Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1400). Services for accessing these data are described at the back of the journal.

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(*R*)- and (*S*)-2-(4-Bromophenyl)-2-oxoethyl 2-Methoxymethylpyrrolidine-1-dithiocarboxylate

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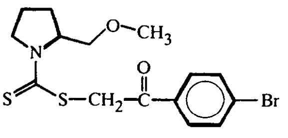
Abstract

The absolute configurations of both the enantiomers of the title compound, $C_{15}H_{18}BrNO_2S_2$, have been determined. As expected, the molecular dimensions of both forms are insignificantly different. The phenacyl and dithiocarbamate fragments are planar and approximately perpendicular to one another. The short N—C(=S) bond length [1.330 (7) Å] indicates involvement of the N-atom lone pair in the thiocarbonyl π system.

Comment

(*R*)- and (*S*)-2-methoxymethylpyrrolidine have long been known as very valuable chiral auxiliaries (Enders & Klatt, 1996, and references therein). Recently, we tried to use these compounds for the synthesis of enantiomerically pure thiols *via* diastereoselective alkylation and subsequent cleavage of chiral dithiocarbamates (Dölling *et al.*, 1997). In the course of those investigations, both enantiomeric title compounds [(*R*)-(1) and (*S*)-(1)] were synthesized and their assumed absolute configurations confirmed by X-ray analyses. The two structure analyses were performed in exactly the same way. Therefore, comparison of the results enables a realistic judgement of geometric parameters (bond lengths, *etc.*) obtained by the present standard routine of X-ray analysis. Considering the *R* values and s.u.'s, the results obtained for (*R*)-(1) seem to be a little more precise than those obtained for (*S*)-(1), possibly due to a small difference in quality of the crystals. But an inspection of the geometric parameters reveals only insignificant differences. The differences in corresponding bond lengths (angles) amount to less than 0.5σ (0.8σ) in most cases and maximally 1.5σ (1.8σ). In the following, only numerical values for (*R*)-(1) are considered; the deposited data include those of (*S*)-(1) [data for (*S*)-(1) have been deposited† in the Cambridge Structural Database (Allen *et al.*, 1983)].



(1)

The essential structural features of (1) can be seen in Fig. 1 and Table 1. The molecule has a chiral centre at atom C1 of the pyrrolidine ring, which adopts an envelope conformation with the C2 atom deviating by 0.502 (9) Å from the plane through the other four atoms. There are two other planar moieties in the molecule, the phenacyl fragment [atoms C8–C15; maximum deviation from planarity 0.039 (8) Å for C11] and the dithiocarbamate moiety (atoms N1, C7, S1 and S2; exactly planar within 3σ), which are nearly perpendicularly oriented [86.2 (2)°] to one another.

Most of the observed bond lengths and angles in (1) are in good agreement with standard values. However, the C7—N1 distance of 1.330 (7) Å is markedly shorter than the normal C_{sp^2}—N_{sp^3} single bond (1.43 Å; Rademacher, 1987) and indicates an obvious participation of the N-atom lone pair in the π system of

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† CCDC deposit No. 100834.

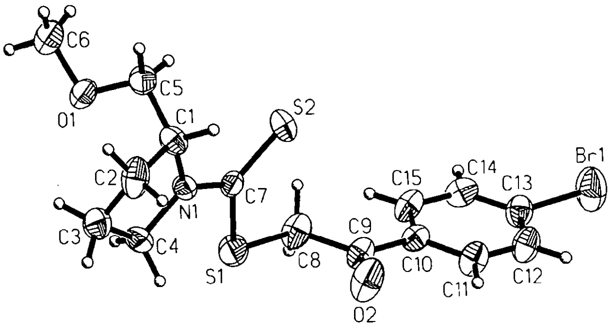

Fig. 1. The molecular structure of the *R* enantiomer of (1) showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms as spheres of arbitrary radii.

the thiocarbonyl group and a substantial contribution of the zwitterionic resonance form (pyrrolidinium structure) to the overall structure. Accordingly, the sum of the three bond angles around the N atom is exactly 360°. A search of the April 1997 version of the Cambridge Structural Database (Allen *et al.*, 1983) revealed only two crystal structures of *N*,*N*-disubstituted phenacyl dithiocarbamates, Ph—C(O)—CH$_2$—S—C(S)—NR_2. The observed molecular structure of (1) is in good agreement with that of phenacyl pentamethylenedithiocarbamate (Baumeister *et al.*, 1989), *i.e.* there are only insignificant differences in corresponding bond lengths and angles, and very similar conformational behaviour, whereas phenyl *N*,*N*-diethyldithiocarbamate (Ng, 1993) shows slight variations in the conformation around bonds C7—S1, S1—C8 and C8—C9; the corresponding torsion angles differ by up to 23.5°.

Experimental

The title compounds were prepared as described recently (Dölling *et al.*, 1997). Single crystals were obtained by recrystallization from ethanol.

Crystal data

$C_{15}H_{18}BrNO_2S_2$
$M_r = 388.33$
Orthorhombic
$P2_12_12_1$
$a = 9.7824\,(7)$ Å
$b = 10.583\,(1)$ Å
$c = 16.344\,(1)$ Å
$V = 1692.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.524$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 80 reflections
$\theta = 10.2$–$12.3°$
$\mu = 2.68$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.30 × 0.28 × 0.17 mm
Brown–yellow

Data collection

Stoe Stadi-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{\min} = 0.396$, $T_{\max} = 0.466$
3432 measured reflections
2969 independent reflections
1891 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\max} = 24.95°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 6.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.133$
$S = 1.242$
2948 reflections
191 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 1.8808P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.330$ e Å^{-3}
$\Delta\rho_{\min} = -0.303$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0019 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (2); 1716 Friedel pairs

Table 1. *Selected geometric parameters (Å, °)*

S1—C7	1.771 (7)	N1—C7	1.330 (7)
S1—C8	1.787 (7)	C8—C9	1.519 (10)
S2—C7	1.655 (7)	C9—C10	1.501 (10)
O2—C9	1.201 (9)		
C7—S1—C8	102.0 (4)	C9—C8—S1	115.2 (6)
N1—C7—S2	125.1 (5)	O2—C9—C8	121.6 (7)
N1—C7—S1	111.3 (5)	C10—C9—C8	117.2 (7)
S2—C7—S1	123.6 (4)		
C8—S1—C7—N1	176.3 (5)	S1—C8—C9—C10	−180.0 (5)
C8—S1—C7—S2	−3.2 (6)	O2—C9—C10—C11	3.6 (12)
C7—S1—C8—C9	87.1 (6)	C8—C9—C10—C11	−179.1 (7)
S1—C8—C9—O2	−2.6 (11)		

All H-atom positions were calculated by geometrical considerations and treated according to a riding model.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP*/*PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper, including data for (*S*)-(1), are available from the IUCr electronic archives (Reference: JZ1254). Services for accessing these data are described at the back of the journal.

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Nonstereospecific 1,3-Dipolar Cycloaddition Reactions of Azomethine Ylides: Proof of the Structures for Four Diastereoisomeric [3+2] Cycloadducts

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Abstract

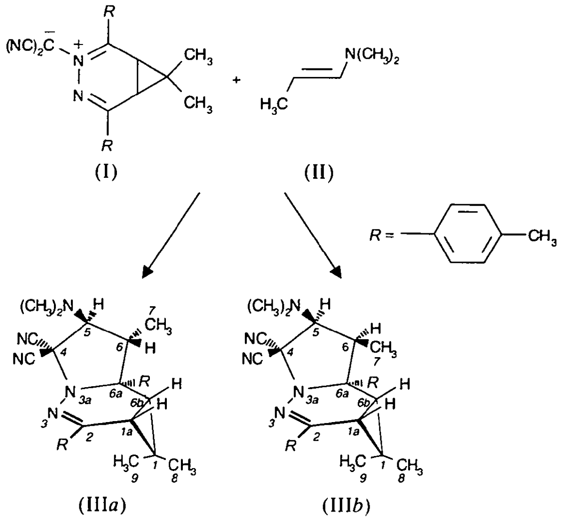
Racemic azomethine ylides [(I) or (IV)] have been found to undergo cycloaddition to a *trans*-enamine [(II)] in a nonstereospecific way to yield mixtures of racemic diastereoisomeric 1:1 adducts: 5-dimethylamino-1,1,6-trimethyl-2,6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-4*H*-3,3a-diazacyclopropa[*e*]indene-4,4-dicarbonitrile, $C_{29}H_{33}N_5$ [(III*a*) and (III*b*)], or 2-dimethylamino-1,5,5-trimethyl-6-(4-methylbenzoyl)-7a-*p*-tolyl-2,3,5,7a-tetrahydro-1*H*-pyrrolizine-3,3-dicarbonitrile (pyrrolizine is pyrrolo[1,2-*a*]pyrrole), $C_{29}H_{32}N_4O$ [(V*a*) and (V*b*)]. Crystal structure analyses prove the structures and configurations for the three diastereoisomeric adducts (III*a*), (III*b*) and (V*b*) unequivocally. In all three cases, the dimethylamino group is *endo* to the five-membered ring formed in the cycloaddition step. In (*cis*-1a-*cis*-4a-*transoid*-8a,8b-*transoid*-8b,8*c*)-1,1-dimethyl-4a-(pyrrolidin-1-yl)-2,8b-di-*p*-tolyl-1,1a,4a,5,6,7,8,8a,8b,8c-decahydro-4*H*-3,3a-diazacyclopropa[*c*]fluorene-4,4-dicarbonitrile, $C_{34}H_{39}N_5$, (VII), the cycloadduct formed using an azomethine ylide [(I)] and a cyclic enamine [(VI)], the amino function is again found in an *endo* position.

Comment

1,3-Dipolar cycloadditions (Huisgen, 1984) are 'symmetry-allowed' reactions (Woodward & Hoffmann, 1969) and occur in a stereospecific manner as suprafacial–suprafacial additions. Only recently have a few exceptions been reported for nonstereospecific 1,3-cycloaddition reactions (Huisgen, 1988). Thiocarbonyl ylides, as electron-rich 1,3-dipoles, react with 2,3-dicyanofumarate (an electron-poor dipolarophile) in a nonstereospecific way, *via* a dipolar intermediate.

Recently, we reported the synthesis of two new classes of coloured stable azomethine ylides [(I) and (IV)], which are electron-poor 1,3-dipoles (Riebel, Weber, Troll, Sauer & Breu, 1996; Riebel, Weber, Troll, Sauer, Breu & Nöth, 1996; Breu *et al.*, 1996). These azomethine ylides preferentially combine with electron-rich dipolarophiles.

In the following, we describe [3+2] cycloaddition reactions of (I) and (IV) with the *trans*-enamine (II), all of which do not obey the Woodward–Hoffmann rules but occur in a nonstereospecific way yielding mixtures of diastereomeric adducts. Since the starting dipoles were racemates, all products were, of course, also isolated as racemates.



When the azomethine ylide (I) was combined with 2.1 equivalents of the enamine (II) at ambient temperature in acetonitrile, the addition occurred immediately with rapid decolourization to yield a mixture of 1:1 adducts in almost quantitative yield (Weber, 1997; Weber & Sauer, 1998). Flash column chromatography separated