One has the chlorine atoms *cis* to this plane and the other has them *trans*. Furthermore, the *cis* isomer should have a permanent dipole moment while the *trans* isomer should not.

The physical properties of $(B_{10}H_{10}C_2PCl)_2$ indicate that only one isomer is isolated from the synthesis[1,3] and X-ray crystallographic data show this to be the *cis* isomer.[2] The dipole moment of this compound was determined to see if this isomer is also the one that exists in solution.

Experimental Section

The exact procedure for obtaining the data has been described previously.[4] For this investigation, ten independent solutions of the dimeric chlorophospha(III)-*o*-carborane in dry cyclohexane were prepared and the dielectric constant and refractive index of each solution was determined at 25.0°.

Results and Discussion

The dipole moment, given below, was calculated using eq 1, which is a modification of the Guggenheim method.[5] The error indicated is experimental. There is a possible error of up to 10% inherent in the method of calculation.[6] The values of ϵ_1, α_ϵ, and α_n are 2.0154, 0.507 ± 0.016, and 0.397 ± 0.011, respectively. The dipole moment calculated from these data is 0.73 ± 0.09 D.

$$\mu^2 = (\text{constant})\left(\frac{1}{d_1(\epsilon_1 + 2)^2}\right)(\alpha^\epsilon - \alpha_n)M_2 \quad (1)$$

A dipole moment calculated by the above procedure is corrected for the electronic contribution to the total polarization. However, the atomic polarization has been neglected as is common practice.[5a]

The dipole moment of 0.73 D indicates that dimeric chlorophospha(III)-*o*-carborane exists in solution as the *cis* isomer in agreement with the results obtained in the crystallographic study of the solid. Of course, since the above dipole moment is rather small, there is a possibility that the *trans* isomer is also present in solution and that the *cis* isomer crystallizes out, preferentially, to give only one isomer in the solid phase.

Acknowledgment.—I wish to thank Dr. A. W. Laubengayer of Cornell University for making available the facilities necessary for obtaining the dipole moment data and Dr. H. Schroeder of Olin Research Center for supplying the dimeric chlorophospha(III)-*o*-carborane.

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[3] H. Schroeder, unpublished data.

[4] R. Maruca, H. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).

[5] (a) J. W. Smith, "Electric Dipole Moments," Butterworth and Co. Ltd., London, 1955; (b) F. Oehme and H. Wirth, "The Determination of the Molecular Dipole Moment," Kahl Scientific Instrument Corp., El Cajon, Calif.

[6] In eq 1, the constant equals 1.474×10^{-1} D^2 at 25.0°; d_1 is the density of the solvent and is 0.7742 g/ml at 25.0° for cyclohexane; ϵ_1 is the dielectric constant of the solvent and is taken as the limiting value of the dielectric constant of the solutions as the weight fraction solute approaches zero; α_ϵ and α_n are the slopes of the graph of the dielectric constant (ϵ) and refractive index squared ($(n_D)^2$) plotted as a function of weight fraction solute; and M_2 is the molecular weight of the solute.

Correspondence

On Vibrational Assignments in Pentacoordinated Molecules and Gillespie-Nyholm Theory[1]

Sir:

In several recent papers, Holmes, *et al.*,[2,3] have discussed the ambiguity in assigning the e′ bending modes in trigonal-bipyramidal molecules. Holmes weighed the evidence for alternative interpretations and concluded that available information does not allow a firm resolution of the problem. In diagnosing the situation, Holmes advanced certain physical arguments which he interpreted as favoring assignment A [ν(equatorial in-plane bend) > ν(axial bend)] over assignment B [ν(eq) < ν(ax.)]. We believe that assignment B is superior, on the basis of (largely unpublished) electron diffraction analyses. Furthermore, we suggest that the arguments offered by Holmes in support of assignment A, while plausible, bear further scrutiny, since they run contrary to implications of the rather successful Gillespie–Nyholm theory of directed valence.[4,5] Therefore, it seems worthwhile to present the diffraction results and to review the discrepant points, showing how the appealingly simple electron pair repulsion theory gives insight into the force field.

The experimental evidence consists of a comparison between rms amplitudes of vibration as measured by gas-phase electron diffraction[6-11] and corresponding amplitudes calculated by Holmes[2] and others[12,13] from vibrational frequencies. It turns out that the amplitudes l_{ae} and l_{ee} calculated for axial–equatorial and equatorial–equatorial nonbonded distances are sensitive to the choice of assignments for the e′ bending

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[1] Research supported by a grant from the National Science Foundation.

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[7] K. W. Hansen and L. S. Bartell, unpublished data.

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[10] H. B. Thompson and L. S. Bartell, unpublished data.

[11] W. J. Adams, Ph.D. Dissertation, The University of Michigan, Ann Arbor, Mich., 1969.

[12] Note that similar arguments for PF_5 (based on an incorrect value for ν_7 according to ref 2) were presented by S. J. Cyvin and J. Brunvoll, *J. Mol. Struct.*, **3**, 151 (1969).

[13] J. Brunvoll, *Acta Chem. Scand.*, **21**, 473 (1967). Brunvoll's PCl_5 amplitudes for 298°K were extrapolated to the 383°K experimental temperature by an approximate method.

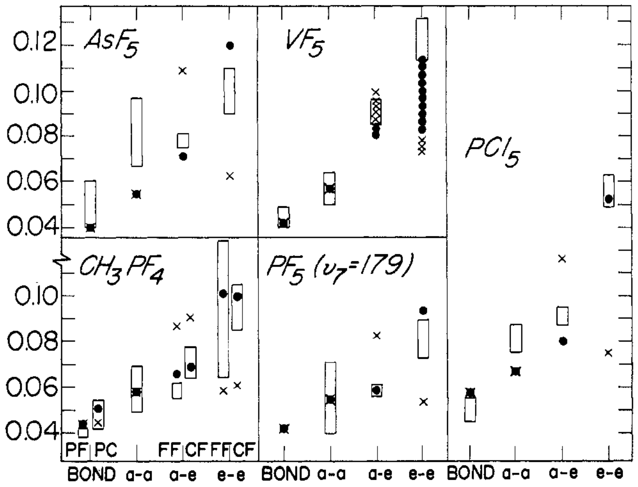

Figure 1.—Mean amplitudes of vibration (Å) of various pentacoordinated molecules for bonded distances (mean of axial and equatorial) and axial–axial, axial–equatorial, equatorial–equatorial nonbonded distances. Rectangles represent experimental electron diffraction values ± esd according to ref 5–10. Crosses (assignment A) and dots (assignment B) represent amplitudes calculated from molecular frequencies according to ref 2 (all molecules except PCl_5) at 298°K and ref 11 and 12 (PCl_5, at 383°K).

modes, with $l_{ae} \gtrless l_{ee}$ for $\nu(\mathrm{eq}) \gtrless \nu(\mathrm{ax.})$. In every one of the 10 l_{ae} and l_{ee} amplitudes available for molecules with established frequencies, the agreement is better for assignment B than for assignment A, as illustrated in Figure 1. In the additional case of VF_5, where ν_7 is uncertain, the range of amplitudes calculated by Holmes, *et al.*,[2] is more compatible with B than A. Just how markedly superior B is to A may be deduced from the sum

$$S_K{}^2 = \sum_{i=1}^{N} (\delta_i/\sigma_i)_K{}^2/N \qquad (1)$$

where, for assignment K = A or K = B, δ_i is the discrepancy between the electron diffraction and the calculated amplitude l_i, and σ_i is the estimated standard deviation for the electron diffraction amplitude. If electron diffraction error theory were rigorous and if the spectroscopic model force fields gave *bona fide* representations of the true fields (neither of which assumptions is strictly correct), the index of discrepancy S_K should be very nearly unity for large N. In fact, S_A and S_B are 1.3 for the nine amplitudes insensitive to the assignment (excluding VF_5) and S_B for the ten sensitive amplitudes is 1.7, a value only modestly larger. By contrast, S_A for the ten sensitive amplitudes is 6.6, a very large value expected by chance (if A were correct) less often than once in 10^{10} such comparisons.[14] Although the actual numerical value of the probability has scant statistical significance, it shows that assignment B is overwhelmingly preferred over A.

The four arguments previously brought to bear[2,3] against assignment B were (1) that axial bonds are longer, (2) that axial bonds have lower stretching force constants than equatorial bonds, (3) that there is no reason to expect in-plane and out-of-plane equatorial bending frequencies to differ drastically, and (4) that axial bending frequencies should differ less than the equatorial in the series $PF_{5-n}(CH_3)_n$ as n is increased. Now, the Gillespie–Nyholm valence shell electron pair repulsion (VSEPR) theory[4] neatly accounts not only for the fact that axial bonds are longer than equatorial bonds but also for the stereochemistry and all of the trends in angles and distances in the series $PF_{5-n}(CH_3)_n$, as explicitly pointed out by Gillespie.[5] Moreover, according to any reasonable variant of Badger's rule,[15,16] observation 2 above follows from observation 1. Holmes and others have reasoned from observations 1 and 2 that, since the axial bonds are weaker, as it were, they might be expected to have the lower bending frequencies. On the other hand, the VSEPR theory embodies the known strong mutual avoidance of occupied, localized molecular orbitals[4,17] to differentiate axial bonds (repelled and constrained by *three* close [90°] equatorial bonds) from equatorial bonds (constrained by only *two* close [90°] axial bonds and, much more weakly, by two remote [120°] equatorial bonds). This environment clearly hampers axial bending motions and equatorial out-of-plane bends severely (and more or less equally), while allowing more freedom of motion for equatorial in-plane bends, consistent with assignment B but contrary to assignment A and to argument 3 above. Indeed, it is pleasing to note that, for assignment B, axial bend and equatorial out-of-plane force constants are similar to each other for all molecules.[3] In the same vein, according to the VSEPR theory,[5] the effect of ligand electronegativity operating in the series $PF_{5-n}(CH_3)_n$ should be felt more strongly along the axis than in the equator,[5] a fact reflected by the noteworthy increase in axial PF bond lengths as n is increased. This clouds deductions from argument 4. Finally, the VSEPR theory suggests a significant coupling between the e′ modes. For example, as an equatorial bond angle opens up, the axial atoms may bend into the void created in the coordination sphere. We are indebted to Professor Holmes for suggesting that interaction constants of this type would give spectroscopic amplitudes in even better agreement with the diffraction results than would the simple force constants of field B.

In support of assignment B, Holmes noted the evidence involving Coriolis coupling constants and the few electron diffraction amplitudes then available. In our opinion, the above experimental and theoretical evidence resolves the ambiguity in favor of a force field much closer to B than to A. Presumably, this conclusion could be tested by purely spectroscopic studies involving isotopic substitution, comparing such pairs as $^{35}Cl_3PF_2$ and $^{37}Cl_3PF_2$.

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(14) The chance is of the order of 10^{-47}, assuming random residuals and renormalizing σ_i with the nonsensitive amplitudes, according to a χ^2 test.

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