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Systematic Errors in Structure Models obtained by X-ray Diffraction

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The bonding maxima on C–C bonds as found in a previous X-ray study of electron distributions on double and triple C–C bonds are approximately a factor of two smaller than the values expected theoretically. The present theoretical study on an ethyne model structure shows that the reduction of the maxima is mainly due to systematic errors in the structural parameters caused by the use of non-bonded atoms during the X-ray diffraction refinement. The systematic errors in the structural parameters can be kept smaller than the standard deviations obtainable for accurate X-ray work, by high-order X-ray refinement based on reflexions with $2\sin\theta/\lambda$ larger than approximately 1·4 Å^{-1}. The height of the maxima on the centres of the bonds is only slightly affected by the omission of weak or high-order reflexions from the difference synthesis.

Introduction

A recent low-temperature X-ray diffraction study of electron density distributions on double and triple C–C bonds (Helmholdt, Ruysink, Reynaers & Kemper, 1972; Ruysink & Vos, 1974*a*) has shown that the observed difference density due to chemical bonding is 0·4 e Å^{-3} on the centre of the C–C bonds. This is about a factor of two smaller than the value expected theoretically, 0·73 e Å^{-3} for ethyne molecules with a thermal motion corresponding with a temperature factor $\exp(-1\cdot07\sin^2\theta/\lambda^2)$ (Ruysink & Vos, 1974*b*). Possible sources of systematic error which might give the observed reduction are:

(*a*) Series termination, as only reflexions with $\sin\theta/\lambda < 0\cdot6$ Å^{-1} were considered in the Fourier syntheses.

(*b*) Errors in the atomic parameters caused by the assumption, usually made during structure refinements, that the model consists of spherically symmetric, non-bonded, atoms.

To check whether the errors in the electron density distribution are mainly due to (*a*) or (*b*) and to see how we can avoid them, a theoretical study has been made on an ethyne model structure. The electron density distributions used in this study are based on the wave functions described by Ruysink & Vos (1974*b*).

Scattering factors for ethyne

We have preferred to use a simple model structure of ethyne for our calculations instead of the real structure determined by Sugawara & Kanda (1952). Our model structure contains only one molecule per unit cell and the intermolecular distances have been chosen such that the electron density distributions of neighbouring molecules do not overlap. The atomic positions of this structure are given in Table 1. In the present section the atoms are assumed not to be subject to thermal motion.

Table 1. *Crystal structure adopted for ethyne*

The cell dimensions are chosen such that at each atomic nucleus the density due to neighboring molecules is smaller than 10^{-5} e Å^{-3} in the static crystal structure.

Space group	$P4/mmm$, $a=b=7\cdot0$, $c=9\cdot0$ Å.
Reflexions	1911 reflexions for $0<H<2\cdot4$ Å^{-1}
Position molecule	Along **z** with inversion centre in origin.
Atomic positions	$z(\text{C})=0\cdot6020$, $z(\text{H})=1\cdot658$ Å
Thermal motion	Rigid-body translations corresponding to $B=1\cdot07$ Å^2 or $U=B/8\pi^2=1355\cdot10^{-5}$ Å^2

The structure factor calculation is based on the well known formula

$$F(\mathbf{H})=\int[\varrho(\mathbf{r})\exp 2\pi i\mathbf{H}\,.\,\mathbf{r}]\mathrm{d}V_r \qquad (1)$$

where **r** is the position vector and $\varrho(\mathbf{r})$ the electron density distribution in the unit cell, **H** is the position vector in reciprocal space, $H=2\sin\theta/\lambda$. The static density distribution $\varrho(\mathbf{r})$ in the ethyne molecules has been calculated by the SCF method, use being made of an extended GTF basis set (Ruysink & Vos, 1974*b*). The structure factors based on this density distribution are designated by $F^0(\text{mol})$. In Fig. 1 these structure factors are compared with the values $F^0(\text{at})$ obtained for a structure consisting of non-bonded, spherically symmetric atoms with $\varrho_{\text{at}}(\mathbf{r})$ values also based on the extended GTF set. Values are given both for **H** perpendicular to **z** (lying along C–C) and **H** parallel to **z**. Fig. 2 shows the average percentage difference expressed by

$$R(\mathbf{H})=100\left[\frac{\sum[F^0(\text{mol})-F^0(\text{at})]^2}{\sum[F^0(\text{mol})]^2}\right]^{1/2}, \qquad (2)$$

the summation being over all vectors **H** with values between H and $H+dH$. It appears that even for high H values the percentage difference is appreciable. As an example some values are given for the reflexion 0,16,0 with $H=2\cdot3$ Å^{-1}, namely $F^0(\text{mol})=1\cdot9327$, $F^0(\text{mol, core})=1\cdot8785$, $F^0(\text{mol, val})=0\cdot0542$, $F^0(\text{at})=1\cdot9447$, $F^0(\text{at, core})=1\cdot8814$, $F^0(\text{at, val})=0\cdot0633$. The figures show that the contribution of the valence electrons to F^0(mol), given by F^0(mol, val), is only 3%. In spite of that, the major part (75% for the reflexion considered) of the difference between F^0(mol) and F^0(at) is caused by the valence rather than by the core electrons.

'Experimental' difference density for ethyne

An X-ray diffraction study was now simulated for the ethyne model structure of Table 1 in which the molecules are subject to isotropic thermal motion. Only rigid-body translations have been considered as it was felt that the systematic errors to be detected would hardly depend on details of the thermal motion. The thermal motion is taken into account by multiplying F^0(mol) by the temperature factor $\exp(-1\cdot07 \sin^2\theta/\lambda^2)$. The F(mol) values obtained in this way are regarded as observed structure factors $F_o(\mathbf{H})$. They have been used in a procedure analogous to that adopted for the determination of the difference density in $C_8H_{16}O_2$ (Ruysink & Vos, 1974*a*, Fig. 3). First the parameters of C and H were adjusted in a least-squares refinement with $w=1$ and based on all reflexions with $H\leq1\cdot92$ Å^{-1}. The scattering factors for the atoms were based on the $\varrho_{at}(\mathbf{r})$ values obtained from the extended GTF set. The shifts in the parameters are given in the legend of Fig. 3 of the present paper. After the refinement all reflexions with $H\leq1\cdot20$ Å^{-1} were used to calculate the (F_o-F_c) difference map. The difference density obtained in this way is given in Fig. 3, curve *b*. The theoretical difference density of Fig. 3, curve *a*, is based on the wave functions, allowance being made

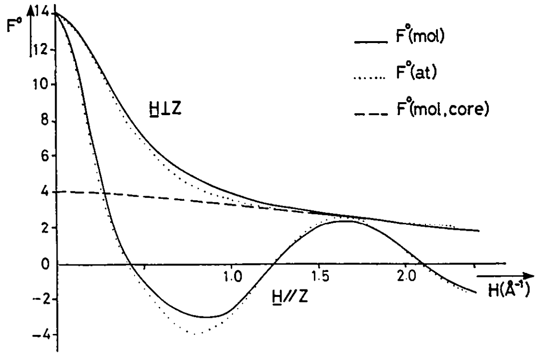

Fig. 1. Structure factors F° *versus* H, for **H** perpendicular and parallel to the molecular axis **z**.

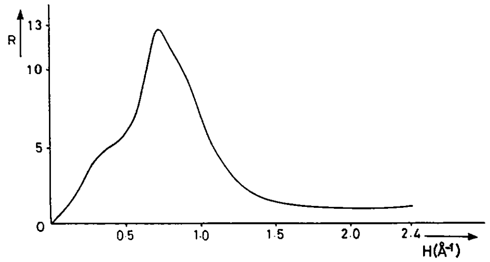

Fig. 2. C_2H_2. The average difference R, defined by formula (2), between F°(mol) and F°(at) *versus* H.

Table 2. *Results of the least squares refinements*

The starting parameters are given in Table 1. Δz=atomic shift in Å; $\Delta U_\perp(\Delta U_\parallel)$=change in U perpendicular (parallel) to C–C, in 10^{-5} Å^2; ΔB=change in $B(H)$, in Å^2; K defined as $KF_c=F_o$. For DA refinements c and v indicate the shifts of the core and valence electrons respectively.

H range	Number of reflexions	Remarks	K	$\Delta z(C)$	$\Delta z(H)$	$\Delta U_\perp$	$\Delta U_\parallel$	$\Delta B(H)$	R(%)
FA									
0–2·4	1911		1·018	−0·0030	−0·106	−3	+161	−1·50	4·61
0–2·4	1911	K fixed	–	−0·0031	−0·122	−39	+120	−1·57	4·81
0–2·4	1911	K and $z(H)$ fixed	–	−0·0026	–	−43	+127	−1·46	5·32
0–2·4	1911	f(SDS)	1·014	−0·0013	−0·113	−10	+145	−0·45	4·30
0–2·4	1911	DA	1·010	$c-0\cdot0002$ $v-0\cdot0674$	−0·139	−11	+124	−1·64	3·82
0–2·4	1288	$I>I(\min)$	1·017	−0·0035	−0·144	−5	+158	−1·51	4·40
HO									
1·6–2·0	525		1·003	+0·0004	−0·019	+6	+30	−0·49	0·28
1·4–2·0	573	$I>I(\min)$	1·009	+0·0004	−0·005	+12	+46	−0·50	0·51
1·4–2·4	1487		1·007	+0·0004	−0·014	+10	+37	−0·50	0·57
1·4–2·4	1487	f(SDS), K fixed	–	+0·0004	−0·015	0	+26	+0·01	0·59
1·4–2·4	1487	*DA*	1·008	$c+0\cdot0004$ $v-0\cdot0004$	−0·014	+11	+38	−0·50	0·56
LO									
0–1·3	346		1·023	−0·0097	−0·093	−138	+730	−2·23	3·20
0–1·3	346	f(SDS)	1·019	−0·0108	−0·103	−153	+664	−0·38	3·08
0–1·3	346	DA	1·014	$c-0\cdot0029$ $v-0\cdot0598$	−0·124	−146	+586	−2·69	2·66
0–1·3	346	DA, $z(H)$ fixed	1·026	$c-0\cdot0051$ $v-0\cdot0354$	–	−123	+753	−2·16	3·74

for the thermal motion mentioned in Table 1. Comparison of curves *a* and *b* shows that the refinement of the structure followed by the calculation of the difference map has reduced the difference density on the C–C bond by approximately a factor of two. This phenomenon corresponds with the observations mentioned in the Introduction, and will be investigated further in the following sections.

Series termination

To estimate the errors due to neglecting part of the terms in the Fourier series, difference density maps have been calculated by use of the formula

$$D(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} [F(\mathrm{mol},\mathbf{H}) - F(\mathrm{at},\mathbf{H})] \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) , \tag{3}$$

where both $F(\mathrm{mol},\mathbf{H})$ and $F(\mathrm{at},\mathbf{H})$ correspond with the structure of Table 1. In Fig. 4 the difference densities obtained in this way are compared with the theoretical density defined in the previous section.

The following curves are given:

(*a*) $D(\mathbf{r})$ from wave functions, $B = 1{\cdot}07$ Å^2.

(*b*) $D(\mathbf{r})$ from all reflexions with $H < 2{\cdot}4$ Å^{-1}.

(*c*) $D(\mathbf{r})$ from all reflexions with $H < 1{\cdot}3$ Å^{-1} (limit for Cu radiation).

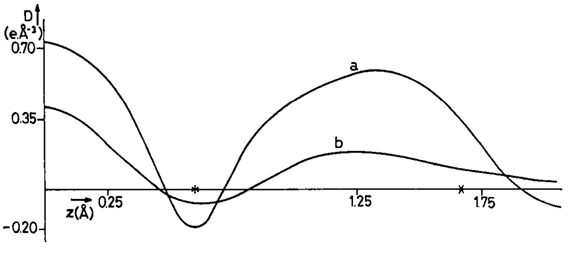

Fig. 3. C_2H_2. Theoretical (*a*) and 'experimental' (*b*) difference density *D* along the *z* axis, $B = 1{\cdot}07$ Å^2, $* = \mathrm{C}$ and $\times = \mathrm{H}$. The $F_c(\mathrm{at})$ values used for the calculation of curve *b* are based on parameters which, as a result of the refinement, show the following differences from those of Table 1: ΔK (multiplication factor of F_c) = 2 %, $\Delta z(\mathrm{C}) = -0{\cdot}0038$, $\Delta z(\mathrm{H}) = -0{\cdot}110$ Å, $\Delta B(\mathrm{C},x) = \Delta B(\mathrm{C},y) = -0{\cdot}01$, $\Delta B(\mathrm{C},z) = 0{\cdot}17$, $\Delta B(\mathrm{H}) = -1{\cdot}66$ Å^2.

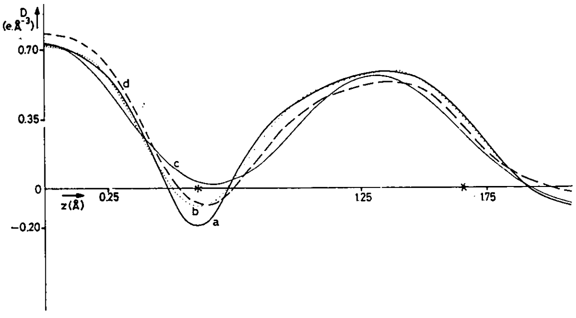

Fig. 4. Difference densities *D* corresponding to the wave functions (*a*) or to Fourier syntheses (*b*, *c* and *d*) based on different series of reflexions (see text), $B = 1{\cdot}07$ Å^2, $* = \mathrm{C}$, $\times = \mathrm{H}$.

(*d*) $D(\mathbf{r})$ as in *b*, but with neglect of all reflexions with $|F \times \mathrm{Lp}^{1/2}| < 0{\cdot}5$. This corresponds with the results obtained from an intensity measurement in which $\frac{1}{3}$ of all reflexions have been classified as unobserved. A similar curve obtained by omitting all reflexions with $|F \times \mathrm{Lp}^{1/2}| < 0{\cdot}3$ ($\frac{1}{5}$ of the reflexions unobserved) closely resembles (*b*) and is not shown in the Figure.

We see that the density given by curve *c*, which is obtained from the smallest number of reflexions, is flattened. For curve *b* flattening occurs only at short distances from the carbon nucleus. On the centres of the bonds only curve *d* differs from curve *a*. For both bonds a deviation of 0·06 e Å^{-3} is found, but in opposite directions. It should further be noticed that both for *c* and *d* the minimum of the curve does not coincide with the position of the carbon nucleus. It can therefore be expected that the position of this atom will change during structure refinement based on the reflexions used for *c* or *d*.

Comparison of Figs. 3 and 4 shows that the reduction in height of the bonding maxima in the 'experimental' difference density of ethyne is not, or only to a slight extent, caused by series termination. Although curve *c* in Fig. 4 is flattened, its deviation from curve *a* is small at the centres of the bonds. This implies that the reduction of the bonding maxima of curve *b* in Fig. 3 has to be ascribed mainly to errors in the atomic parameters. These errors are studied in the next section.

Errors in the assumed structure model

Least-squares refinements based on the (theoretical) $F_o(\mathbf{H})$ values of ethyne, have been made to determine the systematic errors in the adjusted parameters caused by the use of a model consisting of spherically symmetric, non-bonded atoms. The results are given in Table 2. Reflexions with different *H* ranges, indicated as Full Angle (FA), High Order (HO) and Low Order (LO), have been considered. The *H* ranges are given in the first column and the number of reflexions in the second. In some cases reflexions with $|F \times \mathrm{Lp}^{1/2}| < 0{\cdot}5$ were not taken into account; this is indicated by $I > I(\mathrm{min})$ in the third column. All reflexions considered were given unit weight, and the full-matrix method was used throughout. In general, atomic scattering factors based on the wave functions given by Ruysink & Vos (1974*b*) were applied, but in the refinements marked by *f*(SDS) the scattering factor of Stewart, Davidson & Simpson (1965) was used for hydrogen. Refinements with the Double Atom method (Coppens, 1971) in which the core and valence electrons are allowed to shift to different positions, are indicated by DA.

The Table shows that especially for the LO refinements large errors occur in the atomic positions, even in the core positions when the DA method is applied. Also the errors in the thermal parameters are considerable. Although for the FA refinements the systematic errors in the parameters are smaller, their values are in general still larger than the standard deviations expected for accurate structure determinations at low temperatures [for an example, see Verschoor & Keulen, 1971; $\sigma(C)=0{\cdot}0007$ Å]. For the HO refinements, on the other hand, the systematic errors are smaller than the standard deviations obtainable for accurate experimental studies [for $B(H)$ only if f(SDS) is applied]. Our findings agree with the observation that differences between structural parameters obtained by X-ray and neutron diffraction decrease when a higher proportion of high-order X-ray reflexions is included in the X-ray refinement (Coppens & Vos, 1971).

It is easy to see that a change in the isotropic overall temperature factor from $\exp(-1{\cdot}07\sin^2\theta/\lambda^2)$ to $\exp(-B\sin^2\theta/\lambda^2)$ corresponds to a change in the least-squares weighting scheme from the adopted $w=1$ to $w=\exp[-2(B-1{\cdot}07)\sin^2\theta/\lambda^2]$. For increasing B values the weights of the high-order reflexions decrease, so that the shifts of an FA refinement will approach those of an LO refinement. For $B=2{\cdot}12$ Å^2 the FA refinement gives, for instance, $\Delta z(C)=-0{\cdot}0081$ Å.

Discussion

The study in the previous sections has shown that the reduction in height of the bonding maxima as observed for curve *b* in Fig. 3, is mainly due to errors in the atomic parameters rather than to series termination effects. To obtain reliable parameters HO refinements are necessary. This implies that accurately measured high-order reflexions as well as low-order reflexions must be available to obtain reliable difference densities by X-ray diffraction alone. The intensity measurements should therefore be done at low temperatures (preferably 'He temperatures') to reduce the thermal motion of the molecules as much as possible.

As an alternative, one can use neutron diffraction in addition to X-ray diffraction for the accurate determination of the parameters. If this has been achieved, a difference synthesis calculated with X-ray diffraction reflexions up to $H\simeq 1{\cdot}3$ Å^{-1} is expected to give a good picture of the bonding effects, except for regions close to the atomic nuclei.

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The Anomaly of the X-ray Debye Temperature of Chromium in the Temperature Range 35–51°C

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The integrated intensities of the 550 and 651 diffraction lines from a chromium single crystal were measured in the temperature range 35–51°C by steps of 2°C. A plot of the intensities of these lines *versus* temperature showed an abrupt change between 43 and 45°C corresponding to a discontinuity of about $(3{\cdot}6\pm 1{\cdot}1)$°C for the Debye characteristic temperature. This value is in good agreement with the one calculated from the discontinuity of the elastic constants.

Introduction

Chromium, which is antiferromagnetic, has kept the interest of many investigators because of its anomalous properties near the Néel temperature. They were concerned mainly with the specific heat (Beaumont, Chihara & Morrison, 1960), and the elastic constants (Bolef & De Klerk, 1963; Roberson & Lipsitt, 1965; Palmer & Lee, 1971). Similar anomalies were expected in the X-ray Debye temperature. Calculations from elastic constants lead to a discontinuity of 3°C (Wilson, Skelton & Katz, 1966). However, the existence of such