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Acta Cryst. (1981). **B37**, 1703–1706

2-(2-Chlorobenzoylimino)-1,3-thiazolidine: Structure Refinement from Neutron Diffraction Data at 113 K and Charge Density Deformation Maps

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(Received 8 October 1980; accepted 24 February 1981)

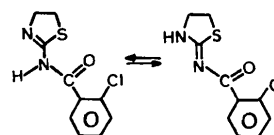
Abstract

The structure of 2-(2-chlorobenzoylimino)-1,3-thiazolidine, C₁₀H₉ClN₂OS, has been redetermined by neutron diffraction at 113 K. The space group is *P2₁/c* with lattice parameters *a* = 19.950 (4), *b* = 7.420 (2), *c* = 11.566 (3) Å, β = 109.10 (3)°, *Z* = 4, *M_r* = 240.7 and *d*_{calc} = 1.52 Mg m⁻³. The final *R*(*F*²) was 0.045 for 1768 reflections. The structural results show unambiguously that the molecule is found in the 'imino' form with an H atom located near the endocyclic N atom of the thiazolidine group. Based on deformation electron density maps and the interatomic distances it is

speculated that the difference in geometry between the two tautomeric forms ('imino' and 'amino') is small and that the occurrence of one or the other is strongly dependent on the substituents. A short intramolecular S—O contact of 2.68 Å is found and is believed to constitute a very weak bond.

Introduction

The title compound can exist in the two tautomeric forms



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where the transition from one form to the other is accompanied by a transfer of a proton between the two N atoms. X-ray analysis (Cohen-Addad & Viallet, 1978; Cohen-Addad, Viallet & Boucherle, 1979) revealed dimers linked together with N...N hydrogen bonds, indicating that proton transfer might be possible in the solid state. Moreover, the C-N distances are in agreement with the 'amino' form whereas the bond angles correspond to an 'imino' form of the molecule (Kálmán, Argay, Ribár & Toldy, 1977). Fourier difference maps showed only one peak located near the endocyclic N atom, indicating the 'imino' form to be the main component of the crystal. In view of the discrepancies in bond lengths and bond angles mentioned above and considering that location of H atoms by X-rays is of limited precision, it was not clear whether some disorder remained in the hydrogen-bond system. It was therefore decided to undertake a neutron diffraction study to settle this problem. If no disorder were found, it would obviously be interesting to study the electron distribution in the molecule, and for this reason the measurement temperature, 113 K, of the X-ray study was also chosen for the neutron analysis.

Experimental details and structure refinement

The compound was prepared by M. P. Viallet at the Laboratoire de Chimie et Toxicologie, Université de Grenoble (Viallet, 1979). A crystal of dimensions $6 \times 5 \times 0.4$ mm was obtained by evaporation of a chloroform solution at room temperature. The crystal was bounded by the faces {001}, {100}, and {011}. Measurements were made at the D8 diffractometer of the Institut Laue-Langevin high-flux reactor at 113 K using a neutron wavelength of 1.26 \AA , and employing an ω - 2θ step scan for the recording of the reflection profiles. The data were reduced to structure factors using the minimum σ/I criteria followed by an approximate correction for the bias (Lehmann & Larsen, 1974), and an absorption correction was made using a Gaussian integration approach (Coppens, Leiserowitz & Robinson, 1965).

H-atom positions were obtained from difference Fourier maps, which, as in the X-ray case, showed one peak near the endocyclic N atom [N(2)] and nothing above the noise level near N(1). Structure refinements were performed using the program ORXFLS3 (Busing & Levy, 1962), minimizing the quantity $\sum w(F_o^2 - F_c^2)^2$, where the weight was defined as $w = 1/[\sigma_p^2(F_o^2) + (0.05F_o^2)^2]^{1/2}$. σ_p originates from counting statistics. 1768 symmetry-independent reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement leading to the disagreement factors $R = \sum (F_o^2 - F_c^2) / \sum F_o^2 = 0.045$ and $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2} = 0.07$. An isotropic extinction correction was included in the calculation (Coppens & Hamilton, 1970) and the

largest correction was 0.42 for the reflection 300. The atomic coordinates are reported in Table 1.* Fig. 1 shows a projection of the molecule onto a plane defined

* Lists of structure factors and anisotropic thermal parameters and details of the mean planes of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36080 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$, for H $\times 10^4$) and equivalent isotropic thermal parameters

	x	y	z	$B_{eq} (\text{\AA}^2)^*$
C(1)	3634 (6)	75010 (10)	-6292 (7)	0.84 (4)
C(2)	-8295 (7)	56339 (12)	-24304 (8)	1.35 (4)
C(3)	-14559 (7)	69045 (11)	-18747 (8)	1.17 (4)
C(4)	21588 (6)	77629 (11)	6483 (7)	0.93 (4)
C(5)	29538 (6)	89990 (10)	15296 (7)	0.88 (4)
C(6)	36232 (6)	101474 (11)	11382 (7)	1.09 (4)
C(7)	43910 (7)	112532 (12)	19543 (8)	1.38 (4)
C(8)	44803 (7)	112183 (12)	31913 (8)	1.35 (4)
C(9)	38099 (7)	101089 (12)	35979 (7)	1.28 (4)
C(10)	30524 (7)	90011 (11)	27700 (7)	1.09 (4)
N(1)	11204 (5)	84303 (8)	2208 (5)	0.98 (2)
N(2)	-6491 (5)	81109 (8)	-10718 (5)	1.09 (2)
O	24595 (8)	62928 (13)	3956 (9)	1.28 (4)
S	5511 (15)	54763 (26)	-13205 (17)	1.01 (8)
Cl	35029 (5)	101910 (9)	-4045 (5)	1.64 (4)
H'(C2)	-1181 (2)	4286 (3)	-2588 (2)	2.66 (11)
H''(C2)	-761 (2)	6146 (3)	-3293 (2)	2.99 (10)
H'(C3)	-1875 (2)	6166 (3)	-1338 (2)	2.59 (10)
H''(C3)	7940 (2)	7684 (3)	-2580 (2)	2.41 (9)
H(C7)	4905 (2)	12127 (3)	1623 (2)	2.68 (10)
H(C8)	5079 (2)	12084 (3)	3831 (2)	2.45 (11)
H(C9)	3853 (2)	10098 (3)	4555 (2)	2.56 (9)
H(C10)	2528 (2)	8137 (3)	3096 (2)	2.29 (9)
H(N2)	-854 (1)	9330 (3)	-753 (2)	2.19 (6)

$$* B_{eq} = (B_1 B_2 B_3)^{1/3}.$$

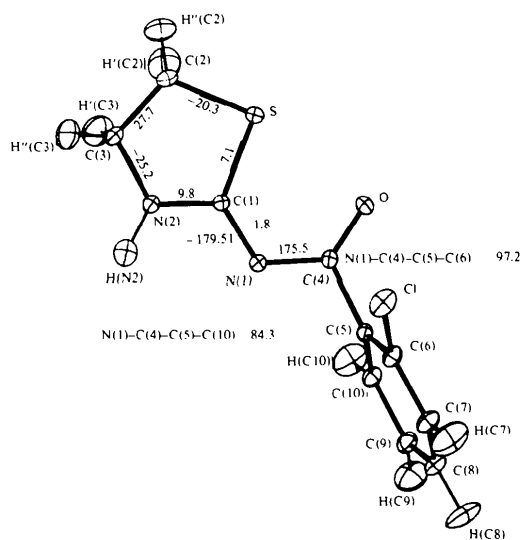


Fig. 1. Projection of the molecule on to the C(1)-N(2)-S plane, and principal torsion angles ($^\circ$) (e.s.d. = 0.1°).

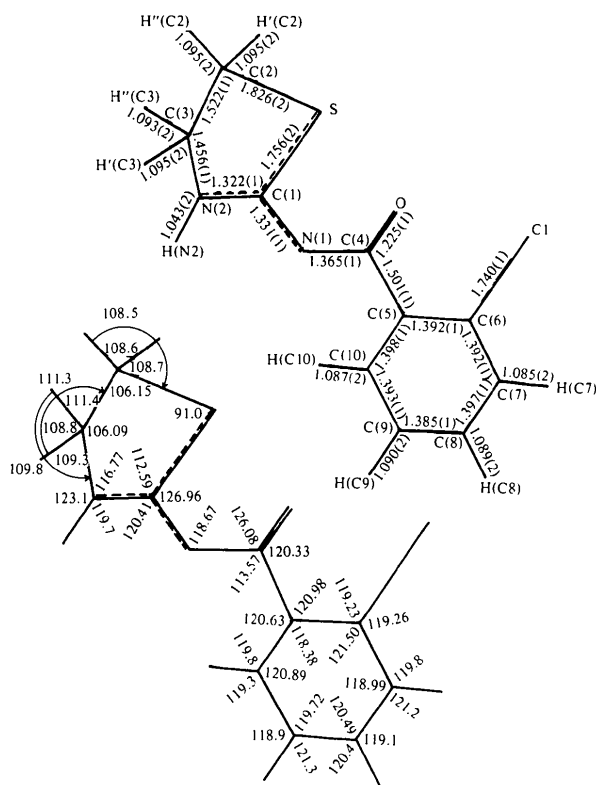


Fig. 2. Interatomic distances (Å) and bond angles ($^{\circ}$). E.s.d.'s on angles are 0.06 to 0.08 $^{\circ}$ for C, O, N, S, and 0.1 $^{\circ}$ for angles involving H atoms.

by C(1), N(2) and S (ORTEP, Johnson, 1965). Interatomic distances and bond angles are shown in Fig. 2.

Discussion

Description of the molecule

The neutron structure analysis leads to results very similar to the X-ray analysis described earlier (Cohen-Addad & Viallet, 1978; Cohen-Addad, Viallet & Boucherle, 1979). The thiazolidine part of the molecule is non-planar with C(3) located at a distance of 0.48 Å from the main plane, and the phenyl ring makes an angle of 84.4(2) $^{\circ}$ with the amide group. The N—H...N hydrogen bond linking the molecules into dimers around the inversion centers has a length of 2.885(1) Å, which is normal for N...N hydrogen bonds. The bond angle N—H...N around H is 175.2(2) $^{\circ}$. After the last refinements difference Fourier sections were made in the region around the hydrogen bond, and again no trace of H was found near N(1). We can thus finally conclude that the 'imino' tautomer is the only form present in the crystal. The nearly identical lengths of the two C(1)—N bonds, which were originally attributed to a tautomeric mixing,

must therefore be explained otherwise. They could well correspond to a mesomeric form as suggested for the β -naphthoquinones (Bechtel, Chasseau, Gaultier & Hauw, 1976), leading to rather similar electronic environments around the two N atoms. This implies that even small changes in other parts of the molecule can shift the H from N(2) to N(1). Indeed, in the compound where Cl is replaced by a methyl group the X-ray analysis (Cohen-Addad, Viallet & Boucherle, 1979) indicated that the H atom is located at N(1). The tautomer found is then a function of the relative proton affinity at the N atoms of the two main groups, and an analysis of angles and distances not involving H might therefore remain inconclusive.

Deformation-density maps

As the neutron diffraction analysis showed the molecule to be ordered and X-ray data were available at the same temperature further analysis can be made using deformation-density maps. These are defined as $\rho_{\text{obs}} - \rho_{\text{calc}}$, where ρ_{obs} is the charge density derived from the X-ray structure amplitudes phased by a model calculation using the neutron parameters, and where ρ_{calc} is a charge density based on neutron parameters and spherical free atoms. The scale factor between the two maps was obtained from a least-squares refinement using fixed neutron parameters. Because of a rather limited data range ($\sin \theta/\lambda_{\text{max}} = 0.56 \text{ \AA}^{-1}$) the peak heights are reduced (Lehmann & Coppens, 1977). Fig. 3 shows a section through the phenyl ring and contains the typical features, namely charge accumulation in the C—C and C—H bonds. The estimated error at approximately 0.4 Å or further from the atom center is 0.09 $e \text{ \AA}^{-3}$. We also note that there is no charge accumulation in the C—Cl bond, in agreement with similar observations in a chloropyridine derivative (Kvick, Thomas & Koetzle, 1976).

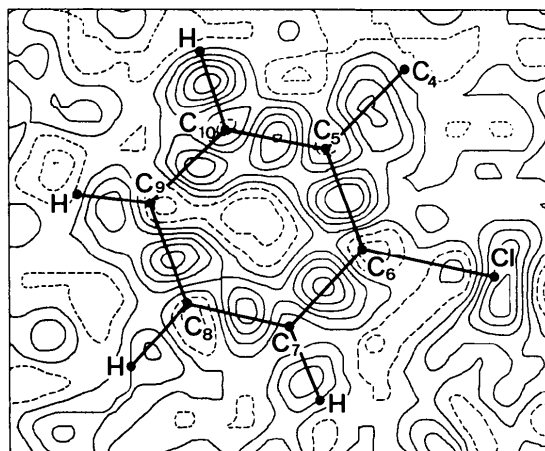


Fig. 3. Deformation-density map in the plane of the phenyl ring. Levels are at 0.05 $e \text{ \AA}^{-3}$, negative contours are broken.

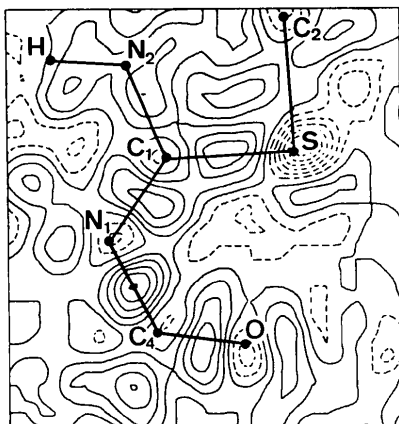


Fig. 4. Deformation-density map in the S-C(4)-O plane. Levels are at $0.05 e \text{ \AA}^{-3}$, negative contours are broken.

Fig. 4 shows the section through the S-C(4)-O plane, which also contains atoms N(1) and N(2). The distance between S and O is $2.684(2) \text{ \AA}$, and very much shorter than the van der Waals contact of 3.2 \AA . The torsion angle S-C(1)-N(1)-C(4) is 1.8° , so there is no indication of a strong repulsive force between S-O, and it would then seem natural to assume a weak bond between S and O. A similar case of a short S-O contact (2.44 \AA) was observed by Hamilton & La Placa (1964) who termed it a 'strong non-bonding attractive interaction', and pointed out that a linear $O \cdots S-O$ bonding geometry is consistent with favorable S *p*- and *d*-orbital participation in the interaction. Recently, Stanković, Ribár, Kálmán & Argay (1980) have found a similar contact with a bond angle $O \cdots S-C$ of 161.0° , very near the value of 162.8° found in this study. As the nucleus of one of the atoms does not penetrate into the charge cloud of the other there is no theoretical reason to expect charge accumulation in the bond (see, for example, Hirshfeld & Rztokiewicz, 1974) and, indeed, the density in the region between S and O is featureless. If there had been strong repulsion one would expect a stronger charge depletion.

The density in the C(4)-N(1)-C(1)-N(2) chain shows a general charge delocalization with nearly

identical charge density in the three C-N bonds. Likewise, the deformation density at the lone-pair region of N(1) and the N(2)-H bond are of the same order of magnitude indicating, as discussed above, that it would take a relatively small rearrangement to shift the H atom to N(1). Presently this remains an hypothesis that only further neutron or precise X-ray measurements on other derivatives can verify.

The authors wish to thank Professors A. Boucherle and J. Lajzéróvicz and Mrs M. P. Viallet for valuable comments.

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