Electronic Supplementary Information for manuscript:

Directionality of π-holes in nitro compounds.

by

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1. Figure S1

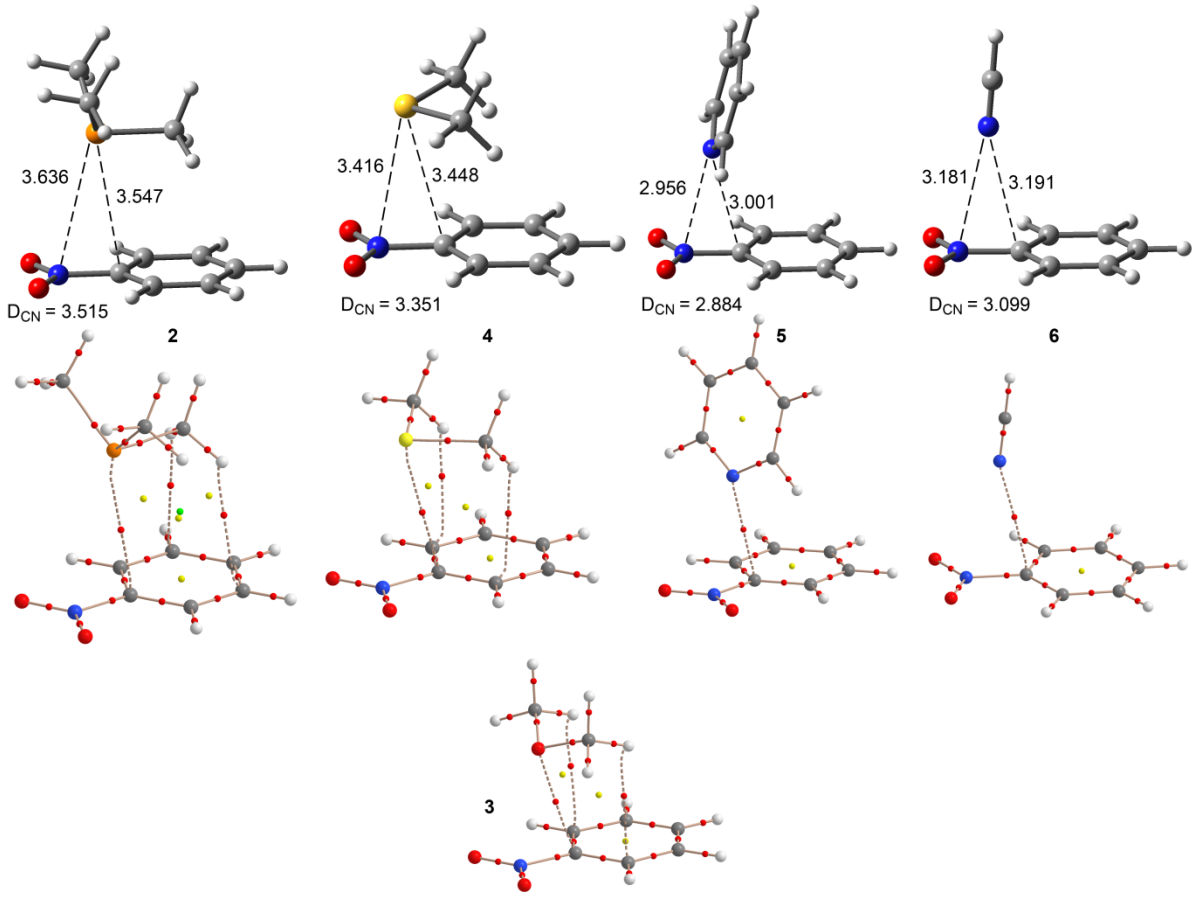

Fig. S1 Top: optimized π-hole complexes **2** and **4-6** with distances in Å (D_{CN} stands for the distance measured from the interacting atom to the C–N centroid). Middle and bottom: distribution of critical points in the complexes, together with paths connecting bond critical points. Bond and ring critical points are represented by red and yellow spheres, respectively.

2. Computational methods:

The energies of all complexes included in this study were computed at the RI-MP2/def2-TZVPD//BP86-D3/def2-TZVPD level of theory. The calculations have been performed by using the program TURBOMOLE version 6.4.[1] The MEP calculations have been performed at the MP2/6-311+G** level of theory using the Spartan v.10 program.[2] The C_s symmetry point group was imposed during the optimization process. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.[3]

3. Cartesian coordinates

1.

C	2.6374991	0.1013410	1.2118175
C	1.5275433	-0.7429689	1.2194612
C	0.9817794	-1.1444913	0.0000000
C	1.5275433	-0.7429689	-1.2194612
C	2.6374991	0.1013410	-1.2118175
H	3.0718053	0.4272579	2.1574575
H	1.0715356	-1.0865804	2.1455825
H	1.0715356	-1.0865804	-2.1455825
H	3.0718053	0.4272579	-2.1574575
N	-0.1935662	-2.0457370	0.0000000
O	-0.6363799	-2.4152279	-1.0938487
O	-0.6363799	-2.4152279	1.0938487
N	-1.5175954	0.3875984	0.0000000
C	-1.2652332	1.1403094	-1.2136149
H	-0.2383463	1.5338346	-1.1979302
H	-1.3621263	0.4733351	-2.0824961
H	-1.9636095	1.9951920	-1.3513848
C	-1.2652332	1.1403094	1.2136149
H	-1.3621263	0.4733351	2.0824961
H	-0.2383463	1.5338346	1.1979302
H	-1.9636095	1.9951920	1.3513848
C	-2.8002738	-0.2944743	0.0000000
H	-2.8718779	-0.9377299	-0.8883216
H	-2.8718779	-0.9377299	0.8883216
H	-3.6642175	0.4060600	0.0000000
C	3.1920422	0.5266925	0.0000000
H	4.0602111	1.1868262	0.0000000

2.

C	2.5948320	0.6163474	1.2124051
C	2.0009842	-0.6457226	1.2201160
C	1.7118881	-1.2554146	0.0000000
C	2.0009842	-0.6457226	-1.2201160
C	2.5948320	0.6163474	-1.2124051
H	2.8257360	1.1089172	2.1572977
H	1.7516234	-1.1609063	2.1454853
H	1.7516234	-1.1609063	-2.1454853
H	2.8257360	1.1089172	-2.1572977
N	1.0763800	-2.5975123	0.0000000
O	0.8347183	-3.1145206	-1.0935577
O	0.8347183	-3.1145206	1.0935577
C	-2.8631266	-0.0019619	1.4140195
H	-3.4667366	0.9135857	1.3095946
H	-3.5362275	-0.8686847	1.4707494

H	-2.2993867	0.0479221	2.3560093
C	-2.8631266	-0.0019619	-1.4140195
H	-3.5362275	-0.8686847	-1.4707494
H	-3.4667366	0.9135857	-1.3095946
H	-2.2993867	0.0479221	-2.3560093
C	-0.8939487	1.4496089	0.0000000
H	-0.2513507	1.5488629	0.8853243
H	-0.2513507	1.5488629	-0.8853243
H	-1.6377943	2.2620743	0.0000000
C	2.8911981	1.2476335	0.0000000
H	3.3536205	2.2352904	0.0000000
P	-1.6834755	-0.2293589	0.0000000

3.

C	0.25858185	-2.21317205	-1.14646590
C	-0.45068938	-1.01041670	-1.20829860
C	-0.79437051	-0.41478427	0.00000000
C	-0.45068938	-1.01041670	1.20829860
C	0.25858185	-2.21317205	1.14646590
H	0.55544444	-2.71899168	-2.06857670
H	-0.72346771	-0.54407712	-2.15253910
H	-0.72346771	-0.54407712	2.15253910
H	0.55544444	-2.71899168	2.06857670
N	-1.55085375	0.86959353	0.00000000
O	-1.84317570	1.35168077	1.09457930
O	-1.84317570	1.35168077	-1.09457930
O	1.11327265	1.81010732	0.00000000
C	1.82899729	1.47909073	1.18116730
H	1.18711755	1.74809758	2.02917120
H	2.05384846	0.39555838	1.22534500
H	2.77985030	2.03978040	1.24954520
C	1.82899729	1.47909073	-1.18116730
H	1.18711755	1.74809758	-2.02917120
H	2.77985030	2.03978040	-1.24954520
H	2.05384846	0.39555838	-1.22534500
C	0.61588886	-2.81336415	0.00000000
H	1.16323293	-3.73277400	0.00000000

4.

C	-0.2042647	-1.9654516	-1.2121617
C	-1.0574924	-0.8617442	-1.2196335
C	-1.4684338	-0.3245208	0.0000000
C	-1.0574924	-0.8617442	1.2196335
C	-0.2042647	-1.9654516	1.2121617
H	0.1277380	-2.3950493	-2.1576769
H	-1.4040531	-0.4074422	-2.1457543

H	-1.4040531	-0.4074422	2.1457543
H	0.1277380	-2.3950493	2.1576769
N	-2.3969692	0.8353928	0.0000000
O	-2.7605568	1.2745157	1.0936114
O	-2.7605568	1.2745157	-1.0936114
S	0.6357152	2.4078204	0.0000000
C	1.4719561	1.5818063	1.3815922
H	1.0340459	1.9774888	2.3067417
H	1.3011110	0.4960145	1.3448931
H	2.5510724	1.7903064	1.3782892
C	1.4719561	1.5818063	-1.3815922
H	1.0340459	1.9774888	-2.3067417
H	2.5510724	1.7903064	-1.3782892
H	1.3011110	0.4960145	-1.3448931
C	0.2221304	-2.5180945	0.0000000
H	0.8884449	-3.3814866	0.0000000

5.

C	2.4895981	0.8822375	1.2125686
C	1.9572617	-0.4068091	1.2194974
C	1.6955489	-1.0286672	0.0000000
C	1.9572617	-0.4068091	-1.2194974
C	2.4895981	0.8822375	-1.2125686
H	2.6974583	1.3850878	2.1575014
H	1.7333377	-0.9336641	2.1447998
H	1.7333377	-0.9336641	-2.1447998
H	2.6974583	1.3850878	-2.1575014
N	1.1108168	-2.3921384	0.0000000
O	0.8908206	-2.9199722	-1.0930252
O	0.8908206	-2.9199722	1.0930252
C	2.7529559	1.5281971	0.0000000
H	3.1667117	2.5373237	0.0000000
C	-1.8380995	-0.2419693	1.1466351
C	-1.8380995	-0.2419693	-1.1466351
C	-2.9568114	0.5942580	-1.2009000
C	-3.5273440	1.0206289	0.0000000
C	-2.9568114	0.5942580	1.2009000
H	-1.3614264	-0.6002123	2.0638979
H	-1.3614264	-0.6002123	-2.0638979
H	-3.3692049	0.9009306	-2.1628069
H	-4.4016226	1.6734152	0.0000000
H	-3.3692049	0.9009306	2.1628069
N	-1.2829351	-0.6585330	0.0000000

6.

C	1.6556495	0.0582097	1.2127043
C	0.4361545	-0.6181956	1.2200097
C	-0.1534098	-0.9454229	0.0000000
C	0.4361545	-0.6181956	-1.2200097
C	1.6556495	0.0582097	-1.2127043
H	2.1306485	0.3235307	2.1575936
H	-0.0682749	-0.8879662	2.1455510
H	-0.0682749	-0.8879662	-2.1455510
H	2.1306485	0.3235307	-2.1575936
N	-1.4595486	-1.6489527	0.0000000
O	-1.9627556	-1.9219358	-1.0933619
O	-1.9627556	-1.9219358	1.0933619
C	2.2651776	0.3965395	0.0000000
H	3.2183601	0.9268275	0.0000000
N	-2.2951530	1.4204978	0.0000000
C	-2.7609462	2.4800961	0.0000000
H	-3.1973240	3.4631295	0.0000000

7.

C	2.0059347	0.2632968	0.0000000
C	1.3215358	0.1110309	-1.2114716
C	-0.0395579	-0.1870880	-1.2188338
C	-0.7042467	-0.3206940	0.0000000
C	-0.0395579	-0.1870880	1.2188338
C	1.3215358	0.1110309	1.2114716
H	3.0695896	0.5089120	0.0000000
H	1.8480549	0.2437758	-2.1582232
H	-0.6074354	-0.2793347	-2.1414316
H	-0.6074354	-0.2793347	2.1414316
H	1.8480549	0.2437758	2.1582232
N	-2.1258049	-0.7473865	0.0000000
O	-2.6623591	-0.9665843	1.0929402
O	-2.6623591	-0.9665843	-1.0929402
Cl	-1.9659494	2.4522722	0.0000000

[1] R. Ahlrichs, M. Bär, M. Hacer, H. Horn and C. Kömel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
[2] Spartan '10, Wavefunction, Inc. (www.wavefun.com)
[3] S. B. Boys, F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.