

**14.3-01** GAS PHASE ELECTRON DIFFRACTION STUDY OF 1-CHLORO-2,4-DIMETHYL-1,2-DIHYDRO-1,5,2,3-PHOSPHOXADIAZOLE. By L.S. Khaikin, O.E. Grikina and L.V. Vilkov, Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R.

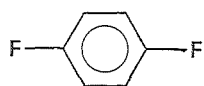
The gas phase electron diffraction data on 1-chloro-2,4-dimethyl-1,2-dihydro-1,5,2,3-phosphaoxadiazole,  $C_3H_6ClN_2OP$  (I), reported in our earlier paper (Dokl. Akad. Nauk SSSR (1969) 187, 1293) have been subjected to detailed analysis. The analysis was carried out using a modern procedure by least-squares treatment of the experimental molecular intensity curve. A considerable elongation of the P-Cl bonds in chlorinated aminophosphines has been confirmed. The bond length,  $r_a(P-Cl)$  2.167 (5) Å, found in (I) is significantly longer than the sum of the covalent radii, 2.09 Å. The  $r_a$  parameters of the five-membered phosphoxadiazole ring containing the N=C double bond were refined to the values (bond lengths in Å, bond angles in degrees): PN 1.698(8), PO 1.630(6), NN 1.405(15), OC 1.406(15), N=C 1.280(13); NPO 91.2(0.5), PNN 110.4(1.5). The heterocycle features a non-planar envelope-like conformation with phosphorus in the "flap" position. The NPO plane and the mean plane of the O-C-N-N fragment make a dihedral angle of 20.9°. The chlorine atom attached to P is in the axial 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.

**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:



$$\begin{aligned} r_g(C-F) &= 135.4 \pm 0.4 \text{ pm} \\ r_g(C-H) &= 108.8 \pm 0.5 \text{ pm} \\ r_g(C-C)_{\text{mean}} &= 139.2 \pm 0.3 \text{ pm} \end{aligned}$$

$$(\text{D}_{2h} \text{ symmetry assumed}) \quad \angle C-C(F)-C = 123.5 \pm 0.1^\circ$$

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,  $123.4 \pm 0.5^\circ$  (Nygaard *et al.*, J. Mol. Struct., 2, 209 (1968)).

The ring deformations observed in the *para*-disubstituted derivatives  $C_6H_4F_2$ ,  $C_6H_4Cl_2$  (Schultz, Hargittai & Domenicano, J. Mol. Struct., 68, 281 (1980)) and  $C_6H_4Me_2$  (Domenicano, Schultz, Kolonits & Hargittai, J. Mol. Struct., 53, 197 (1979)) as well as in the respective monosubstituted derivatives are consistent with the electronegativities 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 *m*-difluorobenzene. According to the empirical angular parameters, considerable deformations would be expected ( $\angle C(F)-C-C(F) = 116.0^\circ$ ,  $C-C(F)-C = 123.9^\circ$ ,  $C(F)-C-C = 117.6^\circ$ ), while a practically undistorted benzene ring has been reported from an electron diffraction analysis (Van Schaick *et al.*, J. Mol. Struct., 16, 389 (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  $\angle C-C(F)-C = 124.4^\circ$ ).

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

**14.3-03** ELASTIC AND INELASTIC SMALL-ANGLE ELECTRON SCATTERING BY GASEOUS MOLECULES.

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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  $CH_4$ ,  $C_2H_2$ ,  $C_6H_6$ ,  $C_2H_2$ ,  $H_2CO$ ,  $CO_2$ ,  $CO$  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. 18 281 (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-MO 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.