A Novel Non Photochemical Ring Contraction of 4-Pyrones to Cyclopent-2-enones

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Unlike comenic acid or most other 4-pyrones, methyl or ethyl comenate reacts with aromatic amines under mild conditions in the sense of ring contraction to 3-arylamino-2,4-dihydroxy-2-cyclopentenone-4-carboxylates. The structure of the new cyclopentenone derivatives were determined from their characteristic spectroscopic behaviour and was confirmed by X-ray crystallographic studies of compound **Vb**.

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A challenging task of heterocyclic chemistry is the study of ring transformations [1]. The transformations of oxygen heterocycles, such as pyrone and related compounds into pyridines [2,3] deserved a good deal of work either in mechanistic studies or for its synthetic interest.

A well known route for preparation of pyridones involves a reaction of suitable pyrone with a primary amine [4]. This reaction was adapted in our laboratory to prepare a number of *N*-aryl- and *N*-heteroaryl-substituted 3-hydroxy-4-pyridones [5,6] which turned out to be suitable selective extractants for a number of metal ions [7].

Comenic acid (5-hydroxy-4-pyrone-2-carboxylic acid) was easily and efficiently converted to *N*-aryl-substituted 5-hydroxy-4-pyridone-2-carboxylic acids by a simple reaction with corresponding the aromatic amine either in diluted acetic acid or in alcoholic solution [5]. Unexpectedly, an attempt to perform the same reaction starting from methyl comenate instead of comenic acid itself, failed since no pyridone but some unidentified crystalline product was detected [8].

Our interest in the field [6,7] prompted us to reinvestigate this result more closely. We found the same behaviour either with methyl or ethyl comenate regardless of the *p*-substituted aniline used. Spectral and chemical characteristics of the main product indicated structural differences either from the expected pyridones or any other compound with the preserved pyrone ring.

In the present paper we wish to discuss a structure elucidation of the product obtained as a result of an unexpected ring contraction of the 4-pyrone nucleus. It should be noted that several ring contraction of 4-pyrones, useful in transformations and synthesis of some natural products were reported, but these reactions were photochemically induced [9].

A reaction of 4-pyrone derivatives with an aliphatic or an aromatic amine is to be regarded as "normal" if the principal isolable product is the corresponding 4-pyridone derivative [12]. The mechanism of this reaction is well documented [13] and there are plenty of literature data showing that the first step in a 4-pyrone to a 4-pyridone transformation is a nucleophilic attack of a base (an amine) to the α- or α'-position of the pyrone nucleus [14] leading to an open-chain intermediate [16]. Such an intermediate in general cyclizes easily to a 4-pyridone derivative ("normal" reaction), but some structural characteristics (*e.g.* steric hindrance) may be of significant disadvantage [17]. Illustrative is a report showing that an open chain reaction product of 2-ethoxycarbonyl-4-pyrone with 3-hydroxyaniline obtained under very mild conditions is stable at room temperature, but cyclizes promptly at elevated temperature [18].

Scheme I

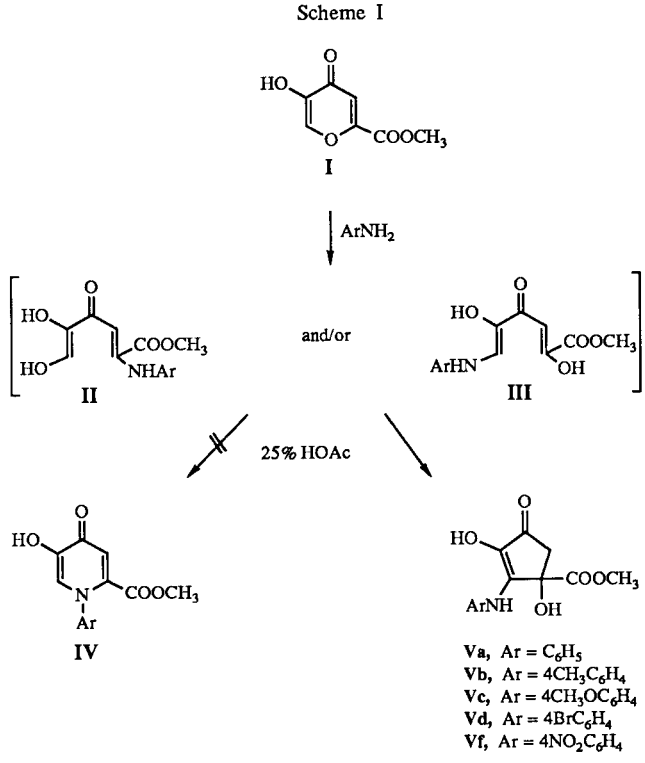
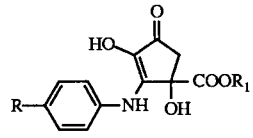


Table I

3-Arylamino-2,4-dihydroxy-4-methoxycarbonyl-2-cyclopenten-1-ones Va-f

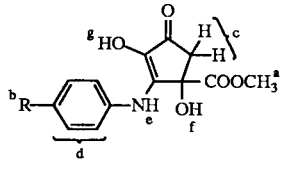


No.	R	R_1	Mp °C	Yield %	Formula	Analysis Calcd./Found % C	% H	% N	UV [a] λ max (log ε)	IR [b] ν C=O (ester)	ν C=O (enone)
Va	H	CH_3	161-162	62	$C_{13}H_{13}NO_5$ [c]	59.31	4.98	5.32	328 (4.41)	1750	1625
						59.25	4.96	5.51	265 (3.34)		
Vb	4-CH_3	CH_3	194-195	73	$C_{14}H_{15}NO_5$	60.64	5.45	5.06	330 (3.48)	1750	1630
						60.72	5.54	5.22	268 (2.54)		
Vc	4-OCH_3	CH_3	163-164	65	$C_{14}H_{15}NO_6$	57.33	5.16	4.78	330 (4.13)	1750	1710
						57.13	5.36	4.84	268 (3.22)		
Vd	4-Br	CH_3	194-195	59	$C_{13}H_{12}NO_5Br$	45.63	3.54	4.10	333 (4.47)	1735	1630
						45.74	3.67	4.19	273 (3.60)		
Ve	4-Br	C_2H_5	154-155	50	$C_{14}H_{14}NO_5Br$ [d]	47.21	3.96	3.93	333 (4.57)	1742	1632
						47.51	4.00	4.06	273 (3.65)		
Vf	4-NO_2	CH_3	224-225	42	$C_{13}H_{12}N_2O_7$	50.65	3.93	9.09	390 (4.28)	1735	1640
						50.85	4.18	9.18	328 (3.54)		

[a] In ethanol. [b] In potassium bromide discs. [c] Mass spectrum: m/z (%) 264 (19), 263 ($M^{+\cdot}$, 100), 204 (99), 176 (16), 162 (10), 148 (10), 130 (29), 104 (36), 93 (14), 77 (23), 43 (16). [d] *Anal.* Calcd. for Br: 22.44, Found: 22.22.

Table II

^{1}H NMR Spectra [a] of Cyclopent-2-enones Va-f



No.	R	Solvent	H_a	H_b	H_c	H_d	H_e, H_f H_g [b]
Va	H	DMSO-d_6	3.64 (s, 3H)	–	2.39 and 2.74 (2H, J_{AB} = 17 Hz)	6.7-7.4 (m, 5H)	6.23 (bs, 1H) 8.20 (s, 1H) 8.70 (bs, 1H)
	H	$(CD_3)_2CO$	3.73 (s, 3H)	–	2.43 and 2.86 (2H, J_{AB} = 17 Hz)	6.9-7.3 (m, 5H)	5.23 (bs, 1H) 7.53 (bs, 1H) 2.93 (bs, 1H)
	H	CD_3OD	3.69 (s, 3H)	–	2.50 and 2.86 (2H, J_{AB} = 17.5 Hz)	6.8-7.4 (m, 5H)	
	H	CF_3COOH	3.91 (s, 3H)	–	3.12 and 3.28 (2H, J_{AB} = 18.5 Hz)	7.2-7.7 (m, 5H)	
Vb	4-CH_3	DMSO-d_6	3.63 (s, 3H)	2.22 (s, 3H)	2.34 and 2.68 (2H, J_{AB} = 17.3 Hz)	6.86 and 7.00 (4H, $J_{A_2B_2}$ = 8.5 Hz)	6.26 (s, 1H) 8.22 (s, 1H) 8.64 (s, 1H)
Vc	4-OCH_3	DMSO-d_6	3.63 (s, 3H) [c]	3.69 (s, 3H) [c]	2.34 and 2.68 (2H, J_{AB} = 17.3 Hz)	6.80 and 6.94 (4H, $J_{A_2B_2}$ = 9.2 Hz)	6.26 (s, 1H) 8.20 (s, 1H) 8.53 (s, 1H)
Vd	4-Br	DMSO-d_6	3.64 (s, 3H)	–	2.38 and 2.73 (2H, J_{AB} = 17.6 Hz)	6.88 and 7.36 (4H, $J_{A_2B_2}$ = 8.8 Hz)	6.33 (s, 1H) 8.44 (s, 1H) 8.99 (s, 1H)
Vf	4-NO_2	DMSO-d_6	3.64 (s, 3H)	–	2.46 and 2.83 (2H, J_{AB} = 18.1 Hz)	6.96 and 8.09 (4H, $J_{A_2B_2}$ = 9.3 Hz)	6.45 (s, 1H) 9.27-9.36 (1H)

[a] The solvent specified. Chemical shifts given in ppm (δ) relative to internal TMS. Coupling constants (J) given in Hz. [b] Exchangeable with deuterium hydroxide. [b,c] Not necessarily respectively.

Our early hypothesis that similar open-chain structures (Scheme I, formulae **II** and **III**) or some other of the possible tautomeric forms, could be attributed to products in our hands and that the compounds are in fact, intermediates toward the expected 4-pyridone **IV**, was soon abandoned on the basis of chemical and spectral evidences. Most significant in this sense were failures to succeed in the cyclization to the corresponding known 4-pyridones [5] in spite of the application of various methods. Finally we concluded that the initial nucleophilic attack at the α'-position is probably alike as in reported examples [16], but the cyclization step must be a different one. Spectral data (uv, ir, nmr) indicated a substituted cyclopent-2-enone structure, confirmed by X-ray structure analysis as 3-arylamino-2,4-dihydroxy-4-methoxycarbonyl-2-cyclopenten-1-ones **Va-f** (Scheme I).

The compounds **Va-f** (Table I) were obtained in a fairly good yield [19] by the reaction of methyl comenate (**I**) and equimolar amounts of corresponding aromatic amine in diluted acetic acid or in methanole. The structure assignments of these products follow from their spectroscopic properties.

NMR Evidence.

The ^{13}C nmr spectra of compound **Va** (Figure I) strongly suggest the presence of carbonyl C-atoms at δ = 192.95

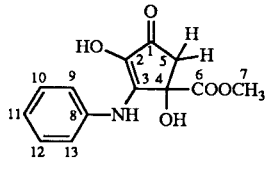


Figure I

and 173.26 ppm (C-1 and C-6 respectively); three saturated C-atoms at δ = 74.87 (C-4), 52.57 (C-7) and 44.97 ppm (C-5); eight unsaturated or aromatic C-atoms at δ = 145.64 (C-3), 139.92 (C-8), 133.92 (C-2), 127.96 (C-10 and C-12), 121.72 (C-11) and 120.23 ppm (C-9 and C-13).

The ^1H nmr spectra of **Va** in hexadeuteriodimethyl sulfoxide undoubtedly pointed out the presence of methylenic group with nonequivalent geminal protons as an AB system centered at δ = 2.39 and 2.74 ppm (2H, J_{AB} = 17 Hz [20]), methoxycarbonyl group at δ = 3.64 ppm (s, 3H), phenyl group at δ = 6.7-7.4 ppm (m, 5H) and three deuteriumoxide exchangeable protons at δ = 6.23 (bs, 1H), 8.20 (s, 1H) and 8.70 ppm (bs, 1H) for OH and NH groups (not necessarily respectively). The ^1H nmr data for compounds **Va-f** are tabulated (Table II).

Both, ^{13}C and ^1H nmr spectra are conformable, as a matter of fact, to several possible cyclopentenone structures **A-C** (Figure II), and were in agreement with those reported [22] for similar compounds.

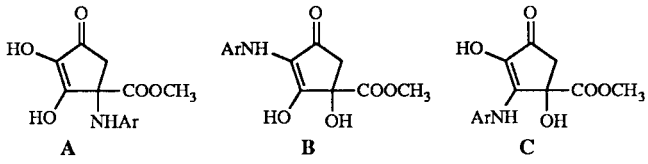


Figure II

Final decision about the structure of novel cyclopent-2-enone compounds was made after the X-ray diffraction measurement on a crystal of 4-tolylamino derivative **Vb** has been performed. It turned out that the compound **Vb** corresponds to 3-(4-tolyl)amino-2,4-dihydroxy-4-methoxycarbonyl-2-cyclopentenone (structure **C**). The view of the molecule is given in the Figure III.

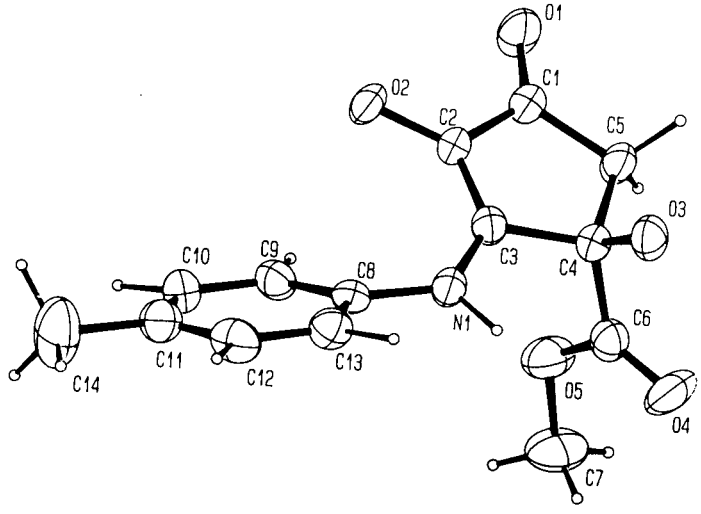


Figure III. An ORTEP [23] representation of the **Vb** with the atom-numbering scheme.

X-ray Structure Determination.

The structure was solved by direct methods [24] and was refined by full matrix least-square refinement. All H-atoms except hydroxy H-atoms H(02) and H(03) were located in difference map. In the final refinement anisotropic thermal parameters were used for nonhydrogen atoms. The hydrogen atoms were included in the structure factor calculations with common thermal parameters and fixed positional parameters. The final R value was 0.052 for 183 parameters, w = 1, S = 1.335, (Δ/σ) max = 0.008, largest peaks in the final difference map of 0.20 and -0.19 e $Å^{-3}$. The final atomic coordinates and equivalent isotropic temperature factors for the nonhydrogen atoms are given in Table III. Bond lenghts and bond angles are presented in Table IV.

Table III

Atomic Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters (x 10^4) with e.s.d.'s in Parentheses for $C_{14}H_{15}HO_5$ (Vb)

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{eq}
O1	7230(4)	3653(3)	6139(6)	522(19)
O2	6570(3)	1948(3)	7621(5)	389(17)
O3	10106(3)	1512(3)	6750(5)	377(14)
O4	9811(4)	837(3)	3688(6)	557(20)
O5	7936(4)	1110(3)	3039(6)	524(20)
N1	8167(4)	351(3)	6910(6)	365(22)
C1	7700(5)	2885(4)	6109(7)	334(22)
C2	7398(5)	1999(4)	6771(7)	290(20)
C3	8104(5)	1288(4)	6507(7)	307(23)
C4	9004(5)	1661(4)	5657(8)	323(24)
C5	8714(5)	2724(4)	5352(8)	389(23)
C6	8981(6)	1145(4)	4028(8)	361(25)
C7	7818(6)	615(5)	1451(8)	601(32)
C8	7374(5)	-218(4)	7493(7)	319(24)
C9	6188(5)	-61(4)	6970(8)	366(25)
C10	5459(5)	-647(5)	7578(9)	439(27)
C11	5869(6)	-1398(5)	8648(8)	452(29)
C12	7035(6)	-1567(4)	9106(8)	445(28)
C13	7785(5)	-979(4)	8531(8)	374(23)
C14	5050(7)	-2032(6)	9315(11)	774(36)

Table IV

Bond Distances (Å) and Angles (°) for $C_{14}H_{15}NO_5$ (Vb)

O1 - C1	1.221(7)	C3 - C4	1.521(9)
O2 - C2	1.354(8)	C4 - C5	1.540(8)
O3 - C4	1.425(6)	C4 - C6	1.525(9)
O4 - C6	1.183(9)	C8 - C9	1.403(8)
O5 - C6	1.322(8)	C8 - C13	1.385(8)
O5 - C7	1.463(8)	C9 - C10	1.384(10)
N1 - C3	1.355(7)	C10 - C11	1.388(10)
N1 - C8	1.416(8)	C11 - C12	1.380(10)
C1 - C2	1.442(8)	C11 - C14	1.527(11)
C1 - C5	1.518(10)	C12 - C13	1.390(10)
C2 - C3	1.362(9)		
C6 - O5 - C7	116.3(5)	C5 - C4 - C6	111.2(5)
C3 - N1 - C8	129.1(5)	C1 - C5 - C4	104.4(5)
O1 - C1 - C5	124.2(5)	O5 - C6 - C4	112.0(6)
O1 - C1 - C2	126.5(6)	O4 - C6 - C4	123.4(6)
C2 - C1 - C5	109.3(5)	O4 - C6 - O5	124.6(6)
O2 - C2 - C1	121.9(5)	N1 - C8 - C13	118.6(5)
C1 - C2 - C3	110.3(5)	N1 - C8 - C9	121.6(5)
O2 - C2 - C3	127.6(5)	C9 - C8 - C13	119.6(6)
N1 - C3 - C2	132.2(6)	C8 - C9 - C10	118.7(6)
C2 - C3 - C4	111.3(5)	C9 - C10 - C11	121.8(6)
N1 - C3 - C4	116.4(5)	C10 - C11 - C14	120.9(6)
O3 - C4 - C3	108.2(5)	C10 - C11 - C12	119.0(6)
C3 - C4 - C6	112.6(5)	C12 - C11 - C14	120.1(6)
C3 - C4 - C5	104.6(5)	C11 - C12 - C13	120.3(6)
O3 - C4 - C6	107.7(5)	C8 - C13 - C12	120.6(6)
O3 - C4 - C5	112.6(5)		

Table V

Hydrogen Atomic Coordinates (x 10^3) in Structure of $C_{14}H_{15}NO_5$ (Vb)

Atom	x	y	z
H1	888	5	675
H71	703	39	108
H72	839	7	160
H73	799	105	046
H141	436	-230	832
H142	468	-166	1021
H143	554	-259	989
H51	853	290	414
H52	944	319	587
H9	584	52	609
H10	453	-63	718
H12	736	-215	1009
H13	875	-107	896

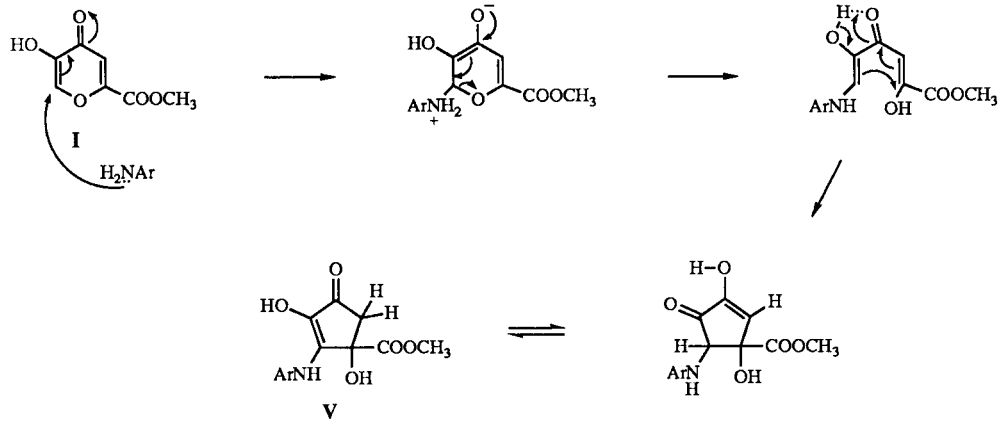
Both hydroxy H-atoms seemed to participate in an extended hydrogen bonding within the crystal structure. These hydrogen bonds are 2.731 (6) and 2.771 (6) Å. The contacts 01 ..... 02 and 03 ..... 04 of 2.889 (6) and 2.647 (6) Å, respectively, suggested also the existence of intramolecular hydrogen bonds. Hydrogen atomic coordinates are given in Table V.

The nonhydrogen atoms of the cyclopentene and benzene rings are in each case planar (x^2 = 5.99 and 7.81), but the nitrogen atom is displaced from the mean planes by distances of 0.002 (5) and 0.011 (5) Å, respectively. The dihedral angle between these planes is 39.6 (2)° and the torsion angles at the N-C bonds are C8-N1-C3-C2 12.2 (10) and C9-C8-N1-C3 33.6 (9)°.

The structure of **Va-f** was supported with mass spectra of compound **Va**, m/z 263 for $M^{+\cdot}$ (Table I), and ir data for ν C=O shifted to 1625 cm^{-1} as a part of a cyclopentenone system maintaining α,β-unsaturation and β-(substituted)-amino group [25].

Nevertheless we wish to stress a high probability of an initial formation of the open-chain intermediate **III** which in our conditions could not be isolated. We would suggest that the presence of an ester group in α-postion would have a directing effect for amine attack in α'-position, opposing "normal" cyclization to 4-pyridone derivative [26] as well. In our hands probable intermediates **IIIa-f** cyclizes by an other route yielding 3-arylamino-2,4-dihydroxy-4-methoxycarbonyl-2-cyclopenten-1-ones **Va-f** by the tentative mechanism proposed by Scheme II.

Scheme II



EXPERIMENTAL

Melting points were determined on an Original Kofler Mikroheiztisch apparatus (Reichert, Wien) and are not corrected. Infrared spectra were taken in potassium bromide pellets with a Perkin-Elmer 297 Infracord Spectrophotometer. Ultraviolet spectra were recorded on a Hitachi-Perkin-Elmer Model 124 double beam spectrophotometer. Proton nmr spectra were obtained using Varian EM-360 or Jeol JNM-FC 90Q spectrometer with tetramethylsilane as internal standard. ^{13}Carbon nmr spectra were taken on a Bruker WH-90 spectrometer at 22.63 MHz or Jeol FX-100 FT instrument at 25.05 MHz. Mass spectra were recorded on a Varian MAT-CH7 spectrometer operating at 70 eV by direct insertion probe. Molecular structure was determined by the X-ray diffraction using Philips PW 1100 diffractometer, graphite monocromator, MoKα radiation. Methyl comenate, mp 185-186°, was prepared according to reported procedure [27].

3-Arylamino-2,4-dihydroxy-4-methoxycarbonyl-2-cyclopenten-1-ones **Va-f**.

General Procedure for Preparation.

To the solution of 5-hydroxy-2-methoxycarbonyl-4-pyrone (methyl comenate) [27] (0.85 g, 0.005 mole) in 10 ml of 25% acetic acid, or in methanol (30 ml), the equimolar quantity of an aromatic amine was added. The mixture was heated at 75-80° for 20-60 minutes. The crude product formed either on cooling or after evaporation under reduced pressure, was triturated with ether/methanol and recrystallized from methanol/water (50%). Yield, analyses, spectroscopic and other data are collected in Tables I-II. The compounds exhibited positive fluorescent test with hydrazine characteristic for α-hydroxyketone [28] and ferric chloride test showing transient green colouration [29].

Crystal Data.

Compound **Vb**, $C_{14}H_{15}NO_5$, M_r = 277.28, yellow, transparent crystal of dimensions 0.15 x 0.15 x 0.11 mm, monoclinic, space group $P2_1/a$, cell dimensions a = 12.022(3), b = 14.046 (3), c = 8.277(2) Å, β = 104.14(2)°, V = 1355.3(6) Å^3, Z = 4, D_m = 1.351, D_x = 1.359 g cm^{-3} μ MoKα = 0.972 cm^{-1}, ω scans, range 2 $\leq$ 0 $\leq$ 30°, three standard reflections every 2 hours, no change; 1046 reflections scaned, 971 unique data, R_{int} = 0.039, 956 reflections with I $\geq$ 2 σ (I) retained, used for structure solution and refinement, no absorption correction.

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