ACTA CHEMICA SCANDINAVICA 27 (1973) 1735–1739

The Molecular Structure of Hexachlorofulvene

ANNE SKANCKE

Department of Chemistry, University of Oslo, Oslo 3, Norway

The molecular structure of hexachlorofulvene has been determined by means of the electron diffraction method. This overcrowded molecule is planar and the structure of the carbon skeleton is strongly alternating. The main conclusions from the electron diffraction investigation are verified by an SCF-MO calculation using the PPP approximation. The results are compared to recent experimental investigations of fulvene.

This work on the hexachlorofulvene molecule is part of an investigation of the aromatic character of some $sp^2\pi$ hybridized ring systems.

Previously, a PPP calculation on the hydrocarbon fulvene and the isomer 3,4-dimethylenecyclobutene has been carried out,[1] and subsequently the calculated geometry of the latter molecule was confirmed by an electron diffraction investigation.[2]

Due to its instability, the fulvene molecule is difficult to investigate by means of electron diffraction. An early investigation has been carried out,[3] but gives by no means an unambiguous solution as to the geometry of the molecule.

In this work, the effect of a substituent, chlorine, on the geometric stability of the ring system is investigated. A valuable supplement to the present studies was given by the completion of a microwave study of fulvene by Brown and coworkers.[4] The main conclusions reached in the present electron diffraction studies have been confirmed by semi-empirical studies of the same type as those applied to the hydrocarbon series.

A sample of the molecule was kindly put at my disposal by Dr. I. Agranat and Professor E. D. Bergmann at the Hebrew University of Jerusalem.

EXPERIMENTAL

The electron diffraction diagrams were taken at the Oslo diffraction unit.[5] Recordings were taken at two nozzle to plate distances, about 48 cm and about 19 cm. The nozzle temperature was about 150°C. Three plates from the longer distance and four from the shorter were used, and their optical densities measured at $\Delta s = 0.125$ Å^{-1} and $\Delta s = 0.25$ Å^{-1}, respectively. A total intensity range from $s = 1.375$ Å^{-1} to $s = 23$ Å^{-1} was covered, the range from $s = 6.75$ Å^{-1} to $s = 19.75$ Å^{-1} being the overlap region.

Recorded data beyond 23 $Å^{-1}$ on the 19 cm curves were found to be too inaccurate to be included in the work. The data were processed at a CDC 6600 computer at the University of Texas at Austin, applying computer programs described elsewere.[6]

The various peaks of the radial distribution curve, shown in Fig. 1, could readily be interpreted in terms of internuclear distances.

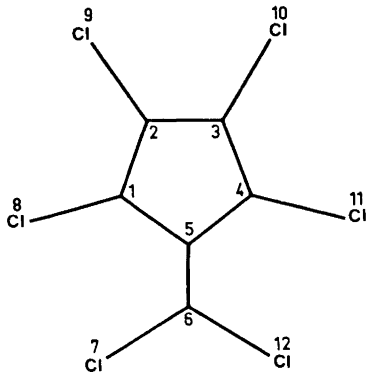

Fig. 1. Hexachlorofulvene. Numbering of atoms.

The first peak at about 1.4 Å has contributions from all C–C bond distances. The next, large peak at about 1.7 Å is composed of the six C–Cl bond distances, and at about 2.3 Å is a small peak due to the next-to-neighbours C···C distances. The peak with maximum at about 6.65 Å gives the longest Cl–Cl distance, and gives immediately an indication of the planarity of the chlorine atoms 8, 9, 11 and 12. For labelling of atoms, see Fig. 2. All other peaks are rather complex and have contributions from several

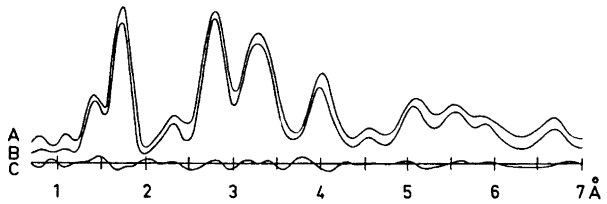

Fig. 2. Radial distribution curve. A. Experimental. B. Theoretical. C. B–A.

distances. Because of the relatively large contribution to the scattering pattern from the chlorine atoms, the radial distribution curve is highly sensitive to even small changes in parameters involving the chlorine atoms.

Little information about the C–C bond distances can be deduced directly from the corresponding peak. This is because there are four different bond distances and the peak is influenced by the large and dominating contribution from the C–Cl bond distances. The C–C bond distances were therefore estimated from the shape of the peak at about 2.3 Å and a general fit of the experimental and theoretical curves. These estimates were refined by the least squares method, but the corresponding amplitudes of vibration were not possible to refine.

Several non-planar models were tested, but none of these fits the experimental data better than the planar model given by the parameters in Table 1.

The standard deviations given in parenthesis are the results from using a diagonal weight matrix only, and may be somewhat too small. The results are compared to existing information of the related compound fulvene.

MO CALCULATIONS

A molecular orbital calculation has been carried out on the system, using the PPP scheme in the ZDO approximation. The parameters for the chlorine atoms are taken from a work by Grabe.[7] That paper also gives a complete list of references pertaining to the method of calculation applied here. The bond distances obtained in the calculation are given in Table 1, which also

Table 1. Bond distances. In Å units. Numbers in parenthesis give the standard deviation corrected for error in wave length.

Distance	Fulvene SCF-MO[a]	Fulvene M.W.[b]	Present work perchlorofulvene SCF-MO	Present work perchlorofulvene E.D.
1 – 2	1.357	1.355	1.362	1.358 (0.005) $u = 0.043$
2 – 3	1.450	1.476	1.447	1.424 (0.005) $u = 0.045$
4 – 5	1.466	1.470	1.460	1.478 (0.002) $u = 0.045$
5 – 6	1.355	1.349	1.360	1.369 (0.012) $u = 0.043$
1 – 7			1.695	1.7070 (0.0021) $u = 0.048$
2 – 8				
6 – 12			1.687	1.6960 (0.0021) $u = 0.048$

[a] Ref. 1. [b] Ref. 4.

gives the results for the hydrocarbon. As is seen from the table, the results of the SCF calculation give nearly identical carbon skeletons for the substituted and unsubstituted molecule. Comparing the SCF results of perchlorofulvene data, the general agreement is good, but there seems to be a slight effect of "smearing out" of bond distances in the perchlorinated molecule. Comparing the SCF results with those from the electron diffraction, the general agreement is good for the two double bonds. Both the calculation and the experimental results give larger double bond distances in the perchlorinated molecule than in fulvene itself. As for the single bonds, the picture is more complicated. A striking difference is seen for the values of bond 2 – 3, where the experimental result is about 0.02 Å shorter than predicted by the SCF calculation. Looking at the atomic charges in Table 2, it is seen that the ring has an increase in

Table 2. Atomic charges.

Atom	Fulvene Theor.	Hexachlorofulvene
1	1.025	1.0537
2	1.028	1.0483
5	0.870	1.0489
6	1.030	0.8714
7		1.9825
8		1.9829
11		1.9725

charge of about 0.3 electrons in going from the hydrocarbon to the perchlorinated molecule. Atoms 5 and 6 have a net positive and negative charge, respectively, in the hydrocarbon, while the reverse is true for the perchlorinated species. This is consistent with the less pronounced single bond-double bond character predicted by the SCF calculation, but the experimentally found difference in the two C – C single bonds cannot be explained in terms of the applied π-electron theory.

A possible explanation may be found by considering the electronic distribution given by the configuration generated by a double excitation from the highest filled to the lowest vacant molecular orbital. This configuration leads to a drastic increase of the mobile bond order for the bond 2 – 3. By an improvement of the molecular ground state through mixing with this configuration, a shortening of the bond 2 – 3 would occur.

The molecular spectrum for hexachlorofulvene has been calculated and compared to the experimentally recorded values.[8] The latter are measured in two solvents, ethanol and benzene, an excellent correspondence is found between the two experimental series.

Table 3. Molecular spectrum for hexachlorofulvene in the UV region. In cm^{-1}. Numbers in parenthesis give the extinction coefficients for the experimental data and the *f*-values for the calculation.

Experimental		Calculated
in EtOH	in C_6H_6	
23.000 (450)	22.500 (420)	26.900 (0.06)
31.100 (10.700)	30.700 (10.000)	
32.300 (18.300)	31.800 (15.400)	
		39.100 (0.67)
33.400 (19.000)	33.000 (15.600)	
34.480 (14.600)	34.000 (13.300)	
		52.400 (0.076)
		58.200 (0.9)
		58.200 (0.2)

The low-lying weak transition predicted at 26 900 cm^{-1} has its experimental counterpart at about 4000 cm^{-1} lower values but this discrepancy may be partly due to solvent effects for this very polar molecule. Experimentally, a series of four close-lying transitions follows, all spaced by about 1200 cm^{-1}. The calculation gives only one electronic transition in this energy range. Since a normal value for the C – Cl vibrational frequency in aromatic molecules is about 1500 cm^{-1}, it is tempting to assume that the experimental sequence is due to vibrational C – Cl transitions rather than to electronic transitions. The center of gravity of the band at about 32 500 cm^{-1} is, however, considerably lower than the calculated band at 39 100 cm^{-1}.

In addition to the above mentioned solvent shift as a possible explanation of the discrepancies between predicted and measured transition energies, it may also be appropriate to include the fact that this molecule is a strained one.

During an electronic excitation such a molecule will most likely undergo drastic deformations leading to electronic distributions deviating significantly from those for which the applied semi-empirical parameters are appropriate.

The dipole moments of the y and z directions vanish by symmetry, and the total, calculated dipole moment is along the x axis. This is calculated as 2.3 D, compared to the experimental value of 1.0 D. This indicates that the sigma core is strongly polarized.

The experimental spectrum has not been recorded in the energy range where the strongest absorptions are predicted to occur.

Acknowledgement. The author is indebted to Cand. real. A. Almenningen and Siv. ing. Birgit Andersen at the University of Oslo for help with the electron diffraction recordings. This work was in part carried out during a stay at the University of Texas at Austin, and thanks are due to Dr. D. Kohl and Dr. J. E. Boggs at that institution for placing facilities at my disposal, and for stimulating discussions. This work has been partially supported by the Robert A. Welch Foundation.

REFERENCES

1. Skancke, A. and Skancke, P. N. *Acta Chem. Scand.* **22** (1968) 175.
2. Skancke, A. *Acta Chem. Scand.* **22** (1968) 3239.
3. Rouault, M. and Waziutynska, Z. L. *Acta Cryst.* **10** (1957) 804.
4. Brown, R. D. *Private communication.*
5. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand.* **9** (1955) 232.
6. Bartell, L. S., Kohl, D. A. Carrol, B. L. and Gavin, R. M., Jr. *J. Chem. Phys.* **42** (1965) 3079.
7. Grabe, B., *Acta Chem. Scand.* **22** (1968) 2237.
8. Agranat, I. *Private communication.*

Received December 4, 1972.