Methods

All calculations were performed using the program package Gaussian 98.[1] The structures and vibrational frequencies of **1** and **2** were calculated using density functional theory (DFT) applying Barone and Adamo's Becke-style one parameter hybrid functional with modified Perdew-Wang exchange and correlation (MPW1PW91).[2] Dunning/Huzinaga's valence double-zeta basis set (D95V) was applied for all period 1 – 3 elements (including Cl);[3] for Se a Stuttgart/Dresden (SDD) effective core potential (ECP28MWB) with a (4s5p)/[2s3p] contraction for the valence electrons was used.[4]

Results and Discussion

The structures of **1** and **2** were fully optimized and the vibrational frequencies (IR and Raman intensities) calculated at the RMPW1PW91/SDD level of theory (Tab. 1).

For compound **1** the computed Se-Cl bond length of 2.456 Å agrees well with the experimentally determined bond length of 2.471(2) Å. Also for the title compound **2** the calculated and experimentally observed (X-ray) structural parameters are in good accord (Tab. 2).

The experimentally observed characteristic IR and Raman frequencies could be assigned on the basis of the computed frequencies and IR and Raman intensities (Tab. 3 and 4).

Table 1. Computational results for compounds **1** and **2**.

	1	**2**
symmetry	C_1	C_1
-*E* / a.u.	874.328141	578.211198
zpe / kcal mol^{-1}	124.2	130.9
NIMAG	0	0
dipole moment, μ / D	8.85	8.34

Table 2. Computed and experimental structural parameters for compound **2**.

	X-ray	RMPW1PW91/SDD
Se(1)-C(1)	1.909(9)	1.951
Se(1)-N(1)	2.204(6)	2.370
Se(1)-N(2)	2.107(8)	2.040
N(2)-N(3)	1.17(1)	1.240
N(3)-N(4)	1.15(1)	1.170
C(1)-Se(1)-N(1)	80.7(3)	79.2
C(1)-Se(1)-N(2)	92.7(4)	89.7
N(1)-Se(1)-N(2)	172.5(3)	168.6
Se(1)-N(2)-N(3)	114.0(7)	116.1
N(2)-N(3)-N(4)	177(1)	175.7

Table 3. Experimental IR and Raman data and computed frequencies and intensities for compound **1**.

IR, exptl. / cm^{-1}	Raman, exptl. / cm^{-1}	computed / cm^{-1}	rel. IR int.	rel. Raman activity	assignment
		3272	19	47	$\nu_{,CH,arom.}$
		3243	9	13	$\nu_{,CH,aliph.}$
		3224	5	13	$\nu_{,CH,aliph.}$
3063 w	3056 (2)	3065	100	100	$\nu_{,CH,aliph.}$
2920 w	2935 (3)	3057	27	16	$\nu_{,CH,aliph.}$
1589/1572 w		1540	20	1	$\delta_{,CH,aliph.}$
	1589/1574 (1)	1539	11	6	$\delta_{,CH,aliph.}$
1461 m		1517	25	0	$\delta_{,CH,arom.}$
1441 m		1498	11	1	$CH_{3,umbrella}$
999 m		1057	32	6	ν_{C-C}
836 s	835 (2)	858	53	2	ν_{C-N}
752 s		795	54	0	$\delta_{,CH,wag.,arom.}$
472 s	473 (8)	437	30	4	$\delta_{,CNC}$
	379 (2)	373	1	1	$\delta_{,CNC}$
304 m		310	46	1	$\delta_{,CNC} + \nu_{Se-Cl}$
		284	18	2	$CH_{3,rot.}$
	261 (2)	275	12	2	$CH_{3,rot.}$

Table 4. Experimental IR and Raman data and computed frequencies and intensities for compound **2**.

IR, exptl. / cm^{-1}	Raman, exptl. / cm^{-1}	computed / cm^{-1}	rel. IR int.	rel. Raman activity	assignment
		3279	1	31	$\nu_{,CH,arom.}$
		3165	2	17	$\nu_{,CH,aliph.}$
		3159	1	12	$\nu_{,CH,aliph.}$
3063 m	3054 (2)	3055	16	100	$\nu_{,CH,aliph.}$
2931 m	2933 (5)	3046	5	21	$\nu_{,CH,aliph.}$
2036/2028 vs	2019 (4)	2081	100	35	$\nu_{,NNN,as.}$
1589 w	1589 (1)	1522	4	4	$\delta_{,CH,arom}$
1572 w	1572 (1)	1498	2	1	$\delta_{,CH,aliph}$
1462 s		1489	1	0	$\delta_{,CH}$
1440 s		1477	1	1	CH_3, umbrella
1265 s		1291	11	4	$\nu_{,NNN,sym.}$
839 s	837 (3)	1062	5	12	$\delta_{,CC}$
748 s		859	5	2	$\delta_{,CC}$
467 m	467 (10)	854	3	4	$\delta_{,CC}$
310 s		796	7	0	$\delta_{,CH,arom,oop}$
282 m		427	3	7	$CH_{3,wag.}$
		352	11	9	$\nu_{,Se-N}$

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