ELECTRONIC SUPPLEMENTARY INFORMATION

Dynamic NMR spectroscopic and computational studies of 1H-pyrazoles: determination of the prototropic barriers

Ibon Alkorta,[a] Rosa M. Claramunt,*[b] José Cumella,[a] José Elguero,[a] Felipe Reviriego,[c] Albert Virgili[d]

[a] *Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain*
[b]*Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, UNED, Avda. Esparta, s/n, Las Rozas-Madrid, E-28232, Spain*
[c]*Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC, Juan de la Cierva 3 E-28006 Madrid, Spain*
[d]*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

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Table 1. Electronic energy, geometry and NMR parameters of the isolated monomers

Electronic energy (Hartree) and geometry (Å)	NMR results (ppm)
1 Electronic Energy= -226.265991267 NIMAG= 0 N,0,0.0350835863,1.0865851359,0. H,0,0.1170172379,2.0902519918,0. N,0,1.1570204554,0.3396247682,0. C,0,-1.1009738268,0.3427550969,0. C,0,0.7163991153,-0.9147706809,0. C,0,-0.6959342496,-0.9760569573,0. H,0,-2.0795936045,0.7953462614,0. H,0,1.4250450086,-1.7292533108,0. H,0,-1.3241431679,-1.8513790231,0.	1 ******** Atom σ δ 1N 38.77 -188.68 2H 22.63 9.05 3N -81.39 -75.01 4C 53.10 124.57 5C 38.13 138.99 6C 73.74 104.69 7H 24.45 7.28 8H 24.20 7.53 9H 25.52 6.25
2 Electronic Energy= -304.927097402 NIMAG= 0 C,1.1227686987,-0.1131146924,0. N,0.7294232747,1.1565235677,0. N,-0.6246203978,1.0973969879,0. C,-1.1103798879,-0.1731420261,0. C,0.0043693636,-0.9887255985,0. H,0.0111658263,-2.0674324282,0. C,-2.5726268833,-0.4834658611,0.	2 ******** Atom σ δ 1C 27.15 149.56 2N -75.54 -80.54 3N 43.39 -193.04 4C 39.65 137.52 5C 74.49 103.97 6H 26.06 5.72 7C 172.08 9.98 8H 29.76 2.14

H,-3.0729446396,- 0.0760458013,0.8843908819 H,-3.0729446396,-0.0760458013,- 0.8843908819 H,-2.7242632429,-1.5632978399,0. C,2.5782501887,-0.4639973793,0. H,2.8446901322,-1.0536763599,- 0.8823338239 H,3.1791548626,0.4462958863,0. H,2.8446901322,- 1.0536763599,0.8823338239 H,-1.1477709498,1.9579182346,0.	9H 29.76 2.14 10H 29.70 2.20 11C 168.18 13.74 12H 29.74 2.16 13H 29.61 2.28 14H 29.74 2.16 15H 23.39 8.31
3 Electronic Energy= -430.825922595 NIMAG= 0 N,0,-0.5949805676,-2.0598564253,0. N,0,0.7607562029,-2.1014551342,0. C,0,1.1384338528,-0.8340436435,0. C,0,0.0080842794,0.0139855312,0. C,0,-1.1001206661,-0.8127196049,0. H,0,-1.1066195006,-2.928932265,0. H,0,2.1806409737,-0.5591054806,0. H,0,-2.1535498582,-0.5890475526,0. N,0,-0.0123130134,1.449303825,0. O,0,-1.1096069098,2.0023078571,0. O,0,1.0696575968,2.0273413728,0.	3 ******** Atom σ δ 1N 38.94 -188.84 2N -81.64 -74.76 3C 40.70 136.51 4C 37.99 139.12 5C 51.36 126.24 6H 22.76 8.92 7H 23.72 7.99 8H 23.86 7.86 9N -135.71 -23.62 10O -315.39 533.22 11O -329.04 545.48
4 Electronic Energy= -509.491826882 NIMAG= 0 C,-1.11559534,-0.78867259,0. N,-0.65147207,-2.02805492,0. N,0.70453017,-1.90658806,0. C,1.15244165,-0.63847028,0. C,-0.01683018,0.12299596,0. C,2.59958784,-0.28486072,0. H,3.21584157,-1.18687592,0. H,2.84918329,0.31753913,-0.87504968 H,2.84918329,0.31753913,0.87504968 C,-2.58349369,-0.52029927,0. H,-2.87475176,0.06365159,-0.87516106 H,-3.11924852,-1.46977239,0. H,-2.87475176,0.06365159,0.87516106 H,1.2659323,-2.7444488,0. N,-0.06936557,1.54947508,0. O,0.99971309,2.16468325,0. O,-1.17642407,2.08454802,0.	4 ******** Atom σ δ 1C 26.55 150.14 2N -66.07 -89.50 3N 41.13 -190.91 4C 35.32 141.68 5C 43.63 133.68 6C 168.56 13.37 7H 30.07 1.84 8H 29.13 2.74 9H 29.13 2.74 10C 166.48 15.38 11H 29.33 2.55 12H 29.54 2.34 13H 29.33 2.55 14H 23.40 8.30 15N -140.32 -19.26 16O -309.12 527.59 17O -321.97 539.13

The δ values are obtained from the σ ones and the equations described in:

[1]H: A. M. S. Silva, et al. Magn. Reson. Chem. 2008, 46, 859-864
[13]C: F. Blanco, I. Alkorta, J. Elguero Magn. Reson. Chem. 2007, 45, 797-800
[15]N: F. Blanco, I. Alkorta, J. Elguero Magn. Reson. Chem. 2007, 45, 797-800
[17]O: D. Sanz, et al. Magn. Reson. Chem. 2012, 50, 246-255

Table 2. Electronic energy (Hartree) and geometry (Å) of the complexes with two methanol molecules in their minimum and TS disposition.

Min	TS
1 Electronic Energy= -457.830459368 NIMAG= 0 N,0.2875674328,1.0083952623,-0.1507978569 H,0.5428724406,1.9872949665,-0.3305893621 N,1.262487152,0.1528249184,0.2197910457 C,-0.915425961,0.4011074948,-0.2360285272 C,0.6566482775,-1.0248547398,0.3725445346 C,-0.7209848531,-0.9280276817,0.0976068009 H,-1.8027651145,0.9436259236,-0.5204214377 H,1.2285336506,-1.8902706231,0.6714136266 H,-1.4629426191,-1.7081232461,0.1363311159 H,2.8952414231,1.0502312917,0.3621712708 O,3.5527617529,1.7820727012,0.3721800987 O,1.5922982985,3.498880593,-0.4387358489 C,4.2934511896,1.7451002938,1.5868840117 H,4.9734164384,2.5983441287,1.5861998315 H,3.6408838291,1.8176789427,2.4650300297 H,4.8890560147,0.828233343,1.6614280284 H,2.4219076282,3.0695148667,-0.1366126611 C,1.8634105093,4.3374530478,-1.5564430492 H,2.2933129505,3.7749402342,-2.3935689039 H,0.9174555644,4.7761725958,-1.8780355281 H,2.5470934355,5.1505651663,-1.2878523195	1 (TS) Electronic Energy= -457.799908918 NIMAG= 1 N,-0.2435061794,0.6322681418,-0.9799206352 H,-0.3979404457,1.0741826126,0.2263248981 N,0.2435061794,-0.6322681418,-0.9799206352 C,-0.3961976188,1.0302555465,-2.2506074828 C,0.3961976188,-1.0302555465,-2.2506074828 C,0.,0.,-3.1057204764 H,-0.7750018029,2.0144431031,-2.4799977183 H,0.7750018029,-2.0144431031,-2.4799977183 H,0.,0.,-4.1832753252 H,0.3979404457,-1.0741826126,0.2263248981 O,0.4240349571,-1.1212880584,1.4270422551 O,-0.4240349571,1.1212880584,1.4270422551 C,-0.3705974849,-2.1550375895,1.9999441815 H,-0.4667586434,-1.9887367881,3.0759569904 H,-1.3743661593,-2.1863821202,1.5587720418 H,0.1164597999,-3.1211076894,1.8417847709 H,0.,0.,1.5935978484 C,0.3705974849,2.1550375895,1.9999441815 H,1.3743661593,2.1863821202,1.5587720418 H,-0.1164597999,3.1211076894,1.8417847709 H,0.4667586434,1.9887367881,3.0759569904
2 Electronic Energy= -536.491485550 NIMAG= 0 N,0.2830984944,1.0166886285,-0.1363596895 H,0.5374190123,1.990920385,-0.3288774431 N,1.270141208,0.1543434147,0.2114817075 C,-0.9297614261,0.418944782,-0.1862537498 C,0.6729069562,-1.0241383099,0.3890814355 C,-0.7161489432,-0.9083528902,0.1500110688 H,-1.4619291559,-1.6849888,0.213748074 H,2.8824282987,1.0454640569,0.3205144808 O,3.5545483886,1.7674195045,0.3229185399 O,1.6170725032,3.5189525317,-0.4726092585 C,4.2790126685,1.7424663499,1.5466059832 H,4.9734460234,2.5841886857,1.5391356896 H,3.6173351812,1.8424364391,2.415478984 H,4.8590500851,0.8178263566,1.6476707431 H,2.4382821905,3.0667145195,-0.1807728251 C,1.8961974656,4.3345100622,-1.6041281641 H,2.2973153105,3.7495388631,-2.4404557351 H,0.958984021,4.7969408699,-1.9186340783 H,2.6074172576,5.1312000971,-1.3574568294	2 (TS) Electronic Energy= -536.461302702 NIMAG= 1 N,-0.11881589,0.66650746,-0.45707086 H,-0.17693107,1.11691627,0.61962226 N,0.11881589,-0.66650746,-0.45707086 C,-0.19428482,1.1014553,-1.72273798 C,0.19428482,-1.1014553,-1.72273798 C,0.,0.,-2.56448274 H,0.,0.,-3.6428692 H,0.17693107,-1.11691627,0.61962226 O,0.21222837,-1.18220406,1.97101211 O,-0.21222837,1.18220406,1.97101211 C,-0.70091286,-2.03036021,2.63986229 H,-0.70252441,-1.82136246,3.71589129 H,-1.72992927,-1.90777634,2.27079917 H,-0.40983408,-3.07803604,2.50311211 H,0.,0.,2.12507977 C,0.70091286,2.03036021,2.63986229 H,1.72992927,1.90777634,2.27079917 H,0.40983408,3.07803604,2.50311211 H,0.70252441,1.82136246,3.71589129

C,1.4556132937,-2.2358848156,0.7895237936 H,2.5185587881,-1.9970898774,0.8490305997 H,1.1335066699,-2.6122006453,1.765130674 H,1.3273895752,-3.0463582283,0.0663020525 C,-2.1770774512,1.1564009352,-0.5549507473 H,-2.329602621,2.0303113433,0.0849661937 H,-2.1457389105,1.5047632046,-1.5919601036 H,-3.043839794,0.503462947,-0.4468662359	C,0.41927276,-2.543101,-2.0516817 H,0.91991703,-3.05725916,-1.22930545 H,-0.52838083,-3.05570774,-2.24336264 H,1.03728024,-2.64240048,-2.94601978 C,-0.41927276,2.543101,-2.0516817 H,-0.91991703,3.05725916,-1.22930545 H,0.52838083,3.05570774,-2.24336264 H,-1.03728024,2.64240048,-2.94601978
3 Electronic Energy= -662.391213607 NIMAG= 0 N,0.2980110022,0.9810085646,-0.1680928273 H,0.5875795948,1.9584867799,-0.3522393973 N,1.2494856028,0.1046578134,0.246057352 C,-0.9099608843,0.4161141768,-0.2827939926 C,0.6290013124,-1.0559354614,0.4005572469 C,-0.7350238971,-0.9116602191,0.0792112701 H,-1.7900867977,0.9510222716,-0.5976065167 H,1.1516367682,-1.9402830836,0.7268241863 H,2.9520896324,1.0303529323,0.4297755602 O,3.5676743076,1.7899524366,0.4188356671 O,1.5657279677,3.4173240671,-0.4444117852 C,4.3754921361,1.7791448297,1.5939066429 H,5.0237590361,2.6550088913,1.5530785393 H,3.7685729184,1.8326409222,2.5047898704 H,5.0040287823,0.8832483708,1.6333440265 H,2.4144859501,3.0416374189,-0.124933435 C,1.8003696779,4.2988911803,-1.5408456925 H,2.2973297731,3.7875474481,-2.3726393614 H,0.8317668753,4.667369283,-1.8809805129 H,2.4083568045,5.1557604654,-1.2330613402 N,-1.7513761264,-1.9222098358,0.1139537162 O,-1.414476696,-3.0497570974,0.4639889014 O,-2.8910375903,-1.5944795747,-0.2082109482	3 (TS) Electronic Energy= -662.365268654 NIMAG= 1 N,-0.2194313359,0.6512467151,0.2244985252 H,-0.3639893102,1.135017066,1.6144038352 N,0.2194313359,-0.6512467151,0.2244985252 C,-0.3562141183,1.0578410989,-1.03466847 C,0.3562141183,-1.0578410989,-1.03466847 C,0.,0.,-1.8791921713 H,-0.690643356,2.0498105622,-1.2926548564 H,0.690643356,-2.0498105622,-1.2926548564 H,0.3639893102,-1.135017066,1.6144038352 O,0.3583885419,-1.1425130854,2.6942830171 O,-0.3583885419,1.1425130854,2.6942830171 C,-0.506447913,-2.1555058777,3.2324538627 H,-0.5595810474,-2.0223375842,4.3129999012 H,-1.5104981691,-2.0849173144,2.8046971134 H,-0.0823092257,-3.1365471552,3.0143106657 H,0.,0.,2.8574463159 C,0.506447913,2.1555058777,3.2324538627 H,1.5104981691,2.0849173144,2.8046971134 H,0.0823092257,3.1365471552,3.0143106657 H,0.5595810474,2.0223375842,4.3129999012 N,0.,0.,-3.307253063 O,-0.3440493393,1.033748422,-3.8803055002 O,0.3440493393,-1.033748422,-3.8803055002
4 Electronic Energy= -741.056796672 NIMAG= 0 N,-0.1411183263,0.7357463652,0.2941048044 H,-0.195741064,1.3222582907,2.1152629744 N,0.0388863347,-0.6151362785,0.2569133024 C,-0.1563318531,1.1458737251,-0.9666145908 C,0.1426659414,-1.1055355652,-0.9840745341 C,0.019674998,0.0159518677,-1.8132639958 H,0.0697904578,-1.1226900968,1.1555957471 O,0.1095449108,-1.439548099,2.9216485783 O,-0.1585090412,1.2643031111,3.0930703365 C,-0.725883388,-2.2619014354,3.7324694503 H,-0.3980531814,-2.2495185734,4.7772964539 H,-1.7746965807,-1.9480057654,3.6839699893 H,-0.6466734127,-3.2838561209,3.3590139611 H,0.0448391169,-0.5048305024,3.2149081307 C,0.7072665759,2.2728218868,3.6067104198 H,1.7219790233,2.1832651733,3.2019992897 H,0.3221754665,3.2747958947,3.388319021 H,0.7506108757,2.1484240418,4.6893560256	4 (TS) Electronic Energy= -741.028805544 NIMAG= 1 N,-0.1255583523,0.6774081441,0.4426527925 H,-0.1906387922,1.1658415636,1.7973623547 N,0.1255583523,-0.6774081441,0.4426527925 C,-0.2068041005,1.1144915974,-0.8109165076 C,0.2068041005,-1.1144915974,-0.8109165076 C,0.,0.,-1.6542311854 H,0.1906387922,-1.1658415636,1.7973623547 O,0.1836035166,-1.1832231366,2.8962398542 O,-0.1836035166,1.1832231366,2.8962398542 C,-0.8288151535,-2.0466988793,3.431173337 H,-0.8702370158,-1.9052789279,4.5116808903 H,-1.8086466896,-1.8249298489,2.997555951 H,-0.5624939407,-3.0836358585,3.2195112581 H,0.,0.,3.0608127567 C,0.8288151535,2.0466988793,3.431173337 H,1.8086466896,1.8249298489,2.997555951 H,0.5624939407,3.0836358585,3.2195112581 H,0.8702370158,1.9052789279,4.5116808903

C,0.3440077226,-2.5548149631,-1.2660628493	C,0.47323144,-2.5468679291,-1.1349665621
H,0.4087856873,-3.1181745766,-0.3335004667	H,0.5968867938,-3.11912583,-0.2138119313
H,-0.4777472174,-2.9474322205,-1.8680725061	H,-0.3447864946,-2.9744701948,-1.7186873779
H,1.2573349655,-2.7100190501,-1.8431254312	H,1.3743061198,-2.6476462359,-1.7433237759
C,-0.3367869668,2.5863455591,-1.3115497348	C,-0.47323144,2.5468679291,-1.1349665621
H,-0.4535561188,3.1676176669,-0.3961818983	H,-0.5968867938,3.11912583,-0.2138119313
H,0.5193101701,2.9637588346,-1.8746609087	H,0.3447864946,2.9744701948,-1.7186873779
H,-1.21490241,2.7287628783,-1.9445753744	H,-1.3743061198,2.6476462359,-1.7433237759
N,0.0659634072,0.0035851894,-3.238323414	N,0.,0.,-3.0754096113
O,-0.0531439083,1.0774664726,-3.8280446806	O,-0.1915381921,1.0719463923,-3.6569483171
O,0.2227021649,-1.0825939699,-3.8007031798	O,0.1915381921,-1.0719463923,-3.6569483171