Supplementary materials for review

Organoelement Compounds Crystallized In Situ: Weak Intermolecular Interactions and Lattice Energies

Alexander D. Volodin [1,*], Alexander A. Korlyukov [1,2] and Alexander F. Smol'yakov [1]

[1] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science. 28 Vavilova str. 119991 Moscow, Russian Federation
[2] Pirogov Russian National Research Medical University, Ostrovityanov str., 1, Moscow, 117997, Russian Federation
* Correspondence: alex.d.volodin@gmail.com; volodin@ineos.ac.ru

Received: 20 November 2019; Accepted: 26 December 2019; Published: 31 December 2019

1. Quantum Chemistry Calculations

Lattice energies were obtained using the energy decomposition procedure implemented into the CrystalExplorer program [1,2]. Molecular volumes and molecular surfaces were obtained using the Hirshfeld surface generation procedure implemented into CrystalExplorer program. CrystalExplorer used a localized basis set 6–31G(d,p) and B3LYP functional if the implemented basis set contains basis functions for all necessary atoms, or HF/3-21G level of theory otherwise.

2. Tables with All Observed in the Review Phases

Table S1. Sublimation energies, melting points, molecular volume and surface area of observed compounds.

No	CSD Refcode	Sublimation Energy (kJ/mol)	Method/Basis	$T_{melt.}$ (K) or Phase at r.t.[1]	Mol. Volume (Å^3) / Surface Area (Å^2)	Reference
1	NITYOE	68	B3LYP/6-31G(d,p)	273	221.18/216.04	[3]
2	NITYUK	87.8	B3LYP/6-31G(d,p)	235	319.56/296.13	[3]
3	NITZAR	100.6	B3LYP/6-31G(d,p)	252	417.80/341.54	[3]
4	NITZEV	112	B3LYP/6-31G(d,p)	262	465.61/392.16	[3]
5	GASVUR01	177.6	B3LYP/6-31G(d,p)	Solid	567.07/495.69	[3]
6	BADZIS	93.8	B3LYP/6-31G(d,p)	263.4	535.91/390.88	[4]
7	YUMFAP	87.2	B3LYP/6-31G(d,p)	272.0	334.63/276.38	[5]
8	YUMFET	92.3	B3LYP/6-31G(d,p)	218.0	351.97/294.94	[5]
9	YUMFIX	94.6	B3LYP/6-31G(d,p)	155.0	377.53/302.59	[5]
10	YUMFOD	-	-	239.8	368.35/293.72	[5]
11	OMCSIO	89.8	B3LYP/6-31G(d,p)	290.6/256.8[2]	412.60/344.71	[6]
12	SEQYUL	89.4	B3LYP/6-31G(d,p)	234	379.63/310.00	[7]
13	NEQZUH	75.6	B3LYP/6-31G(d,p)	125	510.45/369.46	[8]
14	EKEGIM	73.7	HF/3-21G	182	272.34/235.35	[9]
15	EKEGUY	73.4	HF/3-21G	175	219.98/211.87	[9]
16	UKOZUR	84.6	HF/3-21G	181	323.90/268.48	[10]
17	KEJZUX	105.7	HF/3-21G	294	339.85/278.25	[11]
18	IWENUV	-	-	Liquid	299.67/256.94	[12]
19	HIYNUY	54.7	B3LYP/6-31G(d,p)	187	148.87/160.17	[13]
20	HIYPAG	58.9	B3LYP/6-31G(d,p)	284	160.89/168.35	[13]
21	LIQVIQ	54.7	B3LYP/6-31G(d,p)	Liquid	94.44/114.23	[14]
22	LIQVOW	46.8	B3LYP/6-31G(d,p)	Liquid	94.39/112.59	[14]

23	LIQVUC	48.9	B3LYP/6-31G(d,p)	Liquid	105.52/123.49	[14]
24	LIQWAJ	63.2	B3LYP/6-31G(d,p)	Liquid	108.91/125.29	[14]
25	LIQWEN	40.6	B3LYP/6-31G(d,p)	Liquid	112.16/125.37	[14]
26	LIQWIR	49.4	B3LYP/6-31G(d,p)	Liquid	137.81/148.64	[14]
27	CECBAO	-	-	175	110.67/128.03	[15]
28	FACFAQ	46.7	B3LYP/6-31G(d,p)	231	118.58/131.97	[16]
29	FACFOE	51.8	B3LYP/6-31G(d,p)	239	123.36/136.81	[16]
30	FACGEV	47.3	B3LYP/6-31G(d,p)	260	129.89/140.68	[16]
31	PVVAWA01	49.8	B3LYP/6-31G(d,p)	267.5	133.43/144.38	[16]
32	FACJAU	55.7	B3LYP/6-31G(d,p)	277	135.19/149.02	[16]
33	ZELDOJ01	55.6	B3LYP/6-31G(d,p)	231	134.10/146.99	[16]
34a	DCLBEN07	52.1	HF/3-21G	304	148.93/160.48	[17]
34b	DCLBEN06	53.8	HF/3-21G	328	149.02/160.63	[17]
34c	DCLBEN03	58.3	HF/3-21G	273	148.28/160.47	[18]
35	ABUMIT	49.3	HF/3-21G	256	154.65/161.69	[19]
36	ABUMOZ	47.7	HF/3-21G	248	156.40/165.16	[19]
37a	AXUBUR	-	-	224	149.62/162.48	[20]
37b	AXUBUR01	57.4	HF/3-21G	224	147.90/160.16	[20]
38a	AXUCEC	-	-	216	151.70/163.19	[20]
38b	AXUCEC01	56.5	HF/3-21G	216	149.01/161.78	[20]
39	NECMUD01	62.6	HF/3-21G	301	148.82/162.13	[20]
40a	SAXFOO	71.4	HF/3-21G	Liquid	161.07/170.88	[21]
40b	SAXFOO02	66.3	HF/3-21G	Liquid	164.03/173.07	[22]
41	None[3]	79.4	HF/3-21G	Liquid	164.72/174.13	[21]
42	NAFCUV	50.9	HF/3-21G	Liquid	138.97/149.11	[23]
43a	NAFDAC	50.7	HF/3-21G	Liquid	137.13/148.22	[23]
43b	NAFDAC01	-	-	Liquid	-	[23]
44	FACPAA01	-	-	Liquid	138.60/151.00	[23]
45	NAFDOQ	48.8	HF/3-21G	Liquid	145.37/154.36	[23]
46	NAFDUW	-	-	Liquid	143.32/154.06	[23]
47	FACQAB01	-	-	Liquid	146.16/156.65	[23]
48	NAFFEI	46.2	HF/3-21G	Liquid	156.98/163.23	[23]
49	NAFFIM	-	-	Liquid	154.07/162.64	[23]
50	FACQEF01	60.9	HF/3-21G	Liquid	155.25/162.35	[23]
51	MCDENZ03	45.9	HF/3-21G	228	139.23/149.29	[24]
52	YOQWUY	58.9	HF/3-21G	Liquid	134.79/148.45	[25]
53	RUBSUD	58.0	HF/3-21G	Liquid	144.15/154.48	[26]
54	YOQWOS	60.7	HF/3-21G	Liquid	164.56/166.49	[25]
55	INOMET01	71.6	HF/3-21G	Liquid	167.84/169.20	[25]
56	HALWUP	46.6	B3LYP/6-31G(d,p)	146	127.28/138.28	[27]

[1] If the temperature is not available, the state of matter at room temperature is shown instead.

[2] Melting point/phase transition temperature.

[3] This structure hasn't found in the CCDC database, and CIF-file was found on the article website.

24 **Table S2**. Intermolecular interactions in the compounds (shown in percent (%)).

No	CSD refcode	H···H	C(pi)···H	(pi)···pair	N···H	O···H	S···H	P···H	Hal···H	F···F	Hal···Hal	Other	Type of prevail intermol. interaction
1	NITYOE	86.6						13.4					H···H
2	NITYUK	92.4						7.6					H···H
3	NITZAR	96.4						3.6					H···H
4	NITZEV	95.4						4.6					H···H
6	BADZIS	15.8						0.6	62.6	21			Hal···H
7	YUMFAP								41.8	58.2			F···F
8	YUMFET	0.8				1.9			39.2	58.1			F···F
9	YUMFIX	3.6			0.9				50.4	45.1			Hal···H
11	OMCSIO	87.6				12.4							H···H
13	NEQZUH	100											H···H
14	EKEGIM									53.8	46.2		F···F
15	EKEGUY								32.2	67.8			F···F
16	UKOZUR									83.9	16.1		F···F
17	KEJZUX	5							69.8	20.2		5	Hal···H
19	HIYNUY	70.7				10.8	18.5						H···H
20	HIYPAG	66.1					33.9						H···H
21	LIQVIQ	36.8	6.8	5	35.5	15.2						0.7	H···H
22	LIQVOW	41				17.7			39		2.2	0.1	H···H
23	LIQVUC	73.1				26.9							H···H
24	LIQWAJ	31.5	9.4	3.7	31.2		23.1					1.1	H···H
25	LIQWEN	78.3					21.7						H···H
26	LIQWIR	67.3					32.7						H···H
28	FACFAQ	35.1	34.6	1.6					28.7				H···H
29	FACFOE	18.2	29.5	6					38.5	7.8			Hal···H
30	FACGEV	15.7	25.1	5.1					48.4	3.5		2.2	Hal···H

31	PVVAWA01	10	7	6.9		49.6	15.1		11.4	Hal···H
32	FACJAU	0.7	4.4	25.6		42.1	23.9		3.3	Hal···H
33	ZELDOJ01	3.2	5.7	20.4		38.8	27		4.9	Hal···H
34a	DCLBEN07	13.9	14.8	4.3		53.9		5.4	7.7	Hal···H
34b	DCLBEN06	16.5	12.9	4.4		49.8		7.8	8.6	Hal···H
34c	DCLBEN03	9	30.3	4.5		45		10.9	0.3	Hal···H
35	ABUMIT	18.1	10.5	5.9		51.4		5	9.1	Hal···H
36	ABUMOZ	17.9	11.8	4.9		50		6.9	8.5	Hal···H
37b	AXUBUR01	26.4	46.4	6.4		17.4	0.6		2.8	C(pi)···H
38b	AXUCEC01	32.7	31.9	0.4		19.7	2.3		13	H···H
39	NECMUD01	26.2	44.3	4.2		20	0.1		5.2	C(pi)···H
40a	SAXFOO	13	10.8	9.5	17	32.2	1.6	6.1	9.8	Hal···H
40b	SAXFOO02	12.5	5	3.9	19.1	35.2		8	16.3	Hal···H
41	None[3]	5.3	7	12.4	17.3	29.2	4.9	12	11.9	Hal···H
42	NAFCUV	18.6	25.3	9		38.3	0.3	8.3	0.2	Hal···H
43a	NAFDAC	22.2	16.7	11.4		40.1	2.6	3.8	3.2	Hal···H
45	NAFDOQ	21.9	9.8	15.9		46.5		1.2	4.7	Hal···H
48	NAFFEI	16.9	13.6	10.2		50		5.1	4.2	Hal···H
50	FACQEF01	23	13.6	11		41.5		7	3.9	Hal···H
51	MCDENZ03	35.2	32.2	0.6		25.8		6.2		H···H
52	YOQWUY								100	Other
53	RUBSUD								100	Other
54	YOQWOS								100	Other
55	INOMET01								100	Other
56	HALWUP			4.4			70.9		24.7	F···F

25

26 **Table S3**. Intermolecular interactions in halogentrinitromethanes ***52–55*** (shown in percents (%)).

No	CSD Refcode	O O	O N	O Hal	N Hal	Hal Hal
52	YOQWUY	69.5	7.6	22.7	0.2	0
53	RUBSUD	61.2	7.6	31.1	0.1	0
54	YOQWOS	59.9	6.6	33.5	0	0
55	INOMET01	56.9	7	36.1	0	0

27

3. References

1. Jayatilaka, D.; Grimwood, D.J. Tonto: A Fortran Based Object-Oriented System for Quantum Chemistry and Crystallography. In *Computational Science — ICCS 2003*; Sloot, P.M.A., Abramson, D., Bogdanov, A.V., Gorbachev, Y.E., Dongarra, J.J., Zomaya, A.Y., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2003; Vol. 2660, pp. 142–151 ISBN 978-3-540-40197-1.
2. Wang, H.; Xiao, H.; Liu, N.; Zhang, B.; Shi, Q. Three New Compounds Derived from Nitrofurantoin: X-Ray Structures and Hirshfeld Surface Analyses. *Open J. Inorg. Chem.* **2015**, *5*, 63–73.
3. Bruckmann, J.; Krüger, C. Chelating organophosphines: The use of comparative structural investigations to determine ligand properties. *J. Organomet. Chem.* **1997**, *536–537*, 465–472.
4. Waerder, B.; Pieper, M.; Körte, L.A.; Kinder, T.A.; Mix, A.; Neumann, B.; Stammler, H.-G.; Mitzel, N.W. A Neutral Silicon/Phosphorus Frustrated Lewis Pair. *Angew. Chem. Int. Ed.* **2015**, *54*, 13416–13419.
5. Waerder, B.; Steinhauer, S.; Bader, J.; Neumann, B.; Stammler, H.-G.; Vishnevskiy, Y.V.; Hoge, B.; Mitzel, N.W. Pentafluoroethyl-substituted α-silanes: model compounds for new insights. *Dalton Trans.* **2015**, *44*, 13347–13358.
6. Steinfink, H.; Post, B.; Fankuchen, I. The crystal structure of octamethyl cyclotetrasiloxane. *Acta Crystallogr.* **1955**, *8*, 420–424.
7. Arzumanyan, A.V.; Goncharova, I.K.; Novikov, R.A.; Milenin, S.A.; Boldyrev, K.L.; Solyev, P.N.; Tkachev, Y.V.; Volodin, A.D.; Smol'yakov, A.F.; Korlyukov, A.A.; et al. Aerobic Co or Cu/NHPI-catalyzed oxidation of hydride siloxanes: synthesis of siloxanols. *Green Chem.* **2018**, *20*, 1467–1471.
8. Haas, M.; Christopoulos, V.; Radebner, J.; Holthausen, M.; Lainer, T.; Schuh, L.; Fitzek, H.; Kothleitner, G.; Torvisco, A.; Fischer, R.; et al. Branched Hydrosilane Oligomers as Ideal Precursors for Liquid-Based Silicon-Film Deposition. *Angew. Chem. Int. Ed.* **2017**, *56*, 14071–14074.
9. Pelzer, S.; Neumann, B.; Stammler, H.-G.; Ignat'ev, N.; Hoge, B. Synthesis of Bis(pentafluoroethyl)germanes. *Chem. – Eur. J.* **2016**, *22*, 4758–4763.
10. Pelzer, S.; Neumann, B.; Stammler, H.-G.; Ignat'ev, N.; Hoge, B. Synthesis of Tris(pentafluoroethyl)germanes. *Chem. - Eur. J.* **2016**, *22*, 3327–3332.
11. Pelzer, S.; Neumann, B.; Stammler, H.-G.; Ignat'ev, N.; Hoge, B. The Bis(pentafluoroethyl)germylene Trimethylphosphane Adduct $(C_2F_5)_2Ge{\cdot}PMe_3$: Characterization, Ligand Properties, and Reactivity. *Angew. Chem. Int. Ed.* **2016**, *55*, 6088–6092.
12. Solyntjes, S.; Neumann, B.; Stammler, H.-G.; Ignat'ev, N.; Hoge, B. Difluorotriorganylphosphoranes for the Synthesis of Fluorophosphonium and Bismuthonium Salts. *Eur. J. Inorg. Chem.* **2016**, *2016*, 3999–4010.
13. Yokoyama, Y.; Ohashi, Y. Crystal and Molecular Structures of RCH2CH2SCH3 (R = OCH3, SCH3). *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1565–1571.
14. Yokoyama, Y.; Ohashi, Y. Crystal and Molecular Structures of Methoxy and Methylthio Compounds. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2183–2191.
15. Boese, R.; Cutin, E.H.; Mews, R.; Robles, N.L.; Della Védova, C.O. ((Fluoroformyl)imido)sulfuryl Difluoride, FC(O)NS(O)F2: Structural, Conformational, and Configurational Properties in the Gaseous and Condensed Phases. *Inorg. Chem.* **2005**, *44*, 9660–9666.
16. Thalladi, V.R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G.R. C−H···F Interactions in the Crystal Structures of Some Fluorobenzenes. *J. Am. Chem. Soc.* **1998**, *120*, 8702–8710.
17. Wheeler, G.L.; Colson, S.D. Intermolecular interactions in polymorphic *p* -dichlorobenzene crystals: The α, β, and γ phases at 100 °K. *J. Chem. Phys.* **1976**, *65*, 1227–1235.

18. Wheeler, G.L.; Colson, S.D. γ-Phase ıt p-dichlorobenzene at 100 K. *Acta Crystallogr. Sect. B* **1975**, *31*, 911–913.
19. Boese, R.; Kirchner, M.T.; Dunitz, J.D.; Filippini, G.; Gavezzotti, A. Solid-State Behaviour of the Dichlorobenzenes: Actual, Semi-Virtual and Virtual Crystallography. *Helv. Chim. Acta* **2001**, *84*, 1561–1577.
20. Dikundwar, A.G.; Sathishkumar, R.; Guru Row, T.N.; Desiraju, G.R. Structural Variability in the Monofluoroethynylbenzenes Mediated through Interactions Involving "Organic" Fluorine. *Cryst. Growth Des.* **2011**, *11*, 3954–3963.
21. Dikundwar, A.G.; Guru Row, T.N. Evidence for the "Amphoteric" Nature of Fluorine in Halogen Bonds: An Instance of Cl···F Contact. *Cryst. Growth Des.* **2012**, *12*, 1713–1716.
22. Dikundwar, A.G.; Guru Row, T.N. Tracing a Crystallization Pathway of an RT Liquid, 4-Fluorobenzoyl Chloride: Metastable Polytypic Form as an Intermediate Phase. *Cryst. Growth Des.* **2014**, *14*, 4230–4235.
23. Dikundwar, A.G.; Sathishkumar, R.; Guru, R.T.N. Fluorine prefers hydrogen bonds over halogen bonds! Insights from crystal structures of some halofluorobenzenes. *Z. Für Krist. - Cryst. Mater.* **2014**, *229*, 609–624.
24. Nath, N.K.; Naumov, P. In situ crystallization and crystal structure determination of chlorobenzene. *Maced. J. Chem. Chem. Eng.* **2015**, *34*, 63–66.
25. Klapötke, T.M.; Krumm, B.; Moll, R.; Rest, S.F.; Vishnevskiy, Y.V.; Reuter, C.; Stammler, H.-G.; Mitzel, N.W. Halogenotrinitromethanes: A Combined Study in the Crystalline and Gaseous Phase and Using Quantum Chemical Methods. *Chem. – Eur. J.* **2014**, *20*, 12962–12973.
26. Göbel, M.; Tchitchanov, B.H.; Murray, J.S.; Politzer, P.; Klapötke, T.M. Chlorotrinitromethane and its exceptionally short carbon–chlorine bond. *Nat. Chem.* **2009**, *1*, 229–235.
27. Berrueta Martínez, Y.; Reuter, C.G.; Vishnevskiy, Y.V.; Bava, Y.B.; Picone, A.L.; Romano, R.M.; Stammler, H.-G.; Neumann, B.; Mitzel, N.W.; Della Védova, C.O. Structural Analysis of Perfluoropropanoyl Fluoride in the Gas, Liquid, and Solid Phases. *J. Phys. Chem. A* **2016**, *120*, 2420–2430.