Fig. 1. Stereoviews of the molecules of Me/9-^{i}Pr (top), Me/10-^{i}Pr (centre) and Me/10-Men (bottom).

al., 1990) have indicated that electron stabilization was not the controlling factor in the photochemical reactions of those materials, but that intermolecular steric effects were dominant. A qualitative study of intermolecular contacts in the present unsymmetrical esters indicates that bond formation at C12 is favourable. The initial step in the reaction [see Fig. 4 of Garcia-Garibay et al. (1990)] is believed to involve C11···C8a or C9a, or C12···C4a or C10a bond formation; this step results in large motion of a bulky ester group bonded to C11 or C12, which is impeded by intermolecular steric repulsions in the crystal. Since there is no ester group at C12 in the present compounds, reaction at C12 is favoured by these steric effects. It seems likely though that the electron stabilization effect is the dominant factor in determining the photochemical reaction pathway for these unsymmetrical diesters (since solution and solid-state products are identical).

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Structure of 4-Bromo-4'-fluorobiphenyl

By W. B. GLEASON* AND MYLES BROSTROM

Corporate Research Laboratories, 3M Company, 3M Center, St Paul, MN 55144, USA

M. C. ETTER

Department of Chemistry, University of Minnesota, Minneapolis, MN 55144, USA

AND R. B. JOHNSON

Rochelle Crystal Corporation at the College of St Catherine, St Paul, MN 55105, USA

Abstract. $C_{12}H_8BrF$, $M_r = 251 \cdot 1$, monoclinic, $P2_1/c$, $a = 9 \cdot 709$ (2), $b = 13 \cdot 311$ (2), $c = 17 \cdot 487$ (5) Å, $\beta = 116 \cdot 29$ (5)°, $V = 2026 \cdot 2$ Å^3, $Z = 8$, $D_x = 1 \cdot 64$ g cm^{-3}, λ(Mo $K\alpha$) = $0 \cdot 71073$ Å, $\mu = 39 \cdot 7$ cm^{-1}, $F(000) = 992$, $T = 298$ (1) K, $R = 0 \cdot 043$ for 1776 observed reflections. This crystal is isostructural with 4,4'-dibromobiphenyl and has inter-ring dihedral angles

* To whom correspondence should be addressed at: Department of Biochemistry, University of Minnesota, Minneapolis, MN 55455, USA.

of 40·3 (1) and 38·2 (3)°. The shortest intermolecular halogen contacts [3·06 (1), 3·20 (1) Å] involve bromine and fluorine.

Introduction. Crystal data for 4-bromo-4'-fluorobiphenyl, (III), have been previously reported by Brown, Low & Tollin (1986) but intensity data were only observable to low resolution and a full structure was not reported. The crystal structure of 4,4'-dibromobiphenyl, (I), has been previously reported by Kronebusch, Gleason & Britton (1976). In the solid this compound is non-planar with a dihedral angle of approximately 40° between the two phenyl rings. The crystal structure determination of 4,4'-difluorobiphenyl, (II), has been reported by two groups: Bielushkin, Natkaniec, Wasicki, Khomenko, Telezhenko & Wasiutynski (1986) and Lemée, Toupet, Délugeard, Messager & Cailleau (1987). The fluorinated derivative has a planar conformation in the solid similar to that of the parent compound, biphenyl. We have determined the structure of the 'hybrid' 4-bromo-4'-fluorobiphenyl, (III), in order to see which conformation it adopts.

Br—⟨⟩—⟨⟩—Br   (I)

F—⟨⟩—⟨⟩—F   (II)

F—⟨⟩—⟨⟩—Br   (III)
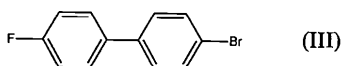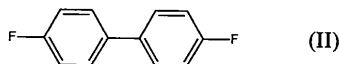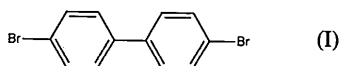
Experimental. 4-Bromo-4'-fluorobiphenyl was obtained from PCR Research Chemicals and suitable crystals were obtained by slow evaporation of an ethanol solution. A crystal of approximate dimensions 0·3 × 0·3 × 0·2 mm was mounted on a glass fiber with epoxy adhesive. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer using variable speed ω–2θ scans. Unit-cell constants were determined from a least-squares fit to data for 25 reflections in the angular range $10 < \theta < 15°$. Data were collected to $(\sin \theta)/\lambda$ of 0·594 Å^{-1}, $-11 \le h \le 11$, $0 \le k \le 15$, $-20 \le l \le 20$. As a check on crystal and electronic stability three reflections ($32\bar{5}$, $15\bar{3}$, 412) were monitored during data collection; these decayed 5% during the course of the experiment and a linear decay correction was applied. 7460 reflections were measured and averaged ($R_{int} = 1·6\%$) to 3565 unique data, 1776 reflections with $I > 2\sigma(I)$ were considered observed. An empirical absorption correction based on a series of ψ scans (North, Phillips & Mathews, 1968) was applied to the data. Relative transmission coefficients ranged from 0·822

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Br(1)	0·49956 (9)	0·86208 (6)	0·13434 (5)	7·04 (3)
Br(2)	0·00551 (7)	0·60234 (5)	0·14578 (4)	5·72 (2)
F(1)	0·4989 (4)	0·0895 (3)	0·1092 (2)	5·8 (1)
F(2)	0·0111 (5)	−0·1652 (3)	0·1009 (2)	7·2 (1)
C(1)	0·5003 (6)	0·5138 (5)	0·1282 (3)	3·7 (1)
C(2)	0·5814 (6)	0·5694 (5)	0·0961 (3)	4·2 (2)
C(3)	0·5821 (6)	0·6698 (5)	0·0981 (3)	4·3 (2)
C(4)	0·4976 (6)	0·7204 (5)	0·1328 (3)	4·8 (2)
C(5)	0·4139 (7)	0·6670 (5)	0·1642 (4)	4·9 (2)
C(6)	0·4155 (6)	0·5653 (5)	0·1624 (3)	4·3 (2)
C(7)	0·4981 (5)	0·4028 (5)	0·1251 (3)	4·1 (2)
C(8)	0·6312 (6)	0·3473 (5)	0·1402 (3)	4·3 (2)
C(9)	0·6267 (7)	0·2438 (5)	0·1364 (4)	5·1 (2)
C(10)	0·4940 (6)	0·1936 (5)	0·1140 (4)	5·3 (2)
C(11)	0·3607 (6)	0·2444 (5)	0·0980 (4)	5·0 (2)
C(12)	0·3630 (6)	0·3477 (5)	0·1039 (3)	4·4 (2)
C(13)	0·0047 (5)	0·2519 (5)	0·1276 (3)	3·7 (1)
C(14)	0·0836 (6)	0·3026 (5)	0·2057 (3)	4·3 (2)
C(15)	0·0807 (6)	0·4068 (5)	0·2102 (3)	4·6 (2)
C(16)	0·0039 (6)	0·4624 (4)	0·1381 (3)	4·0 (1)
C(17)	−0·0739 (6)	0·4158 (5)	0·0614 (3)	4·4 (2)
C(18)	−0·0736 (6)	0·3122 (5)	0·0555 (3)	4·2 (2)
C(19)	0·0066 (6)	0·1424 (4)	0·1226 (3)	3·8 (2)
C(20)	0·1378 (7)	0·0874 (5)	0·1707 (3)	4·6 (2)
C(21)	0·1387 (7)	−0·0141 (5)	0·1628 (4)	5·5 (2)
C(22)	0·0116 (8)	−0·0631 (5)	0·1080 (4)	6·1 (2)
C(23)	−0·1222 (7)	−0·0114 (6)	0·0597 (4)	6·3 (2)
C(24)	−0·1219 (7)	0·0906 (5)	0·0671 (4)	4·8 (2)

to 0·999 with an average value of 0·928. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. All parameters were refined by full-matrix least-squares refinement of F's. H atoms at calculated positions ($r_{C—H} = 0·95$ Å, $B_{iso} = 5·0$ Å^2) were included in the structure-factor calculations but were not refined, all other atoms refined anisotropically for 253 variables. Final $R = 0·043$, $wR = 0·056$, $S = 2·08$; $w = 1/\sigma^2(F)$ was calculated from $\sigma^2(I) = \sigma^2(I)_{cs} + (0·05I)^2$, where $\sigma(I)_{cs}$ is the standard deviation in I based on counting statistics alone. Final $(\Delta/\sigma)_{max} = 0·01$, $\Delta\rho_{max} = 0·59$ (8), $\Delta\rho_{min} = -0·40$ (6) e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs used were those of the Enraf–Nonius (1982) *SDP*.

Discussion. Atomic parameters are given in Table 1,* bond lengths and bond angles are in Table 2. The atomic numbering scheme is shown in Fig. 1. For

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53748 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Br(1)—C(4)	1·886 (5)	C(10)—C(11)	1·375 (7)
Br(2)—C(16)	1·867 (5)	C(11)—C(12)	1·378 (7)
F(1)—C(10)	1·390 (6)	C(13)—C(14)	1·407 (6)
F(2)—C(22)	1·366 (6)	C(13)—C(18)	1·401 (6)
C(1)—C(2)	1·370 (6)	C(13)—C(19)	1·461 (6)
C(1)—C(6)	1·393 (6)	C(14)—C(15)	1·390 (6)
C(1)—C(7)	1·479 (6)	C(15)—C(16)	1·364 (6)
C(2)—C(3)	1·337 (6)	C(16)—C(17)	1·363 (7)
C(3)—C(4)	1·390 (6)	C(17)—C(18)	1·383 (7)
C(4)—C(5)	1·365 (7)	C(19)—C(20)	1·385 (6)
C(5)—C(6)	1·355 (6)	C(19)—C(24)	1·379 (6)
C(7)—C(8)	1·408 (7)	C(20)—C(21)	1·358 (7)
C(7)—C(12)	1·402 (7)	C(21)—C(22)	1·348 (7)
C(8)—C(9)	1·379 (7)	C(22)—C(23)	1·380 (8)
C(9)—C(10)	1·347 (7)	C(23)—C(24)	1·365 (7)

C(2)—C(1)—C(6)	117·9 (4)	C(14)—C(13)—C(18)	116·4 (4)
C(2)—C(1)—C(7)	121·8 (4)	C(14)—C(13)—C(19)	121·4 (4)
C(6)—C(1)—C(7)	120·4 (4)	C(18)—C(13)—C(19)	122·3 (4)
C(1)—C(2)—C(3)	121·8 (5)	C(13)—C(14)—C(15)	121·1 (4)
C(2)—C(3)—C(4)	119·9 (5)	C(14)—C(15)—C(16)	120·4 (4)
Br(1)—C(4)—C(3)	119·1 (4)	Br(2)—C(16)—C(15)	119·4 (4)
Br(1)—C(4)—C(5)	121·2 (5)	Br(2)—C(16)—C(17)	120·5 (4)
C(3)—C(4)—C(5)	119·8 (4)	C(15)—C(16)—C(17)	120·0 (4)
C(4)—C(5)—C(6)	119·8 (5)	C(16)—C(17)—C(18)	120·6 (4)
C(1)—C(6)—C(5)	121·1 (5)	C(13)—C(18)—C(17)	121·5 (5)
C(1)—C(7)—C(8)	121·3 (4)	C(13)—C(19)—C(20)	121·6 (4)
C(1)—C(7)—C(12)	122·0 (5)	C(13)—C(19)—C(24)	120·6 (5)
C(8)—C(7)—C(12)	116·7 (5)	C(20)—C(19)—C(24)	117·7 (4)
C(7)—C(8)—C(9)	120·5 (5)	C(19)—C(20)—C(21)	120·6 (5)
C(8)—C(9)—C(10)	121·1 (5)	C(20)—C(21)—C(22)	120·5 (5)
F(1)—C(10)—C(9)	117·3 (6)	F(2)—C(22)—C(21)	120·8 (6)
F(1)—C(10)—C(11)	122·2 (5)	F(2)—C(22)—C(23)	118·4 (7)
C(9)—C(10)—C(11)	120·5 (5)	C(21)—C(22)—C(23)	120·8 (5)
C(10)—C(11)—C(12)	119·6 (5)	C(22)—C(23)—C(24)	118·5 (6)
C(7)—C(12)—C(11)	121·6 (5)	C(19)—C(24)—C(23)	121·9 (5)

two molecules in the asymmetric unit of (III), the inter-ring torsion angles are 40·3 (1) and 38·2 (3)°. These values are very close to those observed in (I): 38 and 42° (Kronebusch, Gleason & Britton, 1976), while in (II) this angle is zero.

Brock & Minton (1989) have recently reviewed systematic effects of crystal-packing forces in biphenyl systems lacking substituents in the *ortho* positions. They analyzed twist angles in 101 biphenyl fragments including (III). A distribution of twist angles with two (centered at 37 and 0°) and possibly three (centered at 18°) maxima was found. Although the largest number of structures were found in the peak centered at 37° [which included (III)], they concluded that crystal-packing effects systematically stabilized biphenyl fragments with small twist angles. They believe the most likely explanation to be that the solid state systematically favors nearly planar biphenyl fragments because of the better packing arrangement.

Given that (II) is planar in the solid state and that 4-bromobiphenyl has twist angles of 20 and 18° (Brock, 1980) then it might have been expected that the twist angle for (III) would be smaller than observed. However, simple factors such as size or electronegativity do not seem to explain the packing of biphenyl derivatives. The compound bitolyl is

isostructural (Casalone, Mariani, Mugnoli & Simonetta, 1969) with 4,4'-dibromobiphenyl even though the methyl groups in bitolyl are weakly electron donating. That bulky substituents might somehow cause the packing mode of the parent biphenyl to be inefficient seems unlikely because 3,3',5,5'-tetrachloro-4,4'-dihydroxybiphenyl is planar (McKinney & Singh, 1988). However, less intuitive computational approaches may yet prove fruitful. Thus, before definitive experimental results were available, Saito, Atake & Chihara (1987) calculated the energies of crystal structures containing planar and twisted conformations of (II) and correctly predicted that the compound would be planar in the solid.

An interesting feature of the structure is the packing of the Br atoms. The present structure is isostructural with the dibromo derivative, and could be derived from it in two ways. In the dibromo derivative, (I), some bromine contacts are present which are closer (3·46, 3·51 Å) than twice the value of the bromine van der Waals radius (3·70 Å) given by Bondi (1964). If the structure of the dibromo derivative is influenced by some type of weak intermolecular interaction of Br atoms, then the hybrid molecule might be expected to preserve close contacts for bromine. A second possibility is that substitution of a bromine–bromine pair of atoms involved in a 'short' contact by a bromine–fluorine pair might be expected to lead to more efficient packing as expressed by Kitaigorodsky's (1973) 'bumps in hollows' aphorism. The second possibility is supported
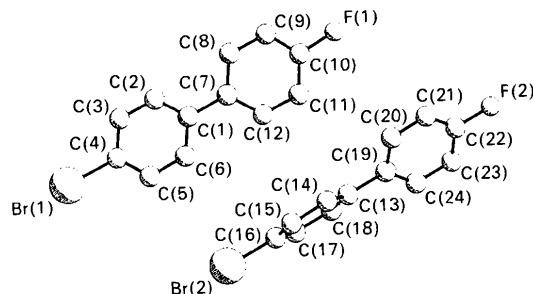

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of two crystallographically independent molecules of 4-bromo-4'-fluorobiphenyl.
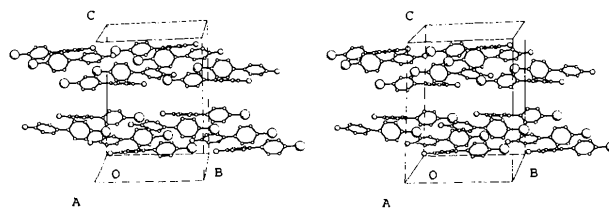

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) stereo packing diagram of 4-bromo-4'-fluorobiphenyl.

by the experimental result. As can be seen from the packing diagram of Fig. 2, there are no significantly short distances in (III) between neighboring Br atoms [the shortest intermolecular distance is 5·63 (1) Å, involving Br(1) and Br(2)]. The shortest intermolecular distances involving F and Br atoms are 3·06 (1) Å [Br(1) and F(1)] and 3·20 (1) Å [Br(2) and F(2)] while the predicted sum of the van der Waals radii for fluorine and bromine is 3·32 Å (Bondi, 1964). Compounds (I) and (III) are isostructural nonetheless with all interhalogen contacts in (III) involving F and Br atoms. Thus, the close Br···Br contacts in (I) may be stabilizing interactions but they apparently are not structure determining because substitution of an F atom for one of the Br atoms does not alter the packing pattern.

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Structure of Thialysine Hydrochloride

BY HERMAN L. AMMON, SATYA M. PRASAD AND JOHN A. GERLT

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

Abstract. 2-Ammonio-3-[(2-ammonioethyl)thio]propionate chloride, $C_5H_{13}N_2O_2S^+.Cl^-$, $M_r = 200.7$, monoclinic, $P2_1$, $a = 5.1275 (4)$, $b = 7.897 (1)$, $c = 11.208 (1)$ Å, $\beta = 104.129 (8)°$, $V = 440.1$ Å^3, $Z = 2$, $D_x = 1.519$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 6.12$ cm^{-1}, $F(000) = 212$, $T = 295$ K, final $R = 0.021$, $wR = 0.027$ for 784 reflections with $I > 3\sigma(I)$. The two ammonium cations form seven hydrogen bonds: α-NH$_3^+$ acts as a donor for three carboxylate O atoms and one Cl$^-$ ion whereas ε-NH$_3^+$ is linked to three Cl$^-$ ions.

Introduction. The alteration of one or more amino-acid residues in a macromolecule is a well established procedure for investigating the influence of the residue(s) on structure and function. The changes, which are introduced by site-directed mutagenesis, are limited to those specified by the genetic code. With these restrictions, for example, it is not possible to replace lysine with a residue in which the distance

between the α- and ε-amino groups has been changed, or to introduce such an altered lysine residue at another location in the polypeptide. The insertion of a thialysine (I) residue might be achieved by the introduction of cysteine with the usual procedures followed by the reaction of the cysteine-containing macromolecule with ethylenimine to convert the cysteine to a thialysine. The structural properties of the Cα-linked chain in thialysine and a comparison with that in lysine was of primary interest in the investigation reported here.
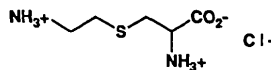
(I)

Experimental. Colorless crystals from aqueous ethanol; 0·2 × 0·35 × 0·4 mm crystal; CAD-4 diffractometer, graphite monochromator, cell parameters