

DIPOLE MOMENTS AND CONFORMATION OF SOME ORGANIC TELLURIUM COMPOUNDS

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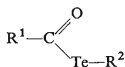
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Dipole moments of ditellurides *I–IV* and telluroesters *V, VI* have been measured in benzene solution. The results are consistent with the non-planar C_2 conformation of ditellurides, the same as in the crystalline state, and with the planar *Z* conformation of telluroesters. In general, there is no obvious difference when compared with corresponding oxygen, sulphur, and selenium compounds.

Although much interest has been devoted to the comparison of corresponding oxygen, sulphur, selenium, and tellurium compounds¹, in the sphere of dipole moments this comparison is prevented by the paucity of data concerning organic tellurium derivatives^{2–4}. In this note we report the dipole moments of ditellurides *I–IV* and telluroesters *V, VI* (Table I). Their approximate conformation has been determined by the same approach as previously for the corresponding selenium compounds⁵; essential is the comparison with an appropriate para derivative⁶.

The conformation of ditellurides is actually known; for the diphenyl derivative the non-planar conformation with the dihedral angle $\tau = 88.5^\circ$ has been found in the crystalline state⁷ and a similar one is considered probable for the dimethyl ditelluride in the gas phase⁸. Hence these compounds served us partly to test the whole approach. The conformation of telluroesters seems to be not known but from the analogy with esters⁹, thioesters¹⁰, and selenoesters⁵ the planar *Z* conformation (*A*) may be *a priori* strongly preferred to the *E* conformation (*B*) or any non-planar form



A(*Z*)



B(*E*)

The experimental dipole moments, listed in Table I, are somewhat less precise than usually^{5,9,10}, since the not exactly known values of molar refraction are of weight when the dipole moments are small. Our calculation of R_D (see Footnotes to Table I) may be even more than $\pm 1 \text{ cm}^3$ in error and introduces the error of some $\pm 0.05 \text{ D}$ in the dipole moment, in addition to the main uncertainty due to the atomic polarization.

In order to calculate theoretical dipole moments for individual conformations, we firstly deduced the $C_{ar}-Te$ bond moment of 0.9 D from the experimental moment of diphenyl telluride². The remaining bond moments were adopted as previously^{5,9,10}. The valence angles used were^{5,7,13} $\sphericalangle C-Te-C = 101^\circ$, $\sphericalangle C-Te-Te = 99^\circ$, $\sphericalangle O=C-Te = 124^\circ$. The calculated and experimental dipole moments are compared using our graphical representation⁶, Figs 1 and 2. Fig. 1 confirms the non-planar C_2 conformation of diaryl ditellurides even in benzene solution. The dihedral angle τ may be estimated to $70^\circ \pm 10^\circ$ in contradistinction to the value of 88.5°

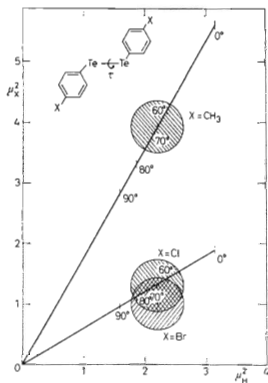


FIG. 1

Comparison of Squared Dipole Moments of Diphenyl Ditelluride *I* (x Axis) and its Derivatives *II*, *III*, *IV* (y Axis)

The hatched circles refer to the experimental moments, the calculated moments are plotted as function of the dihedral angle τ .

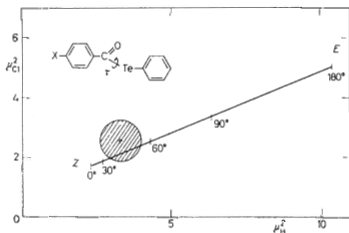


FIG. 2

Comparison of Squared Dipole Moments of Phenyl Tellurobenzoate *V* (x Axis) and its 4-Chloro Derivative *VI* (y Axis)

in the crystalline state⁷. Although the accuracy of our results must not be given too much credit,* we feel that this angle may be anyhow smaller in solution; the smaller value would better fit in the series peroxides-disulphides-diselenides where the dihedral angles (in solution, or in the gas phase) seem to diminish¹⁴⁻¹⁷, from c. 125° to 82° (for Se). Dipole moment of dimethyl ditelluride was interpreted only in terms of possible free or electrostatically controlled rotation³. Assuming a fixed conformation and using the above bond moments, the dihedral angle of 100° ± 10° could be calculated; it is probably less reliable than the estimate from Fig. 1. Of course, the dipole moments themselves do not allow to decide between a single, relatively rigid conformation and various mixtures, *e.g.* of the two extreme forms; the former possibility is, however, generally preferred for compounds of this type^{14,17}. In spite of recent progress the reasons of the stable conformation are not yet fully understood^{14,18}.

The conformation of telluroesters follows from Fig. 2 to be Z (previously denoted⁵ as *trans*). The apparent deviation from planarity, corresponding to the dihedral angle of 40–50°, is more probably due to using unsuitable bond moments than to real liberation around the planar position, although such liberation was claimed in the case of carboxylic esters (phenyl benzoate¹⁹). However, no deviations were

TABLE I
Polarization and Dipole Moments of Tellurium Compounds (Benzene, 25°C)

Compound	∞P_2 cm ³	R_D^a cm ³	$\mu(5\%)^b$ D	$\mu(15\%)^b$ D
I, (C ₆ H ₅ Te-) ₂	141.4	83.2	1.62	1.49
II, (4-CH ₃ C ₆ H ₄ Te-) ₂	186.6	92.6	2.09	1.98
III, (4-ClC ₆ H ₄ Te-) ₂	133.4	93.0	1.32	1.14
IV, (4-BrC ₆ H ₄ Te-) ₂	133.8	98.8	1.21	1.00
V, C ₆ H ₅ COTeC ₆ H ₅	153.1	72.9	1.93	1.84
VI, 4-ClC ₆ H ₄ COTeC ₆ H ₅	143.7	77.8	1.74	1.62

^a Calculated values based on Vogel's atom increments¹¹, the value¹² of 14.5 cm³ for Te and on the following corrections (exaltations) estimated by extrapolation in the series O—S—Se—Te: 1 cm³ for the conjugation Ph—Te, 0.8 cm³ for Te—CO, 1.5 cm³ for Te—Te (*i.e.* 30.5 cm³ for the group Te₂), finally 1.25 cm³ for the conjugation^{5,10} Ph—CO; ^b correction 5% or 15%, respectively, of the R_D value for the atomic polarization.

* Remarkably enough, Fig. 1 does not show the same deviation as similar diagrams for diaryl disulphides and diselenides⁵. Hence, the explanation of this deviation by the mere polarization⁵ may be not sufficient.

observed in similar diagrams concerning phenyl benzoate⁹, phenyl thiobenzoate¹⁰, or phenyl selenobenzoate⁵. The stable *Z* conformation of these esters seems to be a general phenomenon (see also²⁰); the controlling factors were discussed previously¹⁰.

TABLE II

Some Dipole Moment Data of Corresponding Oxygen, Sulphur, Selenium, and Tellurium Compounds (Ref.²)

Compound	Dipole moments (D)			
	O	S	Se	Te
C _{ar} -X ^a	0.74	1.0	1.15	0.9 ^b
Ph ₂ X	1.14	1.55	1.38	1.13
Ph ₂ X ₂	—	1.90	1.78 ^c	1.49 ^b
MeCOXPh	1.67	1.50 ^d	1.65 ^c	—
PhCOXPh	1.80	—	1.05 ^c	1.84 ^b

^a Bond moments, see ref.^{5,9,21}; ^b this work; ^c ref.⁵; ^d ref.²².

Some dipole moment data of corresponding oxygen, sulphur, selenium, and tellurium compounds are compared in Table II. Although some values, particularly the bond moments, are loaded with large errors, it seems certain that the values do not change in the monotonous manner but exhibit sometimes a maximum²³, or even a minimum (see also⁴). The attempt to explain this behaviour by analysing the gross moment into its components²³ is still rather speculative in character.

EXPERIMENTAL

Materials. Ditellurides *I* and *II* were prepared by the reaction of phenyl lithium and *p*-tolyl-lithium, respectively, with pulverized tellurium, and by subsequent acid hydrolysis²⁴. The halogen derivatives *III* and *IV* were obtained by the "dealkylation reaction" of 4-chlorophenyl butyl telluride (4-bromophenyl butyl telluride) by refluxing with 48% hydrogen bromide in acetic acid 6 hours and subsequent cooling²⁵. Telluroesters *V* and *VI* were prepared from natrium tellurophenolate and the appropriate acid chloride²⁶.

Measurements of dipole moments. The same method was used as previously^{5,9,10}.

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