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THERMODYNAMIC AND ENERGY FUNCTIONS OF FLUORINATED BENZENES: THEIR SIGNIFICANCE IN CORRELATION ANALYSIS

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ABSTRACT

Standard thermodynamic functions have been calculated and the term of potential energy change ΔE determined from the $\Delta H_0^\ominus$ term for ideal gas phase fluorobenzene and four of its derivatives, as well as for several of their reactions. The calculations were based on observed structural and vibrational parameters and tabulated heats of formation. The reactions comprised various isodesmic and non-isodesmic processes, treated from the standpoint of applicability to organic correlation analysis. Our analysis indicates that the term $\Delta H_0^\ominus$ is preferable to ΔE as a basis for chemical theories. Its accessibility and applicability to the purposes of correlation analysis are discussed.

INTRODUCTION

The Hammett equation and related "Linear Free Energy Relationships" (LFERs) [1–3] correlate reactivity parameters in related reaction series, i.e. the standard or activation Gibbs energies $\Delta G_T^\ominus$ or $\Delta G_T^\ddagger$, respectively. The evident usefulness and simplicity of these relationships is difficult to understand in view of the relatively complex character of $\Delta G_T^\ominus$. (In the present work we shall limit ourselves to consideration of the standard terms only, but there would be no major difference in the analysis for the activation terms.) Terms of standard enthalpy change at the same temperature $\Delta H_T^\ominus$ or at absolute zero $\Delta H_0^\ominus$, being free of the entropy contribution, should be more closely related to theoretical concepts. The question therefore arises: is $\Delta G_T^\ominus$ actually the most suitable object for simple correlations, or are LFERs

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used so widely only because insufficient data are available for other thermodynamic quantities? An answer has been sought by partitioning $\Delta G_T^\ominus$ into several terms, assuming that some of these can either approach zero or mutually cancel under certain circumstances [1–4]. Thus Hammett [2] has considered a division of $\Delta H_T^\ominus$, and subsequently also of $\Delta G_T^\ominus$, into three terms. In the contemporary notation, his equations can be written as

$$\Delta H_T^\ominus = \Delta H_0^\ominus + \Delta\left(H_T^\ominus - H_0^\ominus\right) = \Delta E + \Delta^{(q)} + \Delta\left(H_T^\ominus - H_0^\ominus\right) \tag{1}$$

$$\Delta G_T^\ominus = \Delta E + \Delta^{(q)} + \Delta\left(H_T^\ominus - H_0^\ominus\right) - T\Delta S_T^\ominus \tag{2}$$

where $\Delta(H_T^\ominus - H_0^\ominus)$ denotes the reaction change in the heat content function, and ΔE and $\Delta^{(q)}$ represent the change in potential energy and in vibrational zero-point energy (so-called 'residual energy'), respectively. The transition from the term ΔE to $\Delta H_0^\ominus$ actually represents the incorporation of quantum effects [5]. In the harmonic-oscillator approximation, these are reduced to

$$\Delta_j^{(q)} = \tfrac{1}{2}h\sum_i \omega_{ij} \tag{3}$$

where ω_{ij} represents the normal vibrational frequencies of the jth reaction component. Further terms of higher orders would appear in relation (3) on transition to more sophisticated types of approximation [6–8] but these are usually neglected.

Hammett [2] reasoned that in certain theoretically important reaction series, $\Delta S_T^\ominus$ can be experimentally found to be constant throughout the series. Then all partition functions should be so similar that even the changes in heat content function and vibrational zero-point energy should be practically constant, with the changes of potential energy ΔE being dominant [1,2]. The latter quantity does not depend on temperature, and can be related to theoretical concepts of organic chemistry such as polar effects, steric hindrance and ring strain, which are also temperature-independent [9]. Most frequently, LFERs are associated with polar effects [1,3].

The condition of constant entropy can be expressed by a double difference

$$\delta\,\Delta S_T^\ominus = 0 \tag{4}$$

where the operator δ [3] relates to the difference between a reaction and the standard reaction of the series. Alternatively, the reaction can be expressed in the isodesmic form [10]. Thus the isodesmic form for the standard series of the Hammett equation reads

$$X\mathrm{C_6H_4COOH} + \mathrm{C_6H_5COO^-} \rightarrow X\mathrm{C_6H_4COO^-} + \mathrm{C_6H_5COOH} \tag{5}$$

However, further investigations have revealed that eqn. (4) is seldom fulfilled. More frequently a less severe condition holds, termed the isokinetic relationship [9].

$$\delta\,\Delta H_T^\ominus = \beta\delta\,\Delta S_T^\ominus \tag{6}$$

When this equation is fulfilled, at least approximately, all the terms in eqns. (1) and (2) can be expected to be mutually proportional. The validity of eqn. (6) has been tested mostly using ionization equilibria [11], but the relations to the values of $\Delta(H_T^\ominus - H_0^\ominus)$ and $\Delta^{(q)}$ are not known.

The aim of the present work was to contribute to the investigation by calculating relevant thermodynamic quantities for several selected gas phase (mostly) isodesmic reactions. Reactions were selected on the basis of: (i) closest possible similarity to reactions popular in LFERs [1–3]; and (ii) availability of necessary data, namely $\Delta H_{298.15}^\ominus$ values from published thermochemical reports, and parameters for the construction of partition functions.

PROCEDURE AND RESULTS

The fluorinated benzenes were selected as the most suitable model. Altogether nine compounds were needed for the various reactions. Two of these were simple diatomic species, HF and F_2. The seven polyatomic species used are given in Table 1. The standard thermodynamical functions were calculated in terms of conventional [12,13] rigid-rotor and harmonic-oscillator (RRHO) approximation to the partition functions. Heats of formation at room temperature were taken from tabulated values [14] and reduced to $\Delta H_0^\ominus$ by application of the heat-content function $H_{298.15}^\ominus - H_0^\ominus$, determined by means of the RRHO partition functions. From these values it was possible to calculate the temperature dependences of the $\Delta H_T^\ominus$ and $\Delta G_T^\ominus$ functions. (A detailed description of the approximations to partition functions used is given in ref. 15.)

The structural and vibrational parameters of the two diatomic molecules, HF and F_2, were taken from tabulated data [16]. For the sake of consistency, the HO type vibrational partition function was used here, too, although it was possible to include correction for the vibrational anharmonicity. This correction is of little significance in our case. The structural parameters of other species were taken from ref. 17. The vibrational frequencies were taken from the following sources: benzene, ref. 18; fluorobenzene, ref. 19; *o*-, *m*- and *p*-difluorobenzene, refs. 20–22; toluene, ref. 23; *p*-fluorotoluene, ref. 22. These data sets are sufficiently homogeneous, and were preferred to earlier sources [24–26]. Nevertheless, the available data were obtained in the condensed phase, and were not corrected for anharmonicity effects. These two drawbacks are insurmountable at present, but make themselves felt only at higher temperatures [12,13]. Table 1 summarizes the calculated thermodynamical functions.

Two out of the nine species considered, namely toluene and *p*-fluorotoluene, show an internal rotation which can be approximated by a free rotation [27]. In the harmonic approximation, this intramolecular motion

TABLE 1

Ideal gas standard [a] heat content function [b] $H_T^\ominus - H_0^\ominus$ and entropy [b] $S_T^\ominus$ for the polyatomic members of the species under investigation

T (K)	Species	$(H_T^\ominus - H_0^\ominus)$ $/RT$	$S_T^\ominus/R$	Species	$(H_T^\ominus - H_0^\ominus)$ $/RT$	$S_T^\ominus/R$
100	$C_6H_6(g)$	4.036	25.718	$C_6H_5CH_3(g)$	4.433	29.642
200		4.582	29.189		5.731	34.385
298		5.724	32.354		7.389	38.626
300		5.751	32.420		7.426	38.713
400		7.257	35.783		9.356	43.040
600		10.359	42.421		13.193	51.409
800		13.048	48.471		16.516	58.995
1000		15.273	53.854		19.281	65.753
100	$C_6H_5F(g)$	4.157	28.612	p-$FC_6H_4CH_3(g)$	4.651	30.724
200		5.088	32.669		6.306	36.085
298		6.520	36.385		8.211	40.854
300		6.552	36.461		8.252	40.949
400		8.230	40.251		10.305	45.656
600		11.471	47.456		14.217	54.502
800		14.180	53.850		17.535	62.380
1000		16.377	59.456		20.270	69.331
100	o-$C_6H_4F_2(g)$	4.351	29.624	m-$C_6H_4F_2(g)$	4.296	29.621
200		5.690	34.355		5.621	34.291
298		7.379	38.621		7.334	38.556
300		7.415	38.706		7.370	38.642
400		9.231	42.905		9.208	42.852
600		12.568	50.635		12.570	50.604
800		15.280	57.349		15.292	57.329
1000		17.445	63.164		17.458	63.150
100	p-$C_6H_4F_2(g)$	4.347	28.939			
200		5.663	33.630			
298		7.377	37.915			
300		7.414	38.001			
400		9.249	42.221			
600		12.604	49.980			
800		15.318	56.707			
1000		17.480	62.528			

[a] Standard state: an ideal gas at 1 atm = 101 325 Pa pressure.

[b] Reduced, dimensionless representation; R denotes the gas constant.

corresponds to a torsional vibration with frequency ω_{tors} which cannot be readily determined from spectroscopic observations [22,23]. We have chosen an approach in which the missing frequency is obtained by fitting to the observed values of standard entropy at one selected temperature [23,25]. With respect to the format of the other frequency values, the fitted ω_{tors}

TABLE 2

Comparison of observed and calculated entropy data for fitted torsional-frequency approach

Species [a]	T (K)	ω_{tors} (cm^{-1})	$S_T^\ominus$ ($\text{J K}^{-1}\text{ mol}^{-1}$)	
			Obs. [b]	Calcd.
$C_6H_5CH_3$(g)	298.15	184	321.2 ± 0.6	321.2
p-$CH_3C_6H_4F$(g)	347.14	160	358.7 ± 0.8	359.1

[a] Standard state: an ideal gas at 1 atm = 101 325 Pa pressure.

[b] Observed standard [a] entropy term for toluene [23] and p-fluorotoluene [25] with estimated accuracy uncertainty.

value was also rounded off to 1 cm^{-1}. Table 2 presents the results of this fitting.

Recently calculated thermodynamic terms available in the literature agree well with the values used in the present work. This is not surprising for the data on the two diatomic species [16] (and the terms are therefore not included in Table 1). However, results for toluene [28] are also in good agreement. (In ref. 28, the internal rotation was treated as a hindered rotation.) Finally, let us comment on the role of benzene ring geometry. For the purposes of the present work, hexagonal symmetry of the ring [17] has been adopted throughout. Deviations from this idealized geometry have been observed [29], but a complete description is not available for the compounds considered here. The effects of the geometry distortion were tested on C_6H_5F, using bond angles [29]. Application of the distorted ring geometry lowers the entropy term $S_T^\ominus/R$ by about 0.006, which has no significance in the present connection.

DISCUSSION

On the basis of the data given in Table 1, one can calculate ΔE and $\Delta H_0^\ominus$ and the temperature dependences of $\Delta H_T^\ominus$ and $\Delta G_T^\ominus$ for various reactions within a relatively broad temperature interval (see Table 3). Of course, not all the reactions will be independent, since they can be added and subtracted mutually. We shall consider the reactions in two separate groups: non-isodesmic reactions (reactions (7)–(11)), which can be classified as fluorination with fluorine; and isodesmic fluorination reactions with fluorobenzene as agent (reactions (12)–(15)). Some of the isodesmic reactions can be classified as redistribution reactions. Other isodesmic reactions involve isomerization (e.g. reaction (16)). Only some of the reactions among those considered can be achieved by using a catalyst, but they would never proceed smoothly. This fact, related to the reaction rate, is not relevant to the present work, in

TABLE 3

Standard[a] changes of Gibbs energy $\Delta G_T^\ominus$, enthalpy $\Delta H_T^\ominus$ and enthalpy at absolute zero $\Delta H_0^\ominus$, and potential-energy changes ΔE along five independent reactions with fluorinated benzenes

Reaction	ΔE (kJ mol^{-1})	$\Delta H_0^\ominus$ (kJ mol^{-1})	T (K)	$\Delta H_T^\ominus$ (kJ mol^{-1})	$\Delta G_T^\ominus$ (kJ mol^{-1})
$C_6H_5F(g)+F_2(g)$ $\rightarrow$ p-$C_6H_4F_2(g)+HF(g)$	−462.48	−463.70	100	−463.62	−461.05
			200	−462.84	−458.73
			298	−461.79	−456.94
			300	−461.77	−456.91
			400	−460.80	−455.43
			600	−459.48	−453.06
			800	−458.78	−451.05
			1000	−458.47	−449.16
$2C_6H_5F(g)$ $\rightarrow$ o-$C_6H_4F_2(g)+C_6H_6(g)$	20.99	21.39	100	21.46	23.02
			200	21.55	24.53
			298	21.55	26.00
			300	21.55	26.02
			400	21.49	27.53
			600	21.32	30.58
			800	21.18	33.69
			1000	21.09	36.82
$2C_6H_5F(g)$ $\rightarrow$ m-$C_6H_4F_2(g)+C_6H_6(g)$	5.63	6.02	100	6.04	7.61
			200	6.07	9.16
			298	6.07	10.67
			300	6.07	10.70
			400	6.04	12.25
			600	5.96	15.38
			800	5.89	18.52
			1000	5.83	21.69
$2C_6H_5F(g)$ $\rightarrow$ p-$C_6H_4F_2(g)+C_6H_6(g)$	8.45	8.68	100	8.74	10.87
			200	8.79	12.98
			298	8.83	15.02
			300	8.83	15.07
			400	8.83	17.14
			600	8.78	21.31
			800	8.72	25.49
			1000	8.67	29.69
$C_6H_5CH_3(g)+C_6H_5F(g)$ $\rightarrow$ p-$FC_6H_4CH_3(g)+C_6H_6(g)$	−0.21	1.40	100	1.48	2.99
			200	1.51	4.48
			298	1.46	5.93
			300	1.46	5.96
			400	1.32	7.48
			600	0.96	10.64
			800	0.65	13.92
			1000	0.44	17.26

[a] Standard state: an ideal gas at 1 atm = 101 325 Pa pressure.

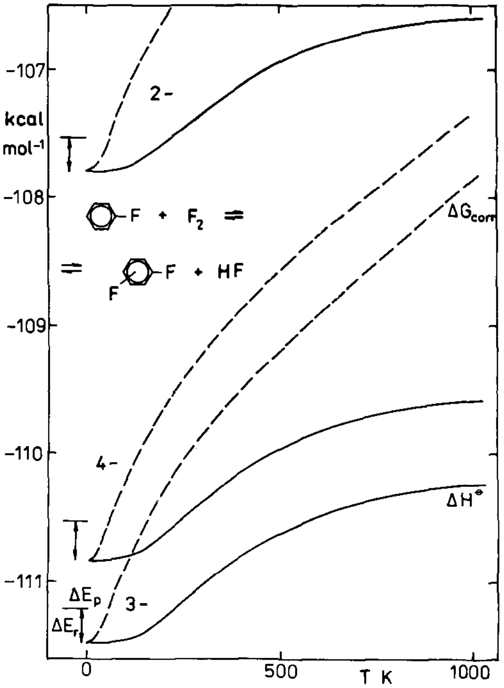

Fig. 1. Temperature dependence of thermodynamic functions of several simple reactions: fluorination of fluorobenzenes.

which our interest is restricted to equilibria.

$C_6H_6(g) + F_2(g) \rightarrow C_6H_5F(g) + HF(g)$ (7)

$C_6H_5F(g) + F_2(g) \rightarrow (o,m,p)\text{-}C_6H_4F_2(g) + HF(g)$ o- (8)

m- (9)

p- (10)

$C_6H_5CH_3(g) + F_2(g) \rightarrow p\text{-}FC_6H_4CH_3(g) + HF(g)$ (11)

$2C_6H_5F(g) \rightarrow (o,m,p)\text{-}C_6H_4F_2 + C_6H_6(g)$ o- (12)

m- (13)

p- (14)

$C_6H_5CH_3(g) + C_6H_5F(g) \rightarrow p\text{-}FC_6H_4CH_3(g) + C_6H_6(g)$ (15)

$m\text{-}C_6H_4F_2(g) \rightarrow p\text{-}C_6H_4F_2(g)$ (16)

The results obtained were very similar within the two groups of reactions, isodesmic and non-isodesmic. For this reason, we present graphically only the results of some typical reactions (Figs. 1 and 2). Let us first compare the terms ΔE and $\Delta H_0^\ominus$ for non-isodesmic ((8)–(10)) and isodesmic ((12)–(14)) reactions (Figs. 1 and 2, Table 3). The change in residual energy is not

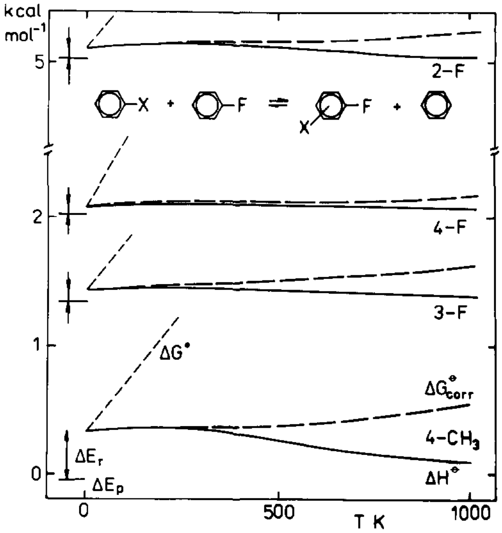

Fig. 2. Temperature dependence of thermodynamic functions of several isodesmic reactions: fluorination of benzene derivatives with fluorobenzene as agent.

negligible in Fig. 1, but is of little significance in Fig. 2. For the purpose of extracting $\Delta H_0^\ominus$ or ΔE values from observable data, the isodesmic reactions appear to be preferable, since they are likely to fulfil the relation $\Delta E \approx \Delta H_0^\ominus$.

Of course, the observed $\Delta H_T^\ominus$ or $\Delta G_T^\ominus$ values are always measured at non-zero temperature, so that an extrapolation to zero temperature appears to be necessary in order to obtain the $\Delta H_0^\ominus$ and/or ΔE terms. In correlation analysis it is usual [1] to unify $\Delta G_T^\ominus$ by subtracting the part of the entropy which is due purely to the symmetry numbers of individual reaction components. Thus

$$\Delta G_{\text{corr}}^\ominus = \Delta G_T^\ominus - RT \sum \ln(\sigma_n) \tag{17}$$

where σ and n represent external and internal symmetry numbers, respectively, or $\Pi(\sigma n)$, the so-called statistical factor. Hence, one works with the quantities $\Delta G_T^\ominus - RT \ln \sigma$. Figure 1 shows that for the non-isodesmic reactions, the temperature courses of the $\Delta G_{\text{corr}}^\ominus$ and $\Delta H_T^\ominus$ functions differ considerably, even at low temperatures. In addition, extrapolation would be made difficult by the distinctly non-linear course of these curves. The situation with the isodesmic reactions is substantially more favourable (Fig. 2). If the correction factor $RT \ln \sigma$ is used, then the $\Delta H_0^\ominus$ term is approximated equally well by the enthalpy or the Gibbs energy terms for temperatures up to e.g. 500 K.

Reaction (15) in Fig. 2, involving an almost non-polar substituent, CH_3, differs quantitatively from the others since the similarity of the values of $\Delta H_0^\ominus$ and ΔE is fulfilled less satisfactorily; the other features found for the isodesmic reactions (12)–(14) are valid in this case, too. It should be noted that this small model gas phase reaction series does not fulfil the preconditions of the Hammett equation, but the one *ortho* substituent present does not cause any deviation.

If a correlation analysis requires that the temperature-dependent terms $\Delta G_T^{\ominus}$ and/or $\Delta H_T^{\ominus}$ be replaced by the temperature-independent quantities $\Delta H_0^{\ominus}$ or ΔE, then $\Delta H_0^{\ominus}$ is certainly more convenient, being more easily obtainable. Generally, ΔE cannot be determined solely from the temperature courses of standard thermodynamical functions. In addition, there are certain theoretical factors which favour the use of $\Delta H_0^{\ominus}$. Although current numerical quantum chemistry has extensively adopted the potential energy term, this is—to a certain extent–an artifact resulting from the Born–Oppenheimer approximation [30]. It is this approximation which can be considered a theoretical justification of the concepts of potential hypersurface or molecular structure [31,32]. If quantum chemistry could avoid this approximation, then the quantities of central importance would be the total wave function and the ground-state energy term, i.e. $\Delta H_0^{\ominus}$. From this rigorous theoretical standpoint, the ΔE term can be considered an auxiliary partial quantity.

Of course, in contemporary quantum chemistry the numerical term most readily accessible is the potential energy change along a chemical reaction ΔE, while the terms $\Delta H_0^{\ominus}$, $\Delta H_T^{\ominus}$ and $\Delta G_T^{\ominus}$ require longer calculations and are rarely evaluated. In any case, the quantum chemical results which are available at present for the reactions considered in the present work [33] are insufficiently accurate.

CONCLUSIONS

Our approach was purely empirical in character, as is usual in correlation analysis; and we have followed only one model reaction series. Nevertheless, we believe that the following conclusions, or mere postulates, may possess a broader validity. We have confirmed the merit and importance of isodesmic reactions by a new line of reasoning. We have confirmed the necessity of symmetry corrections when comparing reactivities across several reactions. Of the temperature-independent reactivity terms, $\Delta H_0^{\ominus}$ is preferable to ΔE as a basis for chemical theories.

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REFERENCES

1 O. Exner, Correlation Analysis of Chemical Data, Plenum, New York, 1988.
2 L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, New York, 1940.
3 J.E. Leffler and E. Grunwald, Rates and Equilibria of Chemical Reactions, Wiley, New York, 1963.
4 L.G. Hepler, J. Am. Chem. Soc., 85 (1983) 3089.
5 G.C. Schatz, Ann. Rev. Phys. Chem., 39 (1988) 317.
6 M. Wolfsberg, A.A. Massa and J.W. Pyper, J. Chem. Phys., 53 (1970) 3138.
7 J. Bron and M. Wolfsberg, J. Chem. Phys., 57 (1972) 2862.
8 M. Wolfsberg, Adv. Chem. Ser., 89 (1969) 185.
9 O. Exner, Progr. Phys. Org. Chem., 10 (1973) 411.
10 W.J. Hehre, R. Ditchfield, L. Radom and J.A. Pople, J. Am. Chem. Soc., 92 (1970) 4796.
11 O. Exner, Coll. Czech. Chem. Commun., 40 (1975) 2762.
12 G.J. Janz, Thermodynamic Properties of Organic Compounds, Academic Press, New York, 1967.
13 S.G. Frankiss and J.H.S. Green, Chem. Thermodyn., 1 (1973) 268.
14 D.R. Stull, E.F. Westrum, Jr., and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
15 Z. Slanina, Contemporary Theory of Chemical Isomerism, Academia and Reidel, Prague and Dordrecht, 1986.
16 D.R. Stull and H. Prophet (Eds.), JANAF Thermochemical Tables, Natl. Bur. Stand., Washington, 2nd edn., 1971.
17 L.E. Sutton (Ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London, 1958.
18 T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Part 1, Natl. Bur. Stand., Washington, 1967.
19 D.W. Scott, J.P. McCullough, W.D. Good, J.F. Messerly, R.E. Pennington, T.C. Kincheloe, I.A. Hossenlopp, D.R. Douslin and G. Waddington, J. Am. Chem. Soc., 78 (1956) 5457.
20 J.H.S. Green, Spectrochim. Acta, Part A, 26 (1970) 1913.
21 J.H.S. Green, Spectrochim. Acta, Part A, 26 (1970) 1523.
22 J.H.S. Green, Spectrochim. Acta, Part A, 26 (1970) 1503.
23 D.W. Scott, G.B. Guthrie, J.F. Messerly, S.S. Todd, W.T. Berg, I.A. Hossenlopp and J.P. McCullough, J. Phys. Chem., 66 (1962) 911.
24 D.H. Whiffen, J. Chem. Soc., (1956) 1350.
25 D.W. Scott, J.F. Messerly, S.S. Todd, I.A. Hossenlopp, D.R. Douslin and J.P. McCullough, J. Chem. Phys., 37 (1962) 867.
26 J.H.S. Green, W. Kynaston and H.M. Paisley, J. Chem. Soc., (1963) 473.
27 J.P. Lowe, Progr. Phys. Org. Chem., 6 (1968) 1.
28 J. Chao, K.R. Hall and J.-M. Yao, Thermochim. Acta, 72 (1984) 323.
29 A. Domenicano and P. Murray-Rust, Tetrahedron Lett., (1979) 2283.
30 M. Born and R. Oppenheimer, Ann. Phys. 4, 84 (der ganzen Reihe 389) (1927) 457.
31 R.G. Woolley, Adv. Phys., 25 (1976) 27.
32 R.G. Woolley and B.T. Sutcliffe, Chem. Phys. Lett., 45 (1977) 393.
33 A. Pross and L. Radom, Progr. Phys. Org. Chem., 13 (1981) 1.