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DIPOLE MOMENTS AND ROTATIONAL ISOMERISM FOR ORGANIC THIO- AND SELENOCYANATES*

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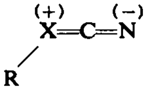
Abstract—From the dipole moments of aromatic thio- and selenocyanates the group moments of the triatomic groups are estimated as $\mu_{SCN} = 2{\cdot}99$ D and $\mu_{SeCN} = 3{\cdot}48$ D; a contribution from a polar structure



appears to be more important in the selenocompounds. No appreciable difference is found in the two series between the moments of aromatic and aliphatic compounds.

The study of the temperature and chain length effects on the moments of aliphatic dithio and diselenocyanates suggests the occurrence of a partial hindrance to free rotation at the bonds between the triatomic groups and the aliphatic chain in these compounds. Electrostatic interactions and steric effects influence remarkably the degree of free rotation, leading possibly for 1,2-dithiocyanatopropane to a greater stability of a *gauche* configuration.

THE relevant body of experimental work with physical methods on thio- and isothiocyanato compounds has given limited structural information as to the orientation of the triatomic group within the molecule. Particular X-ray structural data on inorganic complexes[1] point to an $\widehat{M\text{–}S\text{–}C}$ angle of about 120° for the thiocyanato complexes and an $\widehat{M\text{–}N\text{–}C}$ angle in the range 180° to 120° for the isothiocyanato compounds. The microwave data,[2] for organic derivatives, give for methylthiocyanate, although its spectrum is not of simple interpretation, a $\widehat{C\text{–}S\text{–}C}$ angle of 142° as compared with a 120° from dipole moments.[3] The microwave data, by the same authors, for the corresponding isothiocyanate give again a $\widehat{C\text{–}N\text{–}C}$ angle of 142°, while from dipole moments[4] there is evidence for this angle being around 180° both for methyl and phenylisothiocyanate. On the other hand, the IR spectrum of methylisothiocyanate has been interpreted on the basis of a C_{3v}[5] or C_s[6] symmetry. For isoselenocyanate derivatives there is no structural information. Dipole moment measurements for organic selenocyanates[7] point, as for the corresponding

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* This investigation was supported in part by a research grant from the Italian National Research Council.

[1] I. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.* 4590 (1961).
[2] C. I. Bead and B. P. Dailey, *J. Amer. Chem. Soc.* **71**, 929 (1949).
[3] E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.* 2825 (1932).
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[6] N. S. Ham and J. B. Willis, *Spectrochim. Acta* **16**, 279 (1960).
[7] M. T. Rogers and T. W. Campbell, *J. Amer. Chem. Soc.* **69**, 2039 (1947); **70**, 1029 (1948).

thiocyanates, to an angular structure for the selenium atom. X-ray structural data on inorganic selenides[8] give for $Se(SCN)_2$ an S–$\widehat{Se}$–S angle of 104°, for $Se(SeCN)_2$ an Se–$\widehat{Se}$–Se angle of 95°;[9] for organic selenides[7,10] a mean value of 106 ± 6° appears to be sufficiently reliable.

The present measurements give additional information on the dipole moments of mainly aliphatic organic thiocyanates and selenocyanates. Moreover, through the observation of the temperature dependence of the dipole moment of aliphatic dithio and diselenocyanates—for which dipole moment data were lacking—some evidence has been gained as to the possible occurrence of a partial hindrance to free rotation at the bonds between the triatomic groups and the remainder of the molecule in these compounds.

EXPERIMENTAL

The electric moments have been determined in benzene solution at temp 25 ± 0·05° and 45 ± 05°. For the dielectric constant measurements a Dekameter WTW mod. DKO3 was used, based on the resonance between two oscillating circuits and equipped with a condenser-cell with coaxial cylinders. The sensitivity in the dielectric constant measurements, $\Delta\varepsilon/\varepsilon$ was of the order of 10^{-4} at a 1·8 MHz frequency. The data of distortion polarization $P_E + P_A$ reported in the following were evaluated from the atomic and bond refractions of the molecules concerned; for the atomic refraction a value of 10·75 cc was chosen for selenium and 7·98 cc[11] for sulphur. The rather high electric moment of the compounds studied makes the error negligible. Whenever the index of refraction of the solutions was sufficiently different from that of pure solvent, the calculated molar refraction of solute was also in some cases tested by refractive index measurements referred to sodium D line: $R_{2D} = (R_{12} - R_1)X_2 + R_1$, where R_{12} and R_1 are the molar refractions of solution and solvent respectively, and X_2 the mole fraction of solute; for R_1 a value of 26·2 cc was taken for benzene. The agreement was good between the calculated and experimental values of molar refraction. The refraction indexes were measured on Zeiss and on Bausch-Lomb Abbe refractometers within ±0·0002 and ±0·00003 respectively. The specific volumes were measured on an Ostwald pycnometer of about 10 cc capacity with a precision of ±0·0002. The density of benzene was obtained from the expression $d = 0{\cdot}8737 + 10688{\cdot}10^{-7}$ (25–t)[12] and its dielectric constant from the expression $\varepsilon = 2{\cdot}325 - 0{\cdot}002\,t$ in the range 10–60°.[13] For measurements repeated the specific volumes have not been re-evaluated, considering that even large errors in β do not give appreciable errors in μ.[14] The dependence of dielectric constant and specific volume of the solutions from the mole fraction of solute appeared throughout to be linear within the limits of experimental error.

The total solute polarization P_2, extrapolated at infinite dilution, was evaluated by the method of Halverstadt and Kumler,[15] and the terms α, β, ε_1, v_1 by the mean square method. The electric moment was obtained from the expression $\mu = 0{\cdot}01281\sqrt{(P_2 - R_{2D})T}$ D. The reproducibility of the μ data was ±0·02 D at 25° and ±0·03 D at 45°.

The following compounds have been studied: phenyl, *p*-chlorophenyl, methyl, and ethylselenocyanate; methyl and ethylthiocyanate and phenylisothiocyanate;[16] 1,2-dithiocyanatoethane,

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[15] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).

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1,3-dithiocyanatopropane, 1,4-dithiocyanatobutane, 1,5-dithiocyanatopentane, 1,2-dithiocyanatopropane, 1,2-diselenocyanatoethane, 1,3-diselenocyanatopropane.[17] The compounds were prepared and purified according to the literature, except methyl and ethyl thiocyanate and phenyl isothiocyanate which were commercial BDH products purified by distillation. Benzene, used as solvent, was Erba RP. The moment of phenylisothiocyanate was measured for purposes of standardization, its value being of the same order of magnitude of those now studied.

RESULTS AND DISCUSSION

Table 1 gives in detail the present experimental data, while Table 2 summarizes the μ values, compared with literature data and the parameters for their evaluation.

Comparing the moments of phenyl and *p*-chlorphenylselenocyanate with the 1·59 D figure for chlorobenzene, the selenocyano grouping must be considered out-of-plane with respect to the ring: in fact the difference between the moments of phenylselenocyanate and chlorobenzene does not coincide with the experimental moment of *p*-chlorphenylselenocyanate, differing from it by 0·97 D which cannot be attributed to

TABLE 1. DIELECTRIC CONSTANT AND SPECIFIC VOLUME VS. WEIGHT FRACTION OF SOLUTE

W_2[a]	ε_{12}[b]	v_{12}[c]	W_2	ε_{12}	v_{12}
CH_3SeCN			CH_3SCN		
0·008100	2·3831	1·1401	0·00808	2·4372	1·1429
0·01097	2·4243	1·1382	0·00981	2·4755	1·1423
0·01532	2·4859	1·1359	0·01465	2·5745	1·1411
0·02013	2·5457	1·1333	0·02079	2·6948	1·1401
0·02519	2·6286	1·1305	0·02566	2·8040	1·1387
0·03006	2·6914	1·1274			
			C_2H_5SCN		
C_2H_5SeCN			0·00830	2·4236	1·1433
0·00844	2·3869	1·1406	0·01020	2·4697	1·1429
0·01134	2·4155	1·1396	0·01502	2·5481	1·1419
0·01996	2·5330	1·1355	0·02136	2·6761	1·1411
0·02683	2·6323	1·1322	0·02427	2·7300	1·1403
0·03014	2·6753	1·1303			
0·03478	2·7519	1·1284	C_6H_5NCS		
			0·01427	2·3712	1·1406
C_6H_5SeCN			0·02052	2·4270	1·1313
0·008285	2·3476	1·1407	0·03591	2·5310	1·1355
0·01179	2·3918	1·1389	0·04540	2·5970	1·1330
0·01819	2·4509	1·1358	0·06308	2·7268	1·1282
0·02580	2·5259	1·1321			
0·03204	2·5839	1·1289			
0·03614	2·6275	1·1271			
p-Cl-C_6H_4SeCN					
0·006941	2·3131	1·1398			
0·009213	2·3287	1·1392			
0·01461	2·3617	1·1363			
0·01830	2·3908	1·1330			
0·02407	2·4146	1·1313			

[a] Weight fraction of solute in benzene solution.

[b] Dielectric constant of solution.

[c] Specific volume of solution.

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[17] H. L. Buffs, *Liebig's Ann.* **100**, 229 (1856); J. Hagelberg, *Ber. Dtsch. Chem. Ges.* **23**, 1083 (1890); J. v. Braun and G. Lemke, *Ibid.* **55**, 3550 (1922); J. v. Braun and A Trümpler, *Ibid.* **43**, 550 (1910).

TABLE 1 (*Cont.*)

W_2	$\varepsilon_{12}(25°)$	$\varepsilon_{12}(45°)$	$v_{12}(25°)$	$v_{12}(45°)$
$(CH_2)_2(SCN)_2$				
0·002241		2·2519		1·1709
0·003476	2·2987		1·1429	
0·005441	2·3193		1·1423	
0·005604		2·2796		1·1683
0·007709	2·3369		1·1413	
0·008561		2·3035		1·1679
0·009358	2·3487		1·1409	
0·01303	2·3815		1·1394	
0·01511		2·3571		1·1665
$(CH_2)_3(SCN)_2$				
0·003466	2·3073	2·2689		
0·004160			1·1427	1·1716
0·006698	2·3434	2·3016		
0·007399			1·1413	1·1701
0·009921	2·3787	2·3343		
0·01042			1·1405	1·1690
0·01323	2·4146	2·3676		
0·01541	2·4395	2·3909		
$(CH_2)_4(SCN)_2$				
0·003082			1·1435	1·1724
0·003320	2·3092	2·2700		
0·006164	2·3399	2·2990		
0·006397			1·1499	1·1708
0·009359			1·1410	1·1700
0·01182	2·3993	2·3552		
0·01644			1·1385	1·1671
0·01875	2·4764	2·4286		
$(CH_2)_5(SCN)_2$				
0·003172	2·3092	2·2703	1·1434	1·1721
0·006187	2·3481	2·3059	1·1427	1·1710
0·009084	2·3800	2·3369	1·1416	1·1701
0·01226	2·4179	2·3713	1·1408	1·1690
0·01508	2·4528	2·4040	1·1396	1·1676
$CH_2SCNCH(CH_3)SCN$				
0·002651	2·2985	2·2600	1·1438	1·1724
0·004660	2·3318	2·2911	1·1432	1·1716
0·007670	2·3579	2·3159	1·1420	1·1702
0·01229	2·4055	2·3587		1·1681
0·01315	2·4338	2·3720	1·1399	
$(CH_2)_2(SeCN)_2$				
0·001265		2·2427		1·1719
0·001604		2·2444		1·1713
0·002842		2·2512		1·1706
0·003284		2·2533		1·1707
0·003766	2·2909		1·1421	
0·004230		2·2571		1·1692
0·005819	2·3017		1·1408	
0·007847	2·3119		1·1394	
0·008771	2·3165		1·1388	
$(CH_2)_3(SeCN)_2$				
0·003822	2·3047	2·2643	1·1422	1·1705
0·006874	2·3290	2·2868	1·1402	1·1686
0·01076	2·3575	2·3135	1·1376	1·1663
0·01468	2·3940	2·3473	1·1350	1·1634
0·01661	2·4080	2·3598	1·1339	1·1623

TABLE 2. DIPOLE MOMENTS AND PARAMETERS FOR THEIR EVALUATION

Temp 25°	CH_3SeCN	C_2H_5SeCN	C_6H_5SeCN	p-ClC_6H_4SeCN	CH_3SCN	C_2H_5SCN	C_6H_5NCS
α[a]	14·084	13·860	9·852	6·062	20·634	18·976	7·677
β	−0·597	−0·477	−0·497	−0·552	−0·221	−0·178	−0·258
ε_1	2·2689	2·2620	2·2707	2·2723	2·2712	2·2690	2·2700
v_1	1·1445	1·1451	1·1446	1·1440	1·1444	1·1447	1·1445
R_2	24·7	29·3	44	49	22	27	44·67
P_2	337·98	377·83	373·73	285	302·09	336·58	230·72
μ	3·91[b]	4·12	4·01	3·39 3·28[7]	3·70 3·59[8]	3·89 3·64[8]	3·01 3·00[4]

Temp 25°	$(CH_2)_2(SCN)_2$	$(CH_2)_3(SCN)_2$	$(CH_2)_4(SCN)_2$	$(CH_2)_5(SCN)_2$	$CH_3SCNCH(CH_3)SCN$	$(CH_2)_2(SeCN)_2$	$(CH_2)_3(SeCN)_2$
α[a]	8·624	10·952	10·810	11·944	11·759	5·113	8·095
β	−0·367	−0·44	−0·365	−0·325	−0·354	−0·663	−0·656
ε_1	2·2690	2·2705	2·2729	2·2722	2·2704	2·2714	2·2730
v_1	1·1442	1·1445	1·1444	1·1445	1·1466	1·1444	1·1447
R_2	42	47	51·6	56·2	47	47·2	52·2
P_2	230·44	359·42	390·15	463·97	387·5	263·09	420·42
μ	3·03[b]	3·90	4·06	4·46	4·07	3·24	4·24
Temp 45°							
α[a]	8·166	10·242	10·480	10·983	10·27	5·145	7·50
β	−0·3777	−0·437	−0·389	−0·293	−0·444	−0·793	−0·637
ε_1	2·233	2·233	2·233	2·237	2·235	2·235	2·235
v_1	1·1722	1·1734	1·1734	1·1731	1·1736	1·1728	1·1730
P_2	264·46	351·68	384	448·69	352·3	266·52	410
μ	3·40[b]	3·99	4·16	4·52	3·99	3·38	4·32
$\mu_{45°} - \mu_{25°}$	0·37	0·09	0·1	0·06	−0·08	0·14	0·08

[a] $\alpha = \frac{d\varepsilon_{12}}{dw_2}$; $\beta = \frac{dv_{12}}{dw_2}$; $\varepsilon_1 = \lim_{w_2 \to 0} \varepsilon_{12}$; $v_1 = \lim_{w_2 \to 0} v_{12}$; R_2 and P_2 = solute molar refraction and total polarization, unit cc.

[b] dipole moments, debye units, present measurements.

mesomeric effects, given that the moments of aliphatic and aromatic selenocyanates are almost coincident (See Table 2 and also later).

The direction of the group-moment $-C_{ar}SeCN$, as defined by its angle θ with the axis of benzene ring, may be calculated from the moments of the three molecules mentioned above. The vector diagram is given in Fig. 1. For the angle θ a value of 56°5' is obtained which is in good agreement with 53°30' obtained[7] by comparison of the moments of p-ClPh-SeCN and p-CH_3Ph-SeCN. For the thiocyanates, from the μ values given[18] for the phenylthio and p-chlorphenylthio derivatives a θ value of 53°15' is deduced and close to the value for the selenocyanates.

The mean value for the valence angle at the selenium atom and the dipole moment data for diphenyl (1·38 D) and dimethylselenide (1·32 D)[18] do not give an appreciable difference between the bond moments C_{ar}–Se and C_{al}–Se, with a mean value of

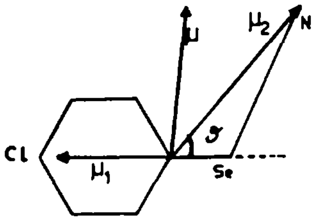
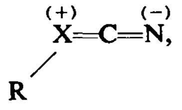


FIG. 1 Vector diagram for p-chlorphenylselenocyanate. μ_1, μ_2 and μ are respectively the moments of Cl–Ph, Ph–SeCN and p-ClPh–SeCN.

$0{\cdot}7_5 \pm 0{\cdot}1$ D. Also for the thiocyanates, using a mean value of 110 ± 10°[19] for the sulphur valence angle and the moments of diphenyl (1·50 D)[18] and dimethylsulphide (1·50 D),[19] a mean value of 0·9 ± 0·1 D is obtained for the C_{ar}–S and C_{al}–S bond moments.

The group-moments μ_{SeCN} and μ_{SCN} of the triatomic groups are calculated from the Eq. (Fig. 1): $\mu^2_{XCN} = \mu^2_{C-X} + \mu_2{}^2 - 2\mu_{C-X}\mu_2 \cos\theta$ where μ_{XCN} = moment of triatomic group, μ_2 = moment of phenylseleno (or thio) cyanate (i.e. group-moment $-C_{ar}XCN$), μ_{C-X} = bond moment C_{ar}–Se (or C_{ar}–S). The group-moments μ_{SeCN} = 3·48 D and μ_{SCN} = 2·99 D were obtained, assuming the CH bond moment 0·4 D. The moments of the –SeCN and –SCN groupings are higher than those calculated by summation of the single bond moments C≡N (3·5 D[20]), C–Se and C–S, the calculated figures being $2{\cdot}7_5$ and 2·6 D respectively. Such a difference may be attributed to a contribution from the polar structure



$$R{-}\overset{(+)}{X}{=}C{=}\overset{(-)}{N},$$

larger in the selenocyanates than in the thiocyanates, the contribution being however small in both cases. The difference between the –SeCN and –SCN group moments,

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[18] E. Bergmann, L. Engel and S. Sandor, *Z. Phys. Chem.* **B10**, 397 (1930); L. Chierici, H. Lumbroso amd R. Passerini, *Bull. Soc. Chim. Fr.* 686 (1955).

[19] L. Pierce and M. Hayashi, *J. Chem. Phys.* **35**, 479 (1961); L. E. Sutton and R. G. A. New, *J. Chem. Soc.* 652 (1933); M. Rolla and M. Sanesi, *Ric. Sci.* **31** (IIA), 43 (1961); **32** (IIA), 29 (1962).

[20] L. P. Smyth, *J. Amer. Chem. Soc.* **60**, 183 (1938).

about 0·5 D, might possibly also include different mesomeric effects in the two classes of compounds; these effects are difficult to estimate, in view of the differences in the moments of the aliphatic and aromatic compounds which are within the limits of experimental error (see Table 2 and the value of $\mu = 3{\cdot}59$ D for phenylthiocyanate[18]).

The high value for the triatomic group moment in the aliphatic derivatives and the bond distances and angles derived by X-ray structural data,[9] suggest that a partial hindrance to free rotation of such a grouping in these molecules cannot be disregarded. Assuming indeed that the interacting dipoles be localized on the CN bond and on the CH bond neighbouring to it, in e.g. CH_3SeCN a mean distance between these two bonds of about 3 Å is obtained. This is somewhat smaller than the minimum distance estimated from Meyer's treatment[21] for the case of free rotation on the basis

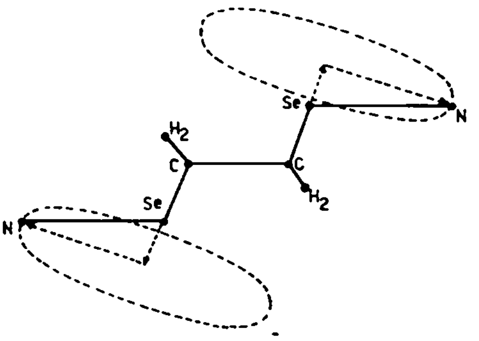

FIG. 2 Vector diagram for 1,2-dithio (or diseleno) cyanatoethane.

of a mutual interaction energy $\mu_1\mu_2/R^3$ of the order of kT/10. This is reasonably supported by the present observations (Tables 1 and 2) of the temperature effect on the dipole moments of aliphatic dithio and diselenocyanates structurally chosen so as to have their total moment depending on their configuration.

Indications as to possible conformations for these molecules come from the IR and Raman spectral data of 1,2-dithiocyanatoethane by Mizushima *et al.*:[22] the molecule is present in the *trans* form in the solid state, and in the *trans* and *gauche* forms in chloroform solution, this last form being also observed in the co-ordination compounds with Pt.

In order to estimate the barrier to free rotation in the simplest case of an aliphatic chain with two carbon atoms, one may admit that the rotation around an axis parallel to the C–X bonds (where X = Se or S) be partially hindered, while that around the C–C axis being totally hindered; this on account of the high value of the moment of the triatomic groups and of their dimensions. In such a situation the mean moment for free rotation, considering as most probable the *trans* configuration to the C–C bond (Fig. 2) may be calculated from the expression: $\bar{\mu} = \sqrt{2}\mu_{XCN}\text{sen}\,(180^\circ - \alpha)$, where α is the selenium (or sulphur) valence angle, μ_{XCN} is the triatomic group moment estimated from the moment of the methyl derivative, the figure having been corrected approximately for the mutual inductive effect of the two groups in the

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[21] J. W. Meyer, *Z. Phys. Chem.* **75**, 138 (1928).

[22] J. W. Quagliano and S. Mizushima, *J. Amer. Chem. Soc.* **75**, 6084 (1953); S. Mizushima *et al.*, *J. Chem. Phys.* **59**, 253 (1955).

disubstituted molecule; the corrected values are $\mu_{\mathrm{SeCN}} = 3{\cdot}3$ D and $\mu_{\mathrm{SCN}} = 3{\cdot}1$ D. The amount of this correction is estimated to be about 0·2 D, such being the difference (Table 2) between the dipole moments of ethyl and methyl derivative both for the thio and the selenocyanates. The values $\bar{\mu} = 4{\cdot}47$ D for the seleno and $\bar{\mu} = 4{\cdot}1$ D for the thio compound were obtained. Also in the case of free rotation in the C–C axis one should have (disregarding the component of the group moment μ_{XCN} perpendicular to the C–X axis):

$$\bar{\mu}_{\mathrm{tot}} = \bar{\mu}(\mathrm{C{-}X}) + \bar{\mu}(\mathrm{C{-}C}) = \sqrt{2}\,\mu_{\mathrm{XCN}}\mathrm{sen}(180^\circ-\alpha) + \sqrt{2}\,[\mu_{\mathrm{C-X}}\mathrm{sen}(180^\circ-110^\circ) + \mu_{\mathrm{XCN}}\cos(180^\circ-\alpha)\mathrm{sen}(180^\circ-110^\circ)]$$

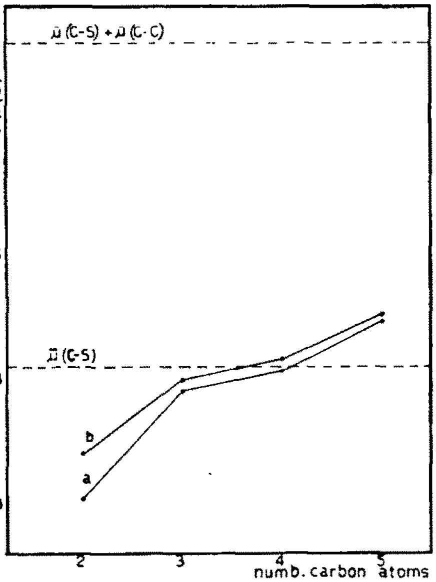
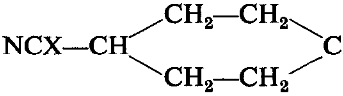


FIG. 3 Plot of dipole moment of aliphatic dithiocyanates vs. chain length. Curve *a* for 25°, curve *b* for 45°.

The figures obtained are $\bar{\mu}_{\mathrm{tot}} = 6{\cdot}7$ D for the seleno and 6·3 D for the thio compound. Taking into account the contribution of the perpendicular component of μ_{XCN}, the above values were raised to 8·8 and 8·04 D.

The difference between such calculated values and the experimental ones may be considered as a measure of the mutual interactions of any kind, possibly active between the two polar groups and among these and the hydrogen atoms of the aliphatic chain. The experimental electric moments (Table 2) are in fact always lower than those calculated on the basis of total free rotation, and in addition they are temperature dependent. Both the interactions and the temperature effect decrease on increasing the aliphatic chain length; the residual temperature increment of 0·06 D observed for the moment of 1,5-dithiocyanatopentane is appreciably higher than the limit of reproducibility of the measurements, but anywhere it should be used with some caution in the absence of information as to the solvent effect on the dipole moments and as to its variation with temperature. Moreover (Fig. 3), for 1,5-dithiocyanatopentane the moment is significantly higher than the mean moment for free rotation to the C–S axis. The situation, therefore, apparently indicates a tendency to a partial free rotation also present in the aliphatic chain.

In this connection, useful information should be obtained from a knowledge of the dipole moment and its temperature dependence for aliphatic ring compounds like  having only the two C–X axis residual for internal rotation. Campbell and Rogers[7] have obtained 4·02 D at 25° for the electric moment of *p*-selenocyano-phenylthiocyanate, estimating a mean moment for free rotation of 4·23 D. This small difference might be interpreted as evidence of an almost free rotation of the two groupings around the ring axis, or as being due to a significant stabilization of a polar form probably active in this molecule.

From the plot of the experimental electric moments vs. the number of carbon atoms of the aliphatic chain (Fig. 3), it is seen that the variation of the electric moment with the number of carbon atoms is greater on going from a compound with an even number of carbon atoms to one with an odd number. This alternation in the value of the electric moment is consistent with an all-*trans* equilibrium configuration of the normal saturated aliphatic chain, as seen by X-ray analysis on n-alkanes[23] in the solid state. Therefore in the n-alkanes substituted at the therminal carbon atoms, the substituent groups are more in opposition for an even than for an odd number of carbon atoms. The occurrence of such an alternation is on the other hand clear evidence of the rigidity of the aliphatic chain.

As to the nature of the potential barrier hindering the free rotation, it seems that both electrostatic interactions and steric hindrance contribute remarkably in the present molecules. The first effect is evident from the significant increase of the electric moment on lengthening the aliphatic chain, the second by the remarkable influence of hydrogen substitution by a methyl group in 1,2-dithiocyanatoethane. In fact the moment at 25° of 1,2-dithiocyanatopropane (4·07 D) is almost 1 D greater than that of 1,2-dithiocyanatoethane (3·03 D). It may be admitted that in benzene solution this molecule exists in the *trans* and *gauche* configurations, the latter predominating owing to steric repulsion of the methyl on the thiocyano group. The small and apparently negative temperature effect in this very case seems to indicate that the steric effect of the methyl hinders the rotation around the neighbouring C–X bond. Also in the case of propylene dichloride[24] the *gauche* form appears to be more stable than the *trans*. The seleno as compared with the thio compounds are more sensitive to the chain than to the temperature effect, which is in agreement with their higher moment and with the greater dimensions of the selenocyano group.

[23] W. J. Taylor, *J. Chem. Phys.* **16**, 257 (1948).

[24] Y. Morino *et al., J. Chem. Phys.* **19**, 791 (1951); **28**, 175 (1958).