

## Molecular Packing Modes of Acyl Halides.

## IV. The Crystal and Molecular Structure of Biphenyl-2,2'-dicarbonyl Chloride

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The structure of biphenyl-2,2'-dicarbonyl chloride,  $C_{14}H_8Cl_2O_2$  (BCl), has been solved from diffractometer data and refined to  $R = 0.071$ ,  $R_w = 0.12$ . Crystals are monoclinic, space group  $C2/c$ , with  $a = 14.5547$  (5),  $b = 6.1935$  (4),  $c = 15.0800$  (10) Å,  $\beta = 106.942$  (4)°,  $Z = 4$ . The two phenylcarbonyl chloride moieties of the molecule are related by a crystallographic twofold axis. The angle between the two phenyl rings is 83.1°; the carbonyl chloride group is rotated 8.6° from the plane of the phenyl ring. No short  $Cl \cdots O$  or  $Cl \cdots Cl$  intermolecular interactions are present. There exists an intramolecular antiparallel  $C^+=O^-$  dipole-dipole interaction, the  $C \cdots O$  distances of which are 3.38 Å. The shortest  $H \cdots O$  intermolecular distances are 2.61 and 2.69 Å.

## Introduction

We have analysed the structure of biphenyl-2,2'-dicarbonyl chloride (BCl). The flexibility of this molecule affords an opportunity to investigate the influence of both the intra- and intermolecular interactions of the carbonyl chloride group on the molecular conformation and packing.

## Experimental

Crystals grow by sublimation on glass wool as thick monoclinic laths or as very thin needles elongated along [010]. In spite of the precaution taken to avoid contact with humidity, all crystals, except one measuring  $0.3 \times 0.4 \times 0.4$  mm, deteriorated in their capillaries within a few days. Cell constants were determined by least squares from 23 medium ( $87 < 2\theta < 110^\circ$ ) reflections measured with Cu  $K\alpha$  radiation.

## Crystal data

Biphenyl-2,2'-dicarbonyl chloride,  $C_{14}H_8Cl_2O_2$ ,  $M_r = 279.13$ , m.p. 94–96°C,  $a = 14.5547$  (5),  $b = 6.1935$  (4),  $c = 15.0800$  (10) Å,  $\beta = 106.942$  (4)°,  $U = 1300.37$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.425$  g cm<sup>-3</sup>,  $F(000) = 568$ ,  $\mu(Cu K\alpha) = 44.05$  cm<sup>-1</sup>. Space group  $C2/c$  or  $Cc$  from systematic absences:  $hkl$  for  $h + k$  odd,  $h0l$  for  $l$  odd;  $C2/c$  was proved correct by the analysis.

Reflection data (one quadrant of the reciprocal sphere) were measured manually on a GE diffractometer with Cu  $K\alpha$  radiation. As high-order reflections were very weak, only reflections up to  $2\theta = 130^\circ$  were measured. Because of the high mosaicity of the crystal, the moving-crystal moving-counter technique was used.

The scan rate was 2° min<sup>-1</sup> over  $2\theta$  angles of  $2.0^\circ + \delta$ , where  $\delta$  is the separation of the  $K\alpha$  doublet. Background counts of 10 s were taken at each end of the scan. Lorentz, polarization and absorption corrections (Coppens, Leiserowitz & Rabinovich, 1965) were applied. Transmission factors, calculated with a Gaussian grid of 1000 points, varied from 0.316 to 0.430. 1104 unique reflections, of which 188 had  $F_o^2 < \sigma(F_o^2)$ , were used in the analysis.

## Structure determination

Statistical  $N(z)$  tests (Foster & Hargreaves, 1963) favoured the centrosymmetric space group  $C2/c$ , thus imposing symmetry 2 or  $\bar{1}$  on the molecule. The structure was solved by the symbolic addition procedure (Karle & Karle, 1966).

An  $E$  map based on the derived phases revealed the positions of all non-hydrogen atoms. Positions of H atoms were calculated from geometrical considerations. The structure was refined anisotropically (H atoms isotropically) by full-matrix least squares. The final  $R = 0.071$  and  $R_w = 0.12$ .\*

## Results and discussion

Table 1 lists the atomic parameters. The e.s.d.'s in the positional parameters are nearly isotropic and average 0.001, 0.003, 0.004 and 0.04 Å for Cl, O, C and H respectively.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33413 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^5$  for C, O and Cl;  $\times 10^4$  for H) and their e.s.d.'s

	x	y	z
C(1)	5181 (21)	32431 (50)	27772 (22)
C(2)	9118 (22)	45952 (55)	35308 (23)
C(3)	18855 (25)	44436 (72)	40256 (26)
C(4)	24635 (28)	29641 (79)	37792 (28)
C(5)	20854 (32)	16012 (76)	30589 (33)
C(6)	11210 (32)	17314 (62)	25540 (30)
C(7)	2899 (26)	62209 (64)	37850 (24)
O	-4952 (19)	66681 (51)	33799 (21)
Cl	8059 (9)	76365 (25)	48332 (9)
H(3)	2116 (27)	5377 (64)	4576 (25)
H(4)	3177 (29)	2838 (65)	4210 (25)
H(5)	2480 (27)	596 (66)	2844 (25)
H(6)	848 (25)	720 (61)	2072 (24)

## Molecular conformation

The two phenylcarbonyl chloride moieties are related by a crystallographic twofold axis (Fig. 1). The angle between the two phenyl rings is  $83.1^\circ$ , the two phenyl rings being rotated about the biphenyl bond by  $41.55^\circ$  from the synplanar conformation. Molecular symmetries, conformations and twist angles of BCl and of some other 2,2'-disubstituted biphenyl molecules both in the gas and in the crystalline state are given in Table 2, which also lists some theoretical results based on conjugation and non-bonded minimum-energy calculations. Since all molecules adopt the *syn* conformation both in the gas phase and in the solid, there exists an appreciable attractive interaction between the substituents. Weaker interactions could result in *anti* conformations, as is predicted by the theoretical calculations which apparently underestimate the attractive forces between the substituents, shown by lower equilibrium energies calculated for the *anti* disposition. The close agreement between the twist angles in the gas and solid phases and the fact that the molecules retain their molecular twofold symmetry in the crystal [the only exception is 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)biphenyl comprising a long side-chain substituent] show that the molecular conformation in the crystal is determined primarily by intramolecular forces and that these molecules behave much more rigidly than might be expected. In biphenyl (Robertson, 1961) the absence of 2,2'-substituents results in much more flexibility and accounts for the difference in conformation in the gas and solid. Indeed, this is also true for biphenyls substituted at other than the 2,2'-position, e.g. 4,4'-diamino-3,3'-dichlorobiphenyl with a twist angle of  $21^\circ$  (Chawdhury,

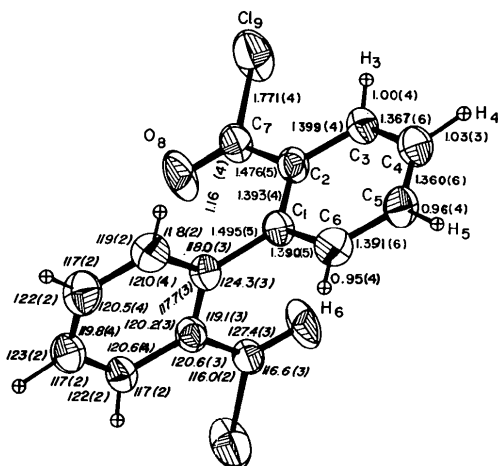
Fig. 1. Bond lengths (Å) and angles ( $^\circ$ ) and their estimated standard deviations.

Table 2. Structural data of some 2,2'-disubstituted biphenyls

Reference	Substituent	Method*	Twist	Conformation	Site symmetry	2...2'
1	COCl	X	$83.1^\circ$	<i>syn</i>	2	3.38 Å
2	CH <sub>3</sub>	X	70.6	<i>syn</i>	2	3.54
3	Cl	X	72	<i>syn</i>	2	
4	Cl	X	69.2	<i>syn</i>	2	3.42
5	Cl	el.g.	74	<i>syn</i>		
6	Cl	calc.	72, 120	<i>syn, anti</i>		
7	Br	X	80	<i>syn</i>	1	3.96
5	Br	el.g.	75	<i>syn</i>		
6	Br	calc.	82, 112	<i>syn, anti</i>		
8	F	el.g.	60	<i>syn</i>		
6	F	calc.	42, 143	<i>syn, anti</i>		
5	I	el.g.	79	<i>syn</i>		
6	I	calc.	93	<i>anti</i>		

References: (1) BCl (present analysis); (2) 2,2'-dimethylbenzidine dihydrochloride (Fowweather & Hargreaves, 1950); (3) 2,2'-dichlorobenzidine (Smare, 1948); (4) 2,2'-dichlorobiphenyl (Rømming, Seip & Oymo, 1974); (5) 2,2'-dichloro-, 2,2'-dibromo-, and 2,2'-diiodobiphenyl (Bastiansen, 1950); (6) 2,2'-difluoro-, 2,2'-dichloro-, 2,2'-dibromo-, and 2,2'-diiodobiphenyl (Almenningen, Hartmann & Seip, 1968); (7) 2,2'-dibromo-4,4'-bis(*p*-methoxybenzylideneamino)biphenyl (Lesser, de Vries, Reed & Brown, 1975); (8) 2,2'-difluorobiphenyl (Bastiansen & Smedvik, 1954).

\* X: single-crystal X-ray diffraction; el.g.: gas-phase electron diffraction; calc.: theoretical minimum-energy calculations.

Hargreaves & Rizvi, 1968) or 4,4'-diamino-3,3'-dimethylbiphenyl (Chawdhury, Hargreaves & Sullivan, 1968) with a twist angle of  $41^\circ$ . In these cases packing forces are the predominant factors in determining the conformations.

However, there is a difference in the nature of the  $2\cdots 2'$  interactions between BCl and the rest of the 2,2'-disubstituted biphenyls listed in Table 2. In the latter it is an atom $\cdots$ atom-type interaction while in BCl the molecular geometry excludes any possibility of  $\text{Cl}\cdots\text{O}$  or  $\text{Cl}\cdots\text{Cl}$  interactions. The conformation is dictated here by a  $\text{C}^+=\text{O}^-$  antiparallel dipole-dipole intramolecular interaction of  $3.38 \text{ \AA}$ , strong enough to bring about a rather short  $\text{O}'\cdots\text{C}(2)$  contact of  $3.05 \text{ \AA}$  and to tilt the carbonyl chloride groups toward each other by  $8.6^\circ$  per group so that the two  $\text{C}=\text{O}$  bonds are closer. In TCl the carbonyl chloride moiety is

Table 3. Equations of planes (through non-hydrogen atoms) in the form  $Ax + By + Cz + D = 0$ , where  $x, y, z$  are fractional atomic coordinates; distances ( $\times 10^3 \text{ \AA}$ ) of relevant atoms from the planes are given in square brackets

Plane A: Phenylcarbonyl chloride moiety

$$-6.5389x - 4.2237y + 10.2998z - 1.0989 = 0$$

[C(1) 53, C(6) 67, C(5) 12, C(4) -69, C(3) -62, C(2) 0, C(7) -18, O -110, Cl 127, H(6) 176, H(5) -42, H(4) -39, H(3) -40]

Plane B: Phenyl ring

$$-6.1422x - 4.1084y + 10.7691z - 1.3485 = 0$$

[C(1) -8, C(6) 2, C(5) 7, C(4) -10, C(3) 3, C(2) 6, C(7) -6, O -144, Cl 224, C(1') 31, C(4') 262, H(6) 66, H(5) -53, H(4) 68, H(3) 71]

Plane C: Carbonyl chloride group

$$-7.3943x - 4.3266y + 9.5013z - 0.6918 = 0$$

[C(2) 1, C(7) -2, O 1, Cl 0, C(1) 161, C(6) 157, C(5) -20, C(4) -205, C(3) -184, C(1') 400]

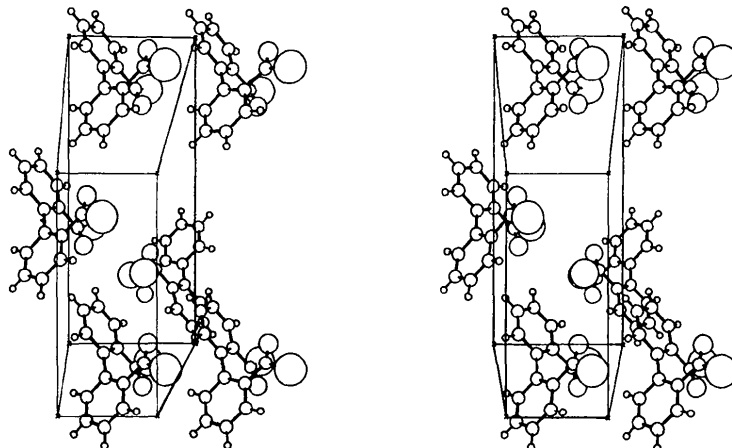


Fig. 3. Stereoscopic view of the packing along [001]. The origin of the unit cell is at the bottom left-hand corner with  $b$  horizontal and  $a$  vertical.

coplanar with the phenyl ring. Antiparallel  $\text{C}^+=\text{O}^-$  dipole-dipole intermolecular interactions are held responsible for the packing arrangement in MCl (part III) and in ACl (part V).

Table 3 lists the best planes through the non-hydrogen atoms of the phenylcarbonyl chloride moiety ( $A$ ), the phenyl ring ( $B$ ) and the carbonyl chloride group ( $C$ ). The phenyl ring is planar within  $0.01 \text{ \AA}$ . C(7) lies in this plane, while C(1'), Cl and O are out of this plane by  $0.03$ ,  $0.22$  and  $-0.14 \text{ \AA}$  respectively. The carbonyl chloride group is rotated  $8.6^\circ$  from the plane of the phenyl group.

#### Bond lengths and angles

Fig. 1 shows the bond lengths and angles as well as the thermal-vibration ellipsoids seen along [010]. Bond lengths and angles of the phenyl ring and the C(1)-C(1') distance agree well with those found in biphenyl (Charbonneau & Delugeard, 1976) and in the 2,2'-disubstituted biphenyls listed in Table 2. The distortion of the exocyclic angle ( $124.3^\circ$ ) is common to biphenyls substituted at the 2 position, e.g. 4-acetyl-2'-nitrobiphenyl ( $125.2^\circ$ ) (Sutherland, Hogg & Williams,

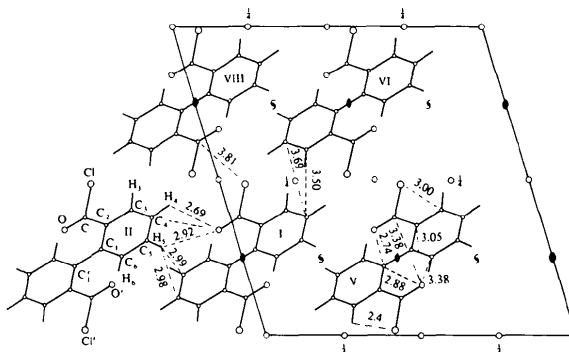


Fig. 2. Packing seen along [010] showing relevant intermolecular contacts. Some of the short intramolecular distances are shown in molecule V.

Table 4. *Short intermolecular contacts* (Å)

O...H(5) <sup>II</sup>	2.92	C(4)...C(4') <sup>VI</sup>	3.69
O...H(4) <sup>II</sup>	2.69	C(4)...C(3) <sup>VI</sup>	3.50
C(5)...O <sup>III</sup>	3.41	C(4)...H(3) <sup>VI</sup>	3.15
C(4)...O <sup>III</sup>	3.30	C(3)...C(3) <sup>VI</sup>	3.82
C(5)...C(5') <sup>III</sup>	3.88	C(3)...H(4) <sup>VI</sup>	3.04
C(5)...C(4') <sup>III</sup>	3.78	C(7)...H(6') <sup>VII</sup>	3.31
C(6)...O <sup>IV</sup>	3.45	O...H(6') <sup>VII</sup>	2.61
C(6)...H(5') <sup>V</sup>	3.31	C(7)...Cl <sup>VIII</sup>	3.81
C(5)...C(5') <sup>V</sup>	3.88	C(4)...Cl <sup>IX</sup>	3.88
C(5)...H(5') <sup>V</sup>	2.99	C(3)...Cl <sup>IX</sup>	3.76
C(4)...H(5') <sup>V</sup>	2.98	Cl...H(4) <sup>IX</sup>	3.30
C(3)...H(5') <sup>V</sup>	3.29	Cl...H(3) <sup>IX</sup>	3.15
		Cl...Cl <sup>X</sup>	3.88

Roman numerical superscripts refer to the molecules in the following equivalent positions.

(I)	$x, y, z$	(VI)	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
(II)	$-\frac{1}{2} + x, \frac{1}{2} + y, z$	(VII)	$x, 1 + y, z$
(III)	$\frac{1}{2} + x, -\frac{1}{2} + y, z$	(VIII)	$-x, 1 - y, 1 - z$
(IV)	$x, -1 + y, z$	(IX)	$\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$
(V)	$\frac{1}{2} + x, \frac{1}{2} + y, z$	(X)	$-x, 2 - y, 1 - z$

1974), 2'-iodobiphenyl-4-carboxylic acid (125.4°) (Sutherland, 1970) and in the compounds listed in Table 2, and is due to the repulsion between C(1') and the substituent on the second phenyl ring [C(1)—C(7') contact of 2.95 Å in BCl]. In contrast to the planar TCl and MCl, the angles at C(2) are not distorted, since the 1,4 C...Cl repulsive interaction is relaxed by the rotation (8.6°) of the carbonyl chloride group from the benzene ring.

#### Packing arrangement

Fig. 2 shows the packing in the *ac* plane. Fig. 3 shows a stereoview of the packing down [001]. No short Cl...O or Cl...Cl interactions are present. The

molecules are stacked along the shortest axis, linked by close O...H contacts of 2.61 Å in the stacks and 2.69 Å between stacks; the configuration of the C—H...O=C system is similar to that observed in *cis*-1,2-bis(*p*-chlorobenzoyl)ethylene (Rabinovich & Shakked, 1970). Other short intermolecular contacts are listed in Table 4.

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