

S—H Bond Dissociation Enthalpies in *para*- and *meta*-Substituted Thiophenols: Correlation with Thiophenolic C—S Bond Length

Lenka Rottmannová, Adam Vagánek, Ján Rimarčík, Vladimír Lukeš, Erik Klein

*Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology,
Radlinského 9, SK-812 37 Bratislava, Slovakia
jan.rimarcik@stuba.sk*

Abstract: For mono-substituted anilines, phenols, and thiophenols it has been found that N—H, O—H and S—H bond dissociation enthalpies (BDE) depend on Hammett constants approximately linearly. For substituents placed in *meta* position, linearity of found dependences is usually considerably worse in comparison to *para*-substituted molecules. Therefore, their applicability for prediction of changes in BDE using substituent Hammett constant may be limited. In this work, we have found that the length of thiophenolic C—S bond, $R(\text{C—S})$, or its shortening after hydrogen atom abstraction, $\Delta R(\text{C—S})$, represent suitable descriptors of substituent induced changes in S—H BDE. For fifteen studied *meta*-substituted thiophenols, these geometry descriptors correlate with S—H BDEs considerably better than Hammett constants.

Keywords: DFT/B3LYP, Bond dissociation enthalpy, Thiophenol, Substituent effect, C—S bond length

Introduction

Sulfur-centered radicals play an important role in variety of chemical processes: organic synthesis, biochemistry, atmospheric chemistry (Griller et al. 1990; Halliwell et al. 1989; Kuwae and Kamachi 1989). Thiophenol and its derivatives are employed also in the synthesis and stabilization of polymers (Griller et al. 1990; Halliwell et al. 1989; Kuwae and Kamachi 1989).

In the case of thiophenol (ArSH) and its derivatives, hydrogen atom transfer (HAT) mechanism of thiophenoxy radical (ArS[•]) formation



is intensively studied in the terms of S—H bond dissociation enthalpy, BDE (Zhu et al. 1997; Bordwell et al. 1994; Borges dos Santos et al. 2002; Chandra et al. 2003; Cabral do Couto et al. 2006; McMillen and Golden 1982; Klein et al. 2006; Rimarčík et al. 2011). The study of the substituent effect on BDE is important for the comparison of reactions differing only in the substitution. The Hammett equation (and its extended forms) is widely applied for the study and interpretation of organic reactions. Hammett constants σ_m (for a substituent in *meta* position) and σ_p (for a substituent in *para* position) obtained from ionization of organic acids in solutions can frequently successfully predict equilibrium and rate constants for a variety of families of reactions (Hansch et al. 1991; Krygowski and Stępień 2005). Usually, Hammett constants correlate with the changes in N—H, O—H and S—H BDEs for *para*-substituted

anilines, phenols or thiophenols well (Klein and Lukeš 2006; Klein et al. 2006; Rimarčík et al. 2011; Gomes et al. 2004). On the other hand, correlations found for *meta*-substituted phenols (Klein and Lukeš 2006) and thiophenols (Rimarčík et al. 2011) were worse, because individual points were more scattered along the regression lines. Gomes et al. (2004) studied 10 anilines with substituents in *para* and *meta* position using (RO)B3LYP/6-311+G(2d,2p)//(U)B3LYP/6-31G* method to obtain N—H BDEs. For *meta*-substituted anilines, linearity of $\text{BDE} = f(\sigma_m)$ dependence is poor, correlation coefficient reached only the value of 0.85. Besides, the published values of a Hammett constant for a substituent may vary in a quite wide range. For strong electron-donating NMe₂ group, published σ_p values lie in the range from -0.24 to -0.83 (Hansch et al. 1991; Krygowski and Stępień 2005; Pytela 1994). Therefore, several attempts to find an alternative substituent effect descriptor were made previously. Brinck et al. (1997) calculated BDEs of 9 *para*-substituted phenols. They did not find any indication that O—H BDE can be related to the properties of the O—H bond. Zhang et al. (2001) found that computed O—H bond parameters, such as bond length, O—H charge difference, O—H Mulliken population and O—H bond stretching force constant of 17 substituted phenols correlated with experimentally determined BDEs poorly. In our previous work (Klein and Lukeš 2006), we have found that O—H BDEs in phenols are actually linearly dependent on the phenolic C—O bond length, $R(\text{C—O})$. Even better linearity was found between BDE and the shortening

of C—O bond after hydrogen atom splitting-off, $\Delta R(\text{C—O})$ (Klein and Lukeš 2006). Very recently, Najafi et. al. (2011) found that in the case of 20 *meta*-substituted chromans (chroman unit is present in tocopherols), calculated BDEs can be correlated with the lengths of phenolic C—O bond in the studied molecules, too.

The aim of this work is to ascertain, whether this concept can be also applied for thiophenols, i.e. to find the dependence of S—H BDE on C—S bond length and $\Delta R(\text{C—S})$. In general, these dependences can be employed in prediction of S—H BDEs for *para*- and *meta*-substituted thiophenols using experimentally determined or calculated bond lengths. Besides, obtained results will be compared with those found for the phenols with the same group of 15 substituents placed in

para and *meta* positions (Klein and Lukeš 2006). Therefore, in this work identical computational approach was used.

Computational details

All calculations were performed using the Gaussian 03 program package (Frisch et al. 2003). The geometry of each compound and corresponding radical was optimized using DFT method with the B3LYP (Becke 1993) functional without using any constraints during geometry optimization (energy cut-off of 10^{-5} kJ mol⁻¹, final RMS energy gradient under 0.01 kJ mol⁻¹ Å⁻¹). For the species having more conformers, all conformers were investigated. Calculations were performed in 6-311++G** basis set (Binkley et al. 1980). The optimized structures

Tab. 1. Calculated B3LYP/6-311++G** gas-phase bond lengths, relative bond dissociation enthalpies of studied thiophenols and Hammett constants.

Substituent	$R(\text{S—H})/\text{Å}$	$R(\text{C—S})/\text{Å}$	$R(\text{C—S}^*)/\text{Å}$	$\Delta R(\text{C—S})/\text{Å}$	$\Delta\text{BDE}/\text{kJ mol}^{-1}$	$\sigma_{\text{m,p}}^{\text{a}}$
-	1.34724	1.78730	1.72812	0.05918	0	-
<i>p</i> -NMe ₂	1.35224	1.80075	1.71595	0.08480	-25	-0.63 ^b
<i>p</i> -NH ₂	1.35196	1.80163	1.71673	0.08490	-21	-0.66
<i>p</i> -OH	1.35139	1.80280	1.72075	0.08205	-12	-0.37
<i>p</i> -MeO	1.35136	1.80238	1.72032	0.08206	-14	-0.27
<i>p-tert</i> -Bu	1.34733	1.78760	1.72437	0.06323	-5	-0.20
<i>p</i> -Me	1.34728	1.78900	1.72496	0.06404	-5	-0.17
<i>p</i> -Ph	1.34731	1.78583	1.72221	0.06362	-5	-0.01
<i>p</i> -F	1.34721	1.79108	1.72463	0.06645	-5	0.06
<i>p</i> -Cl	1.34710	1.78501	1.72435	0.06066	-2	0.23
<i>p</i> -Br	1.34719	1.78528	1.72442	0.06086	-2	0.23
<i>p</i> -MeCO ^c	1.35891	1.78111	1.72603	0.05508	7	0.50
<i>p</i> -CF ₃	1.34740	1.78078	1.72909	0.05169	8	0.54
<i>p</i> -CN ^c	1.35873	1.78044	1.72554	0.05490	7	0.66
<i>p</i> -MeSO ₂	1.34746	1.77945	1.73026	0.04919	10	0.72
<i>p</i> -NO ₂	1.34742	1.77528	1.72808	0.04720	13	0.78
<i>m</i> -NH ₂	1.34734	1.78801	1.72786	0.06015	-1	-0.16
<i>m</i> -NMe ₂	1.34741	1.79088	1.72913	0.06175	-3	-0.16
<i>m-tert</i> -Bu	1.34715	1.78908	1.72739	0.06169	-2	0.10
<i>m</i> -Me	1.34734	1.78803	1.72716	0.06087	-1	0.12
<i>m</i> -Ph	1.34720	1.78782	1.72839	0.05943	0	0.12
<i>m</i> -OH	1.34689	1.78701	1.72631	0.06070	-1	-0.07
<i>m</i> -MeO	1.34694	1.78821	1.72694	0.06127	-2	0.06
<i>m</i> -F	1.34712	1.78468	1.72800	0.05668	4	0.16
<i>m</i> -Cl	1.34717	1.78543	1.72769	0.05774	3	0.34
<i>m</i> -MeCO	1.34731	1.78772	1.72821	0.05951	0	0.39
<i>m</i> -Br	1.34717	1.78554	1.72796	0.05758	3	0.36
<i>m</i> -CF ₃	1.34725	1.78342	1.72877	0.05465	5	0.43
<i>m</i> -CN	1.34727	1.78344	1.73020	0.05324	6	0.56
<i>m</i> -MeSO ₂	1.34730	1.78346	1.72935	0.05411	6	0.60
<i>m</i> -NO ₂	1.34711	1.78264	1.73033	0.05231	7	0.71

^a(Hansch et al. 1991), ^b(Pytela 1994), ^cBP86/6-311++G** results.

were confirmed to be real minima by frequency analysis (no imaginary frequency).

Results and discussion

S—H BDEs of 30 mono-substituted thiophenols employed in this work were taken from our previous work (Rimarčík et al. 2011), the bond lengths of studied thiophenols in Table 1 were not previously published. Calculated B3LYP/6-311++G** S—H and C—S bond lengths, denoted as $R(\text{S—H})$ and $R(\text{C—S})$, in studied thiophenol molecules, as well as C—S bond lengths in corresponding thiophenoxy radicals, $R(\text{C—S}^\bullet)$, are compiled in Table 1. Shortening of C—S bonds after hydrogen atom abstraction, $\Delta R(\text{C—S})$, has been calculated as follows

$$\Delta R(\text{C—S}) = R(\text{C—S}) - R(\text{C—S}^\bullet) \quad (2)$$

The last but one column of Table 1 contains relative BDE values, denoted as ΔBDE . These were obtained as the difference in BDEs of substituted (X—ArSH) and non-substituted thiophenol (ArSH)

$$\Delta\text{BDE} = \text{BDE}(\text{X—ArSH}) - \text{BDE}(\text{ArSH}) \quad (3)$$

In (Rimarčík et al. 2011), for non-substituted thiophenol, gas-phase B3LYP S—H BDE of 316 kJ mol^{-1} was obtained. Results provided by the B3LYP/6-311++G** approach were in good agreement with available experimental values (Rimarčík et al. 2011), although in the case of *para*-substituted thiophenols with electron withdrawing MeCO and CN groups unexpectedly high BDEs and ΔBDE s were obtained. The two BDEs were by 30 kJ mol^{-1} higher than one could anticipate from the observed trends in BDEs. In the two thiophenoxy radicals, B3LYP provided C—S bond lengths significantly longer in comparison to the rest of studied thiophenoxy radicals, too. Therefore, in this paper, for *p*-MeCO and *p*-CN substituted thiophenols, we employed results from BP86/6-311++G** calculations (Rimarčík et al. 2011). For these two molecules, BP86/6-311++G** method provided BDEs corresponding to the rest of computed as well as to experimentally determined values significantly better than the two B3LYP results.

Data in Table 1 show that the electron-donating groups cause an elongation, while electron-withdrawing ones are connected with a shortening of C—S bond in comparison to non-substituted thiophenol. Although the character of substituent influences the length of S—H bond, no correlation between S—H bond length and Hammett constants, σ_p and σ_m , was found. On the other hand, $R(\text{C—S}) = f(\sigma_p)$ and $R(\text{C—S}) = f(\sigma_m)$ dependences can be considered roughly linear. Using linear regression,

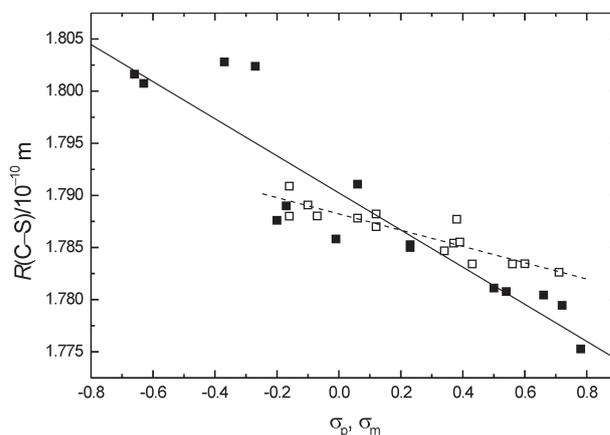


Fig. 1. Dependence of $R(\text{C—S})$ on σ_p (solid squares, solid line) and σ_m (open squares, dashed line).

Fig. 1, we have obtained these equations

$$R(\text{C—S})/\text{Å} = 1.790 - 0.017 \times \sigma_p \quad (4)$$

$$R(\text{C—S})/\text{Å} = 1.788 - 0.0078 \times \sigma_m \quad (5)$$

with correlation coefficients values of -0.921 (*para*) and -0.908 (*meta*). In *para*-substituted thiophenols, points for OH and MeO groups apparently do not follow the observed trend. In these molecules, C—S bonds are the longest.

After removal of the two points from linear regression, for remaining 13 groups, we obtain linear dependence as follows

$$R(\text{C—S})/\text{Å} = 1.789 - 0.015 \times \sigma_p \quad (6)$$

with correlation coefficient value of -0.955 . Similar linearity was also found for $\Delta R(\text{C—S}) = f(\sigma_p)$ and $\Delta R(\text{C—S}) = f(\sigma_m)$ dependences. In the case of phenols, analogous dependences showed better linearity, the two correlation coefficients values were in absolute value higher than 0.950. This has confirmed that the phenolic C—O bond length represents a simple and a reliable descriptor of the substituent effect on O—H BDE especially for the *meta*-substituted phenols, where the linearity of $\Delta\text{BDE} = f(\sigma_m)$ dependence was worse and individual points were considerably more scattered along the regression line (Klein and Lukeš 2006). For the *para*-substituted phenols, σ_p and $R(\text{C—O})$ represented identically reliable descriptor of substituent induced changes in O—H BDE. The linear BDE = $f(R(\text{C—O}))$ dependence found for the *para*-substituted phenols gave reliable estimates of BDEs also for four tocopherols and seven chromans (Klein et al. 2007). It may indicate a wider applicability of the found dependence.

In the case of thiophenols, linear regression of S—H ΔBDE on $R(\text{C—S})$ provided the following

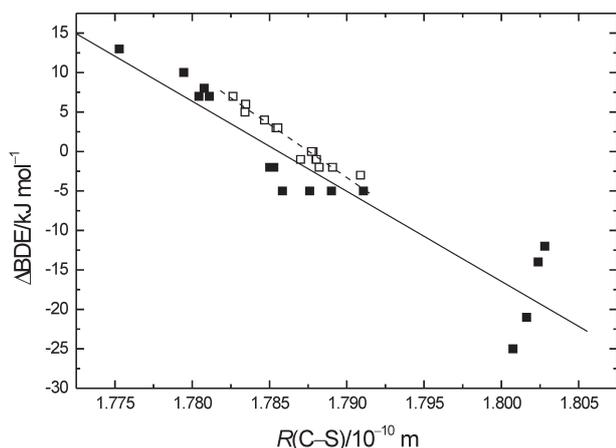


Fig. 2. Dependence of gas-phase ΔBDE on $R(\text{C—S})$ for *para*- (solid squares, solid line) and *meta*-substituted (open squares, dashed line) thiophenols.

equations

$$\Delta\text{BDE}/\text{kJ mol}^{-1} = 2000 - 1100 \times R(\text{C—S})/\text{\AA}, \text{ (para)} \quad (7)$$

$$\Delta\text{BDE}/\text{kJ mol}^{-1} = 2400 - 1350 \times R(\text{C—S})/\text{\AA}, \text{ (meta)} \quad (8)$$

Fig. 2 shows that the C—S bond lengths in *para*-substituted thiophenols bearing four strongest electron-donating groups, i.e. NH_2 , NMe_2 , OH and MeO , are close to each other, while their ΔBDE s are in relatively wide, 13 kJ mol^{-1} , range. This results in worse linearity of $\Delta\text{BDE} = f(R(\text{C—S}))$ dependence. The correlation coefficient reached only the value of -0.936 . On the other hand, for the *meta*-substituted thiophenols, correlation coefficient reached the value of -0.975 . For the sake of easy comparison, we have plotted $\Delta\text{BDE} = f(\sigma_p)$ and $\Delta\text{BDE} = f(\sigma_m)$ dependences in Fig. 3. We can conclude that Hammett-type dependence describes substituent effect better than

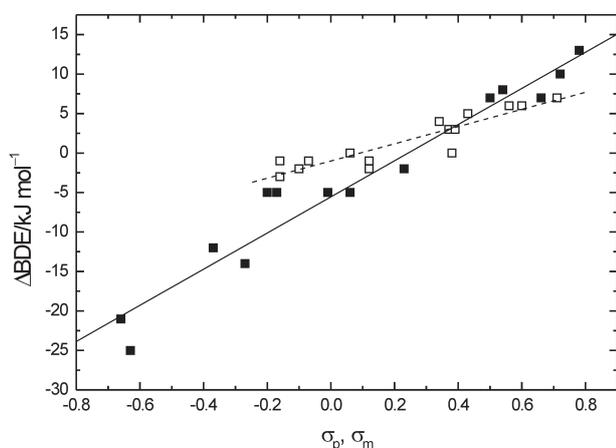


Fig. 3. Dependence of gas-phase S—H ΔBDE on σ_p (solid squares, solid line) and σ_m (open squares, dashed line) in thiophenols.

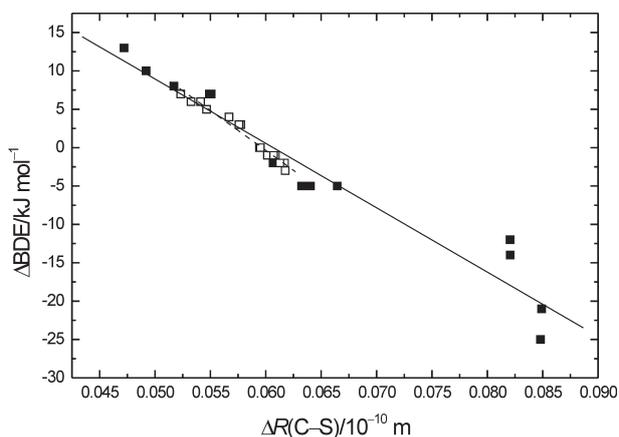


Fig. 4. Dependence of gas-phase ΔBDE on $\Delta R(\text{C—S})$ for *para*- (solid squares, solid line) and *meta*-substituted (open squares, dashed line) thiophenols.

C—S bond length for *para*-substituted thiophenols (Fig. 3). However, for *meta*-substituted thiophenols, $\Delta\text{BDE} = f(R(\text{C—S}))$ in Fig. 2 shows considerably better linearity in comparison to $\Delta\text{BDE} = f(\sigma_m)$ dependence in Fig. 3. Correlation coefficient values for $\Delta\text{BDE} = f(R(\text{C—S}))$ and $\Delta\text{BDE} = f(\sigma_m)$ dependences are -0.975 and -0.918 , respectively. Hence, equation 8 seems to be suited for fast estimations of S—H BDEs of *meta*-substituted thiophenols from the C—S bond length.

For phenols, shortening of C—O bond after homolytic dissociation of O—H bond represented an appropriate descriptor of substituent effect on BDE, too (Klein and Lukeš 2006). Figure 4 confirms that such geometry parameter can be also employed for thiophenols. The following equations were found using linear fits of data shown in Fig. 4

$$\Delta\text{BDE}/\text{kJ mol}^{-1} = 50 - 840 \times \Delta R(\text{C—S})/\text{\AA}, \text{ (para)} \quad (9)$$

$$\Delta\text{BDE}/\text{kJ mol}^{-1} = 62 - 1040 \times \Delta R(\text{C—S})/\text{\AA}, \text{ (meta)} \quad (10)$$

The found values of correlation coefficients are -0.967 (*para*) and -0.985 (*meta*). Fig. 4 clearly indicates that points for *p*-MeO and *p*-OH groups do not follow the overall trend due to the large values of $\Delta R(\text{C—S})$ as it was already pointed out for $R(\text{C—S})$. If we omit the two points from the regression, the correlation coefficient reaches the value of -0.988 and the regression line descent is steeper, similarly to *meta*-substituted thiophenols. Therefore, we have performed the linear regression for all studied thiophenols with exception of *p*-MeO and *p*-OH substituted ones. The overall dependence (for 28 thiophenols)

$$\Delta\text{BDE}/\text{kJ mol}^{-1} = 58 - 960 \times \Delta R(\text{C—S})/\text{\AA} \quad (11)$$

shows excellent linearity with the correlation coef-

ficient of -0.989 . In contrast to Hammett-type dependences, just one equation is able to describe substituent induced changes in BDE for both, *para*- and *meta*-substituted thiophenols. Obtained equation 11 can be used for Δ BDE or BDE estimations from the C—S bond lengths in a thiophenol molecule and corresponding thiophenoxy radical.

Conclusion

In this work, we have found that C—S bond length or its shortening, $\Delta R(\text{C—S})$, after hydrogen atom abstraction for both, *meta*- and *para*-substituted thiophenols represents a suitable descriptor of changes in S—H BDE induced by substituents with various electron-donating and electron-withdrawing character. In the case of *meta*-substituted thiophenols, the two geometry parameters correlate with BDEs significantly better than Hammett σ_m constants. Moreover, $\Delta R(\text{C—S})$ is capable to describe substituent effect of various electron-donating and electron-withdrawing groups regardless of substituent position, while the Hammett-type dependences for *meta*- and *para*-substituted anilines, phenols and thiophenols are usually treated separately. The published results for *meta*-substituted chromans (Najafi et al. 2011), as well as our results for anilines with 20 substituents in *para* and *meta* position (Vagánek, to be published) indicate that C—S, C—O and C—N bond lengths or their shortening after hydrogen atom abstraction linearly correlate with S—H, O—H and N—H BDEs in thiophenols, phenols and anilines, respectively. This fact can be useful also for antioxidants action study, because the three families of aromatic compounds represent the model compounds of primary antioxidants (Zhu et al. 1997; Rimarčík et al. 2011; Klein and Lukeš 2006; Klein et al. 2007; Gugumus 1990).

Acknowledgement

This work has been supported by the Slovak Grant Agency VEGA (Project No. 1/0137/09).

References

- Becke AD (1993) J. Chem. Phys. 98: 5648–5652.
- Binkley JS, Pople JA, Hehre WJ (1980) J. Am. Chem. Soc. 102: 939–947.
- Bordwell FG, Zhang X-M, Satish AV, Cheng J-P (1994) J. Am. Chem. Soc. 116: 6605–6610.
- Borges dos Santos RM, Muralha VSF., Correia CF, Guedes RC, Costa Cabral BJ, Simões JAM (2002) J. Phys. Chem. A 106: 9883–9889.
- Brinck T, Haeblerlein M, Jonsson M (1997) J. Am. Chem. Soc. 119: 4239–4244.
- Cabral do Couto P, Costa Cabral BJ, Simões JAM (2006) Chem. Phys. Lett. 421: 504–507.
- Chandra AK, Nam P-C, Nguyen MT (2003) J. Phys. Chem. A 107: 9182–9188.
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Jr., Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada V, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain M-C, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) GAUSSIAN 03, Revision A.1, Gaussian, Inc., Pittsburgh.
- Gomes JRB, Ribeiro da Silva MDMC, Ribeiro da Silva MAV (2004) J. Phys. Chem. A 108: 2119–2130.
- Griller D, Martinho Simões JA, Wayner DDM (1990). In: Chatgililoglu C, Asmus K-D (Eds.), Sulfur-Centered Reactive Intermediates in Chemistry and Biology, Plenum Press, New York.
- Gugumus F (1990) Oxidation inhibition in organic materials, Vol. 1. CRC Press, Boca Raton.
- Halliwel B, Gutteridge JMC (1989) Free Radicals in Biology and Medicine. Oxford University Press, Oxford.
- Hansch C, Leo A, Taft RW (1991) Chem. Rev. 91: 165–195.
- Klein E, Lukeš V (2006) J. Mol. Struct. (Theochem) 767: 43–50.
- Klein E, Lukeš V, Cibulková Z, Polovková J (2006) J. Mol. Struct. (Theochem) 758: 149–159.
- Klein E, Lukeš V, Ilčin M (2007) Chem. Phys. 336: 51–57.
- Krygowski TM, Stepień BT (2005) Chem. Rev. 105: 3482–3512.
- Kuwae Y, Kamachi M (1989) Bull. Chem. Soc. Jpn. 62: 2474–2479.
- McMillen DF, Golden DM (1982) Ann. Rev. Phys. Chem. 33: 493–532.
- Najafi M, Nazarpour E, Mood KH, Zahedi M, Klein E (2011) Comput. Theor. Chem. 965: 114–122.
- Pankratov AN, Shalabai AV (2004) J. Struct. Chem. 45: 756–761.
- Pytela O (1994) Coll. Czech. Chem. Commun. 381: 159–174.
- Rimarčík J, Lukeš V, Klein E, Rottmannová L (2011) Comput. Theor. Chem. 967: 273–283.
- Vagánek A, Rimarčík J, Lukeš V, Klein E (2012) to be published.
- Zhang HY, Sun YM, Chen DZ (2001) Chin. Chem. Lett. 12: 75–78.
- Zhu Q, Zhang XM, Fry AJ (1997) Polym. Degrad. Stab. 57: 43–50.