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Article

The Enthalpy of Formation of Acetylenes and Aromatic Nitro Compounds for a Group Contribution Method with "Chemical Accuracy"

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Abstract

In this communication we provide the Group Contribution parameters for acetylenes and aromatic nitro compounds fitting with a recently developed Group Contribution method with chemical accuracy (1 kcal/mol) for the heat of formation of organics. These additional parameters widen the applicability of the Group Contribution method. We also provide further G4 quantum calculated values as reference when no experimental data are available and compare to previously reported G4 data.

Keywords: enthalpy of formation; reaction enthalpy; thermodynamics; process design; physicochemical property prediction; group contribution method; chemical accuracy; G4 quantum chemistry

1. Introduction

The heat of formation is a crucial parameter with respect to the stability of molecules and chemical transformations as well as in chemical process design. Due to the lack of experimental data (the space of organic molecules comprises many billions of different molecules) predictive models are highly desired. This communication provides further Group Contribution parameters related to alkynes and aromatic nitro compounds as an extension of earlier work [1–6]. The aim is to have a method available which allows accurate predictions to be obtained for the heat of formation of organic molecules, i.e., with chemical accuracy, previously unprecedented. Peterson et al. [7] formulated chemical accuracy as 'in the thermochemistry literature this is almost universally interpreted as 1 kcal/mol or about 4 kJ/mol', i.e., the aim is to have the difference between experimental and model value less than this value. Apart from being accurate and reliable (very few if any outliers, and certainly not with large deviation), values for the property are to be obtained at one's fingertips.

The GC method [8] is a so-called data-driven model with experimental data being used to parametrize the model; for the heat of formation ΔHf the essential equation reads

$$\Delta Hf = \sum_{j=1,N} Nj.\Delta Hf(j) \quad (1)$$

In Equation (1), Nj represents the number of times Group j occurs in the molecule of interest, whereas ΔHf(j) is the Group Contribution of the chemical Group j to the heat of formation. In this work, the ΔHf (in this paper also indicated as dHf) is the enthalpy of formation for the ideal gas species at the reference temperature of 298.15 K and 101325 Pascal (1 atm.). Additional terms including Group-Group interaction parameters can be introduced to increase the performance. In the present communication we account for ynes and nitro-aromatic compounds and therewith increase the range of applicability of the previously developed model.

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As we will see, the ynes and nitro compounds considered in this Communication prove to be somewhat more difficult for GC models to handle. Therefore, contrary to our previous papers on a new GC method, we will not compare with results from other GC methods as (i) none of these has achieved or truly aimed for chemical accuracy, (ii) they all exhibit very serious outliers without providing a solution, and (iii) with the difficult Groups we handle in the present paper performance is even worse (as we did check but do not report). Key in the extension of our previously developed GC method are both experimental data as well as G4 calculated values for the heat of formation. We will compare our G4 calculated values with previously reported values when such values exist.

2. Computational Methods

Following from our previous works [4–6] we have applied ab initio calculations using the G4 method [9–11] in the present work or, alternatively, refer to G4 computed results reported by other authors. G4 is a procedure that approximates the energy of a CCSD(T)/6-311++G(3df,2p) single-point calculation at the B3LYP/6-31G(2df,p) optimized geometry by using a series of somewhat less expensive calculations. Further details about this so-called composite method can be found in the original references [9–11]. We have been employing Gaussian 16 (G16) [9–11] (including the GaussView visualization tool) for geometry optimization; force constants were calculated analytically and tight convergence criteria were used (fopt = (calcfc, tight)). For structures with multiple conformations, conformational searches were performed systematically and manually as described earlier [4–6].

3. Results

3.1. Alkynes

Table 1 comprises experimental and G4 calculated heats of formation for various alkynes. When available we have used the reliable experimental values from Rossini et al. [12]. We have previously [1] reported on a more limited set of the alkynes and the GC parameters for the C≡C group was found optimal with the value 229 kJ/mol. At that moment this value provided the best average agreement between experimental and GC model values, although it differs from the experimental value reported by Rossini (226.9kJ/mol), but was still within experimental error. We have now added further alkynes with other end groups, both linear and branched, for which either experimental or G4 calculated values are available. Detailed inspection revealed that we should distinguish between terminal and non-terminal C≡C group bonds with slightly different GC parameter values. For the terminal case we now find the experimental value of 226.9 kJ/mol optimal which equals the experimental value due to Rossini (with data among the most reliable in the field) whereas the non-terminal value was established as 230.6 kJ/mol. We note that these values did not result from a simple statistical analysis with minimum average error as we want a reliable model which implies all individual values within experimental error (chemical accuracy). For the hydrocarbon substituted 1-alkynes we obtain an average absolute deviation (AAD) of 1.06 kJ/mol (upper part of Table 1) with all individual values within chemical accuracy. For the last four entries of the upper part of Table 1 we have no reliable experimental data and therefore we have compared with our new conformationally averaged G4 values and at the same time shown the G4 values from Rayne and Forest [13] (Tabel 1, column 7) and from van der Spoel c.s.]14} (Table 1, column 8), respectively, and GC model values compare favourably within chemical accuracy.

The same good agreement was found (lower part of Table 1) for the non-terminal alkynes with an AAD of 1.56 kJ/mol. Disagreement was found for the alkynes having a hetero atom close to the triple bond, i.e., –CH2F, –OH, –CHO, –NH2 and –CN. Apparently, these groups have an additional, mostly strong (the –NH2 excepted), interaction with the triple bond. To confirm this we performed G4 calculations on 2-propyn-1-ol (propargyl alcohol) and 3-butyn-1-ol revealing differences between experimental values and G4 values of 15.4kJ/mol and 0.06 kJ/mol, respectively, compared to 49.7

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kJ/mol for C≡C-OH which confirms that the effect is there and vanishes when the alkyl spacer is sufficiently long to separate the triple bond from the hydroxyl group.

With a few exceptions commented on below, the present alkyne G4 calculations based on the single lowest-energy conformation agree exactly, or nearly exactly, with values reported by Rayne and Forest [13] and by van der Spoel c.s. [14] when available. The values that include conformational averaging are 0-4 kJ/mol higher, depending on the complexity and flexibility of the molecule. Interestingly, the AAD from experiment is 1.9 kJ/mol for the values based on a single conformation, but 2.5 kJ/mol for those based on conformational averaging. Both are generally within the experimental error bars, however, and in principle, the latter (conformationally averaged) values should be preferred. The G4 dHf reported by van der Spoel for 1-octyne is 5.2 kJ/mol higher than the experimental value and even 1.6 kJ/mol beyond the experimental error bar. Our value is significantly closer to experiment, and well within the error bars. We observe similar deviations for 2-, 3-, and 4-nonyne, where the van der Spoel values 54.6, 51.7 and 44.6 kJ/mol are too high and the present G4 values 45.6, 46.6 and 44.9 kJ/mol are closer to experiment. We speculate this might be because van der Spoel c.s. did not identify the lowest-energy conformation, which in each case turns out not to be the fully extended CS-symmetric conformation that one might have guessed without a conformational search. The same seems to apply to the value for 7-methyl-3-octyne. Whereas our G4 value (39.5 kJ/mol) agrees with our GC model value (35.53kJ/mol) within experimental accuracy, the value due to van der Spoel c.s. [14] deviates substantially (43.4 kJ/mol).

Our G4 calculated value for 1-decyne (38.7 kJ/mol) is 3.2 kJ/mol below the experimental value (41.9 kJ/mol) although still within chemical accuracy and experimental error. However, this value does not include conformational averaging, which would have been too time-consuming for this molecule. If we assume a similar increment for dHf as for 1-nonyne, however, it would bring the calculated value up to 42.6 kJ/mol, almost an exact match to the experimental value and within chemical accuracy when compared to the GC model value. The calculated values for 2-, 3-, and 4-decyne are all ~3 kJ/mol higher than the experimental values but within the experimental error bars and very close, within chemical accuracy, to the GC model values

The G4 values we calculated for the heteroalkynes, which are conformationally straightforward, match exactly with previously reported values [13], when they are available, except in the case of 3-fluoropropyne, for which we obtain a value 2 kJ/mol higher than the G4 value reported by Rayne and Forest [13]. This is most likely due to a difference in how fluorine is treated in the atomization scheme as part of the G4 calculation.

In conclusion, we conclude alkynes can be well-treated by our GC method as long as no hetero atoms are close to (within three bonds of) the triple bond. G4 calculated values agree well with these. Because of the generally observed good performance of G4 for heats of formation of organics we believe that the other systems in Table 1 can be accounted for by the G4 results.

Table 1. Experimental, GC model, G4 gas-phase heat of formation values (kJ/mol). In the final column we present the current G4 calculated values based on the minimum energy conformation followed by the conformationally averaged value. In the 5th and 6th column the difference between the GC model and the experimental value is presented. If no experimental value is available, we have taken the second G4 calculated value from the last column representing the conformationally averaged value.

1-alkynes	Rossini [12]	Rogers c.s. [16]	GC model	model-exp (or G4)	ABS (model-exp) (or model - G4)	G4 [13]	G4 [14]	G4 present work
ethyne	226.9		226.9	0	0	228.4		228.4/228.4

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1-propyne	185.6		184.54	-1.06	1.06	185.2	185.1	185.1/185.1
1-butyne	166.2		163.91	-2.29	2.29	166.8	166.7	166.8/166.8
1-pentyne	144.45		143.28	-1.17	1.17		144.9	144.8/144.9
1-hexyne		122.3±1.2	122.65	0.35	0.35		123.8	124.0/124.7
1-heptyne	102.40		102.02	-0.38	0.38		102.40	102.7/104.2
1-octyne		80.7±3.6	81.39	0.69	0.69		85.9	81.1/83.7
1-nonyne	59.8		60.76	0.96	0.96		59.80	59.7/63.2
1-decyne		41.9±3.4	40.13	-1.77	1.77			38.7
3-methyl-1-butyne	136.4±2.1		136.08	-0.32	0.32	139.6		139.6/139.6
3-methyl-1-pentyne			117.55	-0.45	0.45		119.9	116.8/118.0
4-methyl-1-pentyne			115.45	0.85	0.85		114.3	114.5/114.6
C≡C-C-$(CH_3)_3$			102.62	-3.38	3.38	106	106.0/106.0	106.0/106.0
C≡C-C_6H_5			317.4	0.1	0.1	317.4	317.3/317.3	317.3/317.3
averaged absolute difference					1.06			
C≡C-CH_2F			-12.23	36.53	34.43	22.2		24.3/24.3
C≡C-CH_2-CH_2-OH			14.64	-0.06	0.06			12.9/14.7
C≡C-CH_2-OH			35.27	-15.43	15.43			50.4/50.7
C≡C-OH			55.9	-37.2	37.2	93.1		93.1/93.1
C≡C-CHO			102.9	28.0	28.1	131		130.9/130.9
C≡C-NH_2			239.9	-9.0	9	248.9		248.9/248.9
C≡C-CN			342.9	-29.1	29.1	372		372.0/372.0
2-, 3-, 4- and 5-alkynes								
2-butyne	148.1		145.88	-2.22	2.22	147.9		147.8/147.8
2-pentyne	128.95		125.25	-3.7	3.7			129.0/129.0
3-hexyne		105.4±1.9	104.62	-0.78	0.78			109.8/109.8
3-heptyne		82.8±2.4	83.99	1.19	1.19			87.4/87.6
3-octyne		62.5±1.8	63.36	0.86	0.86			66.1/67.3
2-octyne		63.8±1.5	63.36	-0.44	0.44			64.2/66.1
4-octyne		60.1±2.1	63.36	3.26	3.26			64.7/65.3
2-nonyne		43.6±3.0	42.73	-0.87	0.87		54.6	43.5/45.6
3-nonyne		42±2.5	42.73	0.73	0.73		51.70	45.5/46.6
4-nonyne		42±2.8	42.73	0.73	0.73		44.60	44.1/44.9
2-decyne		23.6±3.4	22.1	-1.5	1.5			22.3/25.0
3-decyne		21.8±3.3	22.1	0.3	0.3			23.5

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4-decyne	19.9±3.0	22.1	2.2	2.2		22.7
5-decyne	18.7±3.3	22.1	3.4	3.4		21.9/24.4
4-methyl-2-pentyne		99.52	-1.58	1.58	101	101.1/101.1
7-methyl-3-octyne		35.53	-2.57	2.57	43.4	37.2/38.1
2,6-dimethylhept-3-yne		28.33	-0.27	0.27	28.4	28.5/28.6
averaged absolute difference				1.56		

3.2. Aromatic Nitro Compounds

We have adopted the same value for the nitro Group GC parameter as established earlier for the aliphatic nitro compounds [3]. Table 2 comprises the experimental data quoted in [17] with most of these originating from Pedley and from Verevkin which are generally very reliable and validated sources of thermodynamic data. Furthermore Table 2 contains GC calculated enthalpies of formation using our previously [1–3] established GC parameter values. Suntsova and Dorofeeva [17] have noticed that for the aromatic nitro compounds they found a systematic difference between the G4 result based on atomization energies compared to the experimental values of around 13 kJ/mol and therefore they resorted to isodesmic reactions which generally did reveal good agreement. They have concluded the same for aliphatic nitro compounds [18]. In our own investigation we have similarly found that G4 enthalpies of formation computed in the conventional fashion are about 9 kJ/mol too low per nitro group. If a corresponding correction of 9 kJ/mol per nitro group is added, we in fact obtain G4 enthalpies of formation via the atomization procedure that are very similar to those reported by Suntsova and Dorofeeva using isodesmic reactions [17]. However, it is fair to say that the various isodesmic reaction schemes applied in Ref. [17] led to different values for the heat of formation and the range of values for an individual compound could vary over a range of up to 10 kJ/mol.

Table 2. Experimental, GC model, G4 heat of formation (kJ/mol) and B3LYP relative energies (kJ/mol). The values in bold specifically indicate the species exhibiting steric hinderance. Experimental values were taken from the compilation by Suntsova and Dorofeeva [17] unless indicated otherwise. Most values (for references see Ref. [17]) originate from Pedley c.s. and Verekin c.s., generally very reliable sources. The second experimental values given for the three nitroanilines are those recommended by Suntsova and Dorofeeva. For discussion see text and Ref. [17].

nitro aromatic compounds	experiment [17]t	GC model	GC model -exp	B3LYP relative energies
benzene	82.99 [21]	84.5	1.51	
nitrobenzene	67.5±0.6	64.5	-3	
2-methylnitrobenzene	**37.1±1.0 [19]**	**28.14**	**-8.96**	**12**
3-methylnitrobenzene	29.0±1.5 [19]	28.14	-0.86	2
4-methylnitrobenzene	29.9±1.1 [19]	28.14	-1.76	0
2-ethylnitrobenzene	11.2±6.6	7.51	-3.69	
4-ethylnitrobenzene	7.4±6.6	7.51	0.11	
2-nitrobenzoic acid	**-279.8**	**-314.5**	**-34.7**	**23**
3-nitrobenzoic acid	-304	**-314.5**	-10.5	-2
4-nitrobenzoic acid	-307.7	**-314.5**	-6.8	0
2-nitrophenol	**-127.8**	**-112**	**15.8**	**-12**

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3-nitrophenol	-111.8	-112	-0.2	6
4-nitrophenol	-114.1	-112.0	2.1	0
1,2-dinitrobenzene	**93.7±1.2**	**44.5**	**-49.2**	**39**
1,3-dinitrobenzene	53.8±1.8	54.5	0.7	0
1,4-dinitrobenzene	55.6±0.8	54.5	-1.1	0
1-methyl-2,4-dinitrobenzene	**33.2±3.3**	**18.14**	**-15.06**	
2,4-dinitrophenol	-128.1	-122	6.1	0
2,6-dinitrophenol	**-97.8**	**-132**	**-34.2**	**30**
2-nitroaniline	63.8 / 62.9	70.5	6.7	0
3-nitroaniline	58.4 / 62.5	70.5	12.1	10
4-nitroaniline	58.8 / 57.7	70.5	11.7	0
N,N-dimethyl-3-nitroaniline	72.6±1.8	65.28	-7.32	**11**
N,N-dimethyl-4-nitroaniline	67.3±1.7	65.28	-2.02	0
2-methyl-5-nitrophenol	-147.2	-148.36	-1.16	0
3-methyl-4-nitrophenol	-138.5	-148.36	-9.86	**9**
4-methyl-2-nitrobenzoic acid	-316.9 [22]	-350.9	-34	
6-methyl-3-nitrobenzoic acid	-333.2 [22]	-350.9	-17.7	
2-methyl-4-nitrobenzoic acid	-334.6±3.0 [22]	-350.9	-16.3	

Despite the issues with the G4 results, we observe from the data in Table 2 that all GC model values agree well (within chemical accuracy) with the experimental values up to and including 1,4-dinitrobenzene with the exception of the three marked 1,2-substituted species. As steric hindrance is expected for these species it is not difficult to recognise these as exceptions and avoid treating these with the pure GC method. Following what we already applied in our earlier studies [4] we have used density functional type quantum chemical calculations at the B3LYP//6-311+G** level as a check whether steric hindrance effects, not accounted for by the GC approach, can be accounted for. B3LYP generally delivers reliable relative energies for organics and is also applicable (in terms of computational demand) to larger molecules [20]. Here, we always use the B3LYP calculated energy of the para-substituted isomer as the reference case that is presumed free of steric repulsion. From the results collected in Table 2 it can be corroborated that the deviations can be accounted for very well when the B3LYP calculated energy differences are added to the GC values except for 1,2-dinitrobenzene for which the deviation is larger but still not dramatic. An interesting case is 2-nitrophenol where the experimental value is more negative than the GC model value suggesting this is not pure steric hindrance, and indeed this difference is also due to (and supported by our B3LYP quantum calculations) the hydrogen bond formed between the hydroxy hydrogen and one of the nitro oxygen atoms: the B3LYP energy difference was found as -12 kJ/mol which compares favourably with the 15.8 kJ/mol difference between the experimental and the GC model values. That we observe good agreement between experimental and GC values for 2-methyl-5-nitrophenol is because there is no steric hindrance as we already observed when studying the phenols before [5]. This is different for 3-methyl-4-nitrophenol where we observe a difference of 9 kJ/mol which is the same difference as for 2-methylnitrobenzene earlier on in Table 2. In both cases, a correction by the B3LYP calculated difference (add the relative value to the GC model value) leads to values within chemical accuracy from experiment.

2,4-dinitrophenol is, as we conclude from the reasonably good agreement between experimental and GC value, not just suffering from steric effects. However, there is likely steric hindrance and/or electrostatic repulsion but compensated by the energy resulting from the OH group (B3LYP optimized structure) interacting with the nitro group in a positive way. This is not expected for 2,6-

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dinitrophenol for which we indeed observe steric overlap from a space-filling 3D model and the difference between the dHf's for the two compounds of 30 kJ/mol is close to the B3LYP calculated difference and thus, once more, B3LYP results are useful to obtain a GC model value with correction for steric and presumably also electrostatic effects.

In one of our previous studies [5] we reported a problem related to the GC model value for N,N,dimethylaniline resulting in a model value which was 14.7 kJ/mol too low (less positive) compared to the experimental value. Here we find that for N,N-dimethyl-3-nitroaniline and N,N-dimethyl-4-nitroaniline there are differences between experimental and GC model values which can be well-accounted for by steric affects evaluated using B3LYP calculations for N,N-dimethyl-3-nitroaniline whereas the difference is within chemical accuracy for N,N-dimethyl-4-nitroaniline. This is not totally unexpected when viewing the molecular structures but the problem concerning N,N-dimethyl-aniline itself [5] remains elusive.

2-methylnitrobenzene, 3-methyl-4-nitrophenol and 1-methyl-2,4-dinitrobenzene all have a methyl next to a nitro substituent revealing deviations of -9.0, -9.9 and -15.1 kJ/mol which are relatively close considering experimental errors and therefore revealing a consistent picture of the steric hindrance between adjacent nitro and methyl substituents. Likewise, 4-methyl-2-nitrobenzoic acid has a deviation of 34 kJ/mol whereas for 2-nitrobenzoic acid this reads 34.7 kJ/mol, values being close representing the nitro - benzoic acid steric hindrance. For 6-methyl-3-nitrobenzoic acid we observe a deviation of 17.7 kJ/mol whereas 2-methyl-4-nitrobenzoic acid reveals a deviation of 16.3 kJ/mol and both have a methyl next to a carboxylic acid substituent. All these deviations show internal consistency in agreement with quantifiable steric hindrance. Furthermore, in our earlier work [5] we found just over 10 kJ/mol deviation for 2-methylbenzoic acid, a steric hindrance effect which was in accordance with the B3LYP value of 8.2 kJ/mol compared to 4-methylbenzoic acid, when comparing the experimental with the GC model values.

The three nitroanilines form a somewhat peculiar case as the difference between certain experimental and GC values is on average some 10 kJ/mol, but the B3LYP relative energies do not account well for these as expected because these molecules do not primarily suffer from steric hindrance. According to B3LYP calculations 3-nitroaniline is the least stable species which can be understood when recognizing that the ortho and para isomers are more stable because of the push-pull donor-acceptor interaction. Qualitatively the same conclusion follows from our G4 calculations (52.8, 58.2 and 54 kJ/mol respectively) and the isodesmic reaction scheme results by Suntsova and Dorofeeva (61.2, 66.4, 61.3 kJ/mol) [17]. The latter, however, are averages over about 10 isodesmic reactions. These trends do not agree with the experimental data recommended by Suntsova and Dorofeeva (62.9, 62.5 and 57.7 kJ/mol) though it is not quite clear why these were recommended. Also the values due to Pedley quoted by Suntsova and Dorofeeva (63.8, 58.4, 58.8 kJ/mol), where Pedley which is normally considered a reliable source of verified data, do not agree with this reasoning. Here it should also be noticed that the experimental values have errors given in the range 0.8-4.2 kJ/mol, whereas the isodesmic reactions reported show values within a range of 3-3.5 kJ/mol (different isodesmic reactions reveal a different value). When we look at 2-nitroaniline, when considering experimental errors indicated there is even agreement between the experimental value and our GC model value, but not for the other two isomers. Overall, even though these three molecules do not show any specific issues compared to the other nitro compounds in Table 2, we could not establish a satisfactory explanation for the observed data from various sources.

In conclusion, the GC model values mostly agree well with the experimental values whereas in case of clear deviations these can be accounted for by steric hindrance for which we can obtain a correction value based on B3LYP calculations. The three nitroanilines are problematic, as the exception, but here we have an unclear situation between which experimental values are correct and the GC and quantum results on the other hand.

4. Discussion and Conclusions

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The result of this contribution is an extension to the previously developed GC method [1–6] by adding C≡C Group values characteristic of alkynes and a nitro Group value characteristic of aromatic nitro compounds. As before, the goal of chemical accuracy was largely achieved and deviations due to steric hindrance and intramolecular hydrogen bonding could generally be well-accounted for by additional B3LYP calculated corrections. Following various other publications (see [4–6] and references therein) we have seen once more that G4 calculated values can provide results close to experiment and be a good substitute while developing a GC method for cases where reliable experimental results are absent. However, for the ynes with heteroatoms close to the triple bond the discrepancy between GC and G4 results is generally very significant. For nitro containing compounds we have observed a clear difference between G4 and experimental values in agreement with previous publications [17,18].

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References

1. Meier, R.J. Group contribution revisited: The enthalpy of formation of organic compounds with “chemical accuracy”. *ChemEngineering* **2021**, *5*, 24. https://doi.org/10.3390/chemengineering5020024.
2. Meier, R.J. Group contribution revisited: The enthalpy of formation of organic compounds with “chemical accuracy” Part II. *AppliedChem* **2021**, *1*, 111–129. https://doi.org/10.3390/appliedchem1020009
3. Meier, R.J. Group contribution revisited: The enthalpy of formation of organic compounds with “chemical accuracy” Part III. *AppliedChem* **2022**, *2*, 213–228. https://doi.org/10.3390/appliedchem2040015
4. Meier, R.J.; Rablen, P.R. Group contribution revisited: The enthalpy of formation of organic compounds with “chemical accuracy” Part IV. *Thermo* **2023**, *3*, 289–308. https://doi.org/10.3390/thermo3020018.
5. Meier, R.J.; Rablen, P.R. Group contribution revisited: The enthalpy of formation of organic compounds with “chemical accuracy” Part V. Appl. Sci. 2024, 14, 1929. https://doi.org/10.3390/app140519296.
6. Meier, R.J.; Rablen, P.R. Group contribution revisited: The enthalpy of formation of Organic compounds with “chemical accuracy” Part VI. ApplChem. **2024**, 4, 333–352 https://doi.org/10.3390/appliedchem4040021
7. Peterson, K.A.; Feller, D.; Dixon, D.A. Chemical accuracy in ab initio thermochemistry and spectroscopy: Current strategies and future challenges Theor. *Chem. Acc.* **2012**, *131*, 1079–1098 https://doi.org/10.1007/s00214-011-1079-5 .
8. Van Krevelen, D.W.; Chermin, H.A.G. Estimation of the free enthalpy (Gibbs free energy) of formation of organic compounds from group contributions. *Chem. Eng. Sci.* **1951**, *1*, 66–80; Erratum in *Chem. Eng. Sci.* **1952**, *1*, 238 https://doi.org/10.1016/0009-2509(51)85002-4
9. Curtiss, L.A.; Redfern, P.C.; Raghavachari, K. Gaussian-4 theory. *J. Chem. Phys.* **2007**, *126*, 084108. https://doi.org/10.1063/1.2436888

10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Adamo, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*; Gaussian, Inc., Willingford, CT, 2016
11. Narayanan, B.; Redfern, P.C.; Assary, R.S.; Curtiss, L.A. Accurate quantum chemical energies for 133,000 organic molecules. *Chem. Sci.* **2019**, *10*, 7449. https://doi.org/10.1039/c9sc02834j
12. Wagman, D.D.; Kilpatrick, J.E.; Pitzer, K.S.; Rossini, F.D. Heats, equilibrium constants, and free energies of formation of the acetylene hydrocarbons through the pentynes, to 1,500 K. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 467–496 www.nvlpubs.nist.gov/nistpubs/jres/35/jresv35n6p467_A1b.pdf
13. Rayne, S., Forest, K. Thermochemistry of mono- and disubstituted acetylenes and polyynes at the Gaussian-4 level of theory *Comp. and Theor. Chem.* **2011, *970,*** 15-22 https://doi.org/10.1016/j.comptc.2011.05.018
14. Ghahremanpour, M.M.; van Maaren, P.J.; Ditz, J.C.; Lindh, R.; van der Spoel, D. Large-scale calculations of gas phase thermochemistry: Enthalpy of formation, standard entropy, and heat capacity. *J. Chem. Phys.* **2016**, *145*, 114305. https://doi.org/10.1063/1.4962627
15. NIST Data Base. Available online: https://webbook.nist.gov/ (last accessed October 2025).
16. Rogers, D.W., Dagdagan, O.A., Allinger, N.L. Heats of hydrogenation of linear alkynes and a molecular mechanics interpretation *J.Am.Chem.Soc.* **1979, *101,*** 671-676 https://doi.org/10.1021/ja00497a031
17. Suntsova, M.A., Dorofeeva, O.V. Use of G4 Theory for the assessment of inaccuracies in experimental enthalpies of formation of aromatic nitro compounds *J. Chem.& Eng. Data* **2016**, *61*, 313-329 https://doi.org/10.1021/acs.jced.5b00558
18. Suntsova, M.A., Dorofeeva, O.V. Use of G4 theory for the assessment of inaccuracies in experimental enthalpies of formation of aliphatic nitro compounds and nitramines *J.Chem.& Eng. Data* **2014**, *59* , 2813-2826 https://doi.org/10.1021/je500440y
19. Bikelyte, G.; Hartel, M.; Stierstorfer, J.; Klapötke, T.. M.; Pimerzin, A.A. und Verevkin, S.P. (2017): Benchmark properties of 2-, 3-and 4-nitrotoluene: Evaluation of thermochemical data with complementary experimental and computational methods *In: Journal of Chemical thermodynamics* **2017**, *111*, 271-278 https://doi.org/10.1016/j.jct.2017.03.029
20. Tirado-Rives, J., Jorgensen, W.L. Performance of B3LYP Density Functional Methods for a Large Set of Organic Molecules. *J. Chem. Theory Comput.* **2008**, *4*, 297–306 https://doi.org/10.1021/ct700248k
21. Prosen, E.J.; Johnson, W.H.; Rossini, F.D. Heats of combustion and formation at 25 °C of the alkylbenzenes through C10H14. and of the higher normal monoalkylbenzenes. *J. Res. Natl. Bur. Stand.* **1946**, *36*, 455–461
22. Silva Ferraz, J.M., Emel'yanenko, V.N., Zaiutsau, D.H., Samarov, A.A., Brunetti, B., Ciccioli, A., Ciprioti, S.V., Verevkin, S.P. *ChemPlusChem 2025* e202400703 https://doi.org/10.1002/cplu.2024000703