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# *Z*, *E*-Isomerization mechanism for *N*-arylthio-1,4-benzoquinonimines: DNMR and DFT investigations

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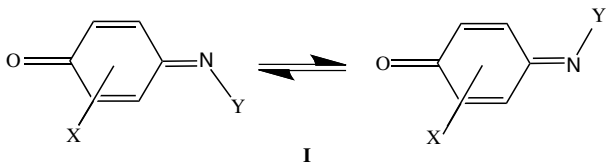
***Z*, *E*-Isomerization has been investigated for the series of the *N*-arylthio-1,4-benzoquinonimines using a line shape analysis in the $^1$H NMR spectra. Thermodynamic parameters and substituent effects have been analyzed for the isomerization process. It has been shown based on the DFT (B3LYP) calculations that the dynamic transformation for *N*-arylthio-1,4-benzoquinonimines should be considered as a combination of the two different processes, a rotation about the N–S bond and an inversion at nitrogen via the transition state with the linear C═N–S moiety. The free energies of activation for the isomerization ($\Delta G_{298\ K}$) measured experimentally depend on the substitution in the quinonimine moiety and phenyl ring and can be referred either to the inversion of the nitrogen atom or to the hindered rotation about the N–S bond.** Copyright © 2008 John Wiley & Sons, Ltd.

*Supporting information may be found in the online version of this article.*

**Keywords:** isomerization; inversion; benzoquinonimines; variable-temperature $^1$H NMR; line shape analysis; DFT calculations; B3LYP

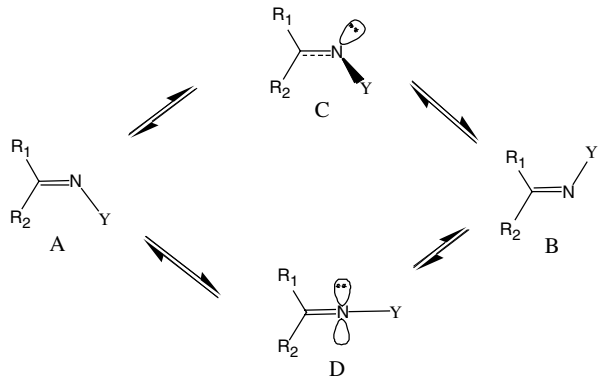
## Introduction

A *Z*,*E*-isomerization is inherent to benzoquinonimines (**I**) as representatives of the class of imino compounds.[1]




Two mechanisms are usually considered for the intramolecular isomerization of imines of general formula $R_1R_2C{=}N{-}Y$: rotation of the *N*-substituent about the C═N bond with the nonplanar transition state (transition state C in Scheme 1) and inversion at the nitrogen atom over the planar transition state with the linear C═N–Y moiety (transition state D), or a combination of both. If states A and B are identical ($R_1 = R_2$), a degenerated isomerization (or topomerization) is considered. The choice between the two mentioned isomerization mechanisms is usually somewhat arbitrary, and the interpretation is based on the influence of the properties of the substituent at the C═N bond on the thermodynamic activation parameters, as well as the solvent effects.[1,2]

For benzoquinonimines (**I**) the measured activation barrier values, which determine the probability of such conformational transformations, strongly depend on the type of the substituents at the nitrogen atom and vary within 40–100 kJ/mol.[2] Therefore, such processes can be investigated using the NMR spectroscopy. Most of the published papers devoted to the *Z*,*E*-isomerization in benzoquinonimines dealt only with the derivatives substituted with the *tert*-butyl groups at positions 2 and 6 of the quinonimine




**Scheme 1.** Possible isomerization mechanisms for imines $R_1R_2C{=}N{-}Y$.

moiety,[3–5] due to the easy analysis of the $^1$H NMR spectra where the *tert*-butyl substituent resonances appeared as singlets. For such cases, the activation $\Delta G_C$ energy values could be estimated from the coalescence temperature $T_C$ using the known approximated expressions.[6] As a consequence, the only effect of the substituents at the imino-nitrogen atom (or at the phenyl ring attached

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to this atom) on the $\Delta G_C$ activation energy was studied previously, to the best of our knowledge. On the basis of these investigations it was established that for 2,6-di-*tert*-butyl-substituted *N*-aryl-,[2a] *N*-aroyl-[4] and *N*-arylsulfonyl-1,4-benzoquinonimines,[2b,c,5] electron acceptor substituents at the *para*-position of the aromatic ring reduced the activation energy for the *Z*, *E*-isomerization process. At the same time, for the structures involving a bivalent sulfur atom such substituents increased the activation barrier.[7] Moreover, a similar trend was also observed for the imino systems with a thioaryl moiety bound to the nitrogen atom, in particular for $Tol_2C{=}N{-}S{-}Ar$,[8] but no explanation was given for such peculiarity of the thioimino compounds. One of the possible versions could be the change of the isomerization mechanism from the inversion to rotation or to the more complicated process.[9]

As it has been already mentioned above, the most available data in the literature on the *Z*, *E*-isomerization were obtained using the approximated expressions,[6] which determined the activation $\Delta G_C$ energy values based only on the coalescence temperature $T_C$ of the singlet peaks. As a consequence, such a comparison was not always reliable because the coalescence for the different structures was achieved by the different temperatures. This effected the $-T\Delta S$ contribution into the $\Delta G_C$ expression. Hence, a satisfactory comparison was sometimes not possible even for structurally very similar species. Additionally it should be noted that most published thermodynamic data on the isomerization processes in benzoquinonimines were obtained using the NMR spectrometers operating at frequencies of 100 MHz or lower. This provided small differences in the chemical shifts for the groups taking part on the exchange processes which adversely affected the accuracy of the determination of the thermodynamic parameters.[10]

We have investigated the *Z*, *E*-isomerization process in the wide series of *N*-arylthio-1,4-benzoquinonimines (**1**–**10**) substituted both in the phenyl ring and in the quinonimine moiety using the $^1$H NMR line-shape analysis. To the best of our knowledge, the influence of the substitution at the various positions of the quinonimine part of the molecule on the *Z*, *E*-isomerization processes in benzoquinonimines has previously not been established. The experimental results are collected in Table 1.

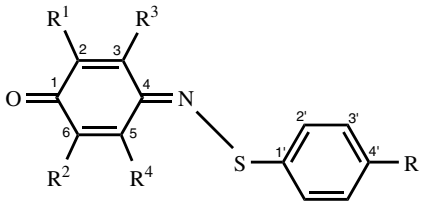


**Table 1.** Thermodynamic activation parameters for the *Z*, *E*-isomerization process for *N*-arylthio-1,4-benzoquinonimines

| Structure | R1 | R2 | R3 | R4 | R | Solvent | $\Delta G_{298K}$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol·K) | n[a] | $\Delta T$ (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | H | H | H | H | OMe | DMSO-$d_6$ | 74.7 | 75.5 ± 0.8 | 2.7 ± 2.3 | 15 | 314–419 |
| **1b** | H | H | H | H | H | DMSO-$d_6$ | 74.1 | 73.3 ± 0.5 | −2.3 ± 1.5 | 14 | 316–397 |
| **1c** | H | H | H | H | Cl | DMSO-$d_6$ | 73.7 | 70.7 ± 0.7 | −9.9 ± 1.5 | 13 | 314–418 |
| **1d** | H | H | H | H | $NO_2$ | DMSO-$d_6$ | 76.3 | 78.5 ± 0.7 | 7.5 ± 1.8 | 12 | 314–418 |
| **2c**[b] | Me | H | H | H | Cl | DMSO-$d_6$ | 75.1 | 68.1 ± 0.7 | −23.4 ± 1.8 | 20 | 331–395 |
| **3a** | Me | Me | H | H | OMe | DMSO-$d_6$ | 75.7 | 72.1 ± 0.7 | −11.9 ± 2.0 | 14 | 323–400 |
| **3c** | Me | Me | H | H | Cl | DMSO-$d_6$ | 76.0 | 69.8 ± 1.0 | −20.8 ± 2.8 | 21 | 325–395 |
| **3d** | Me | Me | H | H | $NO_2$ | DMSO-$d_6$ | 77.2 | 74.9 ± 0.4 | −7.7 ± 1.0 | 23 | 331–393 |
| **4c**[c] | i-Pr | i-Pr | H | H | Cl | DMSO-$d_6$ | 78.2 | 81.3 ± 0.5 | 10.4 ± 1.3 | 24 | 329–405 |
| **5a** | *t*-Bu | *t*-Bu | H | H | OMe | DMSO-$d_6$ | 78.6 | 86.0 ± 1.3 | 24.9 ± 3.6 | 20 | 323–376 |
| **5c** | *t*-Bu | *t*-Bu | H | H | Cl | DMSO-$d_6$ | 79.2 | 83.0 ± 0.6 | 13.0 ± 1.6 | 19 | 334–418 |
| **5d**[d] | *t*-Bu | *t*-Bu | H | H | $NO_2$ | DMSO-$d_6$ | 79.9 | 82.8 ± 0.6 | 10.1 ± 1.5 | 29 | 336–416 |
| **5d** | *t*-Bu | *t*-Bu | H | H | $NO_2$ | $CDBr_3$ | 80.7 | 84.1 ± 0.9 | 11.8 ± 2.6 | 32 | 339–397 |
| **5d** | *t*-Bu | *t*-Bu | H | H | $NO_2$ | $C_6D_5CD_3$ | 79.7 | 83.8 ± 1.0 | 13.5 ± 2.9 | 27 | 311–374 |
| **6c**[b] | Cl | H | H | H | Cl | DMSO-$d_6$ | 73.3 | 75.4 ± 0.5 | 7.0 ± 1.4 | 19 | 315–385 |
| **7a** | Cl | Cl | H | H | OMe | DMSO-$d_6$ | 70.0 | 66.7 ± 0.6 | −11.1 ± 1.6 | 16 | 305–399 |
| **7c** | Cl | Cl | H | H | Cl | DMSO-$d_6$ | 71.2 | 68.0 ± 0.7 | −10.9 ± 1.9 | 22 | 311–391 |
| **7d** | Cl | Cl | H | H | $NO_2$ | DMSO-$d_6$ | 72.3 | 69.7 ± 0.5 | −8.8 ± 1.4 | 15 | 321–391 |
| **8c**[e] | Br | Br | H | H | Cl | DMSO-$d_6$ | 70.9 | 67.3 ± 0.4 | −12.2 ± 1.3 | 12 | 311–400 |
| **9a** | H | H | Cl | Cl | OMe | $CDCl_3$ | 71.1 | 70.4 ± 0.7 | −2.3 ± 2.0 | 10 | 297–334 |
| **9c** | H | H | Cl | Cl | Cl | $CDCl_3$ | 70.2 | 69.5 ± 0.6 | −2.4 ± 1.9 | 10 | 287–334 |
| **9d** | H | H | Cl | Cl | $NO_2$ | $CDCl_3$ | 68.4 | 66.0 ± 0.8 | −8.1 ± 2.6 | 12 | 283–328 |
| **10a** | H | H | Me | Me | OMe | $CDCl_3$ | 60.4 | 55.6 ± 0.6 | −16.1 ± 2.0 | 33 | 268–339 |
| **10c** | H | H | Me | Me | Cl | $CDCl_3$ | 62.4 | 60.9 ± 0.4 | −5.1 ± 1.4 | 23 | 268–346 |
| **10d** | H | H | Me | Me | $NO_2$ | $CDCl_3$ | 66.6 | 64.4 ± 0.7 | −7.4 ± 2.1 | 18 | 280–356 |

[a] Number of points used for the calculation of thermodynamic parameters.
[b] For compounds **2c, 6c**, the thermodynamic characteristics for the isomerization processes are listed for the transformation from the more stable state (*E*) into the less stable one (*Z*). The *E*-/*Z*-isomer ratios for these species are 0.63/0.37 and 0.52/0.48, respectively (298 K).
[c] Data from Ref. [2c]
[d] Data from Ref. [11]
[e] Published data [2c]: $\Delta G_{298K} = 70.4$ kJ/mol, $\Delta H = 65.9$ kJ/mol, $\Delta S = -15.1$ J/mol · K, $\Delta T = 305$–$355$ K (200 MHz).

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## Results and Discussion

As one can see, the activation $\Delta G_{298K}$ energy values for the unsubstituted and 2,6-disubstituted *N*-arylthio-1,4-benzoquinonimines raise with increasing electron acceptor properties of the substituents in the phenyl ring. While this holds true for all types of the investigated 2,6-disubstituted *N*-arylthio-1,4-benzoquinonimines, one can observe such an increase in the case of the unsubstituted compounds only if the strongly electron-attracting nitro group is attached to the *para*-position of the phenyl ring (compound **1d**). Our results demonstrate also an essential dependence of the isomerization barrier energies on the properties of the substituents in the quinonimine moiety. The alkyl substitution at positions 2 and 6 (compounds **2**–**5**) increase the activation energy. Moreover, the latter increases with the raising donor properties of the substituents (from Me to *tert*-Bu) and their number. In contrast, replacing hydrogen at positions 2 and 6 by halogen (compounds **6**–**8**) reduces the activation energy for isomerization. The measured barrier values decrease consecutively from the unsubstituted (**1c**) to the monosubstituted (**6c**) and disubstituted species (**7c**). The solvent polarity does not practically affect the measured activation energies (Table 1, compound **5d**). At the same time, one should note the barriers raising in proton-donor solvents, such as bromoform, which is in line with the inversion isomerization mechanism for the investigated objects.[12]

According to our data, the activation energies for isomerization decrease for 3,5-dimethylsubstituted *N*-arylthio-1,4-benzoquinonimines (Table 1, **10a**–**d**), as compared to all other congeners. This fact also agrees with the inversion isomerization mechanism for *N*-arylthio-1,4-benzoquinonimines. In the case of the rotational mechanism the substituents at positions 3 and 5 would enlarge the activation energy due to the sterical effects.[1a]

It was shown previously[7,8] that the electron acceptor substituents at the *para*-position of the phenyl ring increased activation energies for the isomerization of *N*-arylthio-substituted compounds. However, our results indicate that this trend holds for all investigated series with only exception for the 3,5-dichlorosubstituted thioquinonimines **9a**–**d** where the opposite trend has been found. Indeed, it is evident from Table 1 that within **9a**–**d** the electron attracting substituents in the phenyl ring reduce the activation energy for the *Z*, *E*-isomerization. The reason for such a phenomenon could not be identified by simple terms. Again, a more complicated mechanism could be proposed involving along with inversion a contribution of rotation also. In order to elucidate the isomerization mechanism for thioquinonimines and to interpret the unique behavior of **9a**–**d** we have carried out quantum chemistry investigations for the series of the *N*-arylthio-1,4-benzoquinonimines at the DFT (B3LYP/6–31+G*) level of theory.

## Quantum Chemistry Calculations

To the best of our knowledge, no quantum chemistry calculations have been reported for quinonimines up to date. The theoretically investigated structures together with the ZPE-corrected total energies for all calculated *N*-arylthio-1,4-benzoquinonimines, as well as the relative energies are listed in Table 2. A complete

**Table 2.** Calculated total (*E*)[a] and relative ($\Delta E$) energy values for *N*-arylthio-1,4-benzoquinonimines (**1**–**10**)

| Structure | $E_A$ (a.u.) | $E_B$ (a.u.) | $E_C$ (a.u.) | $E_D$ (a.u.) | $\Delta E_{AB}$ (kJ/mol) | $\Delta E_{AD}$ (kJ/mol) |
|---|---|---|---|---|---|---|
| **1a** (*syn*)[b] | −1105.152461 | −1105.125906 | −1105.146050[c] | −1105.135480 | 69.7 | 44.5 |
| (*anti*) | −1105.152560 | −1105.125813 | | −1105.135523 | 70.2 | 44.8 |
| **1b** | −990.658619 | −990.631540 | −990.650407 | −990.640778 | 71.1 | 46.8 |
| **1d** | −1195.166138 | −1195.137803 | −1195.154069 | −1195.149509 | 74.4 | 43.7 |
| **3a** (*syn*)[b] | −1183.740201 | −1183.712801 | −1183.733157[c] | −1183.723882 | 71.9 | 42.8 |
| (*anti*) | −1183.740214 | −1183.712426 | | −1183.723903 | 73.0 | 42.8 |
| **3b** | −1069.246581 | −1069.218723 | −1069.237667 | −1069.229750 | 73.1 | 44.2 |
| **3d** | −1273.755056 | −1273.725779 | −1273.742123 | −1273.739480 | 76.9 | 40.9 |
| **5a** (*syn*)[b] | −1419.443164 | −1419.415591 | −1419.435405[c] | −1419.426618 | 72.4 | 43.4 |
| (*anti*) | −1419.443084 | −1419.415646 | | −1419.426650 | 72.0 | 43.1 |
| **5b** | −1304.949604 | −1304.921479 | −1304.939990 | −1304.932665 | 73.8 | 44.5 |
| **5d** | −1509.457971 | −1509.428626 | −1509.444672 | −1509.442606 | 77.0 | 40.3 |
| **7a** (*syn*)[b] | −2024.356067 | −2024.330347 | −2024.350241[c] | −2024.338514 | 67.5 | 46.1 |
| (*anti*) | −2024.356108 | −2024.330352 | | −2024.338606 | 67.6 | 46.0 |
| **7b** | −1909.861816 | −1909.835613 | −1909.854242 | −1909.843472 | 68.8 | 48.2 |
| **7d** | −2114.368505 | −2114.340867 | −2114.357091 | −2114.351123 | 72.6 | 45.6 |
| **9a**(*syn*)[b] | −2024.350393 | −2024.332029[c] | −2024.334448[c] | −2024.322699 | 47.9 | 72.7 |
| (*anti*) | −2024.350266 | | | −2024.322726 | | 72.3 |
| **9b** | −1909.856111 | −1909.836483 | −1909.838763 | −1909.827346 | 51.5 | 75.5 |
| **9d** | −2114.362812 | −2114.340855 | −2114.343004 | −2114.335432 | 57.6 | 71.9 |
| **10a**(*syn*)[b] | −1183.730212 | −1183.710021[c] | −1183.714495[c] | −1183.708028 | 53.0 | 58.2 |
| (*anti*) | −1183.730323 | | | −1183.707931 | | 58.8 |
| **10b** | −1069.236104 | −1069.214731 | −1069.218951 | −1069.214564 | 56.1 | 56.6 |
| **10d** | −1273.743892 | −1273.719441 | −1273.723344 | −1273.723888 | 64.2 | 52.5 |

[a] Here the only ZPE-corrected total energy values are shown. The calculated data are presented in more detail in Supporting Information.
[b] Two different conformations with *syn*- and *anti*-orientation of the OMe group relatively to the S–N bond.
[c] Only one isomer exists.



  

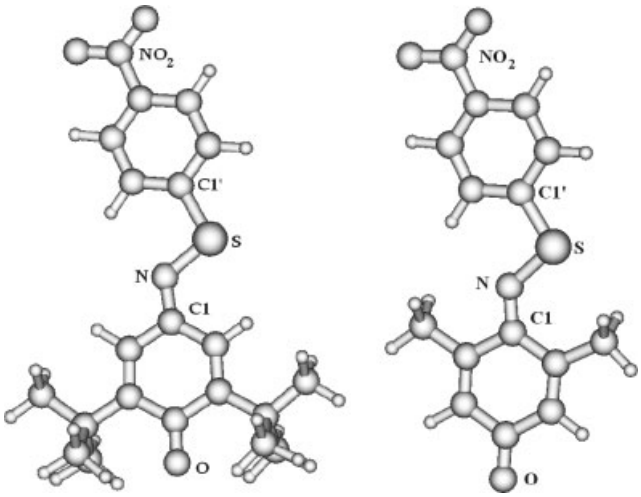


**Figure 1.** MOLDEN plots for the equilibrium structures of *N*-4-nitrophenyl-2,6-bis(*tert*-butyl)-1,4-benzoquinonimine, **5d** (a) and of *N*-4-nitrophenyl-3,5-dimethyl-1,4-benzoquinonimine, **10d** (b). The most important calculated geometry parameters are as follows (bond lengths in Å, bond angles in degrees, in parentheses the experimentally found parameters for **5d**[13]) : C═O 1.233 [1.227(4)] (a), 1.234 (b), C═N 1.309 [1.302(5)] (a), 1.305 (b), N–S 1.684 [1.663(3)] (a), 1.672 (b), S–C1 1.779 [1.761(4)] (a), 1.783 (b), ∠C1NS 121.3 [119.6(3)] (a), 128.1 (b), ∠NSC1′ 100.7 [100.10(17)] (a), 100.7 (b), ∠C1NSC1′ 180.0 (a), 180.0 (b).

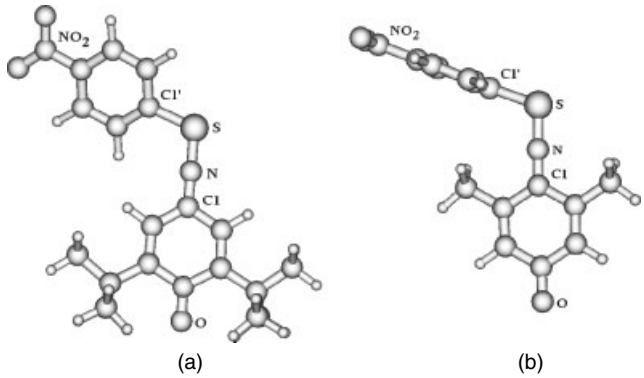


**Figure 2.** MOLDEN plots for the calculated transition-state structures **5d** and **10d** for the inversion reaction. The most important geometry parameters are (bond lengths in Å, bond angles in degrees): C═O 1.234(a), 1.235(b), C═N 1.290(a), 1.283(b), N–S 1.563(a), 1.574(b), S–C1 1.814(a), 1.836(b), ∠C1NS 178.7°(a), 178.2°(b), ∠NSC1′ 110.1°(a), 108.3°(b).

data set can be found in the Supporting Information. The structures have been calculated corresponding to the ground states and transition states. For all series, the species have been studied, substituted with the OMe, H, $NO_2$ groups at the *para*-position of the phenyl moiety. Such a choice of substituents was determined by our wish to reproduce the effects of the $\pi$-donor and $\pi$-acceptor groups and to compare the calculated structural and thermodynamic characteristics with those found in the experiment.

The MOLDEN view for the equilibrium structure of *N*-(4′-nitrophenyl)-2,6-bis(*tert*-butyl)-1,4-benzoquinonimine (**5d**) is presented in Fig. 1(a) and the calculated geometry parameters are compared with those previously found with the single crystal X-ray diffraction method.[13] A good agreement between these two data sets is an evidence of the proper choice of the calculation level.

Our calculation results support the suggestion that the isomerization proceeds via the inversional mechanism and not via rotation. The equilibrium structures for the transition states are characterized by an almost linear configuration of the C═N–S triad (as an example, the transition state for the isomerization for **5d** is shown in Fig. 2(a)). Our attempts to localize transition states for the rotation about the C═N bond (starting the optimization from the structure where the C═N–S triad is nonlinear and the N–S bond is orthogonal to the quinonimine ring) have led to the transition state structures discussed above. This means that the former conformations do not correspond to the real transition states but are the saddle points of the higher order. Most probably the isomerization of the *N*-arylthio-1,4-benzoquinonimines via rotation does not proceed.

The quantum chemistry investigation of the *Z*, *E*-isomerization of thioquinonimines demonstrates that the process considered has a more complicated character than the simple transformation of one conformation into another via the nitrogen inversion. Our calculations predict the second local minima in energy for *N*-arylthio-1,4-benzoquinonimines as the products of the isomerization reaction and additional transition states, which are consistent with the rotation about the N–S bond. A full description of the isomerization in the series of the studied thioquinonimines is demonstrated in Fig. 3 for *N*-phenylthio-1,4-benzoquinonimine (**1b**) as an example. An initial structure **A** converts to the second local minimum in energy (**C**) proceeding via the transition state (**B**). Then, **C** transforms to **A**′ via rotation about the N–S bond. The second transition state **D** exists on the path from **C** to **A**′.

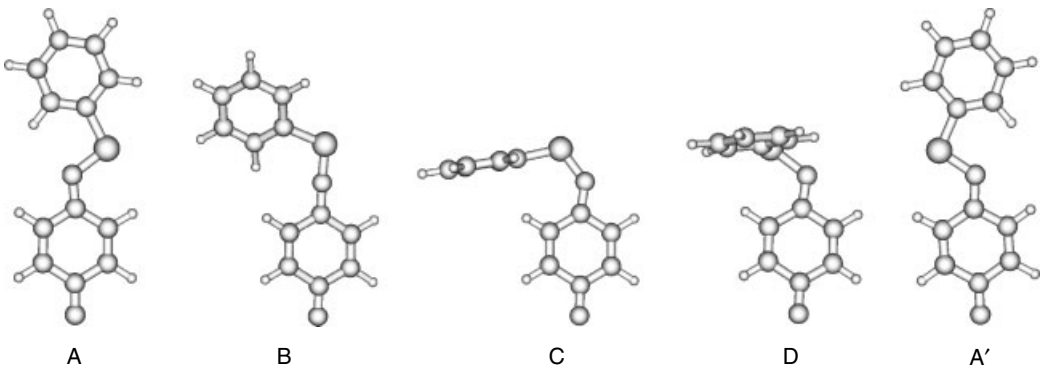


**Figure 3.** Optimized structures for the ground states (**A**, **A**′), second local minimum (**C**) and transition states (**B, D**) for *N*-phenyl-1,4-benzoquinonimine **1b**.

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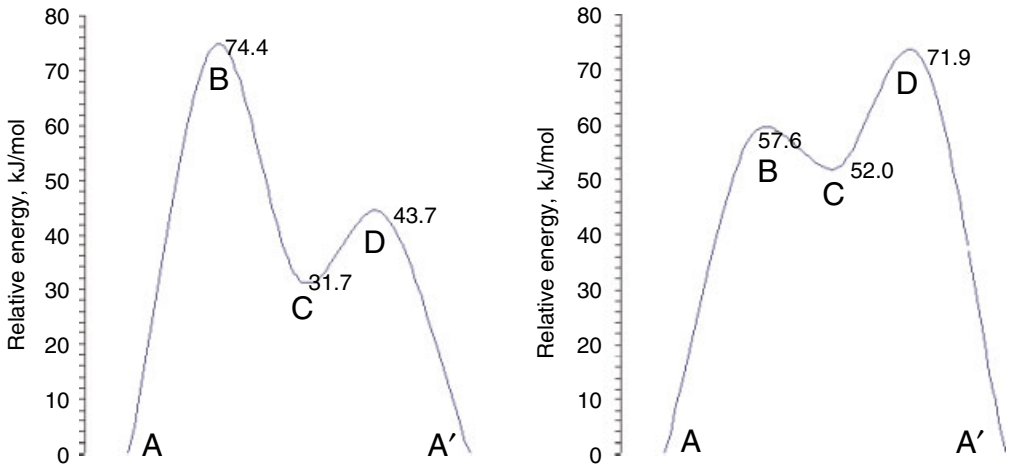


**Figure 4.** Graphical representation of the dynamic processes and relative energies for different states of **1d** (left) and **9d** (right).

Thus, a studied degenerated isomerization really consists of the inversional and rotational parts, but these contribute to the two separate processes. In Table 2, the $\Delta E_{AB}$ values determine the activation barriers for the inversion and $\Delta E_{AD}$ magnitudes are the activation energies for the rotation about the N–S bond. As one can see, the theoretical data are generally in a good agreement with the experimentally found activation barriers for isomerization. In accordance with the experiment, the inversion barrier energies for all 2,6-disubstituted benzoquinonimines raise with increasing electron acceptor properties of the substituents in the aromatic moiety. Theory also reproduces well a trend of the substituent influence on the isomerization barrier height. This becomes obviously higher for the 2,6-dialkylsubstituted species **3**,**5** and lower in the case of the 2,6-dichloro-substituted congeners **7** compared to the unsubstituted compound **1**.

At the same time, theoretical calculations predict lower activation energies $\Delta E_{AB}$ for the inversion reaction for 3,5-disubstituted thiobenzoquinonimines **9**,**10**. The transition state structure for the representative of this series, **10d**, is shown in Fig. 2(b). The obvious difference in comparison with **5d** is the orthogonal orientation of the phenyl ring relative to the C1NS plane but this structural feature is probably not responsible for the low activation energies found in the experiment for **10a**–**d**. For structure **10d** corresponding to the main minimum in energy (Fig. 1(b)) the C1NS bond angle (128.1°) is significantly larger than those calculated for **5d** (121.3°) and **3d** (121.8°) due to the steric effect of the methyl substituents at positions 3,5. This trend is even more pronounced for the 3,5-dichloro-substituted thiobenzoquinonimines **9** (for instance, ∠C1NS = 130.5° for **9d**). This destabilization of the ground states for **9**,**10** diminishes the calculated activation energies for inversion for these structures. At the same time, the calculations suggest for series **9**,**10** increasing barriers of rotation about the N–S bond (larger $\Delta E_{AD}$ values, Table 2). For the unsubstituted (**1**) and 2,6-dialkylsubstituted species (**3**,**5**), the activation barriers for rotation are definitely lower than those for the inversion (by approx. 25–39 kJ/mol). In contrast, for the 3,5-dimethylsubstituted benzoquinonimines **10,** these magnitudes are already commensurable, and in the case of 3,5-dichlorosubstituted congeners (**9**) the $\Delta E_{AD}$ values exceed the $\Delta E_{AB}$ magnitudes. This means that in the case of **9**, the rotation about the N–S bond and not the inversion determines the experimentally measured activation energies. Schematically it can be represented as shown in Fig. 4.

Our calculations predict that the corresponding activation energy on rotation about the S–N bond will decrease with increasing electron-withdrawing properties of the *para*-substituent, i.e. the lowest barrier on rotation is inherent to the compounds with nitro group in the *para*-position of the phenyl moiety (**9d**). This fact is in line with the experiment (Table 1). Therefore, a unique behavior of $\Delta G_{298K}$ values found for series **9** reflects a dominating contribution of the rotation about the N–S bond into the experimentally measured activation energies (Fig. 4(b)).

The calculated energy barriers for **C**–**D**–**A**′ transformation, i.e. for the rotation about the N–S bond for the unsubstituted and 2,6-disubstituted derivatives are in the range of 40–50 kJ/mol, and therefore can be measured using the NMR spectroscopy. However, by the NMR investigation of **5d** at low temperatures (at −80 °C in toluene-$d_8$ and at −60 °C in chloroform-*d*) only remarkable broadening of the signals, but no separation for resonances corresponding to the conformations **A** and **C** has been observed. This is in line with the significant differences in total energies for these two local minima predicted by theory. Due to the negligibly low population of the intermediate **C** calculated for all compounds of interest, the above-mentioned dynamic processes cannot be investigated with the NMR spectroscopy under used experimental conditions.

## Conclusions

The theoretical and experimental data make it possible to affirm that the isomerization of the *N*-arylthio-1,4-benzoquinonimines should be considered as a combination of the two separate dynamic processes, the rotation about the N–S bond and the inversion via transition state **B** with the linear arrangement of the C═N–S triad. The experimentally measured free activation energy for the isomerization process can be determined either by inversion stage or by the rotation about the N–S bond. A good agreement has been found between the experimental $\Delta G_{298K}$ values and theoretically calculated differences in total energies of the ground states and transition states ($\Delta E$). A trend of the substituent influence on the activation barrier energies is reproduced by theory as well. Combining the variable-temperature



  

NMR approach with the quantum chemical calculations is obviously a good way to determine contributions from the different dynamic processes into the experimentally measured free-activation energy values.

## Experimental

The $^1$H (299.95 MHz) NMR spectra were recorded with Varian VXR-300 NMR spectrometer. The thermodynamic parameters for the isomerization processes ($\Delta G_{298K}$, $\Delta H$, $\Delta S$) were calculated using the Eyring equation[6] based on the rate constants determined by the comparison of the experimental and simulated spectra at the different temperatures. The complete set of the simulated and experimental spectra for **3d** as well as the rate constant sets for all experimentally studied compounds are collected in the Supporting Information. The temperature intervals and the number of data points used for the calculation of the thermodynamic parameters are listed in Table 1. The simulation of the theoretical spectra was carried out using the WINDNMR[14] and DNMR[15] program sets and our own modification of the DNMR3 program.[16] The rate constants were estimated either by the visual comparison of the theoretical and experimental spectra (in the case of the WINDNMR and DNMR3 program packets) or using the least-squares-fit of experimental *versus* simulated spectra (for the DNMR program packets) with the following visual comparison of the experimental and simulated spectra. For the more precise calculation of the activation energy values the line shape analyses were carried out both for the quinonimine proton signals and alkyl group resonances. For the correct determination of the rate constants in the fast exchange area, the temperature dependence of the chemical shift values was taken into account for the signals involved in the exchange processes. For this purpose the spectra were additionally recorded at the temperatures 20–30 K lower than the range shown in Table 1. The changes in the population differences of the corresponding isomers with the increasing temperature were considered for the nondegenerated isomerization processes (**2c, 6c** in Table 1). The estimated errors for the activation energy $\Delta$G determination did not exceed 1%. The temperature was determined with a precision of 1 K. The spectra were recorded with a digital resolution 0.10–0.20 Hz per point. The choice of the solvents was determined by the necessary temperature range.

### *N*-Arylthio-1,4-benzoquinonimines (1a–10d)

To the suspension of 2 mmol of *p*-aminophenol in 20 ml of dry diethylether, 6 mmol of the corresponding arylsulfene chloride was added by intensive stirring and cooling to −10 °C. The equivalent quantity of triethylamine was added dropwise to the reaction mixture. Triethylamine hydrochloride was filtered off; the filtrate was evaporated *in vacuo*. The residue was washed with methanol and glacial acetic acid and recrystallized from glacial acetic acid or heptane. The analytical and spectral data for quinonimines were published earlier: (**1b, 3b, 7b**),[17,18] (**1c**),[19] (**1a–c**),[20] (**1d, 3a–3d, 4c, 5c–d, 10a–d**),[21] (**2c, 3a, 5a**),[11,13] (**6c, 7a–d, 8c, 9a–d**).[22]

## Calculation Details

The geometries for all structures were optimized using the GAUSSIAN-03 program set[23] within the DFT approximation. A hybrid functional B3LYP[24,25] was chosen, in combination with the 6–31+G*[26] basis sets. The transition states were localized using the following routine. First the guessed structure for the transition state was optimized as a Z-matrix with a frozen (approx. 180°) C═N–S angle. Then the search of the transition state was performed using option Opt = (CalcFC,TS) with the optimization of all structural parameters. This simple approach can generally be useful for the localization of the low-energy transition states (within few kcal/mol). The vibrational analyses were performed for all the local minima in energy (no imaginary vibrations) and transition states (one imaginary vibration) using the level of theory mentioned above and calculating analytically first and second derivatives (Supporting Information). The MOLDEN program[27] was used for the graphical presentation of the optimized structures.

### Supporting information

Supporting information may be found in the online version of this article.

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