

Supplemental data

Semiexperimental equilibrium structure of 1-methylisatin from gas-phase electron diffraction data and structural changes in isatin due to 1-methyl and 5-fluoro substituents as predicted by coupled cluster computations

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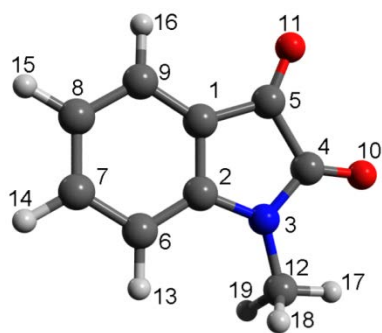


Figure S1. Molecular model of 1-methylisatin with atom numbering (according to the used Z-matrix)

Table S1. Optimized Cartesian coordinates of 1-methylisatin, Å.

| At | MP2_AE/CVTZ | | | MP2_FC/CVTZ | | |
|-----|-------------|-----------|-----------|-------------|-----------|-----------|
| | x | y | z | x | y | z |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.397658 | 0.000000 | 0.000000 | 1.400595 | 0.000000 |
| N3 | 1.302421 | 1.901167 | 0.000000 | 1.304786 | 1.905205 | 0.000000 |
| C4 | 2.229662 | 0.885488 | 0.000000 | 2.234161 | 0.888100 | 0.000000 |
| C5 | 1.403368 | -0.430636 | 0.000000 | 1.406401 | -0.431301 | 0.000000 |
| C6 | -1.184596 | 2.108796 | 0.000000 | -1.186892 | 2.113555 | 0.000000 |
| C7 | -2.373781 | 1.379456 | 0.000000 | -2.378544 | 1.382725 | 0.000000 |
| C8 | -2.378388 | -0.011950 | 0.000000 | -2.383298 | -0.011570 | 0.000000 |
| C9 | -1.179380 | -0.718048 | 0.000000 | -1.181976 | -0.719412 | 0.000000 |
| O10 | 3.433634 | 0.999449 | 0.000000 | 3.439961 | 1.003051 | 0.000000 |
| O11 | 1.878046 | -1.541952 | 0.000000 | 1.882232 | -1.544214 | 0.000000 |
| C12 | 1.641610 | 3.297845 | 0.000000 | 1.644056 | 3.304782 | 0.000000 |
| H13 | -1.198035 | 3.188156 | 0.000000 | -1.200279 | 3.194236 | 0.000000 |
| H14 | -3.313320 | 1.912255 | 0.000000 | -3.319176 | 1.916293 | 0.000000 |
| H15 | -3.318444 | -0.541731 | 0.000000 | -3.324619 | -0.541815 | 0.000000 |
| H16 | -1.155114 | -1.798077 | 0.000000 | -1.157985 | -1.800740 | 0.000000 |
| H17 | 2.724121 | 3.365931 | 0.000000 | 2.727917 | 3.372714 | 0.000000 |
| H18 | 1.248747 | 3.790964 | 0.886628 | 1.250049 | 3.797757 | 0.887895 |
| H19 | 1.248747 | 3.790964 | -0.886628 | 1.250049 | 3.797757 | -0.887895 |

| At | MP2_FC/VQZ | | | MP2_FC/VTZ | | |
|-----|------------|-----------|-----------|------------|-----------|-----------|
| | x | y | z | x | y | z |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.400111 | 0.000000 | 0.000000 | 1.402246 | 0.000000 |
| N3 | 1.304604 | 1.904678 | 0.000000 | 1.305816 | 1.906818 | 0.000000 |
| C4 | 2.233173 | 0.889590 | 0.000000 | 2.235801 | 0.888494 | 0.000000 |
| C5 | 1.406060 | -0.430453 | 0.000000 | 1.407572 | -0.431326 | 0.000000 |
| C6 | -1.185542 | 2.113957 | 0.000000 | -1.188058 | 2.116363 | 0.000000 |
| C7 | -2.376818 | 1.383410 | 0.000000 | -2.381188 | 1.384911 | 0.000000 |
| C8 | -2.381965 | -0.010242 | 0.000000 | -2.386091 | -0.011050 | 0.000000 |
| C9 | -1.181800 | -0.718923 | 0.000000 | -1.183509 | -0.719905 | 0.000000 |
| O10 | 3.437991 | 1.003845 | 0.000000 | 3.443153 | 1.003528 | 0.000000 |
| O11 | 1.882822 | -1.541308 | 0.000000 | 1.884102 | -1.545631 | 0.000000 |
| C12 | 1.641175 | 3.303963 | 0.000000 | 1.645896 | 3.307327 | 0.000000 |
| H13 | -1.198417 | 3.194250 | 0.000000 | -1.201284 | 3.197147 | 0.000000 |
| H14 | -3.317048 | 1.916692 | 0.000000 | -3.321942 | 1.918602 | 0.000000 |
| H15 | -3.323207 | -0.539678 | 0.000000 | -3.327647 | -0.541193 | 0.000000 |
| H16 | -1.158989 | -1.799799 | 0.000000 | -1.159890 | -1.801317 | 0.000000 |
| H17 | 2.724396 | 3.375418 | 0.000000 | 2.730292 | 3.374616 | 0.000000 |
| H18 | 1.245530 | 3.794818 | 0.887608 | 1.251868 | 3.800511 | 0.888384 |
| H19 | 1.245530 | 3.794818 | -0.887608 | 1.251868 | 3.800511 | -0.888384 |

(to be continued)

Table S1. (continued).

| CCSD(T)_FC/VTZ | | | | CCSD(T)_AE/CVQZ | | |
|----------------|-----------|-----------|-----------|-------------------|-----------|-----------|
| At | x | y | z | x | y | z |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.406272 | 0.000000 | 0.000000 | 1.401000 | 0.000000 |
| N3 | 1.309976 | 1.909579 | 0.000000 | 1.307013 | 1.902715 | 0.000000 |
| C4 | 2.241551 | 0.886773 | 0.000000 | 2.234424 | 0.883503 | 0.000000 |
| C5 | 1.410397 | -0.437382 | 0.000000 | 1.405973 | -0.437160 | 0.000000 |
| C6 | -1.189117 | 2.125310 | 0.000000 | -1.183824 | 2.117949 | 0.000000 |
| C7 | -2.385453 | 1.390654 | 0.000000 | -2.375390 | 1.384893 | 0.000000 |
| C8 | -2.395630 | -0.008964 | 0.000000 | -2.385122 | -0.009073 | 0.000000 |
| C9 | -1.188763 | -0.718674 | 0.000000 | -1.183149 | -0.717089 | 0.000000 |
| O10 | 3.445755 | 1.002448 | 0.000000 | 3.434076 | 0.996904 | 0.000000 |
| O11 | 1.886016 | -1.548811 | 0.000000 | 1.880280 | -1.543799 | 0.000000 |
| C12 | 1.656790 | 3.314545 | 0.000000 | 1.650978 | 3.303091 | 0.000000 |
| H13 | -1.200711 | 3.207420 | 0.000000 | -1.195134 | 3.197890 | 0.000000 |
| H14 | -3.326879 | 1.926542 | 0.000000 | -3.315314 | 1.918844 | 0.000000 |
| H15 | -3.338938 | -0.538842 | 0.000000 | -3.326957 | -0.537606 | 0.000000 |
| H16 | -1.166731 | -1.801485 | 0.000000 | -1.160144 | -1.797844 | 0.000000 |
| H17 | 2.743637 | 3.377604 | 0.000000 | 2.734952 | 3.369389 | 0.000000 |
| H18 | 1.262995 | 3.810019 | 0.890445 | 1.256788 | 3.796653 | 0.888319 |
| H19 | 1.262995 | 3.810019 | -0.890445 | 1.256788 | 3.796653 | -0.888319 |
| B2PLYP/VTZ | | | | $r_e(\text{GED})$ | | |
| At | x | y | z | x | y | z |
| C1 | -0.388100 | 0.671634 | 0.000005 | 0.00000 | 0.00000 | 0.00000 |
| C2 | -0.512531 | -0.726691 | 0.000006 | 1.40260 | 0.00000 | 0.00000 |
| N3 | 0.744654 | -1.342700 | 0.000006 | 1.91657 | 1.30374 | 0.00000 |
| C4 | 1.759716 | -0.404663 | 0.000004 | 0.91321 | 2.25032 | 0.00000 |
| C5 | 1.045889 | 0.986137 | 0.000004 | -0.40588 | 1.41712 | 0.00000 |
| C6 | -1.758943 | -1.330856 | 0.000006 | 2.12777 | -1.17986 | 0.00000 |
| C7 | -2.880414 | -0.496204 | 0.000005 | 1.40959 | -2.38232 | 0.00000 |
| C8 | -2.766290 | 0.893353 | 0.000004 | 0.01509 | -2.41951 | 0.00000 |
| C9 | -1.506243 | 1.488657 | 0.000003 | -0.67708 | -1.20741 | 0.00000 |
| O10 | 2.947467 | -0.624653 | 0.000002 | 1.06011 | 3.44692 | 0.00000 |
| O11 | 1.615679 | 2.049817 | 0.000003 | -1.51849 | 1.87723 | 0.00000 |
| C12 | 0.970613 | -2.769684 | 0.000007 | 3.32418 | 1.62273 | 0.00000 |
| H13 | -1.870030 | -2.404691 | 0.000007 | 3.21556 | -1.18412 | 0.00000 |
| H14 | -3.863419 | -0.945549 | 0.000005 | 1.95926 | -3.32102 | 0.00000 |
| H15 | -3.656271 | 1.504374 | 0.000003 | -0.49849 | -3.37843 | 0.00000 |
| H16 | -1.388172 | 2.562889 | 0.000002 | -1.76423 | -1.16999 | 0.00000 |
| H17 | 2.044875 | -2.927290 | 0.000007 | 3.40997 | 2.70513 | 0.00000 |
| H18 | 0.538182 | -3.231048 | 0.887568 | 3.81066 | 1.21964 | 0.88848 |
| H19 | 0.538182 | -3.231050 | -0.887553 | 3.81066 | 1.21964 | -0.88848 |

Note. Atom numbering is given in Fig. S1

Table S2. Optimized Cartesian coordinates of isatin, Å.

| At | MP2_AE/CVTZ | | MP2_FC/CVTZ | | MP2_FC/VQZ | |
|-----|-------------|-----------|-------------|-----------|------------|-----------|
| | x | y | x | y | x | y |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.396784 | 0.000000 | 1.399707 | 0.000000 | 1.399126 |
| N3 | 1.308217 | 1.886374 | 1.310597 | 1.890256 | 1.310277 | 1.889765 |
| C4 | 2.239218 | 0.873184 | 2.243754 | 0.875703 | 2.242488 | 0.876765 |
| C5 | 1.400749 | -0.438919 | 1.403767 | -0.439620 | 1.403222 | -0.439195 |
| C6 | -1.185003 | 2.106009 | -1.187231 | 2.110828 | -1.185818 | 2.111149 |
| C7 | -2.373342 | 1.378547 | -2.378058 | 1.381909 | -2.376215 | 1.382697 |
| C8 | -2.378739 | -0.013986 | -2.383650 | -0.013516 | -2.382313 | -0.012175 |
| C9 | -1.181045 | -0.718663 | -1.183668 | -0.719984 | -1.183646 | -0.719508 |
| O10 | 3.440962 | 0.977590 | 3.447315 | 0.981206 | 3.444948 | 0.981731 |
| O11 | 1.868823 | -1.552869 | 1.872957 | -1.555189 | 1.873475 | -1.552630 |
| H12 | 1.561362 | 2.859100 | 1.563482 | 2.863991 | 1.563205 | 2.863194 |
| H13 | -1.197392 | 3.185902 | -1.199458 | 3.192039 | -1.197453 | 3.191896 |
| H14 | -3.312290 | 1.912216 | -3.318084 | 1.916371 | -3.315787 | 1.916952 |
| H15 | -3.318977 | -0.543320 | -3.325177 | -0.543272 | -3.323815 | -0.541014 |
| H16 | -1.155500 | -1.798589 | -1.158441 | -1.801209 | -1.159707 | -1.800282 |

| At | MP2_FC/VTZ | | CCSD(T)_FC/VTZ | | CCSD(T)_AE/CVQZ | |
|-----|------------|-----------|----------------|-----------|-----------------|-----------|
| | x | y | x | y | x | y |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.401361 | 0.000000 | 1.397628 | 0.000000 | 1.392470 |
| N3 | 1.311685 | 1.891768 | 1.308517 | 1.884858 | 1.304727 | 1.878975 |
| C4 | 2.245331 | 0.875889 | 2.239173 | 0.867268 | 2.231798 | 0.865639 |
| C5 | 1.404909 | -0.439675 | 1.397879 | -0.443562 | 1.393182 | -0.442372 |
| C6 | -1.188421 | 2.113626 | -1.183273 | 2.112243 | -1.178453 | 2.104929 |
| C7 | -2.380694 | 1.384030 | -2.374338 | 1.383984 | -2.365148 | 1.379271 |
| C8 | -2.386427 | -0.013053 | -2.385449 | -0.011454 | -2.376409 | -0.011064 |
| C9 | -1.185176 | -0.720520 | -1.184460 | -0.715083 | -1.180289 | -0.712777 |
| O10 | 3.450469 | 0.981403 | 3.437953 | 0.972336 | 3.426088 | 0.969070 |
| O11 | 1.874800 | -1.556656 | 1.864788 | -1.554999 | 1.859328 | -1.548643 |
| H12 | 1.565143 | 2.865864 | 1.562573 | 2.855739 | 1.558509 | 2.848180 |
| H13 | -1.200621 | 3.194947 | -1.193218 | 3.189710 | -1.188001 | 3.180496 |
| H14 | -3.320858 | 1.918585 | -3.310444 | 1.918321 | -3.299585 | 1.912512 |
| H15 | -3.328190 | -0.542704 | -3.324109 | -0.538630 | -3.313516 | -0.537007 |
| H16 | -1.160343 | -1.801823 | -1.160048 | -1.792630 | -1.156437 | -1.788493 |

Table S3. Optimized Cartesian coordinates of 5-fluoroisatin, Å.

| MP2_AE/CVTZ | | MP2_FC/CVTZ | | MP2_FC/VQZ | | |
|-------------|-----------|-------------|-----------|------------|-----------|-----------|
| At | x | y | x | y | x | y |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 1.396108 | 0.000000 | 1.399022 | 0.000000 | 1.398480 |
| N3 | 1.309373 | 1.886114 | 1.311774 | 1.889976 | 1.311388 | 1.889511 |
| C4 | 2.239757 | 0.873205 | 2.244305 | 0.875720 | 2.243058 | 0.876830 |
| C5 | 1.401715 | -0.439461 | 1.404746 | -0.440167 | 1.404259 | -0.439713 |
| C6 | -1.187751 | 2.101792 | -1.189969 | 2.106595 | -1.188257 | 2.107604 |
| C7 | -2.377062 | 1.377467 | -2.381879 | 1.380933 | -2.380164 | 1.383099 |
| C8 | -2.354957 | -0.009289 | -2.359618 | -0.008721 | -2.357143 | -0.005773 |
| C9 | -1.174718 | -0.729797 | -1.177262 | -0.731306 | -1.177391 | -0.730863 |
| O10 | 3.441472 | 0.974909 | 3.447843 | 0.978492 | 3.445447 | 0.979120 |
| O11 | 1.866100 | -1.554407 | 1.870226 | -1.556747 | 1.870722 | -1.554132 |
| H12 | 1.562636 | 2.858716 | 1.564763 | 2.863588 | 1.564425 | 2.862824 |
| H13 | -1.207227 | 3.181299 | -1.209319 | 3.187419 | -1.206383 | 3.187954 |
| H14 | -3.331061 | 1.881757 | -3.336934 | 1.886016 | -3.334889 | 1.887801 |
| F15 | -3.521077 | -0.665907 | -3.527530 | -0.665992 | -3.526430 | -0.662089 |
| H16 | -1.172079 | -1.809250 | -1.174923 | -1.812027 | -1.177025 | -1.811135 |

| MP2_FC/VTZ | | CCSD(T)_FC/VTZ | | CCSD(T)_AE/CVQZ | | |
|------------|-----------|----------------|-----------|-----------------|-----------|-----------|
| At | x | y | x | y | x | y |
| C1 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 | 0.000000 |
| C2 | 0.000000 | 0.000000 | 0.000000 | 1.403456 | 0.000000 | 1.398300 |
| N3 | 1.312866 | 1.312866 | 1.317152 | 1.894424 | 1.313279 | 1.888547 |
| C4 | 2.245888 | 2.245888 | 2.252471 | 0.875116 | 2.245082 | 0.873485 |
| C5 | 1.405903 | 1.405903 | 1.410305 | -0.445478 | 1.405635 | -0.444249 |
| C6 | -1.191057 | -1.191057 | -1.191458 | 2.119002 | -1.186484 | 2.112198 |
| C7 | -2.384523 | -2.384523 | -2.388562 | 1.390982 | -2.379418 | 1.387131 |
| C8 | -2.362388 | -2.362388 | -2.369698 | -0.003310 | -2.359810 | -0.001831 |
| C9 | -1.178858 | -1.178858 | -1.184519 | -0.730136 | -1.180551 | -0.727793 |
| O10 | 3.451001 | 3.451001 | 3.454476 | 0.980218 | 3.442513 | 0.977031 |
| O11 | 1.872120 | 1.872120 | 1.874976 | -1.560462 | 1.869448 | -1.554026 |
| H12 | 1.566407 | 1.566407 | 1.570864 | 2.867666 | 1.566763 | 2.860124 |
| H13 | -1.210145 | -1.210145 | -1.207232 | 3.201205 | -1.201427 | 3.192495 |
| H14 | -3.339616 | -3.339616 | -3.343883 | 1.898898 | -3.333316 | 1.893781 |
| F15 | -3.531512 | -3.531512 | -3.542365 | -0.660416 | -3.530825 | -0.657132 |
| H16 | -1.177136 | -1.177136 | -1.185224 | -1.812075 | -1.182320 | -1.807991 |

Table S4. Calculated harmonic and anharmonic wavenumbers (cm^{-1}) of 1-methylisatin in comparison with experimental vibrational spectra in the gas phase.

| No | Observed [1] | | Calculated | | Assignment (PED, %) |
|-----------------|--------------|---------|------------|--------|--|
| | IR | Raman | harm | anharm | |
| v ₁ | – | – | 3223 | 3102 | v _{8,15} (45), v _{6,13} (23), v _{7,14} (17), v _{9,16} (15) |
| v ₂ | – | – | 3217 | 3062 | v _{6,13} (63), v _{8,15} (20), v _{9,16} (15) |
| v ₃ | – | – | 3206 | 3051 | v _{9,16} (65), v _{8,15} (17) |
| v ₄ | – | – | 3194 | 3016 | v _{7,14} (66), v _{8,15} (19) |
| v ₅ | – | – | 3164 | 3002 | v _{12,17} (86) |
| v ₆ | 2948 w | 2950 m | 3109 | 2938 | v _{12,19} (50), v _{12,18} (50) |
| v ₇ | – | – | 3049 | 2866 | v _{12,19} (43), v _{12,18} (43) |
| v ₈ | 1743 s | 1740 vs | 1800 | 1781 | v _{4,10} (66), v _{5,11} (20) |
| v ₉ | 1718 vs | 1717 s | 1789 | 1772 | v _{5,11} (68), v _{4,10} (19) |
| v ₁₀ | 1603 vs | 1610 vs | 1660 | 1619 | v _{1,9} (26), v _{2,6} (16) |
| v ₁₁ | – | – | 1641 | 1597 | v _{7,8} (22), v _{2,6} (16), v _{1,2} (15) |
| v ₁₂ | 1486 sh | – | 1533 | 1492 | α _{18,12,19} (43) |
| v ₁₃ | 1467 vs | – | 1513 | 1470 | α _{18,12,19} (15) |
| v ₁₄ | – | 1488 w | 1509 | 1450 | α _{17,12,18} (46), α _{17,12,19} (46) |
| v ₁₅ | – | 1456 w | 1509 | 1450 | α _{8,7,14} (14), α _{7,8,15} (12), v _{6,7} (12), v _{8,9} (12) |
| v ₁₆ | – | – | 1461 | 1420 | α _{3,12,17} (23), α _{17,12,18} (18), α _{17,12,19} (18) |
| v ₁₇ | 1364 s | – | 1406 | 1359 | α _{3,12} (18) |
| v ₁₈ | 1325 vs | 1328 s | 1371 | 1324 | v _{3,4} (11), v _{3,12} (11), v _{8,9} (11) |
| v ₁₉ | – | 1308 w | 1348 | 1311 | v _{2,3} (12), α _{7,6,13} (12) |
| v ₂₀ | 1253 m | 1253 vs | 1273 | 1237 | α _{3,12,7} (15), v _{3,4} (15) |
| v ₂₁ | 1192 m | 1194 m | 1214 | 1188 | v _{1,5} (26) |
| v ₂₂ | 1161 m | 1161 m | 1187 | 1165 | α _{6,7,14} (21), α _{8,7,14} (18) |
| v ₂₃ | – | – | 1160 | 1122 | α _{3,12,19} (46), α _{3,12,18} (46) |
| v ₂₄ | 1111 s | 1117 s | 1138 | 1111 | α _{3,12,17} (13), α _{8,9,16} (10) |
| v ₂₅ | 1089 vs | 1091 sh | 1113 | 1085 | v _{8,9} (11), v _{6,7} (9) |
| v ₂₆ | 1035 m | – | 1052 | 1022 | v _{3,12} (42) |
| v ₂₇ | – | 1019 s | 1042 | 1018 | v _{7,8} (30), v _{6,7} (16), v _{8,9} (15) |
| v ₂₈ | – | – | 987 | 969 | γ _{14,7} (30), γ _{15,8} (27) |
| v ₂₉ | 993 sh | – | 968 | 948 | γ _{16,9} (43), γ _{14,7} (21) |
| v ₃₀ | 955 m | 956 w | 962 | 941 | v _{4,5} (17) |
| v ₃₁ | 880 m | 865 w | 881 | 855 | γ _{13,6} (45) |
| v ₃₂ | 863 s | – | 879 | 864 | α _{3,4,10} (10), α _{7,8,9} (9) |
| v ₃₃ | 816 m | 817 w | 832 | 801 | γ _{11,5} (39), γ _{10,4} (30) |
| v ₃₄ | 757 vs | – | 771 | 747 | γ _{15,8} (35), γ _{14,7} (17), γ _{13,6} (15) |
| v ₃₅ | – | – | 732 | 711 | γ _{6,2} (30), γ _{10,4} (15) |
| v ₃₆ | 701 s | 703 vs | 714 | 702 | α _{2,6,7} (13), α _{1,9,8} (11) |
| v ₃₇ | 684 m | 685 m | 696 | 688 | α _{7,8,9} (11), α _{1,5,11} (10) |
| v ₃₈ | 543 m | – | 561 | 541 | α _{1,5,4} (16) |
| v ₃₉ | 556 m | 560 m– | 558 | 553 | γ _{10,4} (18), γ _{6,2} (17), τ _{7,8} (16) |
| v ₄₀ | – | 527 s | 533 | 523 | v _{3,12} (22), |
| v ₄₁ | – | 483 vs | 487 | 471 | v _{2,3} (11), α _{2,6,7} (10) |
| v ₄₂ | 473 vs | – | 485 | 479 | γ _{10,4} (31), γ _{11,5} (23), γ _{6,2} (15) |
| v ₄₃ | – | – | 407 | 395 | γ _{9,1} (20), τ _{6,7} (16), γ _{11,5} (15) |
| v ₄₄ | – | 328 m | 327 | 324 | α _{5,4,10} (24), α _{3,4,10} (20), v _{5,5} (16) |
| v ₄₅ | – | 296 m | 293 | 291 | α _{2,3,12} (15) |
| v ₄₆ | – | 252 w | 273 | 260 | γ _{12,3} (26), γ _{9,1} (19) |
| v ₄₇ | – | 161 m | 237 | 239 | α _{2,3,12} (17), α _{4,3,12} (16), α _{3,2,6} (15) |
| v ₄₈ | – | – | 157 | 31 | γ _{12,3} (85) |
| v ₄₉ | – | 171 m | 140 | 243 | γ _{9,1} (20), γ _{11,5} (18) |
| v ₅₀ | – | – | 123 | 119 | γ _{12,3} (39), τ _{2,3} (27), τ _{3,4} (21) |
| v ₅₁ | – | – | 102 | 95 | τ _{4,5} (29), τ _{1,5} (23), γ _{12,3} (20) |

v; stretching. α; bending. γ; wagging. τ; torsion.

v; very. s; strong. w; weak. m; medium. sh; shoulder. PED; potential energy distribution.

Table S5. Total corrections $\Delta(r_{ij,e} - r_{ij,a})$ to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ rms vibrational amplitudes (in Å) for 1-methylisatin, Å.

| Parameter | $r_{ij,a}$ | $r_{ij,e} - r_{ij,a}$ ^a | $u_{ij,h1}$ ^b | $u_{ij,exp}$ |
|--------------------|------------|------------------------------------|--------------------------|--------------------------|
| C1–C2 | 1.409 | –0.0066 | 0.0461 | 0.0486(21) ^c |
| C2–N3 | 1.411 | –0.0098 | 0.0467 | 0.0492(21) ^c |
| N3–C4 | 1.390 | –0.0108 | 0.0469 | 0.0494(21) ^c |
| C4–C5 | 1.568 | –0.0080 | 0.0563 | 0.0588(21) ^c |
| C1–C5 | 1.481 | –0.0071 | 0.0501 | 0.0526(21) ^c |
| C2–C6 | 1.392 | –0.0073 | 0.0451 | 0.0476(21) ^c |
| C6–C7 | 1.407 | –0.0066 | 0.0460 | 0.0485(21) ^c |
| C7–C8 | 1.402 | –0.0072 | 0.0458 | 0.0483(21) ^c |
| C8–C9 | 1.402 | –0.0064 | 0.0458 | 0.0483(21) ^c |
| C1–C9 | 1.391 | –0.0069 | 0.0450 | 0.0475(21) ^c |
| C4=O10 | 1.209 | –0.0036 | 0.0376 | 0.0401(21) ^c |
| C5=O11 | 1.208 | –0.0042 | 0.0375 | 0.0400(21) ^c |
| N3–C12 | 1.455 | –0.0119 | 0.0484 | 0.0509(21) ^c |
| C _{Ph} –H | 1.103 | –0.0151 | 0.0751 | 0.0751 |
| C12–H17 | 1.102 | –0.0162 | 0.0759 | 0.0759 |
| C12–H18 | 1.106 | –0.0158 | 0.0767 | 0.0767 |
| O10...O11 | 3.032 | –0.0130 | 0.1030 | 0.1197(103) ^d |
| N3...O10 | 2.317 | –0.0088 | 0.0543 | 0.0601(58) ^e |
| N3...O11 | 3.494 | –0.0110 | 0.0596 | 0.0758 ^f |
| C1...O11 | 2.422 | –0.0074 | 0.0595 | 0.0653(58) ^e |
| C4...O11 | 2.469 | –0.0091 | 0.0673 | 0.0731(58) ^e |
| C5...O10 | 2.513 | –0.0087 | 0.0674 | 0.0732(58) ^e |
| O10...C12 | 2.905 | 0.0029 | 0.1039 | 0.1206(103) ^d |
| C9...O11 | 3.202 | –0.0045 | 0.0975 | 0.1142(103) ^d |
| C2...O10 | 3.470 | –0.0057 | 0.0572 | 0.0734(112) ^f |
| C2...O11 | 3.479 | –0.0066 | 0.0572 | 0.0734(112) ^f |
| C1...O10 | 3.612 | –0.0055 | 0.0604 | 0.0766(112) ^f |
| C8...O11 | 4.566 | –0.0041 | 0.0956 | 0.1932(242) ^g |
| C6...O10 | 4.755 | –0.0061 | 0.0678 | 0.1654(242) ^g |
| C6...O11 | 4.763 | –0.0045 | 0.0652 | 0.1628(242) ^g |
| O11...C12 | 4.851 | –0.0018 | 0.0756 | 0.1732(242) ^g |
| C9...O10 | 4.971 | –0.0031 | 0.0701 | 0.1677(242) ^g |
| C7...O11 | 5.172 | –0.0032 | 0.0842 | 0.1818(242) ^g |
| C7...O10 | 5.843 | –0.0034 | 0.0678 | 0.1519(569) ^h |
| C8...O10 | 5.962 | –0.0028 | 0.0683 | 0.1524(569) ^h |
| C1...N3 | 2.331 | –0.0128 | 0.0532 | 0.0590(58) ^e |
| N3...C5 | 2.340 | –0.0143 | 0.0564 | 0.0622(58) ^e |
| N3...C6 | 2.506 | –0.0138 | 0.0607 | 0.0665(58) ^e |
| N3...C9 | 3.625 | –0.0151 | 0.0589 | 0.0751(112) ^f |
| N3...C7 | 3.736 | –0.0156 | 0.0637 | 0.0799(112) ^f |
| N3...C8 | 4.197 | –0.0167 | 0.0653 | 0.1629(242) ^g |
| C2...C4 | 2.312 | –0.0087 | 0.0542 | 0.0600(58) ^e |
| C2...C5 | 2.307 | –0.0098 | 0.0547 | 0.0605(58) ^e |

(to be continued)

Table S5. (continued).

| Parameter | $r_{ij,a}$ | $r_{ij,e} - r_{ij,a}$ ^a | $u_{ij,h1}$ ^b | $u_{ij,exp}$ |
|-----------|------------|------------------------------------|--------------------------|--------------------------|
| C2...C7 | 2.392 | -0.0100 | 0.0556 | 0.0614(58) ^e |
| C1...C8 | 2.429 | -0.0092 | 0.0556 | 0.0614(58) ^e |
| C1...C4 | 2.437 | -0.0082 | 0.0568 | 0.0626(58) ^e |
| C7...C9 | 2.403 | -0.0083 | 0.0560 | 0.0618(58) ^e |
| C2...C9 | 2.415 | -0.0100 | 0.0561 | 0.0619(58) ^e |
| C1...C6 | 2.441 | -0.0078 | 0.0565 | 0.0623(58) ^e |
| C6...C8 | 2.459 | -0.0097 | 0.0562 | 0.0620(58) ^e |
| C4...C12 | 2.496 | -0.0049 | 0.0692 | 0.0750(58) ^e |
| C2...C12 | 2.528 | -0.0129 | 0.0704 | 0.0762(58) ^e |
| C5...C9 | 2.645 | -0.0063 | 0.0663 | 0.0721(58) ^e |
| C1...C7 | 2.777 | -0.0084 | 0.0637 | 0.0804(103) ^d |
| C2...C8 | 2.801 | -0.0117 | 0.0631 | 0.0798(103) ^d |
| C6...C9 | 2.814 | -0.0088 | 0.0631 | 0.0798(103) ^d |
| C6...C12 | 3.068 | -0.0210 | 0.1070 | 0.1237(103) ^d |
| C4...C6 | 3.650 | -0.0113 | 0.0624 | 0.0786(112) ^f |
| C5...C6 | 3.639 | -0.0106 | 0.0602 | 0.0764(112) ^f |
| C1...C12 | 3.709 | -0.0096 | 0.0669 | 0.0831(112) ^f |
| C5...C12 | 3.744 | -0.0081 | 0.0685 | 0.0847(112) ^f |
| C4...C9 | 3.814 | -0.0083 | 0.0644 | 0.0806(112) ^f |
| C5...C8 | 3.869 | -0.0088 | 0.0682 | 0.0844(112) ^f |
| C5...C7 | 4.221 | -0.0096 | 0.0689 | 0.1665(242) ^g |
| C7...C12 | 4.458 | -0.0188 | 0.1075 | 0.2051(242) ^g |
| C4...C7 | 4.670 | -0.0105 | 0.0650 | 0.1626(242) ^g |
| C4...C8 | 4.765 | -0.0100 | 0.0656 | 0.1632(242) ^g |
| C9...C12 | 4.912 | -0.0110 | 0.0766 | 0.1742(242) ^g |
| C8...C12 | 5.239 | -0.0153 | 0.0962 | 0.1938(242) ^g |

^a Calculated with the B2PLYP/cc-pVTZ cubic force constants (see text).

^b Calculated with the B2PLYP/cc-pVTZ quadratic force constants (see text).

^{c,d,e,f,g,h} Amplitudes with the same superscript were refined in one group. Differences between amplitudes in each group were fixed at the corresponding calculated values. Other amplitudes were assumed at the calculated values. 3σ Values for groups ^{c,d,e,f,g,h} are 0.002, 0.010, 0.006, 0.011, 0.024 and 0.057, respectively

Reference

- [1] T. Polat, F. Bulut, I. Arıcan, F. Kandemirli, and G. Yildirim, J. Mol. Struct. **1101**, 189 (2015).