14. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY

14.3-01 GASEOUS ELECTRON DIFFRACTION STUDY OF 1-CHLORO-2,4-DIMETHYL-1,2-DIHYDRO-1,5,2,3-PHOSPHA­XADIAZOLE

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The gaseous electron diffraction data on 1-chloro-2,4-dimethyl-1,2-dihydro-1,5,2,3-phospha­xadiazole C_6H_4Cl_2N_2P have been subjected to detailed analysis. The analysis was carried out using a modern procedure by least-squares treatment of the experimental molecular intensity curve. A considerable elongation of the PCl bonds in chlorinated aminophosphines has been determined by electron diffraction: r(P-Cl) = 2.167 Å, found in (I) is significantly longer than the sum of the covalent radii, 2.03 Å. The parameters of the five-membered phospha­xadiazole ring containing the NCl double bond were refined to the values (bond lengths in Å, bond angles in degrees): FCl 1.693(8), PO 1.360(6), NN 1.405(9), C-C 1.406(5), N-C 1.280(13); NOP 1.210(5), PNO 1.104(4,5). The heterocycle features a non-planar envelope-like conformation with phosphorus in the "flap" position. The amino nitrogen atom linked to phosphorus has a nearly planar bond configuration (the sum of the valence angles at the nitrogen atom is equal to 356.1°). The amino nitrogen methyl substituent is bent towards an equatorial position.

The internal angle at the ipso carbon is in excellent agreement with the values obtained for fluorobenzene by microwave spectroscopy, 123.4 ± 0.5° (Nygard et al., J. Mol. Struct., 2, 209 (1968)). The ring deformations observed in the para-disubstituted derivatives C_6H_4F_2, C_6H_4Cl_2 (Schult, Hargittai & Domenicano, J. Mol. Struct., 68, 281 (1980)) and C_6H_4F_2N_2P (Domenicano, Schultz, Kolesnik & Hargittai, J. Mol. Struct., 53, 197 (1979)) as well as in the respective monosubstituted derivatives are consistent with the electronacceptivities of the substituents. The internal angles of the ring agree with the values derived from the empirical angular parameters of Domenicano & Murray-Rust (Tetrahedron Lett., 2283 (1979)). (These parameters have been obtained from a large body of data on mono- and para-disubstituted benzene derivatives, assuming additivity of substituent effects. They appear to reproduce well the observed bond angles in other, even highly substituted, benzene derivatives.)

There have been conflicting reports, however, on the structure of p-difluorobenzene. According to the empirical angular parameters, considerable deformations would be expected (C-F-C-F = 116.0°, C-F-C-C = 123.9°, C-F-C = 117.6°), while a practically undistorted benzene ring has been reported from an electron diffraction analysis (Van Schuit et al., J. Mol. Struct., 16, 289 (1973)). On the other hand the findings of an NMR spectroscopic study in nematic solvents pointed to the possibility of considerable ring deformations in this molecule (Den Otter et al., J. Mol. Struct., 16, 379 (1973)).

Earlier, the molecular structure of sym-trifluorobenzene has been studied by electron diffraction under the assumption of an undistorted benzene ring (Bauer et al., Structural Chemistry and Molecular Biology, Eds. Rich & Davidson, Freeman & Co., San Francisco, 1968). Again, in the light of the present results large angular deformations would be expected (the empirical angular parameters give C-F-C = 124.4°).

Reanalyses of p-difluorobenzene and sym-trifluorobenzene are desirable and expected to contribute to further understanding of the origin of the ring deformations in benzene derivatives.

14.3-02 RING DEFORMATIONS IN p-DIFLUOROBENZENE AND IMPLICATIONS FOR RELATED MOLECULES

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The molecular structure of gaseous p-difluorobenzene has been determined by electron diffraction:

\[ \frac{r(F-C)}{r(C-H)} = 135.4 \pm 0.4 \text{ pm} \]
\[ \frac{r(C-H)}{r(C-C)} = 108.8 \pm 0.5 \text{ pm} \]
\[ \frac{r(C-C)}{\text{mean}} = 139.2 \pm 0.3 \text{ pm} \]

(D_{6h} symmetry assumed)

\[ \angle(C-F-C) = 123.5 \pm 0.1° \]

The benzene ring deviates markedly from D_{6h} symmetry. The internal angle at the ipso carbon is in excellent agreement with the value obtained for fluorobenzene by microwave spectroscopy, 123.4 ± 0.5° (Nygard et al., J. Mol. Struct., 2, 209 (1968)). The ring deformations observed in the para-disubstituted derivatives C_6H_4F_2, C_6H_4Cl_2 (Schult, Hargittai & Domenicano, J. Mol. Struct., 68, 281 (1980)) and C_6H_4Cl_2N_2P (Domenicano, Schultz, Kolesnik & Hargittai, J. Mol. Struct., 53, 197 (1979)) as well as in the respective monosubstituted derivatives are consistent with the electronacceptivities of the substituents. The internal angles of the ring agree with the values derived from the empirical angular parameters of Domenicano & Murray-Rust (Tetrahedron Lett., 2283 (1979)). (These parameters have been obtained from a large body of data on mono- and para-disubstituted benzene derivatives, assuming additivity of substituent effects. They appear to reproduce well the observed bond angles in other, even highly substituted, benzene derivatives.)

High-energy electron scattering by molecules has been studied recently by many workers from both the experimental and theoretical viewpoints. In the present study, elastic and total differential cross sections for 30 KeV electrons have been measured on target gases such as CH_4, C_6H_12, C_6H_6, C_2H_5, H_2CO, CO_2, CO and N_2 in a small-angle range up to s=16 by means of the unit providing a retarding-field energy filter and a scintillator and photon-counter system (Shibata et al., Int. J. Quant. Chem. 19, 281 (1980)). The experimental scattering intensities were compared with the independent atomic model intensities and the effect of chemical bonding was found to be particularly remarkable for the hydrogen-rich molecules. On the other hand, the elastic scattering intensities for CH_4, C_2H_2, H_2CO and CO were calculated in the first Born approximation using LCAO-SCF-AO wave function. The results were in good agreement with the experiment. Elastic scattering is related directly to the electron density in a molecule, and thus it was shown that the decreases in the elastic scattering intensities are due to the shrinkage of the electron distribution by formation of chemical bond. Furthermore, the experimental inelastic scattering intensities were much smaller than the sum of atomic inelastic scattering factors with correlation. It is very interesting to note that their decreases are caused by the inelastic scattering from chemical bonding.