A DIPOLE MOMENT STUDY OF THE CONFORMATIONAL PROPERTIES OF DIARYL DISELENIDES AND RELATED COMPOUNDS

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Summary

The electric dipole moments of the diaryl diselenides $(RC_6H_4)_2Se_2$ (R = H, 4-F, 4-Br, 4-CH_3, 3-F) were measured in benzene solution at 25 and 45°C. The conformations of these compounds were deduced by matching experimental moments with values calculated for a variety of possible conformations. In the dissolved state the diselenides exist at 25°C in fixed "skew" conformations characterized by dihedral angles of 75—106° between the C—Se—Se planes, corresponding to the conformational energy minima. At 45°C oscillations about the Se—Se bonds are excited in the diphenyl and bis(4-methylphenyl) diselenides, whereas the 4-bromophenyl derivative exhibits free rotation. The fluoro compounds have temperature-independent dipole moments, suggesting "rigid conformations" with dihedral angles of 106° (4-F) and 74.4° (3-F). An analysis of the dipole moments at 25 and 45°C obtained for the compounds $(RC_6H_4)_2X_2$ (R = H, 3-F, 4-F, 4-Br, 4-CH_3; X = S, Se, Te) showed that the conformational properties of these derivatives change on passing from X = S to X = Te. The observed variations are explicable in terms of a decreasing repulsion between the lone electron pairs of the chalcogen atoms on going from the disulfides to the ditellurides and a concomitant reduction of the energy barrier to rotations about the X—X bonds.

Introduction

Dipole moment measurements have been employed to elucidate the molecular conformation of diaryl disulfides [1—5] and, more recently, diaryl ditellurides [6] in solution. These studies have shown that ditellurides differ from the corresponding sulfur derivatives with respect to their conformational properties. It has been suggested that rotations about the X—X and C—X bonds in diaryl dichalcogenides, Ar—X—X—Ar, are more likely to occur in ditellurides (X = Te)

than in disulfides (X = S). It therefore seemed worthwhile to extend our investigations to the diaryl diselenides in order to make more precise and systematic comparisons of the molecular conformations assumed by Ar_2X_2 compounds (X = S, Se, Te) in solution. Accordingly, we have measured and analyzed the electric dipole moments of the diaryl diselenides $(R—C_6H_4)_2Se_2$ (R = H, 4-F, 4-Br, 4-CH_3, 3-F) in benzene at 25 and 45°C. The temperature dependence of the dipole moments was used to help elucidate the conformations of these molecules in the dissolved state.

Previously, the solid state conformations of diphenyl diselenide [7] and bis-(4-chlorophenyl) diselenide [8] were determined. Molar Kerr constants [9] and dipole moments [10] for diphenyl diselenide and some of its 4-substituted derivatives have been reported. Dipole moments of a series of aromatic diselenides were calculated by quantum mechanical methods [11].

Experimental

Materials

Noranda Brand grey Selenium Powder was obtained from Canadian Copper Refiners Ltd. Diphenyl diselenide was purchased from Eastman Kodak and recrystallized from absolute ethanol.

Diaryl diselenides

The diaryl diselenides, $(RC_6H_4)_2Se_2$ (R = 4-CH_3, 4-Br, 3-F, 4-F) were prepared by addition of an equimolar amount of selenium to the appropriate Grignard reagent (0.5 mols for 4-CH_3; 0.2 mols for 4-Br; 0.025 mols for 4-F and 3-F) in diethyl ether solution, followed by hydrolysis of the reaction mixture with 3 M HCl and air oxidation of the selenol in the ether layer [12].

The bis(4-bromophenyl) diselenide (48% yield) melted at 114°C (lit. [13], 114°C) after recrystallization from absolute ethanol.

Bis(4-methylphenyl) diselenide m.p. at 46°C (lit. [14], 46°C), was obtained in 61% yield. The compound was recrystallized from ethanol.

The bis(fluorophenyl) diselenides are liquids which could not be purified by conventional recrystallization. The selenols were oxidized to the diselenides by bubbling air through the ethereal selenol solution. The liquid remaining after evaporation of the ether was dried for 48 h in a vacuum desiccator over P_2O_5. The dry liquid was dissolved in the minimum amount of an anhydrous mixture of diethyl ether/ethanol (9 : 1 v/v). The solution was chilled in a freezer until crystals had separated. The crystals were quickly filtered through a precooled filtering apparatus and then transferred into a flask, where they melted. The carbon content of the products purified by three low temperature recrystallizations was still 0.6% too high. The compounds were then further purified by preparative high pressure liquid chromatography on a μ-Porasil column with hexane as the mobile phase. The yields of purified products were 36% (4-F) and 30% (3-F). Analysis: Found for 3-F: C, 41.99; H, 2.45. Found for 4-F: C, 41.69; H, 2.30. $(C_6H_4F)_2Se_2$ calcd.: C, 41.41; H, 2.31%.

Physical measurements

The electric dipole moments of the diaryl diselenides were determined in ben-

zene * solution at 25 and 45°C (±0.01°C) using apparatus and techniques described earlier [1]. The total solute polarization was obtained by extrapolation to infinite dilution ($P_{2\infty}$) employing the Halverstadt and Kumler method [16]. The molar refraction (R_D, Na_D line) obtained from the specific refractions of the solutions and taken as equivalent to the distortion polarization was used for the calculation of the dipole moments (μ). The R_D value was assumed to be the same for the two temperatures. Guggenheim's method [17], which does not require determination of R_D values and precise measurements of solution densities

TABLE 1

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

$T = 25°C$				$T = 45°C$			
$100w_2$	ϵ_{12}	v_{12}	n_{12}	$100w_2$	ϵ_{12}	v_{12}	n_{12}
$(C_6H_5)_2Se_2$							
0.0332	2.2730	1.14255	1.49769	0.0601	2.2363	1.16799	1.48492
0.0608	2.2735	1.14242	1.49771	0.1260	2.2369	1.16759	1.48500
0.0931	2.2739	1.14225	1.49774	0.1866	2.2374	1.16726	1.48506
0.1242	2.2744	1.14210	1.49777	0.2346	2.2378	1.16697	1.48511
0.1875	2.2753	1.14178	1.49782	0.2937	2.2383	1.16663	1.48518
0.2066	2.2756	1.14168	1.49784	0.3101	2.2385	1.16484	1.48546
$(4\text{-}FC_6H_4)_2Se_2$							
0.1743	2.2726	1.14213	1.49761	0.1180	2.2331	1.16775	1.48491
0.2675	2.2731	1.14154	1.49772	0.2490	2.2335	1.16703	1.48500
0.3701	2.2735	1.14091	1.49783	0.4069	2.2340	1.16616	1.48511
0.4147	2.2738	1.14065	1.49788	0.6112	2.2346	1.16504	1.48525
0.5612	2.2745	1.13974	1.49804	0.7930	2.2352	1.16404	1.48537
0.7130	2.2752	1.13880	1.49821	0.8892	2.2355	1.16351	1.48544
$(4\text{-}BrC_6H_4)_2Se_2$							
0.0848	2.2728	1.14859	1.49447	0.0925	2.2330	1.16773	1.48493
0.1745	2.2731	1.14804	1.49452	0.1133	2.2331	1.16757	1.48495
0.2420	2.2734	1.14763	1.49456	0.2383	2.2334	1.16659	1.48512
0.4574	2.2744	1.14626	1.49471	0.3638	2.2341	1.16564	1.48527
0.4916	2.2746	1.14605	1.49473	0.4124	2.2342	1.16526	1.48533
0.5102	2.2747	1.14594	1.49474	0.5612	2.2348	1.16412	1.48553
$(4\text{-}CH_3C_6H_4)_2Se_2$							
0.1548	2.2756	1.14201	1.49777	0.0487	2.2346	1.16845	1.48492
0.1877	2.2761	1.14186	1.49780	0.0961	2.2351	1.16783	1.48495
0.2985	2.2780	1.14139	1.49786	0.1649	2.2360	1.16749	1.48501
0.3162	2.2783	1.14131	1.49788	0.2019	2.2364	1.16731	1.48503
0.4016	2.2797	1.14094	1.49793	0.3001	2.2376	1.16684	1.48511
0.6470	2.2839	1.13989	1.49809	0.4616	2.2395	1.16606	1.48523
$(3\text{-}FC_6H_4)_2Se_2$							
0.1260	2.2745	1.14221	1.49767	0.2802	2.2358	1.16706	1.48492
0.3019	2.2767	1.14136	1.49774	0.2867	2.2359	1.16701	1.48494
0.4366	2.2784	1.14071	1.49780	0.3645	2.2372	1.16637	1.48509
0.5003	2.2792	1.14040	1.49783	0.4032	2.2378	1.16605	1.48517
0.5918	2.2803	1.13996	1.49787	0.6098	2.2412	1.16436	1.48558
0.7302	2.2821	1.13929	1.49793	0.9184	2.2463	1.16183	1.48619

* Purified by previously described methods [15].

314

TABLE 2

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

Compound	Temp. (°C)	α [a]	ϵ_{10} [b]	β [c]	v_{10} [d]
$(C_6H_5)_2Se_2$	25	1.500	2.2725	−0.501	1.14272
	45	0.870	2.2358	−0.578	1.16833
$(4\text{-}FC_6H_4)_2Se_2$	25	0.497	2.2717	−0.615	1.14319
	45	0.312	2.2327	−0.550	1.16840
$(4\text{-}BrC_6H_4)_2Se_2$	25	0.460	2.2723	−0.626	1.14913
	45	0.399	2.2326	−0.770	1.16844
$(4\text{-}CH_3C_6H_4)_2Se_2$	25	1.680	2.2730	−0.430	1.14267
	45	1.200	2.2340	−0.483	1.16829
$(3\text{-}FC_6H_4)_2Se_2$	25	1.260	2.2729	−0.484	1.14282
	45	1.660	2.2311	−0.820	1.16936

[a] $\alpha = \Sigma(\epsilon_{12} - \epsilon_{10})/\Sigma w_2$. [b] $\epsilon_{10} = \lim_{w_2 \to 0} \epsilon_{12}$. [c] $\beta = \Sigma(v_{12} - v_{10})/\Sigma w_2$. [d] $v_{10} = \lim_{w_2 \to 0} v_{12}$. [e] $\gamma = \Sigma(n_{12}^2 - n_{10}^2)/\Sigma w_2$. [f] μ calculated by the Halverstadt-Kumler method. [g] μ calculated by the Guggenheim method. [h] Ref. [10]. [i] Ref. [9]. [j] Ref. [11].

was also employed to obtain the dipole moments. Both methods gave the same results within experimental error.

The extimated error in μ is ±0.02 D at 25 and ±0.03 D at 45°C for the diselenides $(RC_6H_4)_2Se_2$ (R = H, CH_3, 3-F). The error in μ is greater, namely ±0.04 D at 25 and ±0.06 D at 45°C, for the compounds with R = 4-F and 4-Br. The experimental results are summarized in Tables 1 and 2.

Results and discussion

The dipole moments for diphenyl and bis(4-methylphenyl) diselenide (Table 2) at 25°C are in exact agreement with those obtained by Sindelar and Exner [10]. Our measured R_D values for these molecules are also in good agreement with those calculated using Vogel's increments [10] supporting the value of 0.7 cm^3 for the exaltation attributable to the C_6H_5—Se conjugation.

In this investigation the theoretical moments for the possible conformations of diselenides were computed by a three-dimensional vector addition method using bond and group moments. This approach was made more reliable by the selection of appropriate group moments which minimized inaccuracies due to interaction effects. The $\mu(C$—$Se)$ bond moment of 1.25 D was deduced from the experimental moment of diphenyl selenide $\mu(Ph_2Se)$ (1.50 D, as calculated by Lumbroso [18]) according to eq. 1.

$$\mu(C\text{—}Se) = \sqrt{\frac{\mu(Ph_2Se)^2}{2(1 + \cos \varphi)}} \tag{1}$$

The value $\varphi = 106°$ was used for the CSeC angle as reported for solid bis(4-methylphenyl) selenide [19]. The calculated dipole moments (μ_{calc}) for the $(4\text{-}RC_6H_4)_2Se_2$ systems were thus obtained as a function of the dihedral angle ϕ between the C—Se—Se plane by means of eq. 2.

$$\mu_{calc} = 2\,\mu(R\text{—}C_6H_4\text{—}Se\text{—}) \sin\theta \cos\frac{\phi}{2} \tag{2}$$

γ^e	$P_{2\infty}$ (cm^3)	R_D (cm^3)	μ^f (D)	μ^g (D)	μ (lit. data)
0.251	147.52	72.6	1.91	1.89	1.88 [h]; 1.68 [i]; 1.67 [j]
0.325	106.76	72.6	1.33	1.32	
0.332	87.25	76.0	0.74	0.73	0.65 [j]
0.204	83.94	76.0	0.64	0.62	
0.194	114.04	89.1	1.10	1.07	1.10 [h]; 0.64 [i]
0.379	91.21	89.1	0.33	0.31	
0.192	179.52	82.1	2.18	2.16	2.49 [i]
0.225	147.77	82.1	1.85	1.84	
0.130	150.68	75.8	1.91	1.90	
0.592	148.62	75.8	1.95	1.95	

The CSeSe angle, θ, was kept constant at the value of 106° as reported for crystalline diphenyl diselenide [7]. The moment of the RC_6H_4Se-group, $\mu(RC_6H_4Se)$, was calculated as the resultant of the moments $\mu(C\text{—}Se)$ and $\mu(C\text{—}R)$, with $\mu(C\text{—}R)$ representing the group moment of the 4-substituent (1.47 D for R = F; 1.57 D for R = Br; 0.37 D for R = CH_3) as taken from literature data [20]. The analysis of the dipole moment of bis(3-fluorophenyl) diselenide is complicated by the two additional angles of internal rotation ω and γ describing the rotation of the phenyl groups about the C—Se bonds (Fig. 1). The dipole moment for this molecule was therefore calculated by means of the equations developed for the analogous ditelluride [6] but employing the bond moments and geometric parameters characteristic of the diselenides. The theoretical averaged moments $\bar{\mu}_{calc}$ expected for molecules with essentially "free rotation" about the Se—Se bond were obtained using a procedure previously described for the diphenyl disulfide system [3].
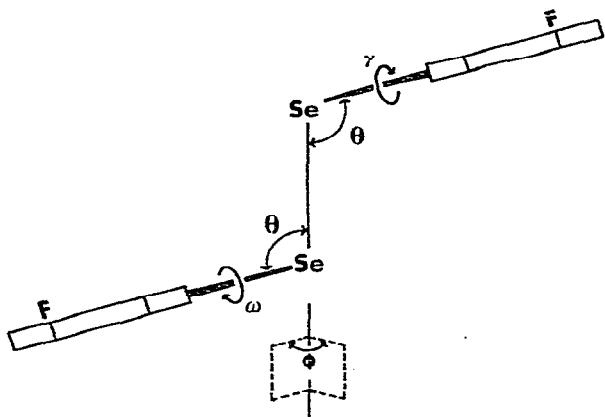

Fig. 1.

TABLE 3

SUMMARY OF THE CONFORMATIONS ASSUMED BY DIARYL DICHALCOGENIDES, Ar_2X_2 (X = S, Se, Te) IN BENZENE AS DERIVED FROM DIPOLE MOMENT MEASUREMENTS

Ar	X	μ_{exp} (D) at 25°C	μ_{exp} (D) at 45°C	Dihedral Angles [j] (φ) (°) 25°C	Dihedral Angles [j] (φ) (°) 45°C	μ_{calc} (D) (free rotation)	Conformation 25°	Conformation 45°
C_6H_5	S	1.77 [a]	1.81 [a]	88.9	88.9	1.75	rigid, φ = 88.9°	rigid, φ = 88.9°
	Se	1.91 [b]	1.33 [b]	74.7	112.8	1.70	rigid, φ = 74.7°	torsions
	Te	1.26 [c]	2.82 [c]	89.7		1.27	rigid, φ = 89.7°	free rotation
$4\text{-}FC_6H_4$	S	0.38 [d]	0.36 [d]	85	85	0.24	rigid, φ = 85°	rigid, φ = 85°
	Se	0.74 [b]	0.64 [b]	(106) [h]	(117.3) [h]	0.30	rigid	rigid
	Te	1.05 [c]	0.36 [c]	47.7		0.80	torsions	free rotation
$4\text{-}BrC_6H_4$	S	0.75 [e]	0.78 [d]	(93.2) [f,h]	(93.2) [f,h]	0.38	rigid, φ = 93.2°	rigid, φ = 93.2°
	Se	1.10 [b]	0.33 [b]	(106.8) [h]	115.1	0.43	rigid, φ = 106.8°	free rotation
	Te	0.89 [c]	0.88 [c]	95.5	95.5	0.95	free rotation	free rotation
$4\text{-}CH_3C_6H_4$	S	2.49 [d]	2.38 [d]	77.5	77.5	2.26	rigid, φ = 77.5°	rigid, φ = 77.5°
	Se	2.18 [b]	1.85 [b]	(91.1) [h]	(109.1) [h]	2.04	rigid, φ = 91.1°	torsions
	Te	2.16 [c]	2.17 [c]	61.1	61.1	1.77	free rotation	free rotation
$3\text{-}FC_6H_4$ [i]	S	not measured	not measured					
	Se	1.91 [b]	1.91 [b]	74.7 [g]	74.7		rigid, φ = 74.7°	rigid, φ = 74.7°
	Te	1.86 [c]	0.66 [c]	89.7 [g]			rigid, φ = 89.7°	torsions

[a] Ref. [1]; [b] Present work; [c] Ref. [6]; [d] Ref. [21]; [e] Ref. [20]; [f] (4-BrC$_6$H$_4$S) group moment calculated from experimental moment of bis(4-bromophenyl) sulfide (0.65 D) [19]. [g] Assumed from unsubstituted compound. [h] These dihedral angles φ were calculated using group moments corrected for interactions between the substituents and the chalcogen atoms. [i] Free rotation about the C—X bonds has been assumed. [j] μ_{exp} is equal to the dipole moment calculated for the dihedral angles listed within ±0.00 D.

The experimental and calculated dipole moments and the conformations assumed by the diselenides are shown in Table 3 together with the corresponding results and conformations obtained for the analogous sulfur and tellurium compounds.

The value of 1.91 D for μ_{exp} at 25° C for diphenyl diselenide can be interpreted either in terms of a single skew conformation in which the C—Se—Se planes form a dihedral angle of about 75°, or, alternatively, in terms of an equilibrium mixture of all possible rotamers, i.e., of free rotation about the Se—Se bond.

This result illustrates the limitation inherent in this method of deducing conformations from experimental dipole moments by matching them with moments calculated as a function of molecular geometric parameters. An unambiguous conformational assignment is not always possible when dipole moments have been measured at only one temperature. The temperature dependence of dipole moments can, however, be used to remove such ambiguities.

Diphenyl diselenide has a dipole moment of 1.91 D at 25 and 1.33 D at 45° C. If free rotation about the Se—Se bond would take place at 25°, free rotation would also be expected at 45° and the dipole moment should be temperature independent. The observed temperature dependence of the dipole moment suggests the existence of diphenyl diselenide in solution in a fixed conformation. The calculated dipole moment (eq. 2) for a conformation with a dihedral angle of 74.7° agrees with the experimental value. This conformation seems to represent the potential energy minimum of the molecule in solution. This dihedral angle of 74.7° agrees well with the angle of 82° derived from molar Kerr constant measurements [9] and from structure investigations [7] as well as with a previous estimate of 75° based on dipole moment measurements [10]. Furthermore, the difference between $\bar{\mu}_{calc}$ for free rotation (1.70 D) and μ_{exp} at 45°C (1.33 D) indicates that even at 45°C free rotation about the Se—Se bond in diphenyl diselenide probably does not occur. The conformational state of the molecule at 45°C certainly is not the same as that at 25°C. The dipole moment calculated (eq. 2) for the conformation characterized by a dihedral angle $\phi = 112°$ does agree with the experimental value obtained at 45° C. It is doubtful, however, that the molecule exists in this conformation. The dipole moment probably decreases with increasing temperature because torsional oscillations about the minimum energy conformation are excited at temperatures higher than 25° C. The electron cloud of the carbon—selenium group is highly polarizable. Oscillations about the Se—Se bond might change the electron distribution within the molecule and thus cause bond and group moments to be dependent on molecular geometry. A value for $\mu(C—Se)$, which in the oscillating molecule might be smaller than in the molecule with a fixed conformation, could account for the low dipole moment observed at 45° C.

When the appropriate C—Se, C—F, C—Br and C—CH$_3$ group moments as given earlier were employed to calculate the dipole moments for bis(4-fluorophenyl) diselenide, bis(4-bromophenyl) diselenide and bis(4-methylphenyl) diselenide according to eq. 2, the experimental moments were outside the range of the calculated values. This failure to achieve agreement between experimental and calculated values must be blamed on interactions occurring between the selenium atoms and the 4-substituents. Therefore, moments for the 4-RC$_6$H$_4$Se groups,

which take into account the pertinent interactions, were derived (eq. 1) from the dipole moments reported for bis(4-chlorophenyl) selenide (0.65 D), bis(4-bromophenyl) selenide (0.77 D) and bis(4-methylphenyl) selenide (1.81 D) [20] assuming a C—Se—C angle = $106°$. The dipole moment for bis(4-fluorophenyl) selenide has not yet been reported. Therefore, the $4\text{-}ClC_6H_4Se$ group moment was assumed to be equal to the $4\text{-}FC_6H_4Se$ moment.

The free rotation dipole moments, $\bar{\mu}_{calc}$ (Table 3), however, were computed using the C—Se and C—R (R—CH_3, F, Cl, Br) group moments and not the interaction moments described above. Internal free rotation implies, that the various groups within the molecule interact only weakly or not at all. Hence, the use of the individual bond moments should give correct free rotation dipole moments.

The dipole moment of bis(4-fluorophenyl) diselenide changes little with temperature (0.74 D at 25, 0.64 D at $45°$C). Neither of these values is close enough to the calculated free rotation moment of 0.30 D to postulate that this molecule is freely rotating. The fixed conformation with a dihedral angle $\phi = 106°$ has a calculated dipole moment equal to the experimental moment at $25°$C. This agreement indicates perhaps that such a conformation is energetically favored and specially stabilized by conjugation across the FC_6H_4Se group.

The bis(4-bromophenyl) diselenide seems to have a rigid conformation at $25°$C characterized by a dihedral angle $\phi = 106.8°$. The dipole moment decreases with increasing temperature (1.10 D at 25, 0.33 D at $45°$C). The value at $45°$C is in reasonably good agreement with the moment calculated for free rotation (0.43 D) indicating the rotational barrier is low enough to allow free rotation at $45°$C.

The dipole moment of bis(4-methylphenyl) diselenide changes little with temperature. The values at 25 (2.18 D) and $45°$C (1.85 D) bracket the calculated free-rotation moment (2.04 D). The assumption that the compound is present at $25°$C in a rigid conformation with a dihedral angle $\phi = 91.1°$ and performs torsional motions at $45°$C is not inconsistent with the experimental results.

The temperature-independent dipole moment of bis(3-fluorophenyl) diselenide (1.91 D) agrees with the calculated values for free rotation about the Se—Se and the C—Se bonds and for a rigid conformation characterized by a dihedral angle $\phi = 75°$. The trend in preferred conformations in the series of diaryl dichalcogenides, Ar_2X_2 (X = S, Se, Te), (Table 3) suggests for the 3-fluoro derivative a rigid conformation of the Se—Se moiety with the fluorophenyl groups freely rotating about the C—Se bonds.

The diaryl dichalcogenides, Ar_2X_2 (X = S, Se, Te) contain the X—X group, whose atoms possess two lone electron pairs each in their valence shells and empty nd-orbitals. These characteristics together with the properties of the X—X bond determine its dynamic behavior, which influences the magnitude of the dipole moment.

The results of dipole moment measurements on a set of five diaryl dichalcogenides, $(RC_6H_4)_2X_2$ (R = H, $4\text{-}CH_3$, 4-F, 4-Br, 3-F) are summarized in Table 3. Comparison of the experimental values with moments calculated for various conformations at 25 and $45°$C suggest possible conformations for these molecules. The conformational assignments given in Table 3 are not always unambiguous. However, in general, the disulfides seem to be frozen in a rigid conformation at both temperatures investigated. The diselenides probably are rigid

at 25°C, but oscillate or freely rotate about the Se—Se bond at 45°C. The ditellurides are less rigid, with some of the compounds performing oscillatory motions even at 25°C. These oscillatory motions occur at rates comparable with the dipole moment measurement time scale.

These trends in the rigidity of the X—X group are explicable in terms of repulsion between the lone electron pairs on the X atoms. The barrier to oscillation or free rotation about the X—X bond decreases with increasing X—X bond distances. At larger interatomic distances the repulsion between lone electron pairs is reduced allowing oscillation or free rotation. The effect of the d-orbitals on the dynamic behavior of these molecules remains to be evaluated.

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