Ten-Membered Heterocyclic Diynes X-ray Structure Analysis and PE-Spectroscopic Investigations

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X-ray investigations on the ten-membered heterocyclodiynes **1**–**4** reveal a chair-like conformation for all four compounds. The triple bonds are oriented parallel to each other, the distances between them varying between 3.10 Å (**2**) and 2.91 Å (**1**). All triple bonds are slightly bent, the deviation from 180° varies between 6–10°. The photoelectron spectra of **1** and **3**–**6** have been recorded. The first six bands have been assigned by comparing them with related species and MO calculations. In the case of **3**–**6**, the HOMO is predicted to be a lone pair combination. The splitting between the in-plane π-linear combinations π_i^-, π_i^+ ranges from 0.9 eV (**5**) up to 1.5 eV (**4**).

The reaction of 1,6-cyclodecadiyne and 1,6-dithia-3,8-cyclodecadiyne with $CpCoL_2$ (L = CO, L_2 = C_8H_{12}) resulted in the formation of new cyclophanes[1–3]. This has prompted us to examine the properties of ten-membered heterocyclic diynes more systematically. In a recent communication we have reported on a general route to some of these species[4]. In this paper we describe our studies concerning the structure and photoelectron (PE) spectra. The compounds in question are 1,6-dioxa-3,8-cyclodecadiyne (**1**), 1,6-dithia-3,8-cyclodecadiyne (**2**), 1-oxa-6-thia-3,8-cyclodecadiyne (**3**), 1-thia-3,8-cyclodecadiyne (**4**), 1-thia-6-selena-3,8-cyclodecadiyne (**5**) and 1,6-diselena-3,8-cyclodecadiyne (**6**). For comparison, we also include the data obtained for 1,6-cyclodecadiyne (**7**)[5].

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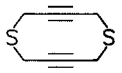

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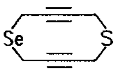

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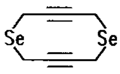

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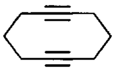
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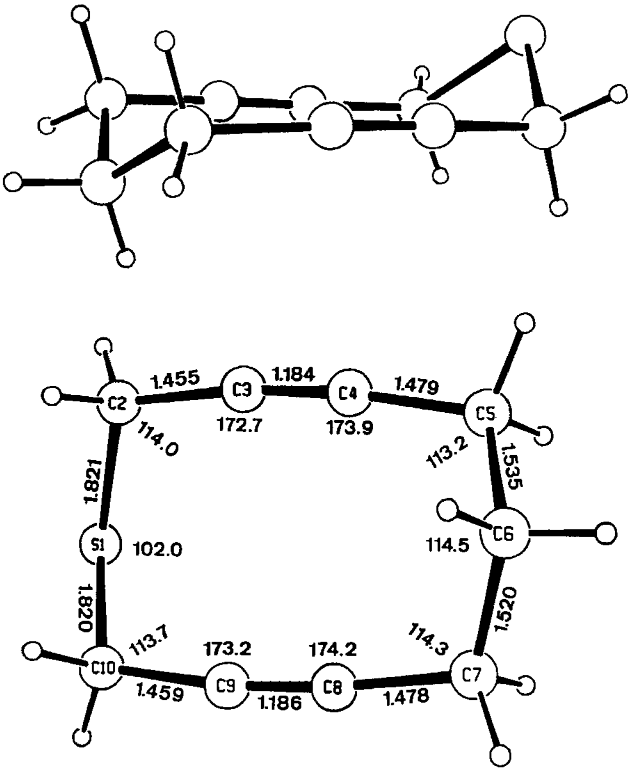


Figure 1. Side view and top view of the structure of **4** as obtained by X-ray investigations

X-ray Structure Determination of the Heterocyclic Diynes 1–4

Compounds **1** and **2** have already been examined by X-ray methods in the early sixties[6,7], but at that time the molecular structures could not be determined. Our investigations now permit a detailed description of the molecular structures of **1** and **2** as well as of the newly synthesized congeners **3** and **4**. In the crystalline state all four cyclodiynes exhibit a chair-like conformation as demonstrated for **4** in Figure 1. The analysis of the X-ray data of **3** reveals a disorder in the crystalline state so that it is not possible to distinguish between the sulfur and oxygen atoms.

Just as in **7**, the two triple bonds are arranged parallel to each other in all four hetero diynes. The transannular distance of the triple bonds depends systematically on the heteroatom (see Table 1). Thus, the ring with two sulfur atoms (**2**) shows the larger distance (3.10 Å), whereas the smallest distance (2.91 Å) is encountered for the ring with two oxygen atoms (**1**). As anticipated the unsymmetric substitution in **4** leads to two acetylenic units which diverge towards the sulfur side of the molecule. Here, the intramolecular distance between the triple bonds amounts to 3.07 Å as compared to 2.98 Å on the side with the trimethylene bridge.

Table 1. Transannular distances of triple bonds, bond angles at C(sp) atoms, deformations and distances between the heteroatoms and the corresponding carbon atoms, respectively, of **1**–**4** and **7**

	1	**2**	**3**	**4**	**7**
Transannular distances [Å]	2.909(2)	3.102(2)	3.014(4)	2.976(3) 3.068(3)	2.991(2)
Bond angles at C(sp) atoms	169.6(1)	174.2(2)	171.4(3)	172.7(2) 173.9(2)	171.7(2)
Cisoid deformations	10.4(1)	5.8(2)	8.6(3)	7.3(2) 6.1(2)	8.3(2)
Distances between atoms 1 and 6	4.935(2)	5.623(2)	5.244(4)	5.422(3)	–

The repulsive transannular interaction of the triple bonds results in a cisoid deformation of the bond angles at the sp carbon atoms (see Table 1). The deviation from linearity amounts to 6° in **2** and rises to 10.4° for **1**. For **4** we encounter a deviation of 7.3° on the carbon side and 6.1° on the sulfur side, the average deviation for **3** is found to be 8.6°.

PE-Spectroscopic Investigations of 1 and 3–6

The PE spectra of **1** and **3**–**6** are illustrated in Figure 2. Common to all of them is a group of three to five peaks below 12 eV. From the size of the different bands we assign

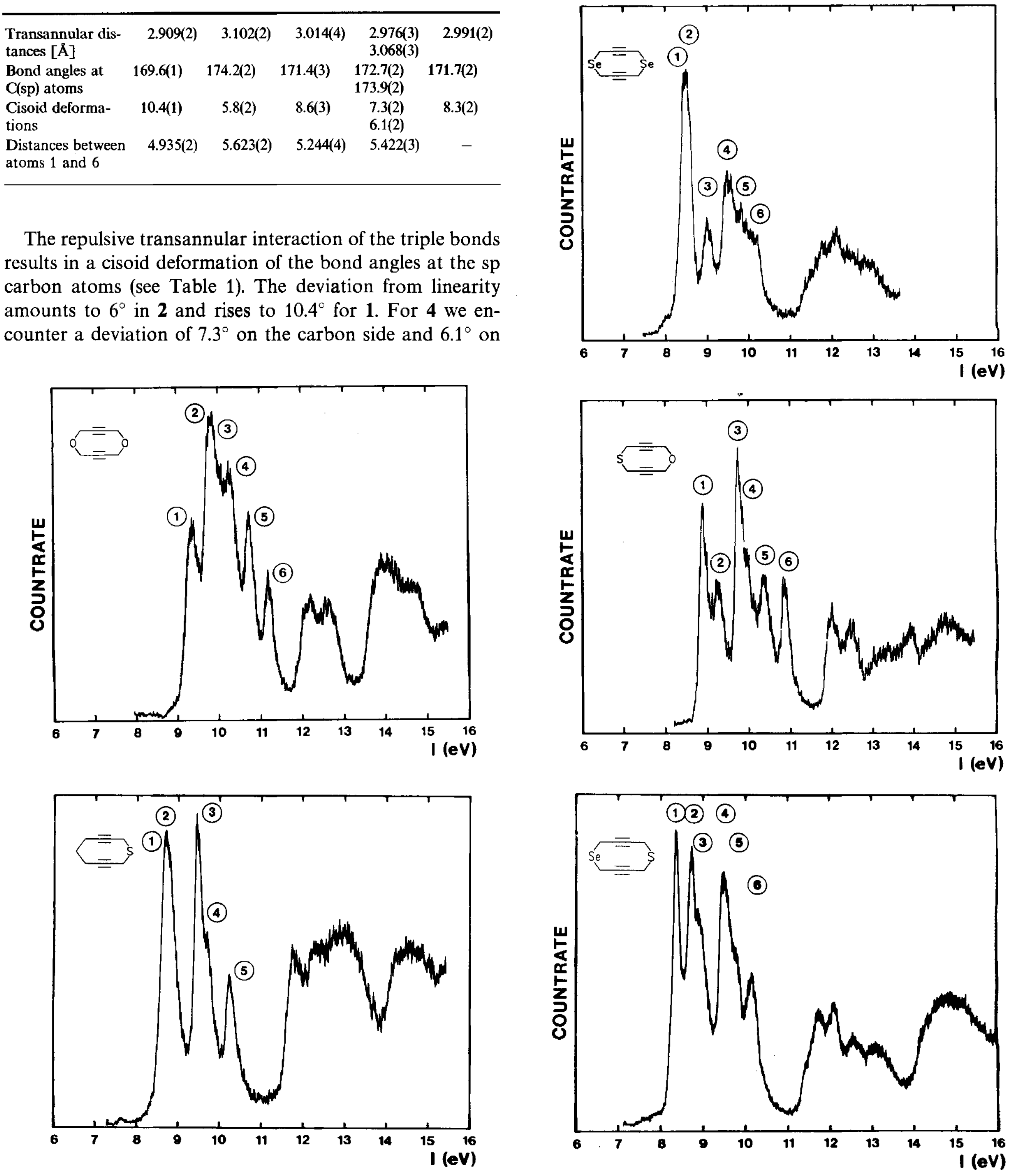
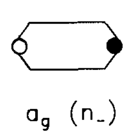
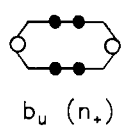


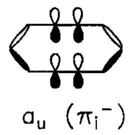
Figure 2. He(I) photoelectron spectra of **1**, **3** and **4**–**6**

to these peaks five or six ionization events as indicated in Figure 2. To interprete the PE spectra of **1**–**6** we proceed in two ways: We correlate the first bands of **1** and **3**–**6** with those of **2** which has already been the object of a detailed investigation[8]. Furthermore, we assume that we can correlate the vertical ionization energies, $I_{v,j}$, directly with the calculated orbital energies, ε_j (Koopmans' theorem[9]), at least for the first bands. The methods applied to the calculations are the Hartree-Fock self-consistent field (HF-SCF) procedure using a STO-3G basis[10] and the semi-empirical MNDO[11] method.

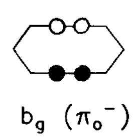
To discuss the PE spectra of **4**, **5** and **6** we first start with that of **2**[8]. The first intensive peak in the PE spectrum of **2** at 8.73 eV is due to three ionization events which have been assigned to the symmetric and antisymmetric linear combinations of the 3 p lone pairs at the sulfur atoms (n_+, n_-) and the antisymmetric linear combination of the "in-plane π-MO" (π_i^-) as shown schematically below.

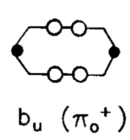


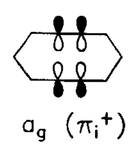




The second peak at 9.6 eV has been assigned to the two "out-of-plane π-MOs" (π_o^+, π_o^-) which are very close in energy. The third peak at 10.31 eV finally is due to the ionization out of the bonding "in-plane π-MO", π_i^+.







A comparison of the PE spectrum of **2** with that of **4** shows a great similarity (see Figure 3). In the latter we observe also three peaks at nearly the same ionization energies as in **2** (see Table 2 and Figures 2 and 3) the only difference is that the ratio of the peaks is 2:2:1. A comparison between the PE spectra of **2** and **4** suggests to assign the first peak in the PE spectrum of **4** to n_s and π_i^-, the second one to π_o^+ and π_o^- and the third one to π_i^+. In line with this assignment are also the results of the calculations (see Table 2), at least as far as the sequence of the bands is concerned.

The PE spectrum of **2** is also a suitable starting point to discuss that of **5**. The replacement of one sulfur atom by selenium should affect the lone-pair combinations only. It seems therefore logical to assign the first two peaks at 8.4, 8.7 and the shoulder at 8.9 eV to the three transitions from n_{Se}, n_S and π_i^-. The band at 9.5 and the shoulder at 9.8 eV can be assigned to π_o^- and π_o^+, while the sixth band at 10.14 is due to the ionization from π_i^+. These assignments are in line with the PE data of **4** and **6** (see Figure 3).

Concerning the PE spectrum of **6** the correlation shown in Figure 3 suggests to assign the first peak to the two lone-pair ionizations n_{Se}^- and n_{Se}^+ which are very close in energy (see also Table 2). This peak is followed by the bands which correspond to the ionizations π_i^-, the pair π_o^+,π_o^-, and π_i^+.

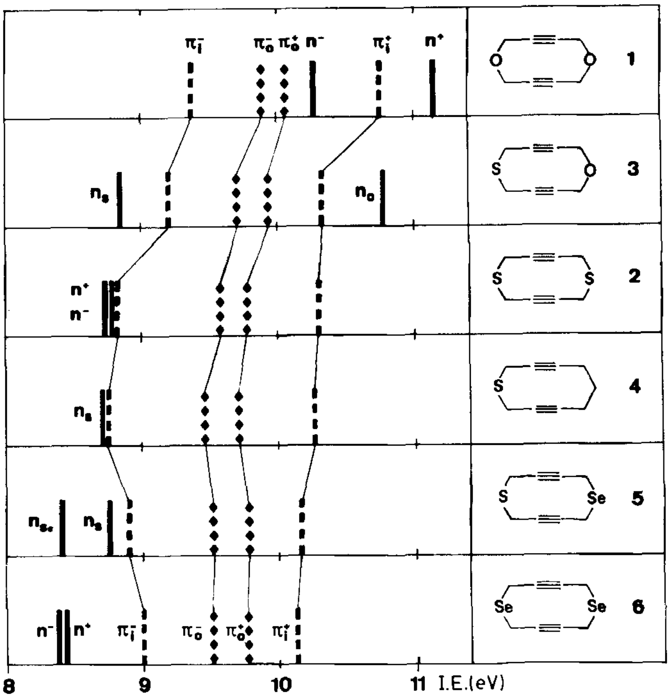


Figure 3. Correlation between the first PE bands of **1**–**6**

In line with this sequence are also the STO-3G calculations carried out on **6** (Table 2).

Also the PE spectrum of **3** can be correlated with that of **2**. Replacement of one sulfur atom by one oxygen atom should leave one sulfur lone pair at around 9 eV. The π_o^+,π_o^- bands should remain slightly above 10 eV. This leaves the lone pair at the oxygen at 10.79 eV, a value which is somewhat higher in energy than that obtained for the dimethyl ether (10.0 eV[12]). We ascribe this difference to the interaction between 13a′(π_i^+) and 12a′(n_o) which destabilizes **13a′** and stabilizes **12a′**. This interpretation rationalizes not only the high ionization energy for the oxygen lone pair, but also the smaller splitting between π_i^- and π_i^+ in the case of **3** (1.1 eV) as compared to the values found for **1** (1.4 eV) and **2** (1.6 eV). If we accept this qualitative reasoning we obtain for band ② the assignment π_i^- and for band ④ π_i^+. In line with this are the results of the calculations (see Table 2). For the PE spectrum of **1** the correlation diagram of Figure 3 predicts π_i^- on top of three closely lying bands assigned to π_o^+,π_o^- and n_-, followed by two bands which belong to ionizations from π_i^+ and n_+. This correlation implies a splitting between n_- and n_+ of about 0.9 eV. At the first glimpse this splitting seems rather high in view of the near degeneracy of the lone-pair combinations in the case of **2** and **6**. The reason for the large splitting is a relatively strong n/σ mixing between $a_g(n_-)$ and a σ-MO of the same symmetry as shown below.

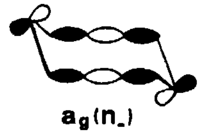


Table 2. Comparison between the recorded vertical ionization energies, $I_{v,j}$ of **1** and **3**–**6** and the calculated orbital energies, ε_j (all values in eV)

Comp.	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$ (MNDO)	$-\varepsilon_j$ (STO-3G)
1	1	9.36	$6a_u(\pi_i^-)$	10.50	7.98
	2	9.9	$7b_u(\pi_o^+)$	10.74	8.63
	3	10.05	$5b_g(\pi_o^-)$	10.90	8.70
	4	10.25	$8a_g(n_-)$	11.37	9.42
	5	10.73	$7a_g(\pi_i^+)$	11.66	9.96
	6	11.18	$6b_u(n_+)$	11.94	10.03
2	1	8.73	$8a_g(n_-)$	9.78	6.96
	2		$7b_u(n_+)$	9.89	7.16
	3		$6a_u(\pi_i^-)$	10.58	7.57
	4	9.6	$6b_u(\pi_o^+)$	10.72	8.07
	5		$5b_g(\pi_o^-)$	11.01	8.41
	6	10.31	$7a_g(\pi_i^+)$	11.00	8.56
3	1	8.85	$15a'(n_S)$	9.80	7.13
	2	9.20	$11a''(\pi_i^-)$	10.66	7.77
	3	9.70	$14a'(\pi_o^+)$	10.67	8.30
	4	9.9	$10a''(\pi_o^-)$	10.97	8.61
	5	10.32	$13a'(\pi_i^+)$	11.27	9.15
	6	10.79	$12a'(n_o)$	11.71	9.80
4	1	8.71	$15a'(n_S)$	9.65	6.92
	2		$11a''(\pi_i^-)$	10.33	7.45
	3	9.45	$10a''(\pi_o^-)$	10.52	8.32
	4	9.8	$14a'(\pi_o^+)$	10.72	8.07
	5	10.23	$13a'(\pi_i^+)$	10.95	8.93
5	1	8.39	$15a'(n_{Se})$		6.90
	2	8.74	$14a'(n_S)$		7.13
	3	8.9	$11a''(\pi_i^-)$		7.54
	4	9.50	$13a'(\pi_o^+)$		8.16
	5	9.8	$10a''(\pi_o^-)$		8.48
	6	10.14	$12a'(\pi_i^+)$		8.58
6	1	8.4	$8a_g(n_-)$		6.93
	2		$7b_u(n_+)$		7.04
	3	9.0	$6a_u(\pi_i^-)$		7.51
	4	9.5	$6b_u(\pi_o^+)$		8.21
	5	9.75	$5b_g(\pi_o^-)$		8.48
	6	10.1	$7a_g(\pi_i^+)$		8.50

This n/σ mixing is much less pronounced in the case of **2** and **6** due to the large energy difference between the lone-pair combinations and the σ energies.

Conclusion

As anticipated from our previous studies on **7**, the heterocyclic diynes **1**–**4** adopt a chair-like conformation. The triple bonds are arranged parallel to each other and are slightly bent (6–10°), depending on the heteroatom.

The PE investigations reveal for the heterocyclodecadiynes **2**–**6** a very similar electronic structure for the valence MOs. In the case of **2**–**6** the HOMO is a lone pair or lone-pair combination localized at the heteroatom(s). For **1** the sequence of the first three bands is the same as in **7**. Thus, we also expect an electrophile to attack the π bonds in an "in-plane" fashion as found for **7**. The splitting between the bands assigned to π_i^-, π_i^+ varies considerably. It is large (1.4 to 1.6 eV) in **1**, **2**, **4** and **7** and of medium size (0.9–1.1 eV) for **3**, **5** and **6**. As anticipated the splitting between π_o^+ and π_o^- is small in all compounds investigated due to the relative large distance between (2.9–3.1 Å) the triple bonds.

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Table 3. Crystallographic data and refinement parameters of **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_8H_8O_2$	$C_8H_8S_2$	C_8H_8OS	$C_9H_{10}O$
Molec. mass	136.2	168.3	152.2	150.2
Crystal size [mm]	0.5 × 0.5 × 0.5	0.55 × 0.55 × 0.4	0.4 × 0.5 × 0.3	0.5 × 0.5 × 0.35
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca
a [Å]	6.836(2)	4.359(1)	7.159(1)	11.665(3)
b [Å]	7.707(1)	11.874(3)	7.820(2)	7.895(2)
c [Å]	6.984(1)	7.889(2)	7.418(2)	17.846(3)
α [°]	90	90	90	90
β [°]	113.83(2)	95.78(2)	113.81(2)	90
γ [°]	90	90	90	90
V [Å^3]	336.6(2)	406.2(3)	379.9(3)	1643.5(11)
$D_{calc.}$ [Mg · m^{-3}]	1.34	1.38	1.33	1.21
Z	2	2	2	8
$F(000)$	144	176	160	640
$(\sin\Theta/\lambda)$max	0.66	0.66	0.66	0.66
Abs. coeff. μ [mm^{-1}]	0.09	0.55	0.33	0.30
Refl. unique	808	975	909	1962
Refl. obs. *	661	848	729	1226
Variables	62	62	62	131
R	0.039	0.038	0.048	0.037
wR	0.049	0.050	0.077	0.045
Goodness of fit S	2.38	2.52	3.74	1.92
max. $\Delta\varrho$ [e · Å^{-3}]	0.140	0.293	0.290	0.163

* Criteria: **1** [$I > 3\sigma(I)$]; **2**, **3**, **4** [$I > 2.5\sigma(I)$].

Table 4. Atomic coordinates and the equivalent atomic displacement parameters (× 10^4 Å^2) of **1**–**4**

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

	Atom	x	y	z	U_{eq} x 10^4[Å^2]
1	O	0.1690(1)	0.1067(1)	0.2169(1)	437(3)
	C1	0.3384(2)	0.0944(1)	0.1485(2)	448(4)
	C2	0.5498(2)	0.0931(1)	0.3248(2)	422(4)
	C3	0.7033(1)	0.0835(1)	0.4853(2)	417(4)
	C4	0.1305(2)	-0.0499(2)	0.3049(2)	439(4)
2	S	0.1522(1)	0.08477(4)	0.83051(4)	447(2)
	C1	0.2268(4)	0.1696(1)	0.6462(2)	472(7)
	C2	0.0322(4)	0.1391(1)	0.4924(2)	414(7)
	C3	0.1242(4)	-0.1047(1)	0.6292(2)	417(7)
	C4	0.3062(4)	-0.0505(2)	0.7729(2)	497(8)
3	S/O	0.6834(1)	0.1396(1)	0.2041(1)	741(3)
	C1	0.6360(3)	-0.0323(4)	0.3086(3)	763(11)
	C2	0.7893(3)	-0.0642(3)	0.5100(3)	628(9)
	C3	0.9296(3)	-0.0797(3)	0.6642(3)	644(8)
	C4	0.8767(5)	0.0887(3)	0.1594(3)	808(11)
4	S1	0.42387(5)	0.15866(6)	0.08043(3)	610(3)
	C2	0.5579(2)	0.2426(3)	0.0437(1)	680(12)
	C3	0.6094(2)	0.3731(2)	0.0904(1)	522(10)
	C4	0.6394(2)	0.4828(2)	0.1312(1)	529(10)
	C5	0.6639(2)	0.6256(3)	0.1824(1)	698(12)
	C6	0.5766(2)	0.7703(3)	0.1760(1)	732(13)
	C7	0.4573(2)	0.7265(3)	0.2043(1)	778(13)
	C8	0.3994(2)	0.5909(2)	0.1614(1)	556(10)
	C9	0.3618(2)	0.4806(2)	0.1236(1)	515(10)
	C10	0.3295(2)	0.3417(2)	0.0740(1)	591(10)

Experimental

The X-ray investigations have been carried out at room temperature with an Enraf-Nonius CAD4 diffractometer with Mo-K_α irradiation, graphite monochromator and ω-2Θ scanning in the region to sin Θ/2 = 0.66 Å^{-1}. The structures of **1**–**4** have been solved with Direct Methods. All calculations have been carried out with a PDP-11/44 computer with the SDP program system[13]. Molecule **3** is disordered around a center of symmetry.

The crystallographic data and the refinement parameters are listed in Table 3, the atomic coordinates of **1**–**4** and the averaged anisotropic thermal parameters (U_{eq}) are given in Table 4[14].

The PE spectra have been recorded with a Perkin-Elmer PS18 instrument. All spectra were recorded at room temperature. The spectra were calibrated with Xe and Ar.

CAS Registry Numbers

1: 6573-64-4 / **2**: 53690-50-9 / **3**: 127793-16-2 / **4**: 115227-74-2 / **5**: 127793-17-3 / **6**: 127793-18-4

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[14] Further details concerning the X-ray investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54528, the names of the authors and the journal citation.

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