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2-[2-(Benzoylmethylene)-4-oxo-3-phenyl-1,3-thiazolidin-5-ylidene]propanedinitrile, a Compound with a C=O···S Interaction

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Abstract. $C_{20}H_{11}N_3O_2S$, $M_r = 357{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}106\,(1)$, $b = 21{\cdot}179\,(2)$, $c = 9{\cdot}833\,(2)$ Å, $\beta = 107{\cdot}53\,(1)°$, $V = 1808{\cdot}28$ Å^3, $Z = 4$, $D_m = 1{\cdot}32$, $D_x = 1{\cdot}31$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}661$ mm^{-1}, $F(000) = 736$, $T = 293$ K, $R = 0{\cdot}038$ for 2901 unique observed reflections. The molecule has a short intermolecular S···O contact of 2·614 Å and C—S···O angle of 165·7°. A similar interaction is believed to be present in the parent carbonyl compound from which the title compound is made, and to be responsible for the resulting reactivity.

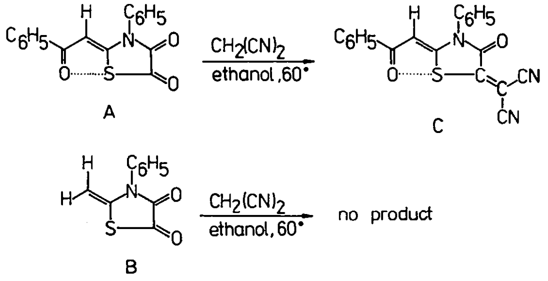

Fig. 1. The Knoevenagel reaction.

Introduction. The crystal structure determination of the title compound was carried out in order to explain the course of the Knoevenagel reaction given in Fig. 1 and studied by Zaleska (1987).

Reactivity of the compound denoted *A* with malonodinitrile and lack of reactivity of compound *B* raised the question of the role of the benzoyl substituent and its conformation with respect to the S atom. Having good single crystals only for the compound *C* we solved its structure, being firmly convinced that the solid-state conformation of the reaction product reflects the initial stage of reaction.

Experimental. The compound was obtained and crystallized from chlorobenzene at room temperature by Zaleska (1987). Yellow flat-plate crystals were obtained. The details of the X-ray measurement and the structure computation are given in Table 1.

Table 1. *Data collection and refinement conditions*

Crystal size (mm)	0·15 × 0·40 × 0·35
Measuring D_m	By flotation
Diffractometer	Enraf–Nonius CAD-4 (graphite-monochromated Cu $K\alpha$ radiation)
Lattice parameter measurement	
θ range (°), number of reflections	$2 \le \theta \le 22°$, 25
Intensity measurement θ range (°)	$2 \le \theta \le 72°$
Indices range	$-11 \le h \le 11 \quad 0 \le k \le 26$ $0 \le l \le 12$
Scan width (°) and mode	$0{\cdot}6 + 0{\cdot}2\tan\theta$, $\omega/2\theta$
Intensity control reflections	$1\bar{4}1$, $1\bar{3}1$, measured every hour
Changes in intensity	< 10%
Number of reflections measured	4332
Criterion for observed reflections	$\lvert F_o \rvert \ge 2\sigma(F)$
Number of observed unique reflections	2901
R_{int}	0·018
Corrections applied	Lorentz–polarization effects
Computer programs	*SHELX76* (Sheldrick, 1976)
Atomic scattering factors	As in *SHELX76*
Solution	Automatic centrosymmetric direct methods with *SHELX76*
Refinement method	Full-matrix least squares on $\lvert F_o \rvert$'s
Parameters refined	279
non-hydrogen atoms	Positional and anisotropic thermal
hydrogen atoms	Positional and isotropic thermal[*]
Weighting scheme	$w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$ k converged to 1·0 and g to 0·00280
R, wR, S	0·038, 0·047, 0·949
Ave., max. Δ/σ	
non-hydrogen atoms:	
positional parameters	0·01, 0·1
thermal parameters	0·08, 0·3
hydrogen atoms:	
positional parameters	0·1, 0·4
thermal parameters	0·3, 0·6
Max., min. height in final difference Fourier synthesis (e Å^{-3})	0·16, −0·23

[*] Initial positional parameters for all H atoms found from difference Fourier maps.

Discussion. Positional and thermal parameters are listed in Table 2, intramolecular distances and angles in Table 3.[*] The conformation of molecule *C* is shown together with the atom-numbering scheme in Fig. 2 and the molecular packing in the crystal unit cell is shown in Fig. 3. Figures were drawn on an IBM PC/AT with *ORTEP* (Johnson, 1971), within the *CRYSRULER*

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51310 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters U_{eq} (Å^2) with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
N1	1·0403 (1)	−0·1413 (1)	0·0266 (1)	0·050 (1)
C3	0·9652 (2)	−0·0897 (1)	0·0622 (2)	0·049 (1)
S1	0·7812 (1)	−0·0796 (1)	−0·0605 (1)	0·052 (1)
C5	0·8076 (2)	−0·1448 (1)	−0·1562 (2)	0·049 (1)
C4	0·9590 (2)	−0·1760 (1)	−0·0891 (2)	0·051 (1)
O2	1·0030 (2)	−0·2240 (1)	−0·1299 (1)	0·064 (1)
C6	0·7071 (2)	−0·1657 (1)	−0·2791 (2)	0·054 (1)
C8	0·7370 (2)	−0·2200 (1)	−0·3554 (2)	0·056 (1)
N2	0·7526 (2)	−0·2623 (1)	−0·4202 (2)	0·072 (1)
C7	0·5650 (2)	−0·1331 (1)	−0·3423 (2)	0·070 (1)
N3	0·4545 (2)	−0·1055 (1)	−0·3889 (3)	0·110 (1)
C1	0·9387 (2)	0·0006 (1)	0·2057 (2)	0·054 (1)
O1	0·8091 (2)	0·0111 (1)	0·1258 (1)	0·064 (1)
C2	1·0260 (2)	−0·0527 (1)	0·1766 (2)	0·052 (1)
C9	1·0077 (2)	0·0415 (1)	0·3318 (2)	0·054 (1)
C10	1·1523 (2)	0·0310 (1)	0·4285 (2)	0·061 (1)
C11	1·2079 (2)	0·0704 (1)	0·5443 (2)	0·070 (1)
C12	1·1193 (3)	0·1202 (1)	0·5659 (1)	0·077 (1)
C13	0·9776 (3)	0·1313 (1)	0·4718 (2)	0·077 (1)
C14	0·9207 (2)	0·0921 (1)	0·3551 (2)	0·064 (1)
C15	1·1936 (2)	−0·1599 (1)	0·1106 (2)	0·050 (1)
C16	1·3189 (2)	−0·1338 (1)	0·0826 (2)	0·063 (1)
C17	1·4646 (2)	−0·1524 (1)	0·1629 (2)	0·073 (1)
C18	1·4822 (2)	−0·1965 (1)	0·2687 (2)	0·070 (1)
C19	0·3573 (3)	−0·2218 (1)	0·2953 (2)	0·079 (1)
C20	1·2092 (2)	−0·2039 (1)	0·2161 (2)	0·070 (1)

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

S—C3	1·758 (1)	C1—C9	1·488 (2)
S—C5	1·727 (2)	C9—C10	1·390 (2)
C3—C2	1·345 (2)	C10—C11	1·379 (3)
C3—N1	1·390 (2)	C11—C12	1·382 (3)
C4—N1	1·369 (2)	C12—C13	1·363 (3)
C4—C5	1·492 (2)	C13—C14	1·384 (3)
C4—O2	1·205 (2)	N1—C15	1·446 (2)
C5—C6	1·352 (2)	C15—C16	1·369 (3)
C6—C7	1·433 (2)	C16—C17	1·381 (2)
C6—C8	1·443 (3)	C17—C18	1·372 (3)
C7—N3	1·135 (3)	C18—C19	1·352 (3)
C8—N2	1·133 (3)	C19—C20	1·391 (3)
C2—C1	1·458 (2)	C20—C15	1·370 (3)
C1—O1	1·225 (2)	C14—C9	1·392 (3)
S···O1	2·614 (1)	C5—S—O1	165·7 (1)
C5—S—C3	91·0 (1)	C4—C5—S	112·0 (1)
S—C3—N1	111·2 (1)	C4—C5—C6	122·5 (2)
S—C3—C2	124·8 (1)	S—C5—C6	125·5 (1)
C2—C3—N1	124·0 (1)	C5—C6—C7	120·6 (2)
C3—N1—C4	116·6 (1)	C8—C6—C7	116·5 (1)
C3—N1—C15	122·2 (1)	C5—C6—C8	122·9 (1)
C4—N1—C15	121·1 (1)	C6—C7—N3	177·6 (2)
N1—C4—C5	109·0 (1)	C6—C8—N2	176·2 (2)
N1—C4—O2	125·3 (1)	C3—C2—C1	120·2 (1)
O2—C4—C5	125·6 (1)	C2—C1—O1	119·4 (1)
O1—C1—C9	120·8 (2)	C2—C1—C9	119·7 (1)
C1—C9—C10	123·5 (2)	N1—C15—C16	119·7 (1)
C1—C9—C14	117·8 (1)	N1—C15—C20	118·7 (2)
C14—C9—C10	118·6 (2)	C16—C15—C20	121·7 (2)
C9—C10—C11	120·3 (2)	C15—C16—C17	119·0 (2)
C10—C11—C12	120·1 (2)	C16—C17—C18	142·7 (3)
C11—C12—C13	120·3 (2)	C17—C18—C19	120·2 (2)
C12—C13—C14	120·1 (2)	C18—C19—C20	121·0 (2)
C13—C14—C9	120·5 (2)	C19—C20—C15	118·1 (2)

package (Rizzoli, Sangermano, Calestani & Andreetti, 1987). The S and the O atoms of the benzoyl group are in an *s-cis* conformation forming a 'single-bond no-bond' interaction characterized by a short intramolecular S···O approach of 2·61 Å and C—S···O angle of 165·6°. These values fit into the ranges 2·55–2·73 Å and 154–174° observed in various compounds with a C counteratom to an O atom and an O=CPh nucleophilic moiety (Kálmán & Párkányi, 1980). The environment of the S atom is coplanar as shown by torsion angles (C5—S1—C3—C2; S1—C3—C2—C1; C3—C2—C1—O1; C3—C2—C1—C9 all equal to zero), and by the least-squares plane calculated for the two fused five-membered rings (one of them a quasi-ring closed by O···S) (Table 4). According to Hamilton & La Placa (1964) the near linearity of the *X*—S···O group is favourable for S *p* and *d* orbital participation in the partial S···O bonding. The existence of such a close S···O approach together with the quasi-linear C—S···O arrangement involves a five-membered conjugated system [O1, C1, C2, C3, S]. We infer from the structure of *C*, solved and presented here,

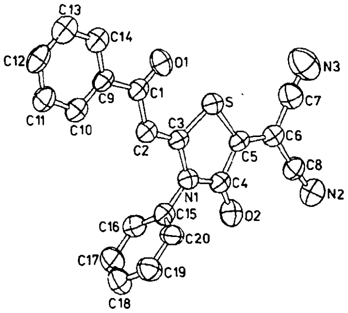

Fig. 2. The title molecule with atom-numbering scheme.

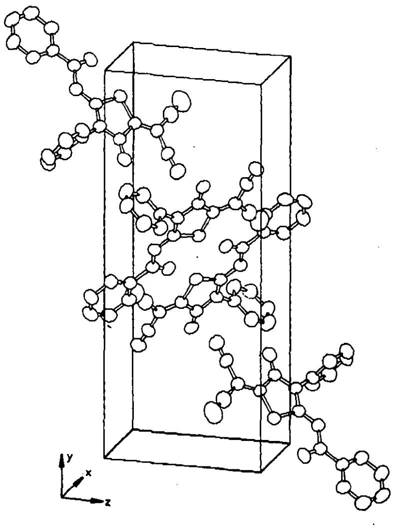

Fig. 3. Packing diagram (Johnson, 1971).

Table 4. *The deviations* (Å) *of the atoms of the least-squares plane in the thiazolidyne part of the molecule*

Plane: $5\cdot339\ x + 12\cdot429\ y - 6\cdot972\ z = 3\cdot592$ (x, y, z are the fractional coordinates along **a**, **b**, **c**).

O(1)	−0·011	S(1)	0·011
C(1)	−0·007	N(1)	0·021
C(2)	0·001	C(4)	−0·038
C(3)	0·014	C(5)	0·010

All e.s.d.'s are 0·002 Å.

that in compound *A* the replacement of the O atom by a dicyanomethylidene group at C5 is possible due to the electron-withdrawing effect of the conjugated system described above.

It can be concluded, as was already suggested by Kucsman, Kapovits, Párkányi, Argay & Kálmán (1984), that the S—O interaction may, by governing the conformation, have a decisive influence on chemical behaviour.

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Structure of (3*S*)-3-*tert*-Butyloxycarbonylamino-2-piperidone

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Abstract. $C_{10}H_{18}N_2O_3$, $M_r = 214\cdot27$, monoclinic, $P2_1$, $a = 15\cdot515\,(2)$, $b = 6\cdot730\,(1)$, $c = 12\cdot541\,(2)$ Å, $\beta = 113\cdot6\,(2)^\circ$, $V = 1200\cdot0$ Å^3, $Z = 4$, $D_x = 1\cdot186$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot54$ cm^{-1}, $F(000) = 464$, $T = 295$ K. The final R value for 1611 observed (3139 unique) reflections is 0·055. In both the independent molecules *A* and *B* of the asymmetric unit of the title compound, the conformation of the urethane moiety is *trans*. The lactam group of molecule *A* is non-planar, the C(9)—N(2)—C(10)—C(6) torsion angle being 12·4 (14)°. One main difference between molecules *A* and *B* is in the value of the φ[C(5)—N(1)—C(6)—C(10)] torsion angle [52·3 (11)° for molecule *A* while −86·5 (10)° for molecule *B*] as a consequence of a rotation of the ring relative to the *tert*-butyloxycarbonylamino substituent. A second major difference is the δ-lactam ring conformation which is approximate half-chair for molecule *A* while boat for molecule *B*.

Introduction. Replacement or modification of the peptide backbone function can lead to enzymatically resistant biologically active analogs. Among the factors contributing to altered chemical and biochemical parameters are changes in electronic properties, differences in solubility characteristics, resistance to proteolytic processes, and, perhaps most important, conformational restrictions and changes that can modify receptor recognition (Spatola, 1983).

In particular, we have recently undertaken the synthesis of a series of conformationally constrained analogs of the neuroactive tripeptide H-L-Pro-L-Leu-Gly-NH$_2$ (Johnson, Yu, Taraporewala, Mishra & Rajakumar, 1985; Yu, Rajakumar, Srivastava, Mishra & Johnson, 1988) in which the γ- and δ-lactam residues developed by Freidinger, Perlow & Veber (1982) have replaced either the leucyl or glycinamide residues. These compounds were synthesized in an attempt to determine whether the *trans* amide bond and the β-bend

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