

## DIPOLE MOMENTS AND CONFORMATION OF DITHIOACETALS AND GEM-DISULFONES

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Dipole moment data on seven dithioacetals and five gem-disulfones in solution have been used to estimate the conformation. The result is rather unexpected in the case of the former compounds, indicating the presence of the unsymmetrical conformation  $g,t$  ( $G$ ) and probably also of others less populated. In the case of gem-disulfones the most populated conformation is  $g,g'$  ( $J$ ) with both alkyl groups on different sides of the S—C—S plane; this is explained by the electrostatic repulsion of oxygen atoms of both sulphonyl groups. The molar refraction of dithioacetals is discussed.

Among various functional groups the conformation of which has been studied by us, those with two equivalent single bonds attached to the same atom deserve special attention. Examples of such molecules are acetals<sup>1</sup>, acylals<sup>2</sup>, carboxylic acid anhydrides<sup>3</sup>, diacyl sulfides<sup>4</sup>, esters of alkaneboronic<sup>5</sup>, alkanephosphinic and alkanephosphonic acid *etc.*

Due to the equivalence of the two bonds, analogous conformations on both are most probable and the whole functional group has most frequently the  $C_2$  or  $C_s$  symmetry. The mutual influence of both parts can be anticipated to be relatively small so that the resulting conformations should be relatively unstable and sensitive to small structural changes. As factors controlling conformation, especially dipole-dipole interaction<sup>6,7</sup>, repulsion of lone electron pairs<sup>1,8,9</sup>, and recently also attractive forces between electrons and atomic nuclei<sup>10</sup> are to be taken into account.

The present paper is concerned with the conformation on the two C—S bonds of dithioacetals and gem-disulfones; the experimental method used was again measurement of dipole moments in solution combined with a graphical evaluation of results<sup>2</sup>. The two classes of compounds were little studied by physical methods; conformational studies of dithioacetals by spectroscopy<sup>11</sup> and of dithioacetals<sup>12</sup> and gem-disulfones<sup>13</sup> by dipole moments were confined to derivatives of formaldehyde. Our graphical method needs the comparison with a *para*-derivative; for this

reason mostly aromatic derivatives have been chosen (2–7, 9–12), the aliphatic ones (1, 8) being included for comparison only. The cyclic derivatives (6, 7, 11, 12) should serve to check the values of bond moments used.

## EXPERIMENTAL AND RESULTS

### Dithioacetals

All the dithioacetals 1–7 are known substances (for references<sup>14–18</sup> see Table I). They were prepared by the following standard procedure: Into the solution of an aldehyde (0.5 mol) and ethanethiol (1.0 mol) or 1,2-ethanedithiol (0.5 mol), respectively, in the equal volume of dichloromethane a stream of dry hydrogen chloride was introduced (1–2 ml/min) during 5 hours, at the beginning under cooling, later at room temperature. The reaction mixture was then refluxed 2 hours, extracted successively with  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHSO}_3$  and  $\text{NaHCO}_3$  solutions and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was taken off and product fractionated at 0.05–0.1 mm Hg.

### Disulfones

The disulfones 9–12 were prepared by the following procedure, based on ref.<sup>19</sup>: To the solution of the corresponding dithioacetal (0.05 mol) in ethyl acetate (150 ml) 4% aqueous potassium permanganate (20.5 g) was added and subsequently diluted sulfuric acid (6.4 g in 100 ml water) under vigorous stirring in the course of 2–3 hours. After the colour of potassium permanganate disappeared, the precipitated manganese dioxide was filtered off and extracted twice with hot ethanol, the extracts combined with the ethyl acetate layer and solvents evaporated. The residue was extracted thoroughly with sodium carbonate solution and the undissolved product recrystallized from aqueous ethanol.

4-Chloro- $\alpha,\alpha$ -bis(ethylsulfonyl)toluene (10), yield 42%, m.p. 138°C. For  $\text{C}_{11}\text{H}_{15}\text{ClO}_4\text{S}_2$  (310.8) calculated: 42.51% C, 4.86% H, 11.41% Cl; found: 42.73% C, 4.75% H, 11.60% Cl.





2-Phenyl-1,1,3,3-tetraoxido-1,3-dithiolane (11), yield 12%, m.p. 118°C. For  $\text{C}_9\text{H}_{10}\text{O}_4\text{S}_2$  (246.3) calculated: 43.89% C, 4.09% H; found: 43.97% C, 4.32% H.

2-(4-Chlorophenyl)-1,1,3,3-tetraoxido-1,3-dithiolane (12), yield 19%, m.p. 218°C. For  $\text{C}_9\text{H}_9\text{ClO}_4\text{S}_2$  (280.7) calculated: 38.51% C, 3.23% H, 12.63% Cl; found: 38.76% C, 3.05% H, 12.44% Cl.

### Measurement of Dipole Moments

The same method was used as previously<sup>1,3</sup>. The experimental results are summarized in Table I. The molar refraction of compounds 7–12 was computed using Vogel's increments<sup>20</sup> and the value  $8.67 \text{ cm}^3$  for the  $\text{SO}_2$  group<sup>21</sup>. With compounds 7, 10, and 12 an exaltation was applied, expressing the conjugation of chlorine atom with the aromatic nucleus and derived from appropriate chloro derivatives. With cyclic compounds 7, 11, and 12 the increment valid for five-membered carbocyclic compounds<sup>20</sup> was added. The inaccuracies in the whole procedure do not influence markedly the values of dipole moments. The theoretical dipole moments were computed graphically with an accuracy of about 0.03 D. The bond moments used were the same as in the previous work<sup>1–3,22</sup>, the angle  $\angle \text{C—S—C} = 102^\circ$  was taken.

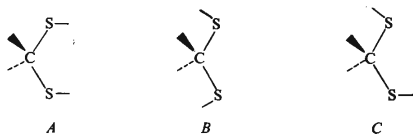
TABLE I  
Polarization and Dipole Moments of Dithioacetals and gem-Disulfones in Benzene at 25°C

Compound	Ref.	$n_D^{20}$	$d^{20}$	$R_D^{20}$	$\infty P_2$	$\mu(5\%)^a$	$\mu(15\%)^a$
1 $(CH_3)_2C(SC_2H_5)_2$	14	1.4965 <sup>b</sup>	0.9482 <sup>b</sup>	50.67 <sup>b</sup>	80.8	1.16	1.05
2 $C_6H_5CH(SC_2H_5)_2$	15	1.5718 <sup>c</sup>	1.0570	66.09	157.2	2.07	1.99
3 $4-CH_3C_6H_4CH(SC_2H_5)_2$	16	1.5660 <sup>c</sup>	1.0394	71.05	154.2	1.97	1.89
4 $4-ClC_6H_4CH(SC_2H_5)_2$	16	1.5805 <sup>c</sup>	1.1531	71.28	215.5	2.62	2.56
5 $4-NO_2C_6H_4CH(SC_2H_5)_2$	16	1.5973 <sup>c</sup>	1.1920	73.60	484.8	4.46	4.43
6 $C_6H_5CH$ 	17	1.6335 <sup>d</sup>	1.2137	53.68	93.0	1.34	1.24
7 $4-ClC_6H_4CH$ 	18	62 <sup>e</sup>		58.5 <sup>f</sup>	178.9	2.40	2.33
8 $(CH_3)_2C(SO_2C_2H_5)_2$	15	127 <sup>e</sup>		54.6 <sup>f</sup>	83.1	1.12	1.00
9 $C_6H_5CH(SO_2C_2H_5)_2$	15	134 <sup>e</sup>		67.0 <sup>f</sup>	312.0	3.41	3.36
10 $4-ClC_6H_4CH(SO_2C_2H_5)_2$	—	138 <sup>e</sup>		71.9 <sup>f</sup>	309.9	3.38	3.33
11 $C_6H_5CH$ 	—	118 <sup>e</sup>		55.4 <sup>f</sup>	321.8	3.59	3.55
12 $4-ClC_6H_4CH$ 	—	218 <sup>e</sup>		60.3 <sup>f</sup>	434.7 <sup>g</sup>	4.25 <sup>g</sup>	4.23 <sup>g</sup>

<sup>a</sup> Values with a correction for the atomic polarization 5% or 15% of the value  $R_D$ , respectively; <sup>b</sup> ref.<sup>14</sup> gives  $n_D^{16}$  1.49392,  $d^{16}$  0.9496,  $R_D^{16}$  50.35; <sup>c</sup> ref.<sup>16</sup> gives  $n_D^{25}$  1.5723, 1.5730, 1.5819 and 1.5980 for compounds 2–5, respectively; <sup>d</sup> ref.<sup>17</sup> gives m.p. 29°C; <sup>e</sup> m.p.; <sup>f</sup> calculated values, see Experimental; <sup>g</sup> in dioxan.

## DISCUSSION

The first task to be dealt with is the choice of appropriate bond moments for a given class of compounds. In the case of dithioacetals we can check our values<sup>1–3,22</sup> on the cyclic compounds 6 and 7, assumed to be planar in the first approximation. The values calculated 0.95 and 2.41 D, respectively, do not agree well with the experimental ones. Using a larger moment 1.0 D for the C—S bond<sup>23</sup> we get the values 1.19 and 2.61 D, respectively, which are not much better. For cyclic acetals<sup>1</sup> and anhydrides<sup>3</sup> high values of dipole moments were previously observed, which would require enhanced bond moments, too. Hence, there are some doubts whether these five-membered heterocycles are a suitable model for open-chain compounds,



or if some specific factors are operating in them. For these reasons we decided to use the original bond moments<sup>1-3,22</sup> without change. A change of the C—S bond moment from 0.7 D to 1.0 D would not affect the main conclusions reached in this paper.

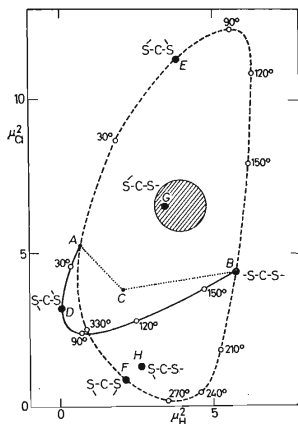


FIG. 1

Comparison of Experimental and Computed Dipole Moments of Dithioacetals 2 and 4

The values of  $\mu^2$  are plotted on the  $x$  axis for the compound 2 and on the  $y$  axis for its 4-chloro derivative 4, the experimental moment is expressed by the hatched circle.

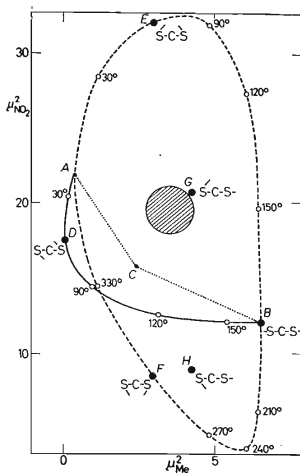


FIG. 2

Comparison of Experimental and Computed Dipole Moments of Dithioacetals 3 ( $x$ -axis) and 5 ( $y$ -axis)

When considering the conformation of acyclic dithioacetals 1–5, we start from the three planar forms *A*–*C*, which are important for the calculations. When the calculated values are plotted as  $\mu^2$  in a graph, the unsubstituted compound being on the *x* axis and its *para*-derivative on the *y* axis, each conformation is represented by a point (see Fig. 1 for compounds 2 and 4). The tie line of two points corresponds either to mixtures or to transitory conformations arising by rotation around one bond<sup>2</sup> in the simple case; in more complex cases curves are generated in the graph. In Fig. 1 the transformation of the form *A* into *B* by several paths is pictured: *a*) by rotating simultaneously both alkylthio groups in the same direction so that the functional group has the  $C_2$  symmetry in transitory conformations (full curve); *b*) by rotating in the opposite directions so that the  $C_s$  symmetry is maintained in the transitory conformations and both ethyl groups are situated above the S–C–S plane, on the side of the hydrogen atom (upper part of the dashed curve); *c*) by rotating in the opposite directions ( $C_s$  symmetry), both ethyl groups being below the S–C–S plane, on the side of the phenyl group (lower part of the dashed curve); *d*) by changing subsequently the conformation on the two C–S bonds so that the unsymmetrical form *C* arises transitorily.

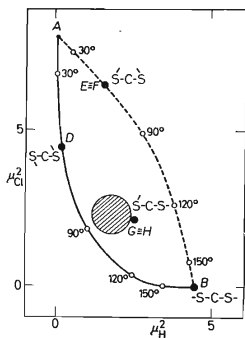


FIG. 3

Comparison of Experimental and Computed Dipole Moments of Bis(phenylthio)methane (*x*-axis) and its 4,4'-Dichloro Derivative (*y*-axis)

Experimental data from ref.<sup>12</sup>.

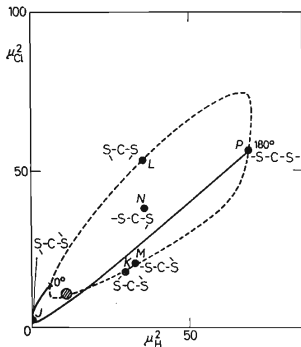
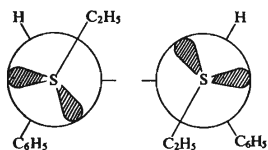
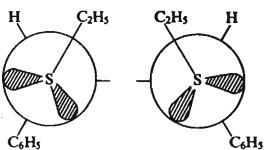
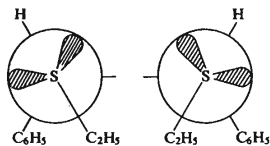
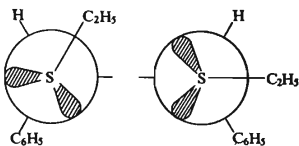
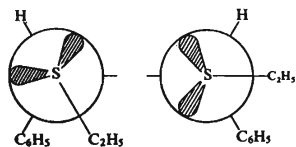
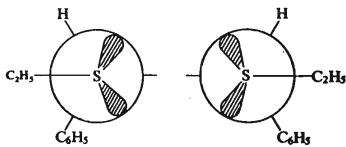


FIG. 4

Comparison of Experimental and Computed Dipole Moments of gem-Disulfones 9 (*x*-axis) and 10 (*y*-axis)

Fig. 1 reveals that no single symmetrical conformation meets with experiment and Fig. 2 concerning derivatives 3 and 5 renders the same picture. The solution of the problem thus needs certain theoretical assumptions, in order to restrict the number of possible conformations. Recent *ab initio* calculations of molecules containing polar bonds and lone electron pairs take into account various kinds of repulsive as well as attractive forces and lead to the following rules<sup>10</sup>: Conformations with a maximum number of gauche interactions between polar bonds and/or lone electron pairs are preferred, except that the conformation which places a polar bond between two electron pairs is disfavoured (the so-called<sup>10</sup> Edward<sup>24</sup>–Lemieux<sup>25</sup> effect). With atoms bearing lone electron pairs the energetical barrier is usually not three-fold since the concept of oriented pairs is essentially an arbitrary one. The rules quoted are supported by a lot of experimental data<sup>10</sup> and agree also with some our of results, discussed previously in terms of lone electron repulsion<sup>1,26</sup>, although not with all<sup>22</sup>.

*D(gg')**E(gg')**F(g'g')**G(gt)**H(g't)**B(tt)*

When applied to dithioacetals these rules predict the gauche forms *D*, *E*, *F* (Newman projections viewed along each S—C bond) to be more stable than *G*, *H* or even *B*. The preference among *D*, *E*, and *F* can be discussed in terms of secondary effects, e.g. steric repulsions  $C_2H_5 - C_6H_5$  in *D* and *F* and electrostatic repulsion between lone electron pairs in *E* and *F*, with the result that the *g, g'* form (*D*) is the preferred conformation as in the case of acetals<sup>1</sup>. The prediction is not supported by experimental findings. Figs 1 and 2 reveal that the only single conformation compatible with experiment is *g, t(G)* (with possible small admixtures of other forms), alternatively mixtures of various composition are also possible. If only *D*, *E*, *F* were taken into account, the actual state would be represented by a 1 : 1 mixture of *g, g'(E)* and *g', g'(F)*; this is hardly compatible with the steric hindrance in the latter. Note that the barrier need not be necessarily three-fold and even the values calculated for completely free rotation are not too far from the experimental ones, however, we consider such a free rotation impossible.

The conformation of the aliphatic derivative *I* cannot be determined by the same method. From the difference between dipole moments of *I* and *2* (or *3*) one can judge that the conformation is similar but not exactly the same. At least the population of individual forms is somewhat different in aliphatic derivative.

The results obtained on bis(arylthio)methanes<sup>12</sup> can be also treated using our graphical method (Fig. 3). The *g, t* form ( $G \equiv H$ ), considered by the original authors<sup>12</sup> as the only one present, seems to be the most populated one but the presence of *g, g'(D)* is also probable. A similar graph is obtained using the 4,4'-dinitro derivative.

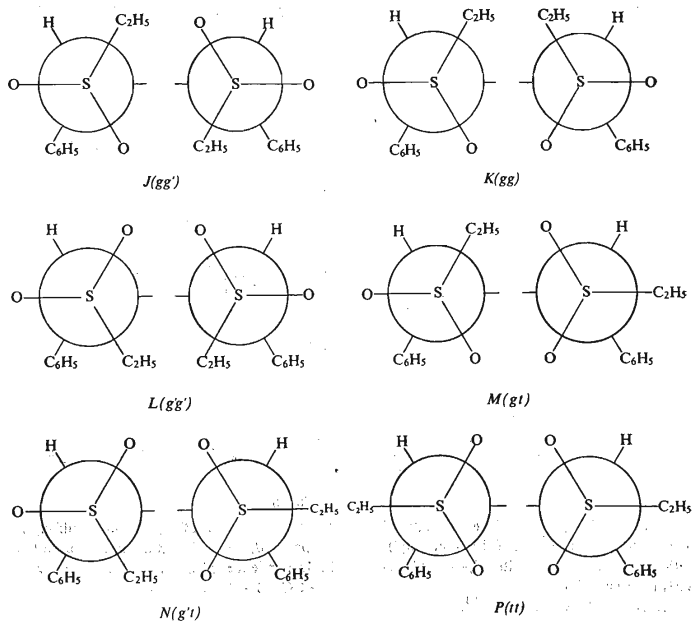
Even when the conformation of dithioacetals is not known into details and should be confirmed by other physical method, it is certainly different from that one of acetals<sup>1\*</sup> and unsymmetrical forms with different conformations on equivalent bonds in both halves of the molecule are probably represented. The difference with respect to acetals is most striking and cannot be explained using the mentioned rules<sup>10</sup> considering only the interactions on one S—C bond. In the case of acetals the explanation was attempted in terms of electrostatic repulsion of electron pairs on the two oxygen atoms<sup>1</sup>. With larger atoms of sulphur this 1,3-interaction is reduced, diminishing the preference of the form *D* and giving the molecule greater conformational freedom. A less probable explanation could make use of *d*-orbitals on sulphur.

With gem-disulfones we followed the same procedure as with dithioacetals, the moment of the  $SO_2$  group being taken as a vector (3.0 D) bisecting the O—S—O angle<sup>22</sup>. Moments computed for cyclic derivatives *11* and *12* (2.65 and 3.88 D, respectively) are again distinctly smaller than the experimental values, however, they are rather sensitive to the values of angles S—C—S and C—S—C. For the same reasons as with dithioacetals we used the original bond moments<sup>1,3,22</sup> to calculate

\* The conformation near to *D* was claimed<sup>27</sup> for bis(*n*-butylthio)methane based on the dipole moment value of this single substance and without considering all possibilities.

moments for individual conformations. The results are compared in a graph (Fig. 4) of the same type as previously. Starting from the conformation corresponding to *A* (denoted  $0^\circ$  in Fig. 4) we can reach that one corresponding to *B* (denoted  $P = 180^\circ$ ) by three paths: *a*) rotation of the two  $\text{SO}_2\text{R}$  groups in the same direction (symmetry  $C_2$ , full curve), *b*) rotation in opposite directions (symmetry  $C_s$ ), both ethyl groups being situated on the side of the hydrogen atom (lower part of the dashed curve), or, *c*), on the side of the phenyl group (upper part of the dashed curve). The discussion of possible conformations is somewhat simpler than with thioacetals since only staggered forms *J*–*P* need be considered.

Jeminet, Pigenet and Lumbroso<sup>13</sup>, when discussing conformation of disulfones  $\text{ArSO}_2\text{CH}_2\text{SO}_2\text{Ar}$ , considered eclipsed forms to be more probable; this opinion was based on the conformation of acetaldehyde the  $=\text{O}$  and  $\text{H}$  atoms of which are





also eclipsed. There is, however, a fundamental difference between both types of compounds: Due to the planar arrangement on the carbonyl carbon a pure staggered conformation of acetaldehyde is not possible, whereas in the case of sulfones even when a weak attracting force exists between O and H atoms, it must be outweighed by repulsion of larger substituents. In fact the staggered form was found by the X-ray investigation of dimethyl sulfone even when the position of hydrogen atoms was determined only approximately<sup>28</sup>. If only staggered forms are taken into account, it follows from our experimental results that the form  $g, g(J)$  is prevailing one, being accompanied either by the form  $g, g(K)$  or  $g, t(M)$ ; the former possibility seems to us more probable.

The experimental data on bis(arylsulfonyl)methanes<sup>13</sup> can now be treated in the same way with a similar result (Fig. 5). In addition to bonds moments used hitherto a mesomeric moment of 1.0 D was applied, expressing formally the conjugation of the  $\text{SO}_2$  group with the benzene ring<sup>22</sup>. The number of possible forms is reduced to four since  $K$  is now identical with  $L$  and  $M$  with  $N$ . A mixture of the prevailing form  $g, g'(J)$  and in addition either  $g, g(K)$  or  $g, t(M)$  is again compatible with

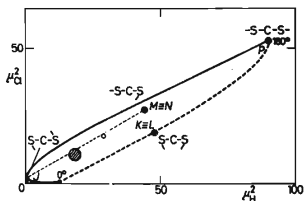


Fig. 5

Comparison of Experimental and Computed Dipole Moments of Bis(phenylsulfonyl)methane ( $x$  axis) and its 4,4'-Dichloro-derivative ( $y$  axis)

Experimental data from ref.<sup>13</sup>.

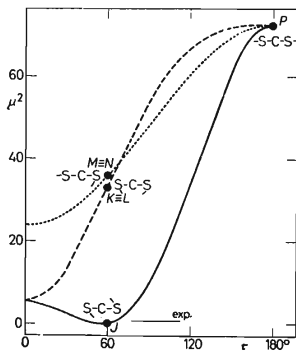


FIG. 6

Dipole Moments of 2,2-Bis(ethylsulfonyl)propane **8**, Experimental and Computed in Dependence of the Dihedral Angle  $\tau = \angle \text{C-S-C-S}$

experiments. The eclipsed conformation supposed by Jeminet and coworkers<sup>13</sup> is marked by a small empty circle in Fig. 5. In fact its presence cannot be disproved on the experimental basis alone and the disagreement between our results and those of ref.<sup>13</sup> thus depends on the presumptions that either staggered or eclipsed conformations are to be preferred.

The conformation of 2,2-bis(ethylsulfonyl)propane 8 cannot be determined by our method<sup>2</sup> but another type of graphical representation brings a decision. In Fig. 6 computed moments are plotted as function of dihedral angle  $\tau = \angle \text{S}-\text{C}-\text{S}-\text{C}$  when both ethylsulfonyl groups are rotated simultaneously in the same direction (full curve), or in opposite directions (broken curve), or finally when only one ethylsulfonyl group is rotated, the other taking the *trans* position (dotted curve). The four staggered conformations are denoted again by black points. Although this kind of graph is less advantageous and in general not sufficient for determining the conformation, the result is unequivocal in the case under consideration; the *g,g'* form (*J*) is the only possible one.

According to the quoted rules<sup>10</sup> the preferred form of gem-disulfones would be *P* with the greatest number of *gauche* interactions of polar bonds. The simplest model compound for one half of the molecule is 1,1,2-trichloroethane; however, the experimental investigations of this compound<sup>29,30</sup> revealed the preference of the "anti" form\* corresponding to *g* conformation of gem-disulfones (in *J*, *K*, *L*). Our experimental results are at variance with the prediction and in agreement with the conformation of 1,1,2-trichloroethane; they can be explained in details starting from the following principles: *a*) The *gauche* conformation is more stable than *trans* for the same reasons as in the case of 1,1,2-trichloroethane<sup>10,29,30</sup>, *b*) the electrostatic interaction between oxygen atoms (*i.e.* of dipoles and/or lone electron pairs) is another important factor. By both these effects the conformation *g,g'*(*J*) would be preferred and it is in fact the only one present in compound 8 and the most populated one in all derivatives. The admixture of other conformations can be explained by secondary effects: With derivatives 9 and 10 especially the form *g,g'*(*K*) comes into play, in which the electrostatic repulsion is partly balanced by releasing the  $\text{C}_2\text{H}_5 - \text{C}_6\text{H}_5$  interaction. With bis-arylsulfonylmethanes forms *g,g'*(*K*) or *g, t'*(*M*) can be considered, one  $\text{C}_6\text{H}_5 - \text{SO}_2$  interaction being released in the latter. The *t, t'* form (*P*) is evidently the least favoured with all compounds, the unfavourable *trans* conformation is combined with the strong electrostatic repulsion of oxygen atoms.

**Molar refraction.** From liquid dithioacetals 1–6 the molar refraction increment for sulfur in the functional group  $-\text{S}-\text{C}-\text{S}-$  can be estimated in an orienting manner. Using Vogel's increments<sup>20</sup> we calculated for one sulfur atom the values

\* There is evidently a misprint in ref.<sup>30</sup> indicating the molar fraction of the *gauche* form (instead of the *anti* form) to be 0.71–0.81.

8.09 cm<sup>3</sup> from the aliphatic derivative 1 and 8.26, 8.39, 8.39 and 8.84 cm<sup>3</sup>, respectively, from aromatic derivatives 2–5, the last abnormal value is due to a near absorption band. From the compound 6 the value 7.80 was obtained even when the negative increment –0.19 cm<sup>3</sup> for the five-membered carbocyclic ring<sup>20</sup> was applied. By comparing to the value for S in sulfides, exaltations of 0.17 cm<sup>3</sup> and 0.44 cm<sup>3</sup> are found in aliphatic and aromatic dithioacetals, respectively. These exaltations indicate non-bonded interactions (probably in the excited state) between the two sulfur atoms on the one hand, and between them and the benzene nucleus on the other hand; both were already found in UV spectra<sup>31</sup>. With respect to acetals, which do not show enhanced refraction<sup>20</sup>, one can judge that either the presence of *d*-electrons is essential, or the conformation of O- and S-derivatives is not the same. The different behaviour of the cyclic derivative 6 is in favour of the latter possibility, the non-bonded interaction seems to be dependent on a favourable conformation of orbitals.

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