Single-crystal structures and electron density distributions of ethane, ethylene and acetylene
Nes, G.J.H. van

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1.1. Accurate studies of electron densities

The research described in this thesis, is part of the project "Accurate determination and interpretation of electron density distributions", performed at the Laboratory of Structural Chemistry of the University of Groningen. Earlier work within this project has been published, in thesis form, by Verschoor (1967), Keulen (1971), Ruysink (1973) and Helmholdt (1975). The experimental method of this project is X-ray diffraction of single-crystals.

X-ray diffraction gives dynamic density distributions for molecules having both internal and external thermal motions in the crystal. In this thesis, the thermal motion of the atoms is deduced from the experimental density by use of the convolution approximation (Coulson & Thomas, 1971). In order to make density changes due to chemical bonding ("bonding effects") clearly visible, experimental deformation densities displaying the differences between the actual electron density distribution and that corresponding to a model of non-bonded spherical atoms, are generally used. The positional and thermal parameters of the atoms in the model must be the same as in the molecule in the solid state. When for this purpose neutron diffraction parameters are used, as is often the case in the literature (Coppens, 1975), care should be taken that these parameters are free from systematic errors caused by, for instance, crystal quality or thermal diffuse scattering.

A summary of the experimental work is given in the upper part of Fig. 1.1. The experimental deformation densities are compared with theoretical deformations obtained as indicated in the lower part of the figure.

Fig. 1.1. Comparison of experimental (above) and theoretical (below) deformation densities.
For molecular crystals, as studied in the present project, it can often be assumed that density changes due to intermolecular interactions can be neglected, so that theoretical densities can be obtained by quantum mechanical calculations on the free molecules.

Usually, theoretical calculations are performed for fixed positions of the nuclei and give the so called static densities. These theoretical static densities can be made comparable with the experimental ones, by smearing the former according to the method described by Ruysink & Vos (1974a). Comparison of the experimental and theoretical densities may reveal possible shortcomings in the theoretical calculations, and in the measurements and interpretation of the experimental deformation density maps.

In addition to the density distributions, accurate X-ray diffraction studies can, in principle, yield information on one-electron properties of the molecules like dipole moments, quadrupole moments, electric field gradients etc. (Stewart, 1972, 1976). To what extent this is feasible, is presently a subject of extensive discussion (Price & Maslen, 1978; Stewart, 1977).

The studies mentioned above require the highest obtainable experimental accuracy, as small effects must be detected. For triple and single C–C bonds, for instance, the total electron surplus due to the bonding is smaller than 0.3 and 0.1 e, respectively (Helmholdt & Vos, 1977). Some necessary requirements for the crystals are:

(a) Good quality (small mosaic spread, and if possible, small extinction);
(b) Centrosymmetric space group, in order to reduce errors due to the phase problem, and (c) Well defined (preferably spherical) shape for obtaining, for instance, accurate corrections for absorption. The X-ray diffraction intensities must be measured with great care on diffractometers of high mechanical and electronic stability. Some further conditions are: (a) Correct choice of scanning method and scanning angle plus counter slit width (Keulen, 1969), (b) Application of the step scan method, which makes analysis of the diffraction profiles feasible, (c) Use of a monochromatic and homogeneous X-ray beam (Helmholdt & Vos, 1977) of preferably high power, and (d) Collection of all reflexions in the Ewald sphere up to the maximum obtainable \( \sin \theta / \lambda \) value. Measurable intensities of molecular crystals at high \( \sin \theta / \lambda \) can only be obtained if the temperature of the crystal is kept low, in order to reduce the thermal motions of the molecules. This has the further advantage that errors due to thermal diffuse scattering (TDS; Kroon, 1977) are kept small. For the compounds studied in this thesis, TDS corrections have not been applied, but research on the calculations of these corrections will be done in the near future.
1.2. Ethane, ethylene and acetylene

Ruysink & Vos (1974b), Helmholdt & Reynaers (1976) and Helmholdt & Vos (1977) have studied the electron density distributions at the central single, double and triple C-C bonds for the series of compounds:

As a continuation of this work, we have chosen to study the small-molecule compounds ethane (C\(_2\)H\(_6\)), ethylene (C\(_2\)H\(_4\)) and acetylene (C\(_2\)H\(_2\)). For these compounds, the intermolecular interactions are so small that density changes due to these interactions can be neglected in good approximation. The small number of atoms per molecule enables us to perform sophisticated theoretical calculations. Moreover, accurate knowledge of the atomic positions in crystals of these small compounds gives a firm basis for the study of the intermolecular interactions, and for the interpretation of spectral data.

Ethane, ethylene and acetylene are all gaseous compounds at room temperature. Therefore we had to reduce the temperature for growing the crystals. Chapter 2 describes the open N\(_2\) cooling equipment which was used during the collection of our data and during the growing of single crystals in situ on the CAD4 diffractometer. A short guide is given there for the preparation of the capillaries. In connection with the homogeneity of the X-ray beam (Fig. 3.1), the diameter of the spherical end of the capillaries in which the crystals had to be grown was kept smaller than 0.6 mm. Most crystals were spherical (\(\phi \approx 0.59\) mm) within some \(\mu\)m\(^2\)'s. Two growing procedures are also reported in that chapter. The smallest mosaic spread is normally obtained by growing the crystals just below the melting point. However, the mosaic spread increases by subsequent cooling of the crystals. As the best compromise, we have grown the crystals directly at the temperature of the diffraction experiment.

Information from the phase diagrams of C\(_2\)H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\) at 1 atmosphere is given in Fig. 1.2. The low melting points of C\(_2\)H\(_4\) and C\(_2\)H\(_6\) necessitate crystal structure determination at temperatures just above the boiling point of liquid nitrogen (77 K). With the exception of C\(_2\)H\(_4\), the compounds show phase transitions in the solid state. For C\(_2\)H\(_2\), the high temperature cubic phase transforms into an orthorhombic phase at 133 K. For C\(_2\)H\(_6\) there is a high temperature (plastic) cubic modification with a stability range of only 0.45° and a monoclinic modification below 90 K.
Fig. 1.2. Information from the phase diagrams of acetylene, ethylene and ethane at 1 atmosphere. Temperatures at which the diffraction experiments for this thesis have been performed, are marked by • together with the space groups of the crystals. b.p. = boiling point; m.p. = melting point; fr.p. = freezing point; p.t. = phase transition. The lowest temperature obtainable with our $N_2$ cooling equipment is 85K (b.p. liquid $N_2$ is 77 K).
In the literature no accurate single crystal structural data are available for \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \). For \( \text{C}_2\text{H}_2 \), the crystal structures of both the high and low temperature modifications have been determined by powder neutron diffraction (Koski, 1975). For solid \( \text{C}_2\text{H}_4 \), different crystal structures have been proposed (§ 5.2), while for \( \text{C}_2\text{H}_6 \) an incorrect crystal structure is described. In Fig. 1.2 the temperatures at which the diffraction experiments have been carried out during the research for this thesis, are marked by •. For \( \text{C}_2\text{H}_2 \), so far, it has not yet been possible to perform a complete single crystal diffraction experiment of the low temperature phase. However, for \( \text{C}_2\text{H}_6 \), the crystal structures of both the cubic and the monoclinic phases have been determined.

The structure determinations are given in chapter 3 for \( \text{C}_2\text{H}_6 \), chapter 4 for \( \text{C}_2\text{H}_2 \) and chapter 5 for \( \text{C}_2\text{H}_4 \). Chapters 2 – 5 are manuscripts of articles accepted by, or submitted to "Acta Crystallographica" or "Journal of Applied Crystallography" (van Nes & van Bolhuis, 1978a; van Nes & Vos, 1978a; van Nes & van Bolhuis, 1978b; van Nes & Vos, 1978b; see also Appendix D). The next sections will give some short experimental notes (§ 1.3) and some results of the structure and electron density distribution determinations (§ 1.4 and § 1.5) of these compounds.

1.3. Experimental data and refinement procedures

A review of the experimental data is given in Table 1.1. The cell dimensions and reflexion intensities were measured on a computer controlled four circle diffractometer (Nonius CAD4). In order to reduce systematic errors and in order to detect multiple diffraction, for \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) all reflexions hkl were collected at two different \( \psi \) values; for \( \text{C}_2\text{H}_2 \) this procedure was done for half of the reciprocal space. Additionally, a frequent change in psi value avoids formation of ice on the capillary. A set of \( |I| \) and/or \( |F| \) values with their weights was deduced from the measured intensities.

Because of the large thermal motion, the resolution of the \( \text{C}_2\text{H}_2 \) experiments is not very high (\( \sin \theta / \lambda < 0.8 \AA^{-1} \)). During the collection of data, the acetylene crystal changed from colourless to deep red, presumably caused by polymerisation of the compound under irradiation by X-rays. For the monoclinic phase of \( \text{C}_2\text{H}_6 \), twinning of the crystals (twinning ratio 4:1) reduced the accuracy of the intensity data. For the data set of \( \text{C}_2\text{H}_4 \), which is the most accurate one, corrections of thermal diffuse scattering are planned for the near future. Further experiments (both X-ray and neutron) will be carried out at He temperatures, in order to reduce the thermal motion of the molecules in the crystal and errors due to TDS.
Table 1.1. Crystallographic data for \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_4 \), and \( \text{C}_2\text{H}_2 \).

<table>
<thead>
<tr>
<th></th>
<th>( \text{C}_2\text{H}_6 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_2\text{H}_2 )</th>
<th>( \text{C}_2\text{H}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>spacegroup</td>
<td>( \text{Im}3\text{m}, Z=2 )</td>
<td>( \text{P}2_1/\text{n}, Z=2 )</td>
<td>( \text{Pa}3, Z=4 )</td>
<td>( \text{P}2_1/\text{n}, Z=2 )</td>
</tr>
<tr>
<td>( \phi ) (crystal:mm)</td>
<td>0.595 ± 0.003</td>
<td>0.595 ± 0.003</td>
<td>0.587 ± 0.004</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>temperature (K)</td>
<td>90</td>
<td>85</td>
<td>141</td>
<td>85</td>
</tr>
<tr>
<td>cell parameters</td>
<td>( a=5.304(2) )</td>
<td>( a=4.226(3) )</td>
<td>( a=6.091(3) )</td>
<td>( a=4.626(1) )</td>
</tr>
<tr>
<td>( (\AA, \text{degrees}) )</td>
<td>( b=5.623(4) )</td>
<td>( b=5.845(4) )</td>
<td>( b=6.620(2) )</td>
<td>( b=4.067(2) )</td>
</tr>
<tr>
<td>( \beta=90.41(6) )</td>
<td>( c=5.845(4) )</td>
<td>( c=4.067(2) )</td>
<td>( \beta=94.39(2) )</td>
<td>( \beta=94.39(2) )</td>
</tr>
<tr>
<td>( D_\chi ) (g.cm(^{-3}))</td>
<td>0.669</td>
<td>0.719</td>
<td>0.765</td>
<td>0.750</td>
</tr>
<tr>
<td>mosaic spread ( m ) (°)</td>
<td>&lt; 0.4</td>
<td>twinning; ( m&lt;0.5 )</td>
<td>&lt; 0.7</td>
<td>&lt; 0.4</td>
</tr>
<tr>
<td>scan method</td>
<td>( \omega )</td>
<td>( \omega )</td>
<td>( \omega )</td>
<td>( \omega )</td>
</tr>
<tr>
<td>( (\sin \theta/\lambda)_{\text{max}} ) (Å(^{-1}))</td>
<td>0.58</td>
<td>0.81</td>
<td>0.80</td>
<td>1.07</td>
</tr>
<tr>
<td>nr. collected refl.</td>
<td>1059</td>
<td>5147</td>
<td>4522</td>
<td>10946</td>
</tr>
<tr>
<td>nr. independent refl.</td>
<td>23</td>
<td>610</td>
<td>164</td>
<td>1295</td>
</tr>
<tr>
<td>nr. refl. ( I &gt; 3\sigma(I) )</td>
<td>10</td>
<td>575</td>
<td>102</td>
<td>801</td>
</tr>
<tr>
<td>( R_w(F) )</td>
<td>0.026</td>
<td>0.052</td>
<td>0.0170</td>
<td>0.0231</td>
</tr>
<tr>
<td>( R_w(I) )</td>
<td>0.026</td>
<td>0.052</td>
<td>0.0170</td>
<td>0.0231</td>
</tr>
<tr>
<td>C-C (lit.) (Å)</td>
<td>1.532</td>
<td>1.532</td>
<td>1.203</td>
<td>1.336</td>
</tr>
<tr>
<td>C-C (ref.) (Å)</td>
<td>1.409</td>
<td>1.510</td>
<td>1.178</td>
<td>1.314</td>
</tr>
<tr>
<td>C-H (lit.) (Å)</td>
<td>1.096</td>
<td>1.096</td>
<td>1.061</td>
<td>1.089</td>
</tr>
<tr>
<td>C-H (ref.) (Å)</td>
<td>constraint</td>
<td>0.92-1.00</td>
<td>constraint</td>
<td>constraint</td>
</tr>
<tr>
<td>( \bar{U}_{ii}(C) ) (Å(^2))</td>
<td>0.166</td>
<td>0.031</td>
<td>0.053</td>
<td>0.036</td>
</tr>
<tr>
<td>( \bar{U}_{ij}(C) ) (Å(^2))</td>
<td>0.014</td>
<td>0.001</td>
<td>-0.006</td>
<td>0.003</td>
</tr>
<tr>
<td>( \bar{U}_{ii}(H) ) (Å(^2))</td>
<td>0.63</td>
<td>0.057</td>
<td>0.100</td>
<td>0.067</td>
</tr>
<tr>
<td>( \bar{U}_{ij}(H) ) (Å(^2))</td>
<td>0.31</td>
<td>0.004</td>
<td>-0.026</td>
<td>0.016</td>
</tr>
<tr>
<td>D(r) at centre</td>
<td>0.28</td>
<td>0.35</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>C-C (eÅ(^{-3}))</td>
<td>constraint</td>
<td>constraint</td>
<td>constraint</td>
<td>constraint</td>
</tr>
</tbody>
</table>

1) data extend further; collection stopped because of twinning
2) collected up to \( \sin \theta/\lambda = 0.90 \) Å\(^{-1}\)
3) obtained for model D (§3.4.2)
4) obtained for model B2 (§3.5.3)
5) obtained for model C5 (§4.8; \( 3P \) refinement)
6) obtained for model A (§5.6; \( \zeta \) refinement)
7) 0.44 for the \( 3P \) refinement
For all refinements, anisotropic least squares techniques were used. For 
$\text{C}_2\text{H}_6$, refinements on $|F|$ and for $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$, refinements on $I$ were carried 
out. Some results are given at the bottom of Table 1.1.

1.4. Description of the structures

In the plastic cubic phase of $\text{C}_2\text{H}_6$, the C-C bonds have preferred 
orientation along the body diagonals of the cubic cell (Fig. 3.3a), while 
there is free rotation around these bonds. The monoclinic $\text{C}_2\text{H}_6$ structure is 
shown in Fig. 3.5. The observed twinning of the monoclinic crystals is discussed 
in § 3.3.3. As is shown in Table 1.1, the thermal motion of the molecules in 
the crystal is not high. Difference Fourier syntheses with amplitudes 
$[F_o - F_c \text{ (C atoms)}]$ clearly show the preferred positions of the H atoms (Fig. 3.9). 
At the centre of the C-C bond, the deformation density has a maximum value of 
0.28 $\text{eA}^{-3}$ for the cubic, and 0.35 $\text{eA}^{-3}$ for the monoclinic phase. No accurate 
analysis of the density distributions of monoclinic $\text{C}_2\text{H}_6$ was attempted because 
of twinning of the crystals. Both the observed cubic and monoclinic structures 
are essentially different from the hexagonal structure proposed by Mark & 
Pohland (1925).

The cubic crystal structure of $\text{C}_2\text{H}_2$, having 4 molecules per cell at 
special position 3, is given in Fig. 4.1. All intermolecular distances are more 
than 0.15 $\text{A}$ longer than the sum of the relevant van der Waals radii, showing 
that the crystal is packed quite loosely, which is also apparent from the 
strong thermal motion (Table 1.1).

The monoclinic structure of $\text{C}_2\text{H}_4$ is shown in Fig. 5.1. The molecules 
lie at inversion centres. Table 1.1 shows, that for $\text{C}_2\text{H}_4$ the thermal motion 
is smaller than for $\text{C}_2\text{H}_2$. The $[F_o - F_c \text{ (C atoms)}]$ map reveals preferred positions 

1.5. Aspherical refinements and analysis of the density distributions for 
$\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$

During the refinements of $\text{C}_2\text{H}_2$, the H atoms were constrained to C by 
use of the bond lengths obtained from Raman spectroscopy and the internal motions 
deduced from IR spectra of the gas. Third and fourth cumulants were applied 
to obtain a good description of the librational motion. For a conventional 
refinement there are only 4 parameters: the first cumulant $x(C)$ (not directly 
obtainable from the Raman values due to librational shortening), the second 
cumulants $U_{11}(C)$ parallel to 3, and $U_{11}(C)$ perpendicular to 3, and the scale 
factor $K$. Due to the limitation of the data set (high thermal motion), the 
correlation between $K$ and the second cumulant is so high, that no reliable
values could be obtained from h.o. refinements. The valence density distribution has been described by a sum of multipole functions $R(r)P_m^l(\Theta, \Phi)$, in which $P_m^l(\Theta, \Phi)$ are associated Legendre functions centered at the atoms (Stewart, 1976). For $R(r)$, Slater type functions with adjustable $\zeta$ exponent (Stewart, 1976) or SCF radial functions for non-bonded atoms have been taken. The corresponding scattering factors are called $\zeta$ and $3P$, respectively. Table 4.6 clearly shows that the structural parameters depend on the radial functions (or scattering factors) applied. The dependence is also clearly seen in the Fourier maps. Filtered and unfiltered deformation maps based on the 138 reflexions with $I > 0$ (§4.9.1), are shown in Fig. 4.5 and 4.6. The filtered deformation density map for the (modified) $3P$ scattering factors agrees best with the theoretical dynamic deformation density map (Fig. 4.8).

During the refinements of $\text{C}_2\text{H}_2$, the positional parameters of H were constrained to those of C. No third and fourth cumulant terms were applied. Despite of the large set of reflexion data, the correlation between the radial parameters (including the scale factor) is high. Both $\zeta$ and $3P$ refinements (see $\text{C}_2\text{H}_2$) were carried out with multipole deformation functions up to octupole on C and up to quadrupole on H. Table 5.5 shows the dependence of the parameter set on the type of scattering factors. Analogous features as for $\text{C}_2\text{H}_2$ (Table 4.6) were observed. Residual density maps and filtered and unfiltered deformation maps were calculated. As in the case of $\text{C}_2\text{H}_2$, the $\zeta$ maps are different from the $3P$ maps. The filtered map for the $3P$ scattering curve shows closer agreement with the theoretical dynamic deformation density map than the map for the $\zeta$ curve (see Figs. 5.2, 5.3 and 5.4).

1.6. Discussion and conclusions

Both for $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$, good qualitative agreement with the theoretical dynamic density distribution is obtained. For the $3P$ refinement, for instance, the difference between the experimental and theoretical dynamic density maps in the C-C regions, is not larger than 0.05 eÅ$^{-3}$ for $\text{C}_2\text{H}_2$ and 0.06 eÅ$^{-3}$ for $\text{C}_2\text{H}_4$. It should be noted, however, that the experimental maps are not directly comparable with the theoretical maps as, due to the correlation between the radial parameters, only experimental maps without the monopole deformations could be calculated. Especially at the H atoms and around the C-H bonds, this is clearly visible. The experimental bonding picture can be improved by supplementing the X-ray work by neutron diffraction (§1.1) and by measuring the X-ray intensities on the absolute scale. The difficulties which may be encountered by combining these techniques are discussed in §4.10.3. Only if
accurate additional information is available, attempts can be made to find better radial distribution functions from the electron density distributions.

The experimental difficulties discussed above and the strong requirements for a correct coupling of X-ray and neutron diffraction data, indicate that for small molecules even experimental deformation density distributions determined by combination of X-ray and neutron diffraction studies, can hardly compete with the theoretical ones. However, the achievable experimental accuracy is such, that density analyses show good prospects for the study of more complicated systems for which only inaccurate or even conflicting theoretical density distributions are available.

1.7. References