O(4)	0.5840 (4)	0.0378 (1)	-0.107 (1)	4.2 (2
O(5)	0.7566 (5)	0.2596(1)	0.308(1)	3.5 (2
O(6)	0.5722 (4)	0.2487 (1)	0.511(1)	3.5 (2
-	Table 7 Salact	ad accompatri	naramatars	(Å °)

Tuble 2. Scieticu geometric purumeters (A,)				
C(1)—C(2)	1.398 (7)	C(10)—O(2)	1.432 (7)	
C(1)—C(6)	1.379 (7)	C(11)—C(12)	1.380 (8)	
C(1)—C(7)	1.471 (7)	C(11)—C(16)	1.389 (7)	
C(2)—C(3)	1.380(7)	C(12)—C(13)	1.376 (6)	
C(3)—C(4)	1.390 (6)	C(13)—C(14)	1.409 (7)	
C(3)O(1)	1.377 (6)	C(13)—O(3)	1.360 (7)	
C(4)—C(5)	1.394 (7)	C(14)—C(15)	1.380 (8)	
C(4)O(2)	1.362 (6)	C(14)—O(4)	1.368 (6)	
C(5)—C(6)	1.385 (7)	C(15)—C(16)	1.384 (7)	
C(7)—C(8)	1.337 (7)	C(17)—O(3)	1.412 (7)	
C(8)—C(11)	1.486 (7)	C(18)—O(4)	1.434 (7)	
C(8)—C(19)	1.505 (8)	C(19)O(5)	1.209 (6)	
C(9)O(1)	1.405 (7)	C(19)O(6)	1.321 (6)	
C(1)—C(7)—C(8)	128.6 (5)	C(8)-C(19)-C	(6) 113.0 (5)	
C(2)—C(3)—O(1)	124.7 (4)	O(5)-C(19)-C	(6) 123.2 (5)	
C(5)—C(4)—O(2)	125.3 (5)	C(3)—O(1)—C(9) 116.8 (4)	
C(12)—C(13)—O(3)	126.1 (5)	C(4)O(2)C(10) 117.4 (5)	
C(15)—C(14)—O(4)	125.8 (5)	C(13)-O(3)-C	(17) 118.3 (4)	
C(8)—C(19)—O(5)	123.8 (5)	C(14)—O(4)—C	(18) 116.5 (5)	
C(1)—C(7)—	-C(8)-C(11)	_	75.9 (5)	
C(1)-C(7)-	-C(8)-C(19)		3.6 (9)	
C(7)—C(8)—	-C(19)O(5)	-	110.5 (6)	
D—H···A	L	DA	D—H···A	
$O(6) - H(O6) \cdots O(5^{i})$	2.0	659 (5)	153 (7)	

Symmetry code: (i) $\frac{3}{3} - x, y, \frac{1}{2} + z$.

The collection of the data was extended to include reflections of the type $h\overline{kl}$. A small number of reflections were affected by a minor contribution from a satellite crystal (usually this was not the case for both a reflection of the type hkl and the corresponding reflection of the type $h\overline{kl}$). The affected reflections were omitted from the data set and average F values were calculated and used in the structure analysis.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1985). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, Hatom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Battersby, A. R. & Greenock, I. A. (1961). J. Chem. Soc. pp. 2592-2593.
- Gadre, S. Y. & Marathe, K. G. (1988). Synth. Commun. 18, 1015– 1027.
- Gierer, J., Lenic, J., Norén, I. & Szabo-Lin, I. (1974). Acta Chem. Scand. Ser. B, 28, 717-729.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Li, S. & Lundquist, K. (1995). Proceedings of the 8th International Symposium on Wood and Pulping Chemistry, June 6–9, Helsinki, Finland, Vol. 1, pp. 163–167, and unpublished data.
- Lundquist, K., Stomberg, R. & von Unge, S. (1987). Acta Chem. Scand. Ser. B, 41, 499-510.

©1995 International Union of Crystallography Printed in Great Britain – all rights reserved Molecular Structure Corporation (1985). TEXSAN. TEXRAY Structure Analysis Package. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pandit, S. B. & Gadre, S. Y. (1988). Synth. Commun. 18, 157-166.

- Russell, J. H. & Hunziker, H. (1969). Tetrahedron Lett. pp. 4035-4036.
- Sheldrick, G. M. (1985). SHELXS86. Program for the Solution of Crystal Structures. Univ. of Göttingen, Germany.
- Stomberg, R., Li, S. & Lundquist, K. (1994). J. Chem. Crystallogr. 24, 407-413.

Acta Cryst. (1995). C51, 2700-2702

2-[2-(3,4-Dichlorophenyl)vinyl]benzo-[*d*]thiazole

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(Received 1 December 1994; accepted 26 June 1995)

Abstract

The title compound, $C_{15}H_9Cl_2NS$, was synthesized by the condensation of 1-(3,4-dichlorophenyl)-4-methyl-1penten-3-one and 2-aminothiophenol. The title compound is essentially planar in the solid state. The C==C double bond has the *E* configuration.

Comment

The synthesis of the title compound, (III), was unexpected and arose presumably by initial formation of an anil between 1-(3,4-dichlorophenyl)-4-methyl-1-penten-3-one, (I), and 2-aminothiophenol, (II), followed by attack on the carbimino C atom by the S atom leading to the extrusion of the isopropyl group and ring closure forming a benzothiazole. Alternatively, attack by the S atom on the carbonyl C atom of (I) could lead to an intermediate, the amino group of which subsequently forms a bond with this C atom, leading to ring closure and the elimination of the isopropyl group.



A review of the literature revealed that while (II) has reacted with certain α,β -unsaturated ketones and α,β unsaturated acids producing benzothiazepines (Lévai, 1979, 1981; Lévai, Toth & Szollosy, 1982) and benzothiazepiones (Mills & Whitworth, 1927; Lévai, 1980), respectively, benzothiazoles were not formed. These heterocycles may be obtained by condensation of aldehydes with (II) (Bogert & Naiman, 1935; Lankelma & Scharnoff, 1932) and in one instance, reaction of the unsaturated aldehyde cinnamaldehyde with (II) produced a benzothiazole (Lankelma & Scharnoff, 1932). However, to the best of the authors' knowledge, this is the first report of a benzothiazole being formed from an α,β - unsaturated ketone and (II). This observation is important for the following reasons. First, a number of benzothiazoles have pronounced bioactivities (Ince, 1990) and hence the discovery of a novel synthetic route to these heterocycles is noteworthy. Second, the expulsion of the isopropyl group of (I) during the formation of the title compound requires an unusual reaction mechanism, the elucidation of which will require further study.

The X-ray crystallographic data revealed that the molecule is essentially planar. The angles between the benzothiazolyl and halogen-containing aryl rings with the olefinic group were 1.9 (4) and 2.1 (3)°, respectively. The maximum deviation from the least-squares plane of the molecule is 0.121 (4) Å. The C9—S—C10 angle is 89.1 (2)°, which suggests that the S atom uses only p orbitals to form bonds with C9 and C10. In order to maintain the planar conformation of the five-membered ring, the other ring bond angles, *i.e.* C9—N—C11, S—C10—C11, N—C11—C10 and N—C9—S, are all in the range 109.0–115.4°, less than the ideal 120° for sp^2 orbital hybridizations of C and N atoms and greater than the ideal 108° required for a regular planar pentagon.

The packing of the molecules is shown in Fig. 2. The molecules are arranged in antiparallel pairs attracted by $\pi-\pi$ interactions. There are two intermolecular N—H distances [N—H15ⁱ = 2.702 and N—H5ⁱⁱ = 2.595 Å; symmetry codes: (i) 1 + x, y, z; (ii) 1 - x, -y, 1 - z] which are slightly less than the sum of the van der Waals radii (2.75 Å). This may indicate two weak N···H—C interactions. Otherwise, only van der Waals interactions are present.



Fig. 2. PLUTON92 (Spek, 1992) drawing of the molecular packing.

Experimental

Crystal data

C₁₅H₉Cl₂NS $M_r = 306.21$ Monoclinic $P2_1/c$ a = 6.2260 (16) Å b = 14.3627 (15) Å c = 14.5505 (22) Å $\beta = 92.783 (17)^\circ$ $V = 1299.6 (4) Å^3$ Z = 4 $D_x = 1.565 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.7107$ Å Cell parameters from 25 reflections $\theta = 8-15^{\circ}$ $\mu = 0.66$ mm⁻¹ T = 123 K Rod $0.40 \times 0.10 \times 0.10$ mm Colorless



Fig. 1. ORTEPII (Johnson, 1976) view of the title compound with non-H-atom displacement ellipsoids at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

2702

C15H9Cl2NS

Data collection Enraf-Nonius CAD-4 diffractometer $\omega/2\theta$ scans Absorption correction: none 2570 magazing appleptions	$R_{int} = 0.021$ $\theta_{max} = 24.92^{\circ}$ $h = -7 \rightarrow 7$ $k = 0 \rightarrow 17$ $l = 0 \rightarrow 17$ 2 cturded a effections	C11-4 C11-4 C2-4 C12-4 C12-4 C3-4 C4-4 C1-4
none 2570 measured reflections 2281 independent reflections 1677 observed reflections $[I > \sigma(I)]$	$l = 0 \rightarrow 17$ 3 standard reflections frequency: 120 min intensity decay: none	C4-C C1-C C1-C The a of 0.
Refinement		atom
Refinement on F R = 0.049 wR = 0.049	$\Delta \rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$ $\Delta \rho_{\text{min}} = -0.40 \text{ e } \text{\AA}^{-3}$ Extinction correction: none	each Cat

wR = 0.049	Extinction correction: none
S = 1.26	Atomic scattering factors
1677 reflections	from International Tables
172 parameters	for X-ray Crystallography
$w = 1/[\sigma^2(F) + 0.0005F^2]$	(1974, Vol. IV, Table
$(\Delta/\sigma)_{\rm max} < 0.001$	2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)

 $U_{ab} = (1/3) \sum \sum U_{ab} a^* a^* a a$

		-cq $(-) = (-) = (j = j) = (j = j)$		
	x	у	z	U_{ea}
C11	0.16566 (17)	0.13504 (8)	0.06737(7)	0.0353 (6)
C12	0.62247 (16)	0.04523 (8)	0.10471 (7)	0.0297 (5)
S	-0.28655 (16)	0.17337 (7)	0.57166 (7)	0.0248 (5)
N	0.0478 (5)	0.1134 (2)	0.6672 (2)	0.023 (2)
C1	0.1962 (6)	0.1037 (3)	0.3411 (3)	0.022 (2)
C2	0.1254 (6)	0.1243 (3)	0.2508 (3)	0.023 (2)
C3	0.2554 (6)	0.1056 (3)	0.1785 (3)	0.023 (2)
C4	0.4564 (6)	0.0666 (3)	0.1943 (3)	0.022 (2)
C5	0.5275 (6)	0.0448 (3)	0.2834 (3)	0.022 (2)
C6	0.3999 (6)	0.0632 (3)	0.3556 (3)	0.023 (2)
C7	0.0564 (6)	0.1244 (3)	0.4168 (3)	0.023 (2)
C8	0.1069 (6)	0.1099 (3)	0.5054 (3)	0.026 (2)
C9	-0.0237 (6)	0.1283 (3)	0.5833 (3)	0.023 (2)
C10	-0.2991 (6)	0.1714 (3)	0.6908 (3)	0.022 (2)
C11	-0.1039 (6)	0.1374 (3)	0.7295 (3)	0.020 (2)
C12	-0.0752 (6)	0.1280 (3)	0.8252 (3)	0.025 (2)
C13	-0.2421 (7)	0.1544 (3)	0.8794 (3)	0.028 (2)
C14	-0.4359 (6)	0.1875 (3)	0.8406 (3)	0.025 (2)
C15	-0.4676 (7)	0.1964 (3)	0.7460 (3)	0.026 (2)

Table 2. Selected geometric parameters (Å, °)

CI1C3	1.737 (4)	C4C5	1.386 (5)
Cl2C4	1.730 (4)	C5—C6	1.373 (6)
S—C9	1.760 (4)	C7—C8	1.330 (6)
S—C10	1.739 (4)	C8—C9	1.450 (6)
NC9	1.297 (5)	C10C11	1.402 (5)
NC11	1.384 (5)	C10-C15	1.399 (6)
C1—C2	1.397 (6)	C11—C12	1.401 (5)
C1C6	1.402 (5)	C12C13	1.388 (6)
C1—C7	1.466 (6)	C13—C14	1.390 (6)
C2C3	1.385 (6)	C14C15	1.387 (6)
C3C4	1.380 (5)		
C9SC10	89.1 (2)	C7—C8—C9	127.9 (4)
C9—N—C11	111.2 (3)	S-C9-N	115.2 (3)
C2C1C6	118.1 (4)	S-C9-C8	123.1 (3)
C2C1C7	119.4 (3)	NC9C8	121.7 (3)
C6—C1—C7	122.5 (3)	SC10C11	109.0 (3)
C1C2C3	120.3 (4)	SC10C15	129.7 (3)

C11—C3—C2	119.1 (3)	C11—C10—C15	121.2 (4)
CI1—C3—C4	120.1 (3)	N-C11-C10	115.4 (3)
C2—C3—C4	120.8 (4)	N-C11-C12	124.7 (3)
CI2—C4—C3	121.2 (3)	C10-C11-C12	119.9 (3)
Cl2—C4—C5	119.3 (3)	C11C12C13	118.4 (4)
C3—C4—C5	119.5 (4)	C12-C13-C14	121.4 (4)
C4—C5—C6	120.2 (4)	C13C14C15	120.9 (4)
C1—C6—C5	121.2 (4)	C10-C15-C14	118.1 (4)
C1—C7—C8	125.1 (4)		

The ω -scan width was $(0.80 + 0.35 \tan \theta)^{\circ}$ with a θ -scan rate of $0.37-2.74^{\circ}$ min⁻¹. The scan angle was extended 25% on each side of each peak for background measurement. All H atoms were placed in calculated positions on the corresponding C atoms (C—H = 1.00 Å) and were not refined. The U_{iso} of each H atom was assigned as equal to the U_{eq} of the attached C atom plus 0.01 Å². Refinement was by full-matrix leastsquares methods.

Data collection: CAD-4 Software (Enraf-Nonius, 1988), Cell refinement: CAD-4 Software. Data reduction: NRCVAX DATRD2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: NRCVAX SOLVER. Program(s) used to refine structure: NRCVAX LSTSQ. Molecular graphics: NRCVAX, ORTEPII (Johnson, 1976). Software used to prepare material for publication: NRCVAX TABLES and UTILITY.

We thank the Natural Sciences and Engineering Research Council of Canada for providing funds for an X-ray diffractometer (to JWQ) and operating grants (to JWQ), and the Medical Research Council of Canada and Apotex Inc., Toronto, Canada, for grants (to JRD). We also thank the University of Saskatchewan for the award of a graduate scholarship (to JY).

Lists of structure factors, anisotropic displacement parameters, Hatom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bogert, M. T. & Naiman, B. (1935). J. Am. Chem. Soc. 57, 1529-1533.
- Enraf-Nonius (1988). CAD-4 Software. Enraf-Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). J. Appl. Cryst. 22, 384-387.
- Ince, F. (1990). Comprehensive Medicinal Chemistry, Vol. 3, edited by J. C. Emmett, p. 309. Oxford: Pergamon.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
- Lankelma, H. P. & Scharnoff, P. X. (1932). J. Am. Chem. Soc. 54, 379 - 381
- Lévai, A. (1979). Pharmazie, 34, 439.
- Lévai, A. (1980). Pharmazie, 35, 680-681.
- Lévai, A. (1981). Pharmazie, 36, 449-450.
 - Lévai, A., Toth, G. & Szollosy, A. (1982). Stud. Org. Chem. (Amsterdam), 11, 41-47; Chem. Abstr. (1983), 98, 34569f.
- Mills, W. H. & Whitworth, J. B. (1927). J. Chem. Soc. London, pp. 2738-2753.
- Spek, A. L. (1992). PLUTON92. Program for the Display and Analysis of Crystal and Molecular Structures. Univ. of Utrecht, The Netherlands.