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Photolysis of Diazo(3-thienyl)methane: A Simple Synthesis of a Methylenecyclopropene

Reinhard Albers and Wolfram Sander*

Lehrstuhl für Organische Chemie II der Ruhr-Universität,
D-44780 Bochum, Germany

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Introduction

Methylenecyclopropene and its derivatives are in general highly reactive species and have been the target of a number of syntheses.[1−6] In solution, the parent compound was synthesized and characterized independently by Billups et al.[5] and Staley and Norden[6a] in 1984. It is stable at temperatures below −90 °C but rapidly decomposes above −75 °C. Simple alkyl-substituted methylenecyclopropenes are still highly reactive.[3] Here, we report on the synthesis and matrix spectroscopic characterization of α-thial methylenecyclopropene utilizing a carbene rearrangement.

Results and Discussion

Diazo(3-thienyl)methane (**1**) was synthesized via the Bamford−Stevens reaction according to a modified procedure by Hoffman and Shechter, who reported the *in situ* generation of **1**.[7] Warming the lithium salt of thiophene-3-carbaldehyde tosylhydrazone to 115 °C resulted in the formation of **1**, which was collected at −78 °C. For matrix isolation experiments diazomethane **1** was directly sublimed from the lithium salt with a large excess of argon on top of a cold spectroscopic window. The orange red **1** exhibits UV absorption maxima at 227, 257, and 290 nm; however, due to the low concentration in the matrix isolation experiments, the weak absorption in the visible region could not be observed. The IR spectrum of **1** shows a very strong absorption at 2066 cm^{-1}, characteristic for the C=N=N moiety.

Irradiation of **1** in argon at 10 K with $\lambda > 435$ nm within several minutes resulted in the complete disappearance of all IR vibrations assigned to **1** and formation of a new compound **2** with intense vibrations at 1718 and 1501 cm^{-1} (Table 1). **2** is photolabile under these conditions, and prolonged irradiation (several hours) produces an isomer with similar strong bands at 1712 and 1480 cm^{-1} (Table 2). The isomerization is not quantitative, and shorter wavelength irradiation results in the decomposition of both isomers. By comparison of the IR spectra with *ab initio* calculated spectra and with related compounds, the isomers were identified as (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**2**).

Table 1. IR Spectroscopic Data of (*s*-*Z*)-2 Matrix Isolated in Argon at 10 K

	argon, 10 K		MP2/6-31G(d)	
Nr^a	ν (cm^{-1})	$I_{rel}{}^b$	ν^c (cm^{-1})	$I_{rel}{}^b$
1			108	0
2			136	0
3			275	0
4			339	0
5			422	1
6	450	6	453	1
7	653	11	645	7
8	754	7	785	1
9	828	12	833	2
10			837	0
11			865	4
12			910	0
13	1005	25	1007	3
14	1013	8	1020	4
15	1098	7	1088	2
16	1182	25	1190	26
17	1253	3	1252	1
18	1405	13	1418	6
19	1501	90	1508	28
20	1718	100	1756	100
21	2956	4	2963	2
22			3083	0
23	3137	3	3155	1
24			3191	1

^{a} Number of vibration. ^{b} Relative intensities based on the most intense band (100). ^{c} Calculated frequencies are scaled by 0.95. The assignment of experimental and calculated frequencies is tentative and based on band positions and relative intensities.

Table 2. IR Spectroscopic Data of *s-trans*-Aldehyde (*s*-*E*)-2, Matrix Isolated in Argon at 10 K

	argon, 10 K		MP2/6-31G(d)	
Nr^a	ν (cm^{-1})	$I_{rel}{}^b$	ν^c (cm^{-1})	$I_{rel}{}^b$
1			129	0
2			137	0
3			228	1
4			326	0
5	445	2	461	1
6	630	14	616	6
7			677	7
8	769	21	743	7
9			790	0
10			847	0
11	863	2	878	1
12	890	4	894	1
13	958	4	940	0
14	1006	19	1010	4
15	1089	6	1096	1
16	1167	44	1178	24
17			1353	0
18	1357	32	1386	30
	1364	38		
19	1480	62	1485	29
20	1712	100	1746	100
	1714	97		
21	2964	3	2987	5
22	3139	2	3081	1
23	3152	5	3158	1
24	3196	3	3204	1

^{a} Number of vibration. ^{b} Relative intensities based on the most intense band (100). ^{c} Calculated frequencies are scaled by 0.95. The assignment of experimental and calculated frequencies is tentative and based on band positions and relative intensities.

The two strongest IR bands in **2** are assigned to the asymmetric and symmetric combination of the C=C stretching vibrations ν_{asym} and ν_{sym} (Tables 1−3, Figure 1). Compared to the parent methylenecyclopropene,[5]

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(1) Kende, A. S. *J. Am. Chem. Soc.* **1963**, *85*, 1882−1884.

(2) Billups, W. E.; Blakeney, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7817−7818.

(3) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 3854−3856.

(4) Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1984**, *25*, 5645−5648.

(5) Billups, W. E.; Lin, L-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698−3699.

(6) (a) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699−3700. (b) Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912−7918.

(7) (a) Hoffman, R. V.; Shechter, H. *J. Am. Chem. Soc.* **1971**, *93*, 5940−5941. (b) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927−7933.

(8) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511−523.

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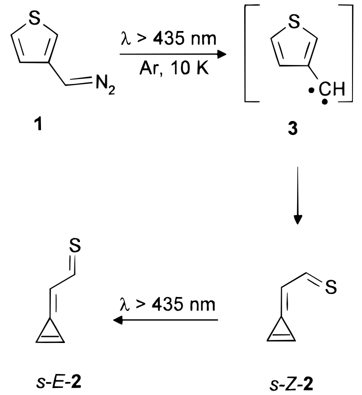
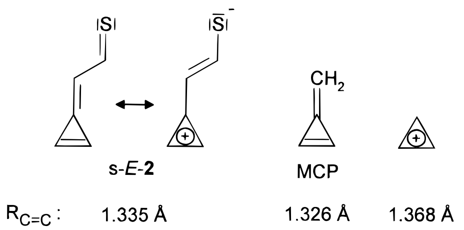


these vibrations are red-shifted by 20−50 cm^{-1}, which indicates a significant contribution of the zwitterionic resonance structure with reduced bond strength of the cyclopropene and the exocyclic methylene double bond.

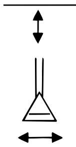
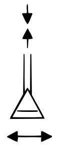


This is in line with calculations at the MP2/6-31G(d) level of theory. The C=C bond length of the three-membered ring in (*s*-*E*)-**2** (1.335 Å) is between that of methylenecyclopropene (1.326 Å) and the cyclopropenyl cation (1.368 Å).[6b]

In the UV (*s*-*Z*)-**2** and (*s*-*E*)-**2** exhibit broad absorptions with maxima at 345 and 320 nm, respectively. Due to the low concentration of **2** in the matrix, the broad and weak visible absorption characteristic of thiocarbonyl compounds was not observed. The *s*-*Z* conformer absorbs at slightly longer wavelength with tailing into the visible region, which explains the slow *s*-*Z* → *s*-*E* interconversion on λ > 435 nm irradiation.

A plausible mechanism for the formation of **2** from **1** is shown in Scheme 1. The primary product of the photolysis of **1** is (3-thienyl)methylene (**3**), which is labile (photochemically or thermally) under these conditions and not directly observed. Indirect evidence for carbene **3** stems from oxygen-trapping experiments. Irradiation of **1** in a 2% O_2-doped argon matrix at 40 K results in the formation of thiophene-3-carbaldehyde **6** as the main product, identified by comparison with an authentic matrix-isolated sample. During the irradiation an absorption around 450 nm appeared that was tentatively assigned to carbonyl *O*-oxide **5**. Similar absorption maxima have been observed for a large number of carbonyl oxides.[9] Due to the low stationary concentration of **5** the characteristic O−O stretching mode of carbonyl oxides around 900 cm^{-1} could not be observed in the IR spectrum of the reaction products.

Table 3. Comparison of the C=C Stretching Vibrations of 2 and 5

		s-E-2	s-Z-2	MCP[a]
	$\tilde{\nu}_{sym}$ [cm^{-1}]	1501	1480	1519
	$\tilde{\nu}_{asym}$ [cm^{-1}]	1718	1712	1770

[a] Methylenecyclopropene, Ar, 15 K (ref 5).

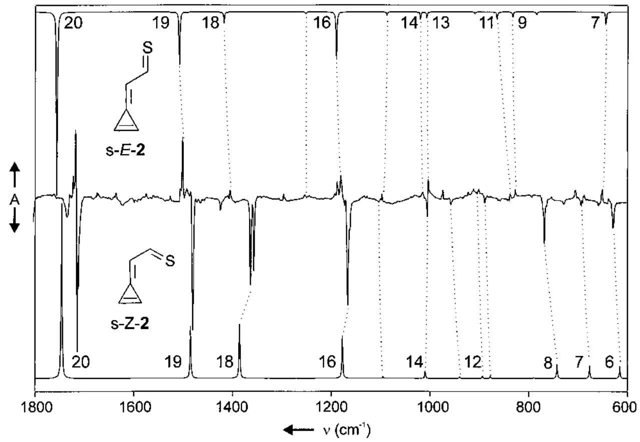
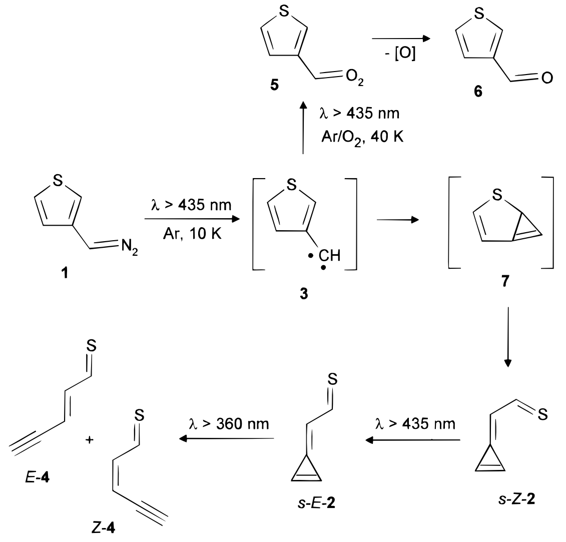


Figure 1. IR difference spectrum showing the photochemical (λ > 435 nm) rearrangement (*s*-*Z*)-**2**, matrix isolated in argon at 10 K, to (*s*-*E*)-**2** (center) compared to the *ab-initio* (MP2-6-31G(d)) calculated spectra of (*s*-*Z*)-**2** (bottom) and (*s*-*E*)-**2** (top). Absorptions pointing downward are disappearing during the irradiation and assigned to (*s*-*Z*)-**2**; absorptions pointing upwards are appearing and assigned to (*s*-*E*)-**2**. The numbering and tentative assignment of vibrations corresponds to Tables 1 and 2 for (*s*-*Z*)-**2** and (*s*-*E*)-**2**, respectively.

Scheme 1



The key intermediate in the reaction sequence leading to **2** is the highly strained 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**7**), which is the product of a vinylcarbene−cyclopropene rearrangement (Scheme 1). Similar carbene rearrangements and the matrix isolation of series of 1,3-bridged cyclopropenes of type **7** was reported in the literature.[10−13] All these cyclopropenes are highly

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(9) Sander, W. *Angew. Chem.* **1990**, *102* , 362−72; *Angew. Chem., Int. Ed. Engl. 29*, 344−354.

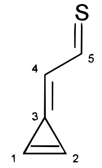
(10) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311−5322.

Table 4. IR Spectroscopic Data of 1*H*-2-Thiabicyclo[3.1.0]hexa-3,5-diene 7, Matrix Isolated in Argon at 10 K

	argon, 10 K		MP2/6-31G(d)	
Nr[a]	ν^{b} (cm^{-1})	I_{rel}[c]	ν^{b} (cm^{-1})	I_{rel}[c]
1			274	10
2			327	5
3			464	10
4			528	15
5	616	56	621	30
6	643	59	640	66
7	660	59	648	44
8	694	100	690	100
9	777	55	769	20
10	795	65	790	23
11			832	10
12	958	64	938	31
13			974	9
14	1024	57	1021	24
15			1077	1
16			1110	22
17	1250	64	1244	16
18			1286	1
19	1425	71	1441	19
20	1681	67	1676	31
21	3179	67	3045	38
22			3103	3
23			3129	2
24			3153	0

[a] Number of calculated vibrations. [b] Relative intensities based on the most intense band (100). [c] Calculated frequencies are scaled by 0.95. The assignment of experimental and calculated frequencies is tentative and based on band positions and relative intensities.

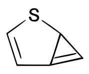
Table 5. Ab-Initio (MP2/6-31G(d)) Calculated Data of (*s-Z*)-2 and (*s-E*)-2



parameter[a]	(*s-Z*)-**2**	(*s-E*)-**2**
C(1)−C(2)	1.3351	1.3311
C(1)−C(3)	1.4231	1.4296
C(2)−C(3)	1.422	1.4321
C(3)−C(4)	1.3499	1.3482
C(4)−C(5)	1.4337	1.4309
C(5)−S	1.6412	1.6352
C(1)−C(3)−C(4)	154.4776	152.8807
C(3)−C(4)−C(5)	121.3048	120.4897
C(2)−C(3)−C(4)	149.5484	151.6805
C(4)−C(5)−S	128.072	125.9421
C(1)−C(3)−C(4)−C(5)	180.1421	180.0545
C(2)−C(3)−C(4)−C(5)	−0.1334	−0.0602
C(3)−C(4)−C(5)−S	0.0336	180.0032
ΔE (MP2)[b]	0	0.21
dipole[c]	6.18	8.41
MP2 (au)	−589.82862	−589.82828

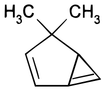
[a] Bond length in pm, angles in deg. From MP2/6-31G(d) calculations. [b] MP2/6-31G(d) energy in kcal/mol, relative to (*s-Z*)-**2**. [c] Mulliken population analysis (D).

labile and rearrange photochemically or even thermally at temperatures as low as 10 K. Under the conditions required for the photolysis of **1** both the carbene **3** and the cyclopropene **7** are labile, and thus, **2** is by far the main product. Several weak absorptions in the IR spectra can tentatively be assigned to **7** by comparison with calculations at the MP2/6-31G(d) level of theory (Table 4). The C=C stretching vibration of the cyclopropene ring at 1681 cm^{-1} is close to that of related 1,3-bridged cyclopropenes. However, due to its low concentration, the rearrangement of **7** to give **2** could not be followed directly.

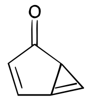


7

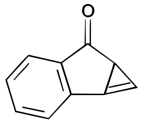
1681 cm^{-1}



1688 cm^{-1}



1665 cm^{-1}



1682 cm^{-1}

Short-wavelength irradiation (λ > 360 nm) of **2** results in the complete disappearance of both conformers and formation of a new compound with absorptions around 3300 and 2100 cm^{-1}, characteristic of a terminal acetylene group. This product was identified as an *E*/*Z* mixture of pent-2-en-4-ynethial **4** by independent synthesis of **4** (see below). Thus, the photochemistry of **2** is analogous to the photochemical ring-opening of matrix-isolated methylenecyclopropene to give vinylacetylene.[8]

Hoffmann and Shechter reported on the synthesis of an *E*/*Z* mixture of pent-2-en-4-ynal **10** by thermolysis of diazo(2-furyl)methane (**8**) at 300 °C (Scheme 2).[7] The mechanism of this rearrangement was recently described by Herges as a concerted reaction of carbene **9**.[15] In contrast to this, thermolysis of diazo(2-thienyl)methane (**11**) under the same conditions was reported to produce the carbene dimers (*E*)- and (*Z*)-**13** as the major products and an oligomer of **4**.[7] In our hands, thermolysis of **11** at 350 °C with subsequent trapping of the products in argon at 10 K resulted in the clean formation of (*Z*)-**4**, which on photolysis (λ > 320 nm) was transformed to a *E*/*Z* mixture of **4**. The photolysis (λ > 435 nm) of **11** directly produces (*E*/*Z*)-**4**; carbene **12** or a methylenecyclopropene was not observed as an intermediate in this case. Thus, both thienyldiazomethanes yield the same final product **4**.

The photolysis of diazomethane **1** provides a novel entry to methylenecyclopropenes. Current investigations in our laboratory are aimed at developing a general synthesis of substituted methylenecyclopropenes of type **2** and to explore the synthetic use of these highly reactive compounds.

Experimental Section

Calculations. Ab initio calculations were carried out with the GAUSSIAN94 program package[14] employing the 6-31G(d) basis set. MP2/6-31G(d) vibrational frequencies were scaled by 0.95.

Materials and General Methods. ^{1}H- and ^{13}C-NMR were recorded with a Bruker AM 400 at 400.1 and 100.6 MHz, respectively, in Freon as solvent. IR spectra were obtained with a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range from 400 to 4000 cm^{-1}. UV spectra were

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(11) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346−1351.

(12) Albers, R.; Sander, W.; Ottosson, C.-H.; Cremer, D. *Chem. Eur. J.* **1996**, *2*, 155−161.

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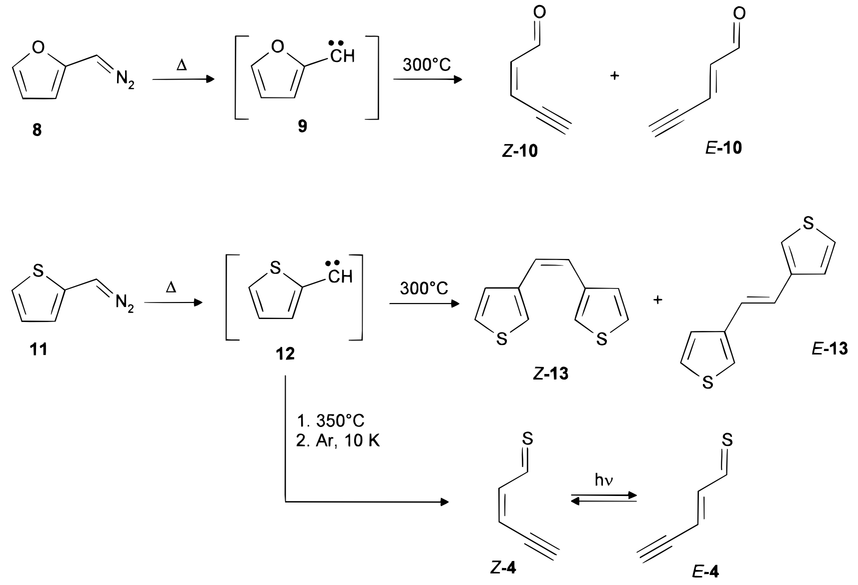
(14) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C*; Gaussian, Inc., Pittsburgh, 1992.

(15) Herges, R. *Angew. Chem.* **1994**, *106*, 261−283; *Angew. Chem., Int. Ed. Engl. 33*, 255.

Scheme 2



taken on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. All reactions involving moisture-sensitive reactants were performed under dry N_2. Solvents were dried as follows: THF was distilled from sodium and methanol from Mg metal. Thiophene-3-carbaldehyde and thiophene-2-carbaldehyde were purchased from Aldrich.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) at 30 K on top of a CsI (IR) or sapphire (UV−vis) window at a rate of approximately 0.15 mmol/min. Irradiations were carried out using Osram HBO 500 W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation of the lamps was absorbed by a 10 cm path of water and by a Schott KG1 filter. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors and cut-off filters were employed.

Diazo(3-thienyl)methane (1). Diazo compound **1** was prepared via the Bamford−Stevens reaction in analogy to a procedure published by Hoffman and Shechter.[7] The tosylhydrazone was prepared by a standard procedure from thiophene-3-carbaldehyde **6** and recrystallized from dry methanol. The lithium salt was synthesized by treating the tosylhydrazone, dissolved in anhydrous THF, with 1.1 equiv of LiH. After being stirred for 30 min at room temperature, the precipitated lithium salt was filtered off and washed thoroughly with dry pentane. The diazo compound was generated by heating the salt in vacuum to 115 °C (10^{-6} mbar). The orange red diazo compound was recovered in a cold trap at 78 K or directly sublimed on the cold window. IR (Ar, 10 K): $\bar{\nu}$ = 3190 (1), 3099 (1), 2871 (1), 2078 (11), 2066 (100), 2046 (41), 1551 (3), 1548 (3), 1532 (3), 1436 (4), 1403 (2), 1346 (1), 1248 (1), 1210 (1), 1081 (2), 1076 (1), 859 (2), 841 (3), 755 (9), 478 (2) cm^{-1} (rel int). UV/vis (Ar, 10 K): λ_{max} (lg ϵ) = 227 nm, 257, 290.

(*Z*)-Pent-2-en-4-ynethial ((*Z*)-4). **(*Z*)-4** was generated by flash vacuum pyrolysis of diazo(2-thienyl)methane (**11**). Diazo compound **11** was prepared via the Bamford−Stevens reaction from the corresponding tosylhydrazone lithium salt following a literature procedure.[7] The gas-phase pyrolysis (350 °C, 10^{-6} mbar) of **11** with subsequent trapping in argon at 10 K yielded (*Z*)-pent-2-en-4-ynthial as the major product. IR (Ar, 10 K): $\bar{\nu}$ = 3315 (100), 2105 (9), 1560 (22), 1554 (53), 1405 (29), 1301 (13), 1252 (30), 1212 (14), 1199 (22), 1138 (43), 1133 (13), 1128 (14), 1036 (19), 896 (10), 888 (7), 779 (31), 696 (22), 667 (9), 658 (5), 639 (78), 629 (88), 470 (2), 465 (3) cm^{-1} (rel int).

(*E*)-Pent-2-en-4-ynethial ((*E*)-4). Short-wavelength irradiation (λ > 320 nm) of matrix-isolated (*Z*)-**4** produced a *E*/*Z* mixture **4**. (*E*)-**4**. IR (Ar, 10 K): $\bar{\nu}$ = 3321 (98), 2111 (10), 1578 (46), 1575 (94), 1361 (23), 1357 (22), 1256 (24), 1252 (26), 1245 (24), 1172 (14), 1166 (31), 1159 (63), 978 (30), 968 (27), 961 (55), 770 (10), 643 (84), 630 (100), 441 (14) cm^{-1} (rel int).

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