What Is Responsible for Conformational Diversity in Single-Crystal Tetraoxazaspiroalkanes? X-Ray, DFT, and AIM Approaches

Arthur R. Tulyabaev, Kamil Sh. Bikmukhametov, Ekaterina S. Mescheryakova, Natalia N. Makhmudiyarova, Rustem Sh. Rakhimov, and Leonard M. Khalilov

Institute of Petrochemistry and Catalysis, Ufa Federal Research Centre, Russian Academy of Sciences
141 Prospekt Oktyabrya, Ufa 450075, Russian Federation
Tel./Fax: +7 347 2842750
tulebeich@gmail.com

Supplementary Information

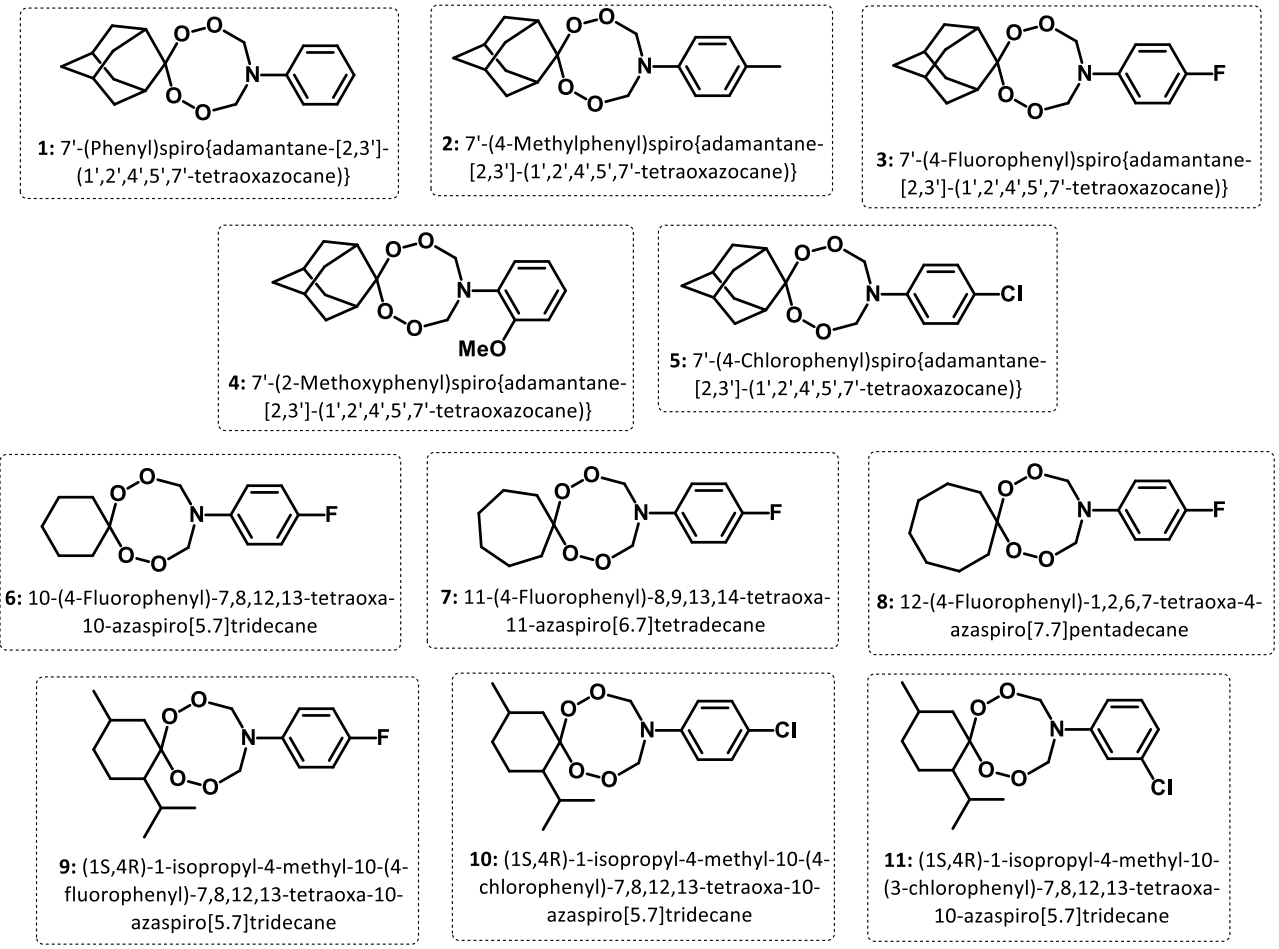


Fig. 1. Structures of the compounds **1–11** and their IUPAC names.

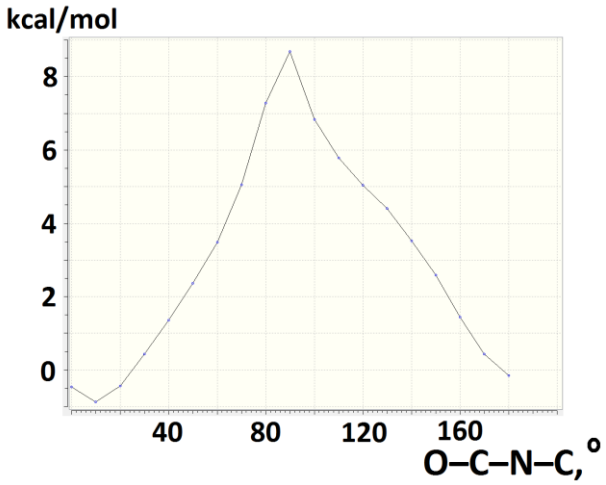


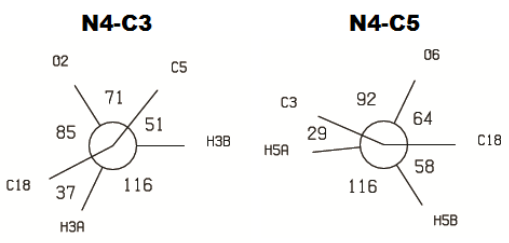
Fig. 2. Potential energy surface *vs*. O–C–N–C torsion angle for the compound **1** calculated at the B3LYP/6-31G(d,2p) level of theory.

Table 1. Experimental and theoretical bond lengths for compounds **1–5**, in Å

Bonds	1		2		3		4		5	
	Exp	Theor	Exp	Theor	Exp	Theor	Exp	Theor	Exp	Theor
O1–O2	1.459	1.459	1.458	1.462	1.463	1.462	1.445	1.458	1.453	1.462
O2–C3	1.440	1.441	1.429	1.424	1.437	1.423	1.448	1.435	1.430	1.422
C3–N4	1.427	1.431	1.419	1.443	1.422	1.444	1.419	1.433	1.426	1.445
N4–C5	1.418	1.443	1.417	1.430	1.426	1.431	1.419	1.435	1.420	1.433
C5–O6	1.436	1.424	1.428	1.442	1.442	1.442	1.440	1.436	1.448	1.439
O6–O7	1.461	1.462	1.475	1.458	1.463	1.458	1.466	1.461	1.469	1.459
O7–C8	1.425	1.425	1.410	1.417	1.419	1.417	1.409	1.412	1.414	1.417

Table 2. Experimental and theoretical bond lengths for compounds **6–11**, in Å

Bonds	6		7		8		9		10		11	
	Exp	Theor	Exp	Theor	Exp	Theor	Exp	Theor	Exp	Theor	Exp	Theor
O1–O2	1.393	1.450	1.450	1.449	1.454	1.448	1.470	1.458	1.456	1.459	1.455	1.459
O2–C3	1.384	1.473	1.468	1.470	1.477	1.471	1.437	1.442	1.425	1.433	1.441	1.433
C3–N4	1.419	1.421	1.411	1.420	1.408	1.421	1.432	1.432	1.422	1.440	1.415	1.441
N4–C5	1.454	1.439	1.437	1.439	1.434	1.439	1.427	1.439	1.407	1.434	1.423	1.435
C5–O6	1.400	1.428	1.420	1.427	1.436	1.427	1.437	1.435	1.426	1.440	1.443	1.439
O6–O7	1.467	1.462	1.474	1.461	1.476	1.463	1.458	1.459	1.458	1.458	1.470	1.458
O7–C8	1.431	1.431	1.430	1.437	1.427	1.432	1.436	1.429	1.415	1.430	1.433	1.430



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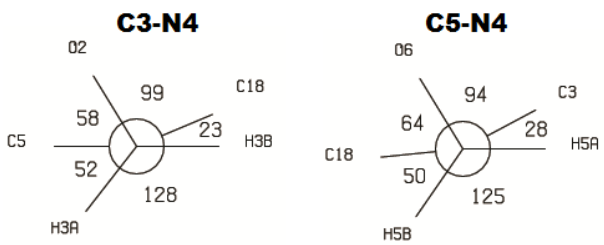

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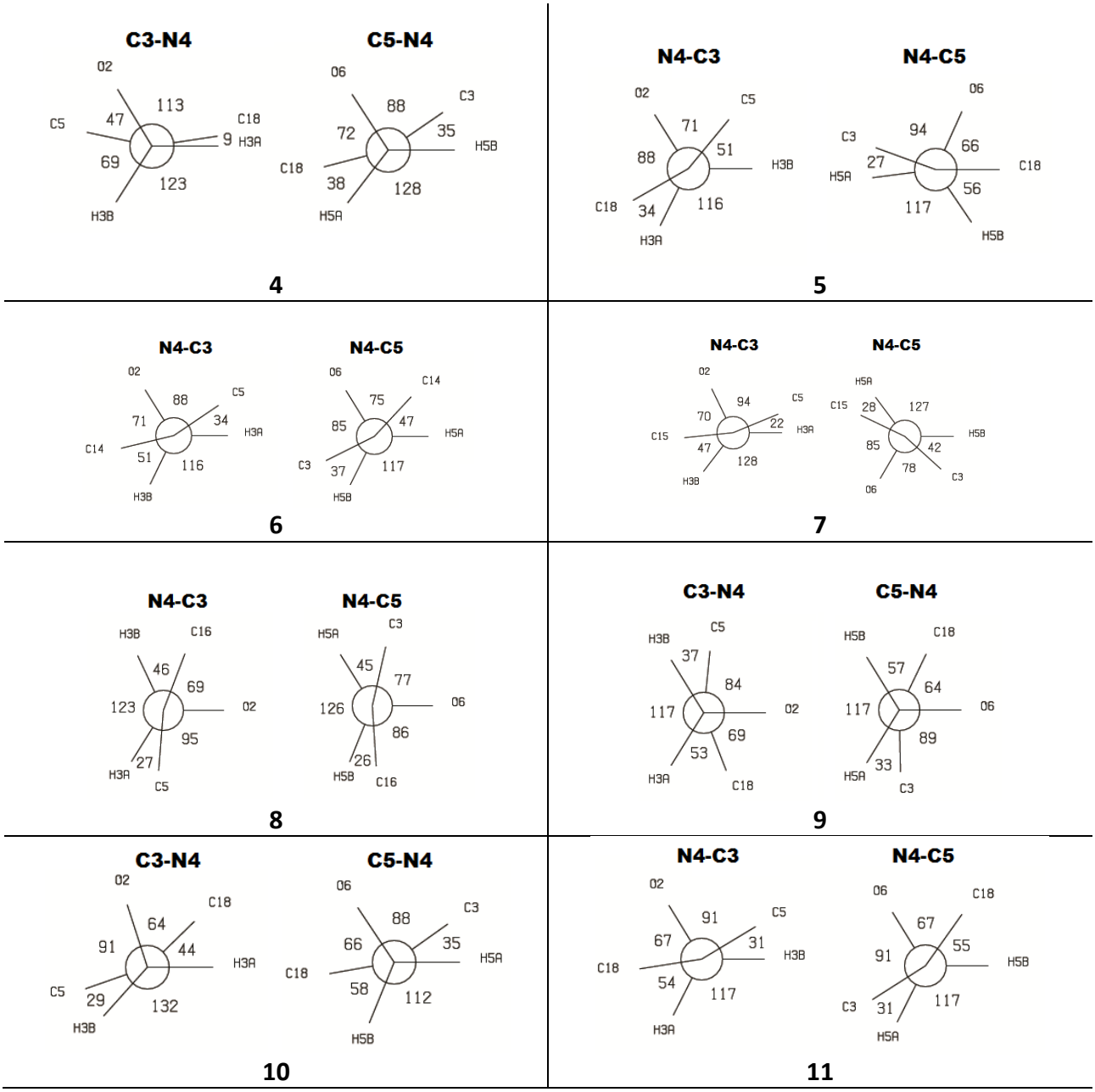


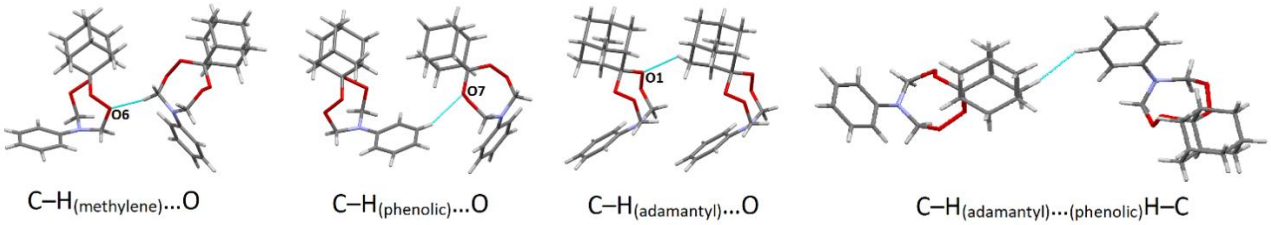
Fig. 3. Newman projections for the compounds **2–11**

Table 3. Topological parameters of electron density in (3, –1) BCPs for compounds **2–11** obtained from experimental X-ray diffraction data and quantum-chemical calculations at B3LYP/6-31G(d,2p) level of theory

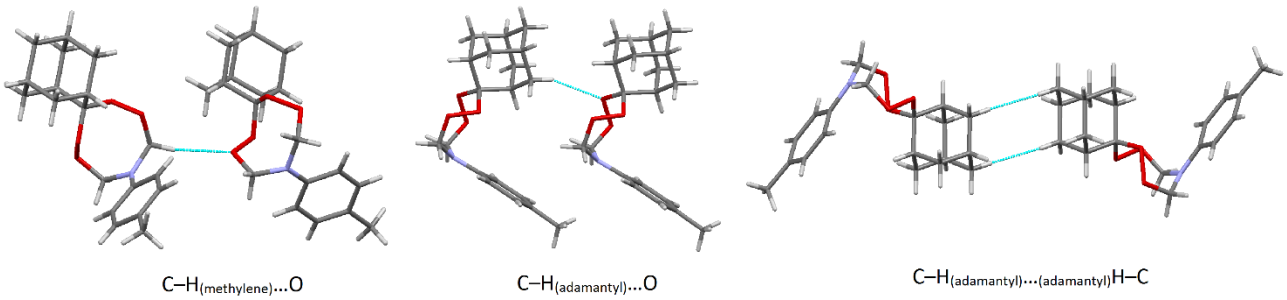
Bonds	X-ray			B3LYP/6-31G(d,2p)		
	Electron density, e/au^3	Laplacian, –e/au^5	Ellipticity	Electron density, e/au^3	Laplacian, –e/au^5	Ellipticity
2						
O1–O2	0.2741	0.0216	0.0485	0.2726	0.0204	0.0723
O6–O7	0.2629	0.0129	0.0338	0.2738	0.0147	0.0289
C3–N4	0.2932	0.9388	0.0248	0.2799	0.8396	0.0880
C5–N4	0.2949	0.9571	0.0427	0.2861	0.8912	0.0227
C3–O2	0.2578	0.5722	0.1572	0.2606	0.5596	0.1147
C5–O6	0.2582	0.5416	0.0898	0.2511	0.5486	0.0785
C8–O1	0.2638	0.5658	0.1554	0.2607	0.5605	0.1524
C8–O7	0.2678	0.5311	0.1386	0.2660	0.5763	0.1351

3						
O1–O2	0.2715	0.0178	0.0661	0.2725	0.0201	0.0726
O6–O7	0.2711	0.0094	0.0310	0.2738	0.0147	0.0290
C3–N4	0.2919	0.9320	0.0492	0.2792	0.8356	0.0870
C5–N4	0.2896	0.9199	0.0431	0.2856	0.8881	0.0228
C3–O2	0.2542	0.5674	0.1325	0.2612	0.5615	0.1154
C5–O6	0.2513	0.5501	0.0746	0.2513	0.5501	0.0789
C8–O1	0.2628	0.5569	0.1575	0.2606	0.5582	0.1529
C8–O7	0.2642	0.5626	0.1348	0.2656	0.5748	0.1365
4						
O1–O2	0.2845	0.0507	0.0667	0.2749	0.0242	0.0644
O6–O7	0.2692	0.0054	0.0370	0.2722	0.0107	0.0329
C3–N4	0.2934	0.9369	0.0805	0.2856	0.8770	0.0772
C5–N4	0.2921	0.9347	0.0312	0.2829	0.8682	0.0317
C3–O2	0.2474	0.5416	0.1128	0.2544	0.5593	0.1185
C5–O6	0.2514	0.5359	0.0805	0.2531	0.5375	0.0901
C8–O1	0.2597	0.5466	0.1570	0.2572	0.5639	0.1504
C8–O7	0.2702	0.5690	0.1362	0.2689	0.5768	0.1335
5						
O1–O2	0.2775	0.0313	0.0521	0.2727	0.0209	0.0729
O6–O7	0.2668	0.0007	0.0329	0.2735	0.0137	0.0285
C3–N4	0.2892	0.9135	0.0215	0.2782	0.8304	0.0852
C5–N4	0.2933	0.9478	0.0407	0.2841	0.8792	0.0256
C3–O2	0.2588	0.5938	0.1530	0.2620	0.5644	0.1162
C5–O6	0.2494	0.5577	0.0692	0.2527	0.5543	0.0805
C8–O1	0.2584	0.5616	0.1509	0.2598	0.5567	0.1552
C8–O7	0.2659	0.5468	0.1396	0.2658	0.5720	0.1372
6						
O1–O2	0.3222	0.1452	0.0139	0.2784	0.0243	0.0055
O6–O7	0.2685	0.0105	0.0390	0.2728	0.0224	0.0449
C3–N4	0.2927	0.9308	0.0265	0.2914	0.9235	0.0237
C5–N4	0.2747	0.7992	0.0118	0.2815	0.8589	0.0182
C3–O2	0.2796	0.4665	0.1765	0.2369	0.5090	0.1392
C5–O6	0.2721	0.4876	0.1082	0.2591	0.5637	0.0977
C8–O1	0.2505	0.5726	0.1223	0.2685	0.5996	0.1212
C8–O7	0.2566	0.5458	0.1402	0.2576	0.5576	0.1304
7						
O1–O2	0.2783	0.0221	0.0062	0.2792	0.0232	0.0112
O6–O7	0.2639	0.0040	0.0461	0.2729	0.0205	0.0438
C3–N4	0.2972	0.9660	0.0295	0.2919	0.9272	0.0261
C5–N4	0.2831	0.8713	0.0139	0.2812	0.8571	0.0198
C3–O2	0.2392	0.5199	0.1369	0.2375	0.5105	0.1352
C5–O6	0.2623	0.5336	0.1052	0.2600	0.5647	0.0972
C8–O1	0.2633	0.5955	0.1169	0.2630	0.5974	0.1114
C8–O7	0.2578	0.5573	0.1307	0.2547	0.5661	0.1295
8						
O1–O2	0.2758	0.0172	0.0058	0.2800	0.0263	0.0101
O6–O7	0.2628	0.0042	0.0482	0.2720	0.0194	0.0444
C3–N4	0.2984	0.9743	0.0308	0.2915	0.9242	0.0257
C5–N4	0.2847	0.8844	0.0150	0.2811	0.8565	0.0193
C3–O2	0.2349	0.4949	0.1356	0.2376	0.5113	0.1358
C5–O6	0.2554	0.5664	0.0882	0.2598	0.5644	0.0973
C8–O1	0.2600	0.5930	0.1114	0.2616	0.5941	0.1131
C8–O7	0.2596	0.5569	0.1396	0.2572	0.5664	0.1339
9						
O1–O2	0.2656	–0.0101	0.0219	0.2736	0.0123	0.0235
O6–O7	0.2735	0.0128	0.0140	0.2731	0.0139	0.0301

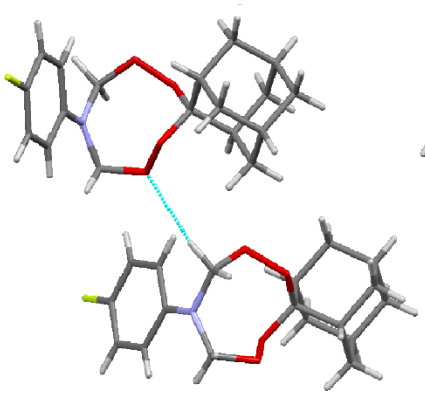
C3–N4	0.2864	0.8959	0.0257	0.2863	0.8893	0.0159
C5–N4	0.2887	0.9125	0.0365	0.2818	0.8570	0.0138
C3–O2	0.2544	0.5620	0.0735	0.2509	0.5464	0.0747
C5–O6	0.2550	0.5706	0.0685	0.2558	0.5628	0.0751
C8–O1	0.2620	0.5276	0.1458	0.2575	0.5625	0.1229
C8–O7	0.2545	0.5614	0.1289	0.2590	0.5794	0.1219
10						
O1–O2	0.2758	0.0182	0.0118	0.2731	0.0138	0.0299
O6–O7	0.2738	0.0124	0.0197	0.2737	0.0122	0.0222
C3–N4	0.2917	0.9347	0.0452	0.2808	0.8525	0.0158
C5–N4	0.3003	0.9906	0.0452	0.2852	0.8832	0.0186
C3–O2	0.2597	0.5427	0.0877	0.2568	0.5667	0.0764
C5–O6	0.2599	0.5511	0.0785	0.2522	0.5511	0.0763
C8–O1	0.2584	0.5417	0.1420	0.2586	0.5773	0.1224
C8–O7	0.2645	0.5356	0.1443	0.2573	0.5611	0.1242
11						
O1–O2	0.2754	0.0158	0.0118	0.2733	0.0145	0.0302
O6–O7	0.2650	0.0119	0.0153	0.2736	0.0121	0.0225
C3–N4	0.2949	0.9582	0.0460	0.2803	0.8500	0.0174
C5–N4	0.2911	0.9329	0.0385	0.2846	0.8801	0.0197
C3–O2	0.2522	0.5528	0.0764	0.2570	0.5672	0.0776
C5–O6	0.2516	0.5607	0.0696	0.2526	0.5525	0.0771
C8–O1	0.2545	0.5560	0.1278	0.2589	0.5776	0.1227
C8–O7	0.2561	0.5602	0.1267	0.2572	0.5606	0.1242



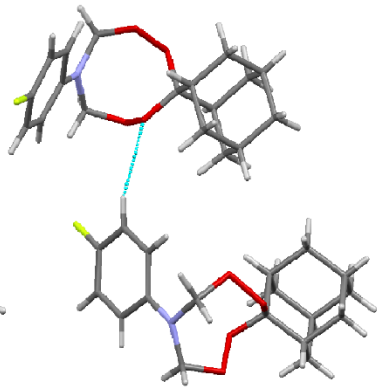
Compound 1



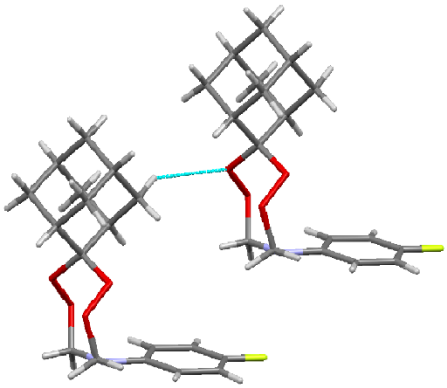
Compound 2



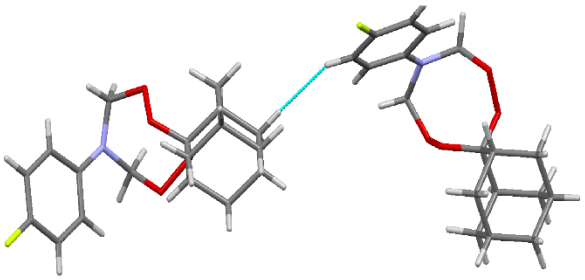
C–H(methylene)…O



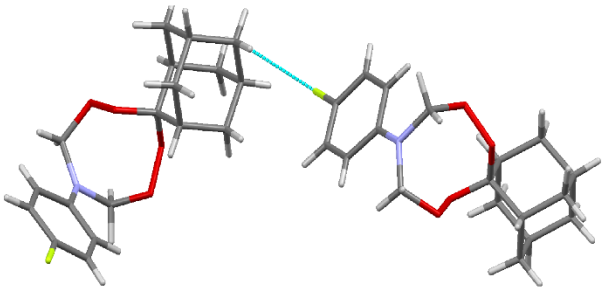
C–H(phenolic)…O



C–H(adamantyl)…O

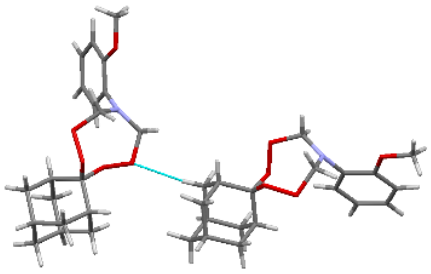


C–H(adamantyl)…(phenolic)H–C



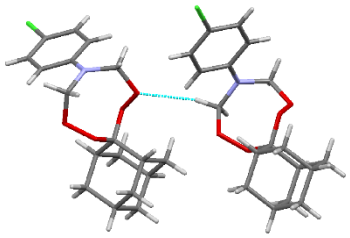
C–H(adamantyl)…F

Compound 3



C–H(adamantyl)…O

Compound 4



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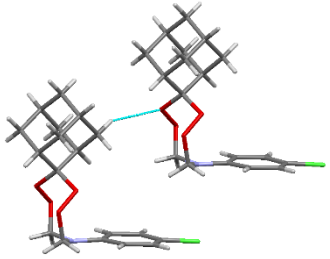
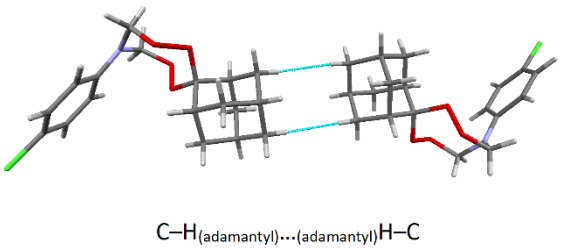
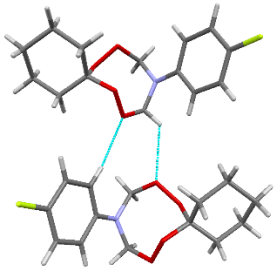


C–H(adamantyl)…O

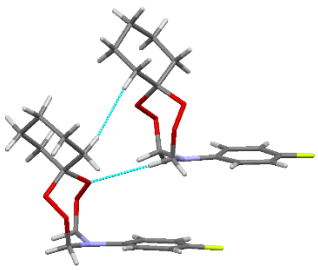


C–H(adamantyl)…(adamantyl)H–C

Compound 5

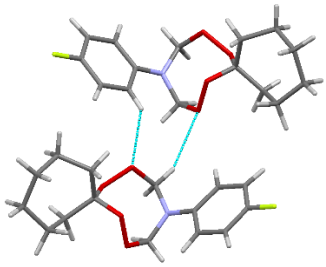


C–H(methylene)…O
C–H(phenolic)…O

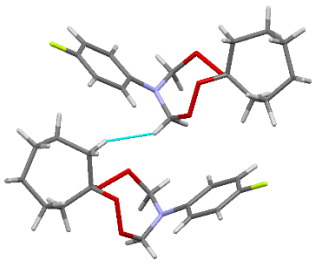


C–H(methylene)…O
C–H(cyclohexyl)…(cyclohexyl)H–C

Compound 6

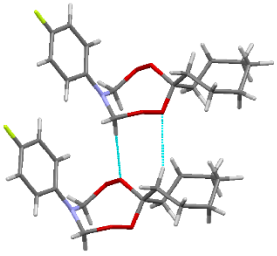


C–H(phenolic)…O
C–H(methylene)…O

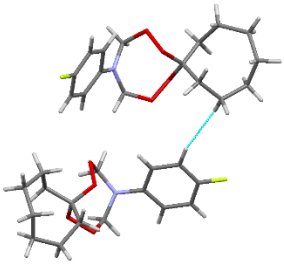


C–H(cycloheptyl)…(methylene)H–C

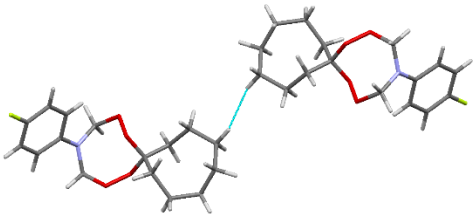
Compound 7



C–H(methylene)…O
C–H(cyclooctyl)…O

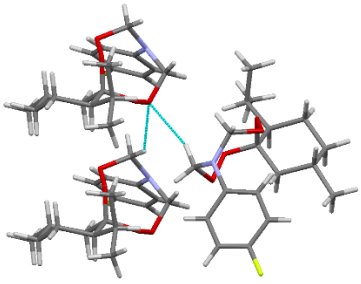


C–H(cyclooctyl)…(phenolic)H–C

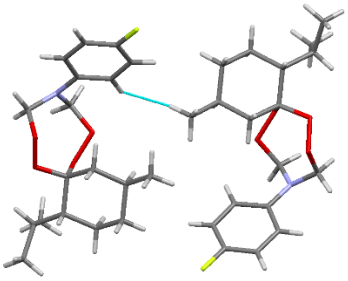


C–H(cyclooctyl)…(cyclooctyl)H–C

Compound 8



C–H(methylene)…O



C–H(menthyl)…(phenolic)H–C

Compound 9

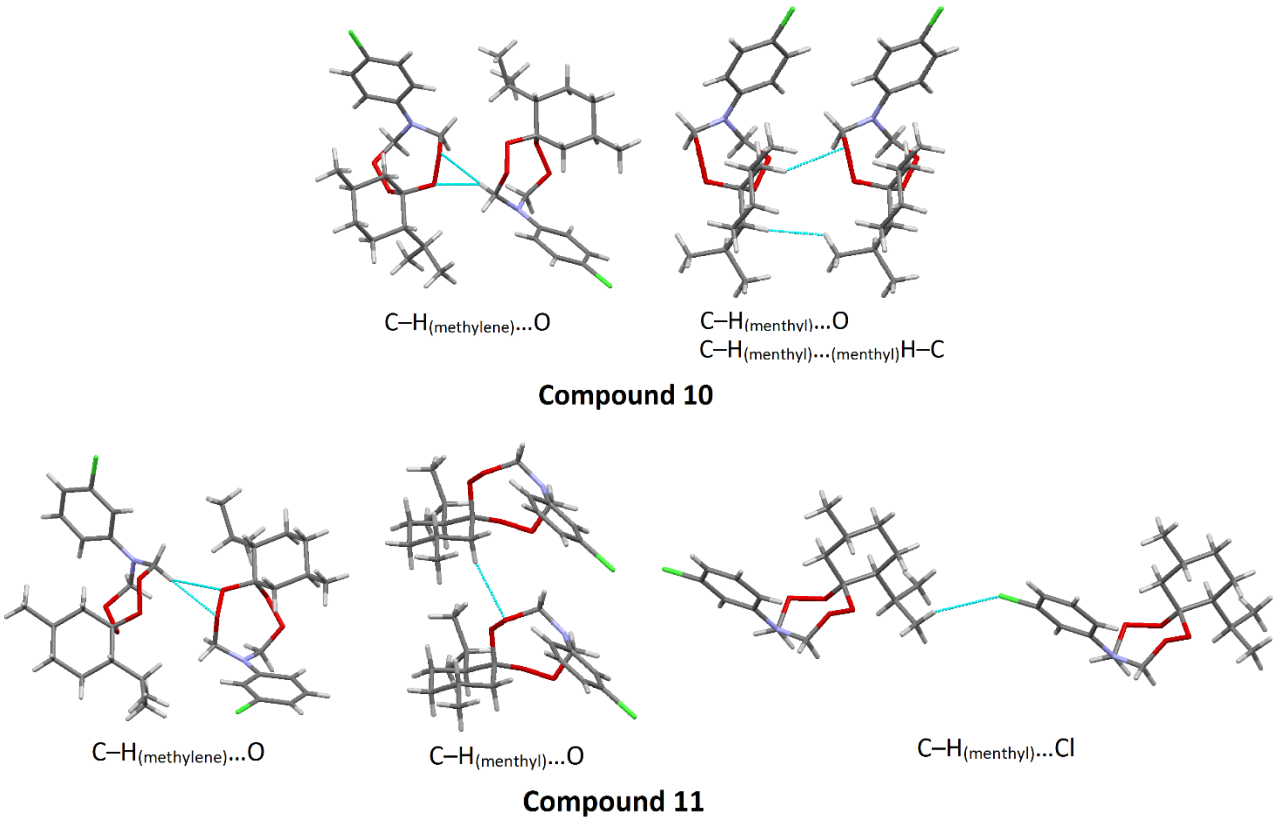


Fig. 4. Dimeric pairs observed in the crystals of compounds **1–11** and used for AIM calculations of intermolecular interactions

Table 4. C–H…O and C–H…H–C intermolecular interactions in crystals of **1–11**: geometry, AIM properties, and AIM energies

Compound	Type	H…A, Å	D–H…A, °	ρ(r), e/au^3	Laplacian, e/au^5	–v(r)	$-E_{int}$, kcal/mol
1	C–H$_{(methylene)}$...O	2.457	170.96	0.0115	0.0364	0.0083	2.60
	C–H$_{(phenolic)}$...O	2.598	153.78	0.0105	0.0362	0.0078	2.45
	C–H$_{(adamantyl)}$...O	2.615	133.20	0.0106	0.0349	0.0073	2.29
	C–H$_{(adamantyl)}$...$_{(phenolic)}$H–C	2.278	142.37	0.0064	0.0223	0.0029	0.91
2	C–H$_{(methylene)}$...O	2.535	170.30	0.0106	0.0346	0.0076	2.38
	C–H$_{(adamantyl)}$...O	2.480	152.10	0.0119	0.0383	0.0085	2.67
	C–H$_{(adamantyl)}$...$_{(adamantyl)}$H–C	2.375	157.88	0.0080	0.0259	0.0039	1.22
3	C–H$_{(methylene)}$...O	2.430	170.10	0.0119	0.0371	0.0086	2.70
	C–H$_{(phenolic)}$...O	2.564	156.80	0.0112	0.0375	0.0083	2.60
	C–H$_{(adamantyl)}$...O	2.590	138.30	0.0098	0.0328	0.0066	2.07
	C–H$_{(adamantyl)}$...$_{(phenolic)}$H–C	2.371	141.20	0.0076	0.0265	0.0037	1.16
4	C–H$_{(adamantyl)}$...O	2.614	157.80	0.0102	0.0315	0.0068	2.13
5	C–H$_{(methylene)}$...O	2.505	165.40	0.0116	0.0372	0.0084	2.64
	C–H$_{(adamantyl)}$...O	2.499	148.50	0.0114	0.0370	0.0080	2.51
	C–H$_{(adamantyl)}$...$_{(adamantyl)}$H–C	2.399	157.45	0.0077	0.0248	0.0036	1.13
6	C–H$_{(methylene)}$...O	2.699	127.10	0.0081	0.0271	0.0051	1.60
	C–H$_{(phenolic)}$...O	2.543	165.50	0.0110	0.0360	0.0080	2.51
	C–H$_{(cyclohexyl)}$...$_{(cyclohexyl)}$H–C	2.394	155.70	0.0067	0.0228	0.0031	0.97
7	C–H$_{(methylene)}$...O	2.699	154.50	0.0072	0.0254	0.0046	1.44
	C–H$_{(phenolic)}$...O	2.510	138.60	0.0092	0.0321	0.0061	1.91
	C–H$_{(cycloheptyl)}$...$_{(methylene)}$H–C	2.356	129.15	0.0066	0.0256	0.0032	1.00
8	C–H$_{(methylene)}$...O	2.445	168.80	0.0134	0.0427	0.0100	3.14
	C–H$_{(cyclooctyl)}$...O	2.664	161.10	0.0074	0.0268	0.0050	1.57

	C–H$_{(cyclooctyl)}$...$_{(cyclooctyl)}$H–C	2.379	131.45	0.0075	0.0257	0.0036	1.13
	C–H$_{(cyclooctyl)}$...$_{(phenolic)}$H–C	2.397	124.16	0.0071	0.0258	0.0034	1.07
9	C–H$_{(methylene)}$...O[a]	2.503	137.44	0.0077	0.0267	0.0049	1.54
	C–H$_{(methylene)}$...O[a]	2.676	161.96	0.0057	0.0223	0.0037	1.16
	C–H$_{(menthyl)}$...$_{(phenolic)}$H–C	2.388	137.09	0.0077	0.0270	0.0038	1.19
10	C–H$_{(menthyl)}$...O[a]	2.599	154.41	0.0072	0.0266	0.0047	1.47
	C–H$_{(methylene)}$...O[a]	2.461	142.89	0.0054	0.0201	0.0031	0.97
	C–H$_{(menthyl)}$...O	2.704	143.14	0.0072	0.0233	0.0040	1.26
	C–H$_{(menthyl)}$...$_{(menthyl)}$H–C	2.396	164.73	0.0077	0.0264	0.0037	1.16
11	C–H$_{(methylene)}$...O[a]	2.560	151.22	0.0097	0.0353	0.0073	2.29
	C–H$_{(methylene)}$...O[a]	2.586	171.03	0.0069	0.0251	0.0043	1.35
	C–H$_{(menthyl)}$...O	2.696	147.96	0.0075	0.0263	0.0048	1.51

[a] bifurcate interactions

Table 5. Intramolecular interactions in crystals of **7**, **8**, and **9–11**: geometry, AIM properties, and AIM interaction energies

Compound	Type	H…A, Å	D–H…A, °	ρ(r), e/au^3	Laplacian, e/au^5	–v(r)	$-E_{int}$, kcal/mol
7	C–H$_{(cycloheptyl)}$...O2	2.340	105.37	0.0157	0.0681	0.0126	3.95
8	C–H$_{(cyclooctyl)}$...O2	2.411	104.22	0.0166	0.0671	0.0128	4.02
9	C–H$_{(menthyl)}$...O1	2.496	117.84	0.0119	0.0418	0.0083	2.60
	C–H$_{(menthyl)}$...O7	2.331	109.37	0.0150	0.0633	0.0115	3.61
	C–H$_{(phenolic)}$...O2	2.407	124.31	0.0128	0.0488	0.0095	2.98
10	C–H$_{(menthyl)}$...O1	2.361	115.67	0.0158	0.0661	0.0122	3.83
	C–H$_{(menthyl)}$...O7	2.415	112.46	0.0132	0.0467	0.0095	2.98
	C–H$_{(menthyl)}$...π	2.705	164.18	0.0071	0.0262	0.0038	1.19
11	C–H$_{(menthyl)}$...O1	2.363	108.48	0.0142	0.0621	0.0109	3.42
	C–H$_{(menthyl)}$...O7	2.369	124.15	0.0129	0.0454	0.0091	2.86
	C–H$_{(menthyl)}$...π	2.802	158.36	0.0071	0.0260	0.0038	1.19