



Fig. 2. Stereoview of a molecule of (3) showing the crystallographic numbering scheme.

[123.4 (2)°]. This set of structural changes, resulting in a less opened-out structure for (3) compared with (2), provides a better precursor for eventual closure to the dodecahedrane nucleus. Further synthetic work on (3) is in progress.

The bond lengths in (3), Table 2, are for the most part unexceptional except for the distances C(6)–C(19)

and C(9)–C(16) [both 1.567 (2) Å] which are much longer than expected for normal C(sp³)–C(sp³) bonds and are considered to be a result of strain in the molecule.

We thank NSERC (Canada) for a grant in aid of research to GF.

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SHORT COMMUNICATION

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Acta Cryst. (1982). **B38**, 2318–2320

Correlations in multipole refinements of ethylene. By R. J. VAN DER WAL and AAFJE VOS, *Department of Chemical Physics, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

(Received 19 January 1982; accepted 22 April 1982)

Abstract

Multipole refinements of C₂H₄ have shown that the positional and thermal parameters of C depend on the radial distribution functions adopted for the dipole and monopole. Values obtained from high-order refinements are approached best for monopole and dipole radial functions derived from SCF (Clementi) wavefunctions, or for a single exponential function $r^n \exp(-ar)$ with $n = 2$ for the dipole.

Introduction

In accurate electron density studies by X-ray diffraction, often the observed one-electron density distribution is given with respect to a reference model consisting of a superposition of non-bonded vibrating atoms: the IAM model. The deformation density

$$D(\mathbf{r}) = K\rho(\text{obs};\mathbf{r}) - \rho(\text{IAM};\mathbf{r}) \quad (1)$$

gives, apart from random errors, a correct picture of the deviations of the observed density from the reference model,

if the scale factor K and the positions and thermal parameters of the IAM atoms are correct. In principle IAM parameters can be determined by neutron diffraction, but in practice difficulties often arise due to a difference in systematic errors for the two experiments (Scheringer, Kutoglu & Mullen, 1978), or because suitable crystals are not available for the neutron diffraction work. In such cases attempts can be made to determine the IAM parameters and K from multipole refinements.

Multipole refinements on C₂H₄

For the volatile compound C₂H₄ no suitable crystals for neutron diffraction were available. Therefore van Nes & Vos (1979) have carried out two types of multipole refinements with the program *VALRAY* (Stewart, 1974) to obtain the IAM parameters. In both refinements the radial function for the carbon core was deduced from the Clementi (1965) wavefunction for the K shell. The H-atom positions were constrained relative to those of the adjacent C atoms on the basis of the molecular geometry of gaseous C₂H₄ (Duncan,

1974). For the valence shells the following radial distribution functions were adopted.

(I) *Single exponentials*

$$R_{n,l}(r) = \frac{1}{4\pi} [\alpha^{n+l+3}/(n+l+2)!] r^n \exp(-\alpha r), * \quad (2)$$

where n is a discrete (integer) variable and α a continuous variable; r gives the distance to the C(H) nucleus. For C the n values taken are $n = 2$ for the monopole up to the quadrupole and $n = 3$ for the octopole. For H, $n = 0, 1, 2$ for monopole, dipole or quadrupole.

(II) *Radial functions derived from SCF wavefunctions*

For the monopole, dipole and quadrupole of C, $R(r)$ was derived from the Clementi (1965) wavefunction for the valence shell; for the octopole of C formula (2) was used with $n = 3$ and $\alpha = 3.44$. For H the SCF scattering factor was taken from Stewart, Bentley & Goodman (1975).

In recent analogous refinements with the Hirshfeld (1971) program, the C=C distance was found to increase from the average value of 1.3130 (3) Å given by van Nes & Vos to

* This function differs from that given by van Nes & Vos (1979) as the present function is normalized according to Stewart (1980); moreover, $\alpha = 2\zeta$.

1.3198 (5) Å, whereas a considerable increase in dipole deformation at C occurred. Analysis of the refinements showed that the difference in the C position is mainly due to the use of a different radial function for the dipole deformation. To study this effect further, a series of refinements with different radial functions has been carried out with the program VALRAY. The data set was corrected for extinction by using the isotropic type I model from Becker & Coppens (1974) in a refinement analogous to refinement (II) with an adjustable α for the octopole on C. The constraint of H to C was maintained. Relevant results of the refinements are listed in Table 1. The slope at C is the slope of the dipole deformation at C at the end of the refinement. This slope is calculated from the C dipole density along z :

$$\rho_C^{\text{Di}}(z_C) = \text{Pop}_C^{\text{Di}} R_C^{\text{Di}}(|z_C|) z_C / |z_C|. \quad (3)$$

z is parallel to C=C with positive direction pointing outwards; Pop_C^{Di} = dipole population of C; R_C^{Di} = dipole radial function of C, z_C = value of z with respect to the C nucleus at position \mathbf{p}_C . Note that for formula (2) with $n = 2$, the slope at C is identical to zero. For the Clementi radial function (CI) the slope lies close to zero.

Table 1(a) shows that C=C increases with decreasing value for the slope at C, as expected. If $n = 2$ or CI is taken for the dipole radial function, the slope remains close to zero. For these refinements the correlation $\rho|\text{Pop}_C^{\text{Di}}, \mathbf{p}_C|$, which is

Table 1. C₂H₄: influence of radial distribution functions

In all cases the Clementi scattering factor is taken for C(core). The centre of C=C lies at an inversion centre in the crystal. CI = fixed Clementi scattering factor for valence shell, Cl(κ) = Clementi scattering factor with κ refinement for C (Coppens, Guru Row, Stevens, Becker & Wang, 1979). A number in column 'radial functions for C' implies that formula (2) is used; the number gives the value of n . mono = monopole, di = dipole, qu = quadrupole, oc = octopole, $R_w = |\sum w(F_o - F_c)^2 / \sum w|F_o|^2|^{1/2}$. $K = F_o$ scale factor.

(a) Influence of dipole $R(r_C)$ on C=C

Number	Radial functions for C				Dipole		Slope at C (e Å ⁻⁴)	C=C (Å)	R_w
	mono	di	qu	oc	α (a.u.)	Pop (a.u.)			
1	CI	1	CI	3	4.4 (5)	-0.24 (4)	-16.5 (91)	1.3204 (9)	1.20
2	CI	1	2	3	3.25 (7)	-0.41 (5)	-6.4 (8)	1.3175 (4)	1.20
3	2	1	2	3	3.36 (2)	-0.36 (3)	-6.6 (5)	1.3170 (4)	1.20
4	Cl(κ)	1	2	3	3.12 (7)	-0.39 (6)	-4.8 (5)	1.3162 (4)	1.19
5	1	1	2	3	2.67 (2)	-0.59 (4)	-3.3 (3)	1.3159 (4)	1.22
6	2	2	2	3	3.41 (2)	-0.56 (4)	0	1.3140 (3)	1.21
7	Cl(κ)	CI	CI	3		-0.58 (6)	-0.47 (5)	1.3140 (3)	1.19
8	CI	2	2	3	3.32 (7)	-0.48 (7)	0	1.3136 (3)	1.22
9	Cl(κ)	2	2	3	3.16 (7)	-0.62 (7)	0	1.3134 (3)	1.20
10	CI	CI	CI	3		-0.34 (5)	-0.27 (4)	1.3130 (3)	1.23

(b) Influence of $R_C^{\text{Mono}}(r_C)$ on $\text{Pop}_C^{\text{Mono}}$ and $U_{\text{eq}}(\text{C})$

Number	Monopole C		$\text{Pop}_C^{\text{Mono}}$	$U_{\text{eq}}(\text{C})$ (Å ²)	K
	n	α or κ			
10	CI		6.00 (5)	0.03693 (7)	0.97
2	CI		6.00 (5)	0.03690 (7)	0.96
8	CI		5.99 (5)	0.03687 (8)	0.96
1	CI		6.12 (5)	0.03861 (7)	0.97
7	Cl(κ)		5.70 (8)	0.03577 (10)	0.99
3	2	1.031 (7)	5.61 (4)	0.03574 (8)	1.00
6	2	3.41 (2)	5.45 (5)	0.03565 (10)	1.00
4	Cl(κ)	1.025 (6)	5.73 (7)	0.03547 (10)	0.98
9	Cl(κ)	1.039 (8)	5.58 (9)	0.03535 (11)	0.98
5	1	2.67 (2)	5.39 (6)	0.03442 (11)	1.00

approximately 0.58 for Cl and -0.53 for $n = 2$, is not large and C=C varies only from 1.3130 (3) to 1.3140 (3) Å. For $n = 1$ the C=C values for all refinements are larger than for $n = 2$. This type of correlation is not printed by the computer program, as n is kept constant during the refinement. For $n = 1$ where the value of the slope varies with Pop_C^{Di} , the correlation $\rho[\text{Pop}_C^{\text{Di}}, \text{p}_C] \approx -0.75$ is larger than for $n = 2$. Consequently, larger values for $\sigma[\text{C}=\text{C}]$ and larger variations in the C=C lengths are found in this case. Finally the table shows that C=C is not determined only by the type of radial function used for the dipole, but also by the radial functions applied for the other multipoles.

According to Table 1(b) an increase in the compactness of $R_C^{\text{Mono}}(r_C)$ decreases both the population and the thermal parameters of C. High-order (HO) refinements with $\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$ have given C=C = 1.3142 (3) Å and $U_{\text{eq}} = 0.03672$ (9) Å². From a recent model study on solid N₂ by Braam (1981) it can be deduced that for volatile compounds with $U_{\text{eq}} \approx 0.04 \text{ \AA}^2$ HO refinements give small systematic errors ($|\Delta r| \approx 3 \times 10^{-4} \text{ \AA}$) for the positions, whereas systematic errors in the HO thermal parameters can be considerable, $\Delta U_{ii} \approx 10^{-3} \text{ \AA}^2$. For C₂H₄ C=C approaches the HO value best if for $R_C^{\text{Di}}(r_C)$ either formula (2) with $n = 2$ or Cl is taken. U_{eq} comes closest to the HO values for $R_C^{\text{Mono}}(r_C) = \text{Cl}$. Use of this monopole function for C also gives the physically most reasonable values for the monopole populations (Table 1), as in C₂H₄ C is slightly electronegative with respect to H. Not too much value should be attached to the atomic charges, however, as they are not observables (Stewart, 1977; Stewart & Spackman, 1981).

In view of the discussion given above we prefer for the dipoles of first-row elements single exponentials with $n = 2$ above single exponentials with $n = 1$. For the monopoles no decision can be taken on the basis of the present refinements, as the uncertainty in the HO thermal parameters is large for crystals with high U_{eq} values.

Part of this research has been supported by the Netherlands Foundation for Chemical Research (SON) with

financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). The authors thank Professor R. F. Stewart for his interest and Dr G. R. Moss and Professor D. Feil for aid with the Hirshfeld program. The computations were carried out at the Computing Center of the University of Groningen.

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Notes and News

Acta Cryst. (1982). **B38**, 2320

Suggested guidelines for the publication of Rietveld analyses and pattern decomposition studies

A letter from R. A. Young, E. Prince and R. A. Sparks to the Editor of *Journal of Applied Crystallography* has been published [*J. Appl. Cryst.* (1982), **15**, 357–359] with the above title. The first paragraph read as follows:

At the request of the Commission on Journals, we drew up some draft guidelines for the publication of Rietveld analyses and of pattern decomposition studies with powder diffraction patterns. The draft was sent for comment to some 25 persons in Europe, Australia, Japan, and the USA. We are grateful for their responses, which both were generally supportive of the idea that there be guidelines and were most helpful in illuminating oversights and other deficiencies. Not all suggestions were incorporated in the revised draft, of

course (in fact, a number were mutually contradictory), but all were carefully considered and many were incorporated in the version which follows.

In presenting these suggested guidelines, we emphasize that we offer them as guidelines, not rigid rules. They are intended primarily to be helpful to the co-editors; they are not intended to infringe on a co-editor's judgement of scientific worth of a submitted manuscript, nor should they be allowed to do so. For the most part, these suggested guidelines address matters of format and presentation of details, and not the fundamental question of scientific interest and worth of the submission. It is primarily for the making of such fundamental judgements that the co-editor system exists; for the health of our science it cannot and should not be replaced with a system of blind rules on a check-off sheet. It is against this background of more overreaching considerations that we offer the following suggestions for guidelines to assist, but not to control or coerce, the co-editors in their acceptance decisions.