

MOLECULAR POLARIZABILITY AND CONFORMATION OF DITHIOACETALS

A. N. VERESHCHAGIN^a and O. EXNER^b

^a A. E. Arbutov Institute of Organic and Physical Chemistry,
USSR Academy of Sciences, Kazan 83, USSR,

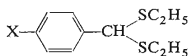
^b J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Prague 1

Received April 8th, 1972

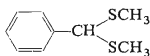
The unsymmetrical *gt* conformation (*C*) of dithioacetals, suggested previously on the basis of dipole moments, has been confirmed from the Kerr constant of *III* when compared with *IV* and *V* (measured in tetrachloromethane). In addition the presence of the second from *gg'* (*D*) not found with certainty from dipole moments has been detected. The conformations of the C—S bonds are closely correlated with the position of the benzene nucleus.

The unsymmetrical conformation of dithioacetals in solution (*trans* = antiperiplanar on one C—S bond, and *gauche* = synclinal on the second one) was suggested in two dipole moment studies using different compounds and somewhat different approach^{1,2}. An admixture of the second form of the *C*₂ symmetry was considered probable, at least in some derivatives¹, but has not been proven. These results are rather unexpected, particularly when compared to the more symmetrical forms of the same compounds in the crystalline state³ and that of their oxygen analogues both in the gas phase and in solution^{4,5}. In all these cases the functional group has a *C*₂ symmetry with one alkyl group above and one below the X—C—X plane, forming a helix. Dithioacetals thus represent a remarkable exception within the stereochemistry of two equivalent single bonds attached to the same atom¹.

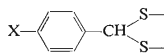
For these reasons we decided to confirm this conformation by determining the molar Kerr constant⁶. This quantity, when combined with dipole moment data, brings new valuable information but in our case also two additional complications arise. On the one hand some groups, perfectly symmetrical as far as the dipole moments are concerned, are anisotropic in their polarizability so that their position influences the Kerr constant. It concerns the ethyl groups and the benzene nucleus, which can rotate around the bonds connecting them with the rest of the molecule. It is for this reason that the previously studied¹ ethyl derivatives *I*, *II* have been now replaced



I, X = H
II, X = Cl



III



IV, X = H
V, X = Cl

by the methyl derivative *III*. However, when we want to study the aromatic compounds, we still have to determine the position of the strongly anisotropic benzene ring. This was done using rigid model compounds *IV*, *V*.

In addition there is the second complication that certain small distortions, as the not exactly planar form of the five-membered ring, were unimportant with respect to the dipole moments, but affect the much more sensitive Kerr constant.

EXPERIMENTAL AND RESULTS

Materials. The dithioacetals *I*, *II*, *IV*, and *V* were the same samples as previously¹. Benzaldehyde dimethyldithioacetal (*III*) was prepared by the same general method¹. Its purity was ascertained from its NMR spectrum, particularly the absence of benzaldehyde was proved by the IR spectrum. The physical constants n_D^{20} 1.5978, d^{20} 1.1103 are in fact valid for the supercooled liquid, literature⁷ gives m.p. 29°C.

Physical measurements. Molar Kerr constants and dipole moments were determined in tetrachloromethane at 25°C as previously described⁸. Coefficients $\alpha-\delta$ and final results are listed in Table I.

TABLE I
Molar Kerr Constants of Dithioacetals (CCl₄, 25°C)

Compound	α	β	γ	δ	μ , D	$mK \cdot 10^{12}$
<i>II</i>	3.422	0.194	0.218	67.611	^a	123
<i>III</i>	3.197	0.085	0.276	-0.850	1.58	-2.1
<i>V</i>	5.212	0.450	0.240	219.450	^a	354

^aThe dipole moments 2.56 and 2.33D of the compounds *II* and *V*, respectively, were determined previously in benzene¹.

DISCUSSION

The solution of the conformational problem is relatively complex and proceeds in three steps. In the first one we attempted to determine more precisely the "effective" conformation of the dithiolane ring in the compounds *IV* and *V*. When discussing the dipole moments, we contented ourselves with the assumption of its approximate planarity, although the agreement of computed and experimental values was not completely satisfactory¹. However, the Kerr constant is in this case much more sensitive to slight conformational changes than the dipole moment, since it is controlled by the orientation of the highly anisotropically polarisable benzene nucleus with respect to the dipoles of the C—S bonds. We took into consideration two kinds

of non-planar forms: The envelope, with atoms $C_{(4)}$ and $C_{(5)}$ on the same side of the $S_{(1)}-C_{(2)}-S_{(3)}$ plane, is characterized by the angle φ between the $S_{(1)}-C_{(2)}-S_{(3)}$ and $S_{(3)}-C_{(4)}-C_{(5)}-S_{(1)}$ planes (taken positive on the side of the H atom), and the half-chair, with atoms $C_{(4)}$ and $C_{(5)}$ on opposite sides of the $S_{(1)}-C_{(2)}-S_{(3)}$ plane, by the angle Ψ between the $S_{(1)}-C_{(2)}-S_{(3)}$ and $C_{(2)}-C_{(4)}-C_{(5)}$ planes.

To decide between the two possibilities the previously described⁹ graphical method was applied. Dipole moments computed for the various forms have been compared with the experimental ones in Fig. 1 by plotting μ^2 of *IV* and *V* on the *x*-axis and *y*-axis, respectively. An envelope with $\varphi \simeq -7^\circ$ is clearly in best agreement with the experimental results, this also means that the previous assumption¹ of an approximately planar form was not too far from reality and sufficient for the given purpose. The conformation of the 1,3-dithiolane ring seems have not been studied and data about similar heterocycles are scarce¹⁰⁻¹². In the case of 1,3-dioxolane both the envelope and half-chair form were claimed^{11,12}; however different valence angles on oxygen and sulphur can cause different conformations of the two heterocycles.

In computing the dipole moments we adopted the bond angles and bond moments as previously¹, except the C-S bond, which was given a larger moment of 1.0 D in order to obtain better agreement with experiment. This value¹³ (appropriate for dialkyl sulphides but not for dimethyl sulphide) was also considered previously¹ instead of the value 0.7 D, but the difference was not critical.

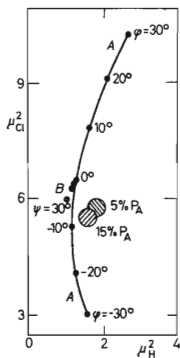


FIG. 1

Comparison of Experimental (dashed points) and Computed Dipole Moments of Cyclic Dithioacetals *IV* (*x*-axis) and *V* (*y*-axis)

A Envelope form, *B* half-chair form.

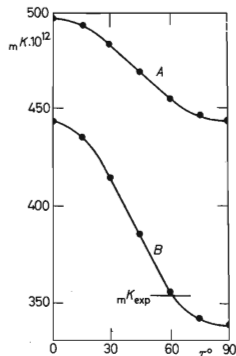


FIG. 2

Dependence of the Kerr Constant of Dithioacetal *V* on the Rotational Angle τ of the Phenyl Group

A $\varphi = 0$, *B* $\varphi = -7^\circ$.

Hence the envelope form with $\varphi = -7^\circ$ can be accepted for the dithiolane ring as a working hypothesis. Of course, the ring is in fact highly flexible and the angle φ represents rather an effective value. In the next step we have to determine the position of the benzene nucleus from the experimental Kerr constant of V . The calculations were carried out with common bond polarizabilities⁷; the values from the benzene ring (including the $C_{ar}-C_{a1}$ bond) were calculated from the polarizability ellipsoid of toluene¹⁴, viz. b_1 13.08 A^3 (along the symmetry axis), b_2 11.10 A^3 (in the ring plane), b_3 4.92 A^3 (perpendicular to the ring). Various values of the angle τ between the plane of the aromatic ring and the symmetry plane of the dithiolane ring were considered, see the Newman projection along the $C_{ar}-C_{a1}$ bond (*A*). Comparison with the experiment (Fig. 2) is in favour of the eclipsed conformation *B* with the angle $\tau = 60^\circ$.



The result seems plausible since in various aromatic derivatives the eclipsed conformation on the $C_{ar}-C_{sp^3}$ bond is typical; it holds particularly for the compounds^{15,16} $ArCHX_2$. By analogy with these compounds one would expect that the H atom, rather than one S atom, is flanked by the benzene ring in V . However, the analogy is not perfect; in the examples mentioned^{15,16} either the groups X are not polar, or ortho substituent are present. We may understand the conformation *B* in terms of a weak interaction between an *ortho* hydrogen and one sulphur atom, or by a conjugation of the lone electrons on sulphur with the atomic π -electrons^{1,17} which need not be restricted to the excited state.

Hence we have adopted the eclipsed conformation *B* as the second working hypothesis. We are aware that the value of τ 60° is rather inaccurate since it is sensitive to the assumed value of φ . However, our hypothesis is supported subsequently by the consistent final results and a planar conformation ($\varphi = 0$) is excluded at any rate since an agreement with the Kerr constant of V could not be reached (Fig. 2A).

Starting from the assumed conformation *B* we may proceed to the last step, determining the conformation of the open-chain dithioacetal *III* on the basis of its experimental Kerr constant and dipole moment. Nine forms have been taken into consideration, corresponding to all combinations of staggered conformations on the two C—S bonds, viz *t* (= antiperiplanar), *g* (= +synclinal), and *g'* (= -synclinal) with respect to the second sulphur atom (Fig. 3). Previously only six forms were distinguished¹; their number is now enhanced since flanked and non flanked C—S

bonds are no more equivalent. In our notation the conformation on the flanked one is named first. Note that the g' conformations are clearly sterically less favourable than g , so that the forms $g't$, tg' , and particularly $g'g'$ are, if not impossible, certainly much less populated than the corresponding not primed forms gt , tg , and gg , respectively.

TABLE II

Polarity and Polarizability of Possible Conformations of Benzaldehyde Dimethyldithioacetal (III)

Conformation	b_{xx}	b_{xy}	b_{zz}	b_{xy}	b_{xz}	b_{yz}	μ, D	$mK \cdot 10^{12}$
tt	16.327	17.431	18.306	2.192	3.109	-1.536	3.02	-204
tg	16.303	17.328	18.433	2.097	3.198	-1.536	2.13	375
tg'	16.303	17.328	18.433	2.097	3.020	-1.536	1.87	63
gt	16.303	17.328	18.433	2.287	3.198	-1.536	2.13	-4.8
gg	16.279	17.225	18.560	2.192	3.307	-1.536	2.39	138
gg'	16.279	17.225	18.560	2.192	3.109	-1.536	0.35	31
$g'g$	16.279	17.225	18.560	2.192	3.109	-1.536	0.35	31
$g't$	16.303	17.328	18.433	2.097	3.020	-1.536	1.90	167
$g'g'$	16.279	17.225	18.560	2.192	2.931	-1.536	1.90	48

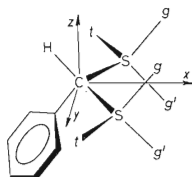


FIG. 3

Possible Conformations of the Benzaldehyde Dimethyldithioacetal III

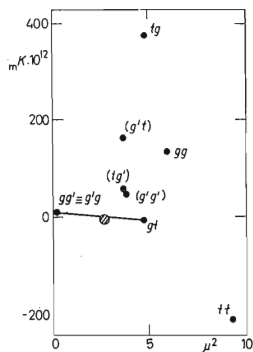
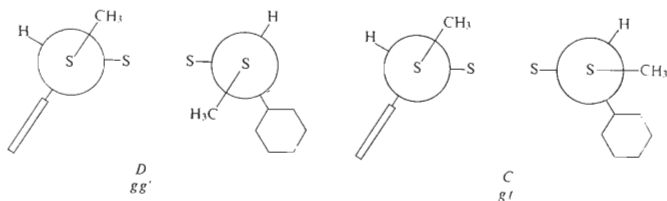


FIG. 4

Comparison of Experimental and Calculated Dipole Moments and Kerr Constants of the Dithioacetal III

The dipole moments and Kerr constants have been computed for all possible conformations of *III*, using the same parameters as in the preceding case (Table II), and compared with experimental values in a two-dimensional graph¹⁸ (Fig. 4). As in our first graphical method⁹, additive quantities have been plotted on both axes, *viz.* μ^2 and ${}_mK$. It follows that mixtures of two forms are represented by the straight line connecting the appropriate points. The two forms *gt* and *tg*, and similarly also *g't* and *tg'*, are of course indiscernible as to the dipole moments but differ in the Kerr constant; the forms *gg'* and *g'g* do not differ in either of the two quantities.

According to the previous dipole moment study¹ we expect the forms *gt* or *tg* to be most probable, but Fig. 4 points out the presence of two forms, almost equally populated, *viz.* *gt* and in addition either *gg'* or *g'g*. Note that particularly the form *tg* is absent, although it differs from *gt* only in the position of the benzene nucleus. It follows that this position is correlated in a unique manner with the conformations on the C—S bonds, see the double Newman projection along each S—C bond (C).



On the flanked C—S bond only the *g* conformation is possible, *i.e.* antiperiplanar to the benzene nucleus. This would support the hypothesis of a certain kind of conjugation between the S atom and the aromatic system^{1,17} but could be partly due to steric effects. On the other hand the benzene nucleus does not affect the second C—S bond with which it is not coplanar. This is why we suppose that the second form present is *gg'* (*D*) with the *g* conformation on the flanked C—S bond and not *g'g*. The findings as to the position of the benzene nucleus and the conformation on the C—S bonds thus support each other and yield a consistent picture.

The results of this paper are essentially in accord with previous dipole moment studies^{1,2} except that the existence of the *gg'* form had only been tentatively assumed in a few compounds and in small amount¹. On the other hand its population of almost 50%, as it follows from Fig. 4, may be somewhat overestimated. Note that this value is determined only from the dipole moment, being independent of the Kerr constant; hence it is not very dependable. The dipole moments of benzaldehyde dimethyldithioacetal (Table I) and diethyldithioacetal¹ differ distinctly, the different solvents may also play some role. Another source of the inaccuracy may be the assumption

of the eclipsed conformation, deduced from the approximate angle φ . However, with a somewhat different conformation of the benzene nucleus the main conclusions would not be essentially altered, only the whole pattern would lack its consistency. At any rate our results are not compatible with the IR study of bismethylthio-methane¹⁹ where just the most probable conformations were rejected.

Finally we attempted to determine the conformation of 4-chlorobenzaldehyde diethylthioacetal (II), considering only the forms *gt* and *gg'*, and different positions of the terminal methyl groups. According to the latter factor the computed Kerr constants vary within the limits 182 to 307 $\cdot 10^{-12}$, or from 330 to 382 $\cdot 10^{-12}$ for the *gt* and *gg'* forms, respectively, in each case higher than the experimental value (Table I). It may be that the mentioned sources of inaccuracy are more significant in this case, or the conformational equilibrium is shifted in comparison to the methyl derivative III; any decision is not possible at the present time.

Thanks are due to Dr J. Firl, München, for supplying kindly the sample of benzaldehyde diethylthioacetal.

REFERENCES

1. Exner O., Jehlička V., Firl J.: This Journal 37, 528 (1972).
2. Pigenet C., Jeminet G., Lumbroso H.: Compt. Rend. 269C, 1587 (1969).
3. Berthou J., Jeminet G., Laurent A., Rérat B., Rérat C.: Compt. Rend. 271C, 516 (1970).
4. Exner O., Jehlička V., Uchytíl B.: This Journal 33, 2862 (1968).
5. Astrup E. E.: Acta Chem. Scand. 25, 1494 (1971).
6. Le Févre R. J. W.: Advan. Phys. Org. Chem. 3, 1 (1965).
7. Backer H. J.: Rec. Trav. Chim. 68, 827 (1949).
8. Vereščagin A. N., Grozina L. A.: Teor. Exp. Chim. 4, 361 (1968).
9. Exner O., Jehlička V.: This Journal 30, 639 (1965).
10. Hanack M.: *Conformation Theory*, p. 301. Academic Press, New York 1965.
11. Le Févre R. J. W., Sundaram A., Pierens R. K.: J. Chem. Soc. 1963, 479.
12. Arbuzov B. A., Juldaševa L. K.: Izv. Akad. Nauk SSSR, Ser. Chim. 1962, 1728.
13. Cumper C. W. N.: Tetrahedron 25, 3131 (1969).
14. Fabelinskij I. L.: *Molekuljarnoje Rassejanije Sveta*, Appendix 3. Izd. Nauka, Moscow 1965.
15. Schaefer T., Schwenk R., Macdonald C. J., Reynolds W. F.: Can. J. Chem. 46, 2187 (1968).
16. Vilkov L. V., Sadova N. I., Močalov S. S.: Dokl. Akad. Nauk SSSR 179, 896 (1968).
17. Fehnel E. A., Carmack M.: J. Am. Chem. Soc. 71, 84 (1949).
18. Vereščagin A. N., Nuretdinova O. N., Nikonova L. Z., Arbuzov B. A.: Izv. Akad. Nauk SSSR, Ser. Chim. 1971, 758.
19. Welti D., Whittaker D.: J. Chem. Soc. 1962, 4372.

Translated by the author (O. E.).