

## Electronic Supporting Information

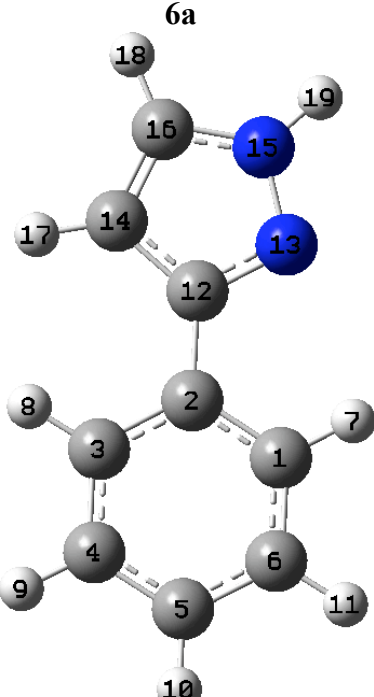
### A Theoretical and Experimental NMR Study of the Tautomerism of two Phenylene-bis-*C*-Substituted Pyrazoles

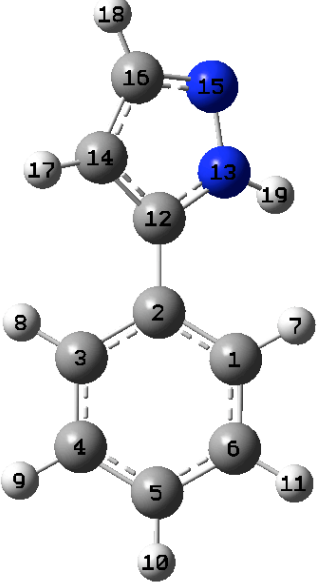
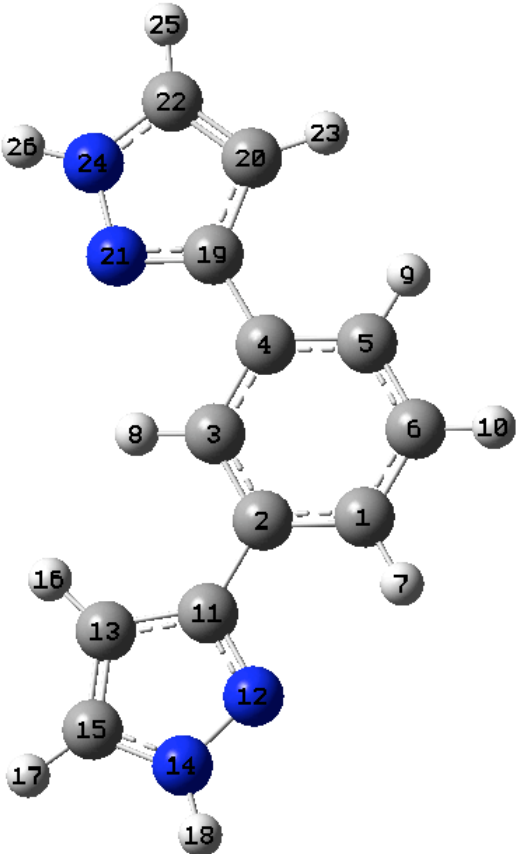
Dionisia Sanz, Rosa M. Claramunt, Ibon Alkorta, José Elguero, Werner R. Thiel and Tobias Rüffer

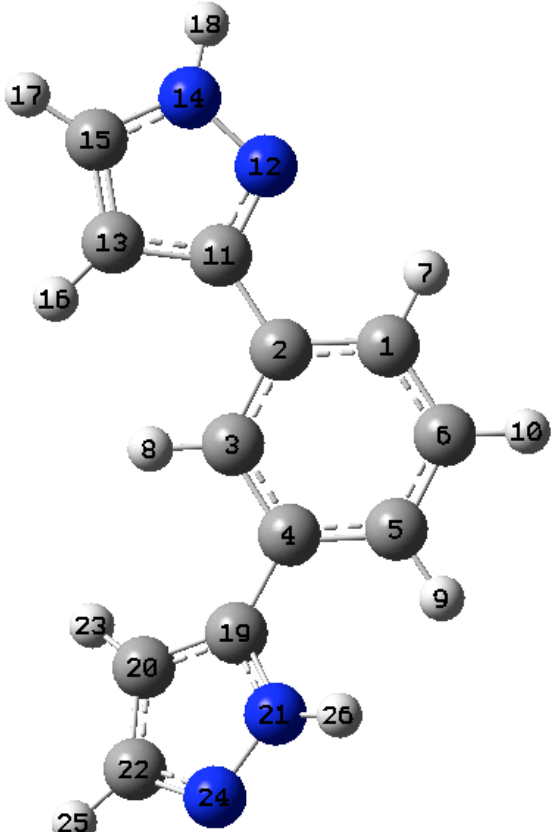
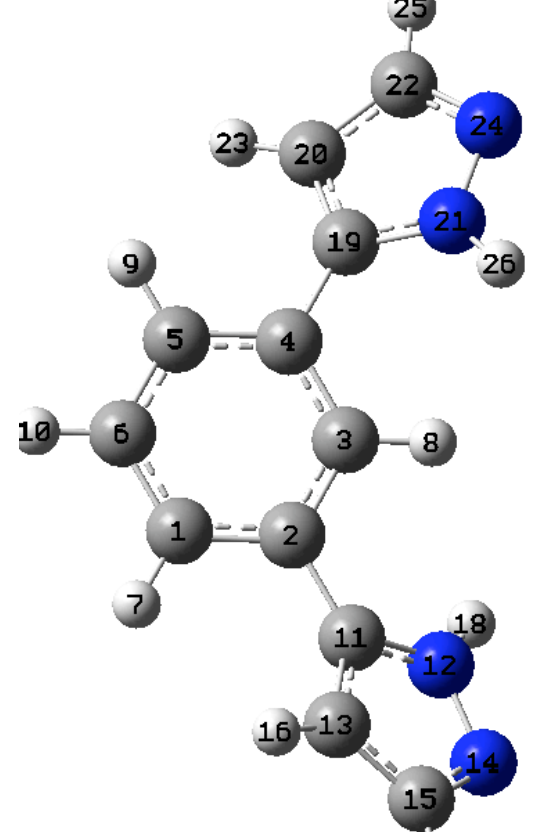
Energies of the optimized structure at the B3LYP/6-311++G(d,p) computational level.

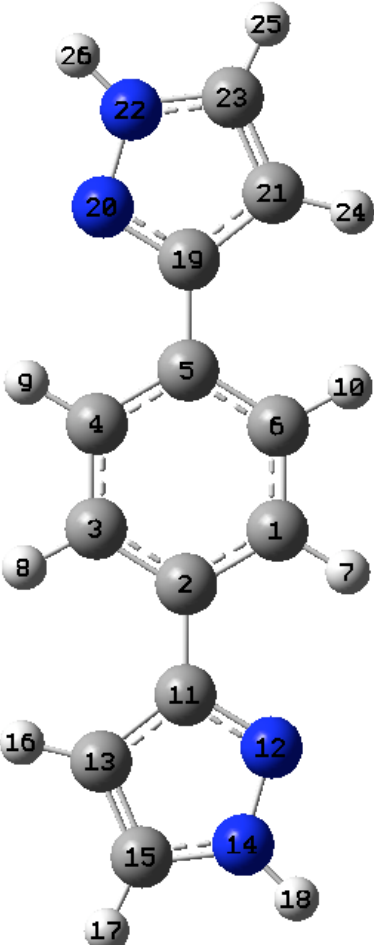
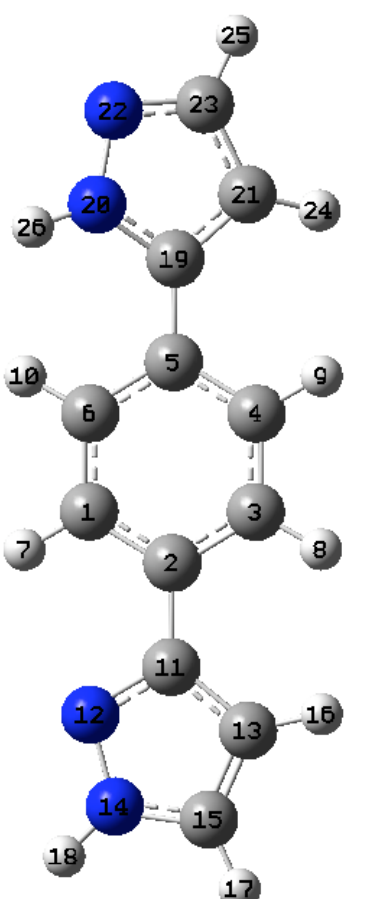
| Molecule  | Gas Phase        |              | DMSO                              |              |
|-----------|------------------|--------------|-----------------------------------|--------------|
|           | Etotal (hartree) | Erel(kJ/mol) | E total + $\Delta G$<br>Solvation | Erel(kJ/mol) |
| <b>1a</b> | -682.450982327   | 0.00         | -682.473389                       | 0.00         |
| <b>1b</b> | -682.450555081   | 1.12         | -682.471605                       | 4.68         |
| <b>1c</b> | -682.448972332   | 5.28         | -682.469908                       | 9.14         |
| <b>2a</b> | -682.451328869   | 0.00         | -682.474428                       | 0.00         |
| <b>2b</b> | -682.451102268   | 0.59         | -682.473021                       | 3.69         |
| <b>2c</b> | -682.449598336   | 4.54         | -682.471127                       | 8.67         |
| <b>6a</b> | -457.381091035   | 0.00         | -457.393745                       | 0.00         |
| <b>6c</b> | -457.380550295   | 1.42         | -457.392315                       | 3.75         |

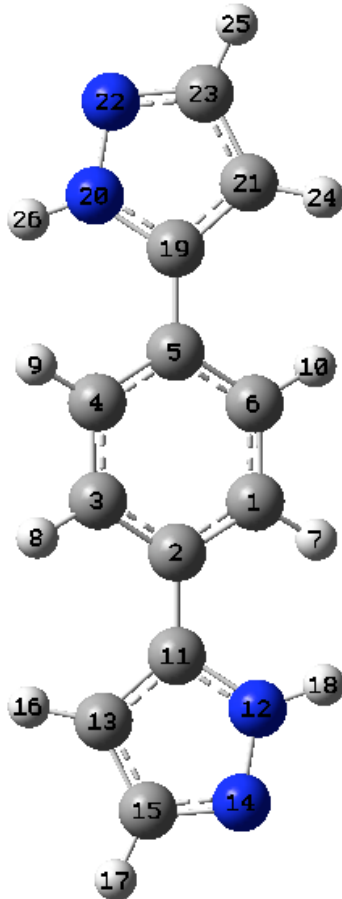
#### Absolute chemical shieldings

| Structure                                                                                            | Gas Phase     | DMSO          |
|------------------------------------------------------------------------------------------------------|---------------|---------------|
|  <p><b>6a</b></p> | 1 C 52.4833   | 1 C 54.2521   |
|                                                                                                      | 2 C 43.1683   | 2 C 43.1459   |
|                                                                                                      | 3 C 53.6403   | 3 C 53.0627   |
|                                                                                                      | 4 C 49.9652   | 4 C 48.7063   |
|                                                                                                      | 5 C 50.7791   | 5 C 50.2666   |
|                                                                                                      | 6 C 49.2492   | 6 C 48.9010   |
|                                                                                                      | 7 H 23.2499   | 7 H 23.2031   |
|                                                                                                      | 8 H 24.0781   | 8 H 23.6843   |
|                                                                                                      | 9 H 24.4667   | 9 H 24.0883   |
|                                                                                                      | 10 H 24.5974  | 10 H 24.2561  |
|                                                                                                      | 11 H 24.4341  | 11 H 24.1160  |
|                                                                                                      | 12 C 24.3252  | 12 C 25.1924  |
|                                                                                                      | 13 N -71.5407 | 13 N -58.9395 |
|                                                                                                      | 14 C 77.3494  | 14 C 77.2859  |
|                                                                                                      | 15 N 42.5667  | 15 N 34.7673  |
|                                                                                                      | 16 C 51.4057  | 16 C 47.1549  |
|                                                                                                      | 17 H 25.0971  | 17 H 24.7220  |
|                                                                                                      | 18 H 24.4795  | 18 H 23.9047  |
|                                                                                                      | 19 H 22.7862  | 19 H 21.6180  |

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| <p style="text-align: center;"><b>6c</b></p>   | <p>1 C 54.6065<br/>2 C 45.3612<br/>3 C 50.7961<br/>4 C 48.4157<br/>5 C 50.2293<br/>6 C 48.7773<br/>7 H 24.3963<br/>8 H 24.1459<br/>9 H 24.3393<br/>10 H 24.4702<br/>11 H 24.3608<br/>12 C 33.8519<br/>13 N 41.6453<br/>14 C 75.6376<br/>15 N -81.3965<br/>16 C 36.2958<br/>17 H 25.3828<br/>18 H 24.2515<br/>19 H 22.5867</p>                                                                                                                         | <p>1 C 52.7625<br/>2 C 46.4345<br/>3 C 50.5318<br/>4 C 48.2247<br/>5 C 48.8128<br/>6 C 48.1673<br/>7 H 23.9223<br/>8 H 23.8455<br/>9 H 23.9941<br/>10 H 24.0829<br/>11 H 23.9881<br/>12 C 31.8875<br/>13 N 37.5711<br/>14 C 75.3188<br/>15 N -63.2176<br/>16 C 35.9664<br/>17 H 24.9798<br/>18 H 24.0108<br/>19 H 21.5660</p>                                                                                                                         |
| <p style="text-align: center;"><b>1a</b></p>  | <p>1 C 53.1946<br/>2 C 43.2431<br/>3 C 56.1319<br/>4 C 44.2386<br/>5 C 54.5238<br/>6 C 49.7286<br/>7 H 23.4025<br/>8 H 22.8991<br/>9 H 24.2763<br/>10 H 24.4752<br/>11 C 23.9005<br/>12 N -71.0516<br/>13 C 76.0761<br/>14 N 43.1309<br/>15 C 51.3732<br/>16 H 24.8401<br/>17 H 24.4663<br/>18 H 22.7838<br/>19 C 24.0439<br/>20 C 76.8849<br/>21 N -70.1966<br/>22 C 51.5830<br/>23 H 25.1079<br/>24 N 43.3716<br/>25 H 24.4836<br/>26 H 22.7704</p> | <p>1 C 54.9908<br/>2 C 43.1956<br/>3 C 58.0276<br/>4 C 43.3252<br/>5 C 53.9102<br/>6 C 48.4504<br/>7 H 23.3518<br/>8 H 22.8826<br/>9 H 23.8742<br/>10 H 24.0996<br/>11 C 25.0644<br/>12 N -59.3066<br/>13 C 76.5192<br/>14 N 34.6943<br/>15 C 46.8739<br/>16 H 24.5498<br/>17 H 23.8772<br/>18 H 21.5766<br/>19 C 25.2917<br/>20 C 76.6755<br/>21 N -59.2161<br/>22 C 47.1616<br/>23 H 24.7327<br/>24 N 34.8090<br/>25 H 23.8925<br/>26 H 21.5479</p> |

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| <p style="text-align: center;"><b>1b</b></p>   | <p>1 C 52.8343<br/>2 C 41.9431<br/>3 C 54.5089<br/>4 C 45.9626<br/>5 C 55.7573<br/>6 C 48.3463<br/>7 H 23.3264<br/>8 H 23.8800<br/>9 H 24.5453<br/>10 H 24.3512<br/>11 C 24.7572<br/>12 N -72.8026<br/>13 C 77.0140<br/>14 N 41.6381<br/>15 C 51.0441<br/>16 H 25.0452<br/>17 H 24.4246<br/>18 H 22.6880<br/>19 C 33.3056<br/>20 C 75.9683<br/>21 N 41.1349<br/>22 C 36.5786<br/>23 H 25.3665<br/>24 N -80.6126<br/>25 H 24.2470<br/>26 H 22.5672</p> | <p>1 C 53.6993<br/>2 C 42.1913<br/>3 C 54.4263<br/>4 C 46.1831<br/>5 C 53.7304<br/>6 C 47.6171<br/>7 H 23.2233<br/>8 H 23.6471<br/>9 H 24.0590<br/>10 H 23.9790<br/>11 C 25.5617<br/>12 N -60.4414<br/>13 C 77.0699<br/>14 N 33.9282<br/>15 C 47.0009<br/>16 H 24.6933<br/>17 H 23.8648<br/>18 H 21.5185<br/>19 C 31.8435<br/>20 C 75.1644<br/>21 N 37.0194<br/>22 C 36.0484<br/>23 H 24.9319<br/>24 N -63.5074<br/>25 H 23.9851<br/>26 H 21.5480</p> |
| <p style="text-align: center;"><b>1c</b></p>  | <p>1 C 51.6432<br/>2 C 44.3953<br/>3 C 58.7647<br/>4 C 44.3954<br/>5 C 51.6436<br/>6 C 47.4468<br/>7 H 24.2403<br/>8 H 24.4676<br/>9 H 24.2403<br/>10 H 24.2850<br/>11 C 34.2928<br/>12 N 41.6345<br/>13 C 74.9749<br/>14 N -83.1742<br/>15 C 36.2062<br/>16 H 25.3461<br/>17 H 24.2109<br/>18 H 22.5832<br/>19 C 34.2931<br/>20 C 74.9737<br/>21 N 41.6347<br/>22 C 36.2055<br/>23 H 25.3461<br/>24 N -83.1750<br/>25 H 24.2108<br/>26 H 22.5832</p> | <p>1 C 50.3376<br/>2 C 45.3554<br/>3 C 55.8063<br/>4 C 45.3559<br/>5 C 50.3382<br/>6 C 47.3146<br/>7 H 23.8740<br/>8 H 23.8754<br/>9 H 23.8735<br/>10 H 23.9088<br/>11 C 32.3331<br/>12 N 37.2237<br/>13 C 74.5895<br/>14 N -64.7282<br/>15 C 36.0066<br/>16 H 24.9358<br/>17 H 23.9802<br/>18 H 21.5532<br/>19 C 32.3364<br/>20 C 74.5877<br/>21 N 37.2330<br/>22 C 36.0060<br/>23 H 24.9359<br/>24 N -64.7402<br/>25 H 23.9802<br/>26 H 21.5570</p> |

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| <p style="text-align: center;"><b>2a</b></p>   | <p>1 C 52.8430<br/>2 C 44.4677<br/>3 C 53.2393<br/>4 C 52.8430<br/>5 C 44.4677<br/>6 C 53.2393<br/>7 H 23.2914<br/>8 H 24.1253<br/>9 H 23.2914<br/>10 H 24.1253<br/>11 C 24.1013<br/>12 N -70.9540<br/>13 C 76.8180<br/>14 N 42.8735<br/>15 C 51.4426<br/>16 H 25.0922<br/>17 H 24.5104<br/>18 H 22.7777<br/>19 C 24.1013<br/>20 N -70.9540<br/>21 C 76.8180<br/>22 N 42.8735<br/>23 C 51.4426<br/>24 H 25.0922<br/>25 H 24.5104<br/>26 H 22.7777</p> | <p>1 C 53.7600<br/>2 C 44.3317<br/>3 C 52.7795<br/>4 C 53.7599<br/>5 C 44.3316<br/>6 C 52.7795<br/>7 H 23.1972<br/>8 H 23.7503<br/>9 H 23.1972<br/>10 H 23.7503<br/>11 C 25.1938<br/>12 N -58.8741<br/>13 C 76.7425<br/>14 N 34.6536<br/>15 C 47.0331<br/>16 H 24.7282<br/>17 H 23.9271<br/>18 H 21.5867<br/>19 C 25.1923<br/>20 N -58.8752<br/>21 C 76.7425<br/>22 N 34.6550<br/>23 C 47.0360<br/>24 H 24.7284<br/>25 H 23.9270<br/>26 H 21.5868</p> |
| <p style="text-align: center;"><b>2b</b></p>  | <p>1 C 51.8158<br/>2 C 43.9577<br/>3 C 52.7152<br/>4 C 51.5350<br/>5 C 47.1917<br/>6 C 54.5469<br/>7 H 23.2526<br/>8 H 24.0194<br/>9 H 24.1645<br/>10 H 24.3919<br/>11 C 25.1979<br/>12 N -72.0200<br/>13 C 76.9623<br/>14 N 41.8399<br/>15 C 50.9721<br/>16 H 25.0770<br/>17 H 24.4610<br/>18 H 22.7354<br/>19 C 33.8755<br/>20 N 42.0526<br/>21 C 76.1416<br/>22 N -80.6162<br/>23 C 36.4356<br/>24 H 25.3784<br/>25 H 24.2574<br/>26 H 22.5445</p> | <p>1 C 53.3266<br/>2 C 43.2709<br/>3 C 52.3648<br/>4 C 50.4158<br/>5 C 48.0286<br/>6 C 52.7476<br/>7 H 23.1623<br/>8 H 23.6139<br/>9 H 23.8074<br/>10 H 23.9246<br/>11 C 25.9832<br/>12 N -60.2455<br/>13 C 76.7150<br/>14 N 33.9509<br/>15 C 46.9180<br/>16 H 24.6866<br/>17 H 23.8965<br/>18 H 21.5583<br/>19 C 32.2734<br/>20 N 38.1054<br/>21 C 75.6012<br/>22 N -63.0022<br/>23 C 35.9360<br/>24 H 24.9589<br/>25 H 24.0020<br/>26 H 21.5434</p> |

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| <p style="text-align: center;"><b>2c</b></p>  | <p>1 C 53.9303<br/>                 2 C 47.1339<br/>                 3 C 50.5022<br/>                 4 C 53.9306<br/>                 5 C 47.1325<br/>                 6 C 50.5027<br/>                 7 H 24.3277<br/>                 8 H 24.1223<br/>                 9 H 24.3280<br/>                 10 H 24.1223<br/>                 11 C 34.7735<br/>                 12 N 41.9898<br/>                 13 C 75.3957<br/>                 14 N -82.8067<br/>                 15 C 36.2018<br/>                 16 H 25.4205<br/>                 17 H 24.2605<br/>                 18 H 22.4740<br/>                 19 C 34.7736<br/>                 20 N 41.9881<br/>                 21 C 75.3933<br/>                 22 N -82.8075<br/>                 23 C 36.2007<br/>                 24 H 25.4206<br/>                 25 H 24.2606<br/>                 26 H 22.4740</p> | <p>1 C 52.2487<br/>                 2 C 46.9520<br/>                 3 C 49.9546<br/>                 4 C 52.2505<br/>                 5 C 46.9511<br/>                 6 C 49.9552<br/>                 7 H 23.8547<br/>                 8 H 23.7426<br/>                 9 H 23.8552<br/>                 10 H 23.7425<br/>                 11 C 32.8249<br/>                 12 N 37.8041<br/>                 13 C 74.7952<br/>                 14 N -64.5032<br/>                 15 C 35.8372<br/>                 16 H 24.9169<br/>                 17 H 23.9873<br/>                 18 H 21.5324<br/>                 19 C 32.8264<br/>                 20 N 37.8054<br/>                 21 C 74.7933<br/>                 22 N -64.5026<br/>                 23 C 35.8358<br/>                 24 H 24.9169<br/>                 25 H 23.9872<br/>                 26 H 21.5326</p> |
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