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SUMMARY

The present study is concerned with the small three membered carbon ring compounds cyclopropane (CP), bicyclopropyl (BCP) and vinylcyclopropane (VCP). Only a brief outline of the research is given in this summary since each of the chapters is already preceded by detailed abstracts. The chosen subject is part of the project "Study of chemical bonding by means of accurate electron density distributions obtained from X-ray analysis". An interesting feature of the compounds considered is the conjugative character of the three membered carbon ring: the carbon ring shows some analogy with an unsaturated double C-C bond. Chapter 1 treats possible influences of conjugation (or electron delocalization) between the two cyclopropyl groups in BCP or between the cyclopropyl and vinyl group in VCP on the molecular geometry and electron density distribution. The BCP ring bonds are expected to be lengthened with respect to the CP C-C bonds. For VCP the qualitative discussion indicates an asymmetry of the ring geometry. For both BCP and VCP the electron density distribution about the central bond is expected to deviate from rotational symmetry.

The crystallization procedure applied for the three volatile compounds is described in Chapter 2. Because the X-ray diffraction measurements require the highest accuracy, special attention is given to the modelling of the glass capillaries in which the crystals are grown. The compounds are crystallized *in situ* on the diffractometer.

The precautions taken to obtain an accurate and extensive set of reflection intensities are treated in Chapter 3. The intensity measurements on four crystals (for CP two crystals of the same sample have been used) are performed at a temperature of ca 100 K. Reduction of several intensity series to one series of independent reflections for each of the compounds renders internal consistency factors of approximately 1 %.

In Chapter 4 the space groups and crystal structures are determined within the scope of the conventional (spherical atom) model. Only BCP turns out to belong to a centrosymmetric (orthorhombic) space group. In contrast with BCP the geometry of VCP clearly points to the presence of conjugation.

Multipole refinements are introduced in Chapter 5. Much attention is paid to obtain the "best" or ultimate multipole models. The use of diffuse deformation functions yields for the low order regions excellent fits of calculated to observed

structure factor amplitudes: the weighted residuals up to $(\sin\theta)/\lambda = 0.65$ Å^{-1} range from 0.32 % for VCP via 0.39 % for CP to 0.57 % for BCP. The ultimate multipole models give the most accurate positional parameters (used for the geometry discussion in Chapter 4). The average σ(C-C) amounts to 4 10^{-4} Å for BCP and VCP, and to 8 10^{-4} Å for CP. The filtered model deformation density maps clearly show the bent bond character for each of the rings (Fig. 5.3(a,b,c)) and the elongation of the deformation density around the VCP double bond in the π-direction (Fig. 5.3(i)).

In Chapter 6 the theoretical deformation densities obtained from quantum chemical calculations without and with polarization functions are used for comparison with the experimental deformation densities. For this purpose the dynamic experimental model densities are made static. If account is taken of the limited resolution of the experimental densities, the overall agreement between experimental and theoretical (with polarization functions) maps is good, apart from the central and double bond region in VCP. Sections perpendicular to and through the midpoints of the VCP central and double bond show that the density in these planes is elongated in the π-direction. This asymmetry is represented by the asymmetry parameter ap defined in Table 6.1. It turns out that for the VCP central bond the theoretical ap is significantly smaller than the experimental ap, whereas the opposite is the case for the VCP double bond. It is not clear yet whether this discrepancy is due to inadequacies in the experimental or in the theoretical model. Both for BCP and VCP the experimental and theoretical central bond ap's point to conjugation. In VCP the elongation of the central bond density in the π-direction gives a significant support to the geometrical evidence for conjugation. In case of BCP the probability that the experimental central bond ap equals the value for rotational symmetry is only 1 %, which makes it most likely that conjugation also occurs in BCP.