Aromatic stabilization of organochalcogen compounds with the intramolecular X←O (X = S, Se, Te) coordination

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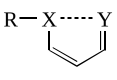
The *ab initio* MP2/LanL2DZ calculations predict a significant contribution of cyclic π-electron delocalization to the stabilization of the *trans–cis–cis* conformation of derivatives of β-chalcogenovinylaldehydes 1 with the intramolecular Chalc←O coordination.

The origin of a sufficiently high strength, as well as structural and chemical consequences, of the attractive interaction between electron-abundant centres suitably oriented within a molecule is of considerable interest.[1–4] It was found that molecular conformations of a variety of organochalcogen (X = S, Se, Te)[3–6] and organopnictogen (X = P, As, Sb, Bi)[7,8] compounds are controlled by the XO or XN interactions, which draw these closed-shell centres together to distances much shorter than the sum of the respective van der Waals radii. This interaction is especially strong, and the X–O distances are short in organochalcogen compounds **1** (X = S, Se, Te). The above bond closes a conjugated chain to form a five-membered ring containing an aromatic π-electron sextet or decet, as is the case with 1,6-dioxa-6a-chalcapentalenes **5** or their pnictogen analogues. The high strength of the ChalcO and ChalcN interactions is illustrated by the computational findings[1,6] that the *trans–cis–cis* conformation of compounds **1** (X = Chalc, Y = O, NR′, R = H) with the tricoordinate T-shaped chalcogen centre is preferable to the *cis–cis–cis* conformation of **2**, ensuring the formation of a sufficiently strong intramolecular hydrogen bond similar to that characteristic of β-hydroxyvinylaldehyde (malonic aldehyde) **2** (X = Y = O), or the sterically unstrained *trans–trans–trans* conformation of **3**. For example, conformation **1** (X = S, Y = O, R = H) with the intramolecular coordination S←O bond was calculated (MP2/6-31+G**) to be preferable by 4.0 kcal mol^{-1} in terms of energy compared to conformation **2**, in which a sufficiently strong intramolecular S–HO hydrogen bond occurs.



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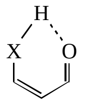

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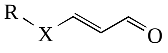

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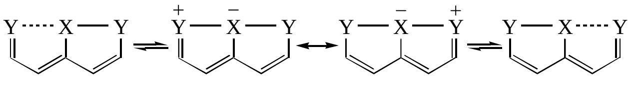
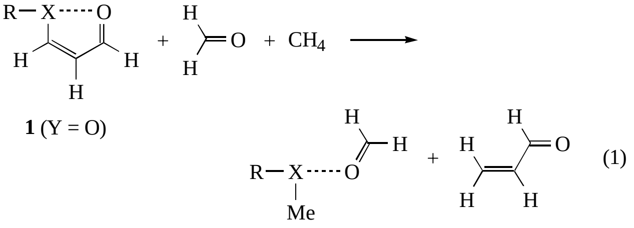


4a **5a** **5b** **4b**

X = S, Se, Te
Y = O, NR′

In compounds **1**, **4** and **5**, the covalency ratio factors[9] calculated for the XO bonds from the experimental or theoretically calculated distances between the formally nonbonded atoms may be as high as 0.8–0.9. Thus, these bonds are almost indistinguishable in their strength and length from the corresponding covalent or three-centre, four-electron hypervalent bonds. The energies of these secondary ('preliminary hypervalent'[1]) bonds in compounds **1** (X = Chalc) were evaluated as differences between the total energies of their *cis*- and *trans*-isomers. According to the *ab initio* (MP2/6-31G** and MP2/LanL2DZ) calculations,[6] the attractive interaction increases in the order S, Se and Te and with increasing electronegativity of a substituent R attached to the chalcogen centre. Isomer **1** (X = S, R = H) is 1.2 (MP2/LanL2DZ) or 0.3 kcal mol^{-1} (MP2/6-31+G**) less stable than its unstrained isomer **3**, whereas in the tellurium (X = Te, R = H) analogues, *cis*-isomer **1** is 3.8 kcal mol^{-1} (MP2/LanL2DZ) energy preferable to **3**.[6] By replacing the substituent R = H by a more electronegative chlorine atom in **1** (X = Te), the energy of the Te–O bond may be increased up to 16.5 kcal mol^{-1} (MP2/Lanl2DZ). In 1,6-dioxa-6a-chalcapentalenes **4** ⇔ **5**, the energies of the 3c, 4e O–X–O bonds estimated in a similar way were found to be 12.1, 19.8 and 27.7 kcal mol^{-1} (MP2/LanL2DZ) for X = S, Se and Te, respectively.[6]

The principal factors responsible for attractive forces between the closed-shell atomic centres in compounds **1** and **4** are the negative hyperconjugation, *i.e.*, the donor–acceptor $n_O \rightarrow s^*_{X-R}$ ineraction, electrostatic interaction and resonance, *i.e.*, aromatic stabilization of the five-membered ring formed by the secondary X–O bond.[1–4,6,10] The goal of this work was to evaluate a contribution of the aromatic stabilization of five-membered rings in compounds **1** using an approach based on homodesmotic reactions. Reactions of this type enable the contribution from the cyclic electron delocalization to be singled out, their energies (HSE) being considered as the analogues of the Dewar resonance energies.[11] Although no unambiguous homodesmotic reaction (in which the number of bonds of each formal type is retained in both reactants and products) can be constructed for compounds **1**, reaction (1) may serve as a reasonable approximation. The only deviation from the above condition is the difference between the numbers of C_{sp^3}–H and C_{sp^2}–H bonds in reactants (4 and 5, respectively) and products (3 and 6, respectively). However, a small difference in the energies of C_{sp^3}–H and a C_{sp^2}–H bonds is included into the HSE values of all compounds **1** and hence does not affect the principal conclusions.



1 (Y = O)

6

(1)

The total energies of all structures involved in equation (1) were calculated by the MP2(fc)/LanL2DZ method using the Gaussian-94 and Gaussian-98 packages of *ab initio* programs. The orbital basis selected allows accounting for some relativistic effects (*via* effective core potentials), which are important for post-third-row atoms. The optimisation of a molecular geometry at stationary points was performed with a 'tight' convergence criterium. To exclude the extraneous stabilization of bimolecular

Table 1 *Ab initio* MP2(fc)/LanL2DZ data for bimolecular complexes **6**.

X	R	E_{tot}/hartree	d_{XO}/Å[a]	E^b_{stab} / kcal mol^{-1}
S	H	–164.236319	3.465	0.66
	Cl	–178.383916	2.833	4.13
Se	H	–163.355948	3.402	1.18
	Cl	–177.519004	2.817	5.17
Te	H	–162.185171	3.409	1.78
	Cl	–176.366829	2.872	6.27

[a] For comparison, the van der Waals contacts are 3.30, 3.40 and 3.60 Å and the bond lengths are: 1.75, 1.90 and 2.08 Å for SO, SeO and TeO, respectively.[12] [b] $E_{stab} = E_{complex} - (E_{MeXR} + E_{CH_2O})$.

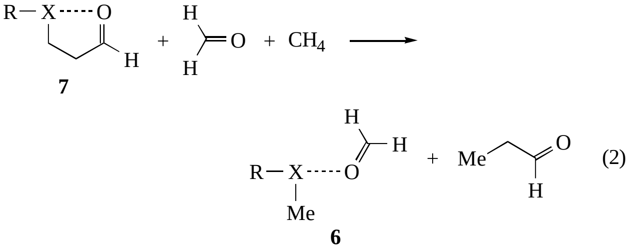
Table 2 Aromatic stabilization energies of cyclic compounds **1** calculated according to equations (1) and (2) by the *ab initio* MP2(fc)/LanL2DZ method.[a]

X	R	**1**, E_{tot}/hartree	**7**, E_{tot}/hartree	**1**, d_{XO}/Å	**7**, d_{XO}/Å	ΔE (**1** – **3**)[6]/ kcal mol^{-1}	HSE/kcal mol^{-1}	E_{str}/kcal mol^{-1}	ASE/kcal mol^{-1}
S	H	–200.998260	–216.328403	2.980	2.917	–3.6[b]	2.0	–6.6	8.6
	Cl	–215.146857	–202.175967	2.395	2.567	5.0	2.6	–3.6	6.2
Se	H	–200.120475	–201.297980	2.935	2.909	0.9	3.6	–5.1	8.7
	Cl	–214.288736	–215.467236	2.307	2.541	10.5	6.9	–1.2	8.1
Te	H	–198.531140	–200.130677	2.845	2.907	3.8	5.6	–2.9	8.5
	Cl	–213.145592	–214.319632	2.294	2.568	16.5	12.5	–1.6	14.1

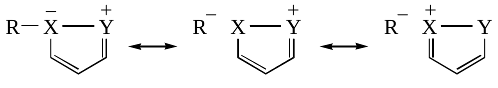
[a] The total energies (hartree) of the components of equations (1) and (2) calculated by the MP2(fc)/LanL2DZ method are the following: CH_4 –40.278267, CH_2=O –114.042055, EtCH=O –192.270511. [b] The negative sign of energy corresponds to destabilization.

complexes **6** through formation of additional hydrogen bonds (X–HO and/or CHCl) between the components,[6] their energies were calculated for the conformation whose stability is provided by solely the RXO interaction (only the RXO distance was optimised, all other geometric parameters were taken to be equal to their values in monomers, the angles XO=C and Me–XO were taken constrained at 120° and 90°, respectively). Table 1 contains the results of calculations for complexes **6**. As expected, the stabilization energy of the bimolecular associates increases, and the XO distances diminish in the order X = S, Se and Te with R = H, Cl.

The HSE values calculated by equation (1) underestimate the stabilising effects of cyclic electron delocalization in compounds **1** by the value of the angle strain of a *cis*-structure. To take this effect into account, the strain energies E_{str} of *cis*-isomers **1** were calculated according to equation (2). The aromatic stabilization energies ASE = HSE – E_{str} of pseudo-heterocycles **1** are given in Table 2.



The ASE values are indicative of a substantial contribution of the cyclic π-electron delocalization to the overall stabilization of compounds **1** with the intramolecular Chalc←O coordination of the hypervalent type. The HSE values of pseudo-heterocycles **1** constitute 10–40% of the HSE value of the prototypic aromatic system of benzene (28.9 kcal mol^{-1}) calculated at a similar level of approximation. This finding lends support to the consideration of derivatives of β-chalcogenovinylaldehydes **1** (X = Te or Se; R = Cl) as true heterocycles, 1,2-oxatellurolyl-1-ium and 1,2-oxaselenolyl-1-ium chlorides,[14] respectively, whose electronic structure was described as a resonance hybrid of the structures with delocalised six-electron π-systems.



1a **1b** **1c**

The chemical behaviour of compounds **1** (the retention of the structural type in reactions with electrophiles and easy ionization of the R–X bond under treatment with supernucleophiles) corresponds to the aromatic structure **1a** ⇔ **1b** ⇔ **1c** rather than heterodiene **1**. The treatment of the type **1** fragments as heterocyclic moieties has been recently used as the basis for the design of new mimic-fused bicyclic heterocycles consisting of stable non-bonded 1,5-type SO interaction.[10]

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References

1 J. G. Ángyán, R. A. Poirier, A. Kucsman and I. G. Csizmadia, *J. Am. Chem. Soc.*, 1987, **109**, 2237.
2 D. H. R. Barton, M. B. Hall, Z. Lin, S. I. Parekh and J. Reibeuspies, *J. Am. Chem. Soc.*, 1993, **115**, 5056.
3 W. R. McWhinnie, I. D. Sadekov and V. I. Minkin, *Sulfur Rep.*, 1996, **18**, 295.
4 V. I. Minkin, *Ross. Khim. Zh.*, 1999, **43**, 10 (in Russian).
5 A. Kucsman and I. Kapovits, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, eds. I. G. Csizmadia, A. Mangini and F. Bernardi, Elsevier, Amsterdam, 1985, pp. 191–245.
6 R. M. Minyaev and V. I. Minkin, *Can. J. Chem.*, 1998, **76**, 766.
7 A. J. Arduengo III and C. A. Stewart, *Chem. Rev.*, 1994, **94**, 1215.
8 T. Murafuji, T. Mutoh, K. Satoh, K. Tsunenari, N. Azuma and H. Suzuki, *Organometallics*, 1995, **14**, 3848.
9 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
10 Y. Nagao, T. Hirata, S. Goto, S. Sano, A. Kakechi, K. Iizuka and M. Shiro, *J. Am. Chem. Soc.*, 1998, **120**, 3104.
11 V. I. Minkin, M. N. Glukhovtsev and B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, 1994.
12 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
13 R. L. Disch and J. M. Schulman, *Chem. Phys. Lett.*, 1988, **152**, 402.
14 M. R. Detty, B. J. Murray, D. L. Smith and N. Zumbulyadis, *J. Am. Chem. Soc.*, 1983, **105**, 875.

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