

susceptibility is -130.5×10^{-6} , as compared with -115.9 for tolane and -102.9 for diphenyl. Pascal's rules would give $\bar{\chi} = -129.7$ for diphenyldiacetylene: he himself found the value -129.3 (corr.). The principal susceptibilities of a single molecule, deduced from the above data and the molecular direction cosines, are $K_L = -109.4$, $K_M = -75.3$, $K_N = -206.7 \times 10^{-6}$.

Comparing these with the corresponding values for tolane², $K_L = -81.5$, $K_M = -67.8$, $K_N = -198.5 \times 10^{-6}$, it will be seen that there is an abnormal increase of susceptibility along the carbon chain axis, indicating a concentration of electron density normal to that axis. This is in sharp contrast to the behaviour of chains of conjugated double bonds, for which the increase of susceptibility is always normal to the plane of the molecule, indicating a concentration of electron density in that plane. An exact Fourier analysis of the structure of diphenyl is very desirable, in order to extend the comparison from tolane to diphenyl.

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¹ Wiebenga, E. H., NATURE, 143, 980 (1939).

² Lonsdale, K., Proc. Roy. Soc., A, 171, 564 (1939).

Crystal Structure of Phosphorus Pentachloride

ALTHOUGH much work has been done on the molecular structure of phosphorus pentachloride, no crystal structure determination of this important substance has previously been made, presumably owing to experimental difficulties. In our separate laboratories, independent X-ray diffraction experiments have given the following results: Crystal system tetragonal, approximate cell dimensions $a_0 = 9.2$, $c_0 = 7.4$ A., density *circa* 2.0 gm./c.c., 4 molecules per unit cell, space group $P4/n$.

This information is sufficient to determine the constitution of the compound. Consideration of the space group symmetry and the available space shows that it is impossible to form a structure containing PCl_5 molecules of any configuration. For similar reasons the constitution $[PCl_4]^+Cl^-$ may also be rejected. An ionic structure containing tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ groups completely satisfies the requirements. For a unit cell with origin as in the "Internationale Tabellen zur Bestimmung von Kristallstrukturen", the centres of $[PCl_4]^+$ groups are at 000 , $\frac{1}{2}\frac{1}{2}0$, and those of $[PCl_6]^-$ at $0\frac{1}{2}z$, $\frac{1}{2}0z$, $z \approx \frac{2}{3}$. Preliminary Fourier analyses have confirmed these conclusions, and further details of the structure will be given later.

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Degeneracy and Dissociation Constants

THE importance of degeneracy in enhancing the stability of radicals such as triphenylmethyl has been emphasized by many authors; for example, Pauling and Wheland¹, Ingold², etc. This being so, it is strange that no relations have been suggested between complexity of degeneracy (which we may define in terms of the number of possible resonating structures) and dissociation constants of series of related acids and bases. It is probable that simple relations will be discovered only in series where the inductive effects of substituent groups are negligible, or can be eliminated.

Consider the series of acids, methyl alcohol (K of the order 10^{-16}), acetic acid ($K = 1.75 \times 10^{-5}$), phenylacetic acid ($K = 4.88 \times 10^{-5}$), and diphenylacetic acid ($K = 11.5 \times 10^{-5}$). (All K values, which are thermodynamic ones, have been taken from Dippy's recent article³.) Now the inductive effect of the C=O group moment fails to account for the enormous increase in strength (the ratio being 10^9) when we proceed from methyl alcohol to acetic acid, for chloroacetic acid is only 100 times as strong as acetic acid. However, two resonating structures ($n = 2$) are possible for the acetic acid molecule ion, and the energy of resonance effects stabilization.

In the same way, the inductive effect of the phenyl group, which must be very small, will not account quantitatively for the acid strengths of phenylacetic and diphenylacetic acids. Even if we assumed (wrongly) that the increase in K in going from acetic to phenylacetic acid is due to an electrical inductive effect of the phenyl group generally designated as $-I$, the strength of diphenylacetic acid is definitely larger than what we should deduce on that hypothesis. It seems fairly obvious that the enhanced stability of the phenylacetic and diphenylacetic acid ions is due to an increase in the number of resonance

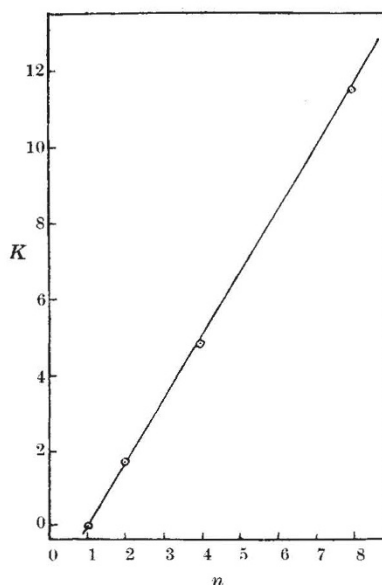


Fig. 1