Concurrent aerogen bonding and lone pair/anion-π interactions in the stability of organoxenon derivatives: A combined CSD and *ab initio* study.

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Electronic Supplementary Information

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Cartesian coordinates

4.

C	1.3605622	1.9684660	-1.2071026
C	1.5965144	0.5944452	-1.2132901
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H	1.2689736	2.5003477	-2.1476997
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H	1.3050355	1.7086649	-2.1462067
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F	-3.5088238	0.1397086	1.1507828
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H	1.2330735	2.4831984	-2.1557858
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F	1.6953809	-0.0681404	-2.3474836
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H	-2.7721189	-1.5233711	-0.8123864
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H	0.7912032	2.0833341	-2.1557609

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C	1.0477305	1.2255803	1.1841836
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C	3.0150120	0.6621194	0.0000000
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O	-0.9813167	-1.2804774	0.0000000
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H	-2.6780930	-1.1519009	-1.1947248
H	-1.1070938	-1.3173684	-2.0216588
H	-1.8452508	-2.7257981	-1.2184394
C	-1.6967603	-1.6412745	1.1653067
H	-1.1070938	-1.3173684	2.0216588
H	-2.6780930	-1.1519009	1.1947248
H	-1.8452508	-2.7257981	1.2184394
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F	0.3979121	1.3910734	2.3476372
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H	2.8969700	0.6911796	-2.1555891

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C	0.254492	-0.060190	1.183992
C	0.032029	1.305619	1.216262

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Xe	0.576100	-2.866641	0.000000
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F	0.351531	-0.718962	2.349435
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F	0.351531	-0.718962	-2.349435
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H	-0.077411	1.832909	2.154073
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C	0.4581634	0.0546835	1.1847259
C	-0.1039336	1.3174516	1.2163818
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F	0.7119558	-0.5647416	-2.3497810
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H	-0.3574935	1.7943265	-2.1531297
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C	0.9872315	-0.1965194	1.1846181
C	1.2081044	1.1690477	1.2162482
C	1.3083622	1.8207180	0.0000000
Xe	0.5345963	-2.9960752	0.0000000
F	0.2960442	-5.1092346	0.0000000
H	1.2623523	1.7057464	2.1534540
H	1.2623523	1.7057464	-2.1534540
F	-1.6801335	1.1070411	0.0000000
F	-1.9845418	-1.1686742	0.0000000
F	-3.4431984	0.1859726	1.1504272
F	-3.4431984	0.1859726	-1.1504272
B	-2.6551556	0.0843581	0.0000000
F	0.8801462	-0.8566826	2.3497525
F	0.8801462	-0.8566826	-2.3497525
F	1.5132406	3.1512294	0.0000000

16.

C	1.3117383	1.9006370	-1.2063758
C	1.5907887	0.5408344	-1.1938637
C	1.7361266	-0.1429427	0.0000000
C	1.5907887	0.5408344	1.1938637
C	1.3117383	1.9006370	1.2063758

C	1.1705286	2.5774469	0.0000000
Xe	2.0118102	-2.2666691	0.0000000
F	2.2542599	-4.3333265	0.0000000
F	1.1724876	2.5588178	2.3533964
F	1.1724876	2.5588178	-2.3533964
F	1.7006402	-0.1008172	2.3602631
F	1.7006402	-0.1008172	-2.3602631
F	0.9048387	3.8792295	0.0000000
N	-1.2260575	-0.9916682	0.0000000
C	-2.3489985	-1.3154219	0.0000000
C	-3.7465814	-1.7231986	0.0000000
H	-4.2462999	-1.3360094	0.8870376
H	-4.2462999	-1.3360094	-0.8870376
H	-3.8146363	-2.8103748	0.0000000

17.

C	0.271022	1.693421	-1.206420
C	0.753760	0.391498	-1.193165
C	1.002983	-0.262990	0.000000
C	0.753760	0.391498	1.193165
C	0.271022	1.693421	1.206420
C	0.027999	2.341150	0.000000
Xe	1.646930	-2.305719	0.000000
F	2.248318	-4.295329	0.000000
F	0.964395	-0.223434	2.360270
F	0.033939	2.322372	2.353483
F	-0.432562	3.586919	0.000000

F	0.033939	2.322372	-2.353483
F	0.964395	-0.223434	-2.360270
N	-1.856553	-1.773510	0.000000
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18.

C	2.2936686	0.7476461	-1.2064228
C	0.9899493	1.2242579	-1.1932169
C	0.3350626	1.4714282	0.0000000
C	0.9899493	1.2242579	1.1932169
C	2.2936686	0.7476461	1.2064228
C	2.9428833	0.5089832	0.0000000
Xe	-1.7267738	2.0527158	0.0000000
F	-3.7428203	2.5602141	0.0000000
O	-0.9510754	-1.1821810	0.0000000
C	-1.6437670	-1.5840780	-1.1663491
H	-2.6498323	-1.1483305	-1.1984345
H	-1.0709010	-1.2310842	-2.0227079
H	-1.7329241	-2.6749676	-1.2170199
C	-1.6437670	-1.5840780	1.1663491
H	-1.0709010	-1.2310842	2.0227079
H	-2.6498323	-1.1483305	1.1984345
H	-1.7329241	-2.6749676	1.2170199
F	4.1900945	0.0542574	0.0000000
F	2.9217414	0.5110300	-2.3534994

F	0.3683795	1.4228174	-2.3604066
F	0.3683795	1.4228174	2.3604066
F	2.9217414	0.5110300	2.3534994

19.

C	-0.1880624	1.2494245	-1.2040891
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C	0.5224791	-0.7042477	0.0000000
C	0.2977070	-0.0474131	1.1944556
C	-0.1880624	1.2494245	1.2040891
C	-0.4302733	1.8955396	0.0000000
Xe	1.0519980	-2.7546456	0.0000000
F	1.6743340	-4.7881388	0.0000000
F	0.4956540	-0.6675162	2.3615495
F	-0.4241713	1.8858842	2.3549574
F	-0.8869331	3.1514873	0.0000000
F	-0.4241713	1.8858842	-2.3549574
F	0.4956540	-0.6675162	-2.3615495
Cl	-2.2938592	-1.6407537	0.0000000

20.

C	0.0466953	1.3066834	-1.2042194
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C	0.4702516	-0.0115153	1.1944409
C	0.0466953	1.3066834	1.2042194

C	-0.1738425	1.9596020	0.0000000
Xe	1.0861694	-2.7541987	0.0000000
F	1.5796491	-4.8217594	0.0000000
F	0.6387487	-0.6420379	2.3618405
F	-0.1672101	1.9487525	2.3542348
F	-0.5851957	3.2280505	0.0000000
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F	0.6387487	-0.6420379	-2.3618405
C	-2.5522518	-0.5412759	0.0000000
N	-2.0056928	-1.5979659	0.0000000

21.

C	0.7748331	1.4454402	-1.2039057
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C	1.1049458	-0.6121179	0.0000000
C	0.9921661	0.0763845	1.1939707
C	0.7748331	1.4454402	1.2039057
C	0.6648613	2.1262818	0.0000000
Xe	1.4202194	-2.7150394	0.0000000
F	1.8310312	-4.7894038	0.0000000
F	-1.8793200	0.5469335	0.0000000
F	-1.5102489	-1.7188211	0.0000000
F	-3.2989014	-0.8464692	1.1503912
F	-3.2989014	-0.8464692	-1.1503912
B	-2.5194033	-0.7163691	0.0000000
F	1.0910813	-0.5670859	2.3621909
F	1.0910813	-0.5670859	-2.3621909

F	0.4472814	3.4409276	0.0000000
F	0.6611374	2.1105348	2.3536079
F	0.6611374	2.1105348	-2.3536079

Additional AIM analyses

In **Fig. S1** the distribution of critical points (CPs) and bond paths for some additional complexes is shown. As noted, for complexes **4**, **6** and **14** only one bond CP connecting the lone pairs of the electron donor molecule to the xenon atom (in **4** and **6**) and the aromatic moiety (in **14**) was found. In addition, for complex **6** two additional bond CPs connect the hydrogen atoms of the methyl groups to the aromatic moiety, thus evidencing the existence of ancillary CH–π interactions. On the other hand, for complexes **17** and **18** two simultaneous bond CPs connect the lone pairs of the nitrogen and oxygen atoms to both the aromatic moiety and the xenon atom. Moreover, in complex **18** ancillary hydrogen bonding interactions are characterized due to the presence of two bond CPs connecting the hydrogen atoms of the methyl groups and the fluorine substituents. Finally, one ring CP (in **17**), two ring CPs (in **6**) and three ring CPs (in **18**) emerge due to the formation of supramolecular rings.

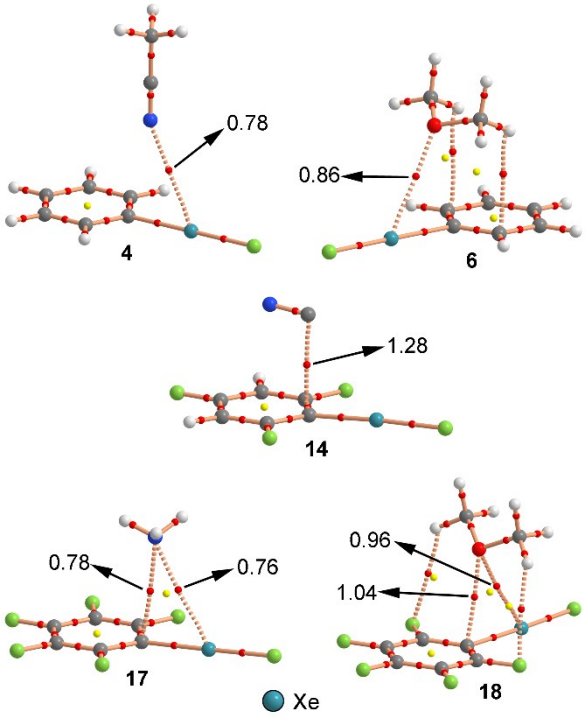

Fig. S1 Distribution of critical points and bond paths in complexes **4**, **6**, **14**, **17** and **18**. Bond, ring and cage critical points are represented by red, yellow and green spheres, respectively. The bond paths connecting bond critical points are also represented. The value of the density at the bond critical point ($\rho \cdot 10^2$) is also indicated.

CIF codes:

COLNAU, DAMROY, IDUQED, JAQCOT, KEDMUB, MOFHOF, MOFHUL, MOFJAT, MOFJEX, QOYRAZ, QOYRED, QOYRIH, ROQQET, TUKFAH, WADHIS, WEJBES, ZOGPIV.