

DIPOLE MOMENTS AND CONFORMATION OF O-ALKYL THIOCARBOXYLATES

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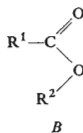
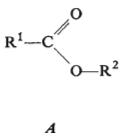
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Dipole moments of ten O-alkyl thiocarboxylates, mostly compounds of the aromatic series, were measured in benzene solution. To determine their conformation, a method previously suggested was used, in which experimental and computed moments of an unsubstituted compound and of its *para* derivative are compared in a simple graphical representation. It follows that the —CS.O-group exists in a practically planar *s-trans* conformation as does the —CO.O-group in carboxylic acid esters, the cause of the rigid conformation being the mesomerism in both cases.

As a part of a broader scheme concerning the stereochemistry of functional groups, we were also interested in the conformation of carboxylic acid esters and analogous compounds^{1,2}.

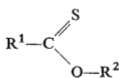
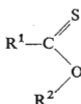
A practically planar and stable *s-trans* conformation (*A*) is now commonly recognized^{3,4} for simple esters although certain authors admit a small deviation from planarity⁵ up to the dihedral angle $\angle \text{O}-\text{C}-\text{O}-\text{R}^2 = 30^\circ$. In a single case a *s-cis* conformation (*B*) was believed to be found⁶ but this finding has been recently disproved⁷.



The *s-trans* form *A* is remarkably stable: in the range of 160°C no change with temperature could be detected⁸ and the free energy difference between *A* and *B* was estimated³ 3.2 kcal mol⁻¹. The reasons of the unusual conformational stability are not quite clear. Although the classical view⁹ is generally adopted that the mesomerism in the group is responsible for the planar arrangement, the mesomerism itself does not explain why the *s-trans* form is energetically favoured.

A supporting hypothesis is thus necessary; either the conjugation should be stronger in the *s-trans* than in the *s-cis* form, or, the difference is due to the interaction between dipoles³ or repulsion between lone electron pairs¹⁰. As an extreme, the latter factor was claimed as the only one controlling the conformation¹¹. In the case of larger groups R^1 and R^2 even the purely steric effect must come into play.

To throw more light upon these questions, we considered it useful to compare systematically the carboxylic acid esters with analogous classes of compounds, in which the individual effects are of different importance. A comparison with sulphonic¹ and sulphinic² esters was already made. In the present paper we are concerned with O-alkyl thiocarboxylates (*C* or *D*), some of which have been made easily accessible by a recent synthesis¹².

*C**D*

Our experimental method of choice was measurement of dipole moments in solution. The results were evaluated using a previously reported¹³ graphical comparison with a *para* substituted derivative; for this reason several aromatic derivatives were included in our selection of compounds *I-X*.

EXPERIMENTAL AND RESULTS

Materials. The preparation of compounds *I-X* has been described^{12,14}, their purity was confirmed by elemental analyses, vpc, IR and NMR. Some characteristic constants are listed in Tables I and II.

Measurements of dipole moments. Dielectric constants of the benzene solutions were measured at 25°C using a heterodyne apparatus at a frequency of 1.2 Mc.p.s. Usually five measurements were carried out in the concentration range $5 \cdot 10^{-3}$ – $5 \cdot 10^{-2}$ M. The dipole moments were computed using the method of Halverstadt and Kumler¹⁵. In the final calculations of the dipole moments μ from the overall polarization ${}_{\infty}P_2$ and molar refraction R_D , an allowance of 5% or 15% of the R_D value was made for the atom polarization. The experimental data are given in Table I.

The molar refraction of liquid compounds was determined from experimental density and refractive index (Table II). The measurement of the latter is, however, difficult with coloured substances and the resulting refraction does not correspond to the theoretically needed R_{∞} value. For the same reason the calculated increments of the S=C—O group, based on Vogel's values¹⁶, are not constant (see Table II). Even when a considerable exaltation in aromatic compounds is accounted for, there are still differences between individual aromatic derivatives. Hence, the molar refraction of solid derivatives was calculated using a constant increment 16.0 cm^3 for the S=C—O group and further atom and group increments of Vogel¹⁶. The inaccuracy in this procedure is not so great as to influence the final values of dipole moments.

Calculation of theoretical dipole moments. The dipole moments for the individual conformations have been determined by vector addition of bond moments. The values of the latter ones were the

TABLE I
Polarization Data and Characterization Constants of O-Alkyl Thiocarboxylates

Compound	B.p. °C	∞P_2^2 cm ³	R_D cm ³	μ (5%) D	μ (15%) D
CH ₃ CSOC ₂ H ₅ (<i>I</i>)	123–125	132.9	30.0	2.22 ^a	2.19
C ₂ H ₅ CSOC ₂ H ₅ (<i>II</i>)	143–145	138.5	34.5	2.23	2.20
C ₆ H ₅ CSOCH ₃ (<i>III</i>)	70–74/4	129.7	46.4	1.99	1.93
C ₆ H ₅ CSOC ₂ H ₅ (<i>IV</i>)	88–89/9	192.4	51.1	2.60 ^a	2.55
4-CH ₃ C ₆ H ₄ CSOCH ₃ (<i>V</i>)	95–96/2	159.6	52.2	2.26	2.21
4-CH ₃ C ₆ H ₄ CSOC ₂ H ₅ (<i>VI</i>)	125–127/5	173.6	57.1	2.35	2.29
4-ClC ₆ H ₄ CSOCH ₃ (<i>VII</i>)	40 ^b	129.3	52.0 ^c	1.91	1.84
4-ClC ₆ H ₄ CSOC ₂ H ₅ (<i>VIII</i>)	34–35 ^b	167.0	56.6 ^c	2.29	2.23
4-CH ₃ OC ₆ H ₄ CSOCH ₃ (<i>IX</i>)	45 ^b	205.4	54.0 ^c	2.70	2.65
4-CH ₃ OC ₆ H ₄ CSOC ₂ H ₅ (<i>X</i>)	28–29 ^b	214.4	58.6 ^c	2.73 ^a	2.68

^a In the literature¹⁸ the values 2.19, 2.24 and 2.82D are given for the compounds *I*, *IV* and *X*, respectively. ^b Melting point. ^c Calculated values, see text.

TABLE II
Refraction Data of Liquid O-Alkyl Thiocarboxylates

Compound	n_D^{20}	d^{20}	R_D^{20} cm ³	Increment of the —C(S)O— group, cm ³
<i>I</i>	1.4625	0.9564	29.97	14.02
<i>II</i>	1.4635	0.9447	34.49	13.89
<i>III</i>	1.6065	1.1330	46.36	15.35
<i>IV</i>	1.5882	1.0958	51.07	15.41
<i>V</i>	1.6075	1.1015	52.15	~ 16.2
<i>VI</i>	1.5905	1.0661	57.10	~ 16.5

same as in our previous communications¹⁻², in addition the moment 2.95 D was used for the C=S double bond (see Discussion). The conjugation of the thiocarboxylate group with the benzene nucleus has been expressed in a formal manner by a mesomeric moment 0.25 D and another mesomeric moment 0.6 D was applied to methoxy derivatives *IX* and *X* to account for the conjugation of the methoxy group.

The values of bond angles used were $\angle R-C=S$ 116°, $\angle S=C-O$ 124°, $\angle C-O-R$ 113°. The calculated moments for individual conformations are not tabulated and only plotted in Figs 1-4.

DISCUSSION

The first step in the solution of our problem is to find the bond moment of the C=S bond. This bond being highly polarizable, a constant moment cannot by far be expected in different compounds, the only task is to assess a value suitable for our set of derivatives. Our value 2.95 D has been derived from C=O bond moment 2.5 D and from the comparison of experimental dipole moments¹⁷ of benzophenone and thiobenzophenone. No doubt it can include a mesomeric component but it can be used with a good approximation in aromatic derivatives at least. Lumbroso and Reynaud¹⁸ used a much smaller C=S bond moment, derived from comparison of fenchone and thiofenchone, and had to add a large mesomeric moment expressing the conjugation inside the S=C-O group. The difference between both conceptions is not essential and the conclusions agree as far as the conformation is concerned.

Our system of the graphical representation¹³ is visualized in Figs 1 and 2. When calculated dipole moments for the unsubstituted and substituted compound (or for

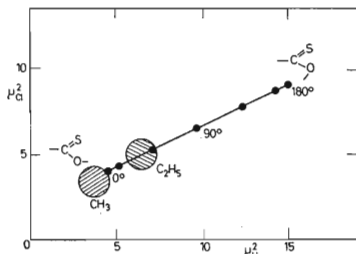


FIG. 1

Comparison of Computed and Experimental (hatched circles for methyl and ethyl derivative respectively) Dipole Moments of O-Alkyl Thiobenzoates *III* or *IV* (*x*-axis) and Their *p*-Chloro Derivatives *VII* or *VIII* (*y*-axis)

The line represents rotation around the C—O bond.

two differently substituted derivatives) are plotted as μ^2 against each other, then each conformation is represented by a point and the comparison with the experimental point is made possible. In this way not only the most probable conformation can be chosen but also the probability estimated with which the other possibilities can be disproved. It can happen that the experimental point does not coincide with any computed one but rather lies on a connecting line of two such points. This fact can be interpreted either as a mixture of two forms or as a transitory conformation arising by rotation around a single bond; finally a disagreement with experiment can be due to an improper choice of bond moments.

We have chosen two combinations of substituents for the graphical comparison of our results, *viz.* 4-chloro derivatives and unsubstituted phenyl compounds in Fig. 1 and 4-chloro and 4-methyl derivatives in Fig. 2. The third possible combination of these substituents is not suitable since the differences between a methyl derivative and the unsubstituted compound are not sufficient. Our results give an unambiguous evidence for the *s-trans* conformation (C) of all compounds III–VIII. A somewhat worse agreement between theory and experiment in Fig. 1 is due to the relatively considerable difference between the experimental moments of the compounds III and IV, which should be equal according to the simple scheme of vector addition of bond moments. This discrepancy originates certainly in the experimental error for the greater part but partly also in failing of this simple scheme.

The basic presumption of our graphical method is the same conformation of the substituted and unsubstituted compound, which we believe to be fulfilled with *para* substitution on the benzene nucleus^{1,2,13}. The substituent should have a known and sufficiently high bond moment and must not introduce a further possibility of rotation

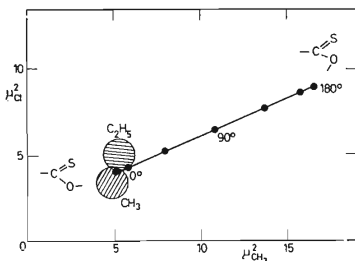


FIG. 2

Comparison of Computed and Experimental Dipole Moments of O-Alkyl 4-Methyl-thiobenzoates V or VI (x-axis) and 4-Chlorothiobenzoates VII or VIII (y-axis)

into the molecule. Therefore the most suitable substituents are halogens and the nitro group. The use of the nitro group in this study was prevented by certain preparative difficulties; instead the methoxy group was used in compounds *IX* and *X* which does not fulfil strictly those requirements. The determination of conformation is more complicated in this case since we have to consider four planar forms corresponding to two possible conformations of the thiocarboxylate group and two positions of the methoxy group. Nevertheless, it follows from Fig. 3 quite conclusively that the conformation of the former is *s-trans*; as to the position of the methoxy group, both forms are populated in an approximate ratio 1 : 1. The same situation is supposed in other simple methoxy derivatives¹⁹.

As to the aliphatic thiocarboxylates *I* and *II*, our graphical method cannot be applied since no possible substitution would be satisfactory with respect to the mentioned requirements. From the comparison with aromatic derivatives *III* and *IV* one can guess that the conformation of the aliphatic ones is not very different. A more exact result can be obtained from another kind of graphical representation in Fig. 4, where the computed dipole moments for an aliphatic thiocarboxylate are plotted against the dihedral angle $\tau = \angle \text{S}=\text{C}-\text{O}-\text{R}$. The excellent agreement for the *s-trans* conformation is partly fortuitous since the determination is much more sensitive to experimental errors than it is in Figs 1 and 2 the case. The advantage of our two-dimensional graphical representation is clearly demonstrated by comparing these two kinds of figures.

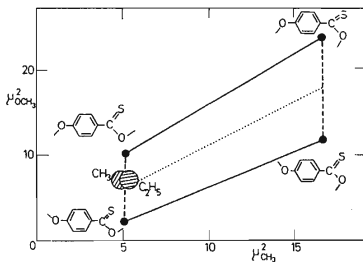


FIG. 3

Comparison of Computed and Experimental Dipole Moments of O-Alkyl 4-Methylthiobenzoates (*x*-axis) and 4-Methoxythiobenzoates (*y*-axis)

The full lines represent change of conformation in the thiocarboxylate group, the broken lines change of mutual position of the methoxy and thiocarboxylate groups, the dotted line corresponds to the mixture 1 : 1.

The conformation of thiocarboxylic esters seems to be fairly rigid. Similarly as Hancock⁸ with carboxylic esters, we were not able to observe any change in the NMR spectra of compounds *III* and *IV* when changing the temperature from -35°C to $+80^{\circ}\text{C}$. Hence the rotation barrier must be of comparable height in both classes of compounds.

The *s-trans* conformation of thiocarboxylates is in agreement with the conclusions reached by Lumbroso and Reynaud¹⁸ on a less extensive set of unsubstituted compounds and is further supported by the same conformation of thioacetic acid²⁰. We believe that this phenomenon is general for all compounds containing the $\text{S}=\text{C}-\text{O}$ -group similarly as for those with the $\text{O}=\text{C}-\text{O}$ -group, the main reason being the mesomerism within both groups. When comparing the two classes of compounds, it is difficult to judge the relative weight of mesomeric structures *E* and *F* since the influence of the lower electronegativity of sulfur in *F* can be counterbalanced by the usual instability of double bonds to atoms of the second row elements. Quantum chemical computations²¹ accounting for these two effects predict a larger relative weight of structure *F* as compared to *E*. In agreement with this prediction, a larger mesomeric moment was derived from dipole moment data^{18,22}.

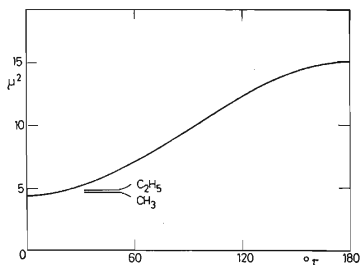


FIG. 4

Computed Dipole Moments of Aliphatic Thiocarboxylates in Dependence on the Dihedral Angle $\tau = \text{V S}=\text{C}-\text{O}-\text{C}$

Comparison to experimental values of $\text{CH}_3\cdot\text{CS}\cdot\text{OC}_2\text{H}_5$ (*I*) and $\text{C}_2\text{H}_5\cdot\text{CS}\cdot\text{OC}_2\text{H}_5$ (*II*) is made.

We tried to test the latter result on the broader experimental material and in a statistically more significant manner. Hitherto, we used our experimental dipole moments to determine the conformation whereas some bond and mesomeric moments were assumed. This procedure can now be reversed: When a strictly planar *s-trans* conformation is once considered to be established, the refined values of bond and mesomeric moments can be derived from the same set of experimental data. In a graphical representation (Fig. 5) similar to that used by van Woerden and Havinga²³ the bond moments of the C—O, O—C, C—H bonds and of the substituent (and — if needed — the mesomeric moment 0.25D for the conjugation with the benzene nucleus) have been plotted from the origin of coordinates in opposite directions. From the end point a circle has been drawn with a radius equal to the experimental moment of the respective compound; this procedure has been repeated for each of compounds I—X. All circles should intersect in a common point and the line connecting the origin with this point represents the vector sum of the C=S bond moment and the mesomeric moment of the S=C—O group. Since the direction of both these moments are known (heavy broken arrows in Fig. 5) their separation is in principle possible. It follows from Fig. 5 that the circles do not intersect exactly in a point but rather in a broader area and further that the resulting vector can be expressed most conveniently as a simple bond moment c. 3 D of the C=S bond. The accuracy of results admits still a mesomeric moment of c. 0.6 D combined with the C=S bond

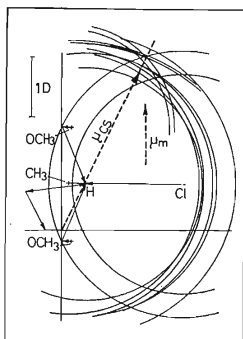


FIG. 5

Determination of the C=S Bond Moment and the Mesomeric Moment of the S=C—O Group from Experimental Dipole Moments of the Compounds I—X

See text.

moment 2.6 D but at any rate the value of the mesomeric moment²², 1.16 D is too high. The accuracy of dipole moment measurements and especially that of the vector addition scheme is not sufficient to decide between the relative weights of structures E and F.

When it is established and substantiated that the molecules of esters and analogous compounds are planar, there remains still a question why the *s-trans* conformation (A and C) are preferred. The explanation based on electrostatic repulsion of lone electron pairs¹⁰ seems reasonable as a working hypothesis at least. The gist of the argumentation lies in the supposed sp^2 hybridization on the ether oxygen. Further experimental support can be seen in the non-planar conformation of sulphinic esters² in which the sp^2 hybridization cannot be considered. We hope to bring more arguments by studying further related classes of compounds.

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