CHEMISTRY LETTERS, pp.1083-1086, 1973. Published by the Chemical Society of Japan

THE X-RAY STUDY ON THE LOW- AND ROOM-TEMPERATURE FORMS OF HEXACHLOROFULVENE

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The X-ray analysis of hexachlorofulvene was undertaken at -130°C and 20°C. The structure of the low-temperature form is in an ordered state and that of the room-temperature form is of a disorder-type. A disorder-model, in terms of the statistical mixture of four molecular orientations, was tentatively proposed.

It has been reported in a previous paper that hexachlorofulvene has a phase transition at 9°C$^{1)}$. Its NQR spectrum indicated the existence of six crystallographically nonequivalent chlorine atoms in a unit cell at -196°C$^{2)}$, and its thermal analysis, NQR experiments and dielectric measurements suggested the existence of a thermal excitation of molecular motion in the crystal lattice above -70°C$^{1)}$.

We undertook the three-dimensional X-ray analysis of hexachlorofulvene at about -130°C and 20°C, to understand its phase transition and molecular motion in the solid state. Samples were recrystallized as deep-red needles from a large amount of n-hexane at 0°C. The crystal data for the low- and room-temperature forms (LTF and RTF) are given in Table 1 along with those of related compounds, hexachlorobenzene and 1,2-dichlorotetramethylbenzene. The intensity data for both forms were collected around the a and b axes by equi-inclination Weissenberg technique with CuKα radiation. The low temperature experiment was carried out in the range from -125°C to -135°C by using a Stoe low-temperature-device. The intensities of 1809 (LTF) and 374 (RTF) independent reflections were estimated visually.

LOW-TEMPERATURE FORM

The structure of the low-temperature form was solved by the inspection of the sharpened Patterson map. The block-diagonal least-squares refinement of the positional and anisotropic thermal parameters of all atoms and one scale factor reduced the R value to 0.11. The final atomic co-ordinates are listed in Table 2. The crystal structure viewed down the b axis and the molecular dimensions are shown in Figs. 1 and 2, respectively. The alternate bond-lengths of 1.36 and 1.47 Å in the five-membered ring are almost equal to those in butadiene$^{3)}$. This fact suggests that each π-electron of carbon atoms is not so significantly delocalized as to give an aromatic character. All of the intramolecular C-Cl distances are equal to one another within the

Table 1. The crystal data for both forms and related compounds.

Compound	Hexachlorofulvene (C_6Cl_6) LTF	Hexachlorofulvene (C_6Cl_6) RTF	Hexachlorobenzene[4] (C_6Cl_6)	1,2-dichlorotetramethylbenzene[4] ($C_{10}H_{12}Cl_2$)
Molecular weight	285		285	203
Temperature	-130°C	20°C	Room temp.	Room temp.
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/\underline{c}$	$P2_1/\underline{c}$	$P2_1/\underline{c}$	$P2_1/\underline{c}$
$\underline{a}$	16.355 Å	8.33 Å	8.08 Å	8.16 Å
$\underline{b}$	3.806	3.84	3.87	3.98
$\underline{c}$	16.779	17.28	16.65	16.95
$\underline{\beta}$	118.87 °	119.8 °	117.0 °	116.4 °
$\underline{V}$	914.64 $Å^3$	479.6 $Å^3$	463.9 $Å^3$	493.1 $Å^3$
ρ_o	——— g/cm^3	1.92 g/cm^3	2.03 g/cm^3	1.34 g/cm^3
ρ_c	2.08	1.97	2.04	1.36
Z	4	2	2	2

Table 2. The final atomic co-ordinates of the LTF.

Atom	$x/\underline{a}$	$y/\underline{b}$	$z/\underline{c}$	Atom	$x/\underline{a}$	$y/\underline{b}$	$z/\underline{c}$
Cl-1	0.1168	0.3925	0.5707	C-1	0.2189	0.3763	0.4717
Cl-2	0.3155	0.7491	0.7215	C-2	0.2090	0.4619	0.5527
Cl-3	0.4655	0.7864	0.6398	C-3	0.2903	0.6057	0.6169
Cl-4	0.3717	0.4346	0.4344	C-4	0.3562	0.6194	0.5806
Cl-5	0.1714	0.1398	0.3030	C-5	0.3143	0.4803	0.4952
Cl-6	0.0445	0.1138	0.3720	C-6	0.1536	0.2237	0.3930

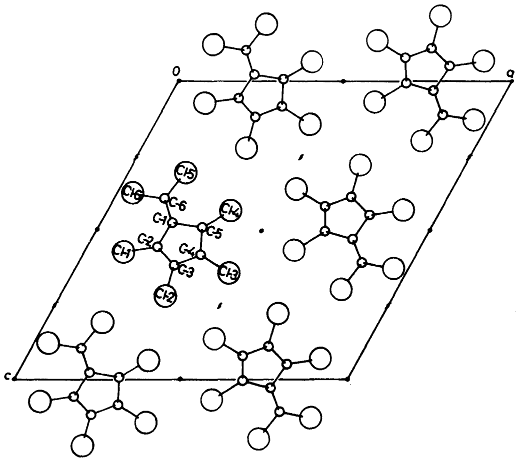

Fig. 1. The crystal structure of the LTF viewed down the $\underline{b}$ axis.

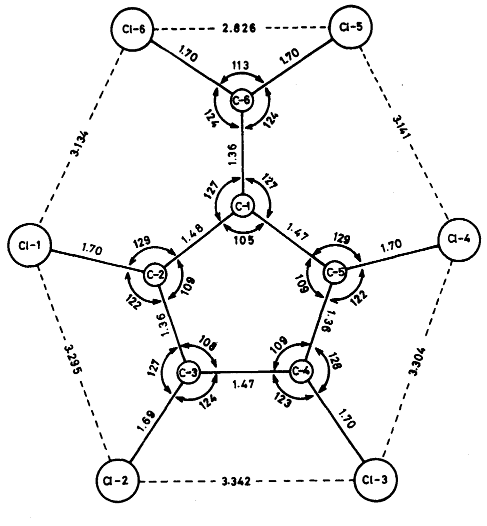

Fig. 2. The molecular dimensions of hexachlorofulvene at -130°C.

experimental error (0.012 Å). All of the distances between the neighboring chlorine atoms in a molecule are much shorter than twice the van der Waals radius of chlorine atom, 3.60 Å. The intramolecular distance between Cl-5 and Cl-6, 2.826(5) Å, is an ordinary value as that in dichloromethylene group5,6) and the mean value of Cl-1---Cl-2, Cl-2---Cl-3 and Cl-3---Cl-4, 3.314(5) Å, is slightly shorter than the corresponding values of octachlorofulvalene7) (3.346 Å) and 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene8) (3.390 Å). The maximum deviation from the least-squares plane of a molecule is 0.067 Å (Cl-4). The dichloromethylene group twists by 1.4° out of the plane of the five-membered ring. These two facts show that the molecule is planar. The planarity of the molecule is noteworthy considering the short contacts between the chlorine atoms in a molecule.

ROOM-TEMPERATURE FORM

The structure of the room-temperature form is nearly isomorphous to those of hexachlorobenzene and 1,2-dichlorotetramethylbenzene. The space-group requirements fix each position of the center of the molecule at the center of symmetry of the crystal. Apparently however, hexachlorofulvene molecule is not centro-symmetrical. Therefore, the structure should be of some disorder-type as the case of 1,2-dichlorotetramethylbenzene4).

The co-ordinates of three chlorine atoms were easily determined by the inspection of the sharpened Patterson map. The positional and anisotropic thermal parameters of the three chlorine atoms were refined by the least-squares method. In this step, the R value was 0.21. A difference Fourier-synthesis (D-map) based on the three chlorine atoms gives three significant peaks revealing that the distribution of electron density associated with carbon atoms was elongated along the [4 3 1] direction as shown in Fig. 3. From the D-map, we tentatively propose a disorder-model which is the assortment of four molecular orientations as superimposed on the D-map in Fig. 3. This model consists with the result of the dielectric studies indicating that all of the molecules reorient at room temperature1). With the model, the R value was finally reduced to 0.11.

The results of further investigation on the molecular motion and the phase transition of the compound will be published with the details of its structure in near future.

The authors are grateful to Professor Akira Fujino, Osaka City University, for valuable suggestions. The authors also wish to thank the Matsunaga Science Foundation for the financial support.

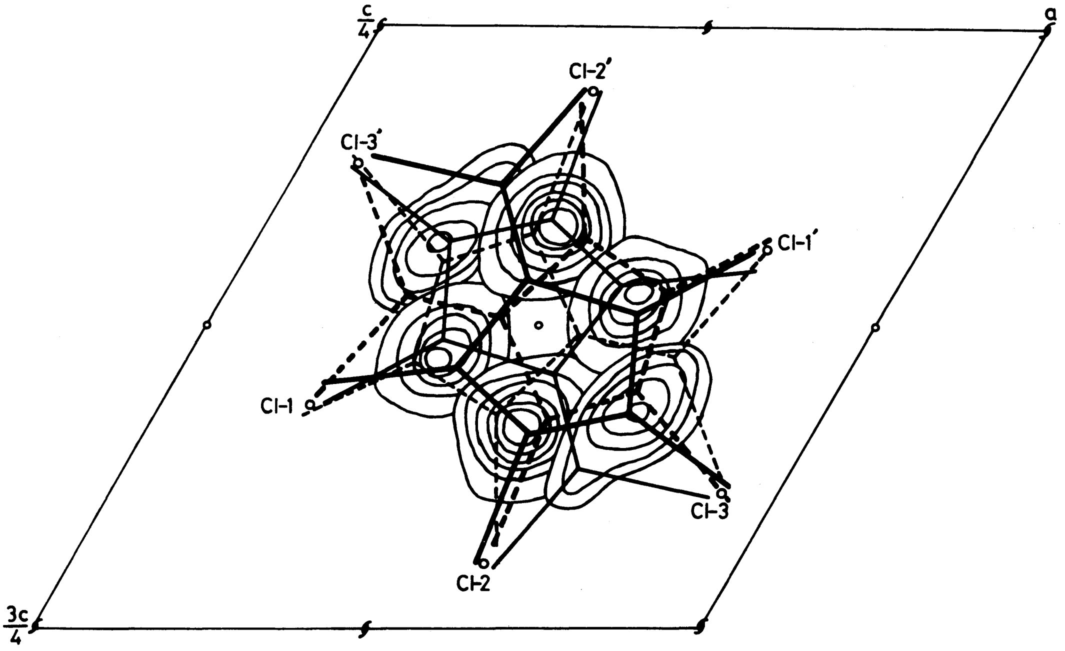

Fig. 3. The electron density associated with carbon atoms and the disorder-model of RTF. The electron density was calculated by using the parameters of Cl-1, Cl-2 and Cl-3. The contours are at intervals of 0.25 e·Å^{-3}, beginning with the 0.25 e·Å^{-3} contour. The two molecular orientations illustrated by thick and fine solid lines are related to each other in regard to the center of symmetry, and another pair with broken lines is also in the same relation.

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(Received July 10, 1973)