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**Supporting information for article:**

# Ionic cocrystals of dithiobispyridines: the role of I···I halogen bonds in the building of iodine frameworks and the stabilization of crystal structures

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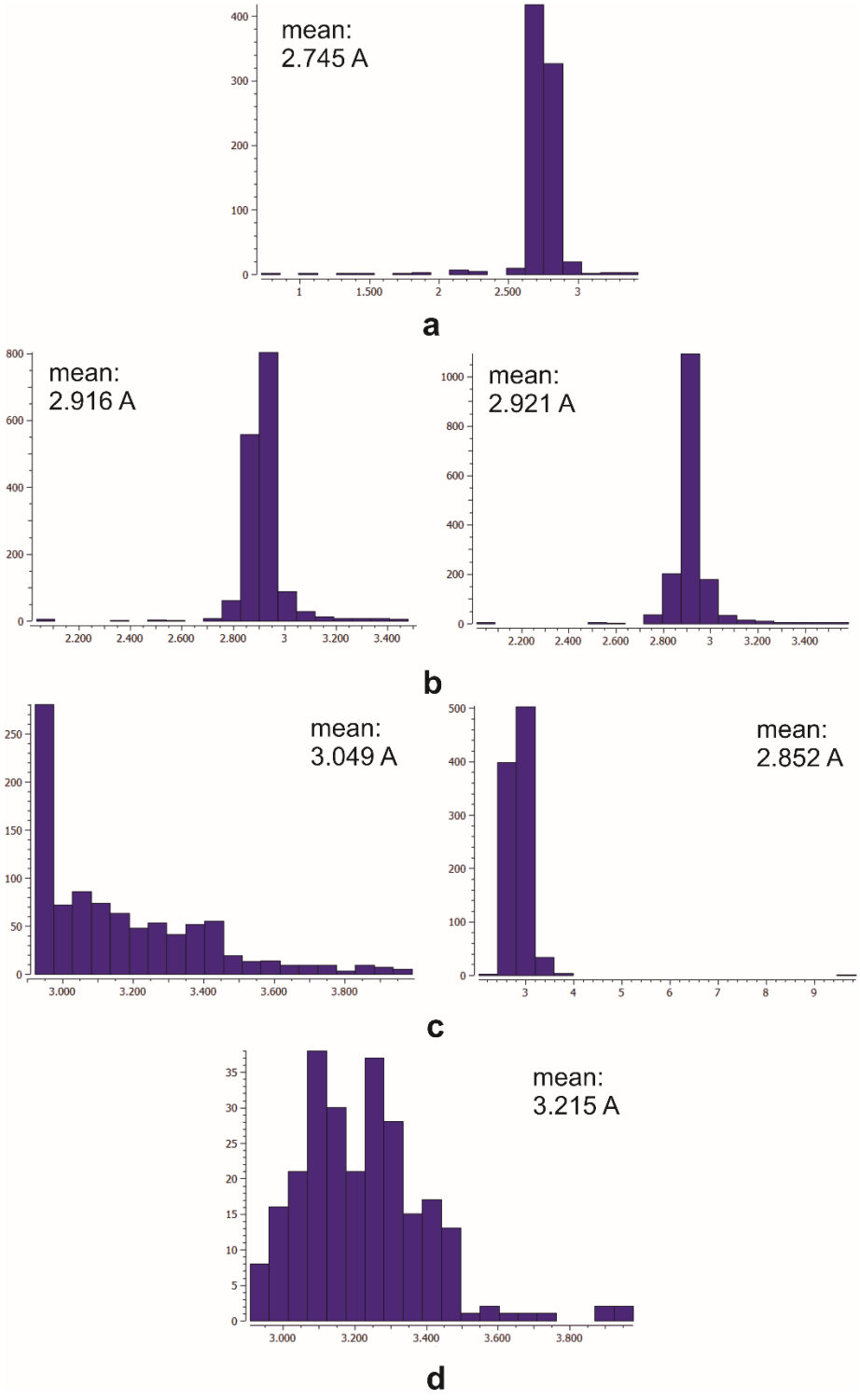


**Figure S1** Histogram presenting distances between iodine atoms in: neutral molecule (**a**), symmetric complex anion $I_3^-$ (**b**), asymmetric complex anion $I_3^-$ (**c**), symmetric complex anion $I_5^-$ (**d**).

**Table S1** Molecular geometries and total energies of organic components of (**I**) and (**II**).

**a) 2,2'-dithiopyridine neutral state**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000017 | 0.000450 | YES |
| RMS Force | 0.000004 | 0.000300 | YES |
| Maximum Displacement | 0.000802 | 0.001800 | YES |
| RMS Displacement | 0.000300 | 0.001200 | YES |

Predicted change in Energy=-5.463303D-09

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.527962 | 0.377006 | -0.946205 |
| 2 | 7 | 0 | 1.518585 | 0.374183 | 0.919667 |
| 3 | 16 | 0 | 0.794232 | -1.694838 | -0.694578 |
| 4 | 16 | 0 | -0.786631 | -1.712204 | 0.634001 |
| 5 | 6 | 0 | 3.604731 | 1.553480 | 0.733376 |
| 6 | 1 | 0 | 4.252459 | 2.341576 | 1.096915 |
| 7 | 6 | 0 | 3.115071 | -0.260748 | -0.759550 |
| 8 | 1 | 0 | 3.374411 | -0.917135 | -1.582062 |
| 9 | 6 | 0 | 2.366670 | 1.328824 | 1.322949 |
| 10 | 1 | 0 | 2.029313 | 1.938786 | 2.155908 |
| 11 | 6 | 0 | -1.892515 | -0.410348 | 0.051158 |
| 12 | 6 | 0 | 1.889669 | -0.394001 | -0.090156 |
| 13 | 6 | 0 | -3.623383 | 1.536432 | -0.740297 |
| 14 | 1 | 0 | -4.277537 | 2.325071 | -1.090921 |
| 15 | 6 | 0 | -2.383772 | 1.331271 | -1.333723 |
| 16 | 1 | 0 | -2.051629 | 1.957323 | -2.156783 |
| 17 | 6 | 0 | 3.980984 | 0.735157 | -0.333454 |
| 18 | 1 | 0 | 4.938173 | 0.870486 | -0.824645 |
| 19 | 6 | 0 | -3.118637 | -0.297696 | 0.722992 |
| 20 | 1 | 0 | -3.372347 | -0.969264 | 1.534937 |
| 21 | 6 | 0 | -3.992665 | 0.698000 | 0.313267 |
| 22 | 1 | 0 | -4.950699 | 0.817721 | 0.806854 |

HF = -1291.9328751 a.u.

**b) 2,2'-dithiopyridine cation**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000020 | 0.000450 | YES |
| RMS Force | 0.000006 | 0.000300 | YES |
| Maximum Displacement | 0.000236 | 0.001800 | YES |
| RMS Displacement | 0.000078 | 0.001200 | YES |

Predicted change in Energy=-8.077824D-09

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.369829 | 0.836651 | -0.013141 |
| 2 | 7 | 0 | 1.389443 | 0.777603 | 0.120131 |
| 3 | 1 | 0 | 0.327261 | 0.917424 | 0.125862 |
| 4 | 16 | 0 | 0.706845 | -1.727870 | -0.678102 |
| 5 | 16 | 0 | -0.723241 | -1.631752 | 0.869972 |
| 6 | 6 | 0 | 3.577163 | 1.659691 | 0.317783 |
| 7 | 1 | 0 | 4.227333 | 2.489181 | 0.560140 |
| 8 | 6 | 0 | 3.225954 | -0.626171 | -0.385099 |
| 9 | 1 | 0 | 3.604140 | -1.597166 | -0.676400 |
| 10 | 6 | 0 | 2.208539 | 1.803745 | 0.423307 |
| 11 | 1 | 0 | 1.728397 | 2.721636 | 0.736515 |
| 12 | 6 | 0 | -1.869351 | -0.364922 | 0.301756 |
| 13 | 6 | 0 | 1.852016 | -0.434290 | -0.257955 |
| 14 | 6 | 0 | -3.601675 | 1.623151 | -0.393362 |
| 15 | 1 | 0 | -4.252119 | 2.439756 | -0.678799 |
| 16 | 6 | 0 | -2.222389 | 1.805354 | -0.374403 |
| 17 | 1 | 0 | -1.782391 | 2.758418 | -0.646945 |
| 18 | 6 | 0 | 4.087563 | 0.428858 | -0.103262 |
| 19 | 1 | 0 | 5.158078 | 0.285595 | -0.191625 |
| 20 | 6 | 0 | -3.232590 | -0.647950 | 0.297027 |
| 21 | 1 | 0 | -3.589237 | -1.640306 | 0.540109 |
| 22 | 6 | 0 | -4.112887 | 0.376911 | -0.046012 |
| 23 | 1 | 0 | -5.180897 | 0.194380 | -0.057733 |

HF = -1292.3270839 a.u.

**c) 2,2'-dithiopyridine proton transfer transition state**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000011 | 0.000450 | YES |
| RMS Force | 0.000003 | 0.000300 | YES |
| Maximum Displacement | 0.001142 | 0.001800 | YES |
| RMS Displacement | 0.000291 | 0.001200 | YES |

Predicted change in Energy=-6.380905D-09

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 7 | 0 | -1.279186 | 0.764239 | -0.091164 |
| 2 | 7 | 0 | 1.292084 | 0.768868 | 0.088766 |
| 3 | 1 | 0 | 0.006183 | 0.853801 | 0.000001 |
| 4 | 16 | 0 | 0.750689 | -1.729844 | -0.790422 |
| 5 | 16 | 0 | -0.724184 | -1.755064 | 0.717916 |
| 6 | 6 | 0 | 3.458000 | 1.697233 | 0.440429 |
| 7 | 1 | 0 | 4.064435 | 2.544763 | 0.730852 |
| 8 | 6 | 0 | 3.217814 | -0.585805 | -0.292394 |
| 9 | 1 | 0 | 3.636502 | -1.546629 | -0.561536 |
| 10 | 6 | 0 | 2.075516 | 1.796807 | 0.453186 |
| 11 | 1 | 0 | 1.567905 | 2.707442 | 0.748643 |
| 12 | 6 | 0 | -1.818036 | -0.426907 | 0.224833 |
| 13 | 6 | 0 | 1.837362 | -0.410125 | -0.260131 |
| 14 | 6 | 0 | -3.450112 | 1.690466 | -0.416553 |
| 15 | 1 | 0 | -4.061177 | 2.542462 | -0.683232 |
| 16 | 6 | 0 | -2.068200 | 1.797749 | -0.426707 |
| 17 | 1 | 0 | -1.565506 | 2.718950 | -0.696713 |
| 18 | 6 | 0 | 4.034043 | 0.488685 | 0.052584 |
| 19 | 1 | 0 | 5.111528 | 0.374673 | 0.037658 |
| 20 | 6 | 0 | -3.197546 | -0.610766 | 0.252433 |
| 21 | 1 | 0 | -3.611023 | -1.580920 | 0.494842 |
| 22 | 6 | 0 | -4.019580 | 0.468518 | -0.062388 |
| 23 | 1 | 0 | -5.096438 | 0.348388 | -0.050498 |

HF = -1292.3236721 a.u.

**d) 4,4’-dithiopyridine neutral state**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000047 | 0.000450 | YES |
| RMS Force | 0.000010 | 0.000300 | YES |
| Maximum Displacement | 0.000563 | 0.001800 | YES |
| RMS Displacement | 0.000203 | 0.001200 | YES |

Predicted change in Energy=-3.202551D-08

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.771979 | -1.574397 | -0.695610 |
| 2 | 16 | 0 | -0.771941 | -1.574003 | 0.696738 |
| 3 | 6 | 0 | 3.179447 | -0.319343 | -0.794387 |
| 4 | 1 | 0 | 3.398999 | -1.005549 | -1.604576 |
| 5 | 6 | 0 | 2.768240 | 1.444889 | 1.229595 |
| 6 | 1 | 0 | 2.628301 | 2.159042 | 2.036205 |
| 7 | 6 | 0 | -1.955616 | -0.352614 | 0.120373 |
| 8 | 6 | 0 | 1.955626 | -0.352639 | -0.119972 |
| 9 | 6 | 0 | -2.768185 | 1.444251 | -1.230102 |
| 10 | 1 | 0 | -2.628191 | 2.158057 | -2.037009 |
| 11 | 6 | 0 | 4.126174 | 0.620962 | -0.399221 |
| 12 | 1 | 0 | 5.084645 | 0.666587 | -0.908372 |
| 13 | 6 | 0 | -3.179536 | -0.319122 | 0.794599 |
| 14 | 1 | 0 | -3.399148 | -1.004995 | 1.605053 |
| 15 | 6 | 0 | -4.126284 | 0.620930 | 0.398883 |
| 16 | 1 | 0 | -5.084831 | 0.666701 | 0.907879 |
| 17 | 6 | 0 | -1.745430 | 0.549630 | -0.918545 |
| 18 | 1 | 0 | -0.820069 | 0.559873 | -1.479612 |
| 19 | 6 | 0 | 1.745514 | 0.550047 | 0.918577 |
| 20 | 1 | 0 | 0.820230 | 0.560465 | 1.479768 |
| 21 | 7 | 0 | 3.941182 | 1.496098 | 0.593828 |
| 22 | 7 | 0 | -3.941220 | 1.495646 | -0.594522 |

HF = -1291.9303193 a.u.

**e) 4,4'-dithiopyridine cation**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000010 | 0.000450 | YES |
| RMS Force | 0.000002 | 0.000300 | YES |
| Maximum Displacement | 0.001159 | 0.001800 | YES |
| RMS Displacement | 0.000302 | 0.001200 | YES |

Predicted change in Energy=-2.336799D-09

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.997096 | -0.440004 | -2.090454 |
| 2 | 16 | 0 | -0.685969 | -1.686915 | -1.033100 |
| 3 | 6 | 0 | 3.103062 | -0.590737 | -0.312476 |
| 4 | 1 | 0 | 3.339741 | -1.553435 | -0.745702 |
| 5 | 6 | 0 | 2.514578 | 1.860987 | 0.837277 |
| 6 | 1 | 0 | 2.351993 | 2.802912 | 1.342662 |
| 7 | 6 | 0 | -1.846669 | -0.446689 | -0.516661 |
| 8 | 6 | 0 | 2.001873 | 0.165174 | -0.829390 |
| 9 | 6 | 0 | -3.261687 | 1.462296 | -0.883859 |
| 10 | 1 | 0 | -3.634216 | 2.253082 | -1.529800 |
| 11 | 6 | 0 | 3.860866 | -0.117526 | 0.713671 |
| 12 | 1 | 0 | 4.704469 | -0.653182 | 1.126620 |
| 13 | 6 | 0 | -2.373105 | -0.490102 | 0.781147 |
| 14 | 1 | 0 | -2.040941 | -1.242947 | 1.485906 |
| 15 | 6 | 0 | -3.330212 | 0.450448 | 1.153848 |
| 16 | 1 | 0 | -3.752227 | 0.424133 | 2.155242 |
| 17 | 6 | 0 | -2.318193 | 0.562414 | -1.367017 |
| 18 | 1 | 0 | -1.951711 | 0.645393 | -2.382367 |
| 19 | 6 | 0 | 1.737186 | 1.417846 | -0.188188 |
| 20 | 1 | 0 | 0.907346 | 2.025727 | -0.523022 |
| 21 | 7 | 0 | 3.575959 | 1.104063 | 1.284795 |
| 22 | 7 | 0 | -3.775216 | 1.423471 | 0.352567 |
| 23 | 1 | 0 | 4.136587 | 1.437954 | 2.052128 |

HF = -1292.5041907 a.u.

**f) 4,4'-dithiopyridine dication**

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000050 | 0.000450 | YES |
| RMS Force | 0.000006 | 0.000300 | YES |
| Maximum Displacement | 0.001068 | 0.001800 | YES |
| RMS Displacement | 0.000375 | 0.001200 | YES |

Predicted change in Energy=-1.468114D-08

Optimization completed.

Input orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 16 | 0 | 0.750270 | -1.067526 | -0.732490 |
| 2 | 16 | 0 | -0.750271 | -1.067128 | 0.733310 |
| 3 | 6 | 0 | 3.264304 | -0.119613 | -0.828531 |
| 4 | 1 | 0 | 3.331688 | -0.671405 | -1.758396 |
| 5 | 6 | 0 | 3.199446 | 1.284818 | 1.546023 |
| 6 | 1 | 0 | 3.254789 | 1.852240 | 2.465991 |
| 7 | 6 | 0 | -2.080569 | -0.096180 | 0.065001 |
| 8 | 6 | 0 | 2.080557 | -0.096203 | -0.064703 |
| 9 | 6 | 0 | -3.199444 | 1.284026 | -1.546432 |
| 10 | 1 | 0 | -3.254763 | 1.851025 | -2.466663 |
| 11 | 6 | 0 | 4.372687 | 0.558876 | -0.378741 |
| 12 | 1 | 0 | 5.313318 | 0.576347 | -0.913753 |
| 13 | 6 | 0 | -3.264371 | -0.119332 | 0.828754 |
| 14 | 1 | 0 | -3.331780 | -0.670708 | 1.758864 |
| 15 | 6 | 0 | -4.372772 | 0.558869 | 0.378575 |
| 16 | 1 | 0 | -5.313442 | 0.576515 | 0.913512 |
| 17 | 6 | 0 | -2.060894 | 0.623114 | -1.138855 |
| 18 | 1 | 0 | -1.181104 | 0.661539 | -1.766272 |
| 19 | 6 | 0 | 2.060916 | 0.623635 | 1.138828 |
| 20 | 1 | 0 | 1.181169 | 0.662281 | 1.766291 |
| 21 | 7 | 0 | 4.316447 | 1.239085 | 0.789075 |
| 22 | 7 | 0 | -4.316497 | 1.238554 | -0.789544 |
| 23 | 1 | 0 | 5.147840 | 1.727801 | 1.111481 |
| 24 | 1 | 0 | -5.147902 | 1.727061 | -1.112232 |

HF = -1292.5891513