A Contribution to the Direct Observation of a Didehydroheteroaromatic with a Five-Membered Ring: 2,3-Didehydrothiophene ☆

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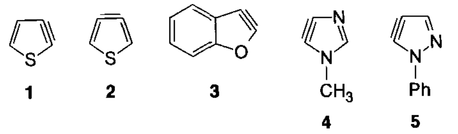
The flash vacuum pyrolysis and the photolysis of 2,3-thiophenedicarboxylic acid anhydride (**6**) were investigated by using the technique of matrix isolation combined with FT-IR spectroscopy. No conclusive proof for the existence of 2,3-didehydrothiophene (**1**) could be found, but two hitherto unknown isomers were isolated and characterized: vinylidenethioketene (**10**) and thioformylvinylidenecarbene (**15**).

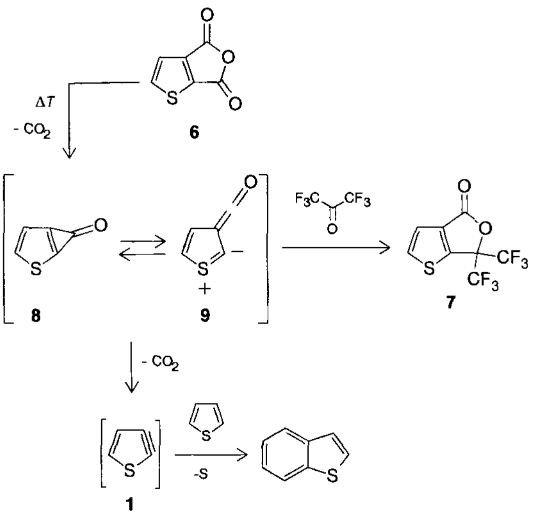
Since Stoermer and Kahlert in 1902[1] first proposed 2,3-didehydrobenzofurane (**3**) as a reaction intermediate, much has been investigated in the field of didehydroaromatics. Although most of the work has concentrated on 1,2-didehydrobenzene, the didehydroheteroaromatics have also received much attention. Reviews[2] on this subject by Reinecke appeared in 1962. Of all the didehydroheteroaromatics with a five-membered ring that have been proposed in the literature, 2,3-didehydrothiophene (**1**) is certainly the best studied. In the early 1960s besides **1**[3] many other didehydroheteroaromatics with a five-membered ring were proposed, e.g. 3,4-didehydrothiophene (**2**)[4], 2,3-didehydrobenzofurane (**3**)[4], 1-methyl-4,5-didehydroimidazole (**4**)[5], and 1-phenyl-4,5-didehydropyrazole (**5**)[6]. Unfortunately, these proposals were based on very little and often not very solid evidence.

Scheme 1



This initial euphoric phase ended with the publication of Hoffmann's excellent book on didehydrobenzene and cycloalkynes[7]. He concluded that no compelling evidence for the intermediacy of didehydroaromatics with a five-membered ring existed. This unleashed a reinvestigation of the earlier experimental data, with the result that by 1971 all the reactions that had been proposed as involving five-membered didehydroheteroaromatics were shown not to proceed by such mechanisms. All attempts to produce five-membered didehydroheteroaromatics have given only negative or ambiguous results. The only exception seems to be the work of Reinecke where he obtained indirect evidence for the formation of 2,3-didehydrothiophene (**1**)[8–10]. He pyrolysed 2,3-thiophenedicarboxylic acid anhydride (**6**) in the gas phase using several traps and isolated the expected adducts of **1** (Scheme 2). This prompted us to reinvestigate the chemistry of **6** by using flash vacuum pyrolysis combined with matrix-isolation and Fourier-transform infrared spectroscopy to try to obtain direct evidence for the existence of **1**.

Scheme 2



Reinecke pyrolyzed **6** at 500 °C using a 4 cm long heated Nichrome wire coil under a stream of pure trapping agent at 1 – 5 Torr[8,10]. Under our pyrolysis conditions (see Experimental for a detailed description) no decomposition was observed at 500 °C and only very little at 600 °C. Total con-

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version of **6** was obtained only at above 850°C. The main products identified in the infrared spectrum of the pyrolyzate (isolated in an argon matrix at 12 K) were CO_2, CO, CS_2, acetylene, OCS, thioketene, and CS together with traces of C_3OS and C_3S_2. Most of the material, however, remained in the quartz pyrolysis tube as a shining black film that covers its inner surface.

Increasing the reaction temperature or the contact time (by placing a thin plug of quartz wool inside the pyrolysis tube) had no influence on the products formed and their distribution. No bands that might be assigned to **1** were found in any of the experiments.

Reinecke[10] also reports that considerable charring took place when no trap was used. When using thiophene as a trap he found very little charring and isolated the expected thianaphthene in an amazingly high (for this kind of experiments) yield of 59%. Probably, if **1** is indeed formed it remains adsorbed on the Nichrome wire surface where it eventually polymerizes or reacts with an adsorbed trap molecule, the product being subsequently desorbed. Under our experimental conditions no trap is present and so the adsorbed pyrolysis products react with each other producing the observed black polymer and the small fragments observed in the matrix. This also explains why CS_2 is a major product in spite of the fact that **6** only contains one sulfur atom. In fact, when Reinecke[9] used hexafluoroacetone as trap he was able to isolate the lactone **7** in 35% yield. He proposed thiophenecyclopropenone (**8**) and the pseudocarbene **9** as intermediates in this reaction and as precursors of **1**.

As discussed later, **9** has been identified as the primary product formed when **6** is photolyzed in an argon matrix. As semi-empirical and ab initio calculations show, it is not even necessary to invoke the intermediacy of **8**. It was probably only invoked by Reinecke in the belief that **9** must be less stable than **8**. Our calculations show that both of them are very close in energy, **9** being probably somewhat more stable[11]. It is possible that the products thought by Reinecke to arise from the trapping of **1** may indeed be simply trapping products of **9**.

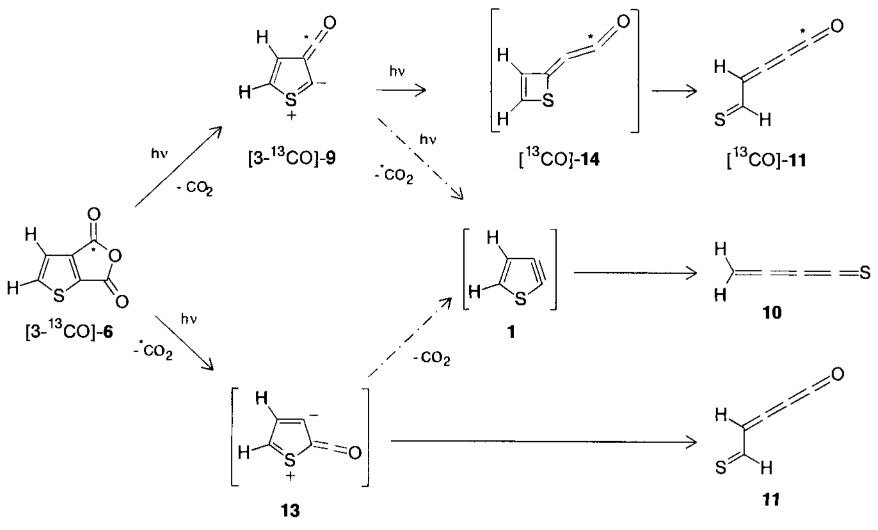
In contrast to the pyrolysis of **6**, the photolysis proved to be much more interesting. Compound **6** has only one absorption in its UV spectrum above 200 nm, clearly consisting of two overlapping unresolved bands [271 nm (ε = 5550, $\lambda_{1/2}$ = 35 nm), 300 nm (ε = 3410, $\lambda_{1/2}$ = 30 nm) measured in 2-methyl-THF]. After deconvolution, the location, intensity and half-width of both bands could be calculated. When **6** is isolated in an argon matrix at 12 K both bands show a smaller half-width, and the band centered at

Table 1. Calculated (MP2/6-31G*) and measured (argon matrix) infrared spectra of **10** and isotopomers[a,b]

10 $\tilde{\nu}$/cm^{-1}	**10** Int[c]	[D]-**10** $\tilde{\nu}$/cm^{-1}	[D]-**10** Int[c]	[D$_2$]-**10** $\tilde{\nu}$/cm^{-1}	[D$_2$]-**10** Int[c]
3128.7	0.1	3089.3 *3070*	0.8 *0.8*	2329.6	0.0
3044.3 *3018*	1.6 *2*	2273.5 *2225*	3.5 *2*	2225.9	9.3
2101.2 *2089*	100.0 *100*	2098.9 *2087*	100.0 *100*	2095.2 *2085*	100.0 *100*
1761.4 *1783*	2.3 *8*	1753.5 *1775*	2.5 *3*	1744.5 *1783*	2.7 *3*
1388.1 *1380*	1.7 *6*	1278.9 *1285*	3.4 *8*	1207.1	6.6
1159.5 *1170*	5.4 *8*	1129.9	3.6	967.2	0.6
952.9	0.2	833.2	0.2	796.2	0.1
704.8 *759*	6.0 *5*	637.2 *685*	5.0 *7*	569.5	2.7
585.0	0.2	576.4	0.2	564.3	1.4

[a] Measured values are given in *italics* below the corresponding calculated ones. — [b] Only the first 9 calculated bands are shown; their frequencies were scaled by 0.95. — [c] All intensities shown are relative intensities in % of the intensity of the strongest band; calculated absolute intensities for the strongest band are: **10**: 1450; [D]-**10**: 1414; [D$_2$]-**10**: 1341 km/mol; measured absolute intensity of the strongest band of **10**: 550 ± 50 km/mol.

Scheme 3. Photochemical transformations of [3-^{13}CO]-**6** when irradiated with light of 313 nm wavelength in an argon matrix at 12 K



300 nm shows a vibrational fine structure with a spacing of 560 ± 110 nm, but the position of the maxima does not change appreciably. In view of this the two wavelengths 254 and 313 nm were selected to photolyze **6**. With 254 nm one excites almost exclusively the highest energy band, while with 313 nm more than 90% of the light is absorbed by the lower energy band. The results obtained when light of 313 nm wavelength is used to photolyze **6** are summarized in Scheme 3. To distinguish two reaction pathways that are indistinguishable for the non-isotopically marked **6**, the photochemistry of [3-^{13}CO]-2,3-thiophenedicarboxylic acid anhydride, [3-^{13}CO]-**6** is shown (Scheme 3).

Table 2. Calculated (SCF/6-31G*) and measured (argon matrix) infrared spectra of **11** and isotopomers[a,b]

11		[4-D]-11		[formyl-D]-11		[D$_2$]-11		[1-^{13}C]-11	
$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]
3044.8	0.1	2992.4	0.1	3044.7	0.2	2251.3	1.1	3044.8	0.1
2992.3	0.1	2259.3	0.7	2209.9	32.6	2209.6	32.7	2992.3	0.1
2198.7 *2226*	100.0 *100*	2198.7 *2225*	100.0 *100*	2195.2 *2226*	100.0 *100*	2195.2 *2229*	100.0 *100*	2150.2 *2188*	100.0 *100*
2018.9 *2002*	12.1 *1*	2013.6 *1997*	11.7 *1*	2018.9 *1999*	16.1 *1*	2013.5 *1995*	15.6 *1*	2009.6 *1987*	4.9 *1*
1491.0 *1470*	11.9 *11*	1470.5 *1450*	13.0 *12*	1478.1 *1461*	14.6 *9*	1460.2 *1446*	15.5 *11*	1490.6	11.8
1355.0 *1342*	0.8 *3*	1349.2 *1337*	1.3 *3*	1274.3 *1262*	5.1 *1*	1233.9 *1230*	15.1 *9*	1355.0	0.7
1211.0 *1199*	0.2 *0.3*	1142.3 *1151*	8.8 *5*	1152.9 *1147*	13.1 *3*	1021.3 *1023*	0.1 *0.1*	1211.0	0.2
1123.2 *1130*	12.2 *8*	984.1 *992*	1.7 *0.2*	1029.7	0.4	926.7 *927*	3.4 *0.7*	1123.1	11.9
988.5 *995*	1.5 *0.3*	930.5 *926*	2.0 *0.7*	866.5	2.0	865.1	1.5	988.5	1.5

[a] Measured values are given in *italics* below the corresponding calculated ones. — [b] Only the first 9 calculated bands are shown; their frequencies were scaled by 0.90. — [c] All intensities shown are relative intensities in % of the intensity of the strongest band; calculated absolute intensities for the strongest band are: **11**: 6733; [4-D]-**11**: 6718; [5-D]-**11**: 5082; [D$_2$]-**11**: 5059; [1-^{13}CO]-**11**: 6934 km/mol.

Table 3. Calculated (SCF/6-31G*) and measured (argon matrix) infrared spectra of **9** and isotopomers[a,b]

9		[4-D]-9		[5-D]-9		[4,5-D$_2$]-9		[3-^{13}CO]-9	
$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]	$\tilde{\nu}$/cm^{-1}	Int[c]
3095.3	0.2	3091.4	0.1	3069.7	0.2	2307.7	0.2	3095.3	0.3
3065.5	0.1	2277.2	0.1	2292.9	0.1	2261.9	0.0	3065.5	0.1
2158.6 *2157*	100.0 *100*	2158.5 *2157*	100.0 *100*	2158.3 *2158*	100.0 *100*	2158.3 *2158*	100.0 *100*	2104.0 *2100*	100.0 *100*
1554.2	2.0	1530.1	2.1	1532.6	1.9	1508.3	1.9	1554.2	2.2
1342.4	0.5	1312.4	0.4	1324.4	0.9	1301.9	0.7	1342.1	0.6
1241.8	3.2	1225.1 *1232*	14.5 *8*	1237.1	8.7	1223.5	14.3	1241.1	3.1
1222.3 *1233*	10.3 *7*	1197.0	0.2	1187.7	4.9	1059.2	0.1	1221.4	11.4

[a] Measured values are given in *italics* below the corresponding calculated ones. — [b] Only the first 7 calculated bands are shown; their frequencies were scaled by 0.90. — [c] All intensities shown are relative intensities in % of the intensity of the strongest band; calculated absolute intensities for the strongest band are: **9**: 1685; [4-D]-**9**: 1684; [5-D]-**9**: 1687; [4,5-D$_2$]-**9**: 1687, [3-^{13}CO]-**9**: 1582 km/mol.

Besides **6** and [3-^{13}CO]-**6** all three possible deuterated variants of **6** have been studied. These are the [4-D_1]-, the [5-D_1]-, and the [4,5-D_2]-2,3-thiophenedicarboxylic acid anhydride. The general designation **6** will be used when a statement applies to all of the isotopomers.

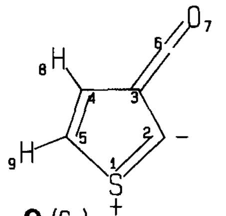
When labeled compounds **6** are photolyzed with 313-nm light CO_2 is lost, and an intermediate with an absorption at ca. 2157 cm^{-1} is formed. This intermediate upon further photolysis yields CO and a mixture of two new products which were identified as vinylidenethioketene (**10**) and thioformylvinylideneketene (**11**) by comparing their infrared spectra with those calculated by ab initio methods. The infrared spectrum of **10** was calculated at the MP2/6-31G* level, while that of the larger molecule **11** could only be computed at the SCF/6-31G* level. The calculated and measured spectra are collected in Tables 1 and 2.

10 shows only one absorption at 234 nm which compares well with the 220-nm band found for the isoelectronic carbon suboxide subsulfide (**12**)[12]. The UV spectrum of **11** shows a strongest band at 252 nm and a weaker one at 362 nm with a clear vibrational progression with a spacing of 650 ± 50 cm^{-1}. This spacing does not change upon deuteration and may be due to coupling with the C=S stretch in the excited state.

As for the intermediate product in the photolysis, the structures **9**, **13** and **14** could be considered. Their infrared spectra and those of their isotopomers were computed at the SCF/6-31G* level and were compared with the observed spectra. In contrast to the computed and measured spectra of **14** those of **9** and **13** correlate well. A distinction between them allowed the photolysis of [3-^{13}CO]-**6**. It produced by irradiation with 313-nm light a mixture of ca. 45% **11** and 55% [1-^{13}C]-**11**[17]; but only one band is observed for the intermediate, shifted by ca. 55 cm^{-1} to lower wavenumbers. If this intermediate had structure **13** only one unshifted band should be observed. If both **9** and **13** were intermediates, absorbing by chance at the same wavenumber, one should observe in the photolysis of [3-^{13}CO]-**6** two bands, one at the original wavenumber and a shifted one. The fact that only one shifted band is observed shows that **9** is the sole intermediate. Its calculated and measured infrared spectra are shown in Table 3.

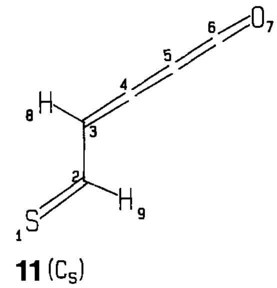
That only **9** is observed as an intermediate and not **13** can be explained with the calculated structures and relative energies of the four isomers **9**, **11**, **13**, and **14** (Figure 1). The two isomers observed are the two most stable.

Ca. 60% of **6e** lose CO_2 to produce **9**. Compound **9** is unexpectedly stable and shows an interesting reactivity. The ratio of **10** to **11** formed on photolysis of **6** can be indirectly calculated by measuring the ratio of intensities of the CO and CO_2 bands and by using their known absolute intensities[13]. **10** accounts for 20% of the products. Whether **1** is an intermediate in the reaction **9** → **10** is not known. Inspecting the structure of **9**, one notices the extremely short C−O bond, only 1.124 Å long. For comparison, the equilibrium bond length in carbon monoxide is 1.128 Å[14]. The bond connecting the CO with the ring is rather long, having a length somewhere between that of a single and that of a double bond. At first sight, this would make **9** an ideally suited precursor of **1**, but a closer inspection also reveals a very long C-5−S bond (1.763 Å compared to only 1.714 Å in thiophene[15,16]). A reaction mechanism where the C-5−S bond breaks first followed by CO expulsion and hydrogen migration would lead to **10** without generation of **1** as intermediate.



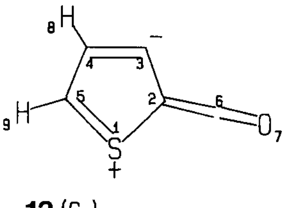
9 (C_s)
E_{rel}= 0.0 kcal/mol

1-2	1.702
2-3	1.422
2-5	1.763
3-4	1.443
3-6	1.350
4-5	1.329
4-8	1.073
5-9	1.072
6-7	1.124
1-2-3	103.9
1-5-4	111.1
2-1-5	96.8
2-3-4	118.8
2-3-6	113.6
3-4-5	109.4
3-6-7	178.9
4-5-9	127.1
5-4-8	125.6



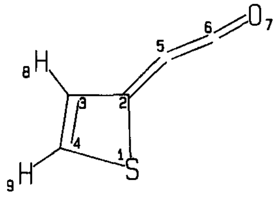
11 (C_s)
E_{rel}= 3.6 kcal/mol

1-2	1.620
2-3	1.443
2-9	1.079
3-4	1.319
3-8	1.075
4-5	1.256
5-6	1.281
6-7	1.140
1-2-3	125.3
1-2-9	119.6
2-3-4	121.2
2-3-8	119.6
3-2-9	115.2
3-4-5	179.9
4-5-6	180.0
5-6-7	180.0



13 (C_s)
E_{rel}= 13.2 kcal/mol

1-2	1.777
1-5	1.729
2-3	1.410
2-6	1.342
3-4	1.452
4-5	1.348
4-8	1.075
5-9	1.074
6-7	1.125
1-2-3	118.0
1-5-4	115.1
1-5-9	118.2
2-1-5	86.4
2-3-4	104.2
2-6-7	179.0
3-2-6	116.4
3-4-5	116.3
3-4-8	122.3



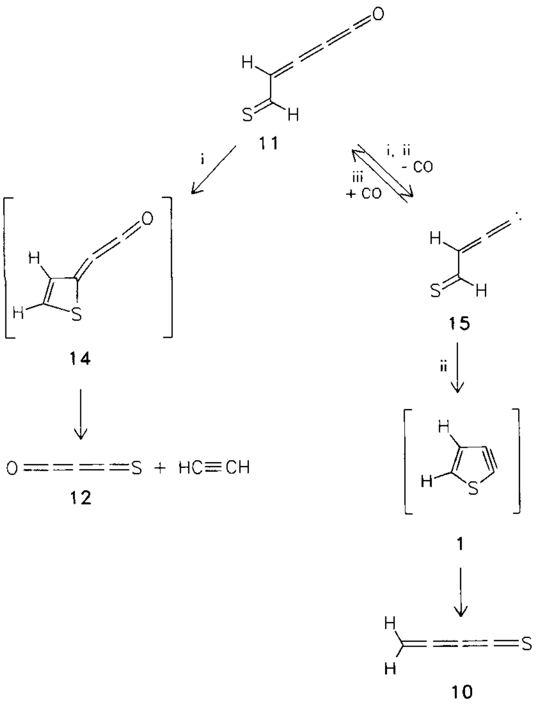
14 (C_s)
E_{rel}= 9.3 kcal/mol

1-2	1.825
1-4	1.793
2-3	1.471
2-5	1.301
3-8	1.072
4-9	1.071
5-6	1.277
6-7	1.149
1-2-3	91.7
1-4-3	98.2
1-4-9	128.0
2-1-4	71.8
2-3-4	98.4
2-3-8	129.0
2-5-6	159.8
3-2-5	135.8
5-6-7	174.7

Figure 1. Calculated structures and relative energies of **9**, **11**, **13**, and **14**; the structures have been optimized at the SCF/6-31G* level (bond lengths are in Å and bond angles in degrees); the energies have been calculated at the MP2/6-31G*//SCF/6-31G* level

In any case, the photolysis of **6** with light of 313 nm wavelength proved to be a good method of producing matrix-isolated samples of **11**. Since **10** is photostable at all the wavelengths used (λ ≥ 254 nm) the photochemistry of **11** could be studied in its presence without problems. If one photolyzes **11** at its first absorption maximum by using light of 254 nm wavelength, it reacts to give two sets of products, as shown in Scheme 4.

Scheme 4. Photochemical transformations of **11** when irradiated with light of 254 or 366 nm wavelenght in an argon matrix at 12 K



i: hv, 254 nm; ii: hv, 366 nm; iii: hv, 254 or 313 nm or annealing to 30 K.

About one quarter of the molecules of **11** reacts to **12** and acetylene while the rest produces CO and **10**. The formation of **12** can be rationalized by assuming that **11** first undergoes ring closure to **14** which is subsequently cleaved to **12** and acetylene. In the formation of **10** an intermediate with a weak absorption at ca. 1930–1940 cm^{-1} was detected. If one irradiates **11** at its second maximum with light of 366 nm wavelength a photoequilibrium is rapidly established between **11** (ca. 10% of the initial concentration) on one side and the above-mentioned intermediate and CO on the other. This intermediate was identified as thioformylvinylidenecarbene (**15**) by comparing the calculated and experimental infrared spectrum (see Table 4).

As a comparison, the unsubstituted vinylidenecarbene has its strongest IR absorption at 1952 cm^{-1} [18].

15 reacts on irradiation with light of 313 nm wavelength with CO back to **11** with a recovery of 50% (i.e. the final concentration of **11** is only 50% of the starting concentration). Indeed, it suffices to anneal the matrix at 30 K for 30 min to bring about recombination of **15** and CO, although in this case the recovery is still lower (no more than 20%). The formation of **15** is rather surprising, because it is computed to be thermodynamically much less stable than **1**, and there is an apparently simple reaction pathway connecting it to **1** (180° rotation about the C–C single bond and ring closure). As can be seen from Figure 2, where the ab initio calculated energies of several C_4H_2S isomers containing the subunit C–C–C–C–S are shown, **15** is even less stable than **2**.

The ab initio calculated infrared spectrum of **1** shows that the strongest band, corresponding to the triple-bond stretching, should be at ca. 1796 cm^{-1} (this value was obtained by scaling the calculated frequency by 0.95). This is considered to be a reliable prediction since very recently the spectrum of 1,2-didehydrobenzene was calculated at the same level of theory and shown to correlate very well with the measured spectrum [13].

When **11** is photolyzed with 366-nm light, there is besides **15** and CO at least one other product formed which shows a very weak band at ca. 1710 cm^{-1}, and disappears on wide-band irradiation ($\lambda \geq 360$ nm) at a slower rate than the band of **15**. This band is too small and too wide to allow any firm statement to be made about the isotope shifts, but they are smaller than 5 cm^{-1}.

In contrast to **6**, 3,4-thiophenedicarboxylic acid anhydride (**16**) and its partially deuterated isotopomer [2/5-D]-**16** proved to be photostable when irradiated with light of 313 nm wavelength in an argon matrix at 12 K. When 254-nm light is used **16** reacts to give exclusively CO, CO_2, and **10**. The very clean reaction is surely the method of choice

Table 4. Calculated (MP2/6-31G*) and measured (argon matrix) data for the strongest band in the infrared spectrum of **15** and isotopomers[a, b]

	MP2/6-31G*			Ar matrix	
	$\tilde{\nu}$/cm^{-1}	Int/km mol^{-1}	D-Shift/cm^{-1}	$\tilde{\nu}$/cm^{-1}	D-Shift/cm^{-1}
15	1938.0	594		1938	
[3-D]-15	1929.5	584	-8.5	1931	-7
[formyl-D]-15	1937.9	594	-0.1	1937	-1
[D_2]-15	1929.4	584	-8.6	1930	-8

[a] All other bands of **15** have calculated intensities of less than 35 km/mol. — [b] Calculated frequencies were scaled by 0.95.

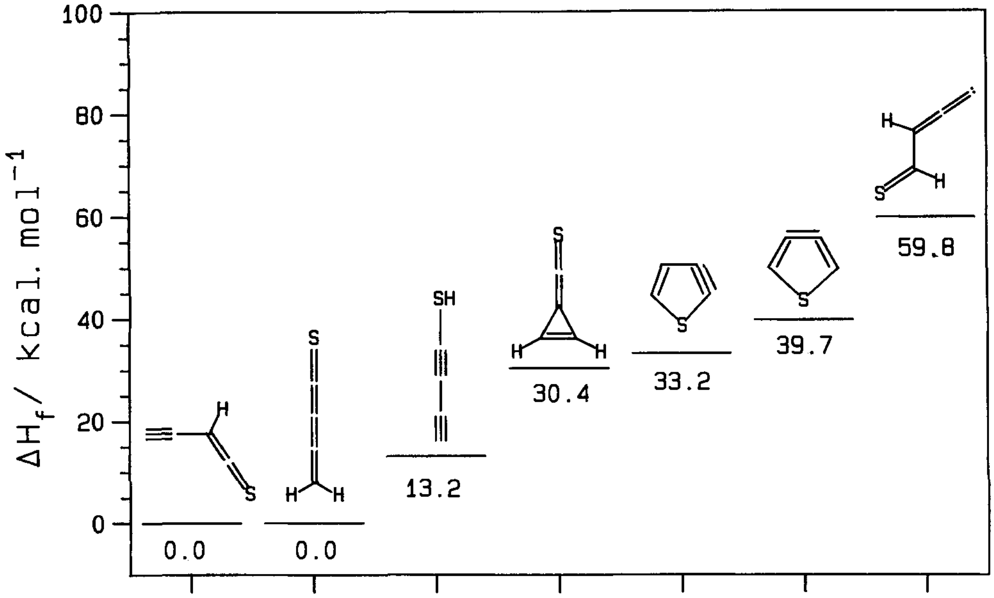
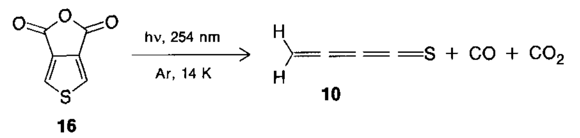


Figure 2. Relative energies of some C_4H_2S isomers containing the C–C–C–C–S subunit; all data were obtained at the fully optimized MP2/6-31G* level

to prepare **10** and allowed the estimation of the absolute intensity of the infrared absorptions of **10** by comparing them with the concomitantly formed CO and CO_2, whose intensities are known[13]. No intermediates were observed in this reaction.

Scheme 5



16 **10**

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Experimental

A. Matrix Isolation

Cryostat: A Displex closed-cycle refrigerator CSA 202 (Air Products) was used.

Spectrometers: A Bruker FT-IR spectrometer with CsI optics operated at 1-cm^{-1} resolution and a UV-Vis spectrometer HP8452A (diode-array type, 4-cm^{-1} resolution) were used.

Light Sources: A mercury high-pressure lamp HBO 200 (Osram) with a monochromator (Bausch & Lomb, band width 20 nm) and a mercury low-pressure lamp "Flächenstrahler 75W" (Gräntzel) were used.

Flash Pyrolysis Oven: A homemade oven with an inner quartz tube (i.d. 8 mm, length of heated zone 5 cm), which could be indirectly heated with a heating wire up to 1000°C, surrounded by a water-cooled metal jacket was used. The oven was directly flanged to the cryostat.

Matrix Preparation: Compounds **6** and **16** were sublimed at 40–45°C/10^{-5} mbar, and the vapors were either passed through the pyrolysis oven or directly condensed with a large excess of argon on the cold optical window. For infrared measurements a CsI window was used, while for the UV measurements a CaF_2 window was chosen.

B. Computational Details

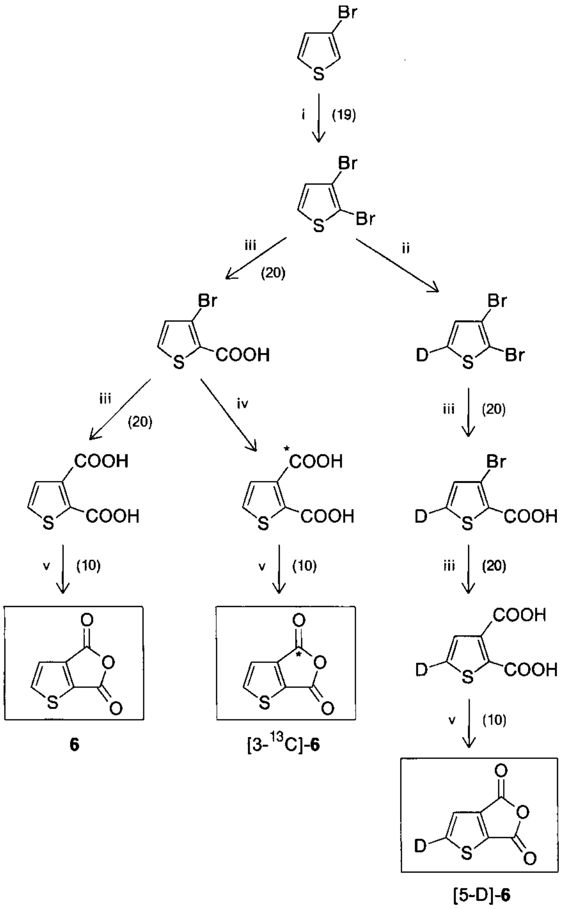
All calculations were carried out by using the program CADPAC[24] on an SCS-40 computer with the internally stored 6-31G* basis set. Both SCF and MP2 second derivatives, and hence vibrational frequencies, were computed analytically. All molecules reported here as energy minima were found, as usual, by searching for structures of zero energy gradient. Vibrational frequencies were then calculated and all found to be positive, thus proving the stationary points to be minima. MP2 total energies were obtained by using the full core.

C. Preparation of Starting Materials

The synthetic routes to **6**, **16** and their isotopomers are shown in Schemes 6 and 7. Roman numerals refer to the reaction conditions (see keys below the Schemes). Arabic numerals in parentheses are literature references for preparations already described and which were not modified. If no literature reference is given, the preparation is described below.

[5-D_1]-3,4-Dibromothiophene: 3,4-Dibromothiophene (12.10 g, 50 mmol) and CF_3CO_2D (50 g, 43 mol-% in D_2O[23]) were placed into a 100-ml round-bottomed flask equipped with a magnetic stirrer. The flask was tightly stoppered with a Teflon-sealed glass stopper (use no grease!) and heated in an oil bath at 80°C with vigorous stirring for 2 weeks (the reaction was complete after 3 d at 100°C but the yield was lower). The reaction mixture was then cooled in an ice bath, diluted with 50 ml of water, and the heavy oily layer was separated and distilled (b.p. 90–92°C/15 Torr), yield 10.45 g (86%), chemical purity >99% (determined by GC); isotope content:

Scheme 6



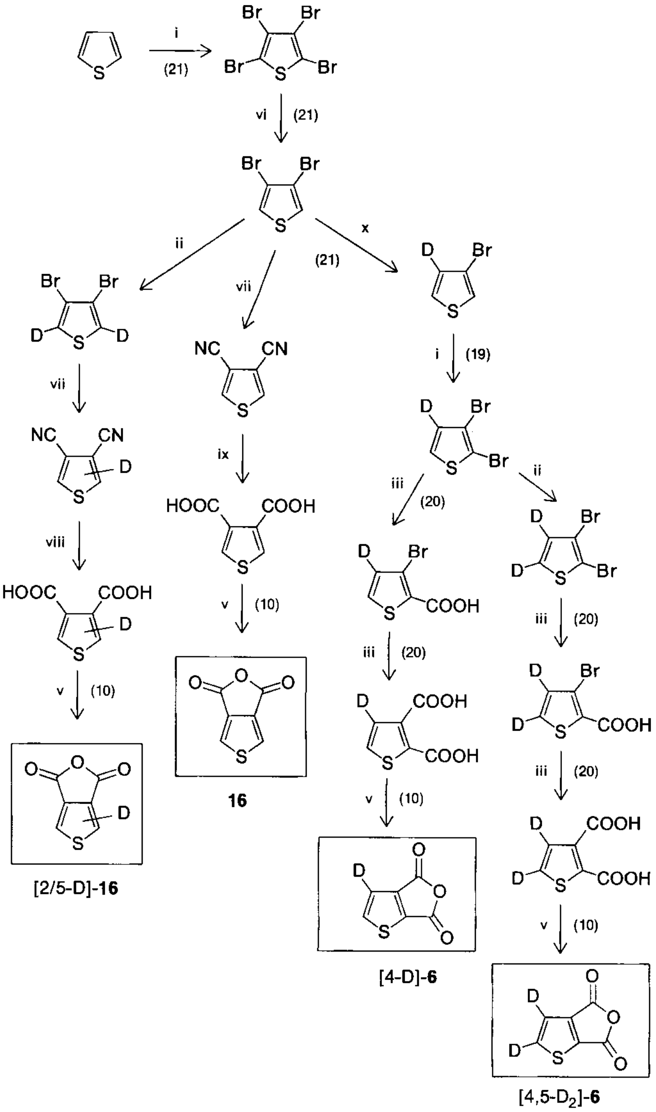
i: Br_2, $CHCl_3$ or CCl_4; ii: CF_3CO_2D/D_2O; iii: 1. *n*BuLi, 2. CO_2; iv: 1. *n*BuLi, 2. $^{13}CO_2$; v: Ac_2O; vi: Zn, AcOH; vii: CuCN, DMF, DCC; viii: H_2SO_4 (10%, v/v); ix: KOH, $HOCH_2CH_2OH$; x: 1. *n*BuLi, 2. $AcOD/Et_2O$.

7% D_0, 93% [5-D_1] (determined by MS and ^{1}H NMR). Deuteration at C-4 was negligible even at 100°C. – IR (neat): $\tilde{\nu}$ = 3101 cm^{-1} (C–H), 1500, 1402, 1313, 1149, 1000, 920, 849, 808, 762, 563. – ^{1}H NMR ($CDCl_3$): δ = 6.90 (s). – MS (70 eV): *m/z* (%) = 241, 243, 245 (50, 100, 53) [M^+], 162, 164 (21, 27) [M^+ – Br], 83 (59) [M^+ – 2 Br].

[4,5-D_2]-2,3-Dibromothiophene: This compound was prepared similarly to the previous one, but starting with [4-D_1]-3,4-dibromothiophene (isotopic purity: 92.3% determined by ^{1}H NMR), yield 77%, chemical purity >99% (GC); isotope content: 1% D_0, 6% 5-D_1, 4% 4-D_1, 89% 4,5-D_2 (MS, assuming no exchange at C-4). – IR (neat): $\tilde{\nu}$ = 2335 cm^{-1} (C–D), 2305 (C–D), 1480, 1392, 1268, 1010, 977, 858, 762, 591, 508. – MS (70 eV): *m/z* (%) = 242, 244, 246 (53, 100, 50) [M^+], 163, 165 (24, 27) [M^+ – Br], 84 (52) [M^+ – 2 Br].

[2,5-D_2]-3,4-Dibromothiophene: This compound was prepared similarly to the two previous ones except that it was heated for 2 weeks at 90°C. After this period, the used trifluoroacetic acid solution was removed by decantation, substituted by a fresh portion and heated for another week. After work-up and distillation (96°C/15 Torr) the yield was 91%, chemical purity >99% (GC); isotope content: 95% [2,5-D_2], 5% [2-D_1]. – IR (neat): $\tilde{\nu}$ = 2328 cm^{-1} (C–D), 1520, 1310, 1280, 975, 942, 887, 762, 620. – MS (70 eV): *m/z* (%) = 242, 244, 246 (48, 100, 53) [M^+], 163, 165 (22, 21) [M^+ – Br], 84 (85) [M^+ – 2 Br].

Scheme 7



i: Br_2, $CHCl_3$ or CCl_4; ii: CF_3CO_2D/D_2O; iii: 1. *n*BuLi, 2. CO_2; iv: 1. *n*BuLi, 2. $^{13}CO_2$; v: Ac_2O; vi: Zn, AcOH; vii: CuCN, DMF, DCC; viii: H_2SO_4 (10%, v/v); ix: KOH, $HOCH_2CH_2OH$; x: 1. *n*BuLi, 2. $AcOD/Et_2O$.

3,4-Dicyanothiophene: This compound was prepared according to ref.[22] with the following simplification. Instead of using dry DMF one can use commercial DMF if an excess of DCC is added to the reaction mixture before heating it to reflux. The DCC can be separated easily by filtration as dicyclohexylurea after the aqueous work-up. This is a very convenient simplification since DMF is quite difficult to dry. The yield obtained is comparable to the one given in the literature.

[2/5-D]-3,4-Dicyanothiophene: This compound was prepared in the way described above for 3,4-dicyanothiophene but starting with [2,5-D_2]-3,4-dibromothiophene. Under the drastic reaction conditions some of the label was lost, but since for our purposes a partly deuterated compound was as suitable as a fully deuterated no effort

was made to correct this; isotope content: 12% D_0, 45% D_1, 43% D_2 (MS).

[2/5-D]-3,4-Thiophenedicarboxylic Acid: [2/5-D]-3,4-Dicyanothiophene cannot be hydrolyzed with KOH in ethylene glycol as described in the literature[22] for the unlabeled compound since all the deuterium will be lost. To avoid this, [2/5-D]-3,4-dicyanothiophene (500 mg, 3.68 mmol) was hydrolyzed by heating it to reflux for 62 h with 10 ml of diluted sulfuric acid (10%, v/v). The solution obtained was filtered while still hot and set aside to cool slowly. The crystals thus formed were separated by filtration, washed with cold water and dried. In this way only ca. 14% of the deuterium is lost; isotope content: 25% D_0, 39% D_1, 36% D_2 (MS).

[3-^{13}CO]-2,3-Thiophenedicarboxylic Acid: The procedure described in the literature[20] for the preparation of the unlabeled compound was modified to reduce the amount of $^{13}CO_2$ needed. The apparatus shown in Figure 3 proved very convenient. All the glassware should be carefully dried before starting. Stopcock S_3 was used as an argon inlet and S_4, which was connccted through a long plastic tube to a bubler, served as argon outlet. The thermometer was a standard low-temperature pentane thermometer. The three-necked flask was equipped with a magnetic stirrer.

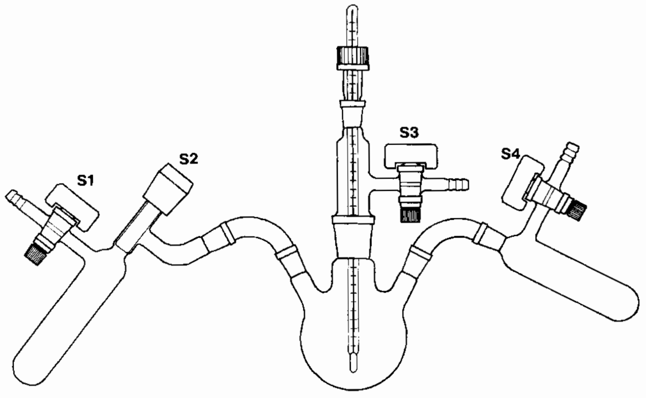


Figure 3. Apparatus for the preparation of [3-^{13}CO]-2,3-thiophenedicarboxylic acid

First, the Schlenk tube of the left side was separately evacuated, and 250 ml (11.2 mmol) of $^{13}CO_2$ (99.2% ^{13}C) was condensed into it by cooling it with liquid N_2. Stopcocks S_1 and S_2 were then closed, and the Schlenk tube was connected to the rest of the apparatus while keeping it cooled with liquid N_2. The three-necked flask was loaded with 0.52 g (2.50 mmol) of 3-bromo-2-thiophenecarboxylic acid dissolved in 26 ml of dry diethyl ether. Into the Schlenk tube to the right was placed 6.60 ml of a 1.13 M solution of *n*-butyllithium in hexane (corresponding to 7.50 mmol of *n*BuLi) and 5 ml of dry diethyl ether. The Schlenk tube on the right side and the three-necked flask were then cooled to −90°C with an ethanol/liq. N_2 slush. When both solutions attained this temperature the Schlenk tube on the right side was rotated upwards to transfer the *n*BuLi solution to the three-necked flask. This caused the temperature in the three-necked flask to rise to −70°C. After stirring for 15 min, the Schlenk tube on the right side was removed from the liquid N_2 bath, the Teflon stopcock S_2 was carefully opened all the way (remember that the Schlenk tube was evacuated!), the contents of the three-necked flask were transferred to the Schlenk tube, and S_2 was again closed. This was done as quickly as possible. The Schlenk tube was then separated from the rest of the apparatus and set aside to warm-up slowly with occasional shaking and relief of pressure through S_1. After the contents had reached room temp., it was worked up as described in the literature[20] for the unlabeled compound, yield after recrystallization from 6.5 ml of water 230 mg (53%), m.p. 268−270°C (ref.[20] 270−272°C). It was immediately dehydrated to the anhydride and analyzed as such.

[4-D]-2,3-Thiophenedicarboxylic Acid Anhydride ([4-D]-**6**): Prepared according to ref.[10], yield 89%, m.p. 138−139°C (ref.[10] 138−140°C for unlabeled **6**), chemical purity >99% (GC); isotope content: 6.5% D_0, 92.9% D_1, 0.6% D_2 (MS). − IR (KBr pellet): $\tilde{\nu}$ = 3128 cm^{-1} (C−H), 1845 (C=O), 1759 (C=O), 1520, 1370, 1292, 1203, 1107, 869, 731, 719. − ^{1}H NMR ($CDCl_3$): δ = 8.015 (s, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 157.438 (3-CO), 156.619 (2-CO), 145.354 (C-3), 141.491 (C-2), 142.339 (C-5). − MS (70 eV): *m/z* (%) = 155 (21) [M^+], 111 (100) [$M^+ - CO_2$], 84 (57) [C_3OS^+], 83 (45) [$M^+ - CO_2 - CO$].

[5-D]-2,3-Thiophenedicarboxylic Acid Anhydride ([5-D]-**6**): Prepared according to ref.[10], yield 86%, m.p. 138−139°C (ref.[10] 138−140°C for unlabeled **6**), chemical purity >99% (GC); isotope content: 6.3% D_0, 93.7% D_1 (MS). − IR (KBr pellet): $\tilde{\nu}$ = 3110 cm^{-1} (C−H), 1845 (C=O), 1760 (C=O), 1528, 1361, 1293, 1193, 1117, 880, 737, 728. − ^{1}H NMR ($CDCl_3$): δ = 7.423 (s, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 157.450 (3-CO), 156.624, (2-CO), 145.439 (C-3), 141.416 (C-2), 121.800 (C-4). − MS (70 eV): *m/z* (%) = 155 (35) [M^+], 111 (100) [$M^+ - CO_2$], 84 (57) [C_3OS^+], 83 (43) [$M^+ - CO_2 - CO$].

[4,5-D_2]-2,3-Thiophenedicarboxylic Acid Anhydride ([4,5-D_2]-**6**): Prepared according to ref.[10], yield 78%, m.p. 130−135°C (ref.[10] 138−140°C for the unlabeled **6**). The low melting point was due to the fact that the compound was only 93% pure (GC). The two impurities present could not be identified, but since they had a retention time almost double that of **6** (and hence a much smaller vapor pressure) they would not interfere in the matrix experiments, and no effort was made to purify the compound further; isotope content: 90% D_2, 10% D_1 (MS). − IR (KBr pellet): $\tilde{\nu}$ = 1840 cm^{-1} (C=O), 1780 (C=O), 1520, 1347, 1290, 1140, 1041, 867, 742, 712. − ^{13}C NMR ($CDCl_3$): δ = 157.401 (3-CO), 156.588 (2-CO), 145.306 (C-3), 141.354 (C-2), 142.099 (t, $^1J_{C,D}$ = 28.9 Hz, C-5), 121.569 (t, $^1J_{C,D}$ = 27.3 Hz, C-4). − MS (70 eV): *m/z* (%) = 156 (9) [M^+], 112 (81) [$M^+ - CO_2$], 84 (100) [$M^+ - CO_2 - CO, C_3OS^+$].

[3-^{13}CO]-2,3-Thiophenedicarboxylic Acid Anhydride ([3-^{13}CO]-**6**): Prepared according to ref.[10], yield 78%, m.p. 138−139°C (ref.[10] 138−140°C for unlabeled **6**); chemical purity >99% (GC); isotope content: 98.5% ^{13}C (MS). − IR (KBr pellet): $\tilde{\nu}$ = 3131 cm^{-1} (C−H), 3110 (C−H), 1820 (C=O), 1730 (C=O), 1520, 1380, 1282, 1235, 1100, 860, 782, 730, 718. − ^{1}H NMR ($CDCl_3$): δ = 7.951 ($J_{H,H}$ = 4.9 Hz, $^1J_{C\text{-}5,H}$ = 188.8 Hz, $^4J_{3\text{-}CO,H}$ = 1.3 Hz, 5-H), 7.354 ($J_{H,H}$ = 4.9 Hz, $^1J_{C\text{-}4,H}$ = 178.3 Hz, $^4J_{3\text{-}CO,H}$ = 0.6 Hz, 4-H). − ^{13}C NMR ($CDCl_3$): δ = 157.384 (t, $^1J_{C\text{-}3,C}$ = 74.6 Hz, 3-CO), 156.589 (2-CO), 142.354 (d, $^3J_{3\text{-}CO,C}$ = 6.7 Hz, C-5), 121.898 (d, $^2J_{3\text{-}CO,C}$ = 4.7 Hz, C-4), 145.393 (d, $^1J_{3\text{-}CO,C}$ = 74.3 Hz, C-3), 141.465 (d, $^2J_{3\text{-}CO,C}$ = 5.4 Hz, C-2). − MS (70 eV): *m/z* (%) = 155 (28) [M^+], 111 (67) [$M^+ - CO_2$], 110 (100) [$M^+ - {}^{13}CO_2$], 84 (27) [C_3OS^+], 85 (78) [$^{13}CC_2OS^+$], 82 (84) [$M^+ - CO_2 - CO$].

CAS Registry Numbers

1: 16180-03-3 / [4-D]-**6**: 137040-68-7 / [5-D]-**6**: 137040-69-8 / [4,5-D_2]-**6**: 137040-70-1 / [3-^{13}CO]-**6**: 137040-71-2 / **9**: 137040-79-0 / [4-D]-**9**: 137040-80-3 / [5-D]-**9**: 137040-81-4 / [4,5-D_2]-**9**: 137040-82-5 / [3-^{13}CO]-**9**: 137040-83-6 / **10**: 137040-88-1 / [D]-**10**: 137040-72-3 / [D_2]-**10**: 137040-73-4 / **11**: 137040-74-5 / [4-D]-**11**: 137040-75-6 / [formyl-D]-**11**: 137040-76-7 / [D_2]-**11**: 137040-77-8 / [1-^{13}C]-**11**: 137040-78-9 / **15**: 137040-84-7 / [3-D]-**15**: 137040-85-8 / [formyl-D]-**15**: 137040-86-9 / [D$_2$]-**15**: 137040-87-0 / [5-D$_1$]-3,4-dibromothiophene: 137040-67-1 / [4,5-D$_2$]-2,3-dibromothiophene: 137040-63-2 / [2,5-D$_2$]-3,4-dibromothiophene: 137040-64-3 / 3,4-dicyanothiophene: 18853-32-2 / [2/5-D]-3,4-dicyanothiophene: 137040-65-4 / [2,5-D$_2$]-3,4-dicyanothiophene: 137040-89-2 / [2/5-D]-3,4-thiophenedicarboxylic acid: 137040-66-5 / [2,5-D$_2$]-3,4-thiophenedicarboxylic acid: 137040-90-5 / [3-^{13}CO]-2,3-thiophenedicarboxylic acid: 137040-67-6 / 3,4-dibromothiophene: 3141-26-2

☆ Dedicated to Professor *Günther Maier* on the occasion of his 60th birthday.

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