

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1972). B28, 318.

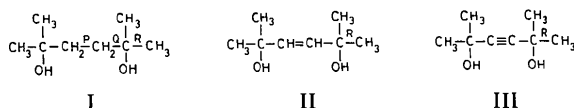
Electron density distributions on single, double and triple C–C bonds. By R. B. HELMHOLDT, A. F. J. RUYSINK, H. REYNAERS* and (in part) G. KEMPER, *Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands*

(Received 21 September 1971)

Preliminary results obtained by X-ray diffraction at 110°K are given.

Introduction and discussion

Experimentally determined electron density distributions have aroused considerable interest (Dawson, 1969; Coppens & Vos, 1971; Coppens, Panther & Griffin, 1971) as they form a powerful means of checking existing valence theories. Accurate densities can be obtained from careful X-ray diffraction studies at low temperature (preferably down to approx. 20°K; cooling by He gas). To study the electron density distributions on a single, a double and a triple C–C bond in analogous compounds, we have chosen the compounds I, II and III.



To check whether these compounds are suitable for very accurate X-ray work, routine structure determinations have been done at 110°K. The preliminary results given in Fig. 1 and in Table 1 justify continuation of this research at lower temperatures.

In Fig. 1 [$\rho(\text{exp}) - \rho(\text{calc})$] maps are given, $\rho(\text{exp})$ being found from the observed X-ray reflexions and $\rho(\text{calc})$ being based on spherically symmetric non-bonded atoms (for details, see Verschoor & Keulen, 1971). The sections given are perpendicular to the double and triple bond of II-*trans* and III respectively, and go through the centres of these bonds. Note that the excess density for the triple bond is extended more than for the double bond. On the central single bond of I no significant difference density maximum has been observed.

In Table 1 average lengths for chemically equivalent bonds are listed. Note that the C–C bonds in II-*cis* and the bonds C–C (type Q) are relatively long. We ascribe the elongation of these bonds to repulsion. Apart from this effect the C–C bond lengths observed for the different molecules show good agreement with each other and with earlier reported values. The strong variations of the C–O bond lengths are tentatively ascribed to the presence of hydrogen bonds in the crystals.

* Present address: Laboratorium voor Macromoleculaire Chemie, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium.

Experimental

The compounds I and III were commercially available (E.G.A. Chemie), while II-*trans* and II-*cis* had to be synthesized from III (Hoffman, 1968; Tedeschi, 1962). Crystals were grown from solutions by slow evaporation of the solvent. The solvents used were a 1:1 mixture of light petroleum (40°–60°) and acetone for I, light petroleum for II-*trans* and II-*cis*, and a 1:2 mixture of benzene and light petroleum for III. Large irregular crystals were obtained which were reduced to reasonable shapes and dimensions by touching their surfaces with cigarette paper soaked with the appropriate solvent. The crystallographic data at 110°K and details of the experimental work are given in Table 2. The cell dimensions were obtained from zero layer line Weissenberg photographs [$\lambda(\text{Cu } K\alpha) = 1.5418$, $\lambda(\text{Cu } K\alpha_1) = 1.54051$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å], except those of II-*trans* and the angle β of I which were measured on a diffractometer [$\lambda(\text{Mo } K\alpha) = 0.7107$ Å]. The intensities (Int) of the independent reflexions were collected with a three-circle Nonius diffractometer at 110°K, Zr-filtered Mo radiation and the θ - 2θ scan method being used. Corrections for Lorentz and polarization effects and for absorption (Busing & Levy, 1957) were applied to obtain the structure amplitudes $|F|$. The structures were determined by the symbolic addition method (Karle & Karle, 1966) and refined by anisotropic block-diagonal least-squares techniques

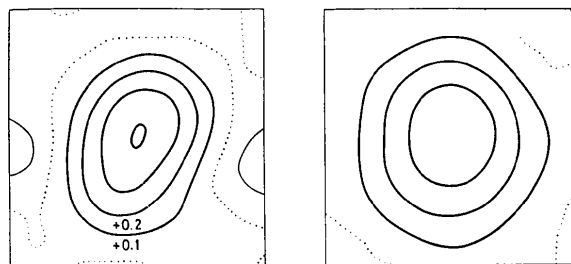


Fig. 1. Difference densities for the double bond of II-*trans* (left) and the triple bond of III (right) (see text). In the Fourier maps only reflexions with $\sin \theta/\lambda < 0.60$ Å⁻¹ are included; $\rho(\text{calc})$ is based on spherically symmetric atoms with parameters obtained from the X-ray refinement discussed in the experimental section. Contours are drawn at intervals of 0.1 e.Å⁻³, the zero line being dotted.

Table 1. Average values of the bond lengths (Å) observed for the different compounds

The standard deviations of individual bond lengths range from 0.002 to 0.003 Å.

Compound	I	II-trans	II-cis	III	Previous measurements
C-C (P)	1.529				1.528*
C-C (Q)	1.534				
C-C (R)	1.525	1.526	1.530	1.527	
C(sp ³)-C(sp ²)		1.514	1.519		1.505†
C(sp ³)-C(sp)				1.479	1.458‡
C=C		1.326	1.338		1.333§
C≡C				1.203	1.207‡
C-O	1.442	1.452	1.436	1.435	

* Davis & Hassel (1963).

† Visser (1969).

‡ Bastiansen (1959).

§ Bartell & Bonham (1959).

Table 2. Crystallographic data at 110°K and details of the experimental work

Standard deviations in parentheses are given in units of the last decimal place.

Compound	I	II-trans	II-cis	III
Space group	P2 ₁ /c	Phcn	P $\bar{1}$	P $\bar{1}$
Z	6	8*	3	3
a	15.583 (3) Å	9.686 (3) Å	8.377 (2) Å	8.495 (2) Å
b	9.948 (4)	10.430 (1)	13.335 (1)	9.970 (4)
c	8.928 (1)	18.298 (2)	6.436 (1)	8.818 (2)
α	90°	90°	102.06 (2)°	95.45 (1)°
β	91.80 (1)	90	74.69 (2)	85.63 (1)
γ	90	90	102.59 (2)	119.56 (1)
Crystal size	0.5 × 0.5 × 0.5	0.4 × 0.4 × 0.4	0.6 × 0.3 × 0.3	ϕ = 0.6 mm
(sin θ / λ) _{max}	0.74	0.96	0.96	0.87 Å ⁻¹
Number of non-zero (Int)	4448	5619	8460	6664
Number of F 's used	3763	3924	6396	5945
P-value in w	0.0295	0.0141	0.02	0.0117
$R = \left[\frac{\sum w(F_o - F_c)^2}{\sum wF_o^2} \right]^{1/2}$	9.9	6.9	7.5	6.7%

* Plus four H₂O molecules lying on twofold axes.

(Cruikshank, 1961) [H atoms fixed at reasonable positions with C-H = 1.08, O-H = 1.0 Å; B(H) refined]. The scattering factors were taken from Stewart, Davidson & Simpson (1965) for hydrogen and Doyle & Turner (1968) for carbon and oxygen. The weighting scheme was $w = [w_c^{-1} + P^2|F^2|]^{-1}$, w_c being the weight based on counting statistics. The structure determinations showed that in the compound called II-cis the molecule at the inversion centre is predominantly trans and to a slight extent disordered cis; in Table 1 only the data for the cis molecule at the general position are given. In compound III one of the $\begin{matrix} \text{OH} \\ \diagdown \\ \text{C} \\ \diagup \\ (\text{CH}_3)_2 \end{matrix}$ groups of the molecule in a general position appeared to show slight disorder. This was accounted for by using fractional ($\frac{1}{2}$) O and methyl C atoms during the refinement (positions fixed during the final refinement stages).

We thank Mr H. Sinnige of the Department of Organic Chemistry for his help in preparing the II-cis compound, Mrs S. Swen and Mr F. van Bolhuis for their practical assistance, and Professor A. Vos for her stimulating discussions. The present investigations have been carried out with financial support of the Dutch Organization for the Advancement of Pure Research. H. Reynaers is indebted to the NFWO of Belgium for a research grant.

References

- BARTELL, L. S. & BONHAM, R. A. (1959). *J. Chem. Phys.* **31**, 400.
 BASTIANSEN, O. (1959). *J. Chim. Phys.* **56**, 817.
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
 COPPENS, P., PANTHER, D. & GRIFFIN, J. F. (1971). *J. Amer. Chem. Soc.* **93**, 1051 and references therein.
 COPPENS, P. & VOS, A. (1971). *Acta Cryst.* **B27**, 146.
 CRUIKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Paper 6. Edited by R. PEPINSKY *et al.* London: Pergamon Press.
 DAVIS, M. & HASSEL, A. (1963). *Acta Chem. Scand.* **17**, 1181.
 DAWSON, B. (1969). *Acta Cryst.* **A25**, 12.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390.
 HOFFMAN, J. K. (1968). *Chem. Abs.* **68**, 39095p.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TEDESCHI, R. J. (1962). *J. Org. Chem.* **27**, 2398.
 VERSCHOOR, G. C. & KEULEN, E. (1971). *Acta Cryst.* **B27**, 134.
 VISSER, G. J. (1969). Thesis, Rijksuniversiteit Groningen, pp. 64, 65.