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Regioselective synthesis of 1,3-thiazines by sequential 4-oxothiazolidine to 1,2-dithiole to 1,3-thiazine transformations: role of intramolecular non-bonded S···O interactions

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Abstract—A new synthetic approach to 2,3-dihydro-4*H*-1,3-thiazine derivatives based upon reductive rearrangement of 1,2-dithiole-3-ylidene thiones has been developed. In turn, the 1,2-dithiole derivatives were prepared by an efficient ring-opening–closing process of 2-alkylidene-4-oxothiazolidines, induced in the presence of Lawesson's reagent by intramolecular non-bonded 1,5-type S···O interactions in the 4-oxothiazolidine precursors.
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1. Introduction

Experimental and theoretical studies have shown that intramolecular non-bonded S···X (X=O or S) interactions in a large number of organosulfur compounds, as exemplified by acetazolamide **1**,[1] thiadiazoline **2**,[2] natural antitumor antibiotic leinamycin **3**,[3] cyclic sulfilimine **4**[4] or 1,3-dithioles **5**,[5] are important in controlling their structural properties and chemical reactivity.[6] Similarly, among specific examples, the reactivity enhancement of ethynyl-1,5-azastibocine **6**[7] with respect to diphenyl(phenylethynyl)stibane, in Pd-catalyzed cross-coupling reactions with organic halides, has been explained in terms of the central role of an intramolecular Sb···N interaction.
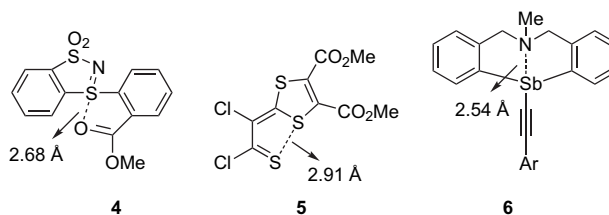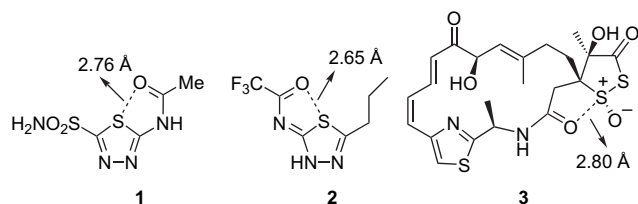
The most important structural feature of the compounds, exhibiting the 1,5-type S···S, S···O or Sb···N interactions, is a much shorter distance between the corresponding atoms than the sum of their van der Waals radii (3.60 Å, 3.32 Å, and 3.74 Å, respectively). Over the last few years we have reported that *push–pull* 2-alkylidene-4-oxothiazolidines of the general structure **7** (Scheme 1), containing the cis-configured –S–C=C–C=O moiety, participate in a number of reactions through activation of (i) the nucleophilic α-carbon atom of the exocyclic C=C bond,[8] or (ii) C(4) and C(5) positions of the heterocyclic ring via activated vinylogous *N*-methyliminium ions.[9] In particular, we anticipated that the 1,5-type S···O close contact, in combination with the rigid and flat 4-oxothiazolidine ring conjugated with the C(2) side chain, can be electronically tuned to induce specific chemical transformation of substrates **7**. As reported in a preliminary communication, this has been confirmed experimentally by a ring-opening–closing transformation of selected 4-oxothiazolidine enaminoketones **7** in the presence of Lawesson's reagent (LR), to produce functionalized 1,2-dithiole-3-ylidene thiones **8**[10] (Scheme 1).
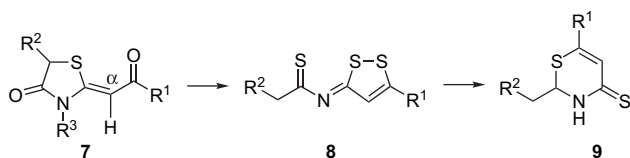
Scheme 1.

Herein, we report the full account of the $7 \rightarrow 8$ conversion initiated by the directional non-bonded 1,5-type S···O interaction in the N-unsubstituted 4-oxothiazolidines **7**. In addition, the range of results obtained on the use of 1,2-dithioles in a subsequent one-pot reductive rearrangement to new 2,3-dihydro-4H-1,3-thiazine-4-thiones **9**, forms the subject of the second part of our paper, demonstrating the ease of interconversion of three structurally different heterocyclic classes via two efficient sequential transformations.[11] The structures **8a** (R^2=H; R^1=Ph) and **9b** (R^2=Me; R^1=Ph), as representatives of the two heterocyclic series, have been unambiguously confirmed by X-ray analyses.
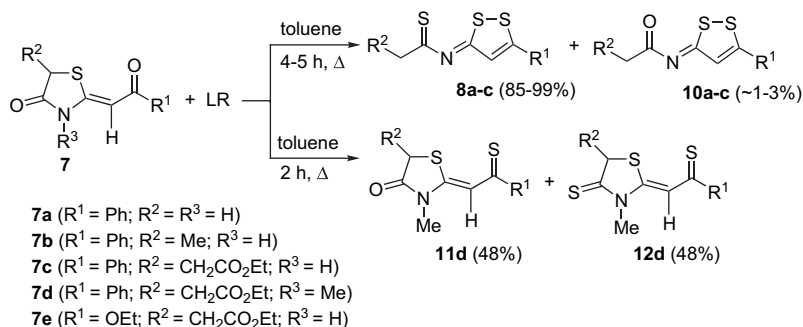
2. Results and discussion

We were attracted to this work by the possibility of inducing the regioselective reaction of (Z)-2-alkylidene-4-oxothiazolidine involving the push–pull moiety as the reactive site, due to the proximity of sulfur and oxygen atoms. An X-ray crystal structure characterization of ethyl (Z)-(5-ethoxycarbonylmethyl-4-oxothiazolidin-2-ylidene)ethanoate (**7e**), in combination with a NOE experiment,[12] gave the evidence for the Z-configuration and short 1,5-O···S non-bonded distance (2.87 Å), which is less than the sum of the van der Waals radii (3.22 Å). The planarity of the U-shaped

–S–C=C–C=O fragment is also reflected in the n,π-donor/acceptor properties of compounds **7**, possessing the two electron donors (–NH– and –S–), the intervening double bond and an electron acceptor (C=O). For the reason of greater reactivity of ketones toward LR, in comparison to that of amides and esters,[13] we chose enaminoketone type thiazolidines **7a–c** (Scheme 2) as substrates for thionation. Thus, colorless **7a–c** (R^3=H) react readily with LR in toluene under reflux to form in one-pot brown-reddish 1,2-dithioles **8a–c** in high yield. When LR was replaced by P_4S_{10} as a thionating reagent in the reaction with **7a**, only 11% of the rearranged 1,2-dithiole **8a** was formed after 6 h, confirming LR as being the superior reagent for this transformation.

An alternative method to prepare 1,2-dithioles **8** in good yields (>55%) involved, in situ base-catalyzed formation of 2-alkylidene-4-oxothiazolidines **7**[12] from the corresponding β-oxonitriles (1 equiv) and α-mercaptoesters (1.2 equiv) in chloroform as a solvent, followed by addition of LR. The formation of a side product, such as oxodithiole **10**, in a very low yield, was also observed in several reactions.[14]

In contrast to the parent enaminoketones **7a–c**, N-methyl substituted thiazolidine derivative **7d** did not give the expected rearranged product with LR, but instead, thionation products **11d** (48%) and **12d** (48%) were formed under similar reaction conditions. The isolation of the thionation derivative **11d** in 64% yield after short reaction time (10 min), establishes for the thiazolidinone reactivity the thionation rates as follows: ketone>lactam ≫ ester. In practice, the ester functionality at C(5) of **7c** and **7d** stayed intact even after prolonged reaction times (5–7 h). Characteristic spectroscopic data of the dithioles **8a–c** and oxodithioles **10b,c** are compiled in Table 1.


7a (R^1 = Ph; R^2 = R^3 = H)
7b (R^1 = Ph; R^2 = Me; R^3 = H)
7c (R^1 = Ph; R^2 = CH_2CO_2Et; R^3 = H)
7d (R^1 = Ph; R^2 = CH_2CO_2Et; R^3 = Me)
7e (R^1 = OEt; R^2 = CH_2CO_2Et; R^3 = H)

Scheme 2.

Table 1. Selected ^{13}C and ^{1}H NMR (CDCl$_3$) chemical shifts (ppm) of 1,2-dithioles **8a–c** and oxodithioles **10b,c**

Entry	Product	C(2′)	C(3)	C(4)	C(5)	C(4)-H	C(3′)-H
1	**8a**[14]	198.6	187.3	125.8	178.3	8.37	2.86
2	**8b**	204.9	187.8	126.0	178.7	8.42	3.12
3	**8c**	201.9	187.4	126.4	177.9	8.37	3.40
5	**10b**	186.4	185.4	122.8	171.0	7.75	2.76
6	**10c**	185.5	183.7	123.0	171.3	7.75	3.05

In the ¹H NMR spectra the C(4) proton of dithioles **8a–c** absorbs at very low field, viz 8.37–8.42 ppm, which indicate the aromatic nature of the dithiole ring. In addition, the ¹³C shifts for C(3), C(4), and C(5) point to highly delocalized derivatives **8a–c**, which implicate a significant aromatic contribution from the 10π electron 3,3aλ^4,4-trithia-1-azapentalene structure **8A**[15] (vide infra). The values matched those obtained in similar 1,2-dithiole-3-ylidene thiones.[16,17] The lowest field signal at δ 198–205 ppm was assigned by an HMBC experiment to the C atom of the C=S group.

The regiochemical control of the 4-oxothiazolidine→1,2-dithiole rearrangement can be traced in the mechanistic features outlined in Scheme 3. Upon direct replacement of the carbonyl oxygen in (Z)-**7** by sulfur, the non-bonded S···S distance in the intermediates **12** and **13**, should be very similar to the original value of 2.87 Å, determined for the S···O distance in enaminoester **7d**. The distance is approximately 0.75 Å shorter than the corresponding van der Waals distance between the two sulfur atoms.[12] Subsequently, the close S···S interaction initiates an intramolecular rearrangement by concerted thioxothiazolidine ring-opening-1,2-
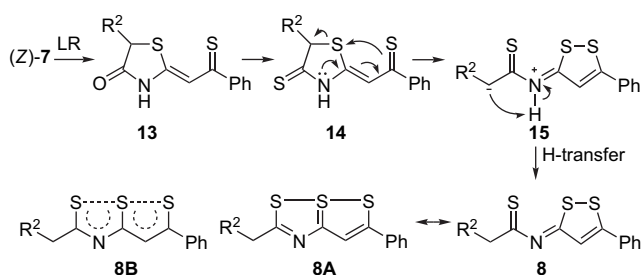
dithiole closing process **14→15**, followed by H-transfer (step **15→8**). The lack of rearrangement in the case of the N-methyl substituted precursor **7d** can be attributed to an unfavorable methyl migration.

In order to prove the 10π electron aromaticity of highly delocalized 1,2-dithioles **8a–c**, the structure of **8a** was theoretically calculated on the B3LYP/6-31G** level of theory.[18,19] As expected, a *planar* [1,2]dithiolo[1,5-b][1,2,4]dithiazole moiety **8B** was obtained; the distances between the three sulfur atoms are more or less the same (vide infra) and the phenyl substituent in position 5 is twisted by 30.6° (Fig. 1). The ring current effect, which proved to be very characteristic of the aromaticity of the 10π electron system **8B** was calculated by the method of Klod and Kleinpeter[20] and is also visualized in Figure 1.

Iso-chemical-shielding surfaces (ICSS) of ±0.1 ppm[21] thus obtained [above and below the plane ca. 10 Å high field shift (yellow), in-plane >10 Å low field shift (red)] show **8B** to have a stronger ring current effect than benzene[20] and, hereby, can be employed as proof for strong pseudo-aromaticity of the planar [1,2]dithiolo[1,5-b][1,2,4]dithiazole moiety **8B**. The chemical shielding in the surrounding of **8B** was calculated based on the idea of NICS by Schleyer et al.[21] Therefore, the molecule was placed in the center of a grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions with a step width of 0.5 Å. This resulted in a cube of 68,921 ghost atoms. The chemical shielding calculations were done with the GIAO method[22,23] using HF/6-31G* on the basis of the geometry optimized B3LYP/6-31G** structure of **8B**. Since GIAO is a coupled HF method that uses gauge independent atom orbital for the calculation of shielding values, it can be applied in the calculation of NICS. From the GIAO calculations the coordinates

Scheme 3.

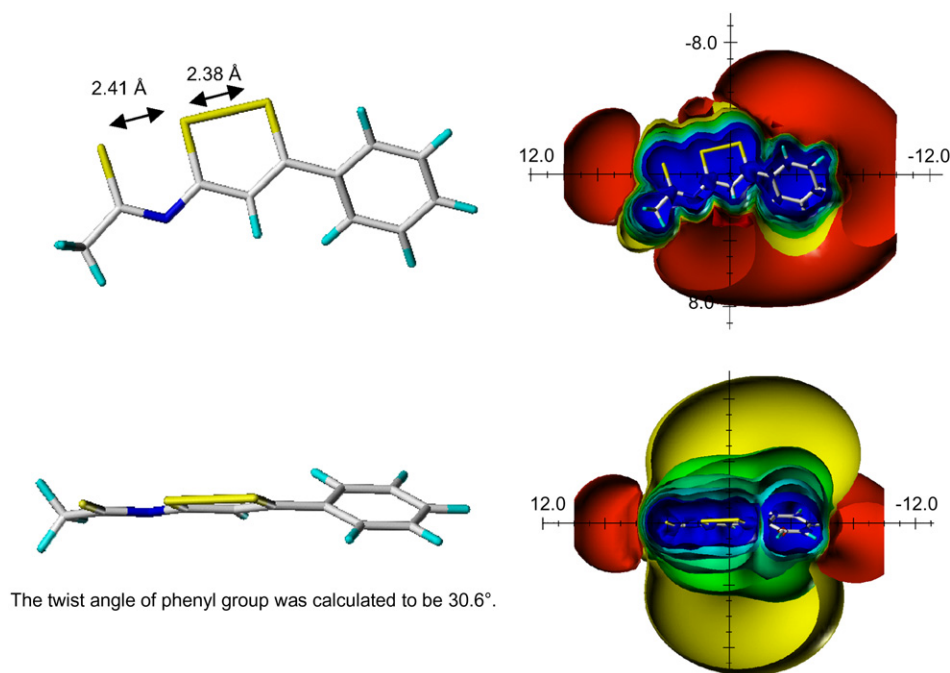The twist angle of phenyl group was calculated to be 30.6°.

Figure 1. Structure and ring current effect of *planar* [1,2]dithiolo[1,5-b][1,2,4]dithiazole moiety of **8a** (ICSSs of different shielding or deshielding: blue stands for 5 ppm shielding, cyan for 2 ppm shielding, green-blue for 1 ppm shielding, green for 0.5 ppm shielding, yellow for 0.1 ppm shielding and red for −0.1 ppm deshielding).

and isotropic shielding values of the ghost atoms were extracted. After the transformation of the tabulated chemical shielding into a contour file the ring current effect of **8B** can be visualized as ICSS. In Figure 1 only ICSSs behind the coordinate system are visualized to show both the different ICSSs and the structure of the molecule. Thus, it is possible to map the spatial extension of the ring current effect at a given chemical shielding value: blue stands for 5 ppm shielding, cyan for 2 ppm shielding, green-blue for 1 ppm shielding, green for 0.5 ppm shielding, yellow for 0.1 ppm shielding, and red for −0.1 ppm deshielding.

It should be emphasized that the above calculations were fully corroborated by a single-crystal X-ray structure determination of **8a** (Fig. 2), which confirms the presence of the $3,3a\lambda^4,4$-trithia-1-azapentalene system as in **8A** or **8B**, depicting full or partial bonding between the sulfur atoms, respectively. It crystallizes as red plates in the monoclinic space group $P2_1/c$. Figure 2 shows a perspective view of the structure along with selected bond lengths and bond angles, which have similar values to those in a previously reported structure containing a heterocyclic ring system of this type.[24]

The [1,2]dithiolo[1,5-*b*][1,2,4]dithiazole ring system is planar [maximum deviation from the mean-plane=0.022(2) Å] and inclined to the plane of the phenyl ring at an angle of $28.0(1)°$. The molecular packing shows the typical herringbone pattern associated with this space group and appears to be controlled by intermolecular S⋯S interactions,[25] the shortest being 3.455(1) Å. From the data above it is apparent that the S1–S2 and S2–S3 bonds, being 2.3374(5) and 2.3408(5) Å, respectively, are shorter than the sum of the van der Waals radii, but relatively long in comparison to a S–S covalent bond (2.08 Å) and not exactly of equal length, as the two fused rings differ. The solid-state structure **8A**, having an internal hypervalent sulfur S(2)[26] within the nearly linear S(1)–S(2)–S(3) array (175.8°) is unequivocal, but not necessarily identical with that in solution. The structure of the major 1,2-dithiol-3-imino species **8** in solution should be considered in conjunction with fused bicyclic
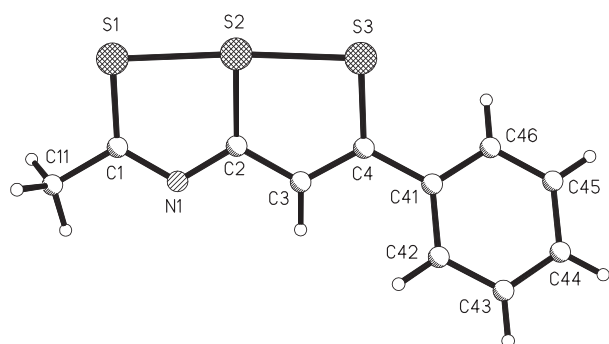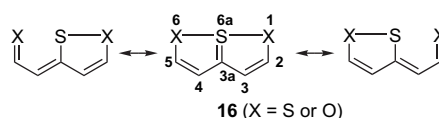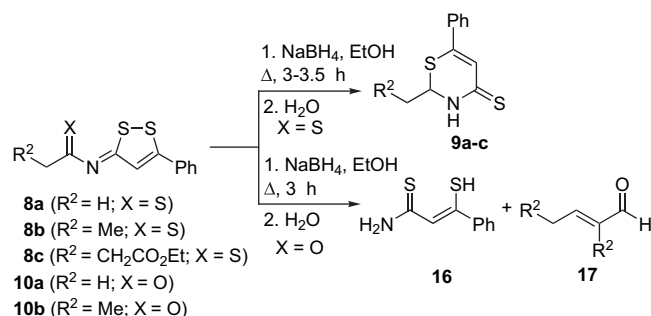
10π-electron system, represented by trithia-1-azapentalene structure **8A** or **8B**.[27] It is worth mentioning that numerous experimental and theoretical investigations presented evidence that the structure of $1,6,6a\lambda^4,4$-trithiapentalene **16** (X=S) and related compounds is characterized by C_{2v} symmetry and no-bond-single-bond-resonance.[15b–d]

16 (X = S or O)

Having studied the synthesis of 3-imino-1,2-dithiole derivatives **8a–c**, which is inherently dependent on the spatial orientation of the U-shaped –S–C=C–C=O fragment of the thiazolidinone precursors **7**, we have focused our interest on their synthetic utility. The aromatic nature of the conjugated 1,2-dithiole ring and nucleophilicity of sulfur atoms reflect the reactivity toward a limited number of electrophilic reagents.[17] On the other hand, reactions are common with a certain number of oxygen, sulfur, nitrogen or carbon nucleophiles, which attack various electrophilic positions of the dithiole nucleus. In some cases after the initial nucleophilic attack, a stepwise pathway involving ring cleavage and subsequent cyclization, sometimes preceded by sulfur extrusion, provide an approach for formation of other heterocyclic systems. These facts prompted us to explore the reductive cleavage of 1,2-dithioles **8** and 1,2-oxodithioles **10** as we assumed that the potential acyclic intermediate can be formed, en route to another heterocyclic ring system.
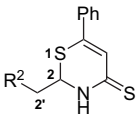
Thus, we found that heating **8a–c** (X=S) with 2 equiv of sodium borohydride in ethanol resulted in ring-opening followed by cyclization to yellowish 2,3-dihydro-4*H*-1,3-thiazine-4-thiones **9a–c** in good yields (Scheme 4).[18,28] In contrast, attempted reductive rearrangement of oxodithioles **10a,b** (X=O) to analogous 1,3-oxothiazine-4-thiones failed, and instead (*Z*)-3-mercapto-3-phenylprop-2-enethioamide (**16**) was isolated, together with the corresponding α,β-unsaturated aldehyde **17**.

Figure 2. Perspective view of the crystal structure of **8a**. Selected bond lengths (Å): S1–S2 2.3374(5), S1–C1 1.701(2), S2–S3 2.3408(5), S2–C2 1.760(2), S3–C4 1.708(2), C1–N1 1.320(2), C1–C11 1.506(2), C2–N1 1.357(2), C2–C3 1.409(2), C3–C4 1.384(2), C4–C41 1.484(2). Selected bond angles (°): S(3)–S(2)–S(1) 175.80(2), C(2)–S(2)–S(3) 88.84(5), C(2)–S(2)–S(1) 86.96(5), C(4)–S(3)–S(2) 94.31(5), N(1)–C(1)–S(1) 121.22(12), C(11)–C(1)–S(1) 119.48(12), N(1)–C(2)–S(2) 122.14(12), C(3)–C(2)–S(2) 118.88(11), C(4)–C(3)–C(2) 121.29(12), C(3)–C(4)–S(3) 116.66(11).

Scheme 4.

The structures of the new products **9a–c** are supported by their spectroscopic data (Table 2) and elemental analysis. 1,3-Thiazines have one strong absorption in their UV–vis spectra at λ_{max} 269 nm and another, nearly identical maximum at 370, 369, and 367 nm, respectively. In comparison to this ring system, 1,2-dithiole precursors **8a–c** exhibit two identical maxima at 333 and 446 nm, indicating that

Table 2. Selected spectroscopic data of 2,3-dihydro-4*H*-1,3-thiazine-4-thiones **9a–c**

	^{13}C and ^{1}H NMR chemical shifts (ppm)					IR (KBr) (ν in cm^{-1})			UV (λ_{max} in nm)
	C(4)	C(2)H	C(2′)H	NH	C(5)H	C=S	C=C	NH	
9a[a]	190.1	4.97–5.06 (m)	1.63 (d, *J*=6.6 Hz)	10.34	6.99	1158	1550	3075	269, 370
9b[b]	191.6	4.74–4.82 (m)	2.00–2.23 (m)	8.07	7.11 (d, *J*=1.2 Hz)[c]	1153	1560	3147	269, 369
9c[b]	191.4	4.91–4.99 (m)	2.28–2.48 (m)	8.30	7.12 (d, *J*=1.2 Hz)[c]	1131	1555	3273	269, 367

[a] DMSO-d_6.
[b] CDCl$_3$.
[c] NH–C(5)H coupling as determined by HH COSY.

different substituents R, i.e., hydrogen, methyl or ethoxycarbonylmethylene, do not alter the UV–vis absorption pattern of heterocycles **8a–c** and **9a–c**. The presence of a strong band in the IR spectra (KBr) around 1150 cm^{-1} and a low-field signal at δ=~191 ppm, unambiguously established the presence of the thiocarbonyl group.

One of the thiazine derivatives, namely 2-ethyl-6-phenyl-2,3-dihydro-4*H*-1,3-thiazine-4-thione (**9b**), has been structurally characterized by X-ray crystallography. This compound crystallizes as yellow blocks in the triclinic space group *P*-1. Figure 3 shows a perspective view of the structure with selected bond lengths. Not shown in the diagram is the fact that there is minor disorder in the conformation of the heterocyclic ring with the sulfur atom occupying two
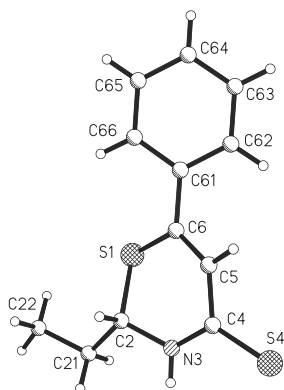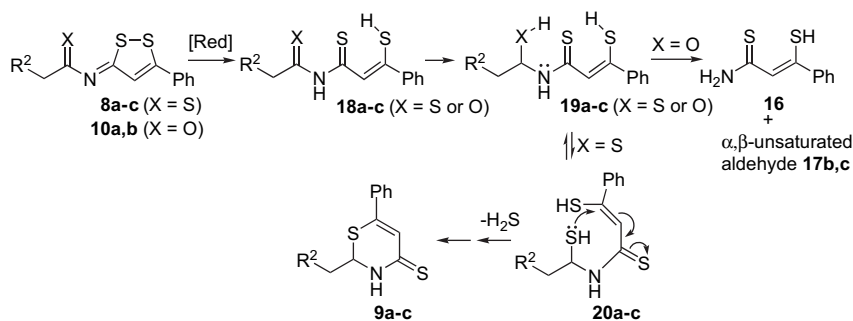
alternative positions with 85:15 relative occupancies. To the best of our knowledge, this is the first X-ray crystal structure of 4*H*-2,3-dihydro-1,3-thiazine-4-thione.

The rearrangement of **8a–c** to **9a–c** can be rationalized by the series of steps, involving an initial hydride ring-opening of the 1,2-dithiole ring to acyclic intermediate **18**, containing the six-atom skeleton, which subsequently appears in the final thiazine ring (Scheme 5). Reduction of the thioxo group (intermediate **19**), followed by rotation around the N–C bond and s-cis → s-trans conformational change **19** → **20**, set the stage for the cyclization. Thus, the mercapto group attack on the C=C bond, occurring with the loss of H$_2$S, gives rise to 1,3-thiazines **9a–c**. Attempts to promote the same type of rearrangement with oxo-1,2-dithioles **10b,c** (X=O) to obtain analogues 1,3-oxazines, resulted in the formation of the α,β-unsaturated thioamide **16** (80%) and **17b** or **17c** via aldol reaction of enolizable aldehyde, formed by degradation of the common open-chain intermediate **19b** or **19c** (X=O). Unsurprisingly, this intermediate, generated by reductive cleavage from the corresponding 1,2-oxodithiole **10** does not undergo cyclization due to the lower nucleophilic ability of the oxygen versus the sulfur atom.

3. Conclusion

The efficient and general procedure for the synthesis of 2,3-dihydro-4*H*-1,3-thiazine-4-thiones via 1,2-dithiole-3-ylidene thiones, prepared from (Z)-2-alkylidene-4-oxothiazolidines, has been developed. The overall 4-oxothiazolidine-1,3-thiazine transformation clearly reveals the importance of the directional non-bonded 1,5-type S···O interaction in 4-oxothiazolidine precursors to induce further chemical reactions.

Figure 3. Perspective view of the major contributor in the crystal structure of **9b**. Selected bond lengths (Å): S1–C6 1.772(3), S1–C2 1.805(3), C2–N3 1.467(4), C2–C21 1.492(4), N3–C4 1.331(3), C4–S4 1.689(3), C4–C5 1.459(4), C5–C6 1.330(4), C6–C61 1.487(4).

Scheme 5.

4. Experimental

Melting points were determined on a Micro-Heiztisch Boetius PHMK apparatus or Büchi apparatus and are uncorrected. The IR spectra were recorded on a Perkin–Elmer FTIR 1725X spectrophotometer and are reported as wave numbers (cm^{-1}). Samples for IR spectral measurements were prepared as KBr disks. The NMR spectra were obtained using a Varian Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50.3 MHz). ^{13}C NMR resonance assignments were aided by the use of the DEPT technique to determine numbers of attached hydrogens. The 2D ROESY has been performed on a Bruker Avance 500 NMR spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale from TMS as an internal standard in the solvents specified. Low-resolution mass spectra were recorded using a Finnigan MAT 8230 BE spectrometer at 70 eV (EI). Isobutane was used as the ionizing gas for the chemical ionization (CI) mass spectra. The UV spectra were measured on a Beckman DU-50 spectrophotometer. Analytical thin layer chromatography (TLC) was carried out on Kieselgel G nach Stahl, and the spots were visualized by iodine. Column chromatography was carried out on SiO$_2$ (silica gel 60 Å, 12-26, ICN Biomedicals). Elemental analyses were performed at the microanalysis laboratory at the Department of Chemistry, University of Belgrade.

4.1. General procedure for the preparation of 1,2-dithioles 8a–c

A colorless solution of (Z)-2-alkylidene-4-oxothiazolidines **7a–c** (0.164 mmol) and LR (0.164 mmol) in dry toluene (3 mL) was heated in an oil bath at 90–95 °C (initially a heterogeneous solution at room temperature becomes homogenous upon heating at around 75 °C). After a few minutes, the color of the reaction mixture turned dark reddish brown. Caution: *All reactions involving Lawesson's reagent, due to the unpleasant odor, should be carried out in a well-ventilated hood*. The mixture was stirred at this temperature for additional 4–5 h when TLC indicated the complete consumption of substrates **7a–c**. After cooling to room temperature, the solvent was evaporated in vacuo. The residue was chromatographed (toluene/ethyl acetate, 10:0 to 8:2, v/v) affording the dark orange crystalline 1,2-dithioles **8a–c** in high yields (85–99%). The structural assignments of all isolated products were made on the basis of spectroscopic data (IR, ^{1}H and ^{13}C NMR, MS, UV) and elemental analysis. Compound **8a** was previously described.[14] The assignments are based on the highly delocalized 1,2-dithiole structures **8** with emphasis on an increased contribution of the 3,3aλ^4,4-trithia-1-azapentalene form **8A**.

4.1.1. *N*-(5-Phenyl-3*H*-1,2-dithiol-3-ylidene)ethanthioamide (8a). From **7a** (50 mg, 0.228 mmol) in toluene (4 mL) and LR (87 mg, 0.228 mmol) after column chromatography (toluene/EtOAc 10:0 to 8:2) the 1,2-dithiole **8a** was isolated; yield 57 mg (99%); R_f (toluene/ethyl acetate, 4:1)=0.76; mp 98 °C. IR (KBr): ν_{max} 3004, 2908, 1638, 1514, 1485, 1447, 1404, 1226, 1205, 989, 846, 757, 690, 642 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.86 (3H, s, CH$_3$), 7.42–7.53 (3H, m, *m*- and *p*-Ph), 7.75–7.84 (2H, m, *o*-Ph), 8.37 (1H, s, =CH). ^{13}C NMR (CDCl$_3$): δ 29.1 (CH$_3$), 125.8 (=CH), 127.4 (*o*-Ph), 129.0 (*m*-Ph), 131.0 (*p*-Ph), 136.2

(C$_{ipso}$-Ph), 178.5 (C=*C*–S), 187.3 (N=C–S), 198.6 (C=S). MS (EI): *m/z* (rel intensity): 251 (M$^+$, 35), 236 (15), 210 (5), 193 (7), 174 (3), 145 (13), 121 (18), 102 (20), 89 (3), 77 (13), 59 (100), 39 (3); UV (DMSO): λ_{max} (ε) 333 nm (15,250) and 446 nm (11,300). Anal. Calcd for C$_{11}$H$_9$NS$_3$: C, 52.56; H, 3.61; N, 5.57; S, 38.26. Found: C, 52.68; H, 3.71; N, 5.63; S, 37.88.

4.1.2. *N*-(5-Phenyl-3*H*-1,2-dithiol-3-ylidene)propanthioamide (8b). From **7b** (40 mg, 0.17 mmol) in toluene (4 mL) and LR (70 mg, 0.17 mmol) after column chromatography (petroleum ether/EtOAc 10:0 to 10:0.4) the 1,2-dithiole **8b** was isolated; yield 39 mg (85%); R_f (toluene/ethyl acetate, 9:1)=0.65; mp 54–56 °C. IR (KBr): ν_{max} 3142, 3013, 2965, 2927, 2891, 1518, 1481, 1448, 1396, 1290, 1227, 1195, 1065, 1000, 944, 841, 761, 693 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.44 (3H, t, *J*=7.4 Hz, CH$_3$), 3.12 (2H, q, *J*=7.4 Hz, CH$_2$), 7.47–7.50 (3H, m, *m*- and *p*-Ph), 7.83–7.88 (2H, m, *o*-Ph), 8.42 (1H, s, =CH). ^{13}C NMR (CDCl$_3$): δ 13.8 (CH$_3$), 35.8 (CH$_2$), 126.0 (=CH), 127.5 (*o*-Ph), 129.1 (*m*-Ph), 131.0 (*p*-Ph), 136.7 (C$_{ipso}$-Ph), 178.7 (C=*C*–S), 187.8 (N=C–S), 204.9 (C=S); UV (DMSO): λ_{max} (ε) 332 nm (15,250) and 446 nm (11,300). Anal. Calcd for C$_{12}$H$_{11}$NS$_3$: C, 54.32; H, 4.15; N, 5.28. Found: C, 54.14; H, 4.18; N, 5.26.

4.1.3. Ethyl 3-(5-phenyl-3*H*-1,2-dithiol-3-ylidenethiocarbamoyl)propanoate (8c). From **7c** (50 mg, 0.16 mmol) in toluene (4 mL) and LR (66 mg, 0.16 mmol) after column chromatography (toluene/EtOAc 3:1 to 1:1) the 1,2-dithiole **8c** was isolated; yield 51 mg (92%); R_f (toluene/ethyl acetate, 4:1)=0.68; mp 65 °C. IR (KBr): ν_{max} 3067, 3006, 2978, 2925, 2855, 1730, 1512, 1483, 1450, 1426, 1401, 1375, 1305, 1177, 1157, 1107, 1049, 1015, 945, 867, 830, 760, 687 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.26 (3H, t, *J*=7.2 Hz, CH$_3$), 2.92 (2H, t, *J*=7.3 Hz, CH$_2$–CO), 3.40 (2H, t, *J*=7.3 Hz, CH$_2$–CS), 4.17 (2H, q, *J*=7.0 Hz, CH$_2$–O), 7.41–7.53 (3H, m, *m*- and *p*-Ph), 7.78–7.87 (2H, m, *o*-Ph), 8.37 (1H, s, =CH). ^{13}C NMR (CDCl$_3$): δ 14.7 (CH$_3$), 32.9 (CH$_2$–CO), 37.5 (CH$_2$–CS), 60.6 (CH$_2$–O), 126.4 (=CH), 127.4 (*o*-Ph), 129.1 (*m*-Ph), 131.1 (*p*-Ph), 136.0 (C$_{ipso}$-Ph), 172.2 (CO$_{ester}$), 177.5 (C=*C*–S), 187.4 (N=C–S), 201.9 (C=S). MS (EI): *m/z* (rel intensity): 337 (M$^+$, 38), 304 (65), 277 (7), 264 (8), 236 (100), 211 (15), 194 (10), 178 (20), 145 (38), 117 (73), 102 (33), 71 (45), 55 (65); UV (DMSO): λ_{max} (ε) 332.6 nm (15,990) and 446.1 nm (12,720). Anal. Calcd for C$_{15}$H$_{15}$NO$_2$S$_3$: C, 53.39; H, 4.48; N, 4.15; S, 28.50. Found: C, 53.15; H, 4.45; N, 4.24; S, 27.97.

4.1.4. *N*-(5-Phenyl-3*H*-1,2-dithiol-3-ylidene)propanamide (10b). A suspension of 1,2-dithiole **8b** (71 mg, 0.27 mmol) and Hg(OAc)$_2$ (86 mg, 0.27 mmol) in acetic acid (6 mL) was kept under reflux for 2.5 h and then cooled down to room temperature. After addition of water (50 mL), the suspension was filtered and extracted with CHCl$_3$ (2×50 mL). The organic layer was dried and concentrated in vacuo. After column chromatography (toluene/EtOAc 20:0 to 20:5) the title compound **10b** was isolated; yield 34.5 mg (52%); R_f (toluene/ethyl acetate, 4:1)=0.36; mp 109–110 °C. IR (KBr): ν_{max} 3223, 3051, 2968, 2931, 2901, 2360, 1585, 1527, 1488, 1450, 1416, 1360, 1295, 1250, 1217, 1176, 1068, 1025, 1001, 911, 845, 805, 758, 727,

682, 652 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.30 (3H, t, J=7.4 Hz, CH$_3$), 2.76 (2H, q, J=7.4 Hz, CH$_2$), 7.49–7.54 (3H, m, *m*- and *p*-Ph), 7.71–7.73 (*o*-Ph), 7.74 (1H, s, =CH). ^{13}C NMR (CDCl$_3$): δ 9.7 (CH$_3$), 31.4 (CH$_2$), 122.8 (=*C*HCPh), 127.2 (*o*-Ph), 129.4 (*m*-Ph), 131.6 (*p*-Ph), 132.9 (C$_{ipso}$-Ph), 171.0 (=*C*SPh), 185.4 (N=CS), 186.4 (CO); CIMS: *m/z*: 250 (M+1); UV (DMSO): λ_{max} (ε) 304.0 nm (10,600) and 381.1 nm (8900). Anal. Calcd for C$_{12}$H$_{11}$NOS$_2$: C, 57.81; H, 4.45; N, 5.62; S, 25.72. Found: C, 57.42; H, 4.46; N, 5.54; S, 25.15.

4.1.5. Ethyl 4-oxo-(5-phenyl-3*H*-1,2-dithiol-3-ylidene-amino)butanoate (10c).

Based on the same procedure as above, from 1,2-dithiole **8c** (101.3 mg, 0.3 mmol) and Hg(OAc)$_2$ (95.7 mg, 0.3 mmol) in acetic acid (6 mL) after column chromatography (toluene/EtOAc 20:0 to 20:5) the title compound **10c** was isolated; yield 50 mg (52%); R_f (toluene/ethyl acetate, 4:1)=0.33; mp 119–121 °C. IR (KBr): ν_{max} 3434, 3056, 2986, 2927, 2335, 1732, 1577, 1522, 1487, 1450, 1414, 1388, 1364, 1329, 1272, 1229, 1186, 1157, 1076, 1022, 965, 940, 917, 868, 848, 762, 684, 660 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.27 (3H, t, J=7.2 Hz, CH$_3$), 2.80 (2H, t, J=6.9 Hz, CH$_2$CO), 3.05 (2H, t, J=6.9 Hz, CH$_2$CON), 4.17 (2H, q, J=7.2 Hz, CH$_2$), 7.50–7.55 (3H, m, *m*- and *p*-Ph), 7.71–7.76 (*o*-Ph), 7.75 (1H, s, =CH). ^{13}C NMR (CDCl$_3$): δ 14.2 (CH$_3$), 29.7 (*C*H$_2$CO), 32.9 (*C*H$_2$CON), 60.6 (OCH$_2$), 123.0 (=*C*HCPh), 127.2 (*o*-Ph), 129.5 (*m*-Ph), 131.7 (*p*-Ph), 132.7 (C$_{ipso}$-Ph), 171.3 (=*C*SPh), 172.7 (N=CO), 183.8 (N=CS), 185.5 (CO$_{ester}$); CIMS: *m/z*: 322 (M+1); UV (DMSO): λ_{max} (ε) 305.6 nm (12,600) and 381.1 nm (10,900). Anal. Calcd for C$_{15}$H$_{15}$NO$_3$S$_2$: C, 56.05; H, 4.70; N, 4.36. Found: C, 56.54; H, 4.97; N, 3.92.

4.2. General procedure for the preparation of 1,3-thiazine derivatives 9a–c

1,2-Dithiole **8** (1 mmol) and sodium borohydride (2 mmol) were suspended in ethanol (ca. 30–35 mL) (initially a heterogeneous solution at room temperature that becomes homogenous upon heating). A dark orange reaction mixture after stirring at room temperature for 1.5–2 h became less colored and cloudy. Stirring was continued at 85–90 °C (oil bath) until the reaction was complete, as monitored by TLC (in most cases, for about 1.5 h). The reaction mixture was brought to room temperature and then the solvent was evaporated in vacuo. The residue was treated with warm water (70 mL) and after stirring (10 min), a cold suspension was extracted with CHCl$_3$ (3×40 mL), followed by drying and concentration of the combined organic phases. The residue was either crystallized or chromatographed on silica gel (toluene/ethyl acetate gradient 100:0 to 50:50, v/v) to afford corresponding thiazine **9**, as a pale yellow solid.

4.2.1. 2-Methyl-6-phenyl-2,3-dihydro-4*H*-1,3-thiazine-4-thione (9a).

The title compound was obtained as a yellow solid in 62% yield (56 mg) from 101.5 mg (0.4 mmol) of 1,2-dithiole **8a** and 30.5 mg (0.8 mmol) of NaBH$_4$. Mp 154–155 °C; R_f (toluene/ethyl acetate, 9:1)=0.50. IR (KBr): ν_{max} 3075, 3031, 2920, 2853, 1550, 1489, 1444, 1385, 1158, 1084, 766, 738, 701 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 1.63 (3H, d, J=6.6 Hz, CH$_3$), 4.97–5.06 (1H, m, CH), 6.99 (1H, s, =CH), 7.49–7.55 (3H, m, *m*- and *p*-Ph),

7.67–7.71 (2H, m, *o*-Ph), 10.34 (1H, s, NH). ^{13}C NMR (DMSO-d_6): δ 19.0 (CH$_3$), 53.7 (CH), 123.2 (=CH), 127.7 (*o*-Ph), 129.4 (*m*-Ph), 131.2 (*p*-Ph), 135.5 (C$_{ipso}$-Ph), 143.0 (=CHPh), 190.1 (C=S). MS (EI): *m/z* (rel intensity): 221 (M$^+$, 100), 206 (14), 193 (11), 178 (77), 145 (31), 121 (96), 102 (17), 77 (23); UV (DMSO): λ_{max} (ε) 269 nm (17,000) and 370 nm (23,900). Anal. Calcd for C$_{11}$H$_{11}$NS$_2$: C, 59.69; H, 5.01; N, 6.33. Found: C, 59.42; H, 5.19; N, 6.10.

4.2.2. 2-Ethyl-6-phenyl-2,3-dihydro-4*H*-1,3-thiazine-4-thione (9b).

The title compound was obtained as a yellow solid in 60% yield (101.5 mg) from 191.0 mg (0.7 mmol) of 1,2-dithiole **8b** and 54.5 mg (1.4 mmol) of NaBH$_4$. Mp 135–136 °C. R_f (toluene/ethyl acetate, 9:1)=0.55. IR (KBr): ν_{max} 3147, 3067, 3028, 2966, 2875, 1560, 1501, 1485, 1416, 1368, 1275, 1153, 1099, 764, 702 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.18 (3H, t, J=7.6 Hz, CH$_3$), 2.00–2.23 (2H, m, CH$_2$), 4.74–4.82 (1H, m, CH), 7.11 (1H, d, J=1.2 Hz, =CH), 7.39–7.50 (3H, m, *m*- and *p*-Ph), 7.67–7.72 (2H, m, *o*-Ph), 8.07 (1H, s, NH). ^{13}C NMR (CDCl$_3$): δ 10.2 (CH$_3$), 26.2 (CH$_2$), 59.9 (CH), 123.0 (=CH), 128.2 (*o*-Ph), 128.9 (*m*-Ph), 131.1 (*p*-Ph), 135.6 (C$_{ipso}$-Ph), 146.0 (=CHPh), 191.6 (C=S). MS (EI): *m/z* (rel intensity): 235 (M$^+$, 100), 220 (54), 206 (28), 193 (52), 178 (26), 145 (33), 121 (95), 104 (30), 77 (25); UV (DMSO): λ_{max} (ε) 269 nm (29,300) and 369 nm (21,400). Anal. Calcd for C$_{12}$H$_{13}$NS$_2$: C, 61.24; H, 5.57; N, 5.95. Found: C, 61.04; H, 5.55; N, 5.99.

4.2.3. 2-Ethyl-3-(6-phenyl-4-thioxo-3,4-dihydro-4*H*-1,3-thiazin-2-yl)propanoate (9c).

The title compound was obtained as a yellow solid in 55% yield (22.0 mg) from 43.8 mg (0.13 mmol) of 1,2-dithiole **8c** and 9.8 mg (0.26 mmol) of NaBH$_4$. Mp 114–116 °C; R_f (toluene/ethyl acetate, 9:1)=0.41. IR (KBr): ν_{max} 3273, 3058, 2961, 2927, 1720, 1555, 1487, 1282, 1201, 1131, 1022, 762, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.29 (3H, t, J=7.0 Hz, CH$_3$), 2.28–2.48 (2H, m, CH$_2$), 2.59–2.69 (2H, m, COCH$_2$), 4.20 (2H, q, J=7.0 Hz, CH$_2$O), 4.91–4.99 (1H, m, CH), 7.12 (1H, d, J=1.2 Hz, =CH), 7.39–7.53 (3H, m, *m*- and *p*-Ph), 7.66–7.70 (2H, m, *o*-Ph), 8.30 (1H, s, NH). ^{13}C NMR (CDCl$_3$): δ 14.1 (CH$_3$), 27.9 (CH$_2$), 30.1 (CO*C*H$_2$), 57.5 (CH), 61.3 (CH$_2$O), 123.0 (=CH), 128.1 (*o*-Ph), 129.0 (*m*-Ph), 131.2 (*p*-Ph), 135.6 (C$_{ipso}$-Ph), 144.6 (=CHPh), 172.5 (C=O), 191.4 (C=S). MS (EI): *m/z* (rel intensity): 307 (M$^+$, 100), 220 (96), 206 (20), 193 (23), 179 (29), 145 (24), 121 (62), 102 (14), 77 (18); UV (DMSO): λ_{max} (ε) 269 nm (18,600) and 367 nm (14,300). Anal. Calcd for C$_{15}$H$_{17}$NO$_2$S$_2$: C, 58.60; H, 5.57; N, 4.56. Found: C, 58.46; H, 5.68; N, 4.51.

4.3. X-ray crystallography

Data were collected with a Bruker APEX CCD area detector, using graphite monochromatized Mo Kα radiation (λ= 0.71073 Å). The structures were solved by direct methods using SHELXS[29] and refined on F^2, using all data, by full-matrix least-squares procedures using SHELXTL.[30] Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of the carrier carbons.

Full tables of atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge

Crystallographic Data Centre. CCDC 607823–607824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (internat.): +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

4.3.1. Crystal data for 8a. $C_{11}H_9NS_3$, MW 251.37, red plate, $0.50 \times 0.41 \times 0.09$ mm, monoclinic, $P2_1/c$, $a=13.4197(7)$, $b=7.2797(4)$, $c=11.8980(6)$ Å, $\beta=108.161(2)°$, $V=1104.4(1)$ Å^3, $Z=4$, $T=-180$ °C, $F(000)=520$, μ(Mo Kα)=0.633 mm^{-1}, $D_{calcd}=1.512$ g cm^{-3}, $2\theta_{max}$ 55° (CCD area detector, 99.6% completeness), $wR(F^2)=0.076$ (all 2532 data), $R=0.030$ (2403 data with $I>2\sigma I$).

4.3.2. Crystal data for 9b. $C_{12}H_{13}NS_2$, MW 235.35, yellow block, $0.22 \times 0.09 \times 0.08$ mm, triclinic, P-1, $a=5.6687(8)$, $b=11.0149(15)$, $c=11.056(2)$ Å, $\alpha=116.540(9)°$, $\beta=94.285(10)°$, $\gamma=102.679(7)°$, $V=590.6(2)$ Å^3, $Z=2$, $T=-180$ °C, $F(000)=248$, μ(Mo Kα)=0.416 mm^{-1}, $D_{calcd}=1.323$ g cm^{-3}, $2\theta_{max}$ 50° (CCD area detector, 97% completeness), $wR(F^2)=0.092$ (all 2033 data), $R=0.044$ (1285 data with $I>2\sigma I$).

Acknowledgements

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