Energetically favoured configurations for cyclohexane are boat, chair and twisted boat; for cycloheptane chair, boat, twisted chair and twisted boat (Hendrickson, 1964). The azabicyclo[3.2.2]nonane ring adopts a boat–boat conformation, with both *L* and *R* rings adopting boat conformations while the base cycloheptane ring *B* adopts the chair conformation. The pyridine rings are planar.

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Structure of Morpholinium 5-Acetyl-3-cyano-1,4-dihydro-6-methyl-4-(2-nitrophenyl)-2-pyridinethiolate, $C_4H_{10}NO^+.C_{15}H_{12}N_3O_3S^-$

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Abstract. $M_r = 402\cdot46$, monoclinic, $C2/c$, $a = 21\cdot221\ (6)$, $b = 11\cdot665\ (4)$, $c = 16\cdot598\ (4)$ Å, $\beta = 108\cdot75\ (2)^\circ$, $V = 3891\ (2)$ Å^3, $Z = 8$, $D_x = 1\cdot374$, $D_m = 1\cdot270$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot027$ cm^{-1}, $F(000) = 1696$, $T = 293$ K. $R = 0\cdot052$ using 2913 independent observed reflections. The crystal has an ionic structure. Two conjugated systems N≡C—C=C—S and O=C—C=C—N exist in the anion and the heterocycle present in it has a flattened boat conformation. The length of the C(1)—S bond to the formally negatively charged S atom is equal to 1·725 (3) Å. The pseudo-axial *o*-nitrophenyl substituent is rotated by 75·6 (1)° with respect to the bottom of the boat. Intermolecular N—H···O, N—H···S and N—H···N hydrogen bonds of 2·729 (4), 3·407 (3) and 2·990 (4) Å are observed in the crystal.

Introduction. The title compound (I) was obtained by reaction of cyano(2-nitrobenzylidene)thioacetamide with acetylacetone in the presence of an excess of morpholine. Salt (I) is also formed on interaction of the enamine, obtained from acetylacetone and morpholine, with cyano(2-nitrobenzylidene)thioacetamide. The present X-ray study was performed to confirm the structure of salt (I).

Experimental. On recrystallization of salt (I) from ethanol prismatic ruby crystals were obtained, one of which with dimensions 0·2 × 0·2 × 0·3 mm was used to measure the cell parameters (using 24 reflections with $33 < 2\theta < 34^\circ$) and intensities of 5381 reflections ($0 \le h \le 28$, $0 \le k \le 15$, $-22 \le l \le 22$) with a Syntex $P2_1$ diffractometer (Mo $K\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\max} = 58^\circ$). No significant variation in intensities of three standard reflections ($0\bar{2}0$, 202, 222) measured after every 100 reflections. No absorption and secondary-extinction corrections. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971), revealing all nonhydrogen atoms, and refined by full-matrix least squares with anisotropic thermal parameters for nonhydrogen atoms, using 2913 independent reflections with $I > 2\sigma$ and minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/[\sigma^2(F_o) + |F_o|^2]$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Hydrogen atoms located by a difference synthesis and refined isotropically. Final *R*

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= 0·052, $wR = 0·045$, max. (shift/σ) = 0·5, final electron density fluctuations $\pm 0·4$ e Å^{-3}. All calculations performed with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Table 1. *Atomic coordinates* ($\times 10^5$ *for* S, $\times 10^4$ *for* O, N, C *atoms*) *and equivalent isotropic thermal parameters of nonhydrogen atoms*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a^*_ia^*_j(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å^2)
S	−9636 (4)	22699 (9)	15906 (6)	2·22 (2)
O(1)	1367 (1)	692 (2)	−134 (2)	3·02 (8)
O(2)	−1310 (1)	1601 (2)	−2204 (2)	3·29 (8)
O(3)	−1920 (1)	3127 (3)	−2558 (2)	4·29 (9)
O(4)	3221 (1)	1318 (2)	−408 (2)	3·95 (9)
N(1)	175 (1)	1853 (2)	1292 (2)	2·09 (8)
N(2)	−2001 (1)	2277 (3)	−689 (2)	2·58 (8)
N(3)	−1388 (1)	2645 (3)	−2185 (2)	2·95 (9)
N(4)	2334 (1)	−520 (2)	−514 (2)	2·22 (8)
C(1)	−501 (1)	2032 (3)	921 (2)	1·78 (9)
C(2)	589 (1)	1512 (3)	856 (2)	1·85 (9)
C(3)	368 (1)	1448 (3)	−11 (2)	1·82 (9)
C(4)	−330 (1)	1847 (3)	−522 (2)	1·65 (8)
C(5)	−751 (1)	1984 (3)	58 (2)	1·65 (9)
C(6)	−1444 (1)	2144 (3)	−338 (2)	2·01 (9)
C(7)	1281 (2)	1229 (3)	1419 (2)	2·56 (10)
C(8)	−330 (1)	2992 (3)	−985 (2)	1·86 (9)
C(9)	171 (2)	3776 (3)	−628 (2)	2·31 (10)
C(10)	184 (2)	4860 (3)	−969 (2)	3·01 (11)
C(11)	−316 (2)	5194 (3)	−1681 (2)	3·23 (12)
C(12)	−827 (2)	4459 (3)	−2056 (2)	3·06 (11)
C(13)	−828 (2)	3370 (3)	−1714 (2)	2·26 (10)
C(14)	787 (2)	1008 (3)	−481 (2)	2·18 (10)
C(15)	503 (2)	928 (4)	−1436 (2)	3·07 (11)
C(16)	2872 (2)	−249 (3)	297 (2)	2·85 (11)
C(17)	3028 (2)	1000 (4)	307 (3)	3·42 (12)
C(18)	2678 (2)	1132 (4)	−1164 (3)	3·82 (13)
C(19)	2496 (2)	−116 (2)	−1276 (2)	2·76 (10)

Table 2. *Bond angles* (°)

SC(1)N(1)	117·5 (3)	C(9)C(10)C(11)	120·1 (4)
SC(1)C(5)	125·1 (3)	C(10)C(11)C(12)	119·8 (4)
N(1)C(1)C(5)	117·4 (3)	C(11)C(12)C(13)	119·5 (4)
C(1)N(1)H(N1)	122 (2)	C(8)C(13)C(12)	122·8 (4)
C(2)N(1)H(N1)	117 (2)	N(3)C(13)C(8)	122·6 (3)
C(1)N(1)C(2)	124·0 (3)	N(3)C(13)C(12)	114·6 (4)
N(1)C(2)C(7)	113·6 (3)	C(13N(3)O(2)	119·4 (3)
N(1)C(2)C(3)	121·0 (3)	C(13)N(3)O(3)	117·4 (3)
C(3)C(2)C(7)	125·4 (4)	O(2)N(3)O(3)	123·1 (3)
C(2)C(3)C(14)	121·6 (3)	O(1)C(14)C(3)	123·0 (4)
C(4)C(3)C(14)	117·6 (3)	O(1)C(14)C(15)	118·3 (4)
C(2)C(3)C(4)	120·8 (3)	C(15)C(14)C(3)	118·7 (3)
C(3)C(4)C(8)	112·7 (3)	C(16)N(4)H(1N4)	111 (2)
C(5)C(4)C(8)	108·7 (3)	C(16)N(4)H(2N4)	111 (3)
C(3)C(4)C(5)	110·1 (3)	C(16)N(4)C(19)	112·4 (3)
C(4)C(5)C(6)	117·0 (3)	C(19)N(4)H(1N4)	112 (2)
C(6)C(5)C(1)	118·6 (3)	C(19)N(4)H(2N4)	106 (3)
C(4)C(5)C(1)	124·3 (3)	H(1N4)N(4)H(2N4)	114 (3)
C(5)C(6)N(2)	177·3 (4)	N(4)C(16)C(17)	108·6 (3)
C(4)C(8)C(9)	118·9 (3)	C(16)C(17)O(4)	111·5 (4)
C(4)C(8)C(13)	125·7 (3)	C(17)O(4)C(18)	109·2 (3)
C(9)C(8)C(13)	115·2 (3)	O(4)C(18)C(19)	111·1 (4)
C(8)C(9)C(10)	122·7 (4)	C(18)C(19)N(4)	108·8 (4)

Angles involving H atoms are given only when these atoms participate in hydrogen bonds.

Discussion. The atomic coordinates are given in Table 1,* bond angles are listed in Table 2. The structure of the anion with bond lengths is shown in Fig. 1. The crystal structure is shown in Fig. 2 with atomic numbering in the ions.

The six-membered 1-azacyclohexa-2,5-diene heterocycle has a flattened boat conformation. The N(1) and C(4) atoms are displaced from the plane of the four

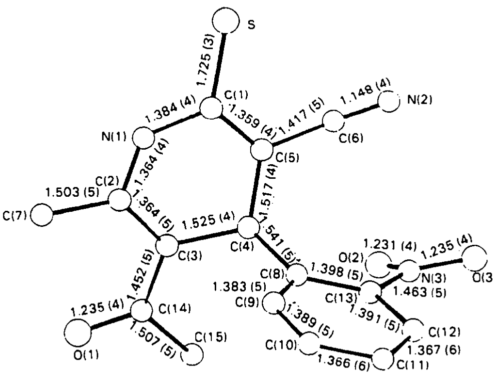

Fig. 1. The structure of the anion of (I), showing bond distances (Å).

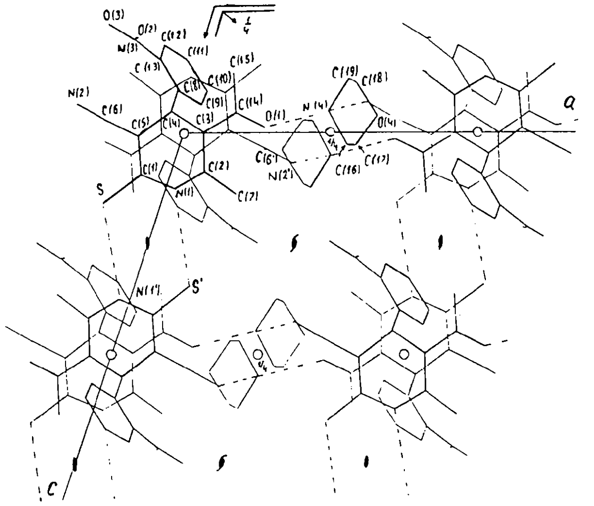

Fig. 2. The crystal structure of (I). Hydrogen bonds are shown by dotted lines.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42108 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

remaining atoms of the cycle by 0·073 (2) and 0·193 (4) Å respectively. This corresponds to the folding of the heterocycle along the N(1)···C(4) line by 12·1 (1)°.

There is a conjugation along the N(2)≡C(6)—C(5)=C(1)—S chain as indicated by the planarity of this moiety and by the bond distances in it. The C(5)—C(6) bond length of 1·417 (5) Å is somewhat shortened and the C(1)=C(5) bond length of 1·359 (4) Å is increased in comparison with the standard values of bond lengths C(sp^2)—C(sp) and C(sp^2)=C(sp^2) of 1·426 and 1·333 Å respectively (Kitaigorodsky, 1973). The length of the C(6)≡N(2) triple bond of 1·148 (4) Å in fact coincides with the value of 1·148 (6) Å in 2-benzoyl-3-dimethylamino-3-methylthio-2-propenenitrile (Adhikesavalu & Venkatesan, 1981). The C(1)—S bond of 1·725 (3) Å with the formally negatively charged S atom is somewhat shorter than the ordinary C(sp^2)—S bond, *e.g.* 1·755 (4) Å (Adhikesavalu & Venkatesan, 1981). Nevertheless the latter bond can be still shorter, *e.g.* 1·73 (1) Å in 1,3-dithiolane-2-thione (Klewe & Seip, 1972). The C(1)—S bond length in the anion of (I) is shortened because of the partial double-bond character of this bond. Such an explanation was used in the description of the S—C bond length of 1·726 (3) Å (coinciding with that found in I) in the molecule of 3-thioxo-2-pyridinecarboxylic acid (Bourne & Taylor, 1983).

The coplanarity of substituents at the C(1)=C(5) bond results in the short non-bonded S···C(6) distance of 3·034 (3) Å, while the sum of van der Waals radii is 3·5 Å (Bondi, 1966). This steric interaction gives rise to an enlargement of the SC(1)C(5) bond angle to 125·1 (3)° as compared with the SC(1)N(1) bond angle of 117·5 (3)°.

Conjugation in the approximately planar O(1)=C(14)—C(3)=C(2)—N(1) chain also may be assumed. The C(14)=O(1) and C(2)=C(3) bonds of 1·235 (4) and 1·364 (5) Å are elongated in comparison with the length of the C(sp^2)=O bond of 1·207 (4) Å in the molecule of acetaldehyde in the vapour phase (Barrow, Long & Millen, 1974) and with the standard C(sp^2)=C(sp^2) bond length of 1·333 Å (Kitaigorodsky, 1973). The C(3)—C(14) bond length of 1·452 (5) Å is somewhat shortened as compared with the standard ordinary C(sp^2)—C(sp^2) bond length of 1·476 Å (Kitaigorodsky, 1973). The N(1)—C(1) and N(1)—C(2) bonds of 1·384 (4) and 1·364 (4) Å are significantly shorter than the normal value of the N—C(sp^2) bond length of 1·426 (12) Å (*International Tables for X-ray Crystallography*, 1968). Therefore these bonds seem to have an increased bond order.

The coplanar arrangement of methyl and acetyl substituents gives rise to the shorter non-bonded O(1)···C(7) distance of 2·714 (4) Å (the sum of van der Waals radii being 3·22 Å; Bondi, 1966). Following Berkovitch-Yellin & Leiserowitz (1984) it is possible that the short O(1)···C(7) contact should be considered a hydrogen bond [H(3C7)···O(1) 2·45 (3) Å, C(7)—H(3C7)···O(1) 96 (2)°].

The C(2)—C(7) and C(14)—C(15) bond lengths of 1·503 (5) and 1·507 (5) Å almost coincide with the standard value for the C(sp^2)—C(sp^3) bond of 1·507 Å (Kitaigorodsky, 1973).

The substituted Ph ring is rotated with respect to the bottom of the heterocycle boat by 75·6 (1)° and occupies a pseudo-axial position. The N=O distances of 1·231 (4) and 1·235 (4) Å in the nitro group, its rotation with respect to the plane of the benzene ring and the C(Ph)—N(O_2) bond length of 1·463 (5) Å are similar to those found for instance in the molecule of *N,N*-difluoroamino-2,4-dinitrobenzene [the corresponding values in the two independent molecules are equal to 1·22 (1) and 1·22 (1) Å, 36·5 and 27·0°, 1·473 (5) and 1·478 (5) Å (Batail, Louër, Grandjean, Dudragne & Michaud, 1976)].

The rotation of the nitro group with respect to the benzene ring plane is such that there is a non-bonded O(2)···C(4) contact of 2·910 (5) Å with an increase in the N(3)C(13)C(8) bond angle as compared with N(3)C(13)C(12) [122·6 (3) and 114·6 (4)° respectively]. This contact should also be considered as a hydrogen bond [H(C4)···O(2) 2·22 (3) Å, C(4)—H(C4)···O(2) 123 (2)°] (Berkovitch-Yellin & Leiserowitz, 1984).

The increase in the endocyclic C(8)C(13)C(12) angle, 122·8 (4) with respect to 120°, is due to the strong electron-accepting action of the NO_2 group (Domenicano, Vaciago & Coulson, 1975).

The morpholinium heterocycle has a chair conformation, the O(4) and N(4) atoms being displaced by −0·685 (3) and 0·625 (3) Å from the C(16), C(17), C(18), C(19) plane. The mean values of the C—C, C—N and C—O bond lengths of 1·498 (6), 1·492 (2) and 1·422 (1) Å, respectively, coincide with the corresponding mean values in the other morpholinium salts, *e.g.* in morpholinium morpholinoformate (1·514, 1·490, 1·425 Å; Brown & Gray, 1982).

An extended hydrogen-bond system is present in the crystal. Anions and cations are linked in chains along the *a* axis *via* the following hydrogen bonds N(4)—H(1N4)···O(1) [N(4)···O(1) 2·729 (4), H(1N4)···O(1) 1·79 (4) Å, N(4)—H(1N4)···O(1) 160 (4)°] and N(4)—H(2N4)···N(2^{i}) ($x+\frac{1}{2}$, $y-\frac{1}{2}$, z) [N(4)···N(2^{i}) 2·990 (4), H(2N4)···N(2^{i}) 2·30 (4) Å, N(4)—H(2N4)···N(2^{i}) 134 (3)°].

Weak hydrogen bonds N(1)—H(N1)···S^{ii} ($\bar{x}$, y, $\frac{1}{2}-z$) [N(1)···S^{ii} 3·407 (3), H(N1)···S^{ii} 2·55 (3) Å, N(1)—H(N1)···S^{ii} 177 (2)°] between anions related by twofold axes link the above-mentioned chains into layers parallel to (010).

All other distances between the ions in the crystal are close to the sums of the van der Waals radii.

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trans-*N*-[3-Methyl-2-*p*-toluenesulphonimido-3-azatricyclo[8.5.0.0^{4,9}]pentadeca-4(9),5,7-trien-10-yl]-*p*-toluenesulphonamide, $C_{29}H_{33}N_3O_4S_2$

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Abstract. $M_r = 551{\cdot}7$, triclinic, $P\bar{1}$, $a = 14{\cdot}67$, $b = 13{\cdot}00$, $c = 8{\cdot}25$ Å, $\alpha = 99{\cdot}9$, $\beta = 109{\cdot}0$, $\gamma = 101{\cdot}9°$, $V = 1406{\cdot}2$ Å^3, $Z = 2$, $D_m = 1{\cdot}312$, $D_x = 1{\cdot}303$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 19{\cdot}22$ cm^{-1}, $F(000) = 584$, $T = 295$ K. Final $R = 0{\cdot}0754$ for 1375 unique reflections. The compound has *trans* stereochemistry. Hydrogen bonds of 2·960 Å link N(1) of one molecule to O(3) of another. The seven-membered ring has the chair conformation. The sulphonyl S—N(imino) distance [1·60 (1) Å] is shorter than the sulphonyl S—N(amino) distance [1·64 (1) Å]. The S—O distances in each sulphonyl group are comparable.

Introduction. The stereochemistry of the title compound is of interest as it was observed (Bailey, 1977) that the related six-membered-ring compound on reaction with 1,5-diaza[4.3.0]bicyclonon-5-ene in base shows *cis* stereochemistry, since elimination of the TosNH group by base does not occur. However, hydrolysis and elimination takes place after boiling the related six-membered sulphone with 1,5-diaza[4.3.0]-bicyclonon-5-ene in alcohol for about 24 hours to form the 10-aza compound.

One would expect the compound containing a seven-membered ring and prepared by a route analogous to that used for the six-membered ring (Bailey & Seager, 1974) also to contain a *cis* junction, since a dramatic change in the mechanistic pathway was not envisaged. However, after boiling the compound for five minutes in ethanol with 1,5-diaza[4.3.0]-bicyclonon-5-ene the TosNH group is eliminated suggesting the seven-membered-ring homologue might have *trans* stereochemistry.

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