

## DIPOLE MOMENTS AND CONFORMATION OF S-ALKYL THIOCARBOXYLATES AND ALKYL DITHIOCARBOXYLATES

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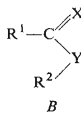
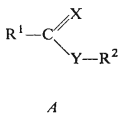
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From dipole moments measurement in solution it has been concluded that S-alkyl thiocarboxylates and dithiocarboxylates possess the *s-trans* conformation, the same as carboxylates and O-alkyl thiocarboxylates. In all cases the rigid planar conformation is controlled by mesomerism within the functional group whereas the repulsion of lone electron pairs is probably the main factor preferring the *s-trans* form. The extent of mesomerism in the compounds mentioned is discussed on the basis of dipole moment data and molar refraction.

In our studies on the conformation of functional groups, we focused our attention to carboxylic esters and some related classes of compounds<sup>1-3</sup>. The rigid and practically planar *s-trans* conformation of esters (*A*) is a dominating feature<sup>4-6</sup> although vibrations undoubtedly take place and the energy minimum need not be exactly connected with the exactly planar form<sup>7,8</sup>. Larger deviations were claimed in the case of some special structures<sup>9</sup> whereas the chloroformates are the only esters believed to exist in the *s-cis* form<sup>10</sup> (*B*).



X, Y = O or S

The mesomerism within the group, resulting in a partial double character of the C—O bond, is generally considered to be the decisive factor compelling the planar conformation<sup>1-7</sup>, while the preference of the form (*A*) over (*B*) is explained either by the electrostatic repulsion of the parallel dipoles<sup>4</sup> C=O and C—O, or of the lone

electron pairs<sup>11</sup> in B. To contribute to this problem we studied all the derivatives arising by replacement of oxygen atoms with sulfur. The same *s-trans* conformation (A) was established for O-alkyl thiocarboxylates<sup>3</sup>; S-alkyl thiocarboxylates and alkyl dithiocarboxylates is the subject of the present paper. The same approach was followed as previously<sup>1-3</sup> in which the dipole moments, measured in solution, are compared in a simple graph<sup>12</sup>. As far as the S-alkyl thiocarboxylates are concerned, dipole moments of some acylated thiophenols were reported without respect to their conformation<sup>13</sup>, whereas the *s-trans* conformation was deduced<sup>14</sup> on the basis of two thioacetates. For chlorothioformates the *s-cis* conformation was claimed<sup>15</sup> similarly as for chloroformates<sup>10</sup>. From dithiocarboxylates two aliphatic derivatives were studied<sup>14</sup> showing the *s-trans* conformation. Compounds studied in this paper (I–VI) included mainly aromatic derivatives with respect to the method<sup>12</sup> which makes use of the comparison with a *para*-substituted derivative.

## EXPERIMENTAL AND RESULTS

### Materials

The compounds I–VI were prepared by known procedures (see ref.<sup>16,17</sup>), the references<sup>17-19</sup> to individual compounds being given in Table I. The compounds IV, not described previously, and III, not characterized<sup>20</sup>, were prepared by the acylation of ethanethiol in pyridine according to ref.<sup>17</sup>.

S-Ethyl 4-methyl-thiobenzoate (III), yield 61%, b.p. 62°C/0.07 Torr. For C<sub>10</sub>H<sub>12</sub>OS (180.3) calculated: 66.62% C, 6.66% H; found: 66.76% C, 6.59% H.

S-Ethyl 4-chlorothiobenzoate (IV), yield 64%, b.p. 155°C/18 Torr. For C<sub>9</sub>H<sub>9</sub>ClOS (200.7) calculated: 53.85% C, 4.53% H; found 53.62% C, 4.70% H.

TABLE I

Polarization and Dipole Moments of S-Alkyl Thiocarboxylates in Benzene at 25°C

Compound	$n_D^{20}$	$d^{20}$	$R_D^{20}$ cm <sup>3</sup>	${}_{\infty}P_2$ cm <sup>3</sup>	$\mu(5\%)^a$ D	$\mu(15\%)^a$ D
I C <sub>2</sub> H <sub>5</sub> .CO.S C <sub>2</sub> H <sub>5</sub> (ref. <sup>17</sup> )	1.4595 <sup>b</sup>	0.9591 <sup>b</sup>	33.72	75.5	1.40	1.34
II C <sub>6</sub> H <sub>5</sub> .CO.S C <sub>2</sub> H <sub>5</sub> (ref. <sup>17</sup> )	1.5695 <sup>c</sup>	1.0962 <sup>c</sup>	49.72	101.7	1.55	1.48
III 4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> .CO.S C <sub>2</sub> H <sub>5</sub>	1.5694	1.0742	55.01	126.5	1.83	1.76
IV 4-Cl-C <sub>6</sub> H <sub>4</sub> .CO.S C <sub>2</sub> H <sub>5</sub>	1.5855	1.2268	54.86	107.9	1.57	1.48
V 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> .CO.S C <sub>2</sub> H <sub>5</sub> (ref. <sup>18</sup> )	67 <sup>d</sup>		56.3 <sup>e</sup>	327.4	3.62	3.58
VI C <sub>6</sub> H <sub>5</sub> .CS.S C <sub>2</sub> H <sub>5</sub> (ref. <sup>19</sup> )	—	1.1472	57.0 <sup>e</sup>	122.0	1.74	1.66

<sup>a</sup> Correction for the atomic polarization 5% or 15% of the  $R_D$  value, respectively; <sup>b</sup> ref.<sup>16</sup> gives  $n_D^{20}$  1.4584,  $d^{20}$  0.9608; <sup>c</sup> ref.<sup>17</sup> gives  $n_D^{20}$  1.5721,  $d^{20}$  1.1003; <sup>d</sup> m.p. °C; <sup>e</sup> calculated values, see Experimental.

## Measurement of Dipole Moments

The same method was used as previously<sup>1,3</sup>. The experimental results are listed in Table I.

The molar refraction of compounds *V* and *VI* which could not be determined experimentally, was computed using Vogel's atom and group increments<sup>21</sup> and the increments 14.36 cm<sup>3</sup> and 21.3 cm<sup>3</sup> for the groups O=C—S and S=C—S, respectively. These values should account for the conjugation with the benzene nucleus; the former was derived from our experimental data (compounds *II*–*IV*), the latter is based on the increment<sup>21</sup> for C=S in xanthates and the exaltation is estimated.

The dipole moments of individual conformations were computed by vector addition of bond moments graphically with an accuracy of about  $\pm 0.03$  D. The bond moments used were listed and discussed previously<sup>1–3</sup>, a mesomeric moment of 0.25 D, denoted later as  $m_2$ , was used throughout to express formally the conjugation of the —CO.S— or —CS.S— group with the benzene nucleus. Our set of bond moments is not essentially different from that one recommended recently by Cumper<sup>22</sup> and based on another convention ( $C_{\text{ar}}\text{-H} = 0$ ). The largest difference is in the moment of the C—S bond which is — according to Cumper<sup>22</sup> — 0.2 D higher than that of the C—O bond whereas our values are practically equal. However, a difference of such order of magnitude does not influence the final conclusions of this paper. The bond angles used in our calculations were  $\angle \text{C—C=O} = \angle \text{C—C=S} = 116^\circ$ ,  $\angle \text{O=C—S} = \angle \text{S=C—S} = 124^\circ$ ,  $\angle \text{C—S—R} = 102^\circ$ .

## DISCUSSION

The dipole moments collected in Table I can be considered consistent with one another, especially the differences between compounds *I* and *II*, and between *II* and *III* are in the expected direction and of reasonable magnitude. The moments of *I*, *II*, *IV* and *V* are higher than those of corresponding carboxylic esters<sup>23</sup> by an almost constant difference  $0.45 \pm 0.07$  D.

Our graphical method to determine the conformation<sup>12</sup> is visualized in Fig. 1. The computed moments of the unsubstituted and substituted compounds are plotted as  $\mu^2$  on the x-axis and y-axis, respectively. When a rotation around the C—S bond takes place, the point in Fig. 1 moves along the straight line connecting the two limiting conformations. Alternatively the points on this line can be interpreted as a mixture of the two limiting forms. The comparison with experimental points shows quite conclusively that the conformation of S-alkyl thiocarboxylates is *s-trans* (*A*); the radius of the hatched circles represents merely the inaccuracy in computing theoretical dipole moments than the experimental error. By this procedure we are thus able not only to assess the most probable conformation but also to judge the reliability of the result and to check ultimately the bond moments used. The same method cannot be applied to the aliphatic derivative *I*; hence, the computed and experimental moments are only compared in another kind of graphical representation<sup>2,3</sup> (Fig. 2).

Our results agree in principle with the findings of Lumbroso and Schuijl<sup>14</sup> reached on two aliphatic derivatives, but our results have a greater statistical weight. Although these authors used bond moments somewhat different from ours, the computed final

values of dipole moments do not differ more than 0.3 D and the conclusion was the same as far as the conformation is concerned.

The dithiocarboxylates were studied less extensively in this paper since the *s-trans* conformation could be anticipated according to the results on two aliphatic deriv-

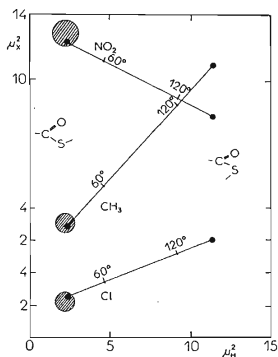


FIG. 1

Determination of Conformation of S-Ethyl Thiobenzoate by Comparing Experimental and Calculated Dipole Moments

The values of  $\mu^2$  are plotted on the  $x$  axis for the unsubstituted compound (II) and on the  $y$  axis for the derivatives (III–V), experimental points are hatched.

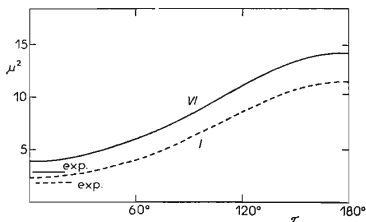
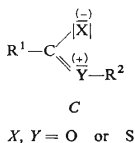


FIG. 2

Comparison of Experimental and Calculated Dipole Moments of S-Ethyl Thiopropionate (I) and Ethyl Dithiobenzoate (VI) for Various Angles  $\tau = \angle \text{X}=\text{C}-\text{S}-\text{C}_2\text{H}_5$ .

atives<sup>14</sup> and to the analogy with other classes of compounds. The comparison of computed and experimental moments (Fig. 2) confirms this assumption although the agreement is somewhat worse than in the case of S-alkyl thiocarboxylates. This graph is more sensitive to experimental errors than Fig. 1 and the comparison of both shows the advantage of our two-dimensional representation<sup>12</sup>.

It follows that the conformation *A* is the more stable one with all combinations of O and S atoms in the place of X and Y, the only possible exception being the chloroformates<sup>10</sup> and chlorothioformates<sup>15</sup>. This conformation is remarkably rigid; the rotational barrier in carboxylates esters was estimated to 5.8 kcal mol<sup>-1</sup> and the free energy difference between *A* and *B* to 3.2 kcal mol<sup>-1</sup> (ref.<sup>4</sup>). In agreement with the extreme position of the conformational equilibrium no change of the NMR spectra of carboxylates<sup>6</sup> and O-alkyl thiocarboxylates<sup>3</sup> was observed between -40° and +120°C, or between -35° and +80°C, respectively. Differences between calculated and experimental dipole moments are either attributed to small deviations from planarity<sup>7</sup>, or to a mesomeric moment<sup>14</sup>, expressed by the limiting structure *C*.



Various values ranging from 0.26 D for S-alkyl thiocarboxylates to 1.16 D for O-alkyl thiocarboxylates were given to this mesomeric moment<sup>14,24</sup>. We attempted to test the latter value but were not able to find any experimental support for it using our own measurements<sup>3</sup>. By the same kind of reasoning, all four classes of compounds can now be treated using our data for aromatic S-alkyl thiocarboxylates O-alkyl thiocarboxylates<sup>3</sup> and alkyl dithiocarboxylates and literature data for carboxylates<sup>23</sup>. When we consider the exactly planar *s-trans* conformation to be proved;

TABLE II

Group Moments of the Functional Groups in Aromatic Esters and their Thio Analogues

Group	Group moment, D	Angle with the C—C bond
O=C—O	1.89 ± 0.07	115° ± 4
O=C—S	1.76 ± 0.07	127° ± 4
S=C—O	2.40 ± 0.15	120° ± 6
S=C—S	1.78 ± 0.20	119° ± 8

the group moments listed in Table II can be calculated by the same procedure as in ref.<sup>3</sup>, except the value for dithioesters which is merely an estimate.

The values given are in fair agreement with some literature data, compare *e.g.* the angle of  $100^\circ$  given for aliphatic carboxylic esters<sup>24</sup> or  $106^\circ$  for aromatic carboxylic acids<sup>25</sup>; according to Cumper<sup>22</sup> the group moment of esters is roughly parallel with the C=O bond.

As these values have been determined on aromatic compounds they can include – in addition to the bond moment C=O (or C=S) and two moments C–O (or C–S) – two mesomeric moments. The first one, denoted  $m_1$ , corresponds to the formula C and is directed from Y to X, the second ( $m_2$ ) represents the conjugation with the aromatic nucleus and is directed from  $C_1$  to  $C_a$ . The situation is pictured in Fig. 3. As can be seen all group moments are of almost equal direction and – except the S=C–O group – also of similar magnitude. Their most important component is apparently the moment of the C=O or C=S double bond which is lessened by the sum of two C–O or C–S bonds the direction of which is almost exactly reverse. One can conclude that the C=S moment is certainly larger than C=O (in agreement with values used by us but not with those of Lumbroso<sup>26</sup>) and probably also the C–S moment somewhat larger than C–O (corresponding better to Cumper's values<sup>22</sup> than to ours). On the other hand no experimental support can be found in Fig. 3 in favour of the mesomeric moments  $m_1$  and  $m_2$ ; it seems only that  $m_2$  could be more important in thioderivatives of all types than in carboxylic esters. In our calculations the moment  $m_2 = 0.25$  D was used throughout. Such a small value cannot be disproved from Fig. 3, on the other hand its existence is substantiated by differences between aromatic and aliphatic derivatives. In general we do not believe that a more detailed analysis of these group moments into individual compo-

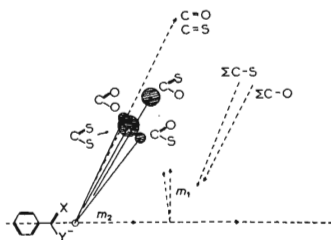


FIG. 3

#### Group Moments of Functional Groups in Esters and their Thio Analogues

Direction and magnitude of group moments and directions of contributing components are shown;  $m_1$  and  $m_2$  are mesomeric moments (see text).

nents could be feasible; it is prevented – besides the experimental uncertainty – by almost the same direction of some of the components. The values given<sup>14,24</sup> for  $m_1$  cannot be considered reliable, especially with the S=C—O and S=C—S groups they are undoubtedly too high. The same applies to the results of LCAO – MO calculations<sup>27</sup>.

Finally we can return to the problem of factors controlling the conformation. In addition to the mesomerism, electrostatic forces of various types are usually discussed; the pure steric effect can be probably neglected if the groups  $R^1$  and  $R^2$  are not very large. This is demonstrated by the conformation *A* of methyl formate<sup>8</sup>, for which *B* should be more stable on pure sterical grounds. The classical point of view<sup>28</sup> is now generally accepted<sup>1-7</sup> that the mesomerism within the functional group is responsible for the planar conformation. However, the mesomerism itself does not explain why the *s-trans* form *A* is preferred to *s-cis* (*B*) unless the mesomeric energy should be different in both forms. Hence, different supporting hypotheses have been advanced: a) The electrostatic attraction<sup>4</sup> of the two almost parallel dipoles C=X and Y—R<sup>2</sup> in *A* and their repulsion in *B*. b) The electrostatic repulsion of lone electron pairs on X (in  $sp^2$  orbitals) and on Y, the latter is assumed to be also in an  $sp^2$  orbital<sup>11</sup>. c) The same repulsion was claimed as the only factor controlling conformation, the mesomerism being insignificant; the lone electron pairs on Y are supposed in a tetrahedral ( $sp^3$ ) arrangement<sup>29</sup>.

An argument against the hypothesis (c) can be seen in dipole moment values of lactones<sup>24,28</sup> which do not change gradually with the increasing size of the ring but rather suddenly; it is supposed that the functional group retains a planar *s-cis* conformation unless the *s-trans* is made possible. In addition the different conformation of sulfonates and carboxylates<sup>1</sup> cannot be understood without taking into account either the mesomerism or different hybridization on oxygen atom. The conformation of sulfonates<sup>1</sup> does not comply even with the hypothesis (a).

In the case of carboxylic esters and their thio-analogues the two hypotheses (a) and (b) afford the same prediction in agreement with experiment but (b) can be preferred with respect to the conformations of alkyl nitrites<sup>11</sup> and sulfinates<sup>2</sup>. Hence we believe that the electrostatic interaction of lone electron pairs is an important factor controlling conformation of functional groups. In the case of esters and their thio-analogues it is operating in addition to the mesomerism of the whole group and it seems to be the decisive factor favouring the conformation *A*.

Based on four liquid S-alkyl thiocarboxylates the refraction increment of the O=C—S grouping can be estimated in an orienting manner. Using Vogel's increments<sup>21</sup> we calculated the values 13.12, 14.06, 14.71 and 14.28 cm<sup>3</sup> from the compounds I–IV, respectively; some of these values include the exaltation due to conjugation with the benzene ring and a *para*-substituent. From the value 13.12 for the aliphatic derivative and increments<sup>21</sup> for C=O and S we can calculate an exaltation 0.60 cm<sup>3</sup> corresponding to the conjugation within the O=C—S group. This value is remarkable when compared to the values -0.16 and +0.19 cm<sup>3</sup> derived for

O=C—O and S=C—O groups, respectively, by the same procedure. The results should be confirmed on further compounds; on the first inspection they agree neither with computed mesomeric moments<sup>14,27</sup> nor with the present analysis, but it must be remembered that the excited state influences the molar refraction. More clear results have been obtained for the conjugation with the benzene nucleus, the values of the exaltation being 0.7, 1.25, and 1.45 cm<sup>3</sup> for O=C—O, O=C—S, and S=C—O, respectively. In these values the greater polarizability of the sulfur atom is apparent.

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