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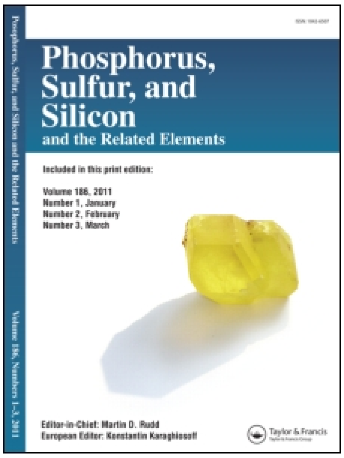

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# Dipole Moments and Conformations of Diphenyl Ditellurides

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# DIPOLE MOMENTS AND CONFORMATIONS OF DIPHENYL DITELLURIDES

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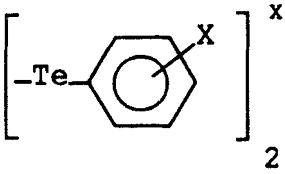
## Abstract

The dipole moments ($\mu_{exp}$) of 15 diphenyl ditellurides $(RC_6H_4)_2Te_2$ (R = 4-$NO_2$, 4-I, 4-β-$CH_3C_{10}H_7$, 4-$OCH(CH_3)_2$, 4-$COOCH_3$, 4-$Si(CH_3)_3$, 4-$COCH_3$, 3-$NO_2$, 3-Br, 3-$OCH_2CH_3$, 3-$N(CH_3)_2$, 2-F, 2-Cl, 2-Br, 2-$SCH_3$) were measured in benzene at 25 °C. The $\mu_{exp}$ values were compared with the calculated ($\mu_{calc}$) for the various conformations.

## INTRODUCTION

The conformational properties of diaryl ditellurides were object of previous investigations in the framework of a systematic study on dichalcogenides by using experimental methods such as dipole moments, p.e. spectroscopy and $^{13}C$-NMR spin-lattice relaxation times[1-4]. In particular, in the case of di-2-pyridyl analogous $(C_6H_4N)_2Te_2$, the NMR approach [4] confirmed the hypotheses based on results of the more classical dipole moment method. The electric dipole moment data for the new substituted derivative compounds **1-15** are here reported and analyzed in terms of conformations in solutions.



X = 4-$NO_2$ (**1**), 4-I (**2**), 4-β-$CH_3C_{10}H_7$ (**3**), 4-$OCH(CH_3)_2$ (**4**), 4-$COOCH_3$ (**5**), 4-$Si(CH_3)_3$ (**6**), 4-$COCH_3$ (**7**), 3-$NO_2$ (**8**), 3-Br (**9**), 3-$OCH_2CH_3$ (**10**), 3-$N(CH_3)_2$ (**11**), 2-F (**12**), 2-Cl (**13**), 2-Br (**14**), 2-$SCH_3$ (**15**)

## EXPERIMENTAL

Materials The diphenyl ditellurides **1** - **15** were prepared according to previously described procedures [5].

Dipole Moment Measurements The electric dipole moments of **1** - **15** were determined in benzene solution at 25 ± 0.01 °C, using apparatus and techniques described earlier [6]. The total solute polarization ($P_{2\infty}$) was obtained by extrapolation to infinite dilution using the Halverstadt-Kumler method [7]. The value of the experimental molar refraction ($R_D$) for the $Na_D$ line was used as the electronic and atomic polarization ($P_e + P_a$) in calculating $\mu$.

The polarization data and $\mu$ values ($\mu_{exp}$, estimated error: ± 0.2 D) are reported in Table 1.

TABLE 1 Polarization data and other measured parameters for evaluation of dipole moments ($\mu$/D) of diphenyl ditellurides in benzene solution at 25 °C.

| Compound | $\alpha$ | $\varepsilon_{10}$ | $\beta$ | $v_{10}$ | $P_{2\infty}/cm^3$ | $R_D/cm^3$ | $\mu$/D |
|---|---|---|---|---|---|---|---|
| **1** | 5.54 | 2.2724 | -0.663 | 1.14254 | 594.8 | 94.1 | 4.94 |
| **2** | 0.38 | 2.2726 | -0.680 | 1.14242 | 136.5 | 110.5 | 1.12 |
| **3** | 1.31 | 2.2726 | -0.617 | 1.14241 | 216.6 | 124.8 | 2.12 |
| **4** | 2.37 | 2.2727 | -0.680 | 1.14290 | 306.6 | 113.2 | 3.07 |
| **5** | 2.34 | 2.2722 | -0.634 | 1.14296 | 310.6 | 104.4 | 3.18 |
| **6** | 0.96 | 2.2724 | -0.533 | 1.14274 | 200.3 | 125.4 | 1.91 |
| **7** | 3.02 | 2.2726 | -0.663 | 1.14282 | 350.1 | 100.6 | 3.49 |
| **8** | 5.19 | 2.2726 | -0.709 | 1.14247 | 538.2 | 94.1 | 4.65 |
| **9** | 0.93 | 2.2727 | -0.842 | 1.14299 | 150.2 | 96.6 | 1.62 |
| **10** | 1.70 | 2.2724 | -0.559 | 1.14275 | 237.5 | 100.4 | 2.59 |
| **11** | 2.98 | 2.2724 | -0.561 | 1.14273 | 363.4 | 110.6 | 3.51 |
| **12** | 1.89 | 2.2722 | -0.641 | 1.14227 | 224.4 | 80.8 | 2.65 |
| **13** | 1.56 | 2.2726 | -0.650 | 1.14329 | 223.7 | 90.9 | 2.55 |
| **14** | 1.41 | 2.2727 | -0.609 | 1.14500 | 240.7 | 96.6 | 2.65 |
| **15** | 2.19 | 2.2725 | -0.679 | 1.14272 | 275.2 | 107.6 | 2.86 |

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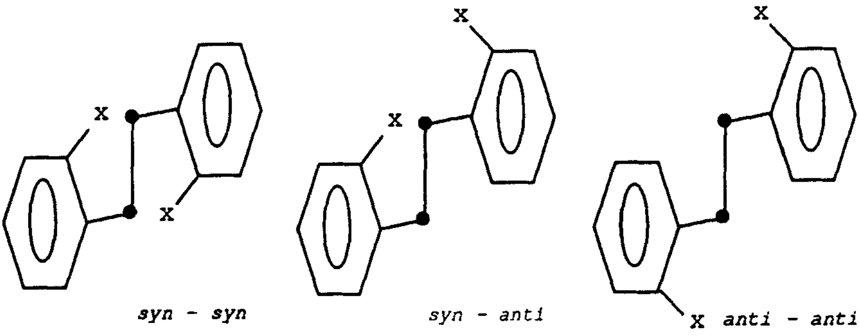
## RESULTS AND DISCUSSION

Theoretical dipole moments ($\mu_{calcd}$) were calculated for three kinds of conformations corresponding to the relative positions of the 2- and 3-substituent groups. The $\mu_{calcd}$ values for the 4-substituted compounds were calculated as a function of the dihedral angle $C_{Ph}$-Te-Te-$C'_{Ph}$ . In the former compounds each Te-Te-$C_6H_4$-X fragment was assumed coplanar (Figure 1) and the dihedral angle was kept fixed at the value of 88.5° found for $Ph_2Te_2$ in the solid [8]. The $\mu_{calcd}$ values were attained by vector addition using the $\mu_{exp}$ of $Ph_2Te_2$[1] and the following group moments [9]: $\mu_F$ = 1.47; $\mu_{Cl}$ = 1.59; $\mu_{Br}$ = 1.57; $\mu_I$ = 1.40; $\mu_{NO_2}$ = 4.01; $\mu_{\beta\text{-}CH_3\text{-}C_{10}\text{-}H_7}$ ≅ 0.5; $\mu_{Si(CH_3)_3}$ = 0.44; $\mu_{COCH_3}$ = 2.96 D (acting at 132° with respect to the $C_{Ph}$-C bond assumig this group coplanar with the ring).



*syn - syn* *syn - anti* *anti - anti*

FIGURE 1 Perspective view of 2-substituted diphenyl ditelluride in the conformations ($\omega_1,\omega_2$): 0,0 ; 0,180; 180,180. The angles are defined in the clockwise sense looking from C to Te and starting from 0 value corresponding to a coplanar arrangement of $C_{Ph}$-Te-Te atoms in which the 2- or 3- substituent is *syn* to Te-Te bond.

Comparison between $\mu_{calcd}$ and $\mu_{exp}$ is shown in Table 2. The analysis of the $\mu_{exp}$ data for ditellurides **4**, **5**, **10**, **11**, **15** was hindered by the additional degrees of rotational freedom of the substituents. The $\mu_{calcd}$ for the 4-substituted ditellurides (assuming the dihedral angle fixed at 88.5°) differ with respect to $\mu_{exp}$ by less than 0.5 D, *i.e.* by an amount that is of the order of magnitude of the accuracy of the method.

**TABLE 2** Comparison of $\mu_{exp}$ with $\mu_{calcd}$ and $\mu_{av}$ for selected conformations of ditellurides. All calculations were carried out with the dihedral angle $C_{Ph}$-Te-Te-$C'_{Ph}$ fixed at 88.5 °.

| Compound | Conformation $\omega_1, \omega_2$ | $\mu_{calcd}$ | $\mu_{av}$ | $\mu_{exp}$ |
|---|---|---|---|---|
| 1 | -- | 0.72 | | 1.16 |
| 2 | -- | 4.41 | | 4.94 |
| 3 | -- | 1.45 | | 2.12 |
| 6 | -- | 1.39 | | 1.91 |
| 7 | 0, 0 | 1.97 | 3.09 | 3.49 |
| | * 0, 180; 180, 0 | 4.64 | | |
| | 180, 180 | 1.11 | | |
| 8 | 0, 0 | 2.27 | 4.32 | 4.65 |
| | 0, 180; 180, 0 | 7.09 | | |
| | 180, 180 | 0.87 | | |
| 9 | 0, 0 | 0.12 | 1.49 | 1.62 |
| | 0, 180; 180, 0 | 2.71 | | |
| | 180, 180 | 0.41 | | |
| 12 | 0, 0 | 2.04 | 2.84 | 2.65 |
| | 0, 180; 180, 0 | 3.40 | | |
| | 180, 180 | 2.55 | | |
| 13 | 0, 0 | 2.11 | 3.0 | 2.55 |
| | 0, 180; 180, 0 | 3.63 | | |
| | 180, 180 | 2.65 | | |
| 14 | 0, 0 | 2.10 | 2.98 | 2.65 |
| | 0, 180; 180, 0 | 3.60 | | |
| | 180, 180 | 2.64 | | |

* The rotation angles $\omega_1, \omega_2$ of the 4-substituted phenyl groups denote in the compound 7 the relative orientation of the -$COCH_3$ groups (assumed coplanar with phenyl rings).

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In the 4-substituted compounds, the "free rotation" about $C_{Ph}$-Te bonds can be inferred on the basis of the agreement between $\mu_{exp}$ and $\mu_{av}$ values only in the case of **7** (see Table 2). Rigid conformations of 3-substituted compounds in which both rings lie on the $C_{Ph}$-Te-Te plane with the substituents being *syn-syn* (0, 0), *syn-anti* (0, 180) and *anti-anti* (180, 180) to the Te-Te group, can be excluded on the basis of the significant disagreement between $\mu_{exp}$ and $\mu_{calcd}$. Conversely, the $\mu_{av}$ values, calculated for equal population of all these rotamers, agree well with the $\mu_{exp}$ ones of compounds **8** and **9**. This result may be extended, by analogy, also to **10** and **11** whose $\mu_{exp}$ could not be analysed.

In the case of the 2-substituted derivatives **12**, **13** and **14** the $\mu_{calcd}$ for the *anti-anti* (180, 180) conformation (2.55, 2.65 and 2.64 D, respectively) are the most compatible ones with the $\mu_{exp}$ values. In the case of **12** and **14** the $\mu_{exp}$ agree also with $\mu_{av}$ values. The *anti-anti* conformation seems however more likely because of steric hindrance which increases the rotational energy barrier about $C_{Ph}$-Te bond. Moreover, such arrangement attains the maximum distance between the substituent groups and the minimum steric repulsive effect between the 2-substituent and the adjacent -Te-Te- group.

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