

DIPOLE MOMENTS AND CONFORMATION OF DIALKYLDITHIOPHOSPHINIC ACIDS AND THEIR DERIVATIVES

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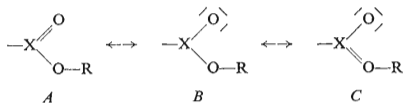
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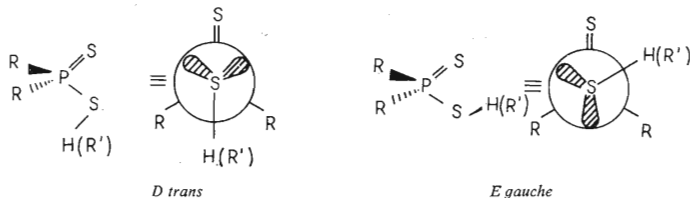
Dipole moments of twenty dialkyldithiophosphinic acid derivatives, including free acids *I–III*, esters *IV–XI*, bisdialkyldithiophosphinyl sulfides *XII*, disulfides *XIII–XVI*, trisulfides *XVII*, *XVIII*, and tetraalkyldiphosphane disulfides *XIX*, *XX*, have been measured in benzene solution. The graphical method was employed to determine their conformation. With the acids and esters the *gauche* conformation prevails in agreement with the concept postulating the maximum number of *gauche* interactions between polar bonds. The *gauche* conformation complies also with the moments of polysulfides; the two moieties of the molecule take often opposite positions (conformation *gg'*), or, at a still longer distance, they behave almost independently, so that the resulting molecular symmetry is lowered. The tetraalkyldiphosphane disulfides are exceptional, since their nearly *trans* conformation is at variance with the mentioned concept.

As a part of the broader program concerned with conformation on functional groups, we have studied^{1–4} derivatives of the general formula *A*. When X represents a IV Group element, the configuration of it is planar and the whole molecule is stable in the planar *trans* conformation due to mesomerism expressed by the formula *C* (carboxylic esters^{2,5}). The situation is not changed by replacing oxygen atoms by sulfur^{1,2} or selenium³. When X is a VI Group element, it bears one lone electron pair and possesses a pyramidal configuration, the conformation of the X—O bond being *gauche* (sulfinic esters⁴).



When we now consider replacing of X by a V Group element (phosphorus), an additional alkyl group must enter the molecule, the configuration of P being tetrahedral. The whole molecule resembles that of sulfinic esters, bearing the second alkyl

group instead of the lone electron pair. From the compounds of this type, the dialkyl-dithiophosphinic acids (*D*, *E*) and their derivatives have been chosen for this study.



Many important studies have been recently devoted to conformation of phosphorus compounds⁶ in solution or in the gas phase, using dipole moments⁷⁻¹², Kerr constant¹³, electron diffraction^{14,15}, IR^{11,12,16-19} and NMR²⁰⁻²³ spectroscopy. In our opinion there is a principal difficulty in almost all these studies in that they deal with complex molecules with several rotational axes before the conformation of simpler derivatives is known. It is why the present study starts from molecules with only one axis of rotation. Sulfur containing compounds are of particular interest since only one of papers quoted deals with conformation on the P—S bond¹⁶. When the conformation of simple derivatives is once established, that of more complex compounds *XII—XVIII* (Table I) with two rotating groups may be approached. The inherent problems are whether the conformation of simple derivatives persists, and whether the two rotating groups behave independently or symmetrically.

Our experimental approach was dipole moment measurement in solution as in our previous studies^{1-4,24}. When possible we made use of the previously suggested method²⁴ of graphical comparison of an aromatic compound with its *para* derivative (Figs 1–3). For this reason several aromatic derivatives were included in our set of compounds (Table I).

EXPERIMENTAL AND RESULTS

Materials: Most compounds were prepared according to literature data, the pertinent references being given in Table I. The remaining ones were obtained by applying known procedures; no attempt was made to find optimum reaction conditions. The samples for physical measurements were purified by crystallization and/or vacuum distillation, and their purity checked by v.p.c. or by determining physical constants. All the values of m.p., b.p., and n_D^{20} agreed well with literature data²⁵⁻³⁷. The methyl esters *IV*, *V*, and *VII* were prepared by esterification of the parent acids *I*, *II* and *III*, respectively, with diazomethane, similarly as described for the compound²⁸ *VI*; yields were 60–65% of the purified material.

Methyl dimethyldithiophosphinate (IV), m.p. 39–40°C. For $C_3H_9PS_2$ (140.2) calculated: 25.70% C, 6.47% H, 22.09% P; found: 26.39% C, 5.99% H, 21.68% P.

Methyl diethyldithiophosphinate (V), b.p. 65°C/0.3 Torr, $n_D^{20} = 1.5617$. For $C_5H_{13}PS_2$ (168.3) calculated: 35.69% C, 7.79% H, 18.41% P; found: 35.79% C, 7.77% H, 18.51% P.

Methyl bis(4-chlorophenyl)dithiophosphate (VII), m.p. 80–81°C (ligroine). For $C_{13}H_{11}Cl_2PS_2$ (333.2) calculated: 46.85% C, 3.33% H, 9.30% P; found: 46.80% C, 3.74% H, 9.19% P.

TABLE I
Polarization Data of Dialkyldithiophosphinic Acids and Their Derivatives (Benzene, 25°C)

Compound	R	R'	M.p. °C	Ref.	R_D^{20} ^a cm ³	∞P_2 cm ³	$\mu(5\%)^b$ D	$\mu(15\%)^b$ D	μ Calc. ^c D
A) dialkyldithiophosphinic acids $R_2P(=S)SH$									
I	CH ₃		54	25	36.2	352.4	3.92	3.90	3.67
II	C ₂ H ₅		68/2.5 ^d	26	45.45 ^e	357.3	3.89	3.86	3.67
III	4-ClC ₆ H ₄		83	27	86.2	239.5	2.70	2.62	2.85
B) dialkyldithiophosphinic esters $R_2P(=S)SR'$									
IV	CH ₃	CH ₃	39	<i>f</i>	41.1	285.6	3.44	3.41	3.63
V	C ₂ H ₅	CH ₃	65/0.3 ^d	<i>f</i>	50.44 ^g	297.6	3.46	3.42	3.63
VI	C ₆ H ₅	CH ₃	83	28	81.2	422.9	4.06	4.01	3.82
VII	4-ClC ₆ H ₄	CH ₃	80	<i>f</i>	91.1	273.3	2.96	2.89	2.91
VIII	CH ₃	C ₆ H ₅	68	29	61.5	400.9	4.05	4.03	3.64
IX	C ₂ H ₅	C ₆ H ₅	126/0.1 ^d	30	70.7	398.2	3.98	3.94	3.64
X	CH ₃	4-ClC ₆ H ₄	105	31	66.4	379.2	3.89	3.85	4.34
XI	C ₂ H ₅	4-ClC ₆ H ₄	61	29	75.7	394.1	3.92	3.87	4.34
C) bis-dialkyldithiophosphinyl sulfides and polysulfides $R_2P(=S)S_nP(=S)R_2$									
XII	CH ₃	n = 1	91	32	63.2	424.4	4.19	4.15	<i>h</i>
XIII	CH ₃	n = 2	56	32	71.2	502.6	4.57	4.54	<i>h</i>
XIV	C ₂ H ₅	n = 2	56	33	89.8	581.3	4.88	4.83	<i>h</i>
XV	C ₆ H ₅	n = 2	147	34	151.5	529.5	4.26	4.18	<i>h</i>
XVI	4-ClC ₆ H ₄	n = 2	124	<i>f</i>	171.2	303.2	2.46	2.28	<i>h</i>
XVII	CH ₃	n = 3	128	35	79.2	463.3	4.31	4.26	<i>h</i>
XVIII	C ₂ H ₅	n = 3	107	35	97.8	510.1	4.46	4.41	<i>h</i>
D) tetraalkyldiphosphane disulfides $R_2P(=S)-P(=S)R_2$									
XIX	CH ₃		227	36	55.4	128.2	1.85	1.78	—
XX	C ₂ H ₅		76	37	74.0	122.4	1.48 ^j	1.35	—

^a Calculated as given in the experimental section, except when otherwise noted; ^b calculated with a correction of 5% or 15% of the R_D value, respectively, for the atomic polarization; ^c calculated for the *gauche* conformation; ^d boiling point; ^e determined experimentally, n_D^{20} 1.5795, d^{20} 1.1269; ^f see Experimental; ^g determined experimentally n_D^{20} 1.5617, d^{20} 1.0814; ^h see Table II; ^j literature gives 1.63 D in benzene³⁸ and 1.57 in tetrachloromethane¹⁹.

Bis-di(4-chlorophenyl)dithiophosphinyl disulfide (XVI) was prepared by oxidation of the corresponding dithiophosphinic acid *III* with iodine as described for the compound³⁴ *XV*; yield 65% of the pure material, m.p. 124–125°C (ligroine). For $C_{24}H_{16}Cl_4P_2S_4$ (636.4) calculated: 45.29% C, 2.54% H, 9.73% P; found: 45.06% C, 2.20% H, 10.00% P.

Physical measurements: The same method was used as in previous papers^{1,4,24}. Molar refractions of the compounds *II* and *V* were determined experimentally and the increment 24.05 cm³ for the P(S)S group deduced thereof, using Vogel's atomic increments³⁹. With this value molar refractions of the remaining compounds were calculated. The bond increments of Gillis⁴⁰ would yield by recalculation the value 22.9 cm³; the discrepancy represents the exaltation due to mesomerism $A \leftrightarrow C$ and is of reasonable magnitude. With compounds *VIII–XI* an additional increment of 0.7 cm³ was introduced to account for the conjugation $S-C_6H_5$, with *III*, *VI*, *VII*, *XV*, and *XVI*, another of 0.4 cm³ for each conjugation $P-C_6H_5$, and finally with all the derivatives *XII–XX* 0.4 cm³ for the conjugation between the two atoms of phosphorus, or along the polysulfide chain. Since the dipole moments are large, all these rather arbitrary corrections do not affect them markedly. The experimental results are listed in Table I. They can be considered to be internally consistent, particularly the values for the corresponding methyl and ethyl derivatives are close as expected. The agreement with literature³⁸ in the case of compound *XX* is also satisfactory. Our moments of *IV* and *V* compare favourably to that of the related O-propyl dipropylthiophosphate⁴¹ (3.71 D).

Calculations of theoretical dipole moments: All the calculations were carried out graphically with an accuracy of about ± 0.03 D. The formal bond moments of the bonds C–P (0.8 D), S–P (0.5 D), P=S (2.9 D), and H–S (0.65 D) are dealt with in the Discussion, the remaining ones were the same as in our previous papers⁴. The bond angles employed were: $\angle VP-S-C = \angle VP-S-S = 105^\circ$, $\angle VP-S-H = 100^\circ$, angles at phosphorus essentially tetrahedral $\angle VR-P-R = 105^\circ$ and $\angle VS=P-S = 108^\circ$, finally the dihedral angles P–S–S–P or P–S–S–S 91° (cf.^{7,42–46}). The calculated dipole moments are plotted in Figs 1–4 or listed in Tables I and II.

TABLE II

Comparison of Computed and Experimental Dipole Moments of Compounds *XII–XVIII*

The symmetry class given in brackets as far as there is any symmetry at all; the most probable actual conformations are printed in boldfaced types.

Conformation	<i>XII</i>	<i>XIII</i>	<i>XIV</i>	<i>XV</i>	<i>XVI</i>	<i>XVII</i>	<i>XVIII</i>
<i>gg</i>	7.71 (<i>C_s</i>)	6.41 (<i>C₂</i>)	6.58 (<i>C₂</i>)	5.77 (<i>C₂</i>)	3.17 (<i>C₂</i>)	4.53 (<i>C₂</i>)	4.53 (<i>C₂</i>)
<i>gg'</i>	3.95 (<i>C₂</i>)	5.02	5.32	4.07	4.07 (<i>C₂</i>)	7.32 (<i>C₂</i>)	7.32 (<i>C₂</i>)
<i>g'g'</i>	—	2.97 (<i>C₂</i>)	3.45 (<i>C₂</i>)	0.39 (<i>C₂</i>)	0.39 (<i>C₂</i>)	7.66	3.05
<i>gt</i>	4.09	6.89	7.23	5.39	7.66	3.05	4.66 (<i>C₂</i>)
<i>g't</i>	—	6.14	6.67	3.91	3.05	4.66 (<i>C₂</i>)	4.41
<i>tt</i>	5.14 (<i>C_{2v}</i>)	0.39 (<i>C₂</i>)	0.73 (<i>C₂</i>)	1.31 (<i>C₂</i>)	4.66 (<i>C₂</i>)	4.41	4.41
Experiment	4.15	4.45	4.83	4.18	2.28	4.26	4.41

DISCUSSION

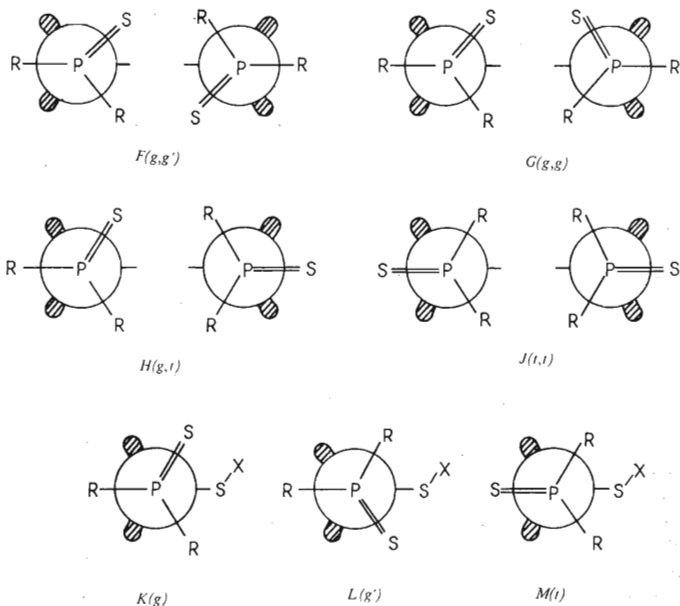
The first step in determining the conformation from dipole moments consists in choosing suitable bond moments, which — even when not completely general — would be applicable within at least the given class of compounds. The task may be particularly difficult for the bonds to phosphorus since the literature data^{7-10,12,41,47-49} are scarce and differ considerably. The reasons for this discrepancy are mainly twofold: Sometimes the determination of bond moments was attempted on molecules with a rotational freedom and unknown conformation; the variable results were either attributed to non-constant bond moments^{9,41,47}, or only group moments were obtained^{7,9,13}. The second reason is connected with the presence of a lone electron pair on trivalent phosphorus, but this difficulty is merely of formal nature.

When the C—P bond moment is determined on the basis of phosphines, neglecting the lone pair moment, one third of the latter, projected into the C—P bond axis, enters into the values obtained^{8,41,48,49}. The same happens with the P—O and P—S bond moments^{7,11,47}. On the other hand the P=O and P=S bond moments, calculated from the difference of dipole moments of phosphine oxides or sulfides and phosphines themselves, represent in fact only the difference between the P=X and lone pair moments^{7,41,47-49}. Nevertheless, correct final values are obtained by vector addition of these formal bond moments for any compound because the corrections cancel. The only shortcoming are the surprising values, and even directions, of the formal moments^{7,11,47}. These lack any physical meaning, cannot be compared with other bond moments, neither estimated on the basis of the electronegativity scale, *etc.* This shortcoming could be removed only when giving the lone pair moment a theoretically computed value; however, no dependable one seems to be available.

For these reasons we decided to use in this work formal bond moments including the components of the lone pair moment. Our values may still somewhat differ from those quoted in the literature as they were related to the moments $H_{ar}-C = 0.3$ D and $H_{ar}-C = 0$ according to our papers¹⁻⁴. Even the choice of these fundamental moments is rather a convention and does not affect the final computed values. Our bond moment $C^{(+)}-P^{(-)} = 0.8$ D is intermediate between those of Cumper⁵⁰, Ishmaeva⁸, and Granzhan⁴⁹. An additional moment comes into play in phenyl phosphines due to a $p\pi \rightarrow d\pi$ conjugation, which makes the P—Ph moment in phosphine oxides effectively equal to the P—R moment⁸. In diaryldithiophosphinic acid derivatives the functional group is a still more powerful acceptor. Hence we gave the mesomeric moment $Ph^{(+)}-P^{(-)}$ the value of 0.6 D, which is substantiated by the differences between the aliphatic and aromatic derivatives in Table I. Our moment $P^{(+)}=S^{(-)} = 2.9$ D agrees with the mean of other estimates^{41,47-49}, while our value of $S^{(+)}-P^{(-)} = 0.5$ D is close to that of ref.¹¹; in the latter value the contribution from the lone electron pair is particularly apparent. The moment $H^{(+)}-S^{(-)} = 0.65$ D is that of Cumper⁵⁰. No mesomeric moments has been introduced to express the $p \rightarrow \pi$ conjugation of the sulfur atom with the benzene nucleus in compounds VIII—XI. The existence of such a conjugation depends

on the position of the aromatic ring, which is not known, but according to the analogy with carboxylic phenyl esters⁵¹ hardly coplanar with the S—P bond.

With these bond moments, and with bond angles given in the experimental section, theoretical dipole moments were computed for various conformations of the dialkyl-dithiophosphinic esters *IV–XI*. The pair *VI*, *VII* is most suitable for determining conformation according to the previously suggested graphical method²⁴. In Fig. 1 values of μ^2 are plotted on the *x*-axis for the unsubstituted compound *VI* and on the *y*-axis for its 4,4'-dichloro derivative *VII*. Each conformation is represented by a point. When the SCH_3 group rotates around the P—S bond, the point on the graph moves along the tie line connecting the two extreme positions²⁴. On the other hand a point on this tie line may be also interpreted as a mixture of the two extreme forms in a ratio corresponding to the pertinent distances. The two possibilities cannot be distinguished on the basis of dipole moments. The basic assumption of the whole method is the same conformation of the substituted and unsubstituted compounds. We believe that it is satisfied by *para* substitution²⁴.



Comparison with the experimental point (hatched in Fig. 1) reveals that the prevailing conformation is *gauche* (*E*). The accuracy of the whole procedure, expressed approximately by the size of the experimental point, does not allow to exclude an admixture of the *trans* form (*D*), say, up to 15%. Alternatively a somewhat larger dihedral angle in *E*, about 75° instead of 60° , may be considered. The remaining couples of compounds (*VIII* and *X*, *IX* and *XI*) yield less definite results when treated in the same way. According to Fig. 2 the *trans* form might be present by some 30%, or, the *gauche* form could be distorted up to the dihedral angle of 90° instead of 60° . We give these results less weight, because even within the class of carboxylic esters and similar compounds, substitution in the alkyl moiety was less successful³.

Among the free dialkyldithiophosphinic acids there is no pair consisting of one substituted and one unsubstituted compound. A comparison is possible, however, with dialkyl derivatives *I* and *II* on the *x*-axis and the bis(4-chlorophenyl) derivative *III* on the *y*-axis (Fig. 3). The agreement with experiment is only moderate, nevertheless the *gauche* conformation is again most probable. We finally calculated the expected dipole moments for the *gauche* conformation of all the compounds *I*–*XI* (last

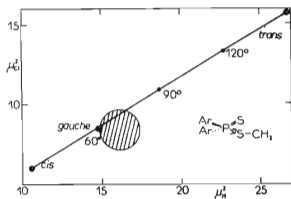


FIG. 1

Comparison of Experimental and Calculated Dipole Moments of Methyl Diphenyldithiophosphate

Values of μ^2 are plotted on the *x*-axis for the parent compound *VI*, on the *y*-axis for its 4,4'-dichloro derivative *VII*; the experimental point is hatched.

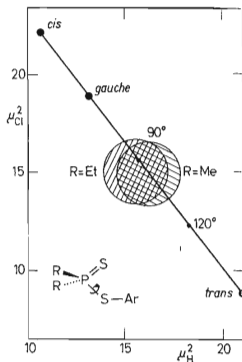


FIG. 2

Comparison of Experimental and Calculated Dipole Moments of Phenyl Dialkyldithiophosphinates *VIII*, *IX* (*x*-axis) and Their 4-Chloro derivatives *X*, *XI* (*y*-axis)

column of Table I). The agreement with experiment is reasonable, the average deviation being 0.26 D. In conclusion our experimental results can be explained by the *gauche* form alone, they do not exclude the presence of the *trans* form in a small amount, but they do not give any support in favour of the *cis* form¹².

The results of this paper agree with the *gauche* conformations of methyl methylphenylphosphinate according to the ¹H NMR spectra²², O-methyl diphenylthiophosphinate in the crystalline state^{4,2}, methyl methylphenylphosphinate and ethyl diphenylphosphinate according our unpublished dipole moment measurements, and with analogous conformation (denoted* "up") prevailing in trialkyl phosphates^{20,21}. On the other hand the ³¹P NMR spectra of menthyl methylphosphinate and of O-menthyl methylthiophosphinate were interpreted in favour of the *trans* ("down") conformation²³. In a cyclic trithiophosphonate the *gauche* form prevails¹¹ in the ratio 2:1. Unique is the claim¹² that the eclipsed *cis* conformation predominates in the case of methyl dimethylphosphinate, which is supported by not very dependable theoretical calculations¹² (small differences of large quantities). In dichlorothiophosphinates two unidentified forms were detected¹⁷. At any rate the situation is somewhat different with our compounds, since the steric hindrance in the *cis* form would be stronger and the stabilizing conjugation weaker than in the oxygen analogues. We do not see any reason for considering the presence of the *cis* form in dialkyldithiophosphinates, although small amounts cannot be detected by our approach.

The *gauche* conformation is certainly an important feature in phosphorus chemistry. Its explanation in terms of steric factors only^{20,23} may be not sufficient, since there are no changes with the size of the substituent. On the other hand there is a full

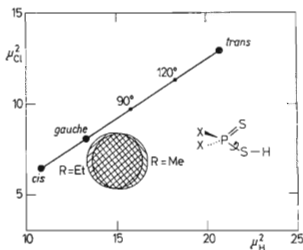


FIG. 3

Comparison of Experimental and Calculated Dipole Moments of Dialkyldithiophosphinic Acids *I*, *II* (*x*-axis) and Bis(4-chlorophenyl)-dithiophosphinic Acid *III* (*y*-axis)

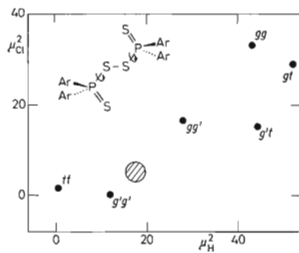


FIG. 4

Comparison of Experimental and Calculated Dipole Moments of Bis-diphenyldithiophosphinic Disulfide *XV* (*x*-axis) and Its 4,4'-Dichloro Derivative *XVI* (*y*-axis)

* The denotation "up" (= *gauche*) and "down" (= *trans*), introduced for trialkyl phosphates²⁰, is in our opinion not very convenient, even less is its extension to alkylphosphinates and alkylthiophosphinates²³.

agreement with the new theoretical approach, taking into account various types of repulsive and attractive forces⁵². Although small differences between large quantities are again involved in the calculations, the final results are in accord with many experimental data. One can state in a simplified manner that conformations with maximum number of *gauche* interactions between polar bonds and/or lone electron pairs are most stable. There is one exception, that the form with a polar bond between two electron pairs is destabilized (the so-called Edwards–Lemieux effect). This can be understood so, that the oriented lone pair is an artificial concept and hence the bond-bond interaction is more important than the bond-pair interaction⁵². In terms of this theory we may state that the stereochemistry of dialkyldithiophosphinic acids and related compounds is dominated by the *gauche* interaction of the P=S and S—R bonds.

Starting from the assumption that the *gauche* conformation (*E*) prevails in simple derivatives of dialkyldithiophosphinic acids, we may attempt to estimate the conformation of more complex ones (*XII–XVIII*) with two or more rotational axes. We shall always suppose that the *gauche* arrangement in each moiety is most probable.

The conformation of bis-dimethyldithiophosphinyl sulfide (*XII*) represents a particular case of a broader problem — conformation of two equivalent single bonds derived from one central atom^{53,54}. *E.g.* in bisbenzenesulfonyl sulfide each moiety preserves the conformation of simple derivatives⁵⁵ and in carboxylic acid anhydrides it is nearly so⁵⁴; in both cases the whole molecule has a C_2 symmetry. However, less symmetrical forms are also encountered in other cases⁵³. When computing the expected dipole moments of various forms of *XII*, we made use of the same bond moments and angles as hitherto, from which we deduced the moment of the whole group $R_2P(S)S$ (*i.e.* including the P—S single bond) to be 3.88 D at the angle of 79°C to the rotational axis (taken from S to P). The computed and experimental moments are compared in Table II. The form denoted *gg'* (see *F*, two Newman projections viewed along each P—S bond) seems to be most probable, although certain amounts of the forms *gg(G)* or even *gt(H)* cannot be excluded. Inspection of the molecular models shows that the *tt* form (*J*) with $R = CH_3$ would be strongly sterically hindered, and from the two *gauche* forms, the *gg'(F)* is preferred.

When considering possible conformations of bis-dialkyldithiophosphinyl disulfides *XIII–XVI*, we supposed *a priori* that the chain of inner atoms P—S—S—P takes the same non-planar form as in all disulfides and analogous compounds. Our task was thus reduced to determining the conformation on the two S—P bonds. There are more possibilities as in the preceding paragraph since two *gauche* positions are to be distinguished; one with the P=S bond directed toward the second moiety is denoted *g* (formula *K* with $X = P$), the other being *g'* (formula *L* with $X = P$). In addition, the *trans* form *M* ($X = P$) may be also considered. Various conformations of the molecule arise from all possible combinations of the three positions in the two moieties.

The computed dipole moments for the compounds *XV* and *XVI* are compared with the experimental ones in Fig. 4. The forms $g'g'$ and gg' seem to be most probable. However, a small admixture of the form gg must also be admitted. According to the molecular models all the forms are sterically hindered to a certain extent; those with one g conformation less than the others. The tt form is practically impossible in the case of phenyl derivatives. Hence the gg form is probably destabilized by the electrostatic repulsion between the two negatively charged sulfur atoms. The remaining two *gauche* conformations gg' and $g'g'$ may be populated in comparable amounts. The same reasoning applies to alkyl derivatives *XIII* and *XIV* (Table II), except the steric hindrance is less pronounced. More definite conclusions are not possible. The X-ray study of bis(O,O-diisopropylthiophosphoryl) disulfide cannot help in understanding the problem since the polysulfide chain has the quite unusual planar conformation⁴³; the intermolecular forces may be very strong in this particular crystal structure.

With the trisulfides *XVII* and *XVIII* we followed the same approach as with disulfides, the P—S—S—P chain being assumed in the zig-zag form. The three possible position *K*, *L*, and *M* ($X = S$) of the terminal groups were considered in all possible combinations, and the expected dipole moments computed. Table II reveals that the form gg' alone can account for the experimental findings but a statistical mixture of the three forms gg , gg' , and $g'g'$ in the ratio 1 : 2 : 1 is also possible. This latter possibility would imply that the two relatively remote groups do not influence each other. According to molecular models there is much less steric hindrance than in the case of disulfides; all possible forms are practically free of steric strain. An apparently analogical compound, bis(dimethoxydithiophosphinyl) telluride exists in the crystalline state in an approximate tt conformation⁴⁴. The intermolecular forces are evidently appreciable and control the conformation. We conclude that the assumption of independent positions of the two groups cannot be rejected and the statement about restricted possibilities of the dipole moment method applies even more to compounds *XVII* and *XVIII* than to *XIII*—*XVI*.

Unlike the preceding classes of compounds the tetraalkyldiphosphane disulfides (*XIX*, *XX*) have been extensively studied by many physical methods⁵⁶. Their structure is now definitely settled in spite of some objections, the deciding factor being several X-ray studies^{45,46}. The problem of the conformation in solution is different in character than in the case of preceding derivatives (*I*—*XVIII*) and resembles that of 1,2-diketones⁵⁷ or of 1,2-diimines⁵⁸. In the latter classes of compounds two double bonds are connected by a single one; their conjugation, if actually present, and electrostatic repulsion would prefer the *trans* conformation, which is opposed by steric strain. The tetraalkyldiphosphane disulfides differ in the tetrahedral configuration on phosphorus atoms and in the kind of conjugation, which uses *d*-orbitals and does not require planar arrangement. As a result equilibrium of *trans* and *gauche* forms

might be expected, the former being preferred by electrostatic factors, the latter by the mentioned *gauche* interaction⁵².

The experimental results are somewhat puzzling. In the crystalline state tetramethyl-diphosphane disulfide⁴⁶ (XIX) as well as the tetraethyl derivative⁴⁵ (XX) exist exclusively in the *trans* form, although the former forms two slightly different kinds of molecules. The same form of the C_{2h} symmetry follows also from the IR spectra in solution with the reservation that less than 5% of another form could not be detected¹⁸. On the other hand the non-zero dipole moment of XX in connection with other spectral features was interpreted¹⁹ by a distorted form with a lower symmetry than C_{2h} . Our findings confirm that the dipole moment is different from zero, and apply also to the tetramethyl derivative XIX, which was believed to be more symmetrical¹⁹ than XX. The moments found are of course much too low for the *gauche* conformation (calculated 6.56 D) and even for a free rotation or for rotation controlled by electrostatic repulsion³⁸. Two explanations are possible: Either an equilibrium mixture with 4–7% of the *gauche* form, or a distorted *trans* form with a dihedral angle S=P–P=S of 155–160° instead of 180°. A decision is not possible on the basis of dipole moment data; the latter possibility seems somewhat more probable considering the analogy with 1,2-diketones⁵⁷ and diimines⁵⁸. At any rate the *gauche* interaction does not control conformation of these compounds, which thus represent an important exception from the quoted rule⁵².

Summarizing our results we may state that they are internally consistent on the one hand, and agree with most findings of other methods and on similar compounds. The evidence is now quite conclusive that steric effects and dipole-dipole interactions are by far not sufficient to explain stability of individual forms. New promising concepts seem to be the lone pair repulsion⁵⁹ and the *gauche* interaction⁵², even when their predictions may disagree in certain cases. Particularly the latter principle was certainly oversimplified in the form used in this paper; the term "polar bond" should be at least specified as to the direction of its polarity. On the other hand a favourable feature is the relative constancy of conformation of the same group in various compounds, as well as the relative independence of remote parts. Hence it may be in principle feasible to estimate conformation of a complex molecule on the basis of simpler ones.

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