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Novel highly energetic pyrazoles: *N*-fluorodinitromethyl and *N*-[(difluoroamino)dinitromethyl] derivatives

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CONTENT

Experimental Section

Caution! All prepared compounds are highly energetic materials and sensitive to various stimuli. Although none of the compounds described herein has exploded or detonated in the course of this research, safety precautions, such as face shields, a leather apron, gloves, and hearing protection should be employed. These compounds should only be prepared by an experienced chemist and should be handled with great care.

General: All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in KBr pellets on a Perkin–Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311 A instrument. The ^{1}H, ^{13}C, ^{14}N, and ^{19}F NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, 21.68, and 282.40 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard without correction nitromethane (^{14}N) and $CFCl_3$ (^{19}F). Analytical TLC was performed using commercially pre-coated silica gel plates (Silufol UV_{254}), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected. The decomposition points were recorded on a thermogravimetric analyzer (TGA) at a scan rate of 5°Cmin^{-1}. Elemental analyses were obtained by using a CHNS/O Analyzer 2400 (Perkin–Elmer instruments Series II).

X-ray crystallography.

Single crystals of compounds **2** and **3** were grown from $CHCl_3$. X-ray experiments were carried out using SMART APEX2 CCD (λ(Mo-Kα)=0.71073 Å, graphite monochromator, *ω*-scans). Collected data were analized by the SAINT and SADABS programs incorporated into APEX2 program package.[25] All structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The positions of hydrogen atoms were found in the difference Furiuer maps and refined isotropically. The refinement was carried out with the SHELXTL program.[26]

In the case of compound **3**, we obtained single crystals of relatively low quality. Compound **3** crystallizes in the form of disordered $CHCl_3$ solvate, and is characterized by extremely weak reflection ability. Due to significant disorder, chloroform solvent was eliminated from the refinement procedure by use of SQUIZZE option included in the SHELXTL program package. Due to that, detailed analisys of all intermolecular interactions that stabilize the crystal packing of compound **3** cannot be carried out. However, we have estimated all molecule interactions of all symmetrically independent molecules with their closest environment which are believed to provide predominant contribution into stabilization of the crystal structure.

Crystal packing analysis of compounds 2 and 3 in comparison with compound 4

General view of compounds **2**, **3** and **4**[15] is depicted in Figure 1S. Selected torsion angles are given in Table 1S.

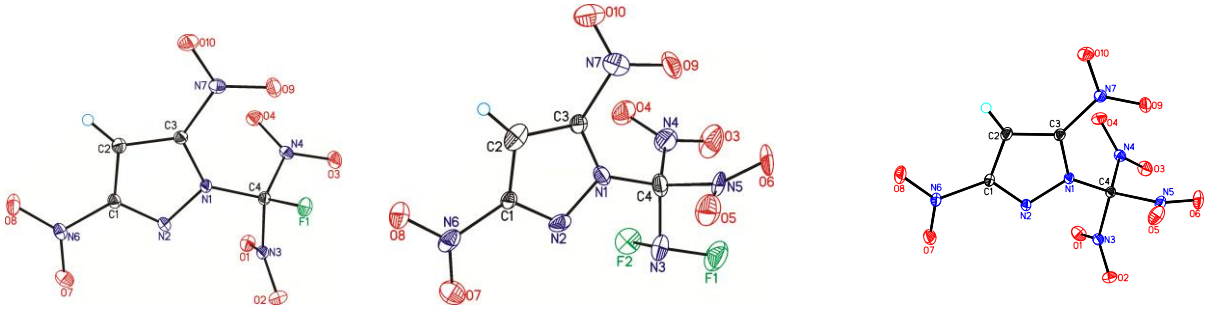

Figure 1S General view of compounds **2** (left) and **3** (middle) studied in the present work and compound **4**[15] (right) showing atomic numbering.

Table 1S Selected torsion angles (deg.) for compounds **2**, **3**, and **4**.[15]

	2	**3**, mol. A	**3**, mol.A'	**3**, mol.A'	**4**, mol. A	**4**, mol.A'
O7-N6-C1-N2	1.4(3)	0.4(9)	2.5(10)	1.2(9)	-2.35(4)	1.64(4)
O8-N6-C1-N2	-175.3(3)	-179.3(6)	-177.8(6)	-176.3(6)	177.22(3)	-178.94(3)
O9-N7-C3-C2	178.2(2)	176.2(7)	-175.5(7)	177.2(7)	176.56(3)	173.21(3)
O10-N7-C3-C2	-2.1(2)	-2.7(11)	2.6(11)	-2.9(11)	-3.26(4)	-6.26(5)
N2-N1-C4-N3	1.9(2)	-3.8(8)	2.8(9)	-2.4(8)	-9.34(3)	-6.21(3)
N2-N1-C4-N4	117.3(2)	118.5(6)	116.1(7)	112.5(6)	108.65(3)	111.58(3)
N2-N1-C4-N5	-118.4(2)[a]	-116.1(6)	-119.2(7)	-119.1(6)	-126.11(3)	-123.99(3)

[a] angle N2-N1-C4-F1

Because compounds **2** and **4** have very close densities (2.012 and 2.020 g/cm^3 for **2** and **4**, respectively at 100K, being different by NO_2/F substituent) we have compared their crystal structures based on estimation of pair intermolecular energies within M052X/6-311G(df,pd) level of theory by the GAUSSIAN program.[24] Results on close intermolecular contacts and energies of interaction of the central molecule with its closest environment are presented in Table 2S in comparison with data for compound **4** (Tables 3S,4S). It appears that the strongest intermolecular interactions are formed between molecules related by a translation, and provided mostly by means of nitro…nitro $\pi\ldots\pi$ interactions (entries 1 and 2 in Tables 2S, 3S and 4S). Both relative orientation of molecules in the pair and system of close contacts are quite similar. At the same time, relative orientations of molecules in other pairs are different. For instance, the second strongest pair interaction in **4** is formed in centrosymmetric C-H…O bonded dimer while in **2**, second strongest interaction is formed by O…π and slightly shortened O…F contacts. In part, such a difference can be related to a participation of the fluorine atom in shortened intermolecular contacts. However the energies of pair interactions are very similar.

Because compound **3** crystallizes in the form of solvate with chloroform, it is impossible to study all the details of its crystal packing. Nevertheless some useful information can be obtained from analysis of pair interaction energies (Tables 5S-7S). Similar to fluorodinitromethyl compound **2** and trinitromethyl compound **4**, all three independent molecules form the strongest interaction with their neighbours related by translation along axis *a*. Energies of such pairs are nearly the same and are close to those calculated for compounds **2** and **4**. However the system of close contacts demonstrates more pronounced differences. Again, as in the case of compound **2**, no double H-bonded dimers are observed in crystal structure of **3**, and distribution of interaction energy over molecular pairs is similar to that of **2** and **4**.

Table 2S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level in the crystal structure of compound **2**.

Entry	Shortened Contact		Symmetry Code	Distance	Energy
1	O2	O3	-1+x,y,z	2.969	-5.6
	O2	O4	-1+x,y,z	3.070	
	O2	O9	-1+x,y,z	2.921	
	O7	O10	-1+x,y,z	2.983	
	O7	C3	-1+x,y,z	3.236	
	N6	O10	-1+x,y,z	3.166	
	C1	O10	-1+x,y,z	3.317	
2	O3	O2	1+x,y,z	2.969	-5.6
	O4	O2	1+x,y,z	3.070	
	O9	O2	1+x,y,z	2.921	
	O10	O7	1+x,y,z	2.983	
	C3	O7	1+x,y,z	3.236	
	O10	N6	1+x,y,z	3.166	
	O10	C1	1+x,y,z	3.317	
3	F1	O6	1-x,-1/2+y,1-z	2.941	-4.4
	N1	O6	1-x,-1/2+y,1-z	3.028	
	C3	O6	1-x,-1/2+y,1-z	3.092	
4	O6	F1	1-x,1/2+y,1-z	2.941	-4.4
	O6	N1	1-x,1/2+y,1-z	3.028	
	O6	C3	1-x,1/2+y,1-z	3.092	
5	O1	O8	-1+x,y,-1+z	3.004	-3.0
	O3	O8	-1+x,y,-1+z	3.010	
	N3	O8	-1+x,y,-1+z	3.133	
	O1	H2	-1+x,y,-1+z	2.497	
6	O8	O1	1+x,y,1+z	3.004	-3.0
	O8	O3	1+x,y,1+z	3.010	
	O8	N3	1+x,y,1+z	3.133	
	H2	O1	1+x,y,1+z	2.497	
7	O3	C2	x,y,-1+z	3.080	-2.6
	O4	O6	x,y,-1+z	3.082	
8	O6	O4	x,y,1+z	3.082	-2.6
	C2	O3	x,y,1+z	3.080	
9	F1	O1	1-x,-1/2+y,-z	2.799	-2.3
	F1	O4	1-x,-1/2+y,-z	2.862	
	O3	O5	1-x,-1/2+y,-z	3.048	
	O3	N5	1-x,-1/2+y,-z	2.959	
	O7	O1	1-x,-1/2+y,-z	3.006	
10	O1	F1	1-x,1/2+y,-z	2.799	-2.3
	O1	O7	1-x,1/2+y,-z	3.006	
	O4	F1	1-x,1/2+y,-z	2.862	
	O5	O3	1-x,1/2+y,-z	3.048	
	N5	O3	1-x,1/2+y,-z	2.959	
11	O2	O5	-x,-1/2+y,-z	2.927	-0.3
12	O5	O2	-x,1/2+y,-z	2.927	-0.3

Table 3S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level for molecule A in the crystal structure of compound **4**. (From Ref 15).

Entry	Shortened contact		Symmetry code	Distance	Type of pair	Energy
1	O2	O4	-1+x,y,z	3.059	A…A	-6.3
	O2	O9		2.939		
	O7	O10		2.990		
	O7	C3		3.180		
	N6	O10		2.873		
	C1	O10		3.043		
2	O4	O2	1+x,y,z	3.059	A…A	-6.3
	O9	O2		2.939		
	O10	O7		2.990		
	O10	N6		2.873		
	O10	C1		3.043		
	C3	O7		3.180		
3	O8	H2	-x,1-y,-z	2.443	A…A	-4.1
	H2	O8		2.443		
4	O4	O4	1-x,-y,-z	2.818	A…A	-2.3
	O4	N4		3.098		
	N4	O4		3.098		
5	O1	O1	-x,-y,-z	3.012	A…A	-2.2
	O1	O7		3.077		
	O1	N2		3.085		
	O3	O7		3.092		
	O7	O1		3.077		
	O7	O3		3.092		
	N2	O1		3.085		
6	O10	O5'	x,y,z	2.790	A…A'	-2.5
	O10	C3'	x,y,z	3.017		
7	O6	O8'	1-x,-y,1-z	3.104	A…A'	-2.4
	O6	N6'		3.121		
	O6	C1'		3.100		
	O9	O8'		3.011		
8	O8	O6'	1-x,1-y,-z	3.048	A…A'	-2.3
	O8	O9'		3.031		
	N6	O6'		3.033		
	C1	O6'		3.083		
9	O5	O10'	-1+x,y,z	2.818	A…A'	-2.3
	C3	O10'		3.032		
10	O3	O2'	x,-1+y,z	3.016	A…A'	-1.7
	O3	O6'		2.886		
	O6	O1'		2.961		
11	O2	O7'	-x,-y,1-z	3.114	A…A'	-1.6
12	O7	O2'	-x,1-y,-z	3.126	A…A'	-1.3
13	O2	O3'	-1+x,-1+y,z	2.857	A…A'	-0.2

Table 4S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level for molecule A' in the crystal structure of compound **4**. (From Ref 15).

Entry	Shortened contact		Symmetry code	Distance	Type of pair	Energy
1'	O2' O2' O2' O7' O7' N6' C1'	O3' O4' O9' O10' C3' O10' O10'	-1+x,y,z	3.119 2.962 3.133 2.946 3.131 2.891 3.066	A'…A'	-6.3
2'	O3' O4' O9' O10' O10' O10' C3'	O2' O2' O2' O7' N6' C1' O7'	1+x,y,z	3.119 2.962 3.133 2.946 2.891 3.066 3.131	A'…A'	-6.3
3'	O8' H2'	H2' O8'	1-x,-y,1-z	2.476 2.476	A'…A'	-4.1
4'	O1' O3' O4' O7'	O4' O7' O1' O3'	1-x,1-y,1-z	2.914 2.978 2.914 2.978	A'…A'	-3.8
5'	O4'	O4'	2-x,1-y,1-z	3.006	A'…A'	-0.4
6'	O5' C3'	O10 O10	x,y,z	2.790 3.017	A'…A	-2.5
7'	O8' O8' N6' C1'	O6 O9 O6 O6	1-x,-y,1-z	3.104 3.011 3.121 3.100	A'…A	-2.4
8'	O6' O6' O6' O9'	O8 N6 C1 O8	1-x,1-y,-z	3.048 3.033 3.083 3.031	A'…A	-2.3
9'	O10' O10'	O5 C3	1+x,y,z	2.818 3.032	A'…A	-2.3
10'	O1' O2' O6'	O6 O3 O3	x,1+y,z	2.961 3.016 2.886	A'…A	-1.7
11'	O7'	O2	-x,-y,1-z	3.114	A'…A	-1.6
12'	O2'	O7	-x,1-y,-z	3.126	A'…A	-1.3
13'	O3'	O2	1+x,1+y,z	2.857	A'…A	-0.2

Table 5S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level for molecule A in the crystal structure of compound **3**.

Entry	Shortened contact		Symmetry code	Distance	Type of pair	Energy
1	O7	C2	-1+x,y,z	3.240	A…A	-5.5
	N2	O10		3.011		
	N6	O10		3.155		
	C1	O10		3.068		
2	O10	N2	1+x,y,z	3.011	A…A	-5.5
	O10	N6		3.155		
	O10	C1		3.068		
	C2	O7		3.240		
3	O5	O5	1-x,2-y,-z	3.107	A…A	-3.9
	O5	C2		3.308		
	O5	C3		3.168		
	C2	O5		3.308		
	C3	O5		3.168		
4	O9	O10	2-x,2-y,-z	2.889	A…A	-2.0
	O10	O9		2.889		
5	O10	O8'	1-x,2-y,-z	2.948	A…A'	-3.1
	H2	O8'		2.506		
6	F1	O5'	1+x,y,z	2.836	A…A'	-2.8
	O6	N6'		3.111		
	O6	C1'		2.906		
	O6	C2'		3.163		
	O3	F2'		3.014		
7	F1	O7'	x,y,z	3.048	A…A'	-1.0
	O6	O7'		3.045		
8	O8	O8'	-x,2-y,-z	2.929	A…A'	-0.4
9	O8	H2"	-1+x,y,-1+z	2.460	A…A"	-3.2
10	F2	O6"	1-x,1-y,-z	2.999	A…A"	-2.9
	O4	F2"		2.911		
	N6	O3"		3.093		
	C1	O3"		2.850		
	C2	O3"		3.094		
11	O7	O3"	-x,1-y,-z	2.971	A…A"	-0.9
12	O8	O8"	x,y,-1+z	2.907	A…A"	-0.8

Table 6S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level for molecule A' in the crystal structure of compound **3**.

Entry	Shortened contact		Symmetry code	Distance	Type of pair	Energy
1	O7'	O10'	1+x,y,z	3.102	A'…A'	-5.4
	O7'	C2'		3.253		
	N2'	O10'		3.029		
	N6'	O10'		3.068		
	C1'	O10'		3.033		
2	O10'	O7'	-1+x,y,z	3.102	A'…A'	-5.4
	O10'	N2'		3.029		
	O10'	N6'		3.068		
	O10'	C1'		3.033		
	C2'	O7'		3.253		
3	O4'	O4'	-x,2-y,1-z	3.065	A'…A'	-3.7
	O4'	C2'		3.280		
	O4'	C3'		3.190		
	C2'	O4'		3.280		
	C3'	O4'		3.190		
4	O9'	O10'	-1-x,2-y,1-z	2.881	A'…A'	-2.4
	O10'	O9'		2.881		
5	O8'	O10	1-x,2-y,-z	2.948	A'…A	-3.1
	O8'	H2		2.506		
6	F2'	O3	-1+x,y,z	3.014	A'…A	-2.8
	O5'	F1		2.836		
	N6'	O6		3.111		
	C1'	O6		2.906		
	C2'	O6		3.163		
7	O7'	F1	x,y,z	3.048	A'…A	-1.0
	O7'	O6		3.045		
8	O8'	O8	-x,2-y,-z	2.929	A'…A	-0.4
9	O10'	O8"	-x,2-y,1-z	3.025	A'…A"	-3.4
	H2'	O8"	-	2.474		
10	F1'	O5"	-1+x,y,z	2.834	A'…A"	-2.9
	O3'	N6"		3.105		
	O3'	C1"		2.928		
	O3'	C2"		3.164		
	O6'	F1"		3.013		
11	F1'	O7"	x,y,z	3.048	A'…A"	-1.0
	O3'	O7"		3.023		
12	O8'	O8"	1-x,2-y,1-z	2.886	A'…A"	-0.1

Table 7S Close intermolecular contacts (Å) and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level for molecule A" in the crystal structure of compound **3**.

Entry	Shortened contact		Symmetry code	Distance	Type of pair	Energy
1	O7"	C2"	-1+x,y,z	3.275	A"…A"	-5.3
	N2"	O10"		2.998		
	N3"	O5"		3.083		
	N3"	O9"		3.108		
	C1"	O10"		3.100		
2	O5"	N3"	1+x,y,z	3.083	A"…A"	-5.3
	O9"	N3"		3.108		
	O10"	N2"		2.998		
	O10"	C1"		3.100		
	C2"	O7"		3.275		
3	O4"	C2"	1-x,1-y,1-z	3.275	A"…A"	-3.0
	O4"	C3"		3.320		
	C2"	O4"		3.275		
4	O9"	O10"	2-x,1-y,1-z	2.896	A"…A"	-2.3
	O10"	O9"		2.896		
5	H2"	O8	1+x,y,1+z	2.460	A"…A	-3.2
6	F2"	O4	1-x,1-y,-z	2.911	A"…A	-2.9
	O3"	N6		3.093		
	O3"	C1		2.850		
	O3"	C2		3.094		
	O6"	F2		2.999		
7	O3"	O7	-x,1-y,-z	2.971	A"…A	-0.9
8	O8"	O8	x,y,1+z	2.907	A"…A	-0.8
9	O8"	O10'	-x,2-y,1-z	3.025	A"…A'	-3.4
	O8"	H2'	-x,2-y,1-z	2.474		
10	F1"	O6'	1+x,y,z	3.013	A"…A'	-2.9
	O5"	F1'		2.834		
	N6"	O3'		3.105		
	C1"	O3'		2.928		
	C2"	O3'		3.164		
11	O7"	F1'	x,y,z	3.048	A"…A'	-1.0
	O7"	O3'		3.023		
12	O8"	O8'	1-x,2-y,1-z	2.886	A"…A'	-0.1

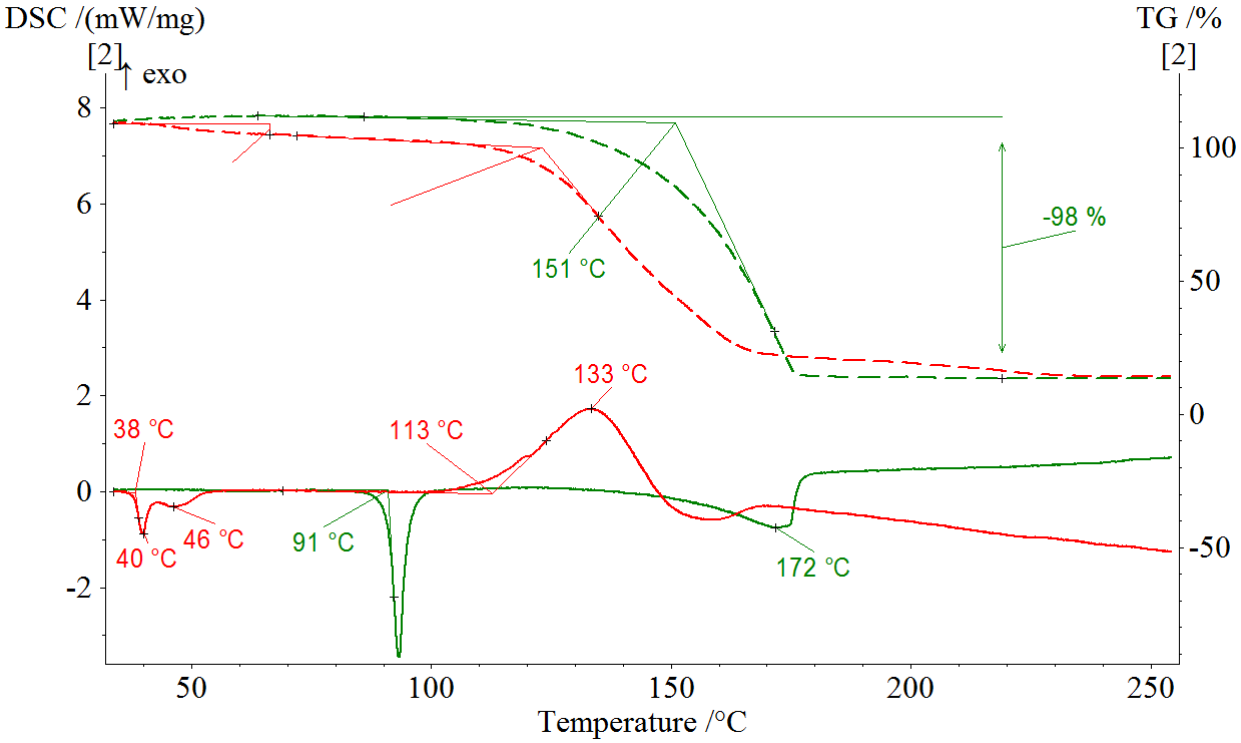

Figure 2S TG−DSC thermogram of compound **2** (green) and **3** (red) at a heating rate of 5°C min^{-1}.

References

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, *Revision E.01*, Gaussian, Inc., Wallingford, 2004.

[25]. *APEX2 and SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.

[26] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.