

Journal of Organometallic Chemistry, 97 (1975) 173–182
© Elsevier Sequoia, S.A., Lausanne — Printed in The Netherlands

DIPOLE MOMENTS AND CONFORMATIONS OF SOME DIARYL DITELLURIDES

GIUSEPPE C. PAPPALARDO*, SALVATORE GRUTTADURIA

Istituto di Chimica Generale, Università di Catania, Viale A. Doria, 95125 Catania (Italy)

and KURT J. IRGOLIC

Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)

(Received January 21st, 1975; in revised form April 3rd, 1975)

Summary

The electric dipole moments of the diaryl ditellurides, $(RC_6H_4)_2Te_2$ ($R = H, 4-F, 4-Br, 4-CH_3, 3-F$) have been measured in benzene solutions at 25 and 45°C. The following values were obtained (R, μ^{25}, μ^{45}): H, 1.26, 2.82; 4-Br, 0.89, 0.88; 4-F, 1.05, 0.36; 4-CH₃, 2.16, 2.17; 3-F, 1.86, 0.66. These data were used to deduce the conformation of these compounds in solution. The ditellurides with $R = 4-Br$ and $4-CH_3$ exhibit free rotation about the Te—Te bond at both temperatures investigated. The remaining three compounds seem to have a rigid conformation characterized by dihedral angles Φ between the C—Te—Te planes of 89.7° ($R = H$), 47.7° ($R = 4-F$), 61.1° ($R = 4-CH_3$) and 89.7° ($R = 3-F$). At the higher temperature these three ditellurides possess torsional motion about the Te—Te bonds. The Te—Te bond is much more flexible than the S—S bond in similar compounds.

Introduction

In previous studies [1-5] we examined the conformational properties of diaryl disulfides by dipole moment and NMR measurements. Those investigations showed that these disulfides adopt a rigid non-planar conformation about the S—S bond with a dihedral angle of $\sim 90^\circ$ and can assume several conformations about the C—S bond depending both on the nature of the aromatic group and the ring substituents.

In the present work we have extended our studies to the corresponding diaryl ditellurides, $(RC_6H_4)_2Te_2$ ($R = H, 4-F, 4-Br, 4-CH_3, 3-F$). Their electric dipole

moments have been measured in benzene at 25° and 45°, and analyzed in terms of molecular solute conformation.

Only very few dipole moments of organic compounds of tellurium have been determined [6-8]. While this work was in progress, Exner et al. [9] reported dipole moment values at 25° for some diaryl ditellurides and certain telluroesters. The difference between our values and their results for diphenyl, bis(4-bromophenyl) and bis(4-methylphenyl) ditelluride is discussed below.

TABLE 1

WEIGHT FRACTIONS OF SOLUTE (w_2), DIELECTRIC CONSTANTS (ϵ_{12}), SPECIFIC VOLUMES (v_{12}) AND REFRACTIVE INDEXES (n_{12}) OF DIARYL DITELLURIDES IN BENZENE SOLUTION AT 25 AND 45°C

$T = 25^\circ\text{C}$				$T = 45^\circ\text{C}$			
100 w_2	ϵ_{12}	v_{12}	n_{12}	100 w_2	ϵ_{12}	v_{12}	n_{12}
<i>(C₆H₅)₂Te₂</i>							
0.1254	2.2734	1.14196	1.49777	0.0944	2.2337	1.16738	1.48512
0.1964	2.2740	1.14147	1.49785	0.1536	2.2349	1.16701	1.48516
0.2859	2.2746	1.14088	1.49794	0.2940	2.2380	1.16613	1.48526
0.2981	2.2747	1.14076	1.49797	0.3638	2.2394	1.16567	1.48532
0.3516	2.2751	1.14041	1.49802	0.4570	2.2414	1.16509	1.48539
0.4101	2.2756	1.14001	1.49809	0.5895	2.2442	1.16425	1.48548
<i>(4-FC₆H₄)₂Te₂</i>							
0.0571	2.2729	1.14242	1.49769	0.0954	2.2338	1.16734	1.48512
0.0941	2.2731	1.14217	1.49772	0.1758	2.2340	1.16682	1.48518
0.1960	2.2736	1.14151	1.49780	0.2565	2.2341	1.16633	1.48521
0.2421	2.2738	1.14122	1.49783	0.3202	2.2342	1.16592	1.48525
0.3162	2.2741	1.14074	1.49789	0.4016	2.2344	1.16541	1.48530
0.3916	2.2745	1.14025	1.49794	0.4515	2.2345	1.16510	1.48532
<i>(4-BrC₆H₄)₂Te₂</i>							
0.0717	2.2729	1.14227	1.49771	0.1308	2.2330	1.16735	1.48500
0.1374	2.2733	1.14175	1.49780	0.2489	2.2336	1.16646	1.48412
0.2766	2.2740	1.14066	1.49797	0.3841	2.2342	1.16536	1.48529
0.3214	2.2742	1.14031	1.49803	0.5012	2.2348	1.16445	1.48542
0.3916	2.2746	1.13976	1.49812	0.5671	2.2351	1.16393	1.48550
0.4510	2.2749	1.13929	1.49819	0.6510	2.2355	1.16327	1.48559
<i>(4-CH₃C₆H₄)₂Te₂</i>							
0.0592	2.2734	1.14228	1.49775	0.1071	2.2339	1.16740	1.48506
0.1074	2.2740	1.14197	1.49779	0.1373	2.2342	1.16718	1.48509
0.1804	2.2749	1.14152	1.49783	0.2481	2.2356	1.16642	1.48518
0.2047	2.2753	1.14135	1.49785	0.2910	2.2362	1.16612	1.48522
0.2832	2.2762	1.14087	1.49789	0.3230	2.2365	1.16590	1.48524
0.3515	2.2771	1.14044	1.49794	0.4921	2.2386	1.16473	1.48539
<i>(3-FC₆H₄)₂Te₂</i>							
0.0649	2.2730	1.14247	1.49764	0.0611	2.2341	1.16798	1.48489
0.1520	2.2739	1.14189	1.49771	0.0977	2.2344	1.16761	1.48498
0.1748	2.2742	1.14175	1.49772	0.1823	2.2351	1.16676	1.48519
0.2348	2.2748	1.14135	1.49777	0.3032	2.2361	1.16554	1.48549
0.3294	2.2750	1.14073	1.49785	0.4154	2.2370	1.16440	1.48477
0.4072	2.2767	1.14022	1.49791	0.4916	2.2376	1.16363	1.48596

TABLE 2
TOTAL POLARIZATIONS ($P_{2\infty}$), MOLAR REFRACTIONS (R_D) AND DIPOLE MOMENTS (μ) TOGETHER WITH OTHER PARAMETERS FOR THEIR EVALUATION

Compound	Temp (°C)	α^a	ϵ_{10}^b	β^c	ν_{10}^d	γ^e	$P_{2\infty,3}$ (cm ³)	$R_{D,3}$ (cm ³)	μ^f (D)	μ^g (D)
(C ₆ H ₅) ₂ Te ₂	25	0.751	2.2725	-0.685	1.14282	0.750	113.58	81.0	1.26	1.25
	45	2.120	2.2317	-0.633	1.16798	0.220	233.59	81.0	2.82	2.82
(4-FC ₆ H ₄) ₂ Te ₂	25	0.490	2.2726	-0.648	1.14278	0.229	106.63	83.9	1.05	1.03
	45	0.186	2.2336	-0.627	1.16793	0.168	86.40	83.9	0.36	0.29
(4-BrC ₆ H ₄) ₂ Te ₂	25	0.531	2.2725	-0.785	1.14283	0.379	117.03	100.6	0.89	0.89
	45	0.473	2.2324	-0.786	1.16839	0.340	115.33	100.6	0.88	0.87
(4-OH ₃ C ₆ H ₄) ₂ Te ₂	25	1.250	2.2727	-0.629	1.14265	0.185	183.57	88.3	2.16	2.15
	45	1.220	2.2326	-0.693	1.16814	0.252	178.51	88.3	2.17	2.17
(3-FC ₆ H ₄) ₂ Te ₂	25	1.070	2.2723	-0.655	1.14289	0.230	154.24	83.6	1.86	1.86
	45	0.820	2.2336	-1.011	1.16860	0.738	91.89	83.6	0.66	0.61

a $\alpha = \frac{\Sigma(\epsilon_{12} - \epsilon_{10})}{\Sigma w_2}$, $\epsilon_{10} = \lim_{w_2 \rightarrow 0} \epsilon_{12}$, b $\beta = \frac{\Sigma(\nu_{12} - \nu_{10})}{\Sigma w_2}$, d $\nu_{10} = \lim_{w_2 \rightarrow 0} \nu_{12}$, e $\gamma = \frac{\Sigma(n_{12}^2 - n_{10}^2)}{\Sigma w_2}$, f μ calculated by the Guggenheim method, g μ calculated by the Halverstadt-Kumier method.

Experimental

Materials

Diphenyl ditelluride, bis(4-fluorophenyl) ditelluride, bis(4-bromophenyl) ditelluride, bis(4-methylphenyl) ditelluride, and bis(3-fluorophenyl) ditelluride have been prepared by the method previously described [10]. The purity, as checked by differential scanning calorimetry [11,12], was 99% for all samples examined. Benzene used as solvent was purified as described in the literature [13].

Dipole moment measurements

The dielectric constant measurements were made with a Dipolmeter WTW DM 01 Type. Densities and refractive indexes of the solutions were measured as described earlier [1].

The total solute polarization was obtained by extrapolation to infinite dilution ($P_{2\infty}$) with the Halverstadt and Kumler method [14]. The value of R_D (for the sodium yellow line) has been found experimentally from measurements of the refractive index and of the density of solutions of the compounds under investigation. The average of the values of R_D (constant at the two temperatures) obtained from solutions of different concentration was used as $P_e + P_a$ in calculating μ from the usual Debye formula.

In order to decrease to the limit the number of parameters to be determined experimentally for calculating the dipole moments of the solutes dealt with, Guggenheim's method [15] has also been used. This is a convenient procedure in that it eliminates precise measurement of solution densities as well as the determination of R_D . Results of both methods are equivalent; differences are within the expected error in the moments, with the Guggenheim moments slightly lower.

The estimated error in μ is ± 0.02 D at 25°C and ± 0.03 D at 45°C for values of $\mu > 1$ D. For moments smaller than 1 D the error clearly increases because small changes in properties with concentration must be determined in order to calculate α , β , γ . In these cases errors in μ are estimated to range from ± 0.03 to ± 0.04 D at 25°C and from ± 0.04 - 0.07 D at 45°C .

Duplicate determinations of μ have shown the level of reproducibility to be ± 0.01 D.

Experimental results at $25^\circ\text{C} \pm 0.01$ and $45^\circ\text{C} \pm 0.01$ are summarized in Tables 1 and 2.

Results and discussion

The expected dipole moments for the possible conformations of the compounds under examination have been calculated by vectorial addition of bond and group moments. The bond moment $\mu(\text{C}-\text{Te}) = 0.89$ D was deduced from the observed moment of diphenyl telluride [6] (1.14 D), using 101° as the C-Te-C angle [16] and $\mu(\text{C}-\text{F}) = 1.47$ D, $\mu(\text{C}-\text{Br}) = 1.57$ D and $\mu(\text{C}-\text{CH}_3) = 0.37$ D were employed as the aryl-halogen group moments [17]. The angle C-Te-Te was kept fixed at the value $\theta = 99^\circ$ reported for crystalline diphenyl ditelluride [18].

The results of these computations show that the experimental moments at

25°C (Table 2) for the diaryl ditellurides (RC₆H₄)₂Te₂ (R = H, 4-F, 4-Br and 4-CH₃) are in agreement with those calculated for non-planar conformations having dihedral angles Φ between the C—Te—Te planes of 89.7° (R = H), 47.7° (R = 4-F), 95.5° (R = 4-Br), and 61.1° (R = 4-CH₃). As discussed below, this agreement does not necessarily imply that a ditelluride will assume in solution a rigid conformation characterized by the calculated dihedral angle. The calculated dihedral angle Φ of 89.7° for diphenyl ditelluride is in very good agreement with the value of 88.5° reported for this molecule in the solid state [18]. The smaller angles in the 4-fluoro and 4-methyl derivatives may be in error because the mesomeric interaction moments between the tellurium atoms and the substituents have been neglected in the calculation.

A surprisingly high dipole moment of 2.82 D has been obtained for diphenyl ditelluride at 45°C. This moment is, in fact, considerably larger than the maximum expected for the fixed conformation with a dihedral angle $\Phi = 0$ ($\mu_{\text{calc}} = 1.77$ D). The observed moment is also in strong disagreement with the value of 1.27 D calculated under the assumption of "free rotation" about the Te—Te bond. Such a large increase of the dipole moment can not be caused by rapid torsional oscillations of the Te—Te linkage about the equilibrium position with a dihedral angle of $\Phi = 89.7^\circ$. The expected mean moment can be calculated by means of eqn. 1 provided that each $\mu(\text{C—Te})$ vector can be considered constant at 0.89 D during the oscillations and that the expression employed for calculating theoretical μ values is a continuous function of the variable Φ in the range $0^\circ \leq \Phi \leq 180^\circ$.

$$\bar{\mu} = 2\mu(\text{C—Te}) \sin \theta \int_{\Phi-x}^{\Phi+x} \cos \frac{\Phi}{2} d\Phi/2ae \quad (1)$$

In this equation, $\Phi - x$ and $\Phi + x$ correspond to the limiting values of the amplitudes of the oscillations. Coincidence of the experimental with the calculated moment, however, cannot be achieved by means of eqn. 1. In our opinion, the following alternative hypotheses can account for the experimental dipole moment at 45°C: (i) the increase in temperature produces dissociation of the compound into two C₆H₅Te[•] radicals; (ii) the conformation of diphenyl ditelluride at 45°C in benzene is more flexible than at 25°C, at the higher temperature the internal motions of rotation about Te—Te and Ar—Te bonds cause a variation in mesomeric and inductive interactions which invalidates the assumed component bond moments.

In the case of bis(4-fluorophenyl) ditelluride the decrease of μ_{exp} with increasing temperature can be accounted for by considering that at 45°C both halves of the molecule oscillate about the Te—Te axis. Use of eqn. 1, in fact, shows that μ_{exp} becomes equal to μ_{calc} for $x = 156^\circ$ assuming $\Phi = 47.7^\circ$ in the equilibrium conformation. Furthermore, the difference between the calculated moment of 0.80 D for "free rotation" (eqn. 2) and the experimental value at 45°C (0.36 D) rules out "free rotation" in this molecule at this temperature.

The constancy of the experimental moments of the 4-bromo and the 4-methyl derivatives within the temperature range studied could be interpreted in terms of an essentially rigid conformation. However, an explanation based on "free rotation" about the Te—Te bond seems to have more merit.

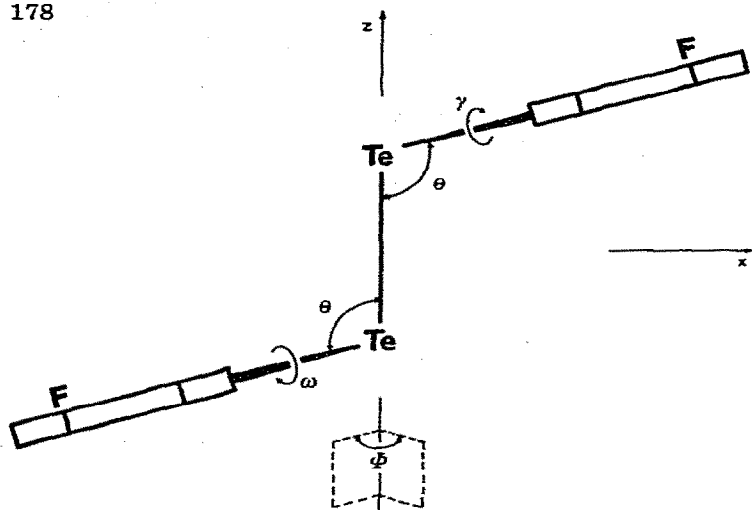


Fig. 1. Coordinate system for bis(3-fluorophenyl) ditelluride. The y axis runs perpendicular to the plane of the paper and intersects the Te—Te linkage at its mid-point. The conformation ($0^\circ, 0^\circ$) is shown.

The average values of the dipole moments which would result from free rotation about the Te—Te bond in the ditellurides $(4\text{-RC}_6\text{H}_4)_2\text{Te}_2$ ($R = \text{Br}, \text{CH}_3$ and also F) were calculated employing the Fuchs—Tiganik formula (eqn. 2) [19,20].

$$\bar{\mu} = (2\mu_R^2 + 2\mu_R^2 \cos^2 \alpha \cos \omega)^{1/2} \quad (2)$$

Here, μ_R is the resulting dipole of the two polar groups that are assumed to rotate freely about the Te—Te axis. The angle formed by the direction of the axes of rotation and vectors of the group moments is $\alpha = 180^\circ - \theta$, and these axes form with one another an angle $\omega = 180^\circ$.

The free rotation moments were thus found to be 0.95 D and 1.77 D for the 4-bromo and the 4-methyl compounds, respectively. The experimental dipole moments of 0.89 D for the bromo derivative and 2.16 for the methyl compound agree well with these calculated values. The difference of 0.4 D between μ_{exp} and μ_{calc} for the bis(4-methylphenyl) ditelluride is probably caused by the inductive effect of the methyl group which increases the dipole moment over the value expected in the absence of this effect.

The moment of bis(3-fluorophenyl) ditelluride has been analyzed in terms of two additional angles of internal rotation about the C—Te bonds. For a fixed dihedral angle Φ the possible rotational isomers are defined by the pair of angles (ω, γ) described by each phenyl ring in clockwise direction starting from the structure $(0^\circ, 0^\circ)$ (Fig. 1). In order to calculate the dipole moments for the various conformations of bis(3-fluorophenyl) ditelluride the external tangent to the angle Φ was chosen as the x axis, the line perpendicular to it in the plane of the paper and bisecting the angle Φ as the y axis, and the Te—Te axis as the z axis (Fig. 1). The component moments on the x, y and z axes in the orientation corresponding to this scheme are expressed by eqns. 3-5.

$$\begin{aligned} \mu_x = & \mu(\text{C-F}) \sin 60^\circ \sin (90^\circ - \theta) (\sin \omega - \sin \gamma) \cos \frac{180^\circ - \Phi}{2} + \\ & + \mu(\text{C-F}) \sin 60^\circ \sin \frac{180^\circ - \Phi}{2} (\cos \gamma - \cos \omega) \quad (3) \end{aligned}$$

$$\begin{aligned} \mu_y &= 2\mu(\text{C—Te}) \cos(90^\circ - \theta) \cos \frac{\theta}{2} - \\ & 2\mu(\text{C—F}) \cos 60^\circ \cos(90^\circ - \theta) \sin \frac{180^\circ - \Phi}{2} - \\ & \mu(\text{C—F}) \sin 60^\circ \sin(90^\circ - \theta) \sin \frac{180^\circ - \theta}{2} (\sin \omega + \sin \gamma) - \\ & \mu(\text{C—F}) \sin 60^\circ \cos \frac{180^\circ - \Phi}{2} (\cos \omega + \cos \gamma) \end{aligned} \quad (4)$$

$$\mu_z = \mu(\text{C—F}) \sin 60^\circ \cos(90^\circ - \theta) (\sin \omega - \sin \gamma) \quad (5)$$

The total moment is then given by eqn. 6.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (6)$$

If the angle Φ is assumed to be fixed at the value of 89.7° obtained for the equilibrium conformation of diphenyl ditelluride and the above group moments and angles are used, the moments for the conformations $(90^\circ, 90^\circ)$, $(90^\circ, 270^\circ)$ and $(270^\circ, 270^\circ)$ are calculated to be 0.51 D, 2.54 D and 0.05 D, respectively. These conformations, shown in Fig. 2, correspond to potential energy minima, since such structures clearly favor π -electron overlap between each phenyl ring and the respective tellurium atom.

By assuming that the compound is present in solution as a mixture of these three equiprobable conformers the average moment is obtained by means of eqn. 7. The conformers $(90^\circ, 270^\circ)$ and $(270^\circ, 90^\circ)$ are equally probable and have the same dipole moment. The coefficient 0.50 in eqn. 7 takes account of this fact.

$$\bar{\mu}^2 = 0.25\mu^2(90^\circ, 90^\circ) + 0.50\mu^2(90^\circ, 270^\circ) + 0.25\mu^2(270^\circ, 270^\circ) \quad (7)$$

The thus calculated dipole moment of 1.81 D agrees well with the experimental value of 1.86 at 25°C .

The theoretical moment for the case of "free rotation" about the C—Te bonds, e.g., equal probability of all possible rotamers, can alternatively be evaluated by means of eqn. 2. By vector triangulation the value $\mu_R = 1.28$ D is obtained for the resultant moment of each rotating fluorophenyl group. The angle between the vector μ_R and the corresponding C—Te axis of rotation is 84° . Keeping the dihedral angle Φ at 89.7° , the angle ω between the axes of rotation

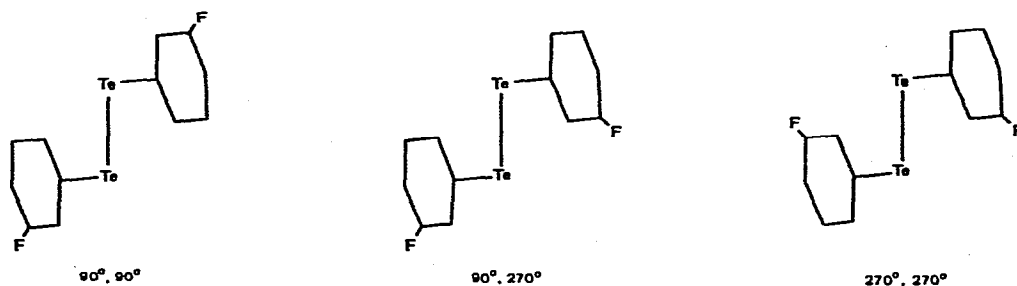


Fig. 2. The possible conformations of bis(3-fluorophenyl) ditelluride having the phenyl rings coplanar with the C—Te—Te group.

has been calculated to be 91.1° using a procedure previously described [21] for model diphenyl disulfide systems. Eqn. 2 then yields a total resultant dipole moment μ of 1.81 D. This result provides additional evidence that "free rotation" about the C—Te bonds occurs in bis(3-fluorophenyl) ditelluride.

The first computational approach adopted is particularly useful to interpret the measured moment at 45°C . The observed dipole moment of 0.66 D at this temperature can best be accounted for on the basis of a molecular solute conformation in which the 3-fluorophenyl groups freely rotate about the C—Te bonds and the Te—Te linkage makes torsional oscillations or freely rotates about the equilibrium position. The amplitude of these oscillations about Φ can adequately be evaluated by rewriting eqns. 3-6 to give μ_{calc} as a function of the dihedral angle Φ for each conformation (ω, γ). The dipole moments for the conformations ($90^\circ, 90^\circ$), ($90^\circ, 270^\circ$) and ($270^\circ, 270^\circ$) will then be obtained through eqns. 8, 9 and 10, respectively, with β representing $(180^\circ - \phi)/2$.

$$\mu^2 = 0.524 \sin^2\beta \quad (8)$$

$$\mu^2 = 0.158 \cos^2\beta + 0.106 \sin^2\beta + 6.32 \quad (9)$$

$$\mu^2 = 0.005 \sin^2\beta \quad (10)$$

By assuming that the amplitudes of oscillations are the same for each conformer, the average dipole moment of a mixture consisting of these equiprobable conformers, in which the dihedral angle is rapidly changing by $\pm x$ can be obtained from eqn. 11.

$$\begin{aligned} \bar{\mu}^2 = & 0.25 \int_{\beta-x}^{\beta+x} \frac{(0.524 \sin^2\beta) d\beta}{2x} + 0.25 \int_{\beta-x}^{\beta+x} \frac{(0.005 \sin^2\beta) d\beta}{2x} + \\ & + 0.50 \int_{\beta-x}^{\beta+x} \frac{(0.158 \cos^2\beta + 0.106 \sin^2\beta + 6.32) d\beta}{2x} \end{aligned} \quad (11)$$

Evaluation of the above integrals shows that reproduction of the experimental moment is impossible for the various possible x values from 0° to 360° . As observed for diphenyl ditelluride, this could indicate that the torsional motions cause changing in the bond moments or that, at higher temperature, some variation occurs in the chemical structure of the solute.

The results obtained during this investigation are summarized in Table 3. The temperature independence of the dipole moments of bis(4-bromophenyl) and bis(4-methylphenyl) ditelluride suggests that the two halves of each of these molecules rotate freely about the Te—Te linkage. A rigid conformation with appropriate dihedral angles as given in Table 3 is unlikely. The results for diphenyl, bis(4-fluorophenyl) and bis(3-fluorophenyl) ditelluride, indicative of little, if any, double bond character in the Te—Te bond and of a low rotational barrier about such a Te—Te bond which is assured by the large covalent radius of the tellurium atom, supports the explanation of the observed dipole moments on the basis of "free rotation".

In contrast to the bromo- and methylphenyl derivatives, the dipole moments of diphenyl, bis(4-fluorophenyl) and bis(3-fluorophenyl) ditelluride are temperature dependent. Free rotation about the Te—Te bond can, therefore, not be involved. At the present time the assumption of a rigid conformation at 25°C

TABLE 3

SUMMARY OF CONFORMATIONS ASSUMED BY DIARYL DITELLURIDES (R_2Te_2) IN BENZENE SOLUTION AS DERIVED FROM DIPOLE MOMENT MEASUREMENTS

R	25°C	45°C	Dihedral angle $\Phi(^{\circ})$ at 25°C	μ_{calc} (D) free rotation	μ_{calc} (D) $\Phi = 0$	Conformation of R_2Te_2	
	(D)	(D)				25°C	45°C
C_6H_5	1.26	2.82	89.7	1.27	1.77	$\Phi = 89.7^{\circ}$, rigid	free rotation (?)
4- BrC_6H_4	0.89	0.88	95.5	0.95		free rotation	free rotation
4- FC_6H_4	1.05	0.36	47.7	0.80		$\Phi = 47.7^{\circ}$; rigid	torsion $\Phi = 47.7^{\circ} \pm 156^{\circ}$
4- $CH_3C_6H_4$	2.16	2.17	61.1	1.77		free rotation	free rotation
3- FC_6H_4	1.86	0.66	89.7 ^a			$\Phi = 89.7^{\circ}$; rigid	torsion $\Phi = 89.7^{\circ} \pm x$ (?)
						free rotation about C—Te	free rotation about C—Te

^a Assumed in calculations.

and of rotational motions about the Te—Te bond at 45°C best reproduces the experimental dipole moments. In the 3-fluoro compound the fluorophenyl groups rotate freely about the C—Te bonds at 25°C and 45°C.

The reason why free rotation about the Te—Te bond occurs in the bromo and methyl derivatives but not in the other three ditellurides investigated, might be found in a more extensive electron delocalization involving the tellurium atoms and the bromo or methyl substituent, than possible in the fluorophenyl compounds and in diphenyl ditelluride. Such a delocalization will lower the barrier to rotation. More definite statements concerning the influence of substituents on this rotation barrier must await the investigation of many more diaryl ditellurides.

These studies have, however, shown that the diaryl ditellurides differ with respect to their conformations adopted in solution from the corresponding sulfur derivatives. Diphenyl disulfides are characterized by a high rotational barrier about the C—S bonds, which is caused by effective $3p-2p$ overlap, and the "rigidity" of the S—S bond, for which the repulsion between the lone electron pairs on adjacent sulfur atoms can be made responsible. The high degree of rotational freedom found in tellurium derivatives clearly suggests that the extent of π -electron overlap between the phenyl groups and the chalcogen atom decreases in the series $O > S > Se > Te$. The "flexibility" of the Te—Te linkage is indicative of a low rotational barrier. Such rotational barriers are expected to decrease in dichalcogenides from oxygen to tellurium because of decreasing repulsion between lone electron pairs with increasing bond length. The chalcogen—chalcogen bond lengths in their crystalline diphenyl derivatives, $C_6H_5-X-X-C_6H_5$, have been determined to be 2.03 Å ($X = S$), 2.29 Å ($X = Se$) and 2.71 Å ($X = Te$) [18,22,23]. On the basis of these considerations, the Te—Te bond in the diaryl ditellurides dealt with in this investigation possess essentially single bond character.

Recently, Exner et al. reported dipole moments at 25° for three diaryl ditellurides. Their experimental results seem to be less accurate than ours, mainly because the R_D values employed were calculated by Vogel's additive increments,

which are not well suited for molecules containing multiple bonds. Errors from this source are, however, not important provided that the measured moment is not too small. This may be the case with bis(4-methylphenyl) ditelluride, for which Exner's moment of 2.09 D agrees well with our value of 2.16 D. The error introduced by R_D is expected to be larger for diphenyl and bis(4-bromophenyl) ditelluride, which have smaller moments than the methyl derivative. However, the disagreement between our values (1.26 D for diphenyl ditelluride, 0.89 D for the 4-bromo derivative) and the reported moments (1.62 D for the phenyl compound, 1.21 D for the bromo derivative) [9] cannot be solely caused by errors in R_D values and discrepancies between the respective polarization data, which have been noted, might also be partially responsible.

Acknowledgement

K.J.I. thanks the Robert A. Welch Foundation of Houston, Texas for partial support of that part of these investigations which was carried out at Texas A&M University.

References

- 1 G.C. Pappalardo and S. Pistara, *J. Chem. Eng. Data*, **17** (1972) 2.
- 2 G.C. Pappalardo and G. Ronsisvalle, *J. Chem. Soc. Perkin Trans. II*, (1973) 701.
- 3 G.C. Pappalardo and E. Tondello, *Int. J. Sulfur Chem.*, **9** (1974) 5.
- 4 G.C. Pappalardo and S. Gruttadauria, *Z. Phys. Chem.*, **91** (1974) 322.
- 5 G.C. Pappalardo and S. Gruttadauria, *Z. Phys. Chem.*, **94** (1975) 179.
- 6 E. Bergmann, L. Engel and S. Sandor, *Z. Phys. Chem. B*, **10** (1930) 397.
- 7 H. Lumbroso, D.M. Bertin, F. Fringuelli and A. Taticchi, *J. Chem. Soc. Chem. Commun.*, (1973) 342.
- 8 H. Lumbroso, D.M. Bertin, F. Fringuelli and A. Taticchi, *C.R. Acad. Sci. Paris, Ser. C*, **277** (1973) 203.
- 9 V. Jehlicka, J.L. Piette and O. Exner, *Coll. Czech. Chem. Commun.*, **39** (1974) 1577.
- 10 W.S. Haller and K.J. Irgolic, *J. Organometal. Chem.*, **38** (1972) 97.
- 11 E.S. Watson, M.J. O'Neill, J. Justin and N. Brenner, *Anal. Chem.*, **36** (1964) 1233.
- 12 Perkin-Elmer Corp., Norwalk, Conn., *Thermal Analysis Newsletter*, Nos. 1-6.
- 13 A. Weissberger and E.S. Proskauer, *Organic Solvents. Techniques of Organic Chemistry*, Vol. VII, Interscience, New York, 1961.
- 14 I.F. Halverstadt and W.D. Kumler, *J. Amer. Chem. Soc.*, **64** (1942) 2988.
- 15 E.A. Guggenheim, *Trans. Faraday Soc.*, **45** (1949) 714.
- 16 W.R. Blackmore and S.C. Abrahams, *Acta Crystallogr.*, **8** (1955) 317.
- 17 C.P. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill, New York, 1955, p. 253.
- 18 G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr. Sect. B*, **28** (1972) 2438.
- 19 O. Fuchs, *Z. Phys. Chem. B*, **14** (1931) 339.
- 20 L. Tiganik, *Z. Phys. Chem. B*, **14** (1932) 135.
- 21 G.C. Pappalardo and G. Ronsisvalle, *J. Mol. Struct.*, **16** (1973) 167.
- 22 J.D. Lee and M.W.R. Bryant, *Acta Crystallogr., Sect. B*, **25** (1969) 2094.
- 23 R.E. Marsh, *Acta Crystallogr.*, **5** (1952) 458.