# Group Electronegativities: as Empirically Estimated from Geometrical and Vibrational Data on Sulphones

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The S=O bond lengths and the S=O bond stretching frequencies characteristically change with changing ligand electronegativities in the $XSO_2Y$ sulphone series. Empirical relationships have been established between the S=O bond length and the sum of the ligand electronegativities ($\chi_X + \chi_Y$) and also between the mean stretching frequency and ($\chi_X + \chi_Y$). These relationships may be used for estimating group electronegativities from geometrical and vibrational data or to predict bond lengths, bond angles and stretching frequencies from ligand electronegativities.

Revised empirical correlation relationships between geometrical and vibrational parameters of a series of sulphone molecules have been communicated recently [1]. The predictive ability of these relationships has been demonstrated by the results of structure determinations of further sulphone molecules, viz. $CCl_3SO_2Cl$ [2], $CF_3SO_2Cl$ [3], $OCNSO_2Cl$ [4], $(CH_2{=}CH)_2SO_2$ [5].

The importance of the ligand electronegativities of $XSO_2Y$ sulphones on the vibrational frequencies and geometry of the $SO_2$ group has been recognized for a long time (see e.g. [6]). As the ligands and their electronegativities change in the sulphone series, the corresponding S=O bond lengths and O=S=O bond angles may differ up to 0.04 Å and 5°, respectively. At the same time the oxygen-oxygen non-bond distance is strikingly constant in the $XSO_2Y$ sulphones as has been noted recently [7, 8]. The O ... O distances in $XSO_2Y$ sulphones can be directly and accurately determined from the rotational spectra (cf. [8]). The mean $r(\mathrm{O} \ldots \mathrm{O})$ value from 9 microwave spectroscopic studies is 2.484 Å ($\sigma = 0.004$ Å) [8]. The empirical relationship correlating $r(\mathrm{S{=}O})$ and the bond angle O=S=O gives nearly the same predictions as yielded by the trigonometrical expression

$$\sphericalangle\, \mathrm{O{=}S{=}O} = 2 \arcsin [2.484/2r(\mathrm{S{=}O})]$$

in which 2.484 Å stands for $r(\mathrm{O} \ldots \mathrm{O})$. This is demonstrated by Fig. 1 incorporating mostly electron diffraction results.

Although the correlation between ligand electronegativity and the geometrical variations seems to be obviously present, no empirical relationship can be established outright because of lack of group electronegativities. As is well known, while the electronegativity of an element is considered to be

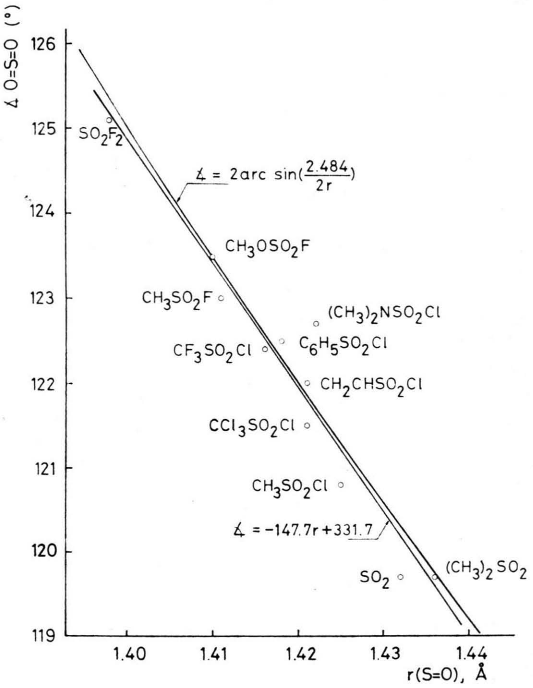

Fig. 1. The O=S=O bond angle ($\sphericalangle$) as a function of the S=O bond length ($r$). Circles: experimental values (for further details see Ref. 8; sources can be found in the Tables). The empirical relationship $\sphericalangle = -147.7\,r + 331.7$ was found by a least squares procedure. The trigonometrical expression utilizes the remarkable phenomenon of the O ... O distance being constant (2.484 Å) in a large series of sulphone molecules.

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a property of this element, the group electronegativity depends on the bond that the group forms. Thus, strictly speaking, there is a specific group electronegativity scale for the sulphone series. The idea to estimate a group electronegativity scale in the sulphone series on the basis of the geometrical, i.e. S=O bond length, variations is attractive since accurate $r(S{=}O)$ values have recently become available (see e.g. [8]). These S=O bond lengths were determined by gas electron diffraction and, accordingly, refer to free molecules.

An initial set of electronegativities was compiled for a few ligands, viz. F, Cl, $CF_3$, $CCl_3$, and $CH_3$. The choice of the first two was obvious, while group electronegativities for the three $CX_3$ ligands have been established by Hinze, Whitehead and Jaffé [9], $\chi_{CF_3}$ 3.29, $\chi_{CCl_3}$ 2.79, and $\chi_{CH_3}$ 2.30. These values were consistent with the experience reported on the relative electronegativities of these five ligands in sulphones [10] and sulphoxides [11] (see also [12]). The geometries of six sulphone molecules with various combinations of these ligands were recently determined. These initial data are given in Table 1.

Table 1. Initial data used in establishing the correlation relationships between S=O bond lengths or stretching frequencies and group electronegativities ($\chi$).

| Compound | $r(S{=}O)$ [Å] | $\tilde{\nu}(S{=}O)$ [cm$^{-1}$] | $\sum\chi$ |
|---|---|---|---|
| $FSO_2F$ | 1.398 [13] | 1390 [16] | 8.0 |
| $FSO_2CF_3$ | | 1356 [17] | 7.3 |
| $FSO_2Cl$ | 1.408 [14, 8] | 1346 [16] | 7.0 |
| $FSO_2CH_3$ | | 1322 [18] | 6.3 |
| $ClSO_2CF_3$ | 1.416 [3] | | 6.3 |
| $ClSO_2Cl$ | | 1303 [16] | 6.0 |
| $ClSO_2CCl_3$ | 1.421 [2] | 1298 [17] | 5.8 |
| $ClSO_2CH_3$ | 1.425 [15] | 1280 [19] | 5.3 |
| $CH_3SO_2CH_3$ | 1.436 [7] | 1257 [20] | 4.6 |

Because of the good experience with the empirical relationships between the S=O bond lengths and S=O bond stretching frequencies, and the available large body of vibrational data, it was decided to parallel the investigation of the correlation between the bond lengths and group electronegativities with another between the bond stretching frequencies and group electronegativities. Note that the correlation relationships between bond distances and vibrational frequencies (and also force constants [1]) refer to vapour-phase geometries and liquid-phase or solution spectra, respectively. One of the relationships, incorporating the results of new studies is demonstrated in Figure 2. Here and in all subsequent calculations the bond stretching frequency $\tilde{\nu}(S{=}O)$ is represented by the average

$$\tilde{\nu} = \{\tfrac{1}{2}[\nu_{as}^2(S{=}O) + \nu_s^2(S{=}O)]\}^{1/2}.$$

The initial frequency data for 8 sulphone molecules with various combinations of the above mentioned ligands are also given in Table 1.

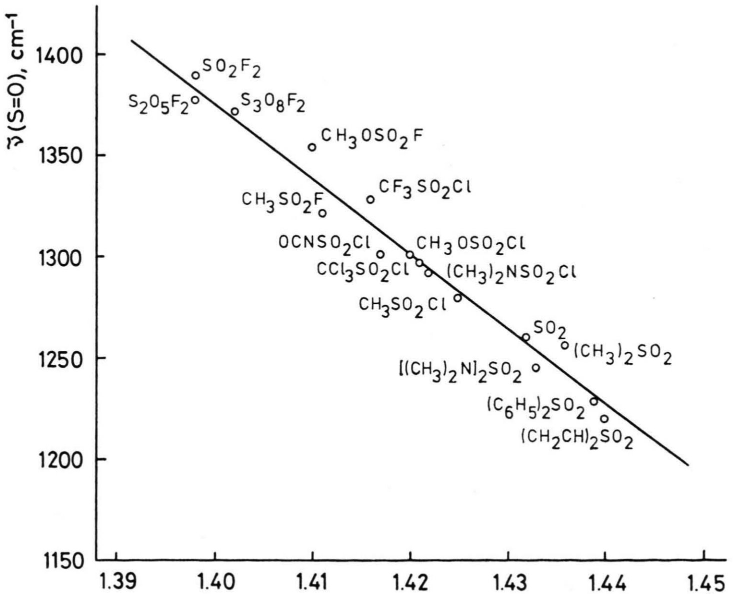


Fig. 2. Correlation relationship between the average stretching frequency, $\tilde{\nu}(S{=}O) = \{\tfrac{1}{2}[\nu_{as}^2(S{=}O) + \nu_s^2(S{=}O)]\}^{1/2}$, and the bond distance, $r(S{=}O)$. Circles: experimental data (for references see Tables 2 and 3). Full line: $\tilde{\nu} = -3695.0\,r + 6549.4\,(\sigma = 9\ \text{cm}^{-1})$.

The following relationships were obtained by least-squares procedure, and are illustrated in Figures 3 and 4.

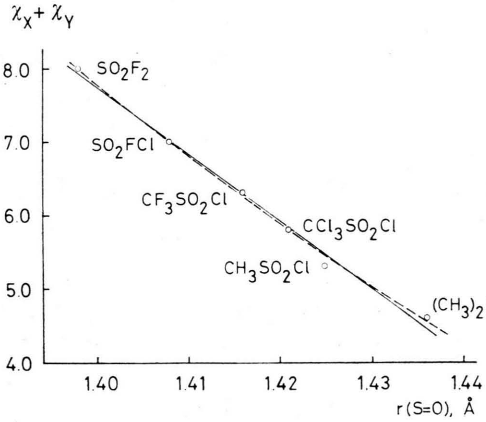


**Fig. 3.** Correlation relationship between the bond length, $r$(S=O) and the sum of the electronegativities of the ligands $X$ and $Y$ in the $XSO_2Y$ sulphone molecules. The circles represent the initial data given in Table 1, the full line and dashed line are determined by the linear and second degree relationships described in the text. The second degree relationship is somewhat superior to the linear one within the interval covered by the initial data. However, the linear relationship is recommended for extrapolation.

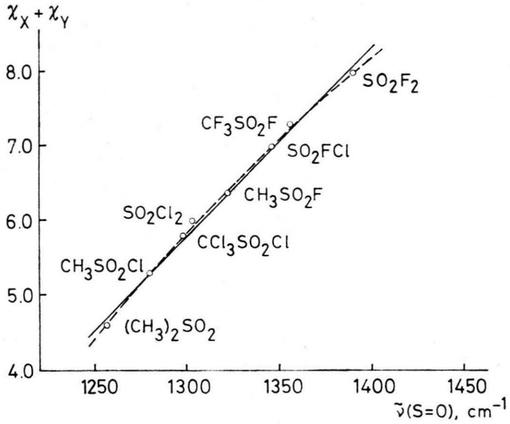


**Fig. 4.** Correlation relationship between the average stretching frequency, $\tilde{\nu}$(S=O) and the sum of the electronegativities of the ligands $X$ and $Y$ in the $XSO_2Y$ sulphone molecules. The circles represent the initial data given in Table 1, the full line and dashed line are determined by the linear and second degree relationships described in the text. The second degree relationship is somewhat superior to the linear one within the interval covered by the initial data. However, the linear relationship is recommended for extrapolation.

*Linear*

$$\sum \chi = -91.28\,r + 135.54 \quad \text{(standard deviation, } \sigma = 0.10\text{)},$$

$$\sum \chi = -0.02546\,\tilde{\nu} - 27.3 \quad (\sigma = 0.08),$$

*Second degree*

$$\sum \chi = 436.69\,r^2 - 1328.65\,r + 1012.00 \quad (\sigma = 0.07).$$

$$\sum \chi = -0.00003247\,\tilde{\nu}^2 + 0.11139\,\tilde{\nu} - 84.1 \quad (\sigma = 0.06).$$

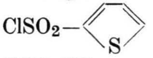
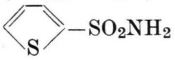
These relationships were then used to estimate other group electronegativities on the basis of available S=O bond lengths and bond stretching frequencies. The results are collected in Tables 2 and 3.

In addition to the usefulness of the group electronegativities, their tentative character should also be emphasized. Only some of the many possible sources of uncertainty are mentioned here. As was stated above, electronegativities of groups linked to identical molecular moieties are comparable in a strict sense. Thus even within the sulphone series the group electronegativities $\chi_X$ in the sulphonyl chloride series ($XSO_2Cl$) should be distinguished from the $\chi_X$ values in the sulphonyl fluoride series ($XSO_2F$), etc. The experimental

Table 2. Group electronegativities of ligands in the $XSO_2Y$ series as estimated from the S=O bond lengths (using the second degree relationship). Parentheses refer to estimated experimental errors of the bond lengths, corresponding deviations of $\sum \chi$ and inplausible values of $\chi_Y$, respectively.

| $XSO_2Y$ | $r$(S=O) [Å] | Ref. | $\sum \chi$ | $\chi_X$ | $\chi_Y$ |
|---|---|---|---|---|---|
| $FSO_2F$ | 1.398(2) | [13] | 8.0(2) | 4.0 | 4.0 |
| $FSO_2\underline{OSO_2F}$ | 1.398(2) | [21] | 8.0(2) | 4.0 | 4.0 |
| $\underline{FSO_2}OSO_2\underline{OSO_2}F$ | 1.402(3) | [21] | 7.6(3) | 3.8 | 3.8 |
| $FSO_2Cl$ | 1.408(6) | [14] | 7.0(6) | 4.0 | 3.0 |
| $FSO_2OCH_3$ | 1.410(2) | [22] | 6.8(2) | 4.0 | 2.8 |
| $FSO_2CH_3$ | 1.411(3) | [23] | 6.7(3) | 4.0 | 2.7 |
| $ClSO_2CF_3$ | 1.416(7) | [3] | 6.2(7) | 3.0 | 3.2 |
| $ClSO_2NCO$ | 1.417(3) | [4] | 6.1(3) | 3.0 | 3.1 |
| $ClSO_2C_6H_5$ | 1.418(12) | [24] | 6.0(12) | 3.0 | (3.0) |
| $ClSO_2OCH_3$ | 1.420(3) | [25] | 5.9(3) | 3.0 | 2.9 |
| $ClSO_2CCl_3$ | 1.421(3) | [2] | 5.8(3) | 3.0 | 2.8 |
| $ClSO_2CHCH_2$ | 1.421(6) | [26] | 5.8(6) | 3.0 | (2.8) |
| $ClSO_2N(CH_3)_2$ | 1.422(4) | [27] | 5.7(4) | 3.0 | 2.7 |
| $ClSO_2CH_3$ | 1.425(3) | [15] | 5.4(3) | 3.0 | 2.4 |
| $SO_2$ | 1.432(2) | [28] | 4.9(2) | 2.4 | 2.4 |
| $(CH_3)_2NSO_2N(CH_3)_2$ | 1.433(10) | [29] | 4.8(10) | 2.4 | 2.4 |
| $CH_3SO_2CH_3$ | 1.436(3) | [7] | 4.6(3) | 2.3 | 2.3 |
| $C_6H_5SO_2C_6H_5$ | 1.439(5) | [30] | 4.3(5) | 2.2 | 2.2 |
| $CH_2CHSO_2CHCH_2$ | 1.440(3) | [5] | 4.3(3) | 2.1 | 2.1 |

Table 3. Group electronegativities of ligands in the $XSO_2Y$ series estimated from the S=O stretching vibrational frequencies.

| $XSO_2Y$ | (S=O) [$cm^{-1}$] | Ref. | $\sum\chi$ | $\chi_X$ | $\chi_Y$ |
|---|---|---|---|---|---|
| | | | * | | |
| $FSO_2F$ | 1390 | 16 | 8.0 | 4.0 | 4.0 |
| $FSO_2\underline{OOF}$ | 1382 | 31 | 7.8 | 4.0 | 3.8 |
| $FSO_2\underline{OF}$ | 1380 | 17 | 7.8 | 4.0 | 3.8 |
| $FSO_2\underline{OSO_2F}$ | 1378 | 17 | 7.7 | 4.0 | 3.7 |
| $FSO_2\underline{OOCF_3}$ | 1375 | 31 | 7.7 | 4.0 | 3.7 |
| $\underline{FO_2SO}SO_2\underline{OSO_2F}$ | 1372 | 17 | 7.6 | 3.8 | 3.8 |
| $FOSO_2CF_3$ | 1356 | 17 | 7.2 | 4.0 | 3.2 |
| $FSO_2OCH_3$ | 1355 | 16 | 7.2 | 4.0 | 3.2 |
| $FSO_2Cl$ | 1346 | 16 | 7.0 | 4.0 | 3.0 |
| $FSO_2OH$ | 1342 | 32 | 6.9 | 4.0 | 2.9 |
| $ClSO_2CF_3$ | 1329 | 33 | 6.6 | 3.0 | 3.6 |
| $FSO_2Br$ | 1326 | 34 | 6.5 | 4.0 | 2.5 |
| $FSO_2C_6H_5$ | 1316 | 35 | 6.3 | 4.0 | 2.3 |
| $ClSO_2OH$ | 1312 | 32 | 6.1 | 3.0 | 3.1 |
| $ClSO_2Cl$ | 1303 | 16 | 5.9 | 3.0 | 3.0 |
| $ClSO_2NCO$ | 1302 | 36 | 5.9 | 3.0 | 2.9 |
| $ClSO_2OCH_3$ | 1302 | 37 | 5.9 | 3.0 | 2.9 |
| $ClSO_2CCl_3$ | 1298 | 17 | 5.8 | 3.0 | 2.8 |
| $ClSO_2N(CH_3)_2$ | 1293 | 38 | 5.6 | 3.0 | 2.6 |
| $ClSO_2C_6H_5$ | 1285 | 39 | 5.4 | 3.0 | 2.4 |
| $HOSO_2OH$ | 1284 | 32 | 5.4 | 2.7 | 2.7 |
|  | 1284 | 33 | 5.4 | 3.0 | 2.4 |
| $ClSO_2CH_3$ | 1280 | 19 | 5.3 | 3.0 | 2.3 |
| $CH_3OSO_2C_6H_5$ | 1279 | 35 | 5.2 | 2.9 | 2.3 |
| $SO_2$ | 1261 | 16 | 4.7 | 2.4 | 2.4 |
| $CH_3SO_2CH_3$ | 1257 | 20 | 4.6 | 2.3 | 2.3 |
| | | | ** | | |
| $C_6H_5SO_2NH_2$ | 1249 | 39 | 4.5 | 2.4 | 2.1 |
| $(CH_3)_2NSO_2N(CH_3)_2$ | 1246 | 38 | 4.4 | 2.2 | 2.2 |
|  | 1243 | 40 | 4.3 | 2.4 | 1.9 |
| $CH_3SO_2NH_2$ | 1233 | 41 | 4.1 | 2.3 | 1.8 |
| $C_6H_5SO_2CHCH_2$ | 1230 | 42 | 4.0 | 2.0 | 2.0 |
| $C_6H_5SO_2C_6H_5$ | 1229 | 43 | 4.0 | 2.0 | 2.0 |
| $CH_3SO_2CHCH_2$ | 1229 | 44 | 4.0 | 2.0 | 2.0 |
| $CH_2CHSO_2CHCH_2$ | 1221 | 4 | 3.8 | 1.9 | 1.9 |

*Using the second degree relationship between $\tilde{\nu}(=[\frac{1}{2}(\nu_{as}^2+\nu_s^2)]^{1/2})$ and $\sum\chi$.

** Using the linear relationship.

errors of the bond lengths and stretching frequencies should not be ignored. $\Delta r(S{=}O) = 0.005$ Å or $\Delta\tilde{\nu}(S{=}O) = 20\ cm^{-1}$ changes the estimated electronegativities by about 0.5. The estimated experimental errors of the bond lengths are indicated in Table 2 and their respective influence in the estimated group electronegativities are also given. It is seen that the relatively large errors of some of the bond lengths render the corresponding estimated group electronegativities meaningless. Unfortunately, no comparable quantities of the experimental error are available for the frequencies. Thus the estimated $\chi$ values should be treated especially carefully. Furthermore, the estimation procedure is somewhat influenced by the choice of the initial data (cf. Table 1). It is true, however, that the emerging pattern of group electronegativities seems to be consistent with expectation and previous experience and thus the initial choice of data is probably fortunate. Finally, it should be remembered that all the bond lengths in our tables refer to free (vapour-phase) molecules while the stretching frequencies originate from spectra of liquid-phase samples.

To summarize, the variations in the S=O bond lengths and bond stretching frequencies well parallel the changes in the ligand electronegativities in the sulphone series. Accordingly, group electronegativities can be estimated from the geometrical and vibrational parameters. The present results support earlier notions as regards the relative electronegativities of the $CF_3$, $CCl_3$, $CH_3$ groups. Furthermore, they indicate the position of some other groups, notably the isocyanate and methoxy groups, on the electronegativity scale. The electronegativities of some of the important ligands follow the relationship:

$$F > OF > CF_3 > NCO > Cl > OCH_3 > CH_3,\ \text{etc.}$$

It is also noted that the numerical $\chi$ values for some groups, e.g. OH, $NH_2$, $C_6H_5$, are very uncertain.

The empirical relationships established above can also be used to predict S=O bond lengths and $\tilde{\nu}(S{=}O)$-values on the basis of the ligand electronegativities. As an illustration let us consider the S=O bond lengths for some individual compounds [45]. Here we shall use the relationship

$$r(S{=}O) = (135.54 - \sum\chi)/91.28\,.$$

Seppelt and Lentz [46] suggested that the ligands $OSeF_5$ and $OTeF_5$ are at least as electronegative as fluorine. Accordingly, the lengths of the S=O bonds in the $SO_2$ groups of the following molecules can be predicted to take the values listed below, assuming 4.0 for the electronegativities of the ligands $OSeF_5$ and $OTeF_5$.

The above relationship yields $r(S{=}O) = 1.419$ Å for sulphuryl chloride, $SO_2Cl_2$. This value is somewhat larger than that reported from an earlier electron diffraction investigation [47]. However, it

| Compound | Predicted $r(S{=}O)$ [Å] |
|---|---|
| $FSO_2OSeF_5$ | 1.397 |
| $FSO_2OTeF_5$ | 1.397 |
| $ClSO_2OSeF_5$ | 1.408 |
| $ClSO_2OTeF_5$ | 1.408 |
| $F_5SeOSO_2OSeF_5$ | 1.397 |
| $F_5TeOSO_2OTeF_5$ | 1.397 |

was suggested that error in the empirical background may have resulted in the determination of a too short S=O distance in $SO_2Cl_2$ ([8], cf. also [48]). The bond length vs. stretching frequencies relationship predicted 1.420 Å for $r(S{=}O)$ [8] in complete agreement with the present prediction based on the ligand electronegativities. Thus an experimental reinvestigation of the sulphuryl chloride structure is warranted.

Using the above relationship, the S=O bond length for some more sulphone molecules are predicted below. Predicted O=S=O bond angles are also listed as estimated from Figure 1.

| | | $r(S{=}O)$ [Å] | $\sphericalangle$ O=S=O [°] |
|---|---|---|---|
| $FSO_2NCO$ | ($\chi_{NCO}$ 3.0) | 1.408 | 123.8 |
| $(OCN)_2SO_2$ | ($\chi_{NCO}$ 3.0) | 1.419 | 122.1 |
| $(OCH_3)_2SO_2$ | ($\chi_{OCH3}$ 2.9) | 1.421 | 121.8 |
| $FSO_2OF$ | ($\chi_{OF}$ 3.8) | 1.399 | 125.1 |
| $FSO_2CF_3$ | ($\chi_{CF_3}$ 3.3) | 1.405 | 124.3 |

The molecular geometry of none of these compounds has been determined yet. It is difficult of course to give a realistic uncertainty estimate for these predicted values. A change of 0.3 in $\sum \chi$, for example, corresponds to $\Delta r = 0.003$ Å and then to $\Delta \sphericalangle = 0.5°$. The uncertainty in the electronegativity values should thus also be considered in addition to the approximate character of the empirical relationships themselves [49].

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[49] Because of the inherent uncertainties of these estimations, we have not been concerned with the exact physical meaning of the internuclear distances appearing in various places of this paper. It is well known that the physical meaning of the $r$-values will be somewhat different as determined by various physical techniques due to the difference is the averaging over the intramolecular motion. These effects are anticipated to be relatively small for $r(S{=}O)$ as a consequence of the relative stiffness of this bond (for more details, see [8]). The estimated bond lengths are considered to represent average distances ($r_g$-values).