catalysts

MDPI

# SUPPLEMENTARY MATERIAL

*Article*

# Chalcogen–Nitrogen Bond: Insights into a Key Chemical Motif

**Marco Bortoli [1], Andrea Madabeni [1], Pablo Andrei Nogara [2], Folorunsho B. Omage [2], Giovanni Ribaudo [3], Davide Zeppilli [1], Joao B. T. Rocha [2,*] and Laura Orian [1,*]**

[1] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy; marco.bortoli@unipd.it (M.B.); andrea.madabeni@studenti.unipd.it (A.M.); davide.zeppilli@studenti.unipd.it (D.Z.)

[2] Departamento de Bioquímica e Biologia Molecular, Universidade Federal de Santa Maria, Santa Maria 97105-900, RS, Brazil; pbnogara@gmail.com (P.A.N.); omagefolorunsho@gmail.com (F.B.O.)

[3] Dipartimento di Medicina Molecolare e Traslazionale, Università degli Studi di Brescia, Viale Europa 11, 25123 Brescia, Italy; giovanni.ribaudo@unibs

* Correspondence: jbtrocha@gmail.com (J.B.T.R); laura.orian@unipd.it (L.O.)

## Table of Contents



**Citation:** Bortoli, M.; Madabeni, A.; Nogara, P.A.; Omage, F.B.; Ribaudo, G.; Zeppilli, D.; Rocha, J.B.T.; Orian, L. Chalcogen–Nitrogen Bond: Insights into a Key Chemical Motif. *Catalysts* **2021**, *11*, 114, https:// doi: 10.3390/catal11010114.

Received: 14 December 2020
Accepted: 11 January 2021
Published: 14 January 2021

**Table S1.** Optimized geometries of compounds of general formula RX–NR′ (X = S, Te).

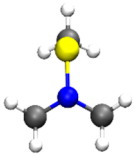
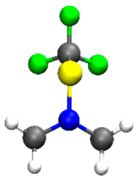
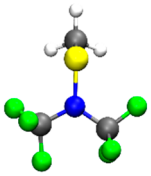
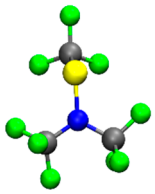
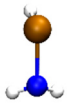
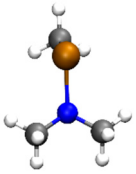
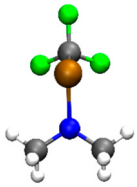
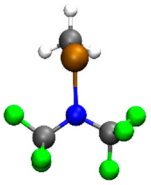
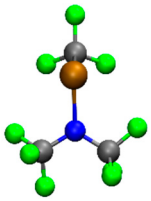
| | | | | |
|---|---|---|---|---|
|  |  |  |  |  |
| $HS–NH_2$ | $H_3CS–N(CH_3)_2$ | $F_3CS–N(CH_3)_2$ | $H_3CS–N(CF_3)_2$ | $F_3CS–N(CF_3)_2$ |
|  |  |  |  |  |
| $HTe–NH_2$ | $H_3CTe–N(CH_3)_2$ | $F_3CTe–N(CH_3)_2$ | $H_3CTe–N(CF_3)_2$ | $F_3CTe–N(CF_3)_2$ |

**Table S2.** EDA for the investigated compounds (energies in kcal $mol^{-1}$). Level of theory ZORA-M06-2X/QZ4Pae // ZORA-BLYP-D3(BJ)/TZ2P.

| | S | | | Se | | | Te | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta V_{elstat}$ | $\Delta E_{Pauli}$ | $\Delta E_{OI}$ | $\Delta V_{elstat}$ | $\Delta E_{Pauli}$ | $\Delta E_{OI}$ | $\Delta V_{elstat}$ | $\Delta E_{Pauli}$ | $\Delta E_{OI}$ |
| **1** | −174.6 | 339.2 | −230.2 | −140.0 | 286.5 | −206.2 | −126.2 | 246.7 | −174.2 |
| **2** | −196.2 | 380.6 | −256.3 | −128.2 | 219.9 | −142.0 | −119.5 | 194.3 | −117.4 |
| **3** | −160.8 | 341.3 | −258.2 | −153.9 | 270.4 | −172.6 | −134.5 | 219.4 | −129.8 |
| **4** | −161.6 | 350.4 | −264.2 | −117.8 | 228.8 | −178.0 | −105.6 | 201.1 | −159.4 |
| **5** | −174.6 | 339.2 | −230.2 | −124.4 | 250.1 | −189.3 | −107.9 | 210.1 | −161.6 |

**Table S3.** Coordinates and energies of optimized structures. Level of theory ZORA-BLYP-D3(BJ)/TZ2P.

**$HSNH_2$** **E= −1.24146483 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.731220040 |
| S | 0.000000000 | 0.000000000 | 0.000000000 |
| H | −0.835058324 | 0.437418830 | 2.117698385 |
| H | 0.835341449 | 0.436877731 | 2.117653475 |
| H | 0.000000000 | 1.333999282 | −0.307387683 |

**$CH_3SN(CH_3)_2$** **E= −3.65417837 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.718242345 |
| S | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.898958366 | 2.298267477 | −0.165061503 |
| H | 1.320297404 | 1.605177017 | 2.293239723 |
| H | 2.095195684 | 0.049775736 | 1.872795474 |
| H | 1.216875447 | 0.224489870 | 3.414208596 |
| C | −1.225799380 | 0.506907036 | 2.353312343 |

| | | | |
|---|---|---|---|
| H | −1.215974049 | 0.227315708 | 3.414404434 |
| H | −1.319459778 | 1.606441223 | 2.291494393 |
| H | −2.095186315 | 0.050815720 | 1.873724006 |
| C | 1.226271028 | 0.505585333 | 2.353490622 |
| C | 0.000000000 | 1.779605388 | −0.510615703 |
| H | 0.001257670 | 1.757191776 | −1.605893197 |
| H | −0.899323342 | 2.298436129 | −0.166475748 |

**$CF_3SN(CH_3)_2$ E= −3.98344121 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.683310175 |
| S | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.092303800 | 2.490751697 | −0.067481550 |
| H | 1.337461775 | 1.482105907 | 2.479044049 |
| H | 2.100124100 | 0.004237407 | 1.831581156 |
| H | 1.225341887 | −0.053021574 | 3.384447052 |
| C | −1.236010655 | 0.400553421 | 2.380435112 |
| H | −1.224284639 | −0.037994905 | 3.385560892 |
| H | −1.327245888 | 1.493813402 | 2.473672097 |
| H | −2.099845593 | 0.017916000 | 1.833006504 |
| C | 1.239108912 | 0.389903748 | 2.381242533 |
| C | 0.000000000 | 1.796302267 | −0.518190068 |
| F | 0.006454482 | 1.835802918 | −1.881886277 |
| F | −1.098125927 | 2.488956955 | −0.081980216 |

**$CH_3SN(CF_3)_2$ E= −4.33286037 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.735108011 |
| S | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.890759409 | 2.268292556 | 0.079489093 |
| F | 1.151566163 | −0.223150622 | 3.721682591 |
| F | 2.210772296 | 0.588762085 | 1.967859383 |
| F | 1.723090319 | −1.544137368 | 2.063103985 |
| C | −1.225926745 | −0.151885719 | 2.483162420 |
| F | −1.354738718 | −1.393170408 | 3.043774506 |
| F | −1.308635173 | 0.752459903 | 3.502583328 |
| F | −2.288132842 | 0.050016781 | 1.672029271 |
| C | 1.254263314 | −0.295463745 | 2.371850340 |
| C | 0.000000000 | 1.798267301 | −0.342325437 |
| H | 0.025285291 | 1.873739100 | −1.435837307 |
| H | −0.913956151 | 2.262814559 | 0.034528546 |

**$CF_3SN(CF_3)_2$ E= −4.65238837 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.714164981 |

| | | | |
|---|---|---|---|
| S | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.117909043 | 2.462058694 | 0.101751077 |
| F | 1.139378999 | −0.195583118 | 3.707658828 |
| F | 2.249131705 | 0.447884080 | 1.920504777 |
| F | 1.618478134 | −1.638025841 | 2.120899416 |
| C | −1.241466354 | −0.161952476 | 2.461626030 |
| F | −1.317026694 | −1.384566753 | 3.063163012 |
| F | −1.351016218 | 0.777116345 | 3.435807078 |
| F | −2.296312818 | −0.033273300 | 1.633497443 |
| C | 1.248665970 | −0.344407736 | 2.368136076 |
| C | 0.000000000 | 1.831781454 | −0.326755362 |
| F | −0.075985843 | 1.948076193 | −1.682119141 |
| F | −1.062359859 | 2.460654119 | 0.232305507 |

**$HSeNH_2$ E= −1.19674260 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.904100901 |
| Se | 0.000000000 | 0.000000000 | 0.000000000 |
| H | −0.827393566 | 0.498716166 | 2.235018680 |
| H | 0.827560185 | 0.498494001 | 2.234993467 |
| H | 0.000000000 | 1.472334641 | −0.284612958 |

**$CH_3SeN(CH_3)_2$ E= −3.60633396 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.921544859 |
| Se | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.896012215 | 2.382783666 | 0.272216586 |
| H | 1.200926928 | −0.502586827 | 3.562453931 |
| H | 2.097604340 | −0.175475622 | 2.058650434 |
| H | 1.253240912 | −1.734088330 | 2.275832946 |
| C | −1.231249840 | −0.591184245 | 2.475157414 |
| H | −1.330237173 | −1.674463652 | 2.279517541 |
| H | −1.221860523 | −0.443684737 | 3.564191008 |
| H | −2.103387218 | −0.079832269 | 2.060244260 |
| C | 1.203425630 | −0.647611964 | 2.473097013 |
| C | 0.000000000 | 1.976923006 | −0.199352247 |
| H | 0.010108347 | 2.176826369 | −1.275259030 |
| H | −0.903827000 | 2.384746120 | 0.255356837 |

**$CF_3SeN(CH_3)_2$ E= −3.93381055 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.861538314 |
| Se | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.091118849 | 2.654772313 | −0.019479549 |
| H | 1.304088010 | 1.589375905 | 2.509028343 |

| | | | |
|---|---|---|---|
| H | 2.103237438 | 0.074945161 | 2.003327691 |
| H | 1.224745694 | 0.143586642 | 3.551995579 |
| C | −1.229323035 | 0.491697315 | 2.510380469 |
| H | −1.225962332 | 0.142496623 | 3.551236304 |
| H | −1.300987542 | 1.590911193 | 2.511286276 |
| H | −2.103210826 | 0.079361195 | 2.001580821 |
| C | 1.229696435 | 0.490329868 | 2.510302227 |
| C | 0.000000000 | 1.979211042 | −0.491098162 |
| F | 0.007698323 | 2.072545271 | −1.853852289 |
| F | −1.100984022 | 2.645802583 | −0.029090545 |

**$CH_3SeN(CF_3)_2$ E= −4.29112877 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.922671784 |
| Se | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.879486253 | 2.381472851 | 0.280563415 |
| F | 1.167642730 | −0.496732522 | 3.854994595 |
| F | 2.260617596 | 0.305391810 | 2.120600011 |
| F | 1.539076764 | −1.765075426 | 2.103127045 |
| C | −1.240582639 | −0.260466454 | 2.599838154 |
| F | −1.480882070 | −1.594952237 | 2.820545261 |
| F | −1.285499623 | 0.352014819 | 3.815570062 |
| F | −2.274141366 | 0.220514318 | 1.865051651 |
| C | 1.219017879 | −0.487269826 | 2.499460399 |
| C | 0.000000000 | 1.968524527 | −0.213555707 |
| H | 0.054394987 | 2.136083667 | −1.294289071 |
| H | −0.926565183 | 2.379282898 | 0.187971786 |

**$CF_3SeN(CF_3)_2$ E= −4.60798207 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 1.891086358 |
| Se | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.106031538 | 2.601490803 | 0.286866358 |
| F | 1.156379399 | −0.352217188 | 3.853281217 |
| F | 2.249121146 | 0.409212289 | 2.101962414 |
| F | 1.606928332 | −1.684287347 | 2.165460127 |
| C | −1.233714109 | −0.241823919 | 2.608480176 |
| F | −1.350168321 | −1.536484028 | 3.039710795 |
| F | −1.324556778 | 0.554114604 | 3.706313206 |
| F | −2.292117821 | 0.026418403 | 1.813366410 |
| C | 1.241641653 | −0.404184135 | 2.503186563 |
| C | 0.000000000 | 2.011905216 | −0.215784244 |
| F | −0.038690655 | 2.224405003 | −1.562649028 |
| F | −1.079493013 | 2.596666932 | 0.351131797 |

**$HTeNH_2$ E= −1.16200015 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 2.084398071 |
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| H | −0.824596389 | 0.503579188 | 2.416532280 |
| H | 0.824581788 | 0.503590953 | 2.416534589 |
| H | 0.000000000 | 1.670416178 | −0.287995132 |

**$CH_3TeN(CH_3)_2$ E= −3.57054950 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 2.098636271 |
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.901025161 | 2.557373955 | 0.376917964 |
| H | 1.209290228 | −0.360209276 | 3.772876894 |
| H | 2.103242911 | −0.130476599 | 2.249738345 |
| H | 1.284452336 | −1.680959245 | 2.582128104 |
| C | −1.218344678 | −0.567633439 | 2.702068010 |
| H | −1.303313351 | −1.664204057 | 2.590284567 |
| H | −1.205676812 | −0.342858447 | 3.778919440 |
| H | −2.103777017 | −0.103879973 | 2.259953891 |
| C | 1.214287237 | −0.583560042 | 2.695646199 |
| C | 0.000000000 | 2.185219055 | −0.111053306 |
| H | −0.001131833 | 2.451769533 | −1.171942742 |
| H | −0.900000238 | 2.557683321 | 0.378555488 |

**$CF_3TeN(CH_3)_2$ E= −3.89315294 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 2.059570401 |
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.090603478 | 2.783841367 | 0.523229998 |
| H | 1.214009120 | −0.120211103 | 3.760073066 |
| H | 2.105747725 | −0.003043704 | 2.226443307 |
| H | 1.358522622 | −1.552123260 | 2.711857413 |
| C | −1.211921176 | −0.527944874 | 2.708490547 |
| H | −1.255965274 | −1.631034532 | 2.725546389 |
| H | −1.223958833 | −0.175367655 | 3.749943003 |
| H | −2.102394773 | −0.146006761 | 2.204656585 |
| C | 1.238747372 | −0.454710971 | 2.713072802 |
| C | 0.000000000 | 2.233789219 | −0.084615687 |
| F | 0.014689396 | 2.618846016 | −1.400351901 |
| F | −1.100087611 | 2.789387393 | 0.498812443 |

**$CH_3TeN(CF_3)_2$ E= −4.26163350 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 2.108897806 |
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.921854302 | 2.555764721 | 0.305604698 |
| F | 1.268991180 | 0.695615411 | 3.922450135 |
| F | 2.277494852 | 0.156726388 | 2.052566608 |
| F | 1.416182417 | −1.414059932 | 3.332071422 |
| C | −1.227242685 | −0.372741088 | 2.732127841 |
| F | −1.638590187 | −1.644968278 | 2.396971977 |
| F | −1.150892505 | −0.332077804 | 4.087157681 |
| F | −2.234561975 | 0.465767131 | 2.342376213 |
| C | 1.215351618 | −0.145138135 | 2.844991415 |
| C | 0.000000000 | 2.175327201 | −0.133592061 |
| H | −0.042198239 | 2.414034021 | −1.200728545 |
| H | −0.885122176 | 2.552352194 | 0.377947714 |

**$CF_3TeN(CF_3)_2$ E= −4.57605003 Hartree**

| | | | |
|---|---|---|---|
| N | 0.000000000 | 0.000000000 | 2.084556829 |
| Te | 0.000000000 | 0.000000000 | 0.000000000 |
| F | 1.096894803 | 2.797622645 | 0.424484590 |
| F | 1.154966078 | −0.260826298 | 4.068482926 |
| F | 2.240331829 | 0.460310159 | 2.295221710 |
| F | 1.631694753 | −1.641102197 | 2.426640870 |
| C | −1.219350801 | −0.159378315 | 2.831662470 |
| F | −1.354624820 | −1.413161352 | 3.369305952 |
| F | −1.299280927 | 0.724545302 | 3.863728436 |
| F | −2.287512664 | 0.057714071 | 2.025265578 |
| C | 1.238060275 | −0.354173602 | 2.719928066 |
| C | 0.000000000 | 2.232725665 | −0.131852035 |
| F | −0.018525658 | 2.544214648 | −1.464621193 |
| F | −1.090090691 | 2.786760160 | 0.453630949 |