**Supplementary material**

**Thermodynamic Stability of Fenclorim and Clopyralid**

Ana R. R. P. Almeida\*, Bruno D. A. Pinheiro, Ana I.M.C. Lobo Ferreira, Manuel J. S. Monte\*

Centro de Investigação em Química (CIQUP), Department of Chemistry and Biochemistry, Faculty of Sciences. University of Porto, Rua do Campo Alegre, P-4169-007 Porto, Portugal

\*Authors for correspondence: [ana.figueira@fc.up.pt](mailto:ana.figueira@fc.up.pt),mjmonte@fc.up.pt

**This Supporting Material file contains the following contents**:

* Specific densities of fenclorim and clopyralid
* DSC results: temperatures, molar enthalpies, and entropies of fusion of fenclorim and clopyralid
* Standard molar heat capacity results, , at *T* = 298.15 K for fenclorim and clopyralid
* Effusion vapor pressure results of fenclorim and clopyralid
* Computational study
* References
* **Specific Densities**

Considering the agreement between the density value of fenclorim reported in the literature, 1.541 g.cm-3 [[[1]](#endnote-1)], and the one determined experimentally in the present work for this compound, (1.43 ± 0.02) g.cm-3, it was decided to perform the experimental determination of the density of clopyralid (3,6-dichloro-2-pyridinecarboxylic acid). The obtained result, (1.64 ± 0.03) g.cm-3, was compared with the value published in the literature for the similar compound, 2-pyridinecarboxylic acid, 1.509 g.cm-3 [[[2]](#endnote-2)].

**Table S1.** Specific densities of fenclorim and clopyralid

|  |  |
| --- | --- |
| Compound | Density / g.cm-3 |
| **Fenclorim** | 1.44 |
| 1.41 |
| 1.44 |
| Meana | **1.43 ± 0.04** |
| Literature | 1.541 [1] |
|  | 1.364 [[[3]](#endnote-3)] |
|  | 1.4 ± 0.1 [[[4]](#endnote-4)] |
|  | 1.5 (20 ºC) [[[5]](#endnote-5),[[6]](#endnote-6)] |
| **Clopyralid** | 1.62 |
| 1.63 |
| 1.67 |
| Meana | **1.64 ± 0.05** |
| Literature | 1.5163 (60.17 ºC) [[[7]](#endnote-7)] |
|  | 1.6 ± 0.1 [4] |

aAverage of three measurements of the volume and mass of three pellets. The uncertainty assigned correspond to the expanded uncertainty determined from the standard deviation of the mean of the three measurements and the coverage factor *k* = 4.30 (0.95 level of confidence)

* **Differential scanning calorimetry**

**Table S2.** DSC results: temperatures, molar enthalpies and entropies of fusion of fenclorim and clopyralid.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Exp. | *T*fus(onset) / K | / kJ·mol-1 |  | / J·K-1·mol-1 |
| **Fenclorim** | | | | |
| 1 | 368.64 | 23.07 |  | 62.6 ± 1.9b |
| 2 | 368.67 | 23.08 |  |
| 3 | 368.50 | 23.05 |  |
| 4 | 368.63 | 23.11 |  |
| Mean | 368.61 ± 0.35a | 23.08 ± 0.69a |  |
| Lit. | 365-366 [[[8]](#endnote-8),[[9]](#endnote-9)] |  |  |  |
|  | 370.1 [[[10]](#endnote-10)-,[[11]](#endnote-11),[[12]](#endnote-12),[[13]](#endnote-13)] |  |  |  |
| **Clopyralid** | | | | |
| 1 | 422.65 | 27.46 |  | 65.3 ± 1.6b |
| 2 | 422.75 | 27.65 |  |
| 3 | 422.68 | 27.58 |  |
| 4 | 422.45 | 27.69 |  |
| Mean | 422.63 ± 0.38a | 27.59 ± 0.67a |  |
| Lit. | 424-425 [[[14]](#endnote-14)] |  |  |  |
|  | 422.8 [[[15]](#endnote-15)] |  |  |  |
|  | 422-424 [[[16]](#endnote-16)] |  |  |  |

aStandard uncertainty calculated through the RSS method combining the expanded uncertainties of the four experimental runs (0.95 level of confidence, *k* = 3.18) with the standard uncertainties of the DSC calibration. bUncertainties calculated through the RSS method.

* **Heat Capacity Drop Calorimetry**

**Table S3**. Standard molar heat capacity results, , at *T* = 298.15 K for fenclorim and clopyralid. The calibration constant used to calculate the was derived from the sapphire [NBS, SRM 720,   
(*α*-Al2O3)] calibration, (6.6809 ± 0.0146 W·V–1).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Exp | *m*sample/g | Ndrop | *<T*furnace>/K | *<T*calorimeter>/K | *T*/K | /J·K–1·mol–1 |
| **Fenclorim** | | | | | | |
| I | 0.48467 | 11 | 303.10 | 293.17 | 298.14 | 214.6 ± 0.6 |
| II | 0.42311 | 36 | 303.08 | 293.18 | 298.13 | 214.1 ± 0.6 |
| III | 0.40059 | 10 | 303.11 | 293.17 | 298.14 | 214.6 ± 0.6 |
| **Clopyralid** | | | | | | |
| I | 0.39698 | 8 | 303.17 | 293.17 | 298.17 | 175.4 ± 0.7 |
| III | 0.39317 | 11 | 303.16 | 293.17 | 298.17 | 175.3 ± 0.5 |

Ndrop = number of drop experiments; *T*furnace = average temperature of the furnace; *T*calorimeter = average temperature of the calorimeter; the uncertainty reported is twice the standard deviation of the mean and the calibration uncertainty is included.

**Effusion vapor pressure results**

**Table S4.** Effusion vapor pressure results for crystalline fenclorim.a

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *T*/Kb |  | *t*/s |  | Orifices |  | *m*/mg | | |  | *p*/Pab | | | | 100*p*/*p*c |
|  |  |  | *m*S | *m*M | *m*L |  | *p*S | *p*M | *p*L | *p*mean |
| 311.11 |  | 22000 |  | A1-B4-C7 |  | 5.48 | 6.71 | 8.35 |  | 0.107 | 0.106 | 0.105 | 0.106 | 0.2 |
| 313.29 |  | 22000 |  | A2-B5-C8 |  | 7.06 | 8.60 | 10.71 |  | 0.138 | 0.136 | 0.135 | 0.136 | -1.2 |
| 315.23 |  | 22000 |  | A3-B6-C9 |  | 8.83 | 10.85 | 13.52 |  | 0.173 | 0.172 | 0.171 | 0.172 | -0.8 |
| 317.10 |  | 15788 |  | A1-B4-C7 |  | 8.06 | 9.95 | 12.34 |  | 0.221 | 0.220 | 0.218 | 0.220 | 1.8 |
| 319.31 |  | 15788 |  | A2-B5-C8 |  | 10.27 | 12.19 | 16.00 |  | 0.282 | 0.271 | 0.283 | 0.279 | 0.0 |
| 321.27 |  | 15788 |  | A3-B6-C9 |  | 12.94 | 15.09 | 19.89 |  | 0.357 | 0.355 | 0.353 | 0.355 | 1.6 |
| 323.10 |  | 18303 |  | A1-B4-C7 |  | 18.30 | 22.27 | 27.65 |  | 0.436 | 0.430 | 0.425 | 0.430 | 0.1 |
| 325.28 |  | 18303 |  | A2-B5-C8 |  | 22.76 | 28.01 | 34.25 |  | 0.545 | 0.542 | 0.528 | 0.538 | -1.8 |
| 327.25 |  | 18303 |  | A3-B6-C9 |  | 28.43 | 34.76 | 43.66 |  | 0.682 | 0.675 | 0.675 | 0.677 | -0.5 |
| 329.11 |  | 10832 |  | A1-B4-C7 |  | 20.66 | 25.39 | 31.52 |  | 0.840 | 0.835 | 0.825 | 0.833 | 0.0 |
| 331.27 |  | 10832 |  | A2-B5-C8 |  | 25.88 | 31.54 | 40.15 |  | 1.056 | 1.041 | 1.055 | 1.051 | 0.0 |
| 333.23 |  | 10832 |  | A3-B6-C9 |  | 32.02 | 38.9 | 49.49 |  | 1.310 | 1.288 | 1.304 | 1.301 | 0.6 |

aResults related to the small (A1, A2, A3), medium (B4, B5, B6) and large (C7, C8, C9) effusion orifices are denoted, respectively, by the subscripts *S*, *M* and *L*. bEstimated standard uncertainties: *u*(*T*/K) = 0.01; *u*(*p*/Pa) = 0.02. cΔ*p* = *p* − *p*calc., where *p*calc is calculated from the Clarke and Glew equation, Eq. (2).

**Table S5.** Effusion vapor pressure results for crystalline clopyralid.a

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *T*/Kb |  | *t*/s |  | Orifices |  | *m*/mg | | |  | *p*/Pab | | | | 100*p*/*p*c |
|  |  |  | *m*S | *m*M | *m*L |  | *p*S | *p*M | *p*L | *p*mean |
| 334.11 |  | 23405 |  | A1-B4-C7 |  | 5.26 | 6.43 | 8.08 |  | 0.108 | 0.107 | 0.107 | 0.107 | 1.9 |
| 336.38 |  | 23405 |  | A2-B5-C8 |  | 6.66 | 8.24 | 10.29 |  | 0.137 | 0.137 | 0.137 | 0.137 | 0.1 |
| 338.46 |  | 23405 |  | A3-B6-C9 |  | 8.33 | 10.23 | 12.98 |  | 0.172 | 0.171 | 0.173 | 0.172 | -1.0 |
| 340.12 |  | 21936 |  | A1-B4-C7 |  | 9.51 | 11.88 | 14.78 |  | 0.210 | 0.212 | 0.210 | 0.211 | 0.5 |
| 342.36 |  | 21936 |  | A2-B5-C8 |  | 12.09 | 14.81 | 18.45 |  | 0.268 | 0.266 | 0.263 | 0.266 | -1.3 |
| 344.36 |  | 21936 |  | A3-B6-C9 |  | 14.84 | 18.27 | 23.17 |  | 0.330 | 0.329 | 0.332 | 0.330 | -1.6 |
| 346.12 |  | 14792 |  | A1-B4-C7 |  | 12.46 | 15.28 | 19.23 |  | 0.412 | 0.409 | 0.409 | 0.410 | 0.8 |
| 348.34 |  | 14792 |  | A2-B5-C8 |  | 15.49 | 18.93 | 23.57 |  | 0.514 | 0.508 | 0.503 | 0.508 | -1.6 |
| 350.40 |  | 14792 |  | A3-B6-C9 |  | 19.34 | 23.72 | 29.89 |  | 0.643 | 0.638 | 0.640 | 0.640 | -0.4 |
| 352.13 |  | 14474 |  | A1-B4-C7 |  | 22.98 | 28.47 | 35.55 |  | 0.783 | 0.785 | 0.780 | 0.783 | 1.4 |
| 354.41 |  | 14474 |  | A2-B5-C8 |  | 28.96 | 35.72 | 44.35 |  | 0.990 | 0.988 | 0.977 | 0.985 | 0.7 |
| 356.38 |  | 14474 |  | A3-B6-C9 |  | 35.09 | 43.52 | 54.27 |  | 1.203 | 1.207 | 1.198 | 1.203 | 0.4 |

aResults related to the small (A1, A2, A3), medium (B4, B5, B6) and large (C7, C8, C9) effusion orifices are denoted, respectively, by the subscripts *S*, *M* and *L*. bEstimated standard uncertainties: *u*(*T*/K) = 0.01; *u*(*p*/Pa) = 0.02. cΔ*p* = *p* − *p*calc., where *p*calc is calculated from the Clarke and Glew equation, Eq. (2).

**Computational Study**

**Table S6.** Calculated absolute standard enthalpies, , (in Hartree, Eh)a of all considered molecules estimated using G3(MP2)/B3LYP. Literature values of (g). 1 a. u. (Hartree) corresponds to 2625.50 kJ.mol-1.

|  |  |  |
| --- | --- | --- |
| Compound | Absolute Enthalpy / Eh |  |
| Methane | -40.420547 | -74.4 ± 0.4 [[[17]](#endnote-17)] |
| Ethane | -79.651017 | -83.8 ± 0.3 [17] |
| Benzene | -231.835164 | 82.9 ± 0.9 [[[18]](#endnote-18)] |
| Chlorobenzene | -690.999276 | 52.0 ± 1.3 [17] |
| *o*-Dichlorobenzene | -1150.160000 | 30.2 ± 2.1 [17] |
| *m*-Dichlorobenzene | -1150.162189 | 25.7 ± 2.1 [17] |
| *p*-Dichlorobenzene | -1150.162055 | 22.5 ± 0.5 [17] |
| Biphenyl | -462.501235 | 180.3 ± 3.3 [18] |
| Pyridine | -247.873431 | 140.4 ± 0.7 [17] |
| 2-Chloropyridine | -707.039096 | 104.5 ± 1.8 [[[19]](#endnote-19)] |
| 3-Chloropyridine | -707.036001 | 107.6 ± 1.7 [19] |
| 2,3-Dichloropyridine | -1166.198732 | 89.5 ± 3.4 [19] |
| 2,5-Dichloropyridine | -1166.200417 | 71.5 ± 2.2 [19] |
| 2,6-Dichloropyridine | -1166.203496 | 71.4 ± 2.2 [19] |
| 3,5-Dichloropyridine | -1166.197590 | 82.2 ± 2.1 [19] |
| Pyrimidine | -263.915002 | 195.7 ± 1.4 [17] |
| 2-Chloropyrimidine | -723.078844 | 155.1 ± 1.6 [19] |
| 2,4-Dichloropyrimidine | -1182.243354 | 125.6 ± 2.2 [17] |
| 4,6-Dichloropyrimidine | -1182.244877 | 126.0 ± 2.2 [17] |
| 2,4,6-Trichloropyrimidine | -1641.407011 | 85.8 ± 1.3 [19] |
| 2,4,5,6-Tetrachloropyrimidine | -2100.562885 | 86.7 ± 2.1 [19] |
| Benzoic acid | -420.210294 | -294.0 ± 2.2 [17] |
| 2-Chlorobenzoic acid | -879.365005 | -304.2 ± 0.7 [[[20]](#endnote-20)] |
| 3-Chlorobenzoic acid | -879.373326 | -321.8 ± 3.7 [20] |
| 4-Chlorobenzoic acid | -879.373923 | -324.8 ± 3.7 [20] |
| 1-Naphthalenecarboxylic acid | -573.594610 | -223.1 ± 1.0 [17] |
| 2-Naphthalenecarboxylic acid | -573.599298 | -232.5 ± 1.7 [17] |
| 2-Pyridinecarboxylic acid | -436.250294 | -243.0 ± 2.6 [[[21]](#endnote-21)] |
| 3-Pyridinecarboxylic acid | -436.247160 | -232.6 ± 1.5 [17] |
| 4-Pyridinecarboxylic acid | -436.246034 | -234.8 ± 4.7 [21] |
| Fenclorim | -1412.917444 | -- |
| Clopyralid | -1354.567694 | -- |

**Table S7.** Working reactions and computed enthalpies of reaction, , and formation, , of fenclorim in the gaseous state, at *T* = 298.15 K.

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | |  |  |
|  | (1) | 17.06  21.05a | 206.34  201.95a |
|  | (2) | 72.15  76.15a | 201.75  197.35a |
|  | (3) | 85.38  79.63b  79.98c | 205.52  206.77b  203.22c |
|  | (4) | 22.25 | 191.85 |
|  | (5) | 34.98  40.73b  40.38c | 201.82  200.57b  204.12c |
|  | (6) | 77.19 | 194.91 |
| Mean valued / kJ.mol-1 | | | **201.35 ± 2.92** |

aReactions (1 and 2) using the isomer 2,4-dichloropyrimidine. bReactions (3 and 5) using the isomer *m*-dichlorobenzene. cReactions (3 and 5) using the isomer *p*-dichlorobenzene. dThe uncertainty assigned correspond to the expanded uncertainty determined from the estimated standard deviation of the mean for the 12 reactions and the coverage factor *k* = 2.20 (0.95 level of confidence).

**Table S8.** Working reactions and computed enthalpies of reaction, , and formation, , of clopyralid in the gaseous state, at *T* = 298.15 K.

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | |  |  |
|  | (1) | -20.62  -16.19a  -28.70b  -13.20c | -284.78  -271.21a  -276.80b  -281.50c |
|  | (2) | -3.26  -25.11d  -26.68e | -279.34  -275.09d  -276.52e |
|  | (3) | -4.86  -16.98d  -18.55e | -284.36  -280.12d  -281.55e |
|  | (4) | -3.46  -5.04a  -17.54b  -2.04c | -292.44  -278.86a  -284.46b  -289.16c |
|  | (5) | -21.77  -17.34a  -29.85b  -14.35c | -289.53  -275.96a  -281.55b  -286.25c |
|  | (6) | -19.52  -25.27f  -24.92g | -276.18  -274.93f  -278.48g |
|  | (7) | -11.29  -17.04f  -16.69g | -274.00  -272.76f  -276.31g |
|  | (8) | -8.34  -14.09f  -13.73g | -279.16  -277.91f  -281.47g |
|  | (9) | -25.17  -20.74a  -33.25b  -17.75c | -286.73  -273.16a  -278.75b  -283.45c |
|  | (10) | -16.94  -12.52a  -25.02b  -9.52c | -284.56  -270.98a  -276.58b  -281.28c |
|  | (11) | -13.98  -9.56a  -22.07b  -6.56c | 289.72  -276.14a  -281.73a  -286.44c |
| Mean valueh / kJ.mol-1 | | | **-280.26 ± 1.72** |

aReaction (1, 4, 5, 9, 10 or 11) using the isomer 2,3-dichloropyridine. bReactions (1, 4, 5, 9, 10 or 11) using the isomer 2,6-dichloropyridine. cReactions (1, 4, 5, 9, 10 or 11) using the isomer 3,5-dichloropyridine.dReactions (2 or 3) using the isomer *m*-chlorobenzoic acid. eReactions (2 or 3) using the isomer *p*-chlorobenzoic acid. fReactions (6, 7 or 8) using the isomer *m*-chlorobenzene. gReactions (6, 7 or 8) using the isomer *p*-chlorobenzene. hThe uncertainty assigned correspond to the expanded uncertainty determined from the estimated standard deviation of the mean for the 39 reactions and the coverage factor *k* = 2.02 (0.95 level of confidence).

* References

1. . Kwon, E.; Kim, J.; Kang, G.; Kim, T.H. Crystal structure of fenclorim. *Acta Cryst*. **2015**. *E71*, o714. [↑](#endnote-ref-1)
2. . Hamazaki, H.; Hosomi, H.; Takeda, S.; Kataoka, H.; Ohba, S. 2-Pyridinecarboxylic Acid. *Acta Cryst.* **1998**, *C54*, IUC9800049. [↑](#endnote-ref-2)
3. . <https://www.lookchem.com/Fenclorim/> [↑](#endnote-ref-3)
4. . <https://www.chemsrc.com/en/cas/3740-92-9_670309.html> [↑](#endnote-ref-4)
5. . <https://www.agropages.com/agrodata/Detail-602.htm> [↑](#endnote-ref-5)
6. . <https://hybris-static-assets-production.s3-eu-west-1.amazonaws.com/sys-master/pdfs/hd0/ha3/9684274741278/EN_ST-WB-MSDS-2213897-1-1-1.PDF> [↑](#endnote-ref-6)
7. . Yaws, C.L. Thermophysical Properties of Chemicals and Hydrocarbons. Elsevier **2014**. [↑](#endnote-ref-7)
8. . <https://www.matrixscientific.com/043477.html> [↑](#endnote-ref-8)
9. . <https://www.chemicalbook.com/ChemicalProductProperty_EN_CB6187251.htm> [↑](#endnote-ref-9)
10. . <https://www.agropages.com/agrodata/Detail-602.htm> [↑](#endnote-ref-10)
11. . <https://pubchem.ncbi.nlm.nih.gov/compound/77338> [↑](#endnote-ref-11)
12. . <http://www.chemspider.com/Chemical-Structure.69755.html> [↑](#endnote-ref-12)
13. . <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/296.htm> [↑](#endnote-ref-13)
14. . <https://pubchem.ncbi.nlm.nih.gov/compound/Clopyralid> [↑](#endnote-ref-14)
15. . <http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/169.htm> [↑](#endnote-ref-15)
16. . <http://www.molmall.net/product/100090> [↑](#endnote-ref-16)
17. . Pedley, J.B. Thermochemical Data and Structures of Organic Compounds Thermodynamics, Research Center, College Station, Texas**, 1994**. [↑](#endnote-ref-17)
18. . Roux, M.V.; Temprado, M.; Chickos, J.S.; Nagano. Y.Critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons, *J. Phys. Chem. Ref. Data* **2008**, *37*, 1855-1996. [↑](#endnote-ref-18)
19. . Ribeiro da Silva, MA.V.; Amaral, L.M.P.F.; Gomes J.R.B. *J. Phys. Chem. B* **2007**, *111*, 792-799. [↑](#endnote-ref-19)
20. . Sabbah, R.; Rojas Aguilar, A., Etude thermodynamique des trois isomeres de l'acide chlorobenzoique. Partie II, *Can. J. Chem*., **1995**, *73*, 1538-1545. [↑](#endnote-ref-20)
21. . Ribeiro da Silva, M.D.M.C.; Matos, M.A.R.; Vaz, M.C.; Santos, L.M.N.B.F.; Pilcher, G.; Acree Jr., W.E.; Powell, J.R. Enthalpies of combustion of the pyridine N-oxide derivatives: 4-methyl-, 3-cyano-, 4-cyano-, 3-hydroxy-, 2-carboxy-, 4-carboxy-, and 3-methyl-4-nitro, and of the pyridine derivatives: 2-carboxy-, and 4-carboxy-. The dissociation enthalpies of the N-O bonds. *J. Chem. Thermodyn.* **1998**, *30*, 869–878. [↑](#endnote-ref-21)