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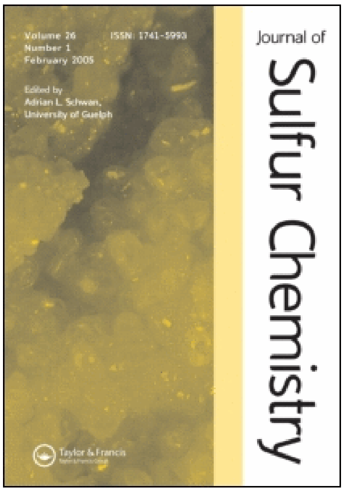

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Theoretical Studies on Heterocumulated Double Bond Systems

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THEORETICAL STUDIES ON HETEROCUMULATED DOUBLE BOND SYSTEMS

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The 21 experimentally known systems of the types C_nX and XC_nY ($X, Y = O, S$; $n = 2–6$) have been calculated at common levels of theory. The geometries, vibrational wavenumbers and absorption intensities, rotational constants, dipole moments, bond dissociation energies, singlet–triplet energy gaps for the 11 diradicals, as well as UV absorptions are presented and discussed, and compared with the experimental values where this is possible. The calculated resonance structures, the C–C bond alternation, the extremely low bending wavenumbers, and the dramatic increase of the dipole moment and IR absorption intensity upon chain lengthening for C_nX strongly suggest the term heteropolyacetylene rather than the name shown in the title. Nevertheless, all these zwitterionic systems exhibit significant π-electron delocalization to an extent which is known from aromatic compounds.

Keywords: Diradicals; heterocumulenes; Lewis structures; molecular properties; quantum chemical calculations

CONTENTS

1. INTRODUCTION

The investigations in the field of carbon chain systems, sometimes called heterocumulated double bond systems, of the types C_nX and XC_nY with $X, Y = O, S$ and $n = 1-6$ go back to the year 1988, when OC_5O and C_4O were observed by matrix IR spectroscopy,[1] and the systems C_4O, C_6O, with even numbers of carbon atoms, were detected by ESR spectroscopy,[2] and SC_2S was identified by neutralization–reionization mass spectroscopy (NRMS).[3] Meanwhile, there are mainly three experimental sources for the discovery of heterocumulenes: (a) matrix IR spectroscopy, with dominant contributions from the groups of Maier (Gießen)[4] and Wentrup (Brisbane), also for $X = NR$;[5] (b) NRMS performed by the groups of Schwarz (Berlin)[6] and Wentrup;[5] (c) microwave spectroscopy (MW), either applied to systems generated by discharge or to circumstellar envelopes. Many of these contributions were made by the group of Endo (Tokyo).[7]

It is easy to understand that unexpected molecular systems such as heterocumulenes represent a challenge for quantum chemical *ab initio* calculations. Most of the publications on these compounds appeared as a fruitful interplay of synthesis, spectroscopy and theory. Most of the aforementioned experiments yield solely the fact of the existence of a new compound rather than its set of molecular properties. In this context, *ab initio* calculations are the only rigorous source for the molecular structure and the nature of the electronic ground state. Furthermore, the comparison of the IR spectrum with the calculated vibrational wavenumbers and absorption intensities enables one to confirm or reject the assumed connectivity of atoms in a new compound.

This report goes beyond a mere compilation of computational efforts from the literature. In addition, a great part of the recently observed systems is calculated at recent state-of-the-art levels of theory. On one hand, these calculations can help to find the degree of reliability of calculated molecular properties, and on the other hand, unappropriate applications of computational methods as well as erroneous interpretations of computational results can be discussed. Moreover, the calculation of a large variety of related systems at a common theoretical level yields interesting trends for molecular properties.

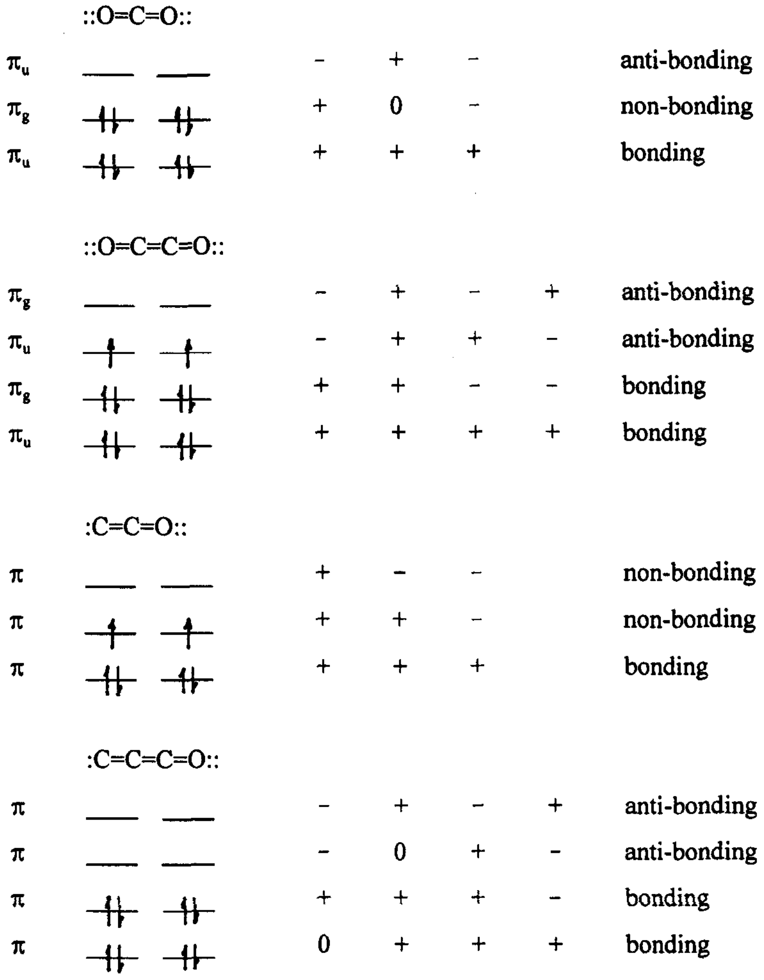
$\underline{CO}$	$\underline{OCO}$	$\underline{OCS}$	$\underline{SCS}$	$\underline{CS}$
C_2O	(OC_2O)	OC_2S	SC_2S	C_2S
C_3O	OC_3O	OC_3S	SC_3S	C_3S
C_4O	OC_4O	OC_4S	SC_4S	C_4S
C_5O	OC_5O	OC_5S	SC_5S	C_5S
C_6O	(OC_6O)	(OC_6S)	SC_6S	(C_6S)

SCHEME 1 Carbon oxides and sulfides. Well known systems with one carbon atom are underlined; still unknown systems are set in parentheses.

The systems under discussion can be presented at best by applying Scheme 1 from the literature[4a] which is modified for our purposes. In Scheme 1 all possible carbon oxides and sulfides with one to six carbon atoms are arranged in a self-explanatory way. The underlined systems at the top have been well known for a long time and their descriptions can be found in textbooks as well as in many articles. The three systems at the bottom and OC_2O, in parentheses, are still unknown. All remaining systems have been experimentally identified and are the topics of this article. Finally, two examples will be described where one of the atoms O, S is substituted by :NH or :NOH.

2. THEORY AND COMPUTATIONAL METHODS

The set of systems in Scheme 1 can be subdivided into two groups. As will be shown, the molecules C_nX and XC_nY ($X, Y = O, S$) exhibit linear structures in their electronic ground states as well as in their low-lying electronically excited states. Under this supposition heterocumulenes with an odd number of carbon atoms have a closed-shell singlet ground state, whereas those with an even number of carbon atoms are diradicals and should have, therefore, a triplet ground state according to Hund's rule. This phenomenon can easily be explained by counting the π-electrons. In Scheme 2 small carbon dioxides and monoxides are represented in localized pictures by means of two-center bonds and free



SCHEME 2 Schemes for counting π-electrons.

electron pairs. These formulae should not be regarded as actual Lewis structures as will be shown later. Instead, they are simple models for counting π-electrons. In addition, delocalized valence π-orbitals are sketched by their nodes. One of the two free electron pairs on oxygen has π character. Therefore, systems with an odd number of carbon atoms have $4n$ π-electrons, and those with an even number of carbon atoms have $4n+2$ π-electrons, where n is an integer which has a different meaning for monoxides (n = number of carbon atoms − 1) and dioxides (n = number of carbon atoms + 1). According to the two-fold degeneracy of π-orbitals, systems with an odd number of carbon atoms have a singlet closed-shell ground state, but systems with an even number of carbon atoms are open-shell systems (diradicals).

Most of the computational methods are tailored for closed-shell systems in their singlet ground states. Doublet and triplet states can be calculated by applying the corresponding methods for open-shell systems. Open-shell singlet states, however, require specific computational procedures. A fundamental task of group theory is the determination of the spectroscopic states of a system such as OC_2O in $D_{\infty h}$ symmetry (Scheme 2) in which two electrons occupy a degenerate pair of orbitals x and y:

After separating the totally symmetric closed-shell core, the pair of degenerate π-orbitals x and y is considered with different possibilities of spin functions α and β according to the Pauli principle. The result is three spectroscopic states with the following wavefunctions (unnormalized) for the two unpaired electrons:

$$\begin{array}{ll} {}^1\Sigma_g^+: & |x\alpha(1)x\beta(2)| + |y\alpha(1)y\beta(2)| \\ {}^1\Delta_g: & |x\alpha(1)x\beta(2)| - |y\alpha(1)y\beta(2)| \\ & |x\alpha(1)y\beta(2)| + |y\alpha(1)x\beta(2)| \\ {}^3\Sigma_g^-: & |x\alpha(1)y\alpha(2)| \end{array} \qquad (1)$$

A simple qualitative analysis of total energies yields the following energetic sequence of states:

$$E(^3\Sigma_g^-) < E(^1\Delta_g) < E(^1\Sigma_g^+).$$

The much discussed singlet–triplet gap of diradicals, $E(^1\Delta_g) - E(^3\Sigma_g^-)$, is twice the exchange integral $K_{xy} = \iint x(1)y(1)1/r_{12}x(2)y(2)\,\mathrm{d}V_1\,\mathrm{d}V_2$ which is a positive number. At the level of (1) Hund's rule is strictly fulfilled:

$$E(^1\Delta_g) - E(^3\Sigma_g^-) = 2K_{xy} > 0. \qquad (2)$$

Actually, however, the pair of orbitals x and y can be different in different states, and the simple form of the wavefunctions (1) can be extended by configuration interaction (CI). Then, the phenomenon of Hund's rule is a matter of experience which cannot easily be explained theoretically, i.e. by simple pictures. Hund's rule can be violated (twisted ethene (D_{2d}), square cyclobutadiene (D_{4h}), Mg atom).

In the literature, singlet diradicals are often calculated in the framework of the restricted Hartree–Fock (RHF) procedure. According to the spectroscopic states (1) the RHF wavefunction does not describe a state,

$$\Psi(\mathrm{RHF}) = |x\alpha(1)x\beta(2)| = \tfrac{1}{2}\{\Psi(^1\Delta_g) + \Psi(^1\Sigma_g^+)\}. \qquad (3)$$

The RHF wavefunction is the average of the two lowest-lying singlet states. Consequently, the erroneously calculated singlet–triplet gap turned out to be too large. Dubious perturbational corrections of the improper use of the unrestricted Hartree–Fock (UHF) method for singlet states yield "singlet–triplet gaps" much too low. In the linear $D_{\infty h}$ arrangement of nuclei Ψ(RHF) is not an irreducible representation of the $D_{\infty h}$ group, but one of D_{2h}. As a consequence, complete optimization of the singlet geometry at the RHF level as well as at MPn, CCSD, CISD levels, which are based on RHF, yields bent structures.

A qualitatively correct treatment of singlet diradicals can be achieved only at the multiconfiguration SCF (MCSCF) level in the framework of the complete active space SCF (CASSCF). The least effort which yields qualitatively correct states can be achieved by CAS(2,2). This term describes the use of all configurations which can be obtained by distributing two electrons in two orbitals (cf. the term (1)). An extended active space is used to calculate the geometries of all open-shell systems XC_nY and C_nX with even numbers of carbon atoms in their states $^3\Sigma_g^-$ and $^1\Delta_g$. At this level (4), which is called CAS(6,6), the complete sets of vibrational wavenumbers are calculated in order to characterize the stationary points. For example, the ground state configuration for XC_2X systems ($D_{\infty h}$), indicating the CAS(6,6) level, is as follows:

$$(2\pi_g)^4(3\pi_u)^2(3\pi_g)^0 \tag{4}$$

Experience has shown that a useful complete active space requires a good balance of occupied and vacant orbitals.

The basis sets cc-pvDZ (correlation consistent polarized valence double zeta) are employed which are, in standard notation: (3s, 2p, 1d) for C and O; (4s, 3p, 1d) for S. These calculations were carried out using the GAUSSIAN 94 package of programs.[8] The CAS(6,6) calculations were redone at the calculated geometries using the program system MOLPRO 96[9] to achieve a multireference wave function for extensive CI (configuration interaction) in the framework of ACPF (averaged coupled pair functional). The latter level is the most reliable one for calculated singlet–triplet gaps. Finally, the ground states of all systems, closed-shell as well as open-shell, were calculated at the density functional theory (DFT) using Becke's gradient-corrected exchange-correlation density functionals (B3LYP), and employing the extended basis sets cc-pvTZ, which are, in standard notation: (4s, 3p, 2d, 1f) for C and O; (5s, 4p, 2d, 1f) for S. The corresponding ground state properties such as geometries, vibrational wavenumbers and absorption intensities, and dipole moments are given in the tables. The IR absorption intensities are given in percent of the most intense absorption; the calculated absolute reference values are given in footnotes. Dissociation energies are calculated in specific cases at the coupled cluster level CCSD(T). For some selected systems the electronic structure was analyzed by means of natural bond orbitals (NBO) which allow to suggest the most relevant Lewis structure or at least a resonance structure and to discuss electron delocalization.[10] The computational procedures and molecular properties are summarized in Table I.

TABLE I Molecular properties and computational methods

Geometries, vibrational wavenumbers of diradicals in the states $^3\Sigma^-$ and $^1\Delta$	CAS(6,6)/cc-pvDZ (not reported)
Singlet–triplet energy gaps $E(^1\Delta)-E(^3\Sigma^-)$ of diradicals	CAS(2,2)/cc-pvDZ (single point calculations) CAS(6,6)/cc-pvDZ CAS(6,6)-ACPF/cc-pvDZ (single point calculations) (Table VI)
Geometries, vibrational wavenumbers, dipole moments, rotational constants, NBO analysis	B3LYP/cc-pvTZ (Tables II, III, IV, V, VII)
Dissociation energies for open-shell (triplet) ground states	UCCSD(T)/cc-pvTZ with geometries and zero-point energies from B3LYP/cc-pvTZ (Table VIII)
Vertical electronic transition energies and oscillator strengths	CIS/aug-cc-pvDZ with geometries from B3LYP/cc-pvTZ (Table IX)

3. HETEROCUMULENES

The computational results should not be discussed system by system. Instead, families will be presented which are columns or rows in Scheme 1.

3.1. Polycarbon Monoxides, C_nO

The closed-shell carbon monoxides C_5O, C_7O and C_9O were identified by their rotational spectra very recently.[7a] Bond lengths are given only for the system C_5O where linearity is assumed. The corresponding values are compared with calculated data in Table II. Apparently the experimental values for C1–C2 and C2≡C3 have been exchanged by mistake. This suspicion is supported by the assumed Lewis structure

$$^-{:}C5{\equiv}C4{-}C3{\equiv}C2{-}C1{\equiv}O{:}^+$$

1

which exhibits bond alternation as is actually observed in the calculated structure. The NBO analysis of C_5O yielded only a resonance structure of the type **1** where strong π-electron delocalization is apparent. Either C≡C triple bond donates 11% of its π-charge into the vacant non-Lewis π^*-orbitals of the C2≡C3 and C1≡O triple bonds. The Lewis π-charge is only 88.66% of the 12 π-electrons. A computational study of the series C_nO, $n = 3$–9, suffers from the limited basis sets used.[11] Their calculated

TABLE II B3LYP/cc-pvTZ calculated molecular ground state geometries (bond lengths in Å) for the C_nX ($C_{\infty v}$) and XC_nY (X, Y = O, S) ($C_{\infty v}$ or $D_{\infty h}$) families

	n	C1=O	C1=S	C1=C2	C2=C3	C3=C4	C4=C5	C5=C6	C=S
C_nO	2	1.1620		1.3556					
	3	1.1488		1.2942	1.2670				
		(1.150)[a]		(1.306)	(1.254)				
	4	1.1631		1.2832	1.2818	1.3044			
	5	1.1555		1.2828	1.2592	1.2897	1.2744		
		(1.1562)[b]		(1.2552)	(1.2881)	(1.2947)	(1.2736)		
	6	1.1628		1.2810	1.2737	1.2734	1.2865	1.2934	
OC_nO	3	1.1597		1.2715					
		(1.1632)[c]		(1.2894)					
	4	1.1721		1.2779	1.2817				
	5	1.1621		1.2757	1.2699				
OC_nS	2	1.1749		1.2791					1.5799
	3	1.1613		1.2765	1.2688				1.5584
		(1.1343)[c]		(1.2696)	(1.2540)				(1.5825)
		(1.163)[d]		(1.289)	(1.289)				(1.554)
	4	1.1696		1.2767	1.2816	1.2721			1.5734
	5	1.1627		1.2765	1.2700	1.2740	1.2711		1.5614
SC_nS	2		1.5767	1.2719					
	3		1.5595	1.2728					
			(1.56)[c]	(1.28)					
	4		1.5716	1.2701	1.2842				
	5		1.5611	1.2720	1.2737				
	6		1.5695	1.2706	1.2816	1.2698			
C_nS	2		1.5712	1.3094					
			(1.567)[e]	(1.310)					
	3		1.5426	1.2892	1.2749				
			(1.5323)[f]	(1.3028)	(1.2724)				
	4		1.5640	1.2735	1.2878	1.2942			
	5		1.5507	1.2783	1.2635	1.2897	1.2765		

[a][13]; [b][7b]; [c][36]; [d][38]; [e][20]; [f][21].

bond lengths for C_5O differ markedly from the experimental values as well as from the recent calculations in Table II which are in close agreement with CCSD(T)/cc-pvTZ calculations.[12] There is a second species among C_nO for which the structure was deduced from microwave spectroscopy.[13] The experimental structure of C_3O is in fair agreement with the recent calculations in Table II. Resonance structures for C_3O, as suggested by Pauling for a proper description of the related systems OCO and OC_3O, are discussed in the literature[14] and are presented in Scheme 3. Nowadays, these resonance structures can be calculated by means of the NBO procedure. The most important result of these calculations is the fact that none of these resonance structures is a good Lewis structure. The criterion of the amount of π-charge, out of the 8 valence electrons, which occupies localized Lewis orbitals is not fulfilled,

Resonance structure		Lewis π-charge in percent of 8 electrons
$^{-}$:C3≡C2−C1≡O:$^{+}$	**2a**	92.15
:C3=C2=C1=O::	**2b**	85.31
$^{+}$:C3−C2≡C1−O:::$^{-}$	**2c**	78.47
C3-----C2-----C1-----O 1.267 1.294 1.149		Bond lengths [Å]
C3-----C2-----C1-----O 0.24 -0.66 0.77 -0.35		Natural net atomic charges
⊖---------------⊕		Dipole moment 2.28 D

SCHEME 3 Different B3LYP/cc-pvTZ calculated resonance structures of C_3O, characterized by the Lewis π-charge in percent of 8 π-electrons, compared with bond lengths, natural net atomic charges and dipole moments.

i.e. the Lewis π-charge is considerably lower than 100%. For comparison, the usual formula with cumulated double bonds for the parent compound $H_2CC_3CH_2$ is a good Lewis structure which is characterized by a weight of 93.97% for the Lewis π-charge of the 8 π-electrons. In contrast, the Kekule formula of benzene is a resonance structure which is characterized by only 83.21% weight for the Lewis π-charge of the 6 π-electrons. For C_3O in the zwitterionic formula **2a**, the C2≡C3 triple bond donates 11% of the π-charge into vacant non-Lewis π^*-orbitals of the C1≡O triple bond. Thus, C_3O is stabilized by electron delocalization, in the description of **2a**, but is the only useful Lewis structure. It is interesting to note that the best resonance structure (in the sense of Lewis) is that where the octet rule is fulfilled (**2a**). This zwitterionic structure with a positively charged oxygen explains correctly the alternation of bond lengths as well as the large dipole moment of 2.39 D[15] in Table III. For comparison, the neutral double bond resonance structure **2b** commonly used is quite irrelevant and unable to explain molecular properties. The natural atomic charges of C_3O where the carbon atom C2 carries much more electronic net charge than the oxygen, which itself is negatively charged, is not in contradiction to the favored resonance formula **2a** where oxygen has a positive sign. The reason can be seen in the C≡O triple bond. Their localized two-center π-bond orbitals are highly polarized to oxygen by 73%. Therefore, the natural net atomic charge at oxygen has actually

TABLE III B3LYP/cc-pvTZ calculated dipole moments (*D*) compared with experimental data. The positive end of the dipole moment is at X for C_nX, and at S for OC_nS

	C_2O	C_3O	C_4O	C_5O	C_6O
Calc.	1.38	2.28	2.66	3.58	3.79
Exp.		2.39[a]			

	OC_2S	OC_3S	OC_4S	OC_5S
Calc.	1.05	0.61	0.95	0.60
Exp.		0.63[b]		

	C_2S	C_3S	C_4S	C_5S
Calc.	3.00	3.66	4.22	4.88
Exp.		3.70[c]		(4.5)[d]

[a][15]; [b][38]; [c][26]; [d][27].

a negative value (electron excess). The direction of the dipole moment can be understood in terms of the large separation of the charged zwitterionic centers.

The results of microwave spectroscopy of triplet carbon monoxides C_2O, C_4O, C_6O and C_8O were published by the same authors at the same time[7a] as those of the closed-shell systems described above.[7b] The triplet ground states of C_4O and C_6O were first identified by ESR spectroscopy.[2] IR spectra are available for C_2O,[16] C_3O[17] and C_4O.[1a] The IR spectra were assigned by different computational methods such as MNDO[1a] or BLYP/6-311G*.[11] In Table IV all experimentally detected systems C_nO up to $n = 6$ are presented by their B3LYP/cc-pvTZ calculated harmonic vibrational wavenumbers and absorption

TABLE IV B3LYP/cc-pvTZ calculated harmonic vibrational wavenumbers (cm^{-1}) and absorption intensities (in percent of the strongest band, absolute intensities ($km\,mol^{-1}$) in footnotes), assigned to the data from IR spectroscopy

State	*Calc.*		*Exp.*	
C_2O				
Σ	2031	(100)[a]	1978[f]	
Σ	1105	(14)	1074	
Π	380	(28)	381	
C_3O				
Σ	2337	(100)[b]	2243	(100)[g]
Σ	1976	(3)	1907	(2)
Σ	967	(0)	939	
Π	602	(2)	580	(3)
Π	147	(0)	120	
C_4O				
Σ	2294	(100)[c]	2222	(100)[h]
Σ	1985	(48)	1920	(65)
Σ	1469	(2)	1431	(4)
Σ	773	(1)	775	(1)
Π	505	(2)	484	(6)
Π	370	(1)		
Π	134	(1)		
C_5O				
Σ	2342	(100)[d]		
Σ	2229	(22)		
Σ	1919	(11)		
Σ	1307	(0)		
Σ	664	(0)		
Π	565	(1)		
Π	548	(0)		
Π	208	(0)		
Π	83	(0)		

TABLE IV (*Continued*)

State	*Calc.*		*Exp.*
C_6O			
Σ	2293	(100)[e]	2164[i]
Σ	2139	(11)	
Σ	1974	(5)	
Σ	1609	(8)	
Σ	1105	(0)	
Σ	569	(0)	
Π	518	(1)	
Π	505	(0)	
Π	360	(0)	
Π	182	(0)	
Π	75	(0)	

[a] 141 km mol^{-1}; [b] 1542; [c] 776; [d] 3549; [e] 2499; [f] [16]; [g] [17]; [h] [1a]; [i] [18], absorption at 1448 cm^{-1} cannot be assigned to a calculated fundamental transition.

OC_3O				
Σ_u	2396	(100)[a]	2258[d]	
Σ_g	2265	(0)	2197	
Σ_u	1647	(3)	1575	
Σ_g	783	(0)	786	
Π_g	589	(0)	573	
Π_u	567	(2)	550	
Π_u	56	(0)	18	
OC_4O				
Σ_g	2365	(0)	2277	(0)[e]
Σ_u	2205	(100)[b]	2130	(100)
Σ_g	1868	(0)	1816	(0)
Σ_u	1306	(4)	1277	(7)
Σ_g	642	(0)	642	(0)
Π_u	488	(1)	467	(2)
Π_g	466	(0)		
Π_g	280	(0)		
Π_u	100	(0)		
OC_5O				
Σ_g	2369	(0)		
Σ_u	2315	(100)[c]	2242	(100)[f]
Σ_u	2131	(7)	2065	(34)
Σ_g	1720	(0)	1665	
Σ_u	1147	(1)	1152	(3)
Σ_g	562	(0)	573	
Π_g	561	(0)	530	
Π_u	561	(1)	542	(3)
Π_u	504	(0)	474	(1)
Π_g	143	(0)	145	
Π_u	56	(0)		

[a] 2942 km mol^{-1}; [b] 2087; [c] 6792; [d] [37]; [e] [33]; [f] [1].

TABLE IV (*Continued*)

State	*Calc.*		*Exp.*	
OC$_2$S				
Σ	2238	(100)[a]	2156	(100)[e]
Σ	1536	(18)	1505	(20)
Σ	692	(0)	685	
Π	470	(2)	452	(9)
Π	186	(0)		
OC$_3$S				
Σ	2331	(100)[b]	2240	(vs)[f]
Σ	2015	(5)	1952	(s)
Σ	1298	(7)	1275	(s)
Σ	609	(0)	602	(vw)
Π	565	(1)	544	(m)
Π	461	(0)	438	
Π	93	(0)	83	
OC$_4$S				
Σ	2295	(100)[c]	2210	(100)[g]
Σ	2071	(26)	1999	(22)
Σ	1667	(0)	1625	(1)
Σ	1065	(5)	1056	(5)
Σ	521	(0)	486	(2)
Π	504	(1)		
Π	458	(0)	428	(1)
Π	258	(0)		
Π	86	(0)		
OC$_5$S				
Σ	2323	(100)[d]	2227	(100)[h]
Σ	2223	(58)	2138	(72)
Σ	1949	(24)	1881	(29)
Σ	1481	(2)	1448	(3)
Σ	954	(4)	945	(4)
Π	555	(0)		
Π	522	(0)		
Σ	469	(0)	463	
Π	445	(0)		
Π	156	(0)		
Π	57	(0)		

[a]553 km mol^{-1}; [b]3127; [c]1621; [d]4234; [e][29]; [f][37]; [g][22]; [h][39].

SC$_2$S				
Σ_g	1972	(0)	1904[f]	
Σ_u	1184	(100)[a]	1179	(100)
Σ_g	554	(0)	546	
Π_g	433	(0)		
Π_u	179	(1)		
SC$_3$S				
Σ_u	2167	(100)[b]	2088	(100)[g]
Σ_g	1720	(0)	1663	
Σ_u	1038	(11)	1030	(19)

TABLE IV (*Continued*)

State	*Calc.*		*Exp.*	
Π_u	508	(0)	502	
Σ_g	502	(0)	485	
Π_g	420	(0)	470	
Π_u	102	(0)	94	
SC_4S				
Σ_g	2127	(0)	2021	(0)[h]
Σ_u	1940	(100)[c]	1872	(100)
Σ_g	1415	(0)	1382	(0)
Σ_u	885	(18)	898	(12)
Π_g	492	(0)		
Σ_g	442	(0)	423	(0)
Π_u	428	(0)		
Π_g	256	(0)		
Π_u	79	(0)		
SC_5S				
Σ_u	2202	(100)[d]	2105	(100)[i]
Σ_g	2127	(0)		
Σ_u	1735	(26)	1688	(36)
Σ_g	1279	(0)		
Σ_u	810	(4)	784	(4)
Π_u	530	(0)		
Π_g	474	(0)		
Π_u	420	(0)		
Σ_g	405	(0)		
Π_g	165	(0)		
Π_u	54	(0)		
SC_6S				
Σ_u	2120	(100)[e]		
Σ_g	2096	(0)		
Σ_g	1920	(0)		
Σ_u	1526	(30)		
Σ_g	1121	(0)		
Σ_u	723	(8)		
Π_g	509	(0)		
Π_u	475	(0)		
Π_g	421	(0)		
Σ_g	367	(0)		
Π_u	293	(0)		
Π_g	140	(0)		
Π_u	46	(0)		

[a]121 km mol^{-1}; [b]3046; [c]801; [d]5999; [e]1976; [f][30]; [g][37]; [h][22]; [i][40].

C_2S				
Σ	1726	(100)[a]	1667[e]	
Σ	863	(24)	863	
Π	281	(16)		
C_3S				
Σ	2140	(100)[b]	2046	(100)[f]
Σ	1567	(4)	1533	(10)

TABLE IV (*Continued*)

State	*Calc.*		*Exp.*	
Σ	739	(1)	726	(1)
Π	504	(0)		
Π	165	(0)		
C_4S				
Σ	2111	(9)		
Σ	1812	(100)[c]	1757	(100)[g]
Σ	1225	(0)		
Σ	613	(1)		
Π	494	(0)		
Π	322	(1)		
Π	128	(1)		
C_5S				
Σ	2231	(100)[d]		
Σ	2085	(0)		
Σ	1656	(15)		
Σ	1091	(2)		
Π	556	(0)		
Σ	544	(0)		
Π	459	(0)		
Π	217	(0)		
Π	84	(0)		

[a]50 km mol^{-1}; [b]1532; [c]522; [d]4015; [e][41]; [f][22]; [g][39].

TABLE V Effective $\bar{r}$(C–C) bond lengths (Å) in C_nO systems by fixing C–O = 1.155 Å (from microwave spectroscopy[7]) compared with calculated (Table II) averaged $\bar{r}$(C–C) values

n	2	3	4	5	6
MW $\bar{r}$(C–C)	1.3704	1.2806	1.2920	1.2777	1.2830
Calc. $\bar{r}$(C–C)	1.3556	1.2806	1.2898	1.2765	1.2816
$\bar{r}$(C–O)	1.1620	1.1488	1.1631	1.1555	1.1628

intensities. All C_nO systems are characterized by one extremely strong absorption near 2000 cm^{-1} and two to four weaker bands at lower wavenumbers. Microwave spectroscopy of the C_nO systems yielded effective C–C bond lengths which decrease gradually to a converging value of roughly 1.28 Å as n becomes larger.[7a] All the C–C bond lengths are assumed to be equal in a molecule with r(C–O) fixed at 1.155 Å. The effective C–C bond lengths as determined by microwave spectroscopy are compared with the averaged calculated C–C bond lengths from Table II. As can be seen in Table V there is excellent agreement, with the exception of the smallest member ($n = 2$) of this series. The excitation energy of the $^1\Sigma^+$ state seems to become smaller as the carbon chain is lengthened, because the spin–spin interaction constant is found to increase rapidly with n; $^1\Sigma^+$ excited states contribute to this constant through second-order perturbation of the spin–spin interaction. In Table VI the calculated energy gaps between the lowest excited singlet state, $^1\Delta$, and the ground state, $^3\Sigma^-$, confirm this trend, too. The comparison of calculated with experimental rotational constants of C_nO species is presented in Table VII.

3.2. Polycarbon Monosulfides, C_nS

The sulfur-containing carbon-chain family is one of the most principal constituents of the interstellar media. In particular, C_2S and C_3S have been found to be ubiquitous and abundant. Different models have been suggested for the production of C_nS in interstellar space where polyacetylene HC_nH and the abundant ion S^+ play a significant role.[19]

TABLE VI Singlet–triplet energy gaps $E(^1\Delta) - E(^3\Sigma^-)$ (kcal mol^{-1}) calculated at three different levels of theory. The CAS(6,6)-ACPF data might be the most reliable ones

	CAS(2,2)	*CAS*(6,6)	*CAS*(6,6)-*ACPF*
O_2[a]	30.7	24.4	24.2
C_2O	23.5	20.7	17.2
OC_2S	13.5	8.4	8.8
SC_2S	12.0	10.9	7.9
C_2S	15.1	11.4	11.6
C_4O	12.0	10.4	7.8
OC_4O	11.5	9.3	5.6
OC_4S	9.0	7.0	5.7
SC_4S	8.8	7.9	4.4
C_4S	6.2	8.7	5.7
C_6O	4.9	8.3	3.6
SC_6S	7.1	6.5	2.4

[a]Experimental value 22.6 kcal mol^{-1}.

TABLE VII B3LYP/cc-pvTZ calculated rotational constants B_e (MHz) compared with B_o values from microwave spectroscopy for C_nO and C_nS species

n	C_nO		C_nS	
	B_e (*calc.*)	B_o (*exp.*)[a]	B_e (*calc.*)	B_o (*exp.*)
2	11614.16	11545.60	6461.55	6477.75[b]
3	4814.51	4810.89	2891.51	2890.38[c]
4	2356.86	2351.26	1520.32	1519.16[d]
5	1369.44	1366.85	924.39	922.70[e]
6	852.05	849.76		

[a][7]; [b][20]; [c][24]; [d][19]; [e][25].

Bond lengths are available from microwave spectroscopy for the small systems C_2S[20] and C_3S.[21] The corresponding values are compared with calculated data in Table II. The IR spectrum of C_3S has been measured and assigned by MNDO calculations[22] (Table IV), and C_2S has been detected by mass spectrometric methods.[23] The complete series C_nS, $n = 2-5$, has been characterized by microwave spectroscopy.[20,24,19,25] The observed rotational constants B_o are in excellent agreement with the calculated B_e values in Table VII. The dipole moment of C_3S was measured to be 3.70 D by microwave spectroscopy,[26] but only a crude estimate of the dipole moment of C_5S (4.5 D) can be found in the literature.[27] The recently B3LYP/cc-pvTZ calculated value in Table III is slightly larger (4.88 D), and coupled cluster CCSD(T)/cc-pvTZ calculations yielded a value as large as 5.4 D (note in Ref. [27]). The dramatic increase of the dipole moment in the series C_nS (cf. Table III) with increasing chain length rules out heterocumulated double bonds in these species. Instead, the assumption of zwitterionic heteropolyacetylenes is confirmed by the sequence of dipole moments. Another interesting sequence can be seen in the most intense IR absorption which increases gradually as the separation of the zwitterionic centers is increased. Singlet and triplet ground states should be discussed separately. In addition, the search for the Lewis structure of C_3S resulted in a resonance structure

$$^{-}{:}C3{\equiv}C2{-}C1{\equiv}S{:}^{+}$$

3

which is stabilized be π-electron delocalization, similar to C_3O in the previous section. Only 89.76% of the π-charge (8 electrons) can be found in Lewis orbitals. In other words, the two π-bonds in C2≡C3 donate 18% of their charge into the non-Lewis C1–S π^*-orbitals. The calculated singlet–triplet energy gaps for C_2S and C_4S indicate the same trend as that for C_2O and C_4O. The excitation energy of the lowest singlet state becomes smaller as the carbon chain is lengthened.

3.3. Dicarbon-chalcogeno Heterocumulenes, OC_2O, OC_2S, SC_2S

The comparison of the systems XC_2Y is interesting in so far that OC_2S as well as SC_2S have been detected mass spectroscopically[28,3] and also by matrix IR spectroscopy,[29,30] in combination with quantum chemical calculations. In contrast, all attempts to isolate OC_2O in a matrix have failed so far; the same is true for the gas phase.[29,4a] The first computational comparison of OC_2O and SC_2S goes back to 1983.[31] Recent calculations of the bond dissociation energies for $XC_2Y \rightarrow CX + CY$ and their comparison in Table VIII reveals a high thermodynamic instability of OC_2O. The reason for this instability of OC_2O can be seen in the high stability of the decay product CO which exhibits one of the strongest bonds (256 kcal mol^{-1}), in contrast to CS (169 kcal mol^{-1}). Thus, the non-existence of OC_2O can be compared, for example, to that of the isoelectronic tetrahedral N_4. No experimental geometries are available for OC_2S and SC_2S. However, the excellent agreement of the calculated vibrational wavenumbers with the IR spectra in Table IV supports the calculated geometries in Table II. Recently calculated CAS(6,6)-ACPF/cc-pvDZ singlet–triplet gaps ($E(^1\Delta) - E(^3\Sigma^-)$) were found to be 8 kcal mol^{-1} for both systems (Table VI). Exploratory calculations for SC_2S where the complete active space is extended to CAS(10,10) (this is the complete valence π-space) leads to a drastic reduction of the singlet–triplet energy gap from 10.9 (CAS(6,6)) to 6.1 kcal mol^{-1}. The extension of the reference wavefunction is prohibitively large for a subsequent CI calculation. Since 1996, the energetic near-equality of singlet and triplet states for SC_2S (44 electrons) in the older literature[30,32] could not be reproduced by recent programs

TABLE VIII UCCSD(T)/cc-pvTZ calculated bond dissociation energies D_0 (kcal mol^{-1}) for $XC_2Y \rightarrow CX + CY$ and $XC_4Y \rightarrow C_3X + CY$ or $CX + C_3Y$ (all systems in their ground states)

$XC_2Y \rightarrow CX + CY$	
$OC_2O \rightarrow CO + CO$	−61.1
$OC_2S \rightarrow CO + CS$	−5.7
$SC_2S \rightarrow CS + CS$	41.7

$XC_4Y \rightarrow C_3X + CY$	
$OC_4O \rightarrow C_3O + CO$	2.9
$OC_4S \rightarrow C_3O + CS$	49.3
$OC_4S \rightarrow C_3S + CO$	14.2
$SC_4S \rightarrow C_3S + CS$	59.8

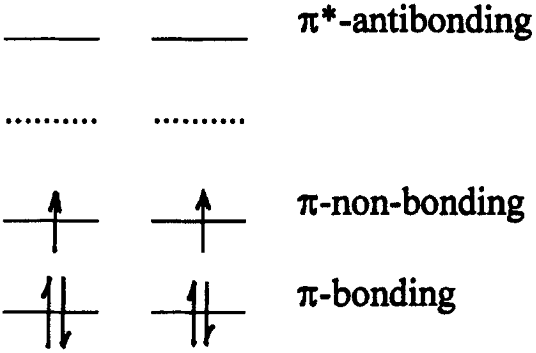
and computers (64 bit). In the past, CAS(6,6) yielded correct results only for small systems (O_2, S_2); for SC_2S such calculations were apparently restricted to CAS(2,2).[32]

3.4. *Tetracarbon-chalcogeno Heterocumulenes, OC_4O, OC_4S, SC_4S*

The only source for geometries of this series of diradicals is again quantum chemical calculations (Table II). Matrix IR spectra are available for these systems, accompanied by semiempirical (MNDO, PM3) calculations.[22,33] Symmetry-forbidden vibrational transitions have been determined from combination bands. A comparison of the IR spectra with recently performed B3LYP/cc-pvTZ calculations can be found in Table IV. The calculated singlet–triplet energy gaps ($E(^1\Delta) - E(^3\Sigma^-)$) for all three systems is reduced, with respect to the previously described XC_2Y series, to roughly 5 kcal mol^{-1} (Table VI). The question of the thermochemical stability of the XC_4Y systems with respect to the different possibilities of decay $XC_4Y \rightarrow C_3X + CY$ or $CX + C_3Y$ can be answered by inspection of Table VIII. Whenever the decay product is CO, there is a strong reduction of the dissociation energy D_0 (cf. also XC_2Y in Table VIII). Since heterocumulenes can be prepared by matrix photolysis, their UV spectra are of interest. For a group of ten systems XC_nY ($X, Y = O, S$ and $n = 2$–5), the UV absorptions can be found summarized.[22] The comparison with improved virtual orbital (IVO) calculated electronic excitations is restricted to systems with $n = 4$. Meanwhile, extended configuration interaction including singly excited configurations, CIS, can be applied to these systems. The excited triplet state energies for XC_4Y systems are related to the corresponding restricted open-shell (ROHF) triplet ground states. Augmented basis sets, aug-cc-pvDZ, have been employed to consider excited Rydberg states. A common result for all three species, OC_4O, OC_4S, and SC_4S, is an extremely dense ladder of excited states. According to the calculated oscillator strengths, almost all electronic transitions are symmetry-forbidden with two exceptions. These are the third (or fourth) state which exhibits low oscillator strength compared with the ninth (or tenth) state which indicates intense transitions at shorter wavelengths. The data in Table IX should be completed by characterizing the two types of excited states by means of the π-orbital space in Scheme 4. The weak transition at longer

TABLE IX CIS/aug-cc-pvDZ calculated vertical electronic transitions (nm), oscillator strengths in parentheses, for XC_4Y diradicals, compared with experimental UV absorption[22]

	Intensive		*Weak*	
	Calc.	*Exp.*	*Calc.*	*Exp.*
OC_4O	195 (2.06)	212	306 (0.19)	340
OC_4S	225 (1.99)	238	403 (0.41)	426
SC_4S	296 (2.50)	272	508 (0.64)	514



SCHEME 4 Orbital scheme for the characterization of electronic transitions.

wavelengths corresponds to the promotion of an electron from a doubly occupied π-bonding orbital to a singly occupied π-non-bonding orbital. The intense transition at shorter wavelengths corresponds to the promotion of an electron from a singly occupied π-non-bonding orbital (SOMO) to one of the higher lying vacant π^*-anti-bonding orbitals. In $D_{\infty h}$ symmetry, these are $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$ transitions. The CIS method fails for the proper description of the UV absorption of closed-shell systems of the type XC_nY (n odd). Most probably, doubly excited configurations are important in these cases. The UV absorptions described lead to photoequilibria of the type

$$XC_nY \rightleftharpoons CX + C_{n-1}Y. \tag{5}$$

All members of the XC_4Y family have been observed in the gas phase by mass spectrometric methods.[34,35,6a,23]

3.5. Tricarbon-chalcogeno Heterocumulenes, OC_3O, OC_3S, SC_3S

These systems have been well known for a long time, but problems arise when the calculated geometries in Table II are to be compared with experimental values. Three different experimental methods have been applied to three different compounds.[36] Electron diffraction (ED) data are available for OC_3O; however, this system exhibits a quasi-linear structure. Two different sets of bond lengths are deduced from microwave spectroscopy for OC_3S, and the crude estimates for the geometry data of SC_3S are based on IR spectroscopy. The excellent agreement of the calculated rotational constant (1411.17 MHz) for OC_3S with the value from microwave spectroscopy (1413.90 MHz)[38] supports the calculated geometry among the three sets of data in Table II. Furthermore, the calculated dipole moment is in perfect agreement with experiment (Table III). The IR spectral data of all members of the XC_3Y group are summarized in Table IV and can be compared with computational results. Considerable attention is paid to the lowest bending vibrations of these species. The calculated wavenumbers (cm^{-1}) are summarized in Table IV, OC_3O 56 (18[37] or 22[38]); OC_3S 93 (83[36–38]); SC_3S 102 (94[37,38]), and compared with the experimentally based values in parentheses. These wavenumbers indicate the exceptional role of carbon suboxide in the XC_3Y series. Compound OC_3O exhibits a quasi-linear behavior due to the extremely low bending wavenumber. The search for an explanation of the quasi-linear structure of OC_3O among the members of the XC_3X family can commence with the NBO analysis. It can be seen in Scheme 5 that only the parent cumulene ($X = CH_2$) has a double bond Lewis structure (**4a**) with 94% Lewis π-charge. For the systems $X = O, S$ the double bond structure is by far the worst presentation, with Lewis π-charges of 73% and 71%, respectively. The zwitterionic triple bond resonance formula **4c** suggested by Pauling is much more favored. However, there is an additional favored formula in which the central carbon atom C2 carries two free electron pairs with two excess electrons **4b**. This resonance structure turned out to be more realistic for $X = O$ than for $X = S$, due to the different Lewis π-charges. A carbon atom in an unusual situation such as in **4b** tends to be a center of bending, due to the separation of the free electron pairs. Two facts are indicated in Scheme 5 which emphasize the importance of the unusual resonance structure **4b** for $X = O$. These are on one hand the extremely

X = O	X = CH_2	X = S	
	$::X{=}C1{=}C2{=}C3{=}X::$		**4a**
73.38	93.97	71.36	
	$^{+}:X{\equiv}C1-{}^{-}:C2:^{-}-C3{\equiv}X:^{+}$		**4b**
87.55		84.14	
	$^{+}:X{\equiv}C1-C2{\equiv}C3-X:::^{-}$		**4c**
87.50		85.36	
O ---- C1 ----C2 --	H_2C --- C1 --- C2 --	S ---- C1 ---- C2 ---	
-0.41 0.71 -0.60	0.01 0.05 -0.12	0.21 -0.05 -0.31	
56 (-20)	154	102 (94)	

SCHEME 5 Comparison of B3LYP/cc-pvTZ calculated resonance structures of OC_3O, $H_2CC_3CH_2$, and SC_3S, characterized by their Lewis π-charges in percent of 12 π-electrons. At the bottom, natural net atomic charges, and the lowest calculated wavenumbers (cm^{-1}) of the bending (at C2) vibrations (experimental values in parentheses).

high electronic charge at the central carbon atom C2 and, on the other hand, the extremely low bending wavenumber. There is an almost perfect linear relation between the net charge on C2 and the bending wavenumber for the three species.

3.6. Pentacarbon-chalcogeno Heterocumulenes, OC_5O, OC_5S, SC_5S

IR spectra are available for these systems which were assigned by quantum chemical calculations in the original literature.[1,39,40] The most intense Σ_u vibration near 2200 cm^{-1} of the XC_5X species has doubled its intensity with respect to the corresponding XC_3X

compounds (Table IV). This implies strong electronic charge separation which is confirmed by the NBO analysis. The system OC_5O prefer C≡O triple bonds like OC_3O (Scheme 5), but the two excess electrons occupy three-center π-orbitals. This new phenomenon is sketched in the resonance structure **5**.

$$^{+}{:}O{\equiv}C1{-}(C2{-}C3{-}C4)^{2-}{-}C5{\equiv}O{:}^{+}$$

5

There are two pairs of three-center π-orbitals where the centers C2, C3, and C4 are involved, the bonding and the non-bonding pair. The latter donates roughly 30% of its four electrons into the antibonding π^*-orbitals of the C≡O triple bonds. The Lewis π-charge of **5** turned out to be 89.94% which is considerably higher than the 87.55% for OC_3O. This sequence, however, could be misleading because three-center bond orbitals are chosen as elements of localization (due to their abundance in chemical structures) like two-center bond orbitals or free electron pairs. The pairs of three-center bond orbitals in **5** can be omitted if they are assumed to be rotated by 45°. Then, the following alternative resonance structure **6** might be important.

$$^{+}{:}O{\equiv}C1{-}{:}C2^{-}{=}C3{=}C4{:}^{-}{-}C5{\equiv}O{:}^{+}$$

6

The Lewis π-charge of **6** resulted to be 85.77%. The π-bond orbitals C2=C3 and C3=C4, and in particular the free π-electron pairs at the carbon centers donate into π^*-orbitals. The advantage of this resonance structure is to indicate the high natural net atomic charges of −0.42 at the carbon atoms C2 and C4 which exceed that of oxygen (−0.40). Similar to the arguments for the central C atom in OC_3O, the C atoms C2 and C4 tend to be centers of bending. Indeed, there is a Π_g bending vibration which exhibits an extremely low wavenumber ($145\,cm^{-1}$).

3.7. Iminoethenethione, HNC_2S, and Ethenedione Oxime, OC_2NOH

The linear geometry of "heterocumulenes" of the type XC_nY ($X, Y = O, S$) cannot be preserved upon substitution of X and/or Y by the NR group. Numerous compounds of the types $R^1NC_3NR^2$, but also $R^1R^2C_2NR^3$ (ketenimines), have been synthesized; concomitantly, the usual computational methods have been applied to yield geometries and vibrational wavenumbers.[5b] However, serious problems arise, even for the smallest compounds, if the energetically closely spaced electronic states and their different conformers are to be studied. Only two examples will be investigated here. One is iminoethenethione, HNC_2S, which has been characterized by NRMS experiments;[5a] the other example is ethenedione oxime, OC_2NOH,[4a] which has been identified by matrix IR spectroscopy.

If HNC_2S is investigated at first as a closed-shell system, the bond angles N–C–C and C–C–S resulted to be roughly 160° and 170°, respectively. Thus, the backbone of the cumulene can be regarded as a slightly disturbed linear arrangement of nuclei. As a consequence, the former $^1\Delta$ state (1) splits into $^1A' + {}^1A''(C_s)$. Application of CAS(6,6) at the ground state geometry yields the following sequence of low-lying electronic states: $1^1A'(0.0\,\text{kcal mol}^{-1})$, $^3A''(5.3)$, $^1A''(17.5)$, and $2^1A'(47.4)$. Hund's rule should be applied to the diradical pair $^3A''$ and $^1A''$ to recognize the feature of the XC_2Y family (Table VI). The other component of the $^1\Delta$ state is the parent state of the closed-shell ground state $1^1A'$, and $2^1A'$ originates from the $^1\Sigma^+$ state. Separate geometry optimization of the lowest singlet and triplet states and employment of the CAS(6,6)-ACPF procedure yielded a singlet–triplet energy gap, $E(1^1A') < E(^3A'')$, of $8.7\,\text{kcal mol}^{-1}$. These comments show how meaningless the application of only singly excited configurations (CIS) is to singlet states of diradicaloid systems. Another dubious point is the characterization of the C=C bond in HNC_2S. Does the value of $r(C{=}C) = 1.295\,\text{Å}$ really indicate a short bond? Certainly not, because the sp-hybridized C=C double bond standard value is 1.285 Å. The elongated C=C bond in HNC_2S can be understood by means of the NBO analysis. This example is the first one in this report which is actually a true heterocumulene. The acceptable Lewis structure is HN:=C=C=S::, however, two free electron pairs at N and S donate 15% of four electrons into the antibonding C=C π^*-orbital.

The system OC_2NOH has a singlet closed-shell ground state (C_s symmetry) according to MP2/6-31G* calculations[4a] as well as CAS(6,6)/cc-pvDZ and B3LYP/cc-pvTZ investigations. The deviation from linearity is characterized by the bond angles O–C–C larger than 160° and C–C–N near 130°. The calculated vibrational wavenumbers and intensities at various levels of theory yield a useful assignment of the

IR spectrum. A problem arises with the calculation of the higher lying triplet state. On one hand, in the MP2/6-31G* approach, C_s symmetry is retained, accompanied by bond angle increase: O–C–C = 177° and C–C–N = 162°. On the other hand, however, at the CAS(6,6)/cc-pvDZ level, rotation around the C=C bond occurs (C_1 symmetry) which leads to C–C bond elongation from 1.375 to 1.477 Å and bond angle decrease to O–C–C = 131°. Paradoxically, the relative energy of the triplet state at MP2/6-31G* and CCSD(T)//CAS(6,6)/cc-pvDZ levels, based on quite different triplet geometries, is identical with 44.4 kcal mol^{-1}. Compound OC_2NOH can be regarded, with some caution, as a true heterocumulene, according to the resonance structure **7** from the NBO analysis.

::O=C=C=N:–O::–H

7

However, the two free π-electron pairs at the oxygen atoms donate 13% of their charge into antibonding π*-orbitals.

4. CONCLUSIONS

This report summarizes computational results for C_nX and XC_nY systems (X = O, S) obtained by present state-of-the-art levels of theory. The most successful results can be seen in the characterization of C_nX systems by the NBO analysis which seeks to find the most relevant Lewis or resonance structures. All C_nX systems are found to be zwitterionic polyacetylenes. The corresponding resonance structures nicely explain the C–C bond alternation as well as the strong gradual increase of dipole moments and IR absorption intensities with the lengthening of the carbon chain. Moreover, even XC_nY systems do not contain cumulated double bonds.

Another progress can be seen in the accuracy of the calculated rotational constants obtained by density functional theory in conjunction with extended basis sets. The mean absolute deviation in percent of the mean value could be reduced with respect to the literature by one order of magnitude from 1% to 0.1%. As a consequence, the reported calculated geometries (bond lengths) are uncertain in the order of only 10^{-3} Å. Some progress is achieved also for the vibrational wavenumbers. The mean absolute deviation turned out to be $42\,\mathrm{cm}^{-1}$; this is 3.3% of the average value.

No satisfying consistency could be achieved for singlet–triplet energy gaps of diradicals. The successful computational methods are restricted in their application only to small systems as was found by exploratory calculations with a stepwise increase of effort. At present, all calculated diradicals possess linear structures for the lowest singlet and triplet states where the triplet is the ground state. Furthermore, the singlet–triplet gaps decrease with lengthening of the carbon chain. Needless to say slightly bent systems of the type XC_2Y ($X = NR$) require careful future investigations. A systematic treatment of electronically excited states (UV transitions) is, at present, out of range.

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REFERENCES

[1] (a) G. Maier, H. P. Reisenauer, U. Schäfer and H. Balli (1988). *Angew. Chem.*, **100**, 590; (1988) *Angew. Chem. Int. Ed. Engl.*, **27**, 566; (b) F. Holland, M. Winnewisser, G. Maier, H. P. Reisenauer and A. Ulrich (1988). *J. Mol. Spectr.*, **130**, 470.

[2] R. J. Van Zee, G. R. Smith and W. Weltner (1988). *J. Am. Chem. Soc.*, **110**, 609.

[3] D. Sülzle and H. Schwarz (1988). *Angew. Chem.*, **100**, 1384; (1988) *Angew. Chem. Int. Ed. Engl.*, **27**, 1337.

[4] (a) G. Maier, H. P. Reisenauer, B. Röther and J. Eckwert (1996). *Liebigs Ann.*, 303; (b) G. Maier (1991). *Pure Appl. Chem.*, **63**, 275; (c) G. Maier (1991). *Chem. Unserer Zeit*, **25**, 51.

[5] (a) R. Flammang, D. Landu, S. Laurent, M. Barbieux-Flammang, C. O. Kappe, M. W. Wong and C. Wentrup (1994). *J. Am. Chem. Soc.*, **116**, 2005; (b) R. Wolf, S. Stadtmüller, M. W. Wong, M. Barbieux-Flammang, R. Flammang and C. Wentrup (1996). *Chem. Eur. J.*, **2**, 1318.

[6] (a) D. Sülzle, N. Beye, E. Fanghänel and H. Schwarz (1990). *Chem. Ber.*, **123**, 2069; (b) D. Sülzle and H. Schwarz (1991). *Fund. Gas Phase Ion Chem.*, 237.

[7] (a) Y. Ohshima, Y. Endo and T. Ogata (1995). *J. Chem. Phys.*, **102**, 1493; (b) T. Ogata, Y. Ohshima and Y. Endo (1995). *J. Am. Chem. Soc.*, **117**, 3593.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople (1995). GAUSSIAN 94, Revision B.3, Gaussian, Inc., Pittsburgh, PA.

[9] H. J. Werner and P. J. Knowles (1996). MOLPRO 96, Version 96.4, University of Birmingham.

[10] E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold (1988). NBO Version 3.1, Wisconsin.

[11] N. Moazzen-Ahmadi and F. Zerbetto (1995). *J. Chem. Phys.*, **103**, 6343.

[12] P. Botschwina, J. Flügge and P. Sebald (1995). *J. Phys. Chem.*, **99**, 9755.

[13] R. D. Brown, P. D. Godfrey, P. S. Elmes, M. Rodler and L. M. Tack (1985). *J. Am. Chem. Soc.*, **107**, 4112.

[14] R. D. Brown and E. H. N. Rice (1984). *J. Am. Chem. Soc.*, **106**, 6475.

[15] R. D. Brown, F. W. Eastwood, P. S. Elmes and P. D. Godfrey (1983). *J. Am. Chem. Soc.*, **105**, 6496.

[16] M. E. Jacox, D. E. Milligan, N. G. Moll and W. E. Thompson (1965). *J. Chem. Phys.*, **43**, 3734.

[17] R. D. Brown, D. E. Pullin, E. H. N. Rice and M. Rodler (1985). *J. Am. Chem. Soc.*, **107**, 7877; D. McNaughton, D. McGilvery and F. Shanks (1991). *J. Mol. Spectrosc.*, **149**, 458; P. Botschwina and H. P. Reisenauer (1991). *Chem. Phys. Lett.*, **183**, 217.

[18] G. Maier, H. P. Reisenauer and A. Ulrich (1991). *Tetrahedron Lett.*, **32**, 4469.

[19] Y. Hirahara, Y. Ohshima and Y. Endo (1993). *Astrophys. J.*, **408**, L113.

[20] S. Yamamoto, S. Saito, K. Kawaguchi, Y. Chikada, H. Suzuki, N. Kaifu, S. Ishikawa and M. Ohishi (1990). *Astrophys. J.*, **361**, 318.

[21] Y. Ohshima and Y. Endo (1992). *J. Mol. Spectrosc.*, **153**, 627.

[22] G. Maier, J. Schrot, H. P. Reisenauer and R. Janoschek (1991). *Chem. Ber.*, **124**, 2617.

[23] D. Sülzle and H. Schwarz (1989). *Chem. Ber.*, **122**, 1803.

[24] F. J. Lovas, R. D. Suenram, T. Ogata and S. Yamamoto (1992). *Astrophys. J.*, **399**, 325.

[25] Y. Kasai, K. Obi, Y. Ohshima, Y. Hirahara, Y. Endo, K. Kawaguchi and A. Murakami (1993). *Astrophys. J.*, **410**, L45.

[26] R. D. Suenram and F. J. Lovas (1994). *Astrophys. J.*, **429**, L89.

[27] M. B. Bell, L. W. Avery and P. A. Feldman (1993). *Astrophys. J.*, **417**, L37.

[28] D. Sülzle, J. K. Terlouw and H. Schwarz (1990). *J. Am. Chem. Soc.*, **112**, 628.

[29] G. Maier, H. P. Reisenauer and R. Ruppel (1997). *Angew. Chem.*, **109**, 1972; (1997) *Angew. Chem. Int. Ed. Engl.*, **36**, 1862.

[30] G. Maier, H. P. Reisenauer, J. Schrot and R. Janoschek (1990). *Angew. Chem.*, **102**, 1475; (1990) *Angew. Chem. Int. Ed. Engl.*, **29**, 1464.

[31] G. P. Raine, H. F. Schaefer and R. C. Haddon (1983). *J. Am. Chem. Soc.*, **105**, 194.

[32] R. Janoschek (1991). *J. Mol. Struct.* (*Theochem*), **232**, 147.

[33] G. Maier, H. P. Reisenauer, H. Balli, W. Brandt and R. Janoschek (1990). *Angew. Chem.*, **102**, 920; (1990) *Angew. Chem. Int. Ed. Engl.*, **29**, 905.

[34] D. Sülzle and H. Schwarz (1990). *Angew. Chem.*, **102**, 923; (1990) *Angew. Chem. Int. Ed. Engl.*, **29**, 908.

[35] D. Sülzle and H. Schwarz (1991). *J. Am. Chem. Soc.*, **113**, 48.

[36] M. Winnewisser and E. W. Peau (1984). *Acta Phys. Hung.*, **55**, 33.

[37] F. M. Nicolaisen and J. J. Christiansen (1979). *J. Mol. Struct.*, **52**, 157.

[38] M. Winnewisser and J. J. Christiansen (1976). *Chem. Phys. Lett.*, **37**, 270.

[39] G. Maier, J. Schrot and H. P. Reisenauer (1991). *Chem. Ber.*, **124**, 2613.

[40] G. Maier, J. Schrot, H. P. Reisenauer and R. Janoschek (1990). *Chem. Ber.*, **123**, 1753.

[41] G. Maier, H. P. Reisenauer and R. Ruppel (1999). *Sulfur Rep.*, **21**, 335.