Regularities of the conformations on a single bond; sulfonic esters and sulfonyl derivatives

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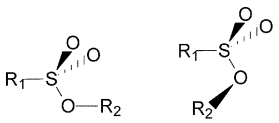
The so-called *gauche* rule preferring the less symmetrical *sc* conformations on sp^3–sp^3 bonds was revised by theoretical calculations of five sulfonyl derivatives: $C_6H_5SO_2OCH_3$, $CH_3SO_2OC_6H_5$, $ClSO_2OC_6H_5$, $C_6H_5SO_2CH_2Cl$ and $C_6H_5SO_2SO_2C_6H_5$. At the same time the limiting possibilities of common theoretical models were tested in predicting exact geometry and minute energy differences between rotamers. With a larger basis set, for instance at the level B3LYP/6-311+G(3df,3pd)//B3LYP/6-311+G(3df,3pd) or MP2/6-311+G(2df,2pd)//MP2/6-311+G(2df,2pd) different methods yielded concordant values of the dihedral angle τ characterizing the conformation. However, the predicted values of energy were not in sufficient agreement to give reliable population of rotamers. Probably the best estimate of this population can be obtained by combining the calculated angle τ with some experimental quantities, for instance with dipole moments. According to these results, the *gauche* rule is not a generally valid law. Preponderance of *sc* conformation in different classes of compounds may have different reasons. In our case, we obtained a qualitative explanation assuming that conformation is determined by destabilizing interaction of two polar bonds in the neighbouring *sc* position, while lone electron pairs have no observable effect.

Introduction

Conformations for single bonds connecting two sp^3 hybridized atoms are usually near to the staggered forms. The number of three possible conformations is reduced to two in simpler, more symmetrical compounds; of them usually the less symmetrical is preferred. To give a simple example, 1,2-dicyanoethane prefers[1] the synclinal, C_2 conformation (once also called "*gauche*") to antiperiplanar, C_{2h}. In 1972 Wolfe attempted to generalize these regularities in the so-called *gauche* rule.[2] A conformation should be stabilized by interactions of two polar bonds or two lone electron pairs in the position *sc* (*gauche*). This conformation is the more stable, the more such interactions exist. This rule was not quite unambiguous: with more complex compounds it may happen that interactions between bonds are opposed by interactions between electron pairs; in this case the bonds should be more important.[2] The rule also does not distinguish the polar bonds according to the orientation of the polarity.

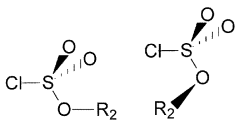
The basic paper[2] has been cited more than 800 times. On the other hand, few attempts were made to formulate the rule more precisely. The problem is still current but is investigated mainly on particular classes of compounds.[3,4] This strategy is followed also in the present communication, which is devoted to sulfonyl derivatives **1–5** investigated formerly by one of the present authors using dipole moments.[5–9] Since the dipole moments of these compounds were generally high, it was possible to estimate roughly the population of the conformers from experiments.[5–12] This approach was sometimes supported by determination of the Kerr constant[10–12] and by IR spectroscopy.[13–15]



1,2*ap* **1,2*sc***

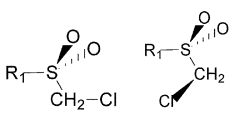
1 $R_1 = C_6H_5$, $R_2 = CH_3$

2 $R_1 = CH_3$, $R_2 = C_6H_5$



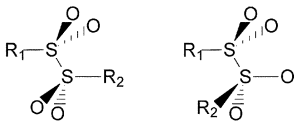
3*ap* **3*sc***

3: $R_2 = C_6H_5$



4*ap* **4*sc***

4 $R_1 = C_6H_5$



5*ap* **5*sc***

5 $R_1 = R_2 = C_6H_5$

The merit of the dipole moment method is that it does not involve any empirical correlations and determination of conformation is commonly straightforward. Thus the dipole moment of **5**, 3.99 D, is evidently not compatible with the conformation *ap*, although the quantitative estimate led to the conclusion that this form still prevails.[9] On the other hand, the dipole moments are of limited experimental accuracy and the estimate of the expected moments from bond moments is rather approximate: recent reinvestigation

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Table 1 Calculated energies and some geometrical parameters of the conformers of methyl benzenesulfonate **1**

Theoretical model	$E(sc)$/a.u.	$E(ap)$/a.u.	ΔE/kJ mol^{-1}	%(sc)	∠O–S–O[a]/°	τ[a]/°	l(S–O)[b]/Å
HF/SVP	−891.2517821	−891.2527022	2.42	43	122.5	82.9	1.457
HF/6-31G(d,p)	−891.7667441	−891.7679113	3.06	37	121.3	70.6	1.424
HF/6-31G(df,pd)	−891.8059815	−891.8073929	3.71	31	121.0	80.6	1.420
MP2/6-31G(df,pd)	−893.6140190	−893.6143070	0.76	60	122.3	75.2	1.449
MP2/6-311 + G(2df,2pd)	−893.9944007	−893.9928307	−4.12	91	122.1	72.0	1.435
B3LYP/SVP	−894.8614221	−894.8616225	0.53	62	122.5	82.8	1.456
B3LYP/6-31G(d,p)	−895.3587582	−895.3593474	1.55	52	122.2	79.9	1.458
B3LYP/6-31G(df,pd)	−895.3860098	−895.3868274	2.15	46	121.9	79.6	1.455
B3LYP/6-311 + G(d,p)	−895.5126393	−895.5131907	1.45	53	122.1	79.3	1.453
B3LYP/6-311 + G(2df,2pd)	−895.5933456	−895.5932924	−0.14	68	121.7	77.5	1.438
B3LYP/6-311 + G(3df,3pd)	−895.6089704	−895.6084389	−1.40	78	121.7	77.0	1.431
	−895.5022810[e]	−895.502582[e]	0.79	59			
CSD/6-311 + G(d,p)	−893.6527771	−893.6524954	−0.74	**73**	122.0	**76.5**	1.441
Experimental X-ray					119.7(18)[c]	**74**[d]	1.422(25)[c]
Experimental in solution				77[f]		(60)[f]	
Experimental combined[g]				**88**		74	

[a] The O–S–O bond angle and the dihedral angle τ = ∠C–O–S–C in the *sc* conformer. [b] Average value of the two S–O bond lengths in the *sc* conformer. [c] Average values (with standard deviation in parentheses) from 512 molecules containing the fragment C–SO_2–O–C, ref. 21. [d] The most frequent value (modus) from 413 molecules containing the fragment C–SO_2–O–C, ref. 21. [e] Calculated Gibbs energy $\Delta G°(298)$. [f] Estimated from the dipole moments in CCl_4 assuming τ = 60°, ref. 11. [g] Estimated here from the experimental dipole moment and geometry of the *sc* form taken from X-ray data. The recommended most trustworthy values are printed in bold.

revealed that this principle holds only for symmetrical structures when the bond moment is collinear with the pertinent bond.[16] However, the main problem is in the interpretation of smaller differences between experimental dipole moments and those estimated from bond moments. For instance when the experimental moment of **1** did not agree with the value anticipated for **1***sc*, one could either assume that some amount of **1***ap* is present in equilibrium or that the form **1***sc* is distorted so that the C–S–O–C dihedral angle deviates from 60°. Both can occur even simultaneously. Determination on the basis of the Kerr constant[11,12] suffers from similar problems, in addition the interpretation is much more complex and some results obtained by this method[17] are questionable. Concerning IR spectroscopy, it gave evidence that several forms are present but their ratio was not estimated.[13–15] Note that all methods mentioned are carried out in solution. In the case of dipole moments, the close relation of gas-phase and solution results was reported recently;[18] on the other hand our experience with theoretical calculations of the solvent effect was very unsatisfactory and is not discussed here.

In contrast to some success in determining conformation, any rule governing it more generally was not found.[5–9] For instance structures **1–3** involve both strongly polar bonds and lone electron pairs, and it was not possible to estimate which are more important for the conformation.

We expected that quantum chemical calculations might contribute significantly to the general problem of the *gauche* effect using just the model compounds **1–5**. We were aware that the energy differences between rotamers are very small and cannot be safely predicted by contemporary quantum chemical methods; on the other hand even the experimental values are not fully dependable as mentioned. We encountered already the problem of whether the calculated or experimental quantities are more reliable, and attempted to solve it referring to a selected series of accurate enthalpies of formation.[19] In our case energies of required accuracy are not obtainable and we proceeded by shifting the interest from the energy to the geometry. In this way individual quantum chemical methods can be evaluated by comparison with relatively reliable experimental data and the experimental methods for determining the population can be improved. We believe that we have obtained more accurate populations than hitherto by properly combining the experimental and theoretical approach.

We calculated the geometry and energy of the two rotamers of **1** by a variety of theoretical models (Table 1), the selected methods were then applied to compounds **2–5** (Tables 2–5).

Calculations

The HF, MP2 and DFT calculations were performed using the Gaussian 03 program.[20] The theoretical models are listed in Table 1; we avoided the single-point calculations and always calculated geometry and energy at the same level. No symmetry conditions were presumed. All final structures were checked by the vibrational analysis and were found to represent energy minima. No correction for the zero-point energy was applied. Population of the conformers at 298 K was calculated assuming that their $\Delta G°(298)$ equals ΔE.

Results and discussion

Comparison of the theoretical models and experiments

In Table 1 are listed energies and some geometric parameters of the ester **1** calculated at a variety of theoretical levels. The energy differences between conformers are rather small and their estimates within the framework of the particular models may differ even more. One cannot decide, which model is better by comparison with the experimental population of rotamers since even this population suffers by great uncertainty (see criticism in the Introduction). We attempted testing on the basis of the geometric parameters, the O–S–O bond angle and S–O bond lengths, obtained as

Table 2 Calculated energies and some geometrical parameters of the conformers of phenyl methanesulfonate **2**

Theoretical model	$E(sc)$/a.u.	$E(ap)$/a.u.	ΔE/kJ mol^{-1}	%(*sc*)	∠OSO[a]/°	τ[a]/°	l(S–O)[b]/Å
MP2/6-311+G(d,p)	−893.6216801	−893.6216033	−0.20	68	122.1	64.9	1.445
B3LYP/6-311+G(d,p)	−895.5194671	−895.5207122	3.27	35	121.6	74.0	1.451
B3LYP/6-311+G(2df,2pd)	−895.6004226	−895.6010777	1.72	50	121.4	76.7	1.436
B3LYP/6-311+G(3df,3pd)	−895.6155419	−895.6157357	0.51	**62**		**75.8**	1.430
Experimental X-ray					119.7(18)[c]	**74**[d]	1.422(25)[c]
Experimental in solution				60[e]		(60)[e]	
Experimental combined[f]				**71**		74	

[a] The O–S–O bond angle and the dihedral angle τ = ∠C–O–S–C in the *sc* conformer. [b] Average value of the two S–O bond lengths in the *sc* conformer. [c] Average values (with standard deviation in parentheses) from 512 molecules containing the fragment C–SO_2–O–C, ref. 21. [d] The most frequented value (modus) from 413 molecules containing the fragment C–SO_2–O–C, ref. 21. [e] Estimated from the dipole moments in benzene assuming τ = 60°, ref. 5. [f] Estimated here from the experimental dipole moment and geometry of the *sc* form taken from X-ray data. The recommended most trustworthy values are printed in bold.

Table 3 Calculated energies and some geometrical parameters of the conformers of phenyl chlorosulfate **3**

Theoretical model	$E(sc)$/a.u.	$E(ap)$/a.u.	ΔE/kJ mol^{-1}	%(*sc*)	∠O–S–O[a]/°	τ[a]/°	l(S–O)[b]/Å
MP2/6-311+G(d,p)	−1313.4689015	−1313.4641197	−12.55	100			
B3LYP/6-311+G(d,p)	−1315.8059785	−1315.8021666	−10.01	99	123.1	69.4	1.441
Experimental in solution[c]				100		(60)	
Experimental combined[d]				100		69	

[a] The O–S–O bond angle and the dihedral angle τ = ∠Cl–S–O–C in the *sc* conformer. [b] Average value of the two S–O bond lengths in the *sc* conformer. [c] Estimated from the dipole moments in benzene assuming τ = 60°, ref. 6. [d] Estimated here from the experimental dipole moment with the calculated dihedral angle τ.

average values from the X-ray data of many sulfonic esters.[21] One assumes generally that these values are almost randomly affected by crystal packing forces; hence their average values should by concordant with the assumed gas-phase values.[23] In this treatment the angles are believed to be more reliable than the bond lengths since they are not controlled by the size of the crystal cell.[24,25] Note that we compare the values calculated for the *sc* rotamer of one compound with the experimental average of many compounds. It is thus assumed that all the compounds investigated were in the *sc* conformation. This was in principle confirmed (Fig. 1). Another problem was that the molecule **1** and most of the molecules investigated experimentally are chiral, hence the two S–O bonds are of different length. Since they can be hardly distinguished and classified in the CSD, we simply used average values.

Both the O–S–O angles and S–O bond lengths calculated with a sufficiently large basis set agreed well with the experiments. The calculated S–O lengths evidently converge to the right value with the increasing basis set (Table 1), while the S–O–S angles are less sensitive and can be obtained with good precision even at low levels. The DFT methods appear to be slightly better than MP2 but the difference is minute. We concluded that our theoretical models with larger basis sets are acceptable and yield reliable geometries. For calculations of the conformers of **2–5** we used only these well-tried models when they were acceptable for technical reasons.

Geometry of the *sc* conformer

Determination of conformation comprises two different problems: first estimating the dihedral angle τ in the rotamer *sc* (τ = ∠C–S–O–C in **1** and **2**, Cl–S–O–C in **3**, C–S–C–Cl in **4**, or C–S–S–C in **5**), second estimating the population of the two rotamers in the equilibrium mixture. Calculations allow the two problems to be solved separately but this has not been possible on the basis of common experimental methods.

The calculated angle τ depends relatively strongly on the theoretical model (Table 1); with the larger basis set it reaches a limiting value but a difference between DFT and MP2

Table 4 Calculated energies and some geometrical parameters of the conformers of chloromethyl phenyl sulfone **4**

Theoretical model	$E(sc)$/a.u.	$E(ap)$/a.u.	ΔE/kJ mol^{-1}	%(*sc*)	∠O–S–O[a]/°	τ[a]/°	l(S–O)[b]/Å
MP2/6-311+G(d,p)	−1277.6022998	−1277.5980749	−11.09	99	122.1	61.5	1.458
B3LYP/6-311+G(2df,2pd)	−1279.9656623	−1279.9630472	−6.87	97	121.2	62.4	1.449
Experimental in solution				100[c]		(60)[c]	
Combined[d]				100		62	

[a] The O–S–O bond angle and the dihedral angle τ = ∠C–S–C–Cl in the *sc* conformer. [b] Average value of the two S–O bond lengths in the *sc* conformer. [c] Estimated from the dipole moments in benzene assuming τ = 60°, ref. 7. [d] Estimated here from the experimental dipole moment with the calculated dihedral angle τ.

Table 5 Calculated energies and some geometrical parameters of the conformers of diphenyl disulfone **6**

Theoretical model	$E(sc)$/a.u.	$E(ap)$/a.u.	ΔE/kJ mol^{-1}	%(*sc*)	$\angle$ O–S–O^a/°	τ^a/°	l(S–O)^b/Å
MP2/6-311 + G(d,p)	−1557.5308351	−1557.5259868	−13.873	100	123.1	43.8	1.459
B3LYP/6-311 + G(2df,2pd)	−1560.8234507	−1560.8264762	7.94	8	122.0	77.7	1.448
B3LYP/6-311 + G(3df,3pd)	−1560.8470360	−1560.8264762	7.58	9	122.1	73.9	1.441
Experimental X-ray[c]					120.2	179.9[c]	1.428
Experimental in solution				27[d]		(60)[d]	
Combined[e]				31		(74)	

[a] The O–S–O bond angle and the dihedral angle τ = $\angle$C–S–S–C in the *sc* conformer. [b] Average value of the two S–O bond lengths in the *sc* conformer. [c] Ref. 22; in the crystalline state the compound is in the conformation *ap*. [d] Estimated from the dipole moments in benzene assuming τ = 60°, ref. 9. [e] Estimated here from the experimental dipole moment with the calculated dihedral angle τ.

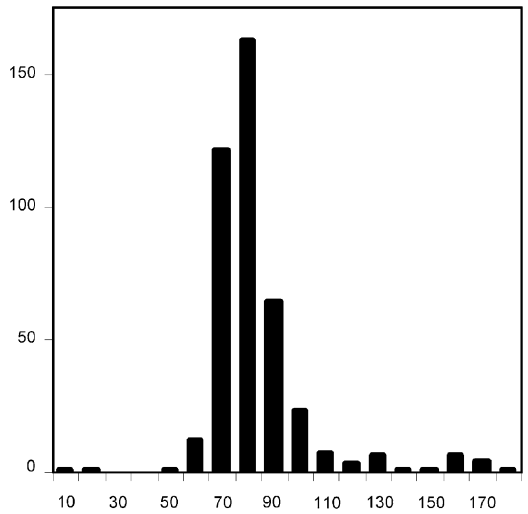


Fig. 1 Histogram of the dihedral angle τ in 413 sulfonic acid esters in the crystalline state with the width of the classes = 10°.

models persists. We may suggest the value τ = 75 ± 3° as a cautious estimate for the sulfonic esters **1** and **2**. Comparison with single trustworthy experiments is not possible; the main problem is that the dipole moments give ambiguous results: an imperfect agreement can be explained either by admixture of the rotamer *ap* or by deformation of the *sc* rotamer (angle τ differing from the standard value of 60°). We searched again a solution in the X-ray structures. In this case it is not possible to take an average from all published structures since the dihedral angles are measured in different directions.[21] (For instance the same structure may be reported as 0 or 180°.) We made a histogram for all investigated sulfonic esters (Fig. 1) and searched for the most populated value (modus). In our opinion, the most probable value of τ is 73–74°. In any case the value 60° used commonly when estimating dipole moments from bond moments[5–12] was significantly in error. Agreement with the best calculations is very good, both for **1** and **2**, in fact better than could be expected. We conclude that theoretical methods at a sufficient level give good estimates of the geometry of the *sc* conformer, even the predicted differences between the compounds **1–5** are in our opinion real.

Population of the *sc* and *ap* conformers

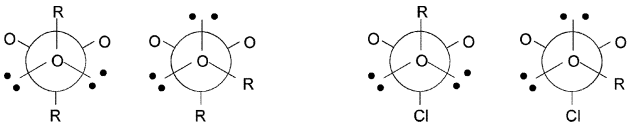
The second problem may become rather difficult since we cannot rely either on calculations or on experiments. (The latter are practically always accompanied by theoretical assumptions.) Contemporary quantum chemical methods are evidently unable to predict the population of rotamers with the accuracy of several percent (see Table 1 where the population is given in percent of the *sc* conformer). They are effective only when the energy difference is some 10 kJ mol^{-1} or more and one rotamer is practically absent; then also agreement with experiments can be simply reached (for instance in Tables 3 and 4). In general it is not possible to recommend any theoretical model since the required accuracy is too high. Calculations useful in practice should for instance clearly differentiate 50% population from say 80% but in energy terms the required accuracy would be 3.4 kJ mol^{-1} and can be hardly achieved by the standard methods.

In our opinion quantum chemical calculations may be useful even in such cases: geometry of the rotamers can be calculated with some reliability and used in empirical determination of the conformational equilibrium. An example is given in Table 5; the resulting estimate of the population is probably the best one can get. The examples in Tables 1 and 2 are less important since the geometry of the *sc* conformer can be obtained either by calculation or from the Cambridge Database[21] with practically equal results.

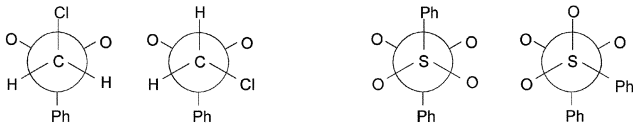
The *gauche* effect

Of the five compounds investigated here, **5** is evidently at variance with the simple *gauche* rule and some examples can be found in other classes of compounds. We agree in principle with Remizov[15] that one cannot consider the "*gauche* effect" as any general preference and one cannot find any kind of interaction, which would explain all observed cases. Wolfe attempted to explain the stability of conformers as a sum of attracting and distracting forces between two groups (and lone electron pairs) in the *gauche* position;[2] this explanation cannot be incorporated into the concept of quantum chemistry and in addition one must make assumptions about the intensity of interaction of various groups. In spite of this, we may attempt this approach within the restricted group of our sulfonyl derivatives. We pictured the *ap* and *sc* conformers of **1–5** in the Newman projections and counted the number of interactions of the adjacent groups in the *sc* (gauche) position. It is possible to get a common picture if one assumes that interaction of two polar bonds is destabilizing and that the lone electron pairs have only a minor effect.

Most evident is the conformation of **5**, which is clearly determined by the interactions of the strongly polar S–O



1,2*ap* **1**,2*sc* **3***ap* **3***sc*



4*ap* **4***sc* **5***ap* **5***sc*

bonds. This makes the *sc* conformer less stable: three interactions compared to two in the *ap* conformer. Any *gauche* rule formulated for the whole molecule would be misleading in this case. Similarly the conformation of **4** is dominated by the interactions of polar S–O and C–Cl bonds: one in the *sc* conformer compared to two in *ap*. The ratio of 2 : 1 is particularly high in this case and preference of the *sc* conformer is also high (Table 4). The effect of the S–C bond is insignificant. With the sulfonic esters **1** and **2** the conformation is determined by the interactions of the S–O bonds with O–R, whether O–CH_3 or O–C_6H_5 (one in *sc*, two in *ap*). Remarkably it is of little consequence that the polarity of the O–R bond is in reversed direction, with the negative end toward the central atom. In the case of chlorosulfates **3**; the polarity of the S–Cl bond is negligible compared to S–O bonds. Conformational preference of all our compounds can be thus explained by a unique principle, although in details referring to *ad hoc* arguments. However, we were not able to devise any general *gauche* rule, not even for this class of compounds.

Conclusions

We may attempt to draw some general conclusions in two different directions. Concerning the evaluation of standard quantum chemical methods, they are certainly at present not able to predict the population of rotamers with the accuracy of several percent. They are thus able to determine conformation only if it is strongly shifted to one side (energy difference of some 10 kJ mol^{-1}); from the point of view of organic chemistry there is only one rotamer existing in such cases. Nevertheless the quantum chemical calculations are useful since they can describe the structure of the individual rotamers with more precision than many experimental methods. This information can be used in calculating the population on the basis of experiments.

Concerning the *gauche* effect we can only support the opinion[15] that any general rule does not exist. When it is valid in some classes of compounds, it may have different reasons in every case. When the conformation should be qualitatively explained in simple terms, the destabilizing interactions of polar bonds in the *sc* position would be in our opinion most important.

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References

1 L. H. L. Chia, H. H. Huang and P. K. K. Lim, *J. Chem. Soc. B*, 1969, 608–612.
2 S. Wolfe, *Acc. Chem. Res.*, 1972, **5**, 102–111.
3 L.-S. Sonntag, S. Schweizer, C. Ochsenfeld and H. Wennemers, *J. Am. Chem. Soc.*, 2006, **128**, 14697–14703.
4 P. R. Rablen, R. W. Hoffmann, D. A. Hrovat and W. T. Borde, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1719–1726.
5 O. Exner, Z. Fidlerová and V. Jehlička, *Collect. Czech. Chem. Commun.*, 1968, **33**, 2019–2028.
6 O. Exner, P. Dembech and P. Vivarelli, *J. Chem. Soc. A*, 1971, 620–622.
7 O. Exner, V. Jehlička and J. B. F. N. Engberts, *Collect. Czech. Chem. Commun.*, 1977, **42**, 3040–3047.
8 O. Exner and J. B. F. N. Engberts, *Collect. Czech. Chem. Commun.*, 1979, **44**, 3378–3384.
9 O. Exner and V. Jehlička, *Collect. Czech. Chem. Commun.*, 1985, **50**, 2245–2251.
10 B. A. Arbuzov, S. G. Vul'fson, G. G. Butenko, O. A. Samarina and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 94–98.
11 G. G. Butenko, A. N. Vereshchagin, A. B. Remizov and R. N. Nurullina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1763–1769.
12 G. G. Butenko, A. N. Vereshchagin and L. S. Lyakisheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1559–1563.
13 B. A. Arbuzov, A. B. Remizov, G. G. Butenko and A. N. Vereshchagin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2006–2009.
14 A. B. Remizov, A. I. Fishman and G. G. Butenko, *Zh. Obshch. Khim.*, 1977, **47**, 1204.
15 A. B. Remizov, F. S. Bilalov and I. S. Pominov, *Spectrochim. Acta, Part A*, 1987, **43**, 475–482.
16 S. Böhm and O. Exner, *Phys. Chem. Chem. Phys.*, 2004, **6**, 510–514.
17 For instance D. Mirarchi and G. L. D. Ritchie, *Aust. J. Chem.*, 1981, **34**, 1443–1450.
18 S. Böhm and O. Exner, *J. Mol. Struct. (THEOCHEM)*, 2007, **803**, 9–16.
19 S. Böhm and O. Exner, *J. Comput. Chem.*, 2006, **27**, 571–577.
20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision B.03)*, Gaussian, Inc., Pittsburgh, PA, 2003.
21 Cambridge Structural Database, Version 5.26, August 2005.
22 C. T. Kiers and A. Vos, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 126–132.
23 F. H. Allen and R. Taylor, *Chem. Soc. Rev.*, 2004, **33**, 463–475.
24 R. Norrestam and L. Schepper, *Acta Chem. Scand., Ser. A*, 1981, **35**, 91–103.
25 S. Böhm and O. Exner, *Acta Crystallogr., Sect. B*, 2004, **60**, 103–107.

