1),C(8),C(21)–N(2),C(9),C(10) 25.13°, *cf.* 19.6, 26.4, and 20.4° in ref. 1] and its lengthening

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1978, Index issue.

[1.374(3); the values given in ref. 1 are 1.317(13), 1.368(6), and 1.354(6) Å] are quite remarkable and show the significant π-delocalisation which involves the piperidine nitrogen atom.

The trigonal C(8) and C(21) carbon atoms are 0.023(2) and 0.046(3) Å out of the planes defined by N(1), C(21), C(9), and C(8), O(3), C(22); comparable values from ref. 1 are 0.050(5) and 0.046(5) Å (mean).

As far as the acetyl group is concerned bond lengths C(8)–C(21) [1.474(3)] and O(3)–C(21) [1.236(4) Å] show some significant shortening and lengthening, respectively, in agreement with the fact that the carbonyl group is also involved in the π delocalisation. On the other side, the length of the C(8)–N(1) bond [1.444(3) Å] is comparable in length with values usually reported for C(sp^2)–N(sp^2) single bonds and this confirms the predictably small influence of the sulphonylamino-group on the conjugate system.

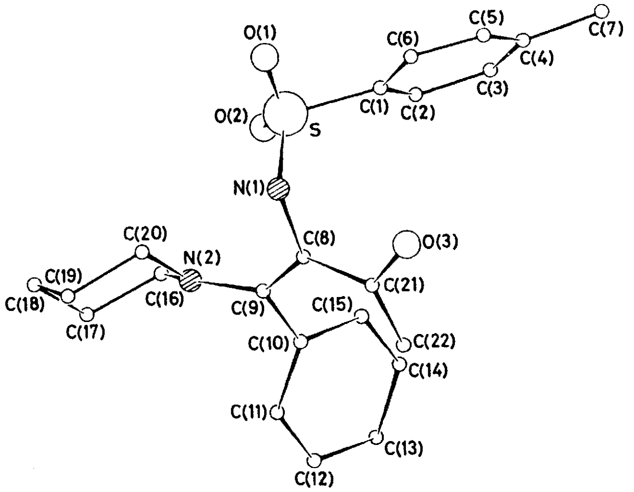

FIGURE 1 Projection of the structure along (001)

The conformation of the molecule can be described by the torsion angles C(1)–S–N(1)–C(8) −45.9, C(9)–C(8)–C(21)–O(3) −172.2, C(8)–C(9)–C(10)–C(11) −124.0, and C(8)–C(9)–N(2)–C(16) 138.7°. Torsion angles within the piperidine ring are unexceptional.

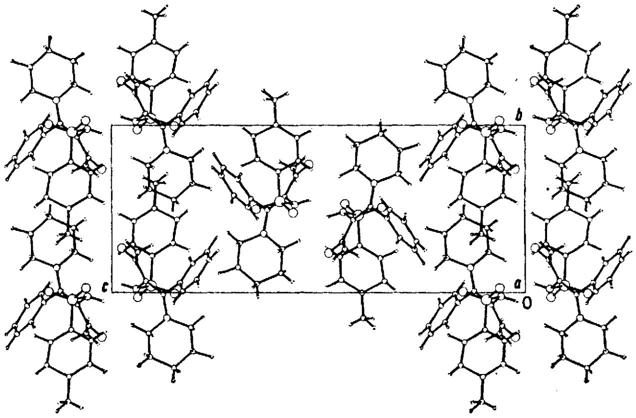

FIGURE 2 Packing of the molecule

Each molecule is linked with a symmetry-related neighbour by a weak hydrogen bond: N(1) · · · O(2) 3.006(3), HN(1) · · · O(2) 2.16(1) Å. Other contacts are consistent with van der Waals interactions.

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