J Mol Model (2014) 20:2343
DOI 10.1007/s00894-014-2343-0

ORIGINAL PAPER

Theoretical study on the structure and stability of [1,2,5] oxadiazolo [3,4-e] [1,2,3,4]-tetrazine-4,6-Di-N-dioxide (FTDO)

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Received: 11 April 2014 / Accepted: 8 June 2014 / Published online: 1 July 2014

Abstract Although many 1,2,3,4-tetrazine-1,3-dioxide derivates have been synthesized, [1,2,5] oxadiazolo [3,4-e] [1,2,3,4]-tetrazine-4,6-di-N-dioxide (FTDO) is the only one with high enthalpy of formation and high detonation velocity. Whereas, its stability has not been studied. In the present work, the structure of FTDO was investigated using density functional theory (DFT) method, and its stability was calculated by potential energy surface scanning and structure interconvert thermodynamics under different temperatures. The spontaneous isomerization of FTDO and its effect on the stability of FTDO were investigated. The dissociation of FTDO to N_2, N_2O and furoxan fragments was studied, and the possibility of synthetic route from FTDO to TTTO was discussed.

Keywords FTDO · Potential energy surface scanning · Stability · Structure · TTTO

Introduction

Since the first 1,2,3,4-tetrazine-1,3-dioxide derivatives were introduced in 1990 [1], many of them have been reported theoretically and experimentally [2–10], and the studies before 2004 have been summarized by Churakov [11]. However, only [1,2,5] oxadiazolo [3,4-e] [1,2,3,4]-tetrazine-4,6-di-N-dioxide (FTDO) could be called high energetic density compounds (HEDCs) among the synthesized compounds, though several other ones with higher predicted properties have been designed, such as TTTO, DTTO, etc., and their structures and predicted properties are listed in Table 1 [10, 12]. From then on N-oxides have also been arousing great interest because of the high detonation performance [14–16].

The first sample of FTDO was obtained by Aleksandr et al. [17] in 1995. Rezchikova et al. [18, 19] reported its IR and Raman spectra at the same year. Li et al. [20] designed a new synthetic route of FTDO with yield of 31 % in 2012, and its density and enthalpy of formation were measured in 2004 and 2011, with the value of 1.85 g cm^{-3} [5] and 160.9 kcal mol^{-1} [9] respectively. Security and combustion properties on this compound are studied. Teselkin et al. [8] reported the mechanical sensibility of FTDO in 2009. They found its mechanical sensibility was close to that of lead azide. In 2009 and 2011, Kalmykov et al. [21, 22] studied the combustibility of co-crystal of FTDO with 2,4-dinitro-2,4-diazapentane. They found it could combust stably at normal pressure, but unstably under several decades atmosphere pressure; and the higher the FTDO's content is, the lower the critical pressure for stable combustion.

FTDO is not only a promising energetic molecule, but also an ideal intermediate for the synthesis of TTTO, one of the most desired high energetic density compounds. A procedure from FTDO to TTTO was proposed by Russian scientists about 10 years ago (see Scheme 1) [12]. However, there is no report on successful synthesis of TTTO up to now.

The stability of FTDO is essential for its applications in explosives or propellants. However, there are not systemic investigations on FTDO's stability until now. The present work investigated the structure of FTDO further using density functional theory (DFT) method, and made systemic calculations on

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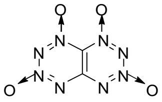
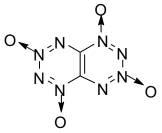
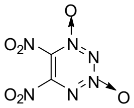
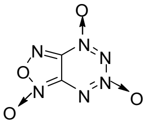
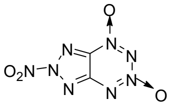
Table 1 Designed 1,2,3,4-tetrazine-1,3-dioxide high energy density compounds by Russian scientists

Compounds	Density (g/cm^3)[a]	Enthalpy of formation (kcal/mol)[a]	Detonation pressure (GPa)[a]	Detonation velocity (m/s)[a, b]	Detonation heat (kJ/kg)[a, b]
 DTTO	1.899[10] 2.419[12]	206[10] 179.5[12]	43.2[10] 131.4[12]	9710[10] 11405.3	8235.44[10] 7693.91
 TTTO	1.897[10] 2.484[12]	205[10] 175.7[12]	43.1[10] 131.8[12]	9700[10] 11607.6	8231.25[10] 7614.35
	2.072[12]	134.3[12]	50.6[12]	9739.5	6615.98
	2.191[12]	128.6[12]	61.8[12]	10514.9	7707.49
	2.179[12]	158.1[12]	61.96[12]	10389.7	7245.85

[a] the data come from references 10 and 12

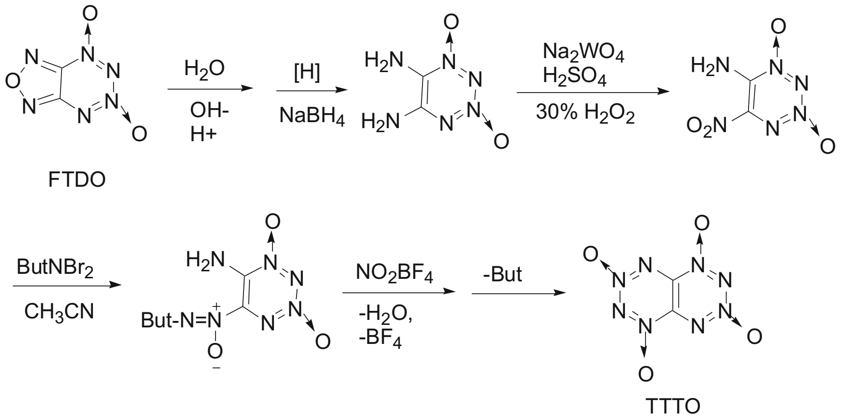
[b] the data calculated by Kamlet-Jacobs formula [13] based on the densities and enthalpy of formations from the reference 12

its stability by the method of potential energy surface scanning and structure interconverted thermodynamics under different temperatures. The synthesis feasibility of TTTO from FTDO was reconsidered.

Calculation details

DFT B3LYP method with cc-pvdz and 6-31G** basis set were carried out to investigate the structure of FTDO using Gaussian 09 program [23]. The geometries were fully optimized, and the frequency calculations were performed. The results indicated that these geometries correspond to be minima (no imaginary frequency) in the potential energy surfaces. FTDO's dissociation barriers in different channels were calculated by the potential energy surface scanning for its dissociation routes and stability. The enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) were calculated at different temperature (25-500 °C) to further confirm its stability.

Scheme 1



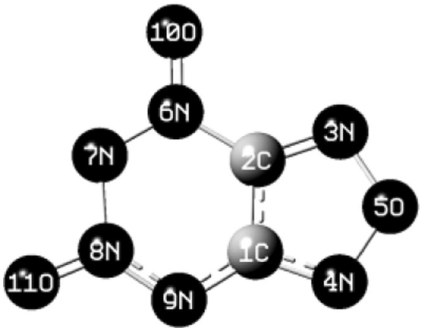


Fig. 1 Optimized geometric configuration of FTDO

Results and discussion

Structure

The optimized structure of FTDO with numbering atoms is presented in Fig. 1, and the bond lengths, bond angles, and dihedral angles are listed in Table 2.

It could be seen that the values of geometric parameters optimized at cc-pvdz and 6-31G** basis sets were nearly consistent. All atoms of FTDO molecule are approximatively in one plane, and the lengths of the bonds are between a typical single bond and a typical double bond to come into being a π conjugate system, which makes it aromatic.

Stability

In our present work, the stability of FTDO was investigated according to its dissociation, and the dissociation process was calculated and analyzed by the means of potential energy surface scanning (see Fig. 2) and Gibbs free energy changes (see Table 3). The results indicate FTDO would isomerize spontaneously (channel b) at ambient condition, in which the O(10) atom transfers from the tetrazine ring to the furazan ring, and the stability decreases after the isomerization. The calculated dissociation energy of the isomer (channel f) is only 13.27 kcal mol^{-1} (cc-pvdz) or 14.08 kcal mol^{-1} (6-31G**), with 12.95 kcal mol^{-1} (cc-pvdz) or 12.38 kcal mol^{-1} (6-31G**) lower than the dissociation energy of FTDO (channel c), which is 26.22 kcal mol^{-1} (cc-pvdz) or 26.46 kcal mol^{-1} (6-31G**). That means the isomer is much easier to dissociate than FTDO. According to the calculation results, the dissociation would begin at the N(7)-N(8) bond in tetrazine ring (channel f), and then be followed by the rupture of N(3)-O(5) bond in furazan ring (channel k). The dissociation energy

Table 2 Optimized geometric parameters of FTDO

Bond length/Å			Bond angle/(°)			Dihedral angle/(°)		
	cc-pvdz	6–31G**		cc-pvdz	6–31G**		cc-pvdz	6–31G**
R(1,2)	1.412	1.412	A(2,1,4)	107.715	107.879	D(4,1,2,3)	0.005	0.006
R(1,4)	1.323	1.322	A(2,1,9)	124.995	124.816	D(4,1,2,6)	−179.995	−179.985
R(1,9)	1.358	1.357	A(4,1,9)	127.290	127.305	D(9,1,2,3)	−179.997	−179.998
R(2,3)	1.308	1.307	A(1,2,3)	111.512	111.656	D(9,1,2,6)	0.003	0.012
R(2,6)	1.410	1.407	A(1,2,6)	119.148	119.101	D(2,1,4,5)	−0.010	−0.017
R(3,5)	1.356	1.360	A(3,2,6)	129.340	129.243	D(9,1,4,5)	179.992	179.986
R(4,5)	1.380	1.384	A(2,3,5)	102.919	102.812	D(2,1,9,8)	0.003	−0.008
R(6,7)	1.320	1.320	A(1,4,5)	103.874	103.775	D(4,1,9,8)	−179.999	−179.989
R(6,10)	1.223	1.229	A(3,5,4)	113.980	113.879	D(1,2,3,5)	0.003	0.009
R(7,8)	1.459	1.455	A(2,6,7)	118.145	118.420	D(6,2,3,5)	−179.997	−179.998
R(8,9)	1.314	1.314	A(2,6,10)	121.461	121.353	D(1,2,6,7)	−0.012	−0.005
R(8,11)	1.210	1.216	A(7,6,10)	120.395	120.227	D(1,2,6,10)	−179.979	−179.983
			A(6,7,8)	117.795	117.568	D(3,2,6,7)	179.988	179.993
			A(7,8,9)	127.691	127.713	D(3,2,6,10)	0.021	0.029
			A(7,8,11)	111.104	111.155	D(2,3,5,4)	−0.010	−0.021
			A(9,8,11)	121.205	121.132	D(1,4,5,3)	0.012	0.025
			A(1,9,8)	112.225	112.381	D(2,6,7,8)	0.014	−0.005
						D(10,6,7,8)	179.981	179.973
						D(6,7,8,9)	−0.008	0.011
						D(6,7,8,11)	179.997	179.996
						D(7,8,9,1)	−0.001	−0.004
						D(11,8,9,1)	179.994	179.997

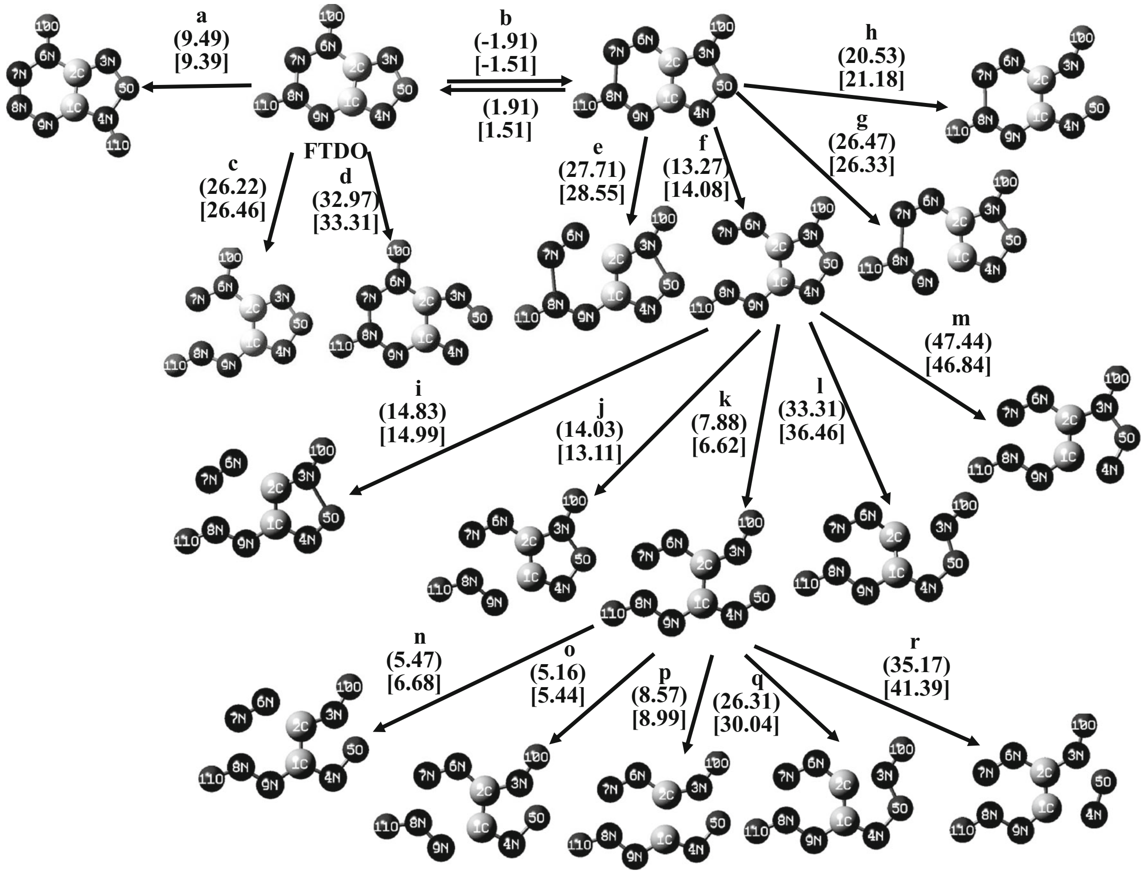


Fig. 2 Potential energy scanning results (the data in parentheses is calculated at B3LYP/cc-pvdz basis set, and that in square brackets is calculated at B3LYP/6-31G**, unit: kcal mol^{-1})

of this process is 7.88 kcal mol^{-1} (cc-pvdz) or 6.62 kcal mol^{-1} (6-31G**). Ultimately, the C(2)-N(6) bond and C(1)-N(9) bond would break at the same time to generate N_2, N_2O, and furoxan fragments (channels n and o). This result is consistent with the mass spectrum data of FTDO [20] and the result of some preliminary research works carried out by other groups [24–27].

The enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) for all channels were calculated in the range of 25–500 °C to investigate the stability further (see Table 3). It could be concluded from the results that the data of Gibbs free energy change at room temperature for each channel is very nearly the energy calculated by potential energy surface scanning. The temperature has little effect on each channel, and the most difference of ΔG is only about 1 kcal mol^{-1}. The conversion from FTDO to isomer 1 (channel b) is a spontaneous process, and the increasing temperature would make the process easier.

It could be seen from the above results that 1,2,3,4-tetrazine ring in FTDO would break first during its dissociation, which means the furazan ring in FTDO is more stable than the 1,2,3,4-tetrazine ring. As a result, the synthetic route from FTDO to TTTO designed by Russian scientist might be impracticable. The low energy barrier for the opening of 1,2,3,4-tetrazine in FTDO indicates its poor stability, and its application would be restricted under the specified conditions.

Conclusions

In the present work, the structure of FTDO was investigated using DFT method with cc-pvdz and 6-31G** basis sets. The results show that all atoms in FTDO are approximatively in one plane and the molecule is aromatic. The potential energy surface scanning and the thermodynamics calculation for FTDO were performed. The results indicated spontaneous conversion from FTDO to its isomer occurred and its stability was decreased, which would dissociate to N_2, N_2O, and furoxan fragments. So the stability of FTDO is poor, and its application would be restricted under specified conditions. The result also indicated the synthetic route from FTDO to TTTO might be infeasible because the furazan ring is more stable than the 1,2,3,4-tetrazine ring, and the tetrazine ring would open first during a reaction.

Table 3 Enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy change (ΔG) for each channel

Channel	T/°C	ΔH/(kcal mol^{-1})		ΔS/(cal mol^{-1}/K)		ΔG/(kcal mol^{-1})	
		cc-pvdz	6-31G**	cc-pvdz	6–31G**	cc-pvdz	6–31G**
a	25	8.67	8.61	0.82	0.67	8.43	8.41
	50	8.70	8.64	0.92	0.77	8.41	8.40
	100	8.76	8.70	1.08	0.92	8.36	8.35
	150	8.81	8.75	1.22	1.05	8.30	8.30
	200	8.86	8.79	1.33	1.15	8.23	8.25
	250	8.91	8.84	1.42	1.24	8.17	8.19
	300	8.95	8.87	1.49	1.30	8.09	8.13
	350	8.98	8.91	1.55	1.36	8.02	8.06
	400	9.01	8.94	1.60	1.41	7.94	7.99
	450	9.04	8.96	1.64	1.44	7.86	7.92
	500	9.07	8.99	1.67	1.48	7.77	7.85
b	25	−2.44	−2.02	2.14	2.11	−3.08	−2.65
	50	−2.39	−1.98	2.30	2.27	−3.13	−2.71
	100	−2.30	−1.89	2.56	2.51	−3.26	−2.83
	150	−2.23	−1.82	2.74	2.69	−3.39	−2.96
	200	−2.17	−1.76	2.87	2.82	−3.53	−3.10
	250	−2.12	−1.72	2.97	2.92	−3.68	−3.24
	300	−2.08	−1.68	3.04	2.98	−3.83	−3.39
	350	−2.05	−1.65	3.10	3.04	−3.98	−3.54
	400	−2.03	−1.62	3.13	3.07	−4.14	−3.69
	450	−2.01	−1.60	3.16	3.10	−4.29	−3.85
	500	−1.99	−1.59	3.19	3.12	−4.45	−4.00
c	25	24.85	25.69	1.29	7.39	24.47	23.49
	50	24.85	25.74	1.29	7.56	24.47	23.49
	100	24.84	25.83	1.26	7.82	24.46	23.50
	150	24.82	25.91	1.20	8.01	24.46	23.52
	200	24.78	25.97	1.12	8.15	24.45	23.54
	250	24.73	26.02	1.03	8.25	24.43	23.56
	300	24.68	26.06	0.93	8.33	24.4	23.58
	350	24.62	26.10	0.82	8.39	24.37	23.60
	400	24.55	26.13	0.72	8.44	24.33	23.62
	450	24.48	26.16	0.61	8.48	24.29	23.63
	500	24.40	26.18	0.51	8.51	24.25	23.65
d	25	31.64	32.01	2.04	0.97	31.04	31.72
	50	31.64	32.01	2.04	0.96	31.04	31.72
	100	31.63	32.00	2.00	0.92	31.03	31.72
	150	31.60	31.97	1.93	0.85	31.03	31.71
	200	31.56	31.93	1.85	0.75	31.01	31.70
	250	31.51	31.88	1.75	0.65	30.99	31.68
	300	31.45	31.82	1.64	0.55	30.97	31.65
	350	31.39	31.75	1.53	0.44	30.93	31.62
	400	31.32	31.68	1.42	0.33	30.90	31.58
	450	31.25	31.61	1.32	0.22	30.85	31.54
	500	31.17	31.53	1.21	0.12	30.81	31.49
e	25	25.65	26.56	4.13	3.78	24.42	25.43
	50	25.69	26.59	4.25	3.90	24.42	25.43
	100	25.75	26.64	4.42	4.04	24.43	25.44

Table 3 (continued)

Channel	T/°C	ΔH/(kcal mol^{-1})		ΔS/(cal mol^{-1}/K)		ΔG/(kcal mol^{-1})	
		cc-pvdz	6-31G**	cc-pvdz	6–31G**	cc-pvdz	6–31G**
	150	25.78	26.67	4.52	4.12	24.44	25.44
	200	25.80	26.68	4.55	4.14	24.44	25.45
	250	25.80	26.68	4.55	4.13	24.44	25.45
	300	25.78	26.66	4.52	4.10	24.43	25.44
	350	25.75	26.63	4.48	4.04	24.42	25.42
	400	25.72	26.59	4.42	3.98	24.40	25.4
	450	25.67	26.54	4.35	3.91	24.37	25.37
	500	25.62	26.48	4.28	3.84	24.34	25.34
f	25	12.6	12.81	5.68	0.54	10.91	12.65
	50	12.64	12.80	5.80	0.51	10.91	12.65
	100	12.71	12.77	6.00	0.43	10.92	12.64
	150	12.77	12.73	6.15	0.33	10.94	12.63
	200	12.82	12.69	6.26	0.23	10.95	12.62
	250	12.86	12.63	6.35	0.12	10.97	12.60
	300	12.90	12.57	6.42	0.00	10.99	12.57
	350	12.93	12.50	6.47	−0.11	11.00	12.53
	400	12.96	12.43	6.51	−0.22	11.02	12.50
	450	12.98	12.36	6.54	−0.33	11.03	12.45
	500	13.00	12.28	6.57	−0.43	11.04	12.41
g	25	25.36	25.25	4.20	3.94	24.10	24.07
	50	25.39	25.29	4.32	4.08	24.11	24.07
	100	25.47	25.36	4.53	4.28	24.12	24.08
	150	25.53	25.42	4.70	4.44	24.13	24.10
	200	25.59	25.48	4.84	4.58	24.15	24.12
	250	25.65	25.54	4.95	4.69	24.18	24.14
	300	25.70	25.59	5.04	4.78	24.20	24.16
	350	25.75	25.63	5.12	4.85	24.22	24.19
	400	25.79	25.67	5.18	4.91	24.24	24.21
	450	25.83	25.71	5.23	4.97	24.26	24.23
	500	25.86	25.74	5.28	5.01	24.29	24.25
h	25	19.96	20.63	8.32	9.02	17.48	17.94
	50	20.01	20.68	8.46	9.47	17.48	17.85
	100	20.09	20.76	8.71	9.72	17.50	17.87
	150	20.16	20.83	8.89	9.89	17.51	17.88
	200	20.22	20.89	9.01	10.01	17.53	17.90
	250	20.26	20.93	9.10	10.10	17.55	17.92
	300	20.30	20.97	9.17	10.17	17.57	17.94
	350	20.33	21.00	9.22	10.22	17.58	17.95
	400	20.35	21.02	9.25	10.25	17.59	17.96
	450	20.37	21.04	9.28	10.28	17.61	17.97
	500	20.39	21.05	9.30	10.30	17.62	17.98
i	25	13.34	14.22	−0.83	3.68	13.58	13.12
	50	13.35	14.27	−0.79	3.84	13.58	13.12
	100	13.35	14.36	−0.78	4.09	13.58	13.14
	150	13.34	14.43	−0.80	4.28	13.58	13.16
	200	13.32	14.50	−0.85	4.43	13.57	13.18
	250	13.28	14.55	−0.93	4.53	13.56	13.20

Table 3 (continued)

Channel	T/°C	*ΔH*/(kcal mol^{-1})		*ΔS*/(cal mol^{-1}/K)		*ΔG*/(kcal mol^{-1})	
		cc-pvdz	6-31G**	cc-pvdz	6–31G**	cc-pvdz	6–31G**
	300	13.24	14.59	−1.01	4.62	13.54	13.22
	350	13.18	14.63	−1.10	4.68	13.51	13.24
	400	13.12	14.67	−1.19	4.73	13.48	13.25
	450	13.05	14.69	−1.29	4.77	13.44	13.27
	500	12.98	14.72	−1.38	4.80	13.40	13.29
j	25	13.57	13.28	−0.25	4.28	13.64	12.01
	50	13.56	13.33	−0.26	4.44	13.64	12.01
	100	13.57	13.43	−0.25	4.73	13.64	12.02
	150	13.57	13.54	−0.23	4.99	13.64	12.05
	200	13.59	13.65	−0.20	5.24	13.65	12.09
	250	13.60	13.76	−0.17	5.46	13.65	12.13
	300	13.62	13.87	−0.14	5.66	13.66	12.18
	350	13.63	13.98	−0.12	5.85	13.67	12.24
	400	13.65	14.09	−0.09	6.02	13.68	12.30
	450	13.66	14.20	−0.07	6.18	13.68	12.36
	500	13.68	14.32	−0.06	6.33	13.69	12.43
k	25	7.35	7.36	−3.13	7.16	8.29	5.23
	50	7.32	7.42	−3.27	7.28	8.29	5.25
	100	7.24	7.53	−3.50	7.60	8.28	5.27
	150	7.15	7.64	−3.72	7.86	8.26	5.29
	200	7.06	7.74	−3.92	8.09	8.23	5.33
	250	6.96	7.84	−4.12	8.29	8.19	5.37
	300	6.86	7.93	−4.30	8.46	8.15	5.41
	350	6.76	8.03	−4.46	8.62	8.09	5.46
	400	6.66	8.12	−4.62	8.77	8.04	5.51
	450	6.56	8.21	−4.77	8.90	7.98	5.56
	500	6.46	8.31	−4.90	9.03	7.92	5.62
l	25	31.43	35.11	−5.20	0.08	32.98	35.09
	50	31.39	35.13	−5.31	0.13	32.97	35.09
	100	31.32	35.16	−5.50	0.23	32.96	35.09
	150	31.26	35.20	−5.65	0.33	32.95	35.10
	200	31.20	35.25	−5.78	0.42	32.93	35.12
	250	31.15	35.29	−5.89	0.51	32.91	35.14
	300	31.09	35.33	−5.99	0.60	32.88	35.16
	350	31.04	35.38	−6.08	0.67	32.85	35.18
	400	30.98	35.42	−6.17	0.74	32.82	35.20
	450	30.92	35.47	−6.26	0.80	32.79	35.23
	500	30.86	35.51	−6.34	0.85	32.75	35.25
m	25	45.04	45.19	−3.30	0.62	46.02	45.00
	50	45.03	45.22	−3.33	0.71	46.02	45.00
	100	45.01	45.28	−3.38	0.88	46.02	45.01
	150	44.99	45.34	−3.43	1.04	46.01	45.03
	200	44.97	45.4	−3.48	1.19	46.00	45.05
	250	44.94	45.47	−3.53	1.31	45.99	45.08
	300	44.91	45.53	−3.58	1.43	45.98	45.1
	350	44.88	45.59	−3.64	1.53	45.96	45.13
	400	44.84	45.64	−3.69	1.61	45.94	45.16

Table 3 (continued)

Channel	T/°C	*ΔH*/(kcal mol^{-1})		*ΔS*/(cal mol^{-1}/K)		*ΔG*/(kcal mol^{-1})	
		cc-pvdz	6-31G**	cc-pvdz	6–31G**	cc-pvdz	6–31G**
	450	44.80	45.7	−3.75	1.69	45.92	45.19
	500	44.76	45.75	−3.81	1.75	45.89	45.22
n	25	4.69	5.30	0.85	−4.58	4.44	6.66
	50	4.72	5.27	0.96	−4.59	4.43	6.64
	100	4.77	5.23	1.12	−4.72	4.44	6.64
	150	4.82	5.18	1.26	−4.84	4.45	6.63
	200	4.87	5.13	1.36	−4.95	4.47	6.61
	250	4.92	5.08	1.45	−5.06	4.48	6.59
	300	4.96	5.02	1.53	−5.17	4.5	6.56
	350	4.99	4.95	1.58	−5.28	4.52	6.53
	400	5.02	4.89	1.63	−5.38	4.54	6.49
	450	5.05	4.82	1.68	−5.48	4.55	6.45
	500	5.08	4.74	1.71	−5.58	4.57	6.41
o	25	5.23	4.90	1.51	−3.88	4.78	6.05
	50	5.26	4.88	1.65	−3.87	4.77	6.04
	100	5.35	4.87	1.89	−3.91	4.79	6.03
	150	5.44	4.87	2.12	−3.91	4.81	6.03
	200	5.55	4.88	2.35	−3.90	4.84	6.04
	250	5.66	4.89	2.57	−3.87	4.89	6.04
	300	5.77	4.90	2.78	−3.85	4.94	6.05
	350	5.88	4.92	2.97	−3.82	5.00	6.06
	400	6.00	4.93	3.15	−3.79	5.06	6.07
	450	6.11	4.95	3.32	−3.77	5.13	6.07
	500	6.23	4.97	3.47	−3.74	5.19	6.09
p	25	8.30	8.11	2.83	−3.59	7.46	9.18
	50	8.36	8.11	3.03	−3.49	7.46	9.16
	100	8.49	8.14	3.39	−3.42	7.47	9.16
	150	8.62	8.17	3.72	−3.33	7.51	9.17
	200	8.75	8.21	4.01	−3.26	7.55	9.18
	250	8.88	8.24	4.28	−3.19	7.61	9.19
	300	9.02	8.28	4.53	−3.13	7.67	9.21
	350	9.15	8.31	4.75	−3.07	7.73	9.23
	400	9.28	8.34	4.95	−3.02	7.80	9.24
	450	9.41	8.37	5.13	−2.98	7.88	9.26
	500	9.53	8.40	5.30	−2.94	7.95	9.28
q	25	24.90	28.49	−1.88	−6.76	25.46	30.51
	50	24.90	28.45	−1.85	−6.84	25.45	30.49
	100	24.92	28.38	−1.80	−7.04	25.46	30.48
	150	24.95	28.32	−1.72	−7.20	25.47	30.46
	200	24.99	28.26	−1.64	−7.32	25.48	30.45
	250	25.03	28.21	−1.55	−7.42	25.49	30.43
	300	25.08	28.17	−1.47	−7.50	25.52	30.40
	350	25.12	28.12	−1.39	−7.58	25.54	30.38
	400	25.17	28.07	−1.32	−7.66	25.56	30.35
	450	25.21	28.02	−1.26	−7.73	25.59	30.33
	500	25.26	27.97	−1.20	−7.80	25.61	30.29
r	25	33.49	38.95	−1.34	−6.34	33.89	40.85

Table 3 (continued)

Channel	T/°C	*ΔH*/(kcal mol^{-1})		*ΔS*/(cal mol^{-1}/K)		*ΔG*/(kcal mol^{-1})	
		cc-pvdz	6-31G**	cc-pvdz	6–31G**	cc-pvdz	6–31G**
	50	33.50	38.93	−1.26	−6.36	33.88	40.82
	100	33.55	38.88	−1.14	−6.50	33.88	40.82
	150	33.60	38.84	−1.01	−6.60	33.90	40.81
	200	33.66	38.81	−0.88	−6.67	33.92	40.80
	250	33.72	38.78	−0.76	−6.74	33.94	40.78
	300	33.78	38.74	−0.65	−6.79	33.97	40.77
	350	33.83	38.71	−0.55	−6.85	34.00	40.75
	400	33.89	38.67	−0.46	−6.91	34.03	40.73
	450	33.95	38.63	−0.38	−6.96	34.06	40.71
	500	34.00	38.59	−0.31	−7.02	34.09	40.68

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