BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2333—2334 (1974)

The Crystal Structure of Tetraiodo-*p*-benzoquinone

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(Received December 20, 1973)

Synopsis. The crystals of tetraiodo-*p*-benzoquinone-(iodanil) are monoclinic, with a space group of $P2_1/c$ and with $a=7.630(1)$, $b=5.268(1)$, $c=14.222(2)$ Å, $\beta=113.07(2)°$, and $Z=2$. The iodanil molecules are stacked to form columns along the b axis, with an interplanar distance of 3.694 Å.

The crystals of iodine molecules have been reported to be metallic under high pressure (>200 kbar).$^{1)}$ On the other hand, those of tetraiodo-*p*-benzoquinone (iodanol) are still semiconductive up to 500 kbar. However, the pressure dependence of the electrical resistivity of the powder crystals of iodanil is quite large (10^{12} Ωcm at 1 bar and 10^{-1} Ωcm at 500 kbar$^{2)}$). Considering the simplicity of the molecular structure, such a large change in conductivity seems noteworthy.

The crystals of iodanil were subjected to X-ray structure analysis in order to obtain structural information.

Experimental

The iodanil was prepared by the reaction of bromanil with NaI and KI and was crystallized from an ethylacetate solution. The crystal data are; $C_6I_4O_2$, F.W. 611.7, monoclinic, $a=7.630(1)$, $b=5.268(1)$, $c=14.222(2)$ Å, $\beta=113.07(2)°$, $U=525.9$ Å^3, $D_x=3.862$ gcm^{-3}, $Z=2$, Space group $P2_1/c$. The intensities were collected on a Rigaku automated four-circle diffractometer with Mo*K*α radiation monochromated by a graphite crystal. The shape of the crystal used was parallelpiped, with dimensions of 0.17×0.16×0.09 mm. The $\omega-2\theta$ scan technique was employed. Data were recorded for 1683 independent reflections up to $2\theta=60°$, of which 831 were observed.

Determination of the Structure and Discussion

The structure was solved by means of three-dimensional Patterson maps. The atomic parameters were refined by the block-diagonal least-squares method. The *R*-value was reduced to 0.069. The positional and thermal parameters are listed in Table 1.

TABLE 1. THE FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (× 10^4)

Temperature factor=exp $[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	2962	3683	2015	240	384	50	−69	3	−15
	3	4	1	4	7	1	5	1	2
I(2)	−2155	4245	1096	264	418	63	45	54	7
	3	4	1	4	8	1	5	2	3
O	3785	−434	725	129	396	46	−1	2	−86
	21	34	12	32	79	10	42	14	23
C(1)	2052	−215	392	122	202	28	−30	0	16
	28	40	14	40	75	10	45	17	24
C(2)	1065	1576	822	163	182	34	−28	20	8
	30	40	14	45	74	11	48	18	25
C(3)	−785	1825	502	131	247	35	−10	22	10
	29	43	15	42	86	12	48	18	26

The iodanil molecules are stacked at equal intervals to form columns parallel to the b axis (Figs. 1a and 1b). The interplanar distance is 3.694 Å. Since no short contact can be observed, the intermolecular interaction between iodanil in the same column seems to be weak. The mode of overlapping is illustrated in Fig. 2. The least-squares plane of iodanil is:

$$-0.3000X-0.7060Y+0.6416Z=0.0,$$

where X, Y, and Z are coordinates (in Å) referred to the a, b, and c* crystal axes respectively. The deviations of atoms from this plane are:

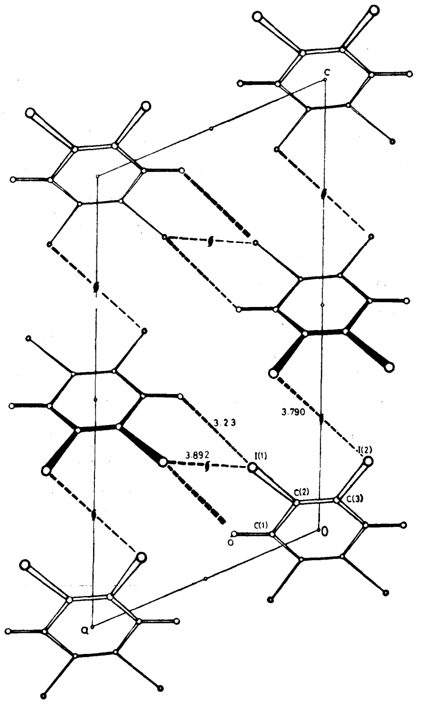

Fig. 1a. Projection of the structure along the b axis.

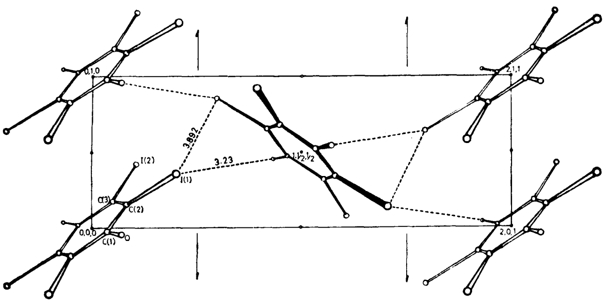

Fig. 1b. The structure viewed along [201].

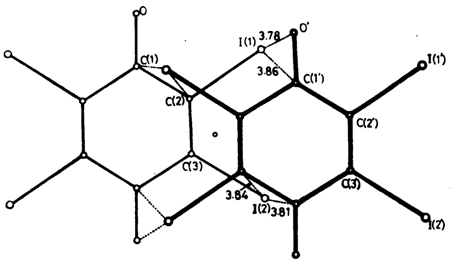

Fig. 2. Nearest-neighbour packing.

I(1), -0.019; I(2), 0.017; O, 0.025; C(1), 0.005; C(2), -0.003; C(3), 0.007 Å.

Few intermolecular short contacts are observed (Figs. 1a and 1b). The interatomic distances, which are shorter than the sum of the van der Waals radii, are as follows:

$$\mathrm{I}(1^{\mathrm{i}})\cdots\mathrm{I}(2^{\mathrm{ii}}),\ 3.790(3);\quad \mathrm{I}(2^{\mathrm{i}})\cdots\mathrm{I}(1^{\mathrm{ii}}),\ 4.181(3);$$

$$\mathrm{I}(1^{\mathrm{i}})\cdots\mathrm{I}(1^{\mathrm{iii}}),\ 3.892(4);\quad \mathrm{I}(1^{\mathrm{i}})\cdots\mathrm{O}^{\mathrm{iii}},\ 3.23(2)\ \text{Å},$$

where the figures in parentheses are the standard deviations and where i, ii, and iii indicate the following equivalent positions:

$$\text{i},\ x, y, z;\quad \text{ii},\ -x,\ -0.5+y,\ 0.5-z;$$

$$\text{iii},\ 1.0-x,\ 0.5+y,\ 0.5-z.$$

The bond lengths and angles are given in Fig. 3; they show a strong quinoid character in iodanil. The mean bond length of C(1)–C(2) and C(1)–C(3′) is 1.50 Å (C(3′) is the atom associated with C(3) (Table 1) by a center of symmetry) and C(2)–C(3) is 1.31 Å. The corresponding values of chroranil are 1.490 and 1.344 Å respectively.$^{3)}$ C(2)–I(1) (2.069 Å) is slightly longer than C(3)–I(2) (2.030 Å).

The visible absorption spectra of the vacuum-deposited thin films on quartz gave two broad maxima (330 and 380 mμ), wheras only one maximum (320 mμ) was observed in the spectra of the benzene solution (7×10^{-5} M). The infrared spectra showed that the C=O stretching frequencies in iodanil are 1665 and 1652 cm^{-1} in solution (carbon tetrachloride) and in a crystalline solid (KBr disks and Nujol mulls) respectively. For chloranil it is 1686 cm^{-1} in a chloroform solution and 1674 cm^{-1} in the crystalline state.$^{4)}$ The magnitudes of the shift of the C=O stretching frequencies are almost equal to each other, while the shift is only 2 cm^{-1} in *p*-benzoquinone.$^{4)}$ A crystal-structure analysis of chloranil has revealed that there is one unusually short contact between carbon and oxygen atoms ($r(\mathrm{C}\cdots\mathrm{O})=2.85$ Å).$^{4)}$ In iodanil crystals O···I(1) is 0.32 Å shorter than the van der Waals radii (Figs. 1a and 1b), which may be noteworthy in this regard.

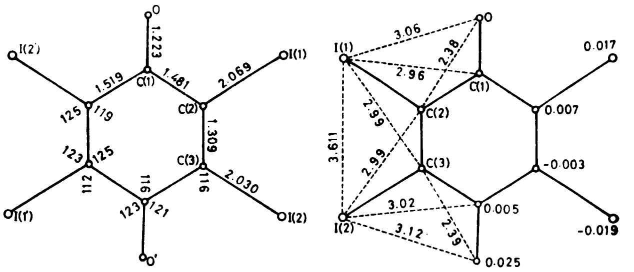

Fig. 3. Geometry of the iodanil molecule.

a) Bond lengths and angles, σ(C–I) = 0.02 Å, σ(remaining bonds) = 0.03 Å, σ(angle) = 1.5–2.0 °.

b) Deviation from the best plane of iodanil and the values for some non-bonded distances.

The large electrical conductivity under high pressure indicates that the interatomic distances between adjacent molecules may be extremly reduced. The contact of O···I and I···I (Figs. 1 and 3) would be important for electric conduction. More information on molecular arrangement under high pressure would be desirable.

References

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