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Single-Crystal Structures and Electron Density Distributions of Ethane, Ethylene and Acetylene.

III.* Single-Crystal X-ray Structure Determination of Ethylene at 85 K

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Abstract

Crystalline C_2H_4 at 85 K is monoclinic, $a = 4\cdot626$ (1), $b = 6\cdot620$ (2), $c = 4\cdot067$ (2) Å, $\beta = 94\cdot39$ (2)°, space group $P2_1/n$, $Z = 2$. The intensities of all reflexions with $\sin\theta/\lambda < 1\cdot07$ Å^{-1} were measured at two ψ values on a Nonius four-circle diffractometer. A valence analysis with multipole deformation terms up to octopole on C and up to quadrupole on H has been performed by anisotropic least-squares refinement on I, including extinction, on the 1295 independent reflexion intensities. Both ζ and SCF scattering factors were considered. The position of H was constrained to that of C. $R_w(I;\zeta) = 0\cdot0231$ and $R_w(I;{}^3P) = 0\cdot0243$ for 38 and 35 independent variables respectively; $\overline{u^2}(C) = 0\cdot036$ Å^2, $(\overline{\varphi^2})^{1/2} = 8°$ for the axis perpendicular to C=C and in the molecular plane. The dipole at H is found to lie along the C–H bond. Although less pronounced, correlation effects as discussed for C_2H_2 [van Nes & van Bolhuis (1979). *Acta Cryst.* B**35**, 2580–2593] still occur. All Fourier maps are based on the reflexions with $I > 0$. Inclusion of monopole terms in the filtered deformation density map is prevented by the correlation between the radial parameters (including the scale). Apart from the omitted monopole deformations the agreement between theory and experiment is satisfactory.

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[*] Part II: van Nes & van Bolhuis (1979).

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1. Introduction

The present paper is the third in the series of papers describing structure determinations of the small hydrocarbons C_2H_6 (van Nes & Vos, 1978; hereafter NV), C_2H_2 (van Nes & van Bolhuis, 1979; hereafter NB) and C_2H_4. A preliminary note on the structure determination of C_2H_4 has been published previously (van Nes & Vos, 1977).

The data set for C_2H_6 was not extremely accurate because of twinning of the crystals (NV) and for the cubic modification of C_2H_2 the data set did not extend beyond $\sin\theta/\lambda = 0{\cdot}80$ Å^{-1}, because of the large thermal motion of the molecules (NB). For C_2H_4, good crystals could be obtained and the thermal motion is appreciably smaller than for C_2H_2.

In the present paper an analysis of the electron density distribution of C_2H_4 is given in terms of multipoles with a restricted radial basis set according to Stewart (1976), with both ζ (STO) and ^3P (SCF) scattering factors (for nomenclature, see NB). Higher cumulants to account for the non-linearity of the librational motion have not been applied because the influence of these terms turned out to be negligibly small for C_2H_2.

2. Earlier structural work on ethylene

In the literature different structures have been proposed for C_2H_4.

(1) An orthorhombic structure with $a = 4{\cdot}9$, $b = 6{\cdot}5$, $c = 4{\cdot}1$ Å, space group $P2_1/n\ 2_1/n\ 2/m$, $Z = 2$. Molecular centres at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, C=C in the *ab* plane at an angle of about 36° to **a**, and C_2H_4 plane perpendicular to the *ab* plane. These data were deduced by Bunn (1944) from X-ray powder data of Mooy (1931) and X-ray single-crystal film data of Keesom & Taconis (1935). The above structure is in conflict with the earlier optical study of Wahl (1913), who reported that crystalline C_2H_4 is moderately doubly refracting and monoclinic.

(2) A monoclinic structure in the subgroup $P1\ 2_1/n\ 1$ with $\beta \simeq 90°$, the so-called '*b* structure' as the 2_1 axis is parallel to **b**. In this structure the symmetry is reduced from orthorhombic to monoclinic by a rotation of the two equivalent molecules in opposite directions by 27° around their C=C axes. The reduction in symmetry is required to interpret the IR data of Brecher & Halford (1961).

(3) A monoclinic structure in the subgroup $P2_1/n\ 1\ 1$, the so-called '*a* structure'. In this case the rotation around C=C has the same sense for the two equivalent molecules. Also this structure has the correct symmetry for the IR data (Dows, 1962).

Lattice-dynamical calculations to interpret IR and Raman frequencies and energy-minimization procedures either have been in favour of the *a* structure (Dows, 1962; Vovelle & Dumas, 1975) or the *b* structure (Elliott & Leroi, 1973) or could not distinguish between these two structures (Brith & Ron, 1969; Taddei & Giglio, 1970). Both the present X-ray study (see also van Nes & Vos, 1977) and the neutron diffraction studies of Ligthart (1975) and Press & Eckert (1976) have shown the *b* structure to be correct. The C=C bond makes a small angle with the *ab* plane in agreement with the energy calculations of Elliott & Leroi (1973).

In addition to its monoclinic form, C_2H_4 has a cubic plastic modification at pressures above 474 atm ($4{\cdot}79 \times 10^7$ Pa) (Trappeniers & Ligthart, 1973), space group $Im3m$, $Z = 2$ (Press & Eckert, 1976). There is a structural analogy between C_2H_4 and C_2H_6 (NV): both compounds have a plastic cubic phase with space group $Im3m$ and a monoclinic form with space group $P2_1/n$ with analogous arrangements of the C—C bonds.

3. Crystal growth

For our experiments, ethylene gas commercially available from the Matheson Company with a quoted purity $> 99{\cdot}5\%$ was used. The crystal-growth technique and equipment used were as described by van Nes & van Bolhuis (1978) and were applied previously for C_2H_6 and C_2H_2. For C_2H_4 good single crystals were obtained as follows: the liquid was solidified rapidly at temperatures below the freezing point of about 92 K (the melting point of C_2H_4 is 104 K). After the solid was heated to about 95 K, the capillary was drawn slowly out of the N_2 stream until one seed crystal was left [method (*a*), van Nes & van Bolhuis, 1978]. From this seed crystal, a single crystal ($\varnothing = 0{\cdot}58 \pm 0{\cdot}02$ mm) with a mosaic spread $m < 0{\cdot}2°$ was grown at 95 K within a few minutes by slowly moving the capillary back into the N_2 stream. As observed for acetylene, subsequent cooling increased the mosaic spread. In the present case, cooling to 85 K increased *m* anisotropically to about 0·3–0·4°. The crystal did not show significant changes during the 15 d required for the intensity measurement.

4. Data collection

Equipment and measuring techniques are as for the C_2H_6 and C_2H_2 work. Cell dimensions were deter-

Table 1. *Crystallographic data for monoclinic* C_2H_4

Space group $P1\ 2_1/n\ 1$
At 100 K: $a = 4{\cdot}669\ (2)$, $b = 6{\cdot}628\ (4)$, $c = 4{\cdot}101\ (2)$ Å, $\beta = 94{\cdot}34\ (4)°$
At 85 K: $a = 4{\cdot}626\ (1)$, $b = 6{\cdot}620\ (2)$, $c = 4{\cdot}067\ (2)$ Å, $\beta = 94{\cdot}39\ (2)°$; $D_x = 0{\cdot}750$ Mg m^{-3} for $Z = 2$

mined at 100 K from the θ, φ, ω and κ values of one set of 24 reflexions (Table 1). At the temperature of the intensity measurement (85 K) six sets of 24 reflexions were used.

At 85 K, 10 946 reflexion intensities (including systematically absent reflexions, full reciprocal space and 2 ψ values for each hkl) were collected up to $\sin\theta/\lambda = 1{\cdot}07$ Å^{-1}, scan range $(0{\cdot}80 + 1{\cdot}00\tan\theta)^\circ$ plus 25% background region on both sides, slit width 1·32°. A correction of ± 1·0%, deduced from the variations of a set of four reference reflexions (measured every 30 min), was made to account for changes in intensity of the primary beam and/or possible changes in the reflecting power of the crystal. The reflexion symmetry $I(hkl) = I(h\bar{k}l)$ and the systematic extinctions $h0l$ with $h+l = 2n+1$ and $0k0$ with $k = 2n+1$ indicated space group $P2_1/n$.

For each set $\mathbf{H}$ of equivalent reflexions $\mathbf{H}_i$ average intensities $I(\mathbf{H})$ were calculated. Ten reflexions with $|I(\mathbf{H}_i)-\bar{I}(\mathbf{H})| > 5\sigma_c[I(\mathbf{H}_i)]$ were removed from the list. From the remaining list 1295 independent $\bar{I}(\mathbf{H})$ values were deduced which were considered as the $I_o(\mathbf{H})$ values of the independent reflexions. As described for C_2H_2, the standard deviations in $I_o(\mathbf{H})$ and in the corresponding $|F_o(\mathbf{H})|$ values were obtained from the variation in the intensities $I_o(\mathbf{H}_i)$. The internal consistency factor

$$R(I) = \left\{\sum_{\mathbf{H},i} [I(\mathbf{H}_i) - \bar{I}_o(\mathbf{H})]^2 / \sum_{\mathbf{H},i} I^2(\mathbf{H}_i)\right\}^{1/2} = 0{\cdot}034.$$

The set of independent reflexions contains 805 reflexions with $I_o(\mathbf{H}) > 3\sigma[I_o(\mathbf{H})]$ and 145 reflexions with $I_o(\mathbf{H}) \le 0$. For the 251 reflexions with $1{\cdot}00 < \sin\theta/\lambda < 1{\cdot}07$ Å^{-1} these numbers are 39 and 68 respectively, showing that significant reflexion intensities still occur in this high-order region.

5. Description of the structure

The crystallographic data are given in Table 1. From the table we see that a and c depend on the temperature. The packing of the molecules is shown in Fig. 1 (*ORTEP*; Johnson, 1970). The two molecules in the cell lie at the inversion centres (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The intermolecular distances have been calculated by use of the molecular geometry found by Duncan (1974) for molecules in the gas phase (Table 5*d*). The direction of C=C, the orientation of the plane of the molecule and the thermal parameters are taken from model A in Table 6 (ζ multipole refinement, § 7.2). The C=C bond makes an angle of 14·6° with the ab plane. None of the intermolecular distances in Table 2 is shorter than the sum of the relevant van der Waals radii ($r_C = 1{\cdot}7$, $r_H = 1{\cdot}2$ Å). For the three compounds C_2H_2, C_2H_4 and C_2H_6, C···H is shortest in C_2H_2, C···C in C_2H_4 and H···H in C_2H_6. The intermolecular distances show that all three compounds are packed quite loosely. The average thermal motion $\overline{u^2}(C)$ is 0·036 Å^2 for C_2H_4 and 0·051 Å^2 for C_2H_2 (ζ multipole refinements). The average librational motion $(\overline{\varphi^2})^{1/2}$ around axes perpendicular to C—C is about 8° for both C_2H_4 and C_2H_2

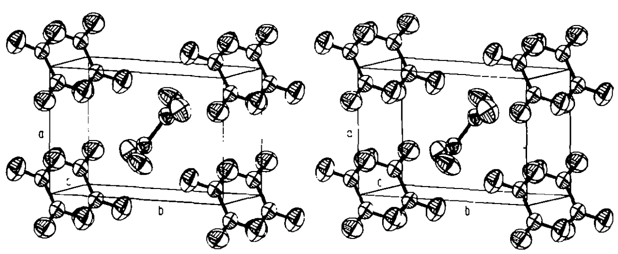


Fig. 1. Stereoview of the packing of the molecules in the monoclinic phase of C_2H_4. Thermal ellipsoids (refinement A, Table 6) are drawn at the 50% probability level.

Table 2. *Short non-bonding distances* (Å) *in* C_2H_4

Distances shorter than the sum of the relevant van der Waals radii [r(C) = 1·7, r(H) = 1·2 Å (Pauling, 1960)] plus 0·4 Å are listed for the structure of model A (Table 6) in which the bond lengths and angles for the molecule in the gas phase (Duncan, 1974) were taken. Standard deviations are of the order of 0·001 Å.

Symmetry code for atom A
$A(n,\mathrm{i}) \equiv A(n; x, y, z)$
$A(n',\mathrm{i}) \equiv A(n; \bar{x}, \bar{y}, \bar{z})$
$A(n,\mathrm{ii}) \equiv A(n; x-1, y, z)$
$A(n,\mathrm{iii}) \equiv A(n; x, y, z+1)$
$A(n,\mathrm{iv}) \equiv A(n; x+\frac{1}{2}, \frac{1}{2}-y, z+\frac{1}{2})$
$A(n,\mathrm{v}) \equiv A(n; x+\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$
$A(n,\mathrm{vi}) \equiv A(n; x-\frac{1}{2}, -\frac{1}{2}-y, z+\frac{1}{2})$
$A(n,\mathrm{vii}) \equiv A(n; x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2})$

C(1,i)—C(1′,ii)	3·642	C(1,i)—H(2′,vii)	3·263
C(1,i)—H(1,v)	3·088	H(1,i)—H(2,iii)	2·720
C(1,i)—H(1′,vi)	3·216	H(1,i)—H(2,iv)	2·834
C(1,i)—H(2,iii)	3·249	H(1,i)—H(2′,vii)	2·725
C(1,i)—H(2′,ii)	3·311		

6. Conventional high-order and full-angle refinements

For the conventional spherical refinements of the structure the 'spherical part' of the program *VALRAY* (Stewart, 1974) has been used. The Q functions, the residuals R and the goodness of fit are defined in NB. High-order (HO) I refinements have been carried out for $\sin\theta/\lambda$ ranges given by $(0{\cdot}60 + 0{\cdot}05n) < \sin\theta/\lambda < 1{\cdot}07$ Å^{-1}, with n = 0–4. Both fixed ζ and ^3P scattering-factor curves were considered for these conventional HO refinements. As preliminary refinements showed that inclusion of H atoms did not affect the parameters of C, all further HO refinements were performed with C atoms only. The results are as follows; for the same $\sin\theta/\lambda$ range, the positional parameters do not change when ζ varies between 1·53 and 1·70 or by intro-

Table 3. *Results for a high-order* (sin $\theta/\lambda > 0{\cdot}60$ Å^{-1}) *conventional refinement including* C *only with scattering factor* $f(\mathrm{C},{}^3P)$

Fractional coordinates and thermal parameters (Å^2) are multiplied by 10^5. For nomenclature see NB.

x(C)	−11642 (3)	$R_w(I)$	0·041
y(C)	5393 (2)	GOF	1·92
z(C)	−4119 (4)	N_o	1077
U_{11}(C)	3913 (8)	N_v	10
U_{22}(C)	3378 (9)		
U_{33}(C)	3726 (9)	K	22·86 (7)
U_{12}(C)	282 (6)	$\langle\rho(U_{ii},K)\rangle_i$	0·88
U_{13}(C)	589 (4)	$\langle\rho(U_{ii},U_{jj})\rangle_{i\neq j}$	0·72
U_{23}(C)	84 (6)	C=C (Å)	1·3142 (3)

duction of the ^3P scattering factor. The temperature-factor parameters hardly depend on ζ, but $U_{ii}(^3P)$ is slightly larger than $U_{ii}(\zeta)$ (about 1·5% for $\zeta = 1{\cdot}70$). Such a trend can be expected from the scattering-factor curves shown in Fig. 3 of NB. Further HO results are given for the ^3P refinements only.

The final data for the I refinement with $n = 0$ (sin $\theta/\lambda > 0{\cdot}60$ Å^{-1}) are listed in Table 3. By analogy to C_2H_2, the present HO refinements show considerable correlation between scale and average temperature-factor parameter, and a dependence of some of the parameters on the sin θ/λ range considered. The scale factor varies by about 3%, whereas for $n = 0$ to $n = 3$, $|z(\mathrm{C})|$ increases from 0·1675 (2) to 0·1701 (3) Å and C=C from 1·3142 (3) to 1·3180 (5) Å. The x(C) and y(C) parameters are reasonably stable. No reason could be found for the changes in the coordinates. It should be noted, however, that the very high-order reflexions do not contribute much to the least-squares refinement with sin $\theta/\lambda > 0{\cdot}60$ Å^{-1} or to a full-angle refinement, because of their relatively weak intensities. This implies that parameters giving the best adjustment for a refinement based on very high-order reflexions only may not be optimal for the complete reflexion set.

In order to compare the results of I and $|F|$ refinements, full-angle conventional refinements were performed with $f(\mathrm{C},{}^3P)$ for C and f(H,pol) for H. Just as in the C_2H_2 case, no parameter differences occur between weighted I and $|F|$ refinements, but changes are induced by taking $w[|F_o(\mathrm{H})|] = 1$ in the $|F|$ refinements. Values for the residuals are $R_w(I) = 0{\cdot}075$, $R_w(|F|) = 0{\cdot}038$ and $R(|F|, w = 1) = 0{\cdot}044$.

7. Multipole refinements

7.1. *General*

The multipole refinements for C_2H_4 are set up analogously to those for C_2H_2, apart from the fact that third and fourth cumulant terms have been neglected. All multipole refinements were carried out on I. Scattering factors with fixed ζ values were not considered. As no reliable neutron parameters are available, it was decided to constrain the positions of H to those of C (no constraints were used for the ζ values or the temperature factors of H). To this end use was made of the geometry observed by Duncan (1974) for the molecule in the gas phase. As distortions due to intermolecular interactions may be assumed to be small for the present van der Waals crystal, the symmetry *mmm* observed in the gas phase was adopted for the molecules in the crystal, for calculating both the constraints for the H atoms and the multipole populations.

Multipoles and reference frame

The multipole functions applicable for *mm*2 symmetry at C are listed in Table 4, where multipole functions consistent with local symmetry $\bar{6}m2$ at C (C=C and C–H bonds assumed to be equivalent) are indicated by an asterisk.

In the program *VALRAY* [(Stewart, 1974), extended by van der Wal (1978)], all multipole functions are referred to a single Cartesian reference frame. The picture in Table 5(*a*) gives the location of the frame used relative to the molecule. To find its orientation in the crystal a preliminary full-angle least-squares multipole refinement with multipoles up to hexadecapole on C and up to dipole on H was carried out with a fixed dipole moment and variable position for H. In the final stages of the refinement with H constrained to C (see Table 6 for parameters used), a slight readjustment of the orientation appeared to be necessary. The final orientation of the frame in the crystal is given in Table 5(*a*).

Table 4. *Multipole functions up to octopole, used for* C_2H_4 (*symmetry mm*2 *assumed*)

For nomenclature see NB. q_x, q_y and q_z give the direction cosines of the Bragg vector with respect to the reference frame **X,Y,Z** defined in Table 5(*a*).

(*a*) Functions for C

$C(1,0)\mathrm{Pop}(1,0)P_1^0(\cos\theta) = 4 \times \mathrm{Pop}(1,0) \times q_z$

$^*C(2,0)\mathrm{Pop}(2,0)P_2^0(\cos\theta) = 3\sqrt{3} \times \mathrm{Pop}(2,0) \times 3(q_z^2 - \tfrac{1}{3})/2$

$C(2,2)\mathrm{Pop}(2,2)P_2^2(\cos\theta)\cos 2\varphi = \pi/2 \times \mathrm{Pop}(2,2) \times 3(q_x^2 - q_y^2)$

$^*C(3,0)\mathrm{Pop}(3,0)P_3^0(\cos\theta) = 40/7 \times \mathrm{Pop}(3,0) \times (5q_z^2 - 3)q_z/2$

$C(3,2)\mathrm{Pop}(3,2)P_3^2(\cos\theta)\cos 2\varphi = 4\pi/15 \times \mathrm{Pop}(3,2) \times 15(q_x^2 - q_y^2)q_z$

(*b*) Functions for H

$C(1,0)\mathrm{Pop}(1,0)P_1^0(\cos\theta) = 4 \times \mathrm{Pop}(1,0) \times q_z$

$C(1,1)\mathrm{Pop}(1,1)P_1^1(\cos\theta)\cos\varphi = 4 \times \mathrm{Pop}(1,1) \times q_x$

$C(2,0)\mathrm{Pop}(2,0)P_2^0(\cos\theta) = 3\sqrt{3} \times \mathrm{Pop}(2,0) \times 3(q_z^2 - \tfrac{1}{3})/2$

$C(2,1)\mathrm{Pop}(2,1)P_2^1(\cos\theta)\cos\varphi = \pi \times \mathrm{Pop}(2,1) \times 3(q_xq_z)$

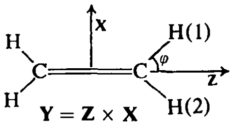
$C(2,2)\mathrm{Pop}(2,2)P_2^2(\cos\theta)\cos 2\varphi = \pi/2 \times \mathrm{Pop}(2,2) \times 3(q_x^2 - q_y^2)$

* C multipole functions applicable for local symmetry $\bar{6}m2$.

Table 5. *Reference frame* **X,Y,Z**, *internal and external motions, and geometry of* C_2H_4

(*a*) Choice of reference frame **X,Y,Z** and its orientation (given as direction cosines, × 10^4), with respect to the crystal system

	a	**b**	**c**
X	759	5098	8486
Y	5931	6678	−4939
Z	−8016	5423	−1896



(*b*) **U**(int.) (10^{-4} Å^2) for C and H in C_2H_4, calculated from the normal frequencies in the gas, as given by Cyvin & Cyvin (1963)

	U(int., **X**)	*U*(int., **Y**)	*U*(int., **Z**)
C	5·7	6·3	5·2
H	99·3	263·9	112·4

(*c*) **T** (Å^2) and **L** (rad^2) tensors for solid C_2H_4 (molecular symmetry *mmm* assumed)

T_{xx}	0·031	L_{xx}	0·024
T_{yy}	0·025	L_{yy}	0·014
T_{zz}	0·034	L_{zz}	0·012

(*d*) Molecular geometry, symmetry *mmm*

	Gas phase (Duncan, 1974)	With librational deformations
C=C	1·3384 (10) Å	1·3130 Å
C–H	1·0870 (20)	1·071
H–C–H	117·37 (25)°	117·67°

Constraining H *to* C

Linear constraints of H to C were applied, as rigid-body refinements are not yet possible with *VALRAY* (Stewart, 1974). For each of the H atoms **r**(H) − **r**(C) was calculated first by making use of the position of C and the orientation of the molecular plane found in the preliminary multipole refinement (see above), and of the geometry observed by Duncan (1974) (Table 5*d*). Deformations in the model resulting from libration were taken into account. The libration tensor was found from the shortening of C=C and analysis of the thermal parameters. In this analysis, internal vibrations (Table 5*b*) were subtracted and *mmm* symmetry was assumed. Towards the end of the refinement the analysis was repeated on the basis of the average parameter values for the ^3P and ζ refinements (§ 7.2). The final values for the **T** and **L** tensors and the model as deformed by libration are given in Table 5.

7.2. *Refinements with adjustable-*ζ *and SCF scattering factors*

As preliminary ζ refinements indicated a significant extinction effect, in all further refinements extinction corrections were carried out according to Zachariasen (1967, 1968) with sin θ corrections as given by Becker & Coppens (1974). By restricting the symmetry to $\bar{6}m2$

Table 6. *Final parameter results of refinements with* (*variable*) ζ *and* ^3P *scattering vectors, given as A and B, respectively*

Numbers in parentheses are the estimated standard deviations in the last digits; constrained parameters are indicated with a hyphen between parentheses. Fractional coordinates and thermal parameters (Å^2) are multiplied by 10^5 for C and by 10^4 for H. Multipoles for C are defined in the **X,Y,Z** reference frame (Table 5*a*), and for H in a local $\mathbf{x}_H,\mathbf{y}_H,\mathbf{z}_H$ frame, obtained by rotating **X,Y,Z** around **Y** over an angle φ (see Table 5*a*).

	C		H(1)		H(2)	
	A	*B*	*A*	*B*	*A*	*B*
ζ	1·692 (8)		1·026 (22)		0·986 (19)	
x	−11656 (4)	−11646 (3)	−1869 (–)	−1868 (–)	−2430 (–)	−2429 (–)
y	5382 (2)	5375 (2)	1698 (–)	1697 (–)	287 (–)	286 (–)
z	−4075 (3)	−4072 (3)	1185 (–)	1186 (–)	−2689 (–)	−2688 (–)
U_{11}	3804 (9)	3912 (7)	750 (29)	842 (21)	608 (26)	764 (25)
U_{22}	3318 (8)	3426 (6)	577 (28)	647 (31)	804 (30)	938 (21)
U_{33}	3647 (9)	3779 (8)	685 (28)	695 (36)	601 (28)	682 (48)
U_{12}	340 (6)	324 (6)	162 (15)	115 (31)	142 (15)	103 (32)
U_{13}	555 (3)	577 (4)	150 (13)	150 (32)	−215 (16)	−192 (35)
U_{23}	54 (6)	79 (6)	−143 (15)	−172 (35)	−150 (16)	−196 (36)
Pop(core)	2·00 (–)	2·00 (–)				
Pop(0,0)	3·63 (4)	4·30 (3)	1·22 (3)	1·05 (2)	1·22 (–)	1·05 (–)
Pop(1,0)	−0·092 (6)	−0·076 (10)	−0·232 (13)	−0·352 (29)	−0·232 (–)	−0·352 (–)
Pop(1,1)			−0·007 (1)	−0·002 (1)	0·007 (–)	0·002 (–)
Pop(2,0)	0·146 (4)	0·168 (5)	0·098 (9)	0·523 (142)	0·098 (–)	0·523 (–)
Pop(2,1)			0·006 (4)	0·225 (89)	−0·006 (–)	−0·225 (–)
Pop(2,2)	0·095 (6)	0·072 (8)	−0·013 (2)	−0·183 (35)	−0·013 (–)	−0·183 (–)
Pop(3,0)	0·142 (5)	0·133 (4)				
Pop(3,2)	−0·145 (3)	−0·118 (3)				

at C, the $R_w(I)$ value for the ζ refinements did not decrease below 0·0285 for multipoles up to hexadecapole on C, and up to quadrupole on H. A considerable decrease in $R_w(I)$ to 0·0230 was obtained by lowering the symmetry to $mm2$. Further ζ refinements for symmetry $mm2$ showed that omission of hexadecapoles on C did not affect $R_w(I)$ significantly, but that omission of quadrupoles on H increased $R_w(I)$ to 0·0244. Therefore, the ζ refinement for symmetry $mm2$, with multipoles up to octopole on C and up to quadrupole on H, is considered as the final ζ refinement.[*] Results are given as refinement A in Tables 6 and 7. Refinement A was repeated with the same set of variables, but with $f(\mathrm{C},{}^3P)$ instead of $f(\mathrm{C},\zeta)$ for C, and $f(\mathrm{H,pol})$ instead of $f(\mathrm{H},\zeta)$ for H. Results are given as refinement B in Tables 6 and 7.

The refinement results are similar to those observed for C_2H_2:

(1) Rather high correlation (Table 7) is still present, although the reflexion set of C_2H_4 extends much further than that for C_2H_2. The correlation between the radial parameters especially (including the scale) is large.

(2) For ${}^3P$, the extinction correction is higher than for ζ. Part of this correction, however, has to be considered as a modification of $f(\mathrm{C},{}^3P)$.

(3) For ${}^3P$ the sum of the monopole populations (8·4) for a CH_2 unit exceeds the number of electrons; this is hardly the case for ζ.

(4) The scale factor $K(\zeta) = 22{\cdot}40$ is considerably lower than $K({}^3P) = 23{\cdot}17$. In the high-order region nearly equal values are obtained, however, for $K \times f(\mathrm{C})$, in which $f(\mathrm{C})$ includes thermal motion and core and refined valence populations. The product is, for instance, 12·16 for the ζ and 12·09 for the ${}^3P$ refinement for $\sin\theta/\lambda = 0{\cdot}75$ Å^{-1}.

Table 7. *Data from refinements A and B in Table 5*

Correlation coefficients $\rho(a,b)$ with $a \neq b$ larger than 0·80 are given.

	$R_w(I)$	GOF	K	y(ext.)*	C=C
A	0·0231	2·00	22·41 (6)	0·86	1·3137 (3)
B	0·0243	2·10	23·14 (4)	0·81	1·3124 (3)

a,b	A	B	a,b	A	B
$K, U_{22}(\mathrm{C})$	0·91	0·83	$P_1^1(\mathrm{H}), P_1^0(\mathrm{H})$	0·86	0·81
$K, U_{33}(\mathrm{C})$	0·82	0·83	$P_1^1(\mathrm{H}), P_0^0(\mathrm{H})$	−0·83	−0·93
$P_0^0(\mathrm{H}), P_1^0(\mathrm{H})$	−0·80	−0·89	$P_1^1(\mathrm{H}), P_1^0(\mathrm{C})$	0·83	0·95

a,b	A	a,b	A	a,b	A
$K, U_{11}(\mathrm{C})$	0·85	$P_0^0(\mathrm{H}), \zeta(\mathrm{H}_1)$	−0·85	$\zeta(\mathrm{H}_1), U_{11}(\mathrm{H}_1)$	0·87
$K, \zeta(\mathrm{C})$	−0·81	$P_0^0(\mathrm{H}), \zeta(\mathrm{H}_2)$	−0·80	$\zeta(\mathrm{H}_1), U_{22}(\mathrm{H}_1)$	0·83
$P_0^0(\mathrm{C}), \zeta(\mathrm{C})$	−0·88	$U_{22}(\mathrm{H}_2), \zeta(\mathrm{H}_2)$	0·81		
$P_1^0(\mathrm{C}), x(\mathrm{C})$	0·81	$\zeta(\mathrm{H}_1), \zeta(\mathrm{H}_2)$	0·86		

a,b	B	a,b	B	a,b	B
$P_0^0(\mathrm{H}), P_1^0(\mathrm{C})$	−0·91	$U_{33}(\mathrm{H}_2), P_1^0(\mathrm{C})$	−0·86	$U_{23}(\mathrm{H}_2), P_2^2(\mathrm{H})$	−0·84
$P_0^0(\mathrm{H}), P_2^2(\mathrm{C})$	−0·85	$U_{33}(\mathrm{H}_2), P_0^0(\mathrm{H})$	0·80	$U_{23}(\mathrm{H}_2), U_{33}(\mathrm{H}_1)$	0·81
$P_1^0(\mathrm{H}), P_2^2(\mathrm{C})$	0·87	$U_{33}(\mathrm{H}_2), P_1^1(\mathrm{H})$	−0·91	$P_1^0(\mathrm{H}), U_{13}(\mathrm{H}_2)$	−0·84
$P_1^1(\mathrm{H}), P_0^0(\mathrm{C})$	0·86	$U_{33}(\mathrm{H}_2), U_{23}(\mathrm{H}_1)$	0·86	$P_2^0(\mathrm{H}), U_{12}(\mathrm{H}_2)$	0·84
		$P_1^1(\mathrm{H}), U_{23}(\mathrm{H}_1)$	−0·87	$P_2^1(\mathrm{H}), U_{13}(\mathrm{H}_1)$	0·83

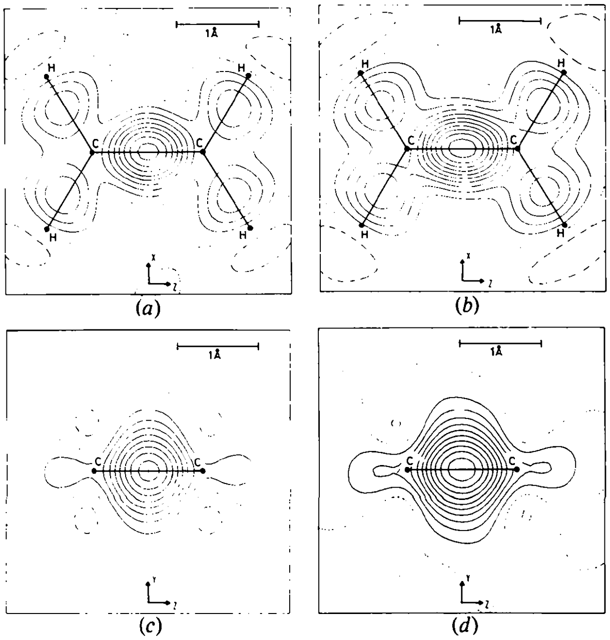
* Extinction parameter for reflexion 011, defined as $I_c^{\mathrm{ext}} = I_c y$.

8. Electron density distributions

8.1. *Experimental densities*

Correlations between radial parameters as discussed for C_2H_2 (NB, § 7) have also been observed for C_2H_4. Because of the resulting errors in the monopole deformations (NB, § 8.3) it was decided to omit these from the deformation maps. Therefore, again the three types of maps used for C_2H_2 have been calculated for the ζ and ${}^3P$ refinements of C_2H_4 (Table 6). Only reflections with $I_o(\mathrm{H}) > 0$ were taken into account (see NB).

(1) Residual density distributions $D_f(r)$ based on amplitudes $[K^{-1}F_o - F_c(\text{final model})]$. With the formula $\sigma(D_f) = V^{-1}\{\sum_{\mathrm{H}}[K^{-1}F_o - F_c(\text{final model})]^2\}^{1/2}$, the standard deviation is estimated at 0·02 e Å^{-3} for general positions, and 0·03 e Å^{-3} at the inversion centre. The $D_f(\mathbf{r})$ maps are flat within $3\sigma(D_f)$ apart from a minimum and a maximum of *ca* $5\sigma(D_f)$ close to the C atom. The slope at C corresponds to the variation in the z(C) parameter observed during the high-order refinements (§ 6). It shows up in the $D_f(\mathbf{r})$ maps be-



(*a*) (*b*)

(*c*) (*d*)

Fig. 2. Filtered deformation density distributions $D_{fl}(\mathbf{r})$. Shown are sections through the molecular plane (*a* and *b*), and sections perpendicular to the molecular plane and through C=C (*c* and *d*), (*a*) and (*c*) from ${}^3P$ refinement (B in Table 6), (*b*) and (*d*) from ζ refinement (A in Table 6). Contours in this and following figures are at intervals of 0·05 e Å^{-3}. Full lines are positive, dotted lines zero and long-dashed lines negative contours.

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34534 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cause, for the very high-order reflexions, w(Fourier) = 1 is much too high in comparison with their accuracy.

(2) Deformation density distributions $D(\mathbf{r})$ based on amplitudes $[K^{-1}F_o - F_c(\text{monopole})]$ where F_c(monopole) includes both the core and valence monopole populations of Table 6. These maps are not given as they do not show systematic features in addition to those revealed by the filtered deformation density maps discussed below and the $5\sigma(D_f)$ peaks discussed above.

(3) Filtered deformation density distributions $D_{\rm fi}(\mathbf{r})$ based on amplitudes $[F_c(\text{final model}) - F_c(\text{monopole})]$. As for C_2H_2 the two F_c values are based on parameters, including the radial functions, of the same refinement. Sections of the $D_{\rm fi}(\mathbf{r})$ maps are given in Fig. 2. The ^3P maps closely obey the $mm2$ symmetry around C. For the ζ maps, small deviations from this symmetry are observed due to (small) differences between the ζ values and between the thermal parameters of the two H atoms (Table 6). In spite of the use of multipole functions only, the density around C is not equal to zero. This must be ascribed mainly to the contributions of multipole functions centred at neighbouring atoms and to a minor extent to the anisotropy of the thermal motion.

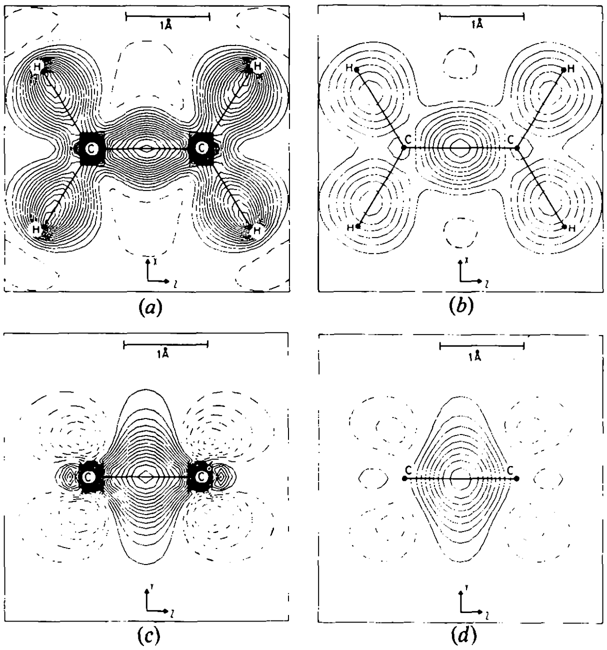

Fig. 3. Static (a and c) and dynamic (b and d) theoretical deformation densities for C_2H_4. Given are sections through the molecular plane (a and b), and perpendicular to the plane and through C=C (c and d).

8.2. *Theoretical densities*

The static and dynamic density distributions for the C_2H_4 molecule and for the free-atom model were calculated analogously and with the same basis functions as for C_2H_2. For the molecular geometry, the bond lengths and angles observed by Duncan (1974) for molecules in the gas phase (Table 5d) were taken. The thermal parameters used for the smearing of the static density were obtained, with the assumption of mmm symmetry, from the average values of corresponding thermal parameters of the ζ and ^3P refinements (Table 6). Because of restrictions of the program *BEDGOLV* (Ruysink & Vos, 1974), only displacements along **X**, **Y** and **Z** (see Table 5a) could be considered, without coupling between the displacements in the different directions. The molecule as a whole was given a translation corresponding to $T_{ii} = U_{ii}(\text{C})$, i = 1, 2 and 3 for **X**, **Y** and **Z** respectively. The remaining U values of H, given by $\Delta U_{ii}(\text{H}) = U_{ii}(\text{H}) - U_{ii}(\text{C})$, were accounted for as uncoupled vibrations. Fig. 3 shows two sections of both the static and dynamic theoretical deformation density distribution $D_{\rm th}(\mathbf{r}) = \rho_{\rm th}^{\rm mol}(\mathbf{r}) - \rho_{\rm th}^{\rm atom}(\mathbf{r})$.

9. Discussion

9.1. *ζ values and gross populations*

The ζ values of refinement A may be compared with the values $\zeta(\text{C}) = 1{\cdot}70$, $\zeta(\text{H}) = 1{\cdot}22$ obtained for C_2H_4 by energy minimization (Hehre, Stewart & Pople, 1969), and with the values $\zeta(\text{C}) = 1{\cdot}52$, $\zeta(\text{H}) = 1{\cdot}12$ obtained by adjustment of molecular 'ζ density distributions' to SCF density distributions (Bentley & Stewart, 1976). For C the refined ζ(C) lies close to the energy-optimized value, whereas for H the best agreement is obtained with the density-optimized value.

For both types of refinement the trend of $P(\text{H/C}) = P(\text{monopoles,H})/P(\text{monopoles,C})$ observed for C_2H_2 and C_2H_4 follows the theoretical trend (Clementi & Popkie, 1972). The values are:

	$P(\text{H/C};^3P)$	$P(\text{H/C};\zeta)$	P(H/C;theory)
C_2H_4	0·167	0·217	0·165
C_2H_2	0·129	0·188	0·138.

The two sets of radial functions give strongly different P(H/C) values, however, showing that population parameters are not observables, but depend on the radial functions used. The relatively high H populations for the ζ refinements are connected to the fact that, in comparison with the density-optimized values, the ζ(H) values are too small and the ζ(C) values too high [C_2H_2: $\zeta(\text{H}) = 0{\cdot}92$ (3), $\zeta(\text{C}) = 1{\cdot}69$ (1); C_2H_4: $\zeta(\text{H}) = 1{\cdot}00$ (1), $\zeta(\text{C}) = 1{\cdot}69$ (1)]. For the present ζ refinements the contraction expected for an H atom in a molecule thus does not result in an increase in ζ, but in an increase of the H monopole population.

9.2. *Dipoles and quadrupoles on* H

In Table 6, the dipoles and quadrupoles on H are given in a local axial frame with $\mathbf{z}_H$ along C—H. The table shows that both for the ζ and the ^3P refinement, the dipole component perpendicular to C—H is, as should be expected, considerably smaller than along C—H. For the ^3P refinement, the perpendicular component is zero within the experimental error. The dipole moment corresponds to a transfer of electrons from the H atom to the inner side of the C—H bond. For the ζ refinement, the major component of the quadrupole moment lies along C—H. This multipole describes a transfer of electrons from a plane perpendicular to C—H to the C—H axis. For the ^3P refinement, the standard deviations of the quadrupole components are high, evidently due to a relatively high correlation with the thermal parameters which also have high standard deviations (Tables 6 and 7). From the above discussion, it can be concluded that at the H atom the C—H bond has rotational symmetry in good approximation.

9.3. *Comparison of experimental and theoretical densities*

The experimental C_2H_4 densities in Figs. 2 and 4 do not contain the monopole deformations and therefore do not represent the complete bonding effects, especially at the atomic positions. In C_2H_2 good agreement between theory and experiment (without monopole deformations) was obtained by replacing the diffuse SCF H atoms in $\rho_{\rm th}^{\rm atoms}(\mathbf{r})$ in the formula $D_{\rm th}(\mathbf{r}) = \rho_{\rm th}^{\rm mol}(\mathbf{r}) - \rho_{\rm th}^{\rm atoms}(\mathbf{r})$ by polarized H atoms with the scattering factor f(H,pol) (NB, § 6.3). In the present case this replacement reduces $D_{\rm th}(\mathbf{r})$ at the H position by 0·09 e Å^{-3} to 0·11 e Å^{-3}. This is still higher than the value 0·04 e Å^{-3} in the experimental maps of Fig. 2. In contrast, Fig. 4 shows that for C the experimental non-monopole deformations are higher than the (total) theoretical deformation. This indicates that for C_2H_4 good agreement with theory can be obtained by adding small monopole deformations to the $D_{\rm fl}(\mathbf{r})$ maps such that electrons are transferred from C to H. Such a replacement of electrons in C_2H_4, which was not required for C_2H_2, agrees with the fact that in C_2H_4 the population of H, relative to that of C, was found to be higher than in C_2H_2 (§ 9.1). Fig. 4 shows that the average value of the ζ and ^3P bonding maximum at C=C, which will not be influenced strongly by omission of the monopole deformations, is nearly equal to the theoretical value. Comparison of Figs. 2 and 3 reveals that the theoretical and experimental non-monopole deformations are similar. In both cases at the C=C bond centre the deformation density is elongated along the **Y** direction (perpendicular to the C_2H_4 plane), whereas at a distance of about 0·4 Å along **Y** from C, a minimum is encountered. In the theoretical map the elongation of the C=C bond maximum along **Y** is more pronounced than in the theoretical map. Finally Figs. 2(*c*),(*d*) and 3(*d*) show that at the outer sides of the C=C bond the deformation density is not negative.

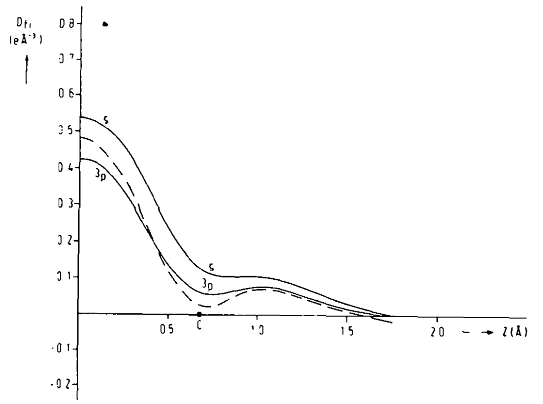

Fig. 4. Filtered deformation densities $D_{\rm fl}(Z)$ along the C=C direction of the C_2H_4 molecule, plus dynamic theoretical deformation density. Solid lines: densities from refinements *A* (ζ scattering factors) and *B* (^3P scattering factors). Dashed line: theoretical values.

Although an exact calculation of the monopole deformations has not been possible from the present C_2H_2 and C_2H_4 data, the above discussion reveals that the experimental data are able to show quantitative trends in the bonding features predicted by extensive theoretical *ab initio* calculations. A clearer picture of the bonding features may be obtained by supplementing the X-ray diffraction experiment with neutron diffraction data. In view of the difficulties which may be encountered in a combined X-ray and neutron diffraction study and in the determination of the scale factor (NB, § 9.3) it is not certain, however, whether densities with higher accuracies than the theoretical ones can be obtained for the present small molecules. On the other hand, the present study has shown that accurate density analyses by diffraction methods will give valuable information for more complicated systems for which only inaccurate or even conflicting theoretical densities are available.

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The Crystal and Molecular Structure of 3,3-Dimethyl-1,1-diphenylphosphetanium Iodide

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Abstract

$C_{17}H_{20}P^+.I^-$ is monoclinic, space group $P2_1/n$, $a = 11.264$ (1), $b = 12.276$ (3), $c = 12.193$ (3) Å, $\beta = 94.60$ (15)°, $Z = 4$. The structure was refined to $R = 0.029$ for 2529 counter reflections. The phosphetane ring is puckered with a dihedral angle of 18·6°.

Introduction

During the past decade the chemistry of the four-membered heterocycle, phosphetane, has been studied extensively (Trippett, 1970–1976). The ring constraints in this system provide a structural asset for the analysis of P stereochemistry, particularly where pseudo-rotational processes are involved (Westheimer, 1968). A ring methyl substituent *cis* or *trans* to a functional group provides a convenient probe to enable the following stereochemical changes (retention and inversion) about the P atom in chemical reactions (Trippett, 1970–1976; Cremer & Trivedi, 1969).

X-ray studies have provided confirmation of stereochemical assignments and important data on a number of phosphetane derivatives (Swank & Caughlan, 1968; Moret & Trefonas, 1969; Mazhar-ul-Haque, 1970,

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