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On the Usefulness of Bond Orders and Overlap Populations to Chalcogen–Nitrogen Systems

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Bond orders calculated using the Mayer, Wiberg or NAO methodologies are incompatible with the observed bond lengths in chalcogen–nitrogen systems. To study this discrepancy four types of bond orders and three types of (scaled) overlap populations have been used to determine the bonding in these systems. A new overlap population based on the Hirshfeld partitioning of the electron density is compared to the Mayer, Wiberg, NAO and Fuzzy bond order schemes and the Mulliken and Fuzzy overlap population schemes. The correlation between the investigated bond orders and overlap populations is excellent for common organic molecules, but the (scaled) Hirshfeld and Fuzzy overlap population schemes produce the best results for a series of chalcogen-nitrogen systems.

Introduction

There has been an increasing interest in low-molecular-weight derivatives of $(SN)_x$ polymer since the latter's metallic properties[1] and low-temperature superconductivity[2] were discovered in the 1970′s. In our earlier work we have dealt with various compounds containing an $(SN)_2$ fragment such as 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazine (**1**),[3] its fluorinated derivatives[4] and Roesky's ketone (**4**).[5] 3$\lambda^4\delta^2$,1,2,4-Benzothiaselenadiazine (**2**) and 1,3$\lambda^4\delta^2$,2,4-benzodiselenadiazine (**3**), the mono- and diselena analogues of **1**, are also of considerable interest and are presently targets for synthesis.[6] Figure 1 presents structural formulas of these compounds. According to single-crystal X-ray diffraction (XRD) studies,[7] the structure of **1** is planar in the solid state, whereas both gas-phase electron diffraction (GED) and quantum chemical calculations indicate a bent structure in the gas phase.[3] Compound **1** possesses a cyclic 12π-electron system, and the deviation from the planar structure was attributed to a pseudo-Jahn–Teller distortion to minimize the antiaromaticity.[3,8] Furthermore, the energy barrier to planarity is low (1.17 kJ·mol^{-1} at the HF/6-31G* level) and in the crystal phase the molecule can be flattened without great effort.

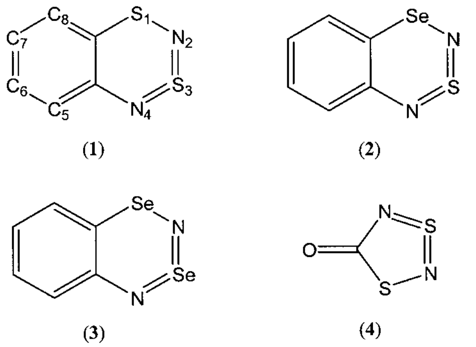

Figure 1. Structural formulas and atomic numbering of the chalcogen–nitrogen compounds under consideration. For compound **4** the formal Lewis structure is given.

Despite the different conformations in the two phases the measured (by XRD and GED) and calculated geometrical parameters of **1** reflect similar bonding. In the heteroatomic part there are two virtually equally short N=S bonds (bond length about 1.55 Å) and one longer N–S bond (bond length about 1.70 Å). On the basis of a comparison between the average bond lengths for the N=S and N–S bonds, the two short bonds could be identified as being double bonds while the longer one fell within the range for a single bond. Indeed, according to the analysis of the Cambridge Structural Database by Allen et al.,[9] an average N–S single bond lies between 1.64 and 1.70 Å, while a N=S double bond is approximately 1.54 Å long [we note that the N=S bond length is only tabulated for conjugated N=S=N systems].

In many cases, conclusions on the structures of compounds are based on bond order considerations, and therefore, it is essential to obtain reliable values for it. According to the IUPAC Compendium of Chemical Terminology, a

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bond order is a "theoretical index of the degree of bonding between two atoms relative to that of a single bond, i.e. the bond provided by one localized electron pair".[10] However, there exists no unique formula to calculate the bond order. Every bond order is partly arbitrary since it is based on a population analysis scheme which is arbitrary itself: different schemes for the partitioning of the electron density give rise to different definitions of bond orders.

Regardless of the differences between the various bond order methodologies, it is important that each one of them produces consistent results, and this is often the case for common organic molecules. This requirement is, however, not fulfilled in the case of compound **1** for which the Mayer,[11–13] Wiberg[14] and NAO (atom-atom-overlap-weighted Natural Atomic Orbital bond order)[15,16] methodologies predict a bond order value for the NS double bond which is much smaller than expected on the basis of the bond length. The same controversy is observed in the case of compounds **2**, **3** and **4**.

Since the early definition of Wiberg[14] there has been a long debate on the appropriate quantum chemical definition of bond orders (see ref.[17] and refs. 1–18 therein). Recently, Mayer and Salvador[18] have proposed bond orders based on 'fuzzy' atoms which are characterized by soft overlapping boundaries and defined using the Becke partitioning scheme. Clark and Davidson proposed a method for controlling the region of overlap between atoms and thoroughly examined the effect of the shape and sharpness of the interatomic boundaries on the obtained fuzzy atomic populations.[19] Mayer's fuzzy atom bond order, together with several other methods, was used by Clark et al.[20] in their investigation of the bonding properties of a number of actinide complexes. It was found that the fuzzy atom method[18] performed well for these compounds, even though the Natural Population Analysis (NPA) method exhibited the best performance of all the orbital-based partitioning schemes for these molecules.

Pauling was the first to suggest that bond orders can be related to bond lengths, and since then several relationships have been proposed.[21–24] These curves have found widespread applications. Among others, Lendvay[25] has reconfirmed the exponential relationship between the bond length and bond order using Equation (1),

$$n = \exp[-(r - r_0)/b] \tag{1}$$

where n is the bond order, r_0 the equilibrium bond length of a single bond, r the real bond length in the compound considered, and b is a constant.

It is the purpose of this paper to address the discrepancies between observed bond lengths and the corresponding bond orders calculated using different methodologies, in particular for NS and NSe bonds in chalcogen-nitrogen compounds. For this purpose we have calculated and compared the Mulliken, Fuzzy and Hirshfeld overlap populations with the Mayer, Wiberg, NAO and Fuzzy bond orders. We have also investigated the relationship between these bond orders, overlap populations and the corresponding bond lengths. It has been known for decades that Mulliken overlap populations correlate reasonably well with Mayer bond orders,[26] even though Mayer insists that overlap populations and bond orders reflect different aspects of bonding, i.e. charge accumulation and exchange interactions, respectively. In the recent past the Hirshfeld partitioning scheme[27,28] has received considerable interest in relation to the calculation and interpretation of a variety of molecular quantities such as charges and dipoles,[28–33] enthalpies of formation,[34–36] global QMSI (quantum molecular similarity index) values[37] and Fukui functions (see ref.[38] and refs. therein).

Theory and Computational Details

In the Hirshfeld Scheme[27,28] the number of electrons attributed to an atom A in a molecule, N_A, is defined as in Equation (2),

$$N_A = \int d\boldsymbol{r} \frac{\rho_A(\boldsymbol{r})}{\sum_X \rho_X(\boldsymbol{r})} \rho_M(\boldsymbol{r}) \tag{2}$$

in which $\rho_M(\boldsymbol{r})$ is the molecular density at position $\boldsymbol{r}$, $\rho_A(\boldsymbol{r})$ is the atomic density and $\sum_X \rho_X(\boldsymbol{r})$ constitutes the pro-molecular density. In a way similar to the definition of the atomic charge,[28–33] the Hirshfeld overlap population (HOP), B_{AB}, can be defined by Equation (3),

$$B_{AB} = \int d\boldsymbol{r} \frac{\rho_A(\boldsymbol{r})\rho_B(\boldsymbol{r})}{\left(\sum_X \rho_x(\boldsymbol{r})\right)^2} \rho_M(\boldsymbol{r}) \tag{3}$$

which is the special case of the fuzzy atom overlap population defined earlier[18] in which the weight factors have been replaced by those specified by Hirshfeld. Full geometry optimisations of the structures of all the molecules studied in this work were performed using the Gaussian 03 program package[39] applying Density Functional Theory (DFT) with the hybrid B3LYP functional[40] and the cc-pVTZ basis set; the basis set was used as it is implemented in the program. The Wiberg and NAO bond orders and the NPA charges were calculated using the NBO 3.0 program[41] as it is implemented in the Gaussian 03 program package. Mayer and Fuzzy bond orders and Mulliken and Fuzzy charges were calculated using the program Fuzzy.[42] The Hirshfeld overlap populations and stockholder charges were calculated using the BRABO program package.[43]

Results and Discussion

Comparison of Overlap Populations and Bond Orders for Homodiatomic and Simple Organic Molecules

In order to evaluate our new Hirshfeld overlap populations (HOP) as they are defined by Equation (3), the values were compared to the corresponding Mulliken and Fuzzy overlap populations and to the Mayer, Wiberg, NAO and Fuzzy bond orders for a set of simple organic and inorganic molecules. The results have been compiled in Table 1. The values of the overlap populations are considerably smaller than those of the bond orders. In order to make comparison of the data easier, we have scaled the overlap populations in such a way that they are in line with the formal bond orders of 1, 1.5, 2, and 3 for the CC bonds in ethane, benzene, ethene, and ethyne, respectively. Therefore, these four compounds and their bond order values were used to construct a linear function between the calculated and formal bond orders and this has been presented graphically in Figure 2; the relevant data of the trendlines have been given in Table 2. Although this scaling is arbitrary it does have the advantage that it produces numbers comparable to the bond orders expected by chemical intuition. For reasons of comparison similar linear regression curves were calculated for the bond order schemes as well. Figure 2 and Table 2 indicate that the slopes of the regression lines for the Wiberg, Mayer and Fuzzy bond orders are close to 1, precluding any form of scaling. The values of the NAO bond orders and of the three overlap populations are lower in absolute value, but correlate very well linearly with the formal bond orders as can be seen from the R^2 values given in Table 2. On the basis of the equations of the regression lines obtained for the three overlap populations and the NAO bond orders, scaled equivalents of these were calculated, and these are also given in Table 1 as sHOP (scaled Hirshfeld overlap population), sMOP (scaled Mulliken overlap population), sFOP (scaled Fuzzy overlap population) and sNAO (scaled NAO bond order).

The bond orders and overlap populations of the different bonds in a series of substituted ethynes (RC≡CH), ethenes ($RHC=CH_2$) and ethanes ($RH_2C–CH_3$) were calculated and the changes of the bond order or overlap population as a function of the substituents (R = H, CH_3, F, Cl and CHO) were examined. All schemes used reflect the expected trends. For the homodiatomic molecules, basic chemical knowledge suggests that there is a single bond in H_2, F_2 and Cl_2, a double bond in O_2 and a triple bond in N_2; the respective bond orders are then 1, 2 and 3. The scaled Hirshfeld overlap population of 1.91 for O_2 is remarkable, as is the value of 1.87 obtained with the Mayer scheme; the other methods show much lower or higher values, despite the commonly accepted bond order value of 2. In contrast, the values of sHOP for both H_2 and F_2 are quite low. It is important to note that there is a significant difference between the Wiberg and Mayer bond orders on the one hand, and the Hirshfeld and Fuzzy overlap populations and the NAO bond order on the other. In each case, the Wiberg/Mayer values are very close to the formal bond order of 1 but are independent of the strength of the bond, while the Hirshfeld/NAO/Fuzzy values seem to provide additional information on the bond strength (i.e. they give larger numbers for stronger single bonds and smaller values for weaker single bonds). The Wiberg bond order of the F–F bond is 1.01 and virtually equal to that of the H–H bond, while both sNAO and sHOP suggest a weaker bond in F_2 which is in accordance with the small dissociation energy of the F–F bond.[44] Table 1 also contains a number of negative values which are clearly due to the scaling procedure. Even though these values have lost their quantitative meaning they are still useful on a qualitative level.

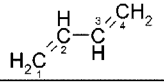
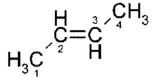
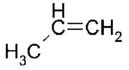
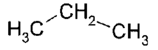
In order to compare the values of the scaled Hirshfeld overlap population with those of the other investigated quantities, the latter were plotted against the scaled Hirshfeld overlap populations in Figure 3; all carbon–carbon bonds compiled in Table 1 have been included. As can be seen from Figure 3 the Hirshfeld overlap population correlates quite well with all the other bond order and overlap population schemes except with the Mulliken overlap population. The correlation with NAO is the best.

As mentioned in the introduction, since Pauling's original suggestion several authors have confirmed the bond orders' exponential decrease with the bond length. In Figure 4 the values of the bond orders and overlap population calculated using the different methods were plotted against the

Table 1. Calculated bond lengths (r_e in Å), the corresponding Hirshfeld (HOP), Fuzzy (FOP) and Mulliken (MOP) overlap populations together with their scaled equivalents (sHOP, sFOP and sMOP), and the NAO (NAO), scaled NAO (sNAO), Wiberg (WBO), Mayer (MBO) and Fuzzy (FBO) bond orders for a number of organic and diatomic compounds. See text for details. * These compounds were used for scaling.

			Overlap populations						**Bond orders**				
	bond	r_e	**HOP**	**FOP**	**MOP**	**sHOP**	**sFOP**	**sMOP**	**NAO**	**sNAO**	**WBO**	**MBO**	**FBO**
$HC\equiv CH^*$	C≡C	1.1960	0.82	0.46	0.83	3.00	2.96	2.93	2.00	3.01	3.00	2.73	2.85
$H_2C=CH_2^*$	C=C	1.3242	0.59	0.38	0.62	1.98	2.11	2.09	1.43	1.98	2.05	1.91	1.97
$H_3C-CH_3^*$	C–C	1.5262	0.37	0.28	0.33	0.99	1.09	0.92	0.90	1.02	1.05	0.96	1.14
Benzene*	CC	1.3907	0.49	0.31	0.49	1.53	1.33	1.57	1.16	1.49	1.44	1.37	1.37
$H_3\underset{1}{C}-\underset{2}{C}\equiv\underset{3}{C}-\underset{4}{C}H_3$	C≡C	1.2010	0.80	0.44	0.52	2.92	2.76	1.68	1.94	2.91	2.78	2.50	2.64
	C–C	1.4566	0.44	0.29	0.52	1.31	1.19	1.68	0.97	1.16	1.09	1.09	1.20

Table 1. *(continued)*

	C–C	1.4527	0.44	0.28	0.42	1.28	1.10	1.26	0.96	1.14	1.13	1.07	1.19
	C=C	1.3339	0.57	0.36	0.60	1.88	1.87	2.01	1.37	1.87	1.89	1.77	1.82
	C=C	1.3283	0.57	0.35	0.65	1.88	1.82	2.20	1.38	1.90	1.92	1.85	1.83
	C–C	1.4976	0.40	0.28	0.36	1.11	1.06	1.05	0.89	1.01	1.06	0.98	1.14
$H_3C-C\equiv C-H$	C–C	1.4549	0.44	0.29	0.39	1.30	1.19	1.14	0.98	1.17	1.10	1.02	1.20
	C≡C	1.1989	0.81	0.45	0.80	2.96	2.86	2.80	1.98	2.98	2.88	2.65	2.74
	C–C	1.4968	0.40	0.28	0.36	1.10	1.06	1.02	0.90	1.02	1.06	0.97	1.14
	C=C	1.3265	0.58	0.37	0.64	1.93	1.97	2.15	1.41	1.95	1.98	1.87	1.90
	C–C	1.5277	0.36	0.27	0.34	0.95	0.94	0.97	0.85	0.94	1.04	0.95	1.11
$FC\equiv CH$	F–C	1.2777	0.49	0.30	0.38	1.55	1.29	1.10	0.87	0.97	1.00	1.21	1.25
	C≡C	1.1917	0.82	0.43	0.64	3.04	2.67	2.16	1.95	2.94	2.84	2.62	2.64
$FHC{=}CH_2$	F–C	1.3462	0.43	0.28	0.36	1.24	1.10	1.03	0.77	0.79	0.90	1.10	1.17
	C=C	1.3172	0.59	0.34	0.56	1.99	1.65	1.83	1.43	1.98	1.96	1.84	1.81
FH_2C-CH_3	F–C	1.3974	0.38	0.27	0.33	1.02	0.91	0.91	0.62	0.51	0.85	1.02	1.11
	C–C	1.5094	0.38	0.24	0.33	1.02	0.68	0.90	0.90	1.02	1.04	0.97	1.05
Fluorobenzene	F–C	1.3503	0.42	0.27	0.39	1.19	0.95	1.15	0.76	0.78	0.89	1.11	1.11
$ClC\equiv CH$	Cl–C	1.6424	0.53	0.34	0.41	1.72	1.73	1.24	0.99	1.19	1.18	1.29	1.46
	C≡C	1.1977	0.81	0.43	0.68	2.95	2.68	2.33	1.93	2.89	2.80	2.58	2.64
$ClHC{=}CH_2$	Cl–C	1.7452	0.43	0.30	0.29	1.24	1.29	0.75	0.85	0.93	1.06	1.06	1.29
	C=C	1.3198	0.58	0.35	0.63	1.95	1.76	2.09	1.42	1.97	1.97	1.85	1.84
ClH_2C-CH_3	Cl–C	1.8185	0.36	0.27	0.25	0.93	0.91	0.57	0.75	0.75	0.99	0.99	1.19
	C–C	1.5131	0.37	0.26	0.34	1.00	0.80	0.95	0.88	0.98	1.05	0.96	1.08
$OH\underset{1}{C}-\underset{2}{C}\equiv\underset{3}{C}H$	C–C	1.4458	0.46	0.28	-0.02	1.37	1.09	-0.49	1.00	1.22	1.08	0.88	1.18
	C≡C	1.2012	0.79	0.44	0.75	2.90	2.74	2.60	1.95	2.92	2.84	2.63	2.68
	C=O	1.2066	0.64	0.40	0.78	2.19	2.36	2.71	1.35	1.83	1.85	2.18	2.24
$OH\underset{1}{C}-H\underset{2}{C}{=}\underset{3}{C}H_2$	C–C	1.4707	0.42	0.28	0.16	1.21	1.01	0.22	0.95	1.11	1.07	0.90	1.14
	C=O	1.2082	0.64	0.41	0.00	2.19	2.39	-0.41	1.34	1.82	1.83	2.13	2.23
	C=C	1.3310	0.57	0.36	0.00	1.88	1.86	-0.41	1.37	1.87	1.91	1.75	1.83
$OH\underset{1}{C}\text{-}H_2\underset{2}{C}-\underset{3}{C}H_3$	C_1–C_2	1.5059	0.38	0.26	0.16	1.03	0.88	0.22	0.90	1.02	1.01	0.90	1.09
	C_2–C_3	1.5223	0.37	0.27	0.25	0.97	0.90	0.61	0.85	0.93	1.03	0.95	1.10
	C=O	1.2040	0.64	0.41	0.77	2.19	2.39	2.66	1.35	1.85	1.88	2.20	2.27
CH_4	C–H	1.0883	0.34	0.15	0.40	0.85	-0.32	1.18	0.77	0.79	0.96	0.97	0.98
CH_3NH_2	C–N	1.4636	0.39	0.30	0.34	1.05	1.25	0.96	0.83	0.90	1.03	0.99	1.27
CH_3OH	C–O	1.4194	0.39	0.31	0.35	1.09	1.38	0.99	0.74	0.74	0.96	1.03	1.38
CH_3SH	C–S	1.8304	0.39	0.29	0.26	1.06	1.11	0.64	0.79	0.83	1.04	1.01	1.26
CH_3SeH	C–Se	1.9738	0.34	0.26	0.25	0.85	0.85	0.57	0.74	0.73	1.03	1.00	1.20
CH_2O	C=O	1.1990	0.65	0.42	0.71	2.26	2.56	2.45	1.37	1.87	1.95	2.14	2.36
H_2	H–H	0.7429	0.31	0.12	0.42	0.72	-0.58	1.26	0.80	0.84	1.00	1.00	1.00
N_2	N≡N	1.0914	0.83	0.47	0.75	3.07	3.08	2.60	1.92	2.88	3.03	2.93	3.11
O_2	O=O	1.2058	0.57	0.40	0.16	1.91	2.29	0.23	0.94	1.10	1.52	1.87	2.49
F_2	F–F	1.3976	0.31	0.29	0.03	0.69	1.16	-0.28	0.33	-0.01	1.01	0.96	1.58
Cl_2	Cl–Cl	2.0231	0.44	0.39	0.09	1.29	2.25	-0.04	0.52	0.33	1.04	1.07	1.81

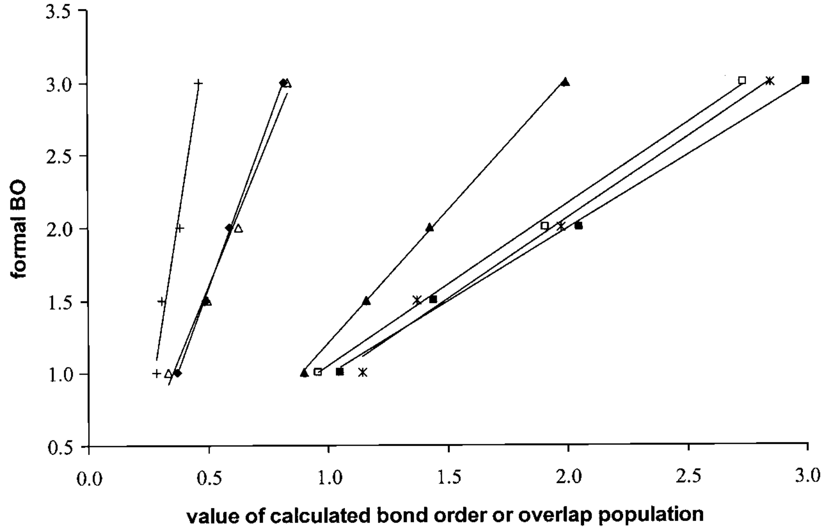


Figure 2. Calculated bond orders within the NAO (▲), Mayer (□), Fuzzy (*) and Wiberg (■) schemes and calculated overlap populations within the Hirshfeld (♦), Fuzzy (+) and Mulliken (Δ) schemes for ethane, ethene, ethyne and benzene plotted against their formal bond orders of 3, 2, 1 and 1.5. The relevant data regarding the trendlines is given in Table 2.

Table 2. Relevant data regarding the trendlines in Figure 2.

		Equation	R^2
Bond orders	NAO (▲)	$y = 1.814\,x - 0.607$	1.000
	Wiberg (■)	$y = 1.005\,x - 0.020$	0.996
	Mayer (□)	$y = 1.110\,x - 0.058$	0.998
	Fuzzy (*)	$y = 1.113\,x - 0.163$	0.985
Overlap populations	Hirshfeld (♦)	$y = 4.518\,x - 0.686$	0.999
	Fuzzy (+)	$y = 10.55\,x - 1.900$	0.977
	Mulliken (Δ)	$y = 4.005\,x - 0.410$	0.989

bond length for the carbon–carbon bonds presented in Table 1. The function in Equation (4),

$$n = A\cdot\exp[-r/b] \tag{4}$$

was then fitted to the data. Compared to Equation (1) a parameter A was introduced which results from two considerations. First, instead of plotting $(r - r_0)$ against n, only r was, which resulted in a right-shift of the curve by r_0. This does not effect the goodness of the exponential fit, the correlation coefficients or the decay parameter b. Secondly, the non-scaled bond orders and overlap populations were used in these fits in order to avoid confusion because of the scaling, taking into account that the latter values are much lower than the formal bond orders, which are present in Equation (1). Table 3 contains the parameters A and b used in the different fits. Our results are in accordance with the earlier findings: with the exception of the Mulliken overlap population all investigated quantities decrease exponentially with the bond length, with R^2 values above 0.97 (except for the fuzzy overlap population). The R^2 values are largest for the NAO bond order and the Hirshfeld overlap population. For the Wiberg and Mayer bond orders, the

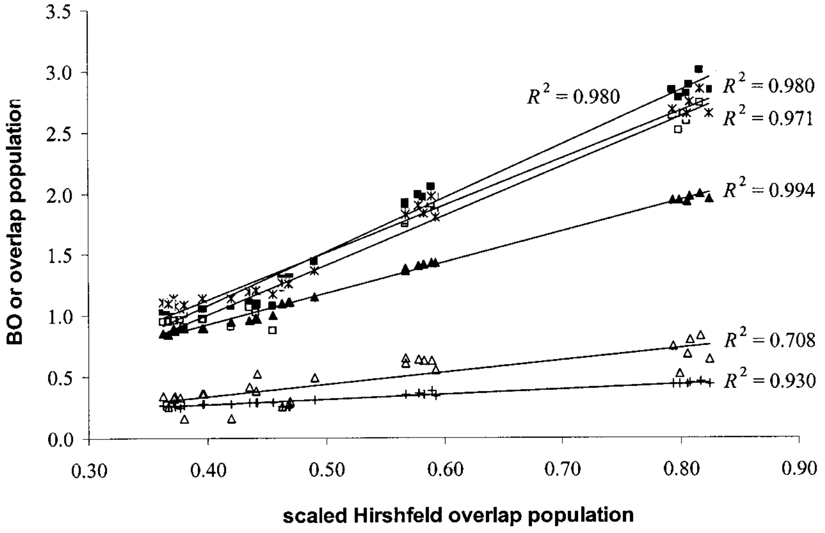


Figure 3. The scaled Hirshfeld overlap population vs. the Wiberg (■), the Fuzzy (*), the Mayer (□) and the scaled NAO (▲) bond orders and the scaled Fuzzy (+) and scaled Mulliken (Δ) overlap populations for the carbon–carbon bonds in the compounds of Table 1.

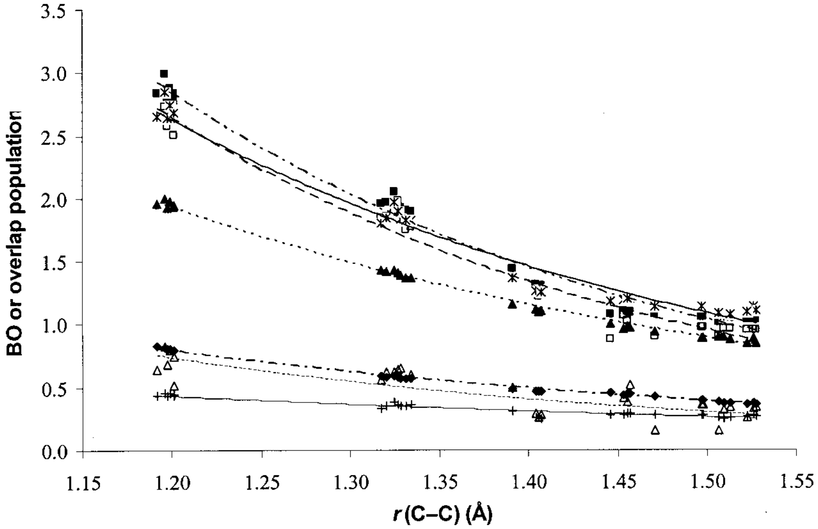


Figure 4. Exponential fit of the Wiberg (■), the Fuzzy (*), the Mayer (□) and the NAO (▲) bond orders and the unscaled Hirshfeld (♦), Fuzzy (+) and Mulliken (Δ) overlap populations vs. the *r*(C–C) of Table 1. See Table 3 for the values of the fitting parameters and the correlation coefficients.

Table 3. Parameters *A* and *b* (in Å) used in the exponential fits in the bond length vs. bond order/overlap population curves in Figure 4 and Figure 5, combined with the correlation coefficients of these fits.

			r(C–C)			*r*(N–S)	
		A	*b*	R^2	*A*	*b*	R^2
Bond orders	NAO (▲)	42.11	0.389	0.994	112.6	0.337	0.859
	Wiberg (■)	162.10	0.297	0.973	3878	0.198	0.797
	Mayer (□)	157.67	0.293	0.962	2674	0.211	0.878
	Fuzzy (*)	88.88	0.341	0.965	2309	0.220	0.902
Overlap populations	Hirshfeld (♦)	13.83	0.419	0.994	54.32	0.344	0.989
	Fuzzy (+)	3.117	0.607	0.872	35.57	0.342	0.921
	Mulliken (Δ)	26.22	0.336	0.605	54.46	0.321	0.367

value of the *b* parameter is about 0.29 Å, which is close to Pauling's "universal" value of 0.26 Å.

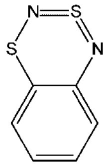
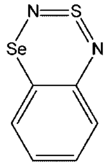
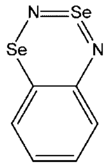
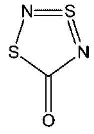
Chalcogen–Nitrogen Compounds

For common organic compounds, all methodologies except the Mulliken overlap population give virtually equally good results. Consequently, it is logical to investigate their performance for more exotic systems, in particular compounds **1**–**4**, which are of special interest to our research.[3–6] First, a number of simple compounds which contain formal single, double and triple NS and NSe bonds were studied. The results are given in Table 4. On the basis of these the values, the bond orders and overlap populations calculated for compounds **1**–**4** can be interpreted in the second part of this discussion.

It is important to note that while the values of the scaled Hirshfeld overlap population (sHOP) and the Wiberg and Mayer bond orders correspond to a single NX (X = O,S,Se) bond in NH_2OH, NH_2SH and NH_2SeH and a double NX bond in HN=O and HN=S, the values of the scaled NAO bond order and the Mulliken overlap population are lower, and those of both the scaled Fuzzy overlap population and the Fuzzy bond order are larger. In every case the sulfur–nitrogen bonds have a larger bond order/overlap population than the corresponding selenium–nitrogen bonds (except in the case of the scaled Mulliken overlap population) which can be explained by the fact that heavier elements do not prefer to form double or triple bonds. Furthermore, the weakening of the double bond in the N=O > N=S > N=Se series is confirmed by all except the Mayer and Mulliken schemes.

While the NS bond length is considerably shorter in HN=S=NH and HN=Se=NH than in HN=S and HN=Se, respectively (in both cases by about 0.03 Å), the Wiberg, Mayer and Fuzzy bond orders are smaller in the diimino species. The Hirshfeld and NAO methods, on the contrary, show approximately the same bond order for the di- and monoimino species. As there seems to be a contradiction between the conclusions based on bond orders and bond lengths, we calculated the ellipticity and the electron density in the bond critical points of the N=X (X = S,Se) bonds of these four molecules with the Atoms In Molecules (AIM) theory.[45,46] Table 5 collects the results. The relatively large ellipticity values for all four compounds indicates the presence of NS and NSe double bonds in the compounds, but the values obtained for HN=X=NH are particularly large. The increase of the electron density in the bond critical point upon going from the monoimino to the diimino species

Table 4. Calculated bond lengths (r_e in Å), the corresponding Hirshfeld (HOP), Fuzzy (FOP) and Mulliken (MOP) overlap populations together with their scaled equivalents (sHOP, sFOP and sMOP) and the NAO (NAO), scaled NAO (sNAO), Wiberg (WBO), Mayer (MBO) and Fuzzy (FBO) bond orders for a number of systems containing NS and NSe bonds and compounds **1**–**4**. See text for details.

			Overlap populations						**Bond orders**				
	bond	r_e	**HOP**	**FOP**	**MOP**	**sHOP**	**sFOP**	**sMOP**	**NAO**	**sNAO**	**WBO**	**MBO**	**FBO**
NH_2OH	N–O	1.4268	0.34	0.28	0.17	0.83	1.06	0.25	0.61	0.50	1.00	0.95	1.38
NH_2SH	N–S	1.7337	0.41	0.32	0.23	1.18	1.48	0.49	0.74	0.74	1.00	1.05	1.51
NH_2SeH	N–Se	1.8798	0.36	0.30	0.24	0.92	1.25	0.56	0.68	0.63	0.97	1.06	1.47
HN=O	N=O	1.1985	0.61	0.41	0.34	2.07	2.37	0.96	1.18	1.53	2.02	1.95	2.40
HN=S	N=S	1.5715	0.59	0.40	0.36	1.96	2.31	1.04	1.12	1.43	1.97	1.96	2.37
HN=Se	N=Se	1.7210	0.51	0.37	0.37	1.61	1.98	1.09	1.02	1.24	1.93	1.97	2.34
N≡SH	N≡S	1.5040	0.69	0.44	0.56	2.44	2.77	1.82	1.37	1.87	2.13	2.28	2.61
N≡SeH	N≡Se	1.6581	0.60	0.42	0.54	2.04	2.51	1.75	1.22	1.60	2.07	2.26	2.58
HN=S=NH	N=S	1.5464	0.60	0.39	0.35	2.01	2.26	0.99	1.12	1.42	1.54	1.71	2.10
	N···N	2.5289	0.02	0.00	-0.04				0.00		0.00	0.22	0.00
HN=Se=NH	N=Se	1.7039	0.51	0.37	0.39	1.63	2.01	1.14	0.99	1.18	1.50	1.71	2.07
	N···N	2.7072	0.01	0.00	-0.03				0.00		0.00	0.26	0.00
	CC	1.4052	0.46	0.26	0.26	1.40	0.83	0.62	1.10	1.39	1.30	1.22	1.27
	$C_{4a}-N_4$	1.4104	0.43	0.26	0.41	1.24	0.79	1.21	0.94	1.10	1.09	1.13	1.19
	$N_4=S_3$	1.5556	0.59	0.38	0.46	1.96	2.13	1.44	1.09	1.36	1.39	1.61	1.91
	$S_3=N_2$	1.5600	0.58	0.36	0.40	1.93	1.94	1.21	1.10	1.39	1.43	1.59	1.88
	N_2-S_1	1.7032	0.44	0.30	0.24	1.32	1.25	0.53	0.80	0.85	0.99	1.05	1.39
	S_1-C_{8a}	1.8098	0.40	0.26	0.27	1.11	0.86	0.67	0.81	0.86	0.99	0.98	1.15
	$N_2\cdots N_4$	2.6817	0.01	0.00	-0.06				0.00		0.00	0.22	0.00
	CC	1.4041	0.47	0.26	0.29	1.43	0.80	0.77	1.11	1.41	1.31	1.25	1.27
	$C_{4a}-N_4$	1.4069	0.43	0.26	0.41	1.26	0.80	1.21	0.94	1.10	1.09	1.13	1.20
	$N_4=S_3$	1.5532	0.59	0.38	0.46	1.98	2.13	1.43	1.09	1.37	1.41	1.62	1.92
	$S_3=N_2$	1.5559	0.59	0.36	0.40	1.99	1.90	1.21	1.12	1.43	1.46	1.62	1.88
	N_2-Se_1	1.8587	0.38	0.29	0.23	1.02	1.14	0.50	0.72	0.71	0.92	1.00	1.36
	Se_1-C_{8a}	1.9524	0.35	0.26	0.26	0.90	0.80	0.61	0.79	0.83	0.97	0.97	1.12
	$N_2\cdots N_4$	2.7025	0.01	0.00	-0.06				0.00		0.00	0.23	0.00
	CC	1.4071	0.47	0.25	0.28	1.43	0.77	0.71	1.11	1.41	1.30	1.24	1.25
	$C_{4a}-N_4$	1.3996	0.45	0.25	0.42	1.33	0.78	1.28	1.00	1.21	1.14	1.17	1.22
	$N_4=Se_3$	1.7184	0.50	0.36	0.46	1.57	1.87	1.41	0.92	1.06	1.29	1.53	1.85
	$Se_3=N_2$	1.7203	0.50	0.34	0.40	1.58	1.68	1.19	0.95	1.12	1.36	1.54	1.81
	N_2-Se_1	1.8489	0.39	0.29	0.23	1.09	1.12	0.51	0.75	0.76	0.96	1.04	1.38
	Se_1-C_{8a}	1.9557	0.35	0.25	0.24	0.89	0.75	0.57	0.78	0.81	0.96	0.95	1.11
	$N_2\cdots N_4$	2.9175	0.00	0.00	-0.04				0.00		0.00	0.24	0.00
	C=O	1.1935	0.66	0.39	0.78	2.28	2.22	2.72	1.39	1.91	1.74	2.14	2.15
	C_5-S_1	1.9134	0.33	0.23	0.28	0.81	0.50	0.72	0.75	0.75	0.87	0.90	1.01
	S_1-N_2	1.6397	0.49	0.32	0.33	1.52	1.43	0.92	0.96	1.14	1.21	1.28	1.56
	$N_2=S_3$	1.5972	0.53	0.33	0.38	1.69	1.63	1.13	1.04	1.28	1.36	1.49	1.74
	$S_3=N_4$	1.5832	0.54	0.36	0.43	1.77	1.87	1.32	1.03	1.27	1.28	1.45	1.74
	N_4-C_5	1.3700	0.47	0.27	0.44	1.43	0.97	1.34	1.11	1.40	1.24	1.28	1.31
	$N_2\cdots N_4$	2.5642	0.01	0.00	-0.05				0.00		0.00	0.18	0.00

indicates a strengthening of the N=S and N=Se bonds as well. A possible explanation for the decrease of the values of the Wiberg, Mayer and Fuzzy bond orders and the Mulliken and Fuzzy overlap populations is that these methods are much more sensitive to the valence state of the atom than the other methods; after all, HN=X contains a divalent and HN=X=NH a tetravalent chalcogen atom. As a further possibility, we checked whether there is any bonding between the two nitrogen atoms in these molecules. The Mayer bond order value of about 0.24 shows weak bonding between these atoms, but none of the other methods supports this. The overlap-population-based methodologies can not be used for non-bonded atoms as the overlap populations in theses cases are always very low if not zero.

Table 5. Ellipticity (ε) and electron density in the bond critical point (ρ_{BCP}) of the N=S and N=Se bonds in HN=S, HN=S=NH, HN=Se and HN=Se=NH.

	ε	ρ_{BCP}
HN=S	0.083	0.250
HN=S=NH	0.392	0.275
HN=Se	0.125	0.206
HN=Se=NH	0.244	0.220

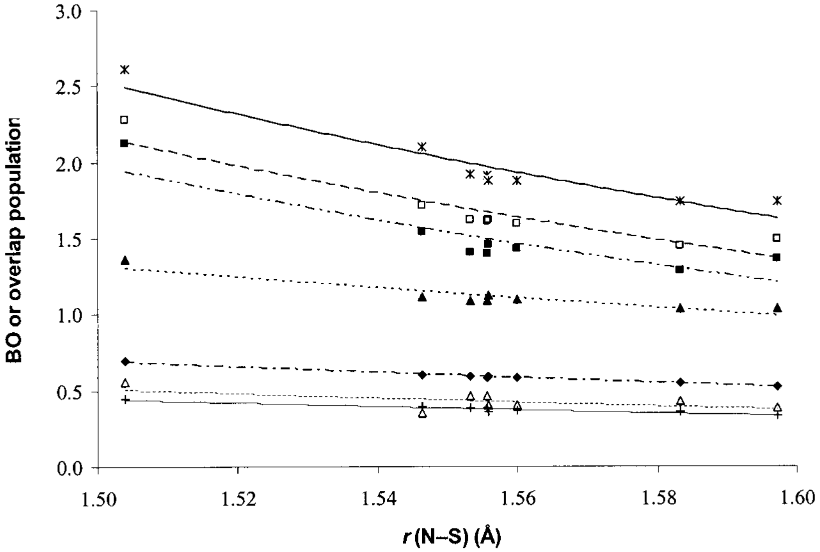


Figure 5. Exponential fit of the Wiberg (■), the Fuzzy (*), the Mayer (□) and the NAO (▲) bond orders and the unscaled Hirshfeld (♦), Fuzzy (+) and Mulliken (Δ) overlap populations vs. the *r*(N–S) of Table 4. See Table 3 for the values of the fitting parameters and the correlation coefficients.

In the second part of this discussion we will consider the bonding in compounds **1**–**4** with the above conclusion in mind. The calculated geometrical parameters and conformation of **1** are in accordance with earlier results.[3] An isolated molecule of **1** has a bent geometry and two short and one long NS bonds (see Table 4). Compounds **2** and **3** have the same conformation as **1** in the gas phase, and the bond lengths indicate similar bonding patterns in all three molecules. The scaled Hirshfeld and Fuzzy overlap populations and the Fuzzy bond orders in Table 4 are much larger than the other values for the N=S double bonds and they are in accordance with the conclusions based on the bond lengths. Only the Hirshfeld, Fuzzy bond order and NAO schemes suggest that the N=S bonds in **1** are of similar strength as those in HN=S=NH. In contrast, the Wiberg and Mayer bond orders are even smaller for the ring compounds than for HN=S=NH. As the NAO values are too small, only the scaled Hirshfeld overlap populations and Fuzzy bond orders are consistent with the conclusion based on the bond lengths. As was shown above, the AIM theory showed that for these compounds a shorter bond length indicates a stronger bond, and we can conclude that **1** contains two double and one single NS bonds. It is clear from Table 4 that the same conclusions can be drawn for compounds **2** and **3**. For the latter the bond order values have decreased in agreement with the observations made on the model compounds.

Comparison of the bond orders and bond lengths calculated for Roesky's ketone (**4**) further supports π-electron delocalisation and the aromaticity of Roesky's ketone. It was shown earlier that Roesky's ketone (**4**) is aromatic which is indicated by both the NICS value and the equalisation of the bond lengths within the ring.[5] When going from **1** to Roesky's ketone (**4**) the N=S double bond lengths increase from about 1.55 Å to about 1.58 and 1.59 Å, while the N–S single bond shortens from about 1.70 Å to about 1.64 Å. In accordance with this, the scaled Hirshfeld overlap populations of the double bonds in **4** are only 1.69 and 1.77, compared to 1.93 and 1.96 in **1**; the bond order of the single NS bond is 1.52 in **4**, while only 1.32 in **1**. The same trends can be seen in the Fuzzy, the Wiberg, the NAO and the Mayer bond orders, although the differences are far less pronounced.

Although it is known that for inorganic systems the relationship between bond order and bond length is much weaker than in organic molecules, we investigated whether Pauling's curve is applicable to our chalcogen-nitrogen systems. The calculated NS bond lengths were plotted against the values obtained from the different methodologies in Figure 5 for the tetravalent sulfur atoms; Table 3 contains the data relevant to the plots. The divalent sulfur atoms were not included in the fit, as the valence state of the atom may seriously influence this type of relationship. From Figure 5 and Table 3 it is clear that for these systems the exponential relationship between bond length and bond order/overlap population holds, but that the best correlation was found in the case of the Hirshfeld and Fuzzy overlap populations. The correlation in the case of bond orders is definitely inferior.

Conclusions

Several types of overlap populations and bond orders were compared for a large set of common organic and diatomic molecules and applied to the description of chalcogen-nitrogen systems. It has been shown that the different overlap populations (with the exception of Mulliken) and bond orders correlate very well with bond lengths. In addition, the values obtained from the different methodologies correlate well amongst themselves. The particular usefulness of these schemes was demonstrated by examining the bonding in a set of chalcogen-nitrogen compounds which exhibit unusual bonding between heteroatoms. Only the (scaled) Hirshfeld and Fuzzy overlap population schemes produce results that are compatible with the observed bond lengths.

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