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# 3-Nitrobiphenyl

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## Abstract

The crystal structure of 3-nitrobiphenyl, $C_{12}H_9NO_2$, has been determined as a part of a systematic study of crystallization and crystal growth of biphenyl derivatives. It crystallizes with two similar molecules in the asymmetric unit. Unlike biphenyl itself, the torsion angles between the phenyl rings in each molecule are $-26\,(1)$ and $23\,(1)°$. The nitro groups are parallel to the phenyl groups [$\tau = -6\,(1)$ and $-4\,(1)°$].

## Comment

The title biphenyl, (I), and its derivatives have been studied extensively in the past because of the differences found in the inter-ring torsion angle, $\varphi$, in the solid state (Hargreaves & Rizvi, 1962; Charbonneau & Delugeard,

1976, 1977; Brock, Blackburn & Haller, 1984; Brock & Haller, 1984*b*; Brock & Minton, 1989; Samdal, 1985) and the gas phase (Almenningen & Bastiansen, 1958; Bastiansen & Traetteberg, 1962). These systems have also been investigated because of the differences found in the dihedral angle between the phenyl rings (Cailleau & Baudour, 1979; Brock, 1980, and references therein; Sutherland & Rawas, 1983).



(I)
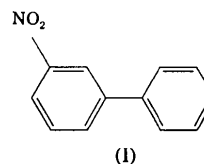
In continuation of our research on the systematic analysis of growth conditions and morphology modifiers for the preparation of substituted biphenyls from organic solvents (Rajnikant, Watkin & Tranter, 1995*a,b*), the crystal structure of the title compound, (I), was determined.

A perspective view of the molecule with atomic labelling is depicted in Fig. 1 and the unit-cell packing is shown in Fig. 2.
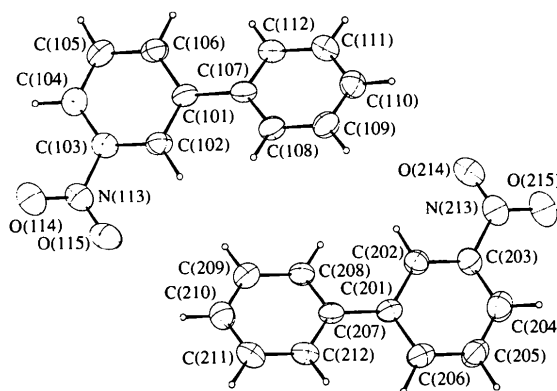


Fig. 1. View of the two independent molecules along the *a* axis. The molecules are separated in the view direction by approximately *a*/2. The ellipsoids are drawn at the 50% probability level.
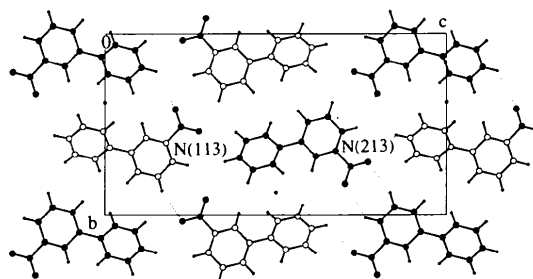


Fig. 2. The layer of molecules lying close to the plane perpendicular to the *a* axis at $x \simeq \frac{1}{2}$. The molecules of types 1 and 2 are shown by open and filled circles, respectively. The pseudo-centres of symmetry at $\frac{9}{16}, \frac{3}{8}, 0$ and $\frac{7}{16}, \frac{7}{8}, \frac{1}{2}$ are shown. O···H contacts less than 3.0 Å are shown dotted.

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The bond distances and angles in 3-nitrobiphenyl are in good agreement with those of 4-nitrobiphenyl (II) (Casalone, Gavezzotti & Simonetta, 1973), 4,4'-dinitrobiphenyl, (III) (Boonstra, 1963; Brock & Haller, 1984a), 2-nitrobiphenyl, (IV), and 2,2'-dinitrobiphenyl, (V) (Sekine, Ohashi, Yoshimura, Yagi & Higuchi, 1994), whereas the torsion angles around the central C—C bond of the biphenyl group [−26 (1) and 23 (1)°] are significantly different from those of the *ortho*- and *para*-substituted biphenyl molecules [33, 2 and −62.9° in (II), (III) and (IV), respectively].

The torsion angles around the C—N bond [−6 (1) and −4 (1)°] are significantly different from those of the aforementioned *ortho*- and *para*-substituted biphenyl complexes [37.2, 6.6, −44.2 and −38.3° in (II), (III), (IV) and (V), respectively]. The N—O bonds [1.22 (1), 1.21 (1), 1.203 (9), 1.217 (9) Å] are comparable with the values quoted for some similar nitro-substituted compounds (Sutherland, Hogg & Williams, 1974, and references therein; Sutherland & Ali-Adib, 1986; Sekine *et al.*, 1994).

The crystal structure consists of layers of molecules in van der Waals contact. Each layer contains both independent molecules. The shortest contacts are between the nitro group of molecule 2 and the H atoms on C(110) and C(111) of molecule 1 [O(215')···H(1110)(−x, y + ½, ½ − 2) 2.79 (1), O(215)···H(1111)(−x, y + ½, ½ − z) 2.61 (1) Å]. These loose dimers are joined end to end by a short O···H—C contact, and the chains are cross-linked by other O···H—C contacts to form sheets. Fig. 2 shows the contents of one layer. All O···H intermolecular contacts less than 3.2 (1) Å are shown as dotted lines. In the molecular packing diagrams, molecule 1 is shown by open circles, molecule 2 by filled circles.

Each molecule of type 1 is surrounded by four close neighbours of type 2 in the sheet and because the layers are related to each other by a twofold screw axis at (x = ¼, y = 0), there is also a close neighbour of type 2 in the adjacent sheet. A corresponding similar environment exists for the type 2 molecules. Although the space group P2₁2₁2₁ is non-centrosymmetric, there are molecules of each hand in the cell related to each other by a pseudo-centre of symmetry at ¹⁄₁₆, ⅛, 0.

## Experimental

The material was supplied by Aldrich and crystallization from various solvents was carried out with the aim of obtaining good quality crystals. Methanol yielded a very large hexagonal-shaped crystal (approximate dimensions 3.0 × 1.5 × 1.0 mm) of 3-nitrobiphenyl at room temperature, as well as some small crystals. The other solvents resulted in poor morphology crystallization.

### Crystal data

C₁₂H₉NO₂
$M_r$ = 199.2
Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å

Orthorhombic
$P2_12_12_1$
$a$ = 7.414 (2) Å
$b$ = 11.981 (2) Å
$c$ = 22.826 (6) Å
$V$ = 2027.57 Å³
$Z$ = 8
$D_x$ = 1.305 Mg m⁻³

Cell parameters from 250 reflections
$\theta$ = 0–24°
$\mu$ = 0.084 mm⁻¹
$T$ = 290 K
Thick hexagonal plate
0.80 × 0.30 × 0.25 mm
White

### Data collection

Enraf–Nonius FAST diffractometer
$\omega/2\theta$ scans, area detector
Absorption correction: none
8063 measured reflections
1781 independent reflections

805 observed reflections
$[I > 3\sigma(I)]$
$R_{int}$ = 0.0127
$\theta_{max}$ = 25°
$h$ = 0 → 8
$k$ = 0 → 13
$l$ = 0 → 24

### Refinement

Refinement on $F$
$R$ = 0.0450
$wR$ = 0.0571
$S$ = 0.83
805 reflections
272 parameters
All H-atom parameters refined
$w = (weight)\{1 - [\delta(F)/6\sigma(F)]^2\}^2$
weighting coefficients:
21.1, −3.6, 12.9

$(\Delta/\sigma)_{max}$ = 0.260
$\Delta\rho_{max}$ = 0.167 e Å⁻³
$\Delta\rho_{min}$ = −0.383 e Å⁻³
Extinction correction: secondary (Larson, 1969)
Extinction coefficient: 87.06
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

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

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(101) | 0.060 (1) | −0.1518 (6) | −0.0779 (3) | 0.058 (2) |
| C(102) | 0.080 (1) | −0.0706 (6) | −0.1201 (3) | 0.064 (2) |
| C(103) | 0.064 (1) | −0.0993 (7) | −0.1784 (3) | 0.078 (2) |
| C(104) | 0.029 (1) | −0.2052 (7) | −0.1975 (4) | 0.082 (2) |
| C(105) | 0.008 (1) | −0.2860 (7) | −0.1549 (4) | 0.081 (2) |
| C(106) | 0.025 (1) | −0.2598 (6) | −0.0961 (4) | 0.070 (2) |
| C(107) | 0.077 (1) | −0.1243 (6) | −0.0140 (3) | 0.054 (2) |
| C(108) | 0.177 (1) | −0.0342 (6) | 0.0050 (3) | 0.061 (2) |
| C(109) | 0.192 (1) | −0.0087 (7) | 0.0641 (4) | 0.070 (2) |
| C(110) | 0.104 (1) | −0.0739 (8) | 0.1052 (4) | 0.074 (2) |
| C(111) | 0.000 (1) | −0.1627 (7) | 0.0870 (3) | 0.073 (2) |
| C(112) | −0.014 (1) | −0.1885 (6) | 0.0284 (3) | 0.065 (2) |
| N(113) | 0.082 (1) | −0.0094 (7) | −0.2219 (4) | 0.104 (2) |
| O(114) | 0.085 (1) | −0.0342 (6) | −0.2736 (3) | 0.134 (2) |
| O(115) | 0.094 (1) | 0.0866 (6) | −0.2058 (3) | 0.113 (2) |
| C(201) | 0.081 (1) | 0.4066 (6) | 0.0742 (3) | 0.056 (2) |
| C(202) | 0.055 (1) | 0.3249 (6) | 0.1181 (3) | 0.064 (2) |
| C(203) | 0.048 (1) | 0.3547 (7) | 0.1750 (3) | 0.077 (2) |
| C(204) | 0.067 (1) | 0.4638 (8) | 0.1936 (4) | 0.085 (2) |
| C(205) | 0.090 (1) | 0.5430 (7) | 0.1527 (4) | 0.085 (2) |
| C(206) | 0.097 (1) | 0.5154 (6) | 0.0937 (4) | 0.071 (2) |
| C(207) | 0.087 (1) | 0.3755 (6) | 0.0111 (3) | 0.054 (2) |
| C(208) | 0.005 (1) | 0.2799 (6) | −0.0086 (3) | 0.061 (2) |
| C(209) | 0.013 (1) | 0.2503 (6) | −0.0683 (3) | 0.069 (2) |
| C(210) | 0.103 (1) | 0.3163 (7) | −0.1066 (3) | 0.074 (2) |
| C(211) | 0.187 (1) | 0.4123 (7) | −0.0882 (3) | 0.074 (2) |
| C(212) | 0.178 (1) | 0.4413 (6) | −0.0296 (3) | 0.064 (2) |
| N(213) | 0.022 (1) | 0.2667 (7) | 0.2187 (3) | 0.104 (2) |
| O(214) | −0.003 (1) | 0.1725 (6) | 0.2024 (3) | 0.121 (2) |
| O(215) | 0.019 (1) | 0.2922 (6) | 0.2703 (3) | 0.130 (2) |

In spite of the relatively large sample, the diffraction data were not extensive, yielding only 805 reflections with $I > 3\sigma(I)$ out of 8063 measured. The large thermal motion of the molecules required the refinement of anisotropic displacement parameters. The least-squares refinement was completed without restrictions on the positional parameters, but with the displacement parameters restrained between adjacent atoms (Rollett, 1970). The good agreement between equivalent bonds within each molecule and between molecules indicated that there was no need to add geometric restraints.

The structure was solved by SHELXS86 (Sheldrick, 1985) and refined by CRYSTALS (Watkin, Carruthers & Betteridge, 1985). Molecular graphics: CAMERON (Pearce, Watkin & Prout, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1254). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (1S,2S)-(+)-1,2-Bis[(dicyclohexyl)phosphinomethyl]cyclopentane.2CS2 and (±)-1,2-Bis(dicyclohexylphosphinomethyl)cyclopentane

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## Abstract

The molecular structures of $C_{33}H_{56}P_2S_4$, (1), and $C_{31}H_{56}P_2$, (2), are reported. The structure analysis of (1) is the first of a $CS_2$ adduct of an optically active diphosphine. The optically active compound (1) is not a simple $CS_2$ adduct but contains two zwitterionic structures, i.e. 1,2-cyclopentylenedimethylenebis[(dicyclohexyl)phosphoniocarbodithioate], $C_5H_8[CH_2P^+(C_6H_{11})_2(CS_2)^-]_2$.

## Comment

Optically active peralkyl diphosphines are electron-rich phosphorus compounds and are expected to be effective ligands in asymmetric catalyses, such as asymmetric hydrogenation of various ketones (Tani, Suwa, Yamagata & Otsuka, 1982). The title compounds, (1) and (2), were prepared according to the scheme shown below (see Experimental also).