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Crystal structures and energy refinement of some 2,2′-disubstituted biphenyl compounds

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Synthesis and structural determination by X-ray crystallography of three substituted biphenyl structures are reported: (2) is monoclinic $P2_1/n$ with a = 10.805(4), b = 8.079(3), c = 16.232(6) Å, β = 100.96(5)°; (4) is monoclinic $P2_1/n$ with a = 9.966(3), b = 10.007(3), c = 13.053(4) Å, β = 96.74(5)°; (5) is triclinic $P\bar{1}$ with a = 12.033(5), b = 16.903(8), c = 9.752(4) Å, α = 94.70(3)°, β = 112.56(3)° γ = 76.12(3)°. In all compounds the biphenyl has two identical substituents in an ortho position to the center inter-ring bond and present variable inter-ring twist angles. In the process of investigating molecular geometry, we are interested in studying whether the calculated conformations of our molecules can fit the crystallographic structures.

Introduction

Biphenyl and substituted biphenyl molecules are the most famous examples which illustrate that molecular conformation in the crystalline state results from a delicate balance between antagonist intramolecular and intermolecular forces. Structure analyses of the biphenyl molecule in the gas or in the solid state have revealed interesting conformational changes. The inter-ring twist angle τ is equal to 42° in the gas phase (Bastiansen and Tratteberg, 1962) whereas crystallographic studies (Trotter, 1961; Hargreaves and Rizvi, 1962; Charbonneau and Delugeard, 1976, 1977) have shown the molecule to be planar. For substituted biphenyls the situation is somewhat more complicated, the values of τ angles observed in the solid state or calculated by molecular mechanics depend on the nature and the position of the substituents on the phenyl cycles. The steric hindrance brought by various substituents in the 2,2′-position such as COOH (Fronczek *et al.*, 1987), Cl (Romming *et al.*, 1974), and $N(CH_3)_2$ (van der Sluis and Spek, 1990a), gives rise to large values of τ, between 68° and 83° in the solid state, and 66° to 90° for the calculated angles (Benmenni, unpublished results), with a maximum of discrepancy of 22° between observed and calculated τ, and an averaged difference of 12°. With 3,3′- or 4,4′-substituents and in the absence of noticeable intermolecular interactions, the observed τ angles scatter around the value found in gas phase for the biphenyl molecule: 21° to 50° (van der Sluis *et al.*, 1990b) with calculated values between 34° (Singh *et al.*, 1987) and 71° (Benmenni, unpublished results). Intermolecular hydrogen bonds lead to a flattening of the torsion angle τ. Thus, in the solid state, 4-hydroxy biphenyl (Brock and Haller, 1984) and 3,3′-5,5′-tetrachloro-4,4′-dihydroxybiphenyl (McKinney and Sing, 1988) are flat (τ = 0) although the calculated values are 45° (Benmenni, unpublished results) and 36° (McKinney and Sing, 1988), respectively.

Substituted biphenyls are molecules we used as ligands in the preparation of copper(II) complexes which are supposed to be chemical models of the active site of cupro-proteins (Müller *et al.*, 1988; Knapp *et al.*, 1982; Réglier *et al.*, 1990, 1993). In order to understand whether the molecular conformation of the ligands and later of the copper complexes can be simulated by empirical molecular modeling, we have undertaken crystal structure investigations and conformational calculations

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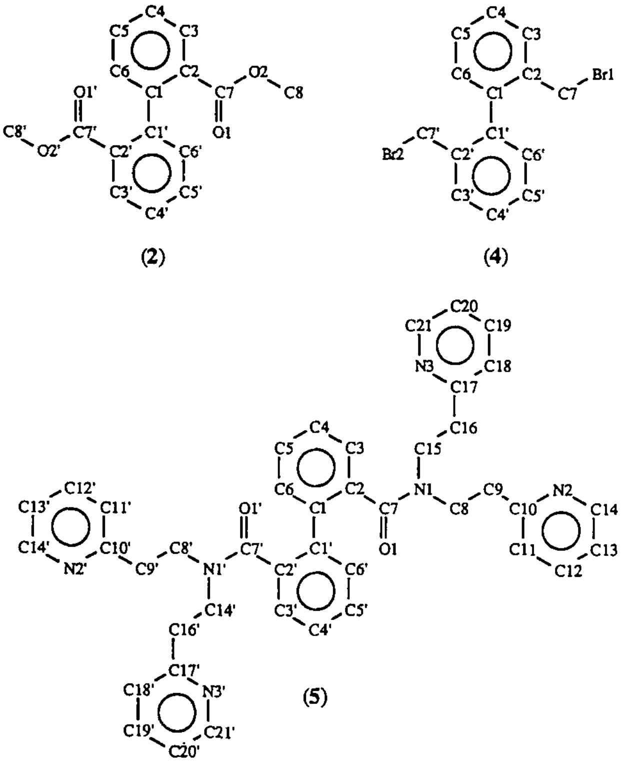


Scheme 1. Numbering scheme for compounds (2), (4), and (5) using in X-ray analysis and the definition of torsion angles τ (C2C1C1'C2'), $\tau 1$ (C1C2C7x) and $\tau 2$ (C1'C2'C7'x') with x,x' = O1, O1' for (2) and (5) and x,x' = Br1, Br2 for (4).

of three biphenyl derivatives identically substituted in the 2,2'-positions. These compounds hereafter named **(2)**, **(4)**, and **(5)** are described in Scheme 1 with the atom numbering used for the discussion.

Experimental

2,2'-Dimethyl diphenate (2)

In a 250 ml flask, diphenic acid **(1)** (5 g; 21 mmol) is refluxed over night in dry methanol (100 ml) containing concentrated sulfuric acid (5 ml). After cooling and methanol evaporation under vacuum, the crude oil obtained is dissolved in dichloromethane (50 ml), successively washed with a saturated $NaHCO_3$ solution, brine and dried on magnesium sulfate. After solvent evaporation under vacuum, distillation (130°C/0.1 mm Hg) affords 5.6 g (83%) of 2,2'-dimethyl diphenate **(2)**. Ir (film): $\nu_{C=O}$, 1724 cm^{-1}; δ_{C-O}, 1254 cm^{-1}. ^1H nmr (200 MHz, $CDCl_3$), δ ppm/TMS 8.01 (dd, J_1 = 7.7 and J_2 = 1.7 Hz; 2H); 7.53 (td, J_1 = 7.5 and J_2 = 1.7 Hz; 2H); 7.42 (td, J_1 = 7.5 and J_2 = 1.7 Hz; 2H); 7.20 (dd, J_1 = 7.5 and J_2 = 1.7 Hz; 2H); 3.61 (s, 6H). ^{13}C nmr (50 MHz, DEPT, $CDCl_3$), δ ppm/TMS 167.41 (2 $COOCH_3$), 143.29 (2 C), 131.49 (2 CH), 130.20 (2 CH), 129.85 (2 CH), 129.34 (2 C), 127.18 (2 CH), 51.82 (2 $COOCH_3$).

2,2'-Bis(hydroxymethyl)biphenyl (3)

In a 250 ml trinecked flask, lithium aluminum hydride (2 g; 53 mmol) is carefully suspended in anhydrous THF (50 ml) and maintained at 0°C with an ice bath. To this suspension, 2,2'-dimethyl diphenate **(2)** (5.6 g; 21 mmol) dissolved in anhydrous THF (50 ml) is added dropwise. After addition, this mixture is refluxed for 3 hr. Careful hydrolysis with water, filtration of the aluminate precipitate, drying on sodium sulfate and THF evaporation under vacuum, afford 2.8 g (64%) of 2,2'-bis(hydroxymethyl) biphenyl **(3)** which are crystallized in methanol at −20°C. Melting point: 110°C. Anal. calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found C, 78.55; H, 6.63. Ir (film) ν_{OH}; 3374 cm^{-1}; δ_{C-O}, 1032 cm^{-1}. ^1H nmr (200 MHz, $CDCl_3$), δ ppm/TMS 7.50–7.20 (m; 6H), 7.12 (dd, J_1 = 7.7 and J_2 = 2.1 Hz; 2 H). ^{13}C nmr (50 MHz, DEPT, $CDCl_3$), δ ppm/TMS 139.97 (2 C), 138.61 (2 C), 129.60 (2 CH), 128.03 (2 CH), 127.58 (2 CH), 62.61 (2 CH_2).

2,2'-Bis(bromomethyl) biphenyl (4)

To a carbon tetrachloride (10 ml) solution of phosphorus tribromide (3 g, 11 mmol), a suspension of alcohol **(3)** (2.8 g, 13 mmol) in carbon tetrachloride (25 ml) are added dropwise. After 3 hr at room temperature, the homogeneous solution is successively washed with saturated bicarbonate solution and brine, and dried on magnesium sulfate. Solvent evaporation under vacuum affords the crude dibromide **(4)** which is recrystallized in hot hexanes (3.65 g, 82%). Anal. calcd. for $C_{14}H_{12}Br_2$: C, 49.71; H, 3.58. Found C, 49.80; H, 3.61. ^1H nmr (200 MHz, $CDCl_3$), δ ppm/TMS 7.70–7.30 (m; 8 H), 4.35 (d, J = 10 Hz; 4 H); 4.19 (d, J = 10 Hz; 4 H). ^{13}C nmr (50 MHz, DEPT, $CDCl_3$), δ ppm/TMS 139.38 (2 C), 135.85 (2 C), 130.66 (2 CH), 129.70 (2 CH), 128.96 (2 CH), 128.93 (2 CH), 31.91 (2 CH_2Br).

2,2'-Bis{N,N'-bis[2-(2'pyridyl)-ethyl] biphenyldicarboxamide; 2,2'-BIPHAMID[PY2]$_2$ (5)

A diphenic acid **(1)** suspension (4.2 g, 20 mmol) in dry toluene (50 ml) is treated by thionyl chloride (3.2 ml). This suspension is refluxed until SO_2 ceases to evolve (3 hr). Then, the solution is cooled, the toluene is evaporated, the crude product obtained is dried under vacuum (1 mm Hg) and dissolved in dichloromethane (50 ml). To this solution bis-2-[2′pyridylethyl]amine (8 g, 59 mmol) in dichloromethane (25 ml) is added dropwise. The mixture is agitated for 16 hr. After that, the solution is successively treated with saturated bicarbonate solution, brine and dried on sodium sulfate. After dichloromethane evaporation, the diamide (**5**) is obtained as a white solid which is recrystallized in dimethylsulfoxide at 25°C (6.1 g, 60%). Anal. calcd. for $C_{42}H_{40}N_6O_2$: C, 76.34; H, 6.10; N, 12.72. Found C, 76.50; H, 6.30; N, 13.01. Ir ($CHCl_3$), $\nu_{C=O}$, 1600 cm^{-1}. ^1H nmr (200 MHz, $CDCl_3$), δ ppm/TMS 8.53 (d, J = 4.3 Hz; 2 H), 8.45 (d, J = 4.2 Hz; 2 H), 4.44 (td, J_1 = 7.6 and J_2 = 1.8 Hz; 2 H), 4.44 (td, J_1 = 7.6 and J_2 = 1.8 Hz; 2 H), 7.35–7.25 (m, 6H), 7.20–7.10 (m, 6H), 7.05–6.95 (m, 4H), 4.30–2.70 (m, 16H). ^{13}C nmr (50 MHz, DEPT, $CDCl_3$), δ ppm/TMS 170.37 (2 C_{amid}); 158.80 (2 C_{py}); 157.95 (2 C_{py}); 148.80 (4 CH_{py}); 136.26 (2 C_{biph}), 136.18 (2 C_{biph}), 135.99 (4 CH_{py}); 129.84 (2 CH_{biph}); 128.01 (2 CH_{biph}); 127.06 (2 CH_{biph}); 126.51 (2 CH_{biph}); 123.01 (2 CH_{py}), 122.97 (2 CH_{py}); 121.11 (2 CH_{py}); 121.02 (2 CH_{py}); 48.40 (2 CH_2); 44.45 (2 CH_2); 36.62 (2 CH_2); 34.88 (2 CH_2).

Crystal data

For each compound a unique data set was measured at 293°K, by using an Enraf Nonius CAD4 diffractometer with monochromated Mo$K\alpha$ (λ = 0.71073 Å). Cell constants and orientation matrix for data collection were obtained from a least squares fit of 25 reflections with $14° < \theta < 18°$. The intensity of three standard reflections measured every 60 min showed no significant variation during the data collection. Crystal orientation was monitored every 400 reflections. Further details of the crystals and the data collections are reported in Table 1.

Lorentz and polarization corrections were applied to the raw data which were not corrected for absorption or secondary extinction. The structures were solved by direct methods calculations using Multan (Main *et al.*,

Table 1. Data collection and processing parameters

Compounds	(2)	(4)	(5)
Formula	$C_{16}H_{14}O_4$	$C_{14}H_{12}Br_2$	$C_{42}H_{40}N_6O_2$
M_w	270.29	340.06	618.81
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Unit cell parameters			
a, Å	10.805(4)	9.966(3)	12.033(5)
b, Å	8.079(3)	10.007(3)	16.903(8)
c, Å	16.232(6)	13.053(4)	9.752(4)
α, °			94.70(3)
β, °	100.96(5)	96.74(5)	112.56(3)
γ, °			76.12(3)
V, Å^3	1391(1)	1292(1)	1778(2)
Z	4	4	2
Density calcd., g cm^{-3}	1.29	1.74	1.298
F(000)	568	664	736
μ (MoK_α), cm^{-1}	0.86	61.8	1.3
Scan type; θ_{max}	θ-2θ; 24	θ-2θ; 24	θ-2θ; 24
h, k, l range	−10/10, 0/7, 0/15	−11/11, 0/11, 0/14	−13/13, −19/19, 0/11
Scan range θ, °	1–24	1–24	1–24
Scan width	0.35 + 2.7 tan θ	0.35 + 2.7 tan θ	0.35 + 2.7 tan θ
Number of reflections:			
Measured	2277	2147	5344
Unique	2109	1891	4710
Used in refinement	1822	1235	3823
Number of variables	181	145	451
R (Rw)	0.042 (0.040)	0.054 (0.062)	0.051 (0.055)
W	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
max Δe/Å^3	0.157	1.1	0.261
Goodness of fit	2.205	2.825	1.07
Max shift	0.004	0.02	0.002

Table 2. Table of positional parameters and their estimated standard deviations for compound **(2)**

Atom	x	y	z	B (Å^2)
O1	−0.0258(2)	−0.2410(2)	0.6855(1)	6.83(5)
O1′	0.1808(2)	−0.4102(2)	0.8557(1)	5.89(5)
O2	−0.1444(2)	−0.4634(2)	0.6673(1)	6.68(5)
O2′	0.3574(2)	−0.2633(2)	0.8850(1)	5.62(5)
C1	−0.0431(2)	−0.2395(3)	0.8630(1)	3.61(5)
C1′	0.0397(2)	−0.0994(3)	0.8464(1)	3.39(5)
C2	−0.1049(2)	−0.3499(3)	0.8021(1)	3.57(5)
C2′	0.1694(2)	−0.1140(3)	0.8502(1)	3.40(5)
C3′	0.2412(2)	0.0260(3)	0.8403(1)	4.18(6)
C3	−0.1843(2)	−0.4709(3)	0.8246(2)	4.63(7)
C4′	0.1860(2)	0.1801(3)	0.8274(2)	4.72(6)
C4	−0.2023(2)	−0.4842(4)	0.9063(2)	5.33(7)
C5′	0.0580(2)	0.1955(3)	0.8243(2)	5.07(7)
C5	−0.1412(2)	−0.3775(4)	0.9667(2)	5.57(7)
C6	−0.0632(2)	−0.2550(3)	0.9445(2)	4.81(6)
C6′	−0.0136(2)	0.0574(3)	0.8343(2)	4.46(6)
C7′	0.2324(2)	−0.2787(3)	0.8637(1)	3.96(6)
C7	−0.0855(2)	−0.3412(3)	0.7143(2)	4.07(6)
C8	−0.1346(3)	−0.4679(4)	0.5801(2)	7.33(9)
C8′	0.4278(3)	−0.4170(4)	0.8926(2)	7.21(9)

Table 3. Table of positional parameters and their estimated standard deviations for compound **(4)**

Atom	x	y	z	B (Å^2)
BR1	0.2199(2)	0.1556(2)	0.9366(1)	4.85(3)
BR2	0.5547(2)	0.4482(2)	0.6918(1)	5.80(4)
C1	0.566(1)	0.128(1)	0.8241(9)	3.2(3)
C1′	0.587(1)	0.205(1)	0.9204(9)	3.1(2)
C2	0.615(1)	0.171(1)	0.7337(9)	3.5(3)
C2′	0.483(1)	0.278(1)	0.9573(9)	3.5(3)
C3	0.595(1)	0.093(1)	0.6455(9)	4.1(3)
C3′	0.506(1)	0.345(1)	1.052(1)	4.1(3)
C4′	0.631(1)	0.341(1)	1.109(1)	4.7(3)
C4	0.530(1)	−0.029(1)	0.646(1)	4.6(3)
C5′	0.736(1)	0.274(1)	1.073(1)	5.2(3)
C5	0.480(1)	−0.071(1)	0.734(1)	4.0(3)
C6	0.499(1)	0.004(1)	0.822(1)	3.7(3)
C6′	0.713(1)	0.202(1)	0.979(1)	4.2(3)
C7′	0.351(1)	0.292(1)	0.896(1)	3.9(3)
C7	0.688(1)	0.301(1)	0.730(1)	4.7(3)

1980); the remaining nonhydrogen atoms were located in successive Fourier difference synthesis. Hydrogen atoms were introduced at idealized positions but not refined. All nonhydrogen atoms were refined anisotropically. Full-matrix least-squares refinement with the SDP package (Frenz, 1978) was applied. The function $\Sigma w(|F_o|-|F_c|)^2$ was minimized where $w = \sigma(F_o)^{-2}$; $\phi(F_o)$ was based on counting statistics. Atomic scattering factors were those of the *International Tables of Crystallography*. Refinement parameters and results are given in Table 1. The final coordinates and thermal parameters are listed in Tables 2–4 for compounds **(2)**, **(4)**, and **(5)**, respectively. Selected bond distances and angles are given in Tables 5–7. (The authors have deposited atomic coordinates, bond lengths and bond angles for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.)

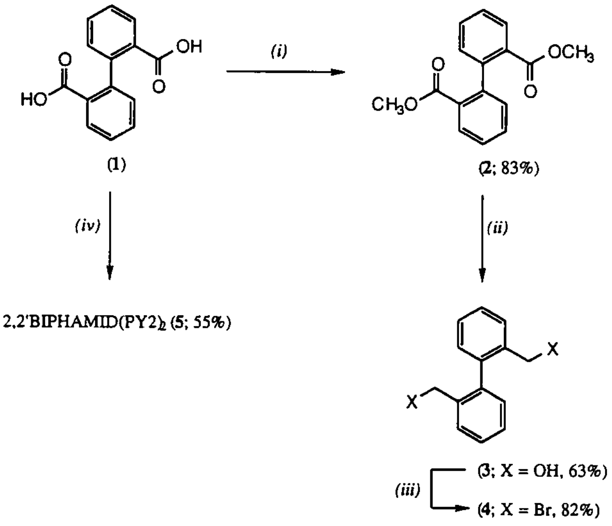
Results and discussion

Synthesis

Diester **(2)** was obtained from commercially available diphenic acid **(1)** by an acid catalyzed esterification reaction (Hiatt *et al.*, 1979). Alcohol **(3)**, obtained by reduction of diester **(2)** with lithium aluminum hydride, has been transformed to the dibromo derivative **(4)** by treatment with phosphorus tribromide in carbon tetrachloride. The reaction of diphenic acid **(1)** with thionyl chloride in toluene followed by amidation with bis[2-(2′-pyridyl)ethyl]amine in dichloromethane afforded diamide 2,2′-BIPHAMID(PY2)$_2$ **(5)**.

X-ray analysis

All attempts to obtain good crystals of diol **(3)** have failed. However, crystallization of saturated: (i) ether



Scheme 2. Synthesis of compounds (2)–(5) from diphenic acid (1) [(i) MeOH/5% H_2SO_4; (ii) $AlLiH_4/Et_2O$; (iii) PBr_3-CCl_4; (iv) $SOCl_2$ Toluene then bis[2-(2′-pyridyl)ethyl]amine CH_2Cl_2].

Table 4. Table of positional parameters and their estimated standard deviations for compound **(5)**

Atom	x	y	z	B (Å^2)
O1′	0.3140(2)	0.2370(2)	0.0396(3)	4.56(7)
O1	0.5585(2)	0.3124(2)	0.6230(3)	4.14(7)
N1′	0.1182(2)	0.3095(2)	−0.0636(3)	3.19(7)
N1	0.5933(2)	0.2181(2)	0.4580(3)	3.03(7)
N2′	−0.0750(3)	0.0922(3)	−0.1598(4)	7.0(1)
N2	0.6117(3)	−0.0324(2)	0.2366(3)	4.33(8)
N3′	0.0528(3)	0.5299(2)	−0.2291(3)	4.42(9)
N3	0.8135(3)	0.2289(2)	0.2513(3)	4.28(8)
C1	0.2930(3)	0.3056(2)	0.3527(3)	2.62(7)
C1′	0.3143(3)	0.3697(2)	0.2775(3)	2.65(8)
C2	0.3882(3)	0.2575(2)	0.4687(3)	2.76(8)
C2′	0.2789(3)	0.3721(2)	0.1223(3)	2.76(8)
C3	0.3622(3)	0.2024(2)	0.5427(4)	3.68(9)
C3′	0.2966(3)	0.4343(2)	0.0547(4)	3.63(9)
C4′	0.3459(3)	0.4969(2)	0.1383(4)	4.2(1)
C4	0.2429(3)	0.1922(2)	0.5023(4)	4.03(9)
C5′	0.3797(3)	0.4956(2)	0.2908(4)	4.0(1)
C5	0.1480(3)	0.2387(2)	0.3852(4)	3.85(9)
C6	0.1735(3)	0.2945(2)	0.3135(4)	3.23(8)
C6′	0.3648(3)	0.4330(2)	0.3594(4)	3.24(9)
C7′	0.2381(3)	0.3007(2)	0.0303(3)	2.99(8)
C7	0.5206(3)	0.2658(2)	0.5221(3)	2.96(8)
C8′	0.0843(3)	0.2377(2)	−0.1488(4)	4.0(1)
C8	0.5526(3)	0.1584(2)	0.3418(3)	3.14(8)
C9′	0.0722(4)	0.1756(3)	−0.0555(5)	6.4(1)
C9	0.5772(4)	0.0740(2)	0.4066(4)	4.0(1)
C10′	0.0327(3)	0.1032(2)	−0.1463(4)	4.4(1)
C10	0.5301(3)	0.0156(2)	0.2854(4)	3.33(8)
C11′	0.1049(4)	0.0537(3)	−0.2111(6)	7.8(2)
C11	0.4071(4)	0.0131(3)	0.2280(5)	5.3(1)
C12′	0.0679(6)	−0.0119(3)	−0.2910(7)	9.2(2)
C12	0.3674(4)	−0.0412(3)	0.1170(5)	7.0(1)
C13′	−0.0372(6)	−0.0264(3)	−0.3009(7)	9.5(2)
C13	0.4500(4)	−0.0905(3)	0.0665(4)	6.1(1)
C14′	−0.1081(5)	0.0260(4)	−0.2398(7)	9.8(2)
C14	0.5696(4)	−0.0843(3)	0.1268(4)	5.5(1)
C15′	0.0186(3)	0.3803(2)	−0.0708(4)	3.56(9)
C15	0.7246(3)	0.2211(3)	0.5149(4)	4.0(1)
C16′	−0.0440(3)	0.4222(2)	−0.2224(4)	4.2(1)
C16	0.7456(3)	0.2906(3)	0.4448(4)	4.5(1)
C17′	0.0412(3)	0.4537(2)	−0.2692(4)	3.8(1)
C17	0.7237(3)	0.2795(2)	0.2834(4)	3.58(9)
C18′	0.1099(4)	0.4061(3)	−0.3430(4)	5.3(1)
C18	0.6167(4)	0.3194(3)	0.1759(5)	5.2(1)
C19′	0.1930(4)	0.4362(3)	−0.3753(5)	6.8(1)
C19	0.6031(4)	0.3093(3)	0.0288(5)	6.5(1)
C20′	0.2053(4)	0.5148(3)	−0.3351(5)	6.1(1)
C20	0.6960(4)	0.2587(3)	−0.0062(5)	6.4(1)
C21′	0.1329(4)	0.5585(3)	−0.2634(4)	5.1(1)
C21	0.7988(4)	0.2190(3)	0.1097(5)	5.6(1)

Table 5. Selected bond distances and angles with esd's in parentheses for compound **(2)**

(a) Bond Distances in Å

C1−C1′	1.498(3)	C7−O2	1.333(3)
C2−C7	1.481(3)	C7′−O2′	1.335(3)
C2′−C7′	1.492(3)	O2−C8	1.441(3)
C7−O1	1.185(3)	O2′−C8′	1.449(3)
C7′−O1′	1.196(3)		

(b) Bond Angles in °

C1−C2−C7	120.8(2)	C2−C7−O2	112.0(2)
C7′−O2′−C8′	115.6(2)	C1′−C2′−C7′	120.5(2)
C2′−C7′−O2′	111.5(2)	O1−C7−O2	121.2(2)
C2−C7−O1	126.8(2)	C7−O2−C8	117.6(2)
O1′−C7′−O2′	122.6(2)	C2′−C7′−O1′	125.9(2)
C7′−O2′−C8′	115.6(2)		

Table 6. Selected bond distances and angles with esd's in parentheses for compound **(4)**

(a) Bond Distances in Å

C1−C1′	1.47(2)	C7−Br2	2.01(1)
C2−C7	1.50(2)	C7′−Br1	2.00(1)
C2′−C7′	1.46(2)		

(b) Bond Angles in °

C1−C2−C7	121.1(1)	C2−C7−Br2	109.4(8)
C1′−C2′−C7′	121.1(1)	C2′−C7′−Br1	111.3(9)

solution for **(2)**; (ii) hexane solution for **(4)**; (iii) and dimethylsulfoxide solution for **(5)** give rise to suitable crystals for X-ray analysis. The conformation of the molecules and the molecular packing arrangement in the unit cell are indicated in Fig. 1. Both phenyl rings are planar to within ±0.01 Å. Intraring C−C bond lengths lie within the range 1.373(6) Å to 1.41(2) Å and the pivot bond has an average length of 1.487(13) Å. As expected for 2,2′-disubstituted biphenyls, all these mol-

Table 7. Selected bond distances and angles with esd's in parentheses for compound **(5)**

(a) Bond Distances in Å

C1−C1′	1.479(5)	C7−N1	1.344(5)
N1′−C8′	1.464(5)	C2−C7	1.513(5)
C7′−N1′	1.359(4)	C8′−C9′	1.511(7)
C2′−C7′	1.506(5)	N1−C8	1.471(4)
C9′−C10′	1.511(6)	C7−O1	1.224(4)
C8−C9	1.524(5)	C7′−O1′	1.218(4)
C9−C10	1.501(5)		

(b) Bond Angles in °

C1−C2−C7	122.2(2)	C2′−C7′−O1′	119.1(3)
C1′−C2′−C7′	119.9(3)	C2−C7−N1	117.1(3)
C2−C7−O1	120.1(3)	C2′−C7′−N1′	119.1(3)

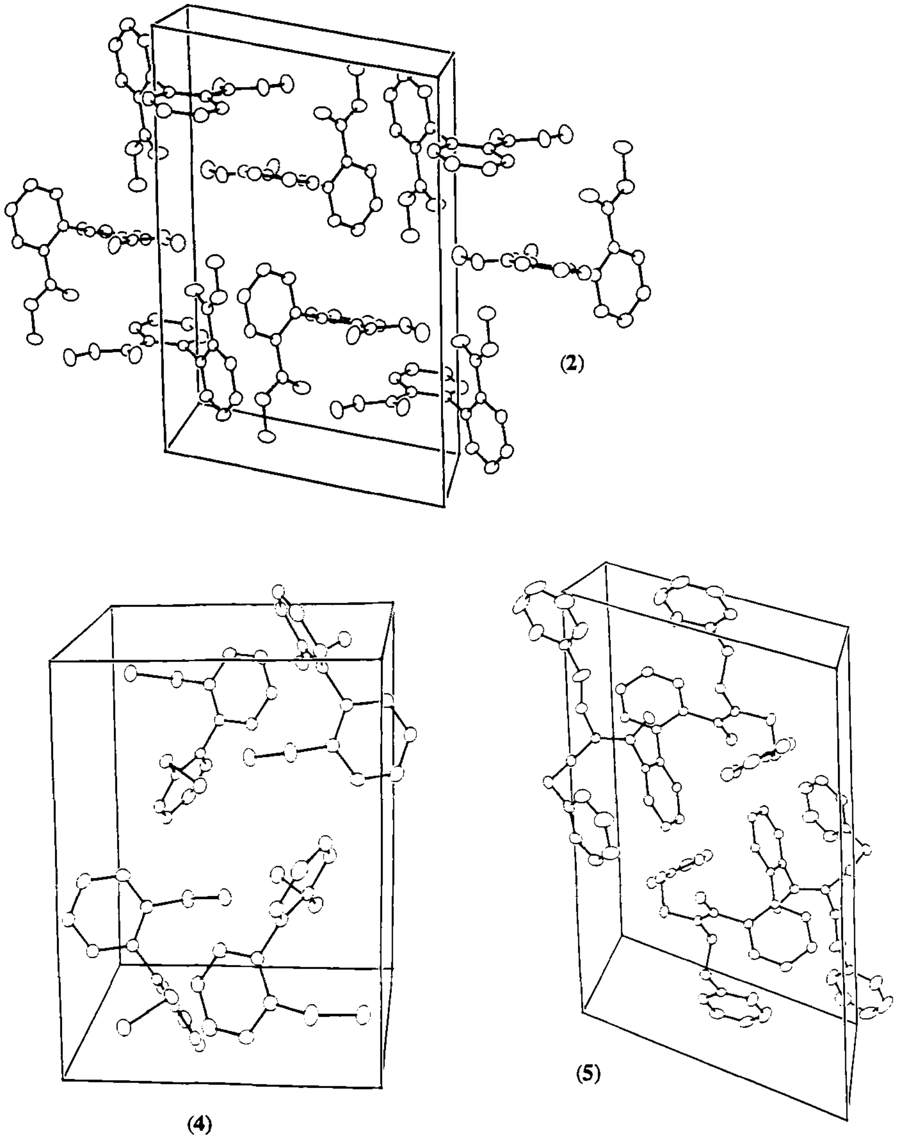


Fig. 1. Unit cell contents of compounds (2), (4), and (5).

ecules adopt a twist conformation with relatively large values of the τ angles: 89.8°, 76.3°, and 126.1°, respectively, for compounds **(2)**, **(4)**, and **(5)** (Table 8).

The bromo derivative **(4)** is symmetrically substituted, the torsion angles $\tau1$ and $\tau2$ as defined in Scheme 1 are equal within the experimental errors: $\tau1 = 88(1)°$ and $\tau2 = 87(1)°$. This is not the case with compounds **(2)** and **(5)** when an asymmetry in conformation of the substituents appears: the difference between torsion angles of the phenyl planes and the substituents is more significant in compound **(5)** ($\tau1 = 91.1(4)°$, $\tau2 =$

Table 8. Values of torsion angles τ^* for compounds **(2)**, **(4)**, and **(5)**[a]

Compounds	(2)	(4)	(5)
τ_{obs}	89.8(3)	76.3(1.5)	126.1(3)
τ_{calc}	83.1/*85.3*	92.2	120.7/*113.1*
$\tau1_{obs}$	4.6(4)	88.(1)	91.1(4)
$\tau1_{calc}$	45.2/*57.2*	101.6	81.1/*87.6*
$\tau2_{obs}$	15.8(4)	87.(1)	69.4(4)
$\tau2_{calc}$	70.1/*74.9*	93.6	76.4/*76.4*

[a] Italic values were obtained by dynamics calculations.

69.4(4)°) than in compound **(2)** ($\tau 1$ = 4.6(4)°, $\tau 2$ = 15.8(2)°). Moreover, the values of these torsion angles indicate that orientation of the carbonyl groups is different in compounds **(2)** and **(5)**: the ester groups in **(2)** are nearly coplanar to the phenyl ring whereas the carbonyls are almost perpendicular to the phenyl groups in **(5)**. As can be seen in Figure 1 the packing of these molecules is rather different in crystals **(2)** and **(5)**, the CO groups in **(2)** being external and exposed to intermolecular contacts. However the calculation of intermolecular distances doesn't bring any information explaining the asymmetry of the substitution and the difference of the CO orientation.

Molecular mechanics and dynamics calculations

These calculations were performed with Pro-Simulate software (Oxford Molecular Ltd., The Magdalen Centre, Oxford Science Park, Oxford OX4 4GA) and Gromos Vacuum Force Field running on a Silicon Graphics workstation. Parameters for the pivot bond were adapted in order to allow the torsion of biphenyl and test calculations were performed on some biphenyl crystal structures known in the literature (Benmenni, unpublished results). All compounds were first energy minimized by 1000 steps of steepest descent followed by conjugated gradient. Dynamics calculations were performed for compounds **(2)** and **(5)** using the following parameters: MD simulation of 60 ps at constant temperature (300°K) with a time step of 1 fs.

Calculated values for the torsion angles τ, $\tau 1$, and $\tau 2$ are given in Table 8 and deserve some comments, keeping in mind that the calculated conformation in vacuum gives an approximation of the experimental structure observed in the solid state. In all these compounds the torsion angle τ is reproduced well, the maximum discrepancy being obtained for **(4)**: 92.2° compared to 76.3° observed in the crystal. The conformation of the ortho-substituents defined by torsion angles $\tau 1$ and $\tau 2$ leads to different situations. For compounds **(4)** and **(5)** the agreement between observed and calculated values is satisfactory, the larger difference being less than 10°. More interesting is the difference between $\tau 1$ and $\tau 2$ in the same compound: 8° in **(4)** and 5° in **(5)**; a tentative explanation will be given by compound **(2)** where all these features are magnified. In the calculated conformation **(2)** the ester group is not coplanar with the phenyl ring as observed in the crystal structure: the torsional angles $\tau 1$ and $\tau 2$ are equal to 45.2° and 70.1° instead of 4.6° and 15.8° in the solid state. However, the graph (Fig. 2) of steric energy versus dihedral angle $\tau 1$ obtained by a 360° rotation of one substituent, the second one being fixed, reveals a low rotation barrier of about 5.5 KJ/mol: clearly the differences between observed and calculated $\tau 1$ and $\tau 2$ values can be attributed to intermolecular forces in the crystal structure even if as mentioned above any particular interaction can not be pointed out. Moreover when giving to one arm (C2—C7 for instance) the conformation of the deepest minimum in Figure 2: $\tau 1$ = 75°, and then rotating the second arm C2′—C7′, the conformation is optimized for $\tau 1$ = 57° and $\tau 2$ = 88.3°, values which seem to prove that the asymmetric conformation is solely due to intramolecular forces. These results are neither improved nor changed by molecular dynamics calculations as it can be seen in Table 8 for compounds **(2)** and **(5)**.

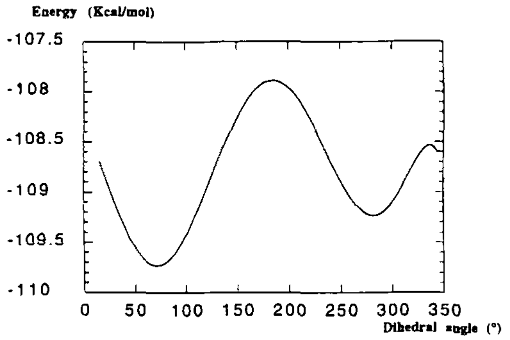


Fig. 2. Diagram of energy vs dihedral angle for compounds (2).

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