

Table 2. *Selected geometric parameters* (Å, °)

|              |           |               |            |
|--------------|-----------|---------------|------------|
| N1—C1        | 1.465 (4) | N13—C12P      | 1.57 (2)   |
| N1—C2        | 1.369 (3) | O2—C2         | 1.217 (3)  |
| N1—C8        | 1.370 (3) | O4—C4         | 1.243 (3)  |
| N3—C2        | 1.396 (4) | O16—C15       | 1.401 (5)  |
| N3—C3        | 1.467 (3) | O16—C17       | 1.418 (5)  |
| N3—C4        | 1.405 (3) | C4—C9         | 1.384 (4)  |
| N5—C6        | 1.353 (3) | C8—C9         | 1.373 (4)  |
| N5—C9        | 1.401 (3) | C10—C11       | 1.517 (4)  |
| N5—C10       | 1.464 (3) | C11—O11       | 1.390 (3)  |
| N6—C6        | 1.326 (3) | C11—C12       | 1.473 (4)  |
| N7—C6        | 1.353 (3) | C11—O11P      | 1.289 (16) |
| N7—C8        | 1.350 (3) | C11—C12P      | 1.44 (2)   |
| N13—C14      | 1.449 (4) | C14—C15       | 1.491 (5)  |
| N13—C18      | 1.441 (4) | C17—C18       | 1.521 (5)  |
| N13—C12      | 1.467 (4) |               |            |
| C1—N1—C2     | 118.0 (2) | N5—C6—N7      | 112.4 (2)  |
| C1—N1—C8     | 121.5 (2) | N6—C6—N7      | 124.2 (2)  |
| C2—N1—C8     | 120.3 (2) | N1—C8—N7      | 126.2 (2)  |
| C2—N3—C3     | 115.3 (2) | N1—C8—C9      | 120.9 (2)  |
| C2—N3—C4     | 125.9 (2) | N7—C8—C9      | 112.9 (2)  |
| C3—N3—C4     | 118.7 (2) | N5—C9—C4      | 132.3 (2)  |
| C6—N5—C9     | 106.6 (2) | N5—C9—C8      | 104.3 (2)  |
| C6—N5—C10    | 125.4 (2) | C4—C9—C8      | 123.4 (2)  |
| C9—N5—C10    | 127.9 (2) | N5—C10—C11    | 111.7 (2)  |
| C6—N7—C8     | 103.8 (2) | C10—C11—O11   | 106.8 (2)  |
| C14—N13—C18  | 109.3 (3) | C10—C11—C12   | 113.2 (3)  |
| C14—N13—C12  | 107.4 (3) | C10—C11—O11P  | 112.4 (7)  |
| C14—N13—C12P | 127.4 (8) | C10—C11—C12P  | 119.8 (9)  |
| C18—N13—C12  | 115.5 (3) | O11—C11—C12   | 114.8 (3)  |
| C18—N13—C12P | 84.9 (9)  | C12—C11—O11P  | 132.3 (8)  |
| C15—O16—C17  | 110.2 (3) | O11P—C11—C12P | 108.7 (12) |
| N1—C2—N3     | 116.7 (2) | N13—C14—C15   | 111.2 (3)  |
| N1—C2—O2     | 122.2 (3) | O16—C15—C14   | 112.0 (3)  |
| N3—C2—O2     | 121.1 (3) | O16—C17—C18   | 110.4 (3)  |
| N3—C4—O4     | 120.5 (2) | N13—C18—C17   | 110.5 (3)  |
| N3—C4—C9     | 112.8 (2) | N13—C12—C11   | 113.3 (3)  |
| O4—C4—C9     | 126.7 (3) | N13—C12P—C11  | 109.9 (14) |
| N5—C6—N6     | 123.4 (2) |               |            |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| D—H...A                      | D—H      | H...A    | D...A     | D—H...A |
|------------------------------|----------|----------|-----------|---------|
| N6—H61...O11 <sup>i</sup>    | 0.74 (4) | 2.26 (3) | 2.953 (3) | 156 (4) |
| N6—H62...N7 <sup>ii</sup>    | 0.99 (3) | 1.94 (3) | 2.933 (3) | 176 (3) |
| O11—HO11...O4 <sup>iii</sup> | 0.92 (4) | 1.86 (4) | 2.737 (4) | 160 (3) |

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 - x, -y, 1 - z$ ; (iii)  $x, 1 - y, \frac{1}{2} + z$ .

The systematic absences showed the space group to be  $C2/c$  or  $Cc$ . The normalized structure-factor statistics favoured the centrosymmetric space group  $C2/c$  and subsequent analysis confirmed this. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976). All H atoms, except those of the amino and hydroxy groups, which were located from a  $\Delta\rho$  map, were placed in calculated positions and refined using a riding model with isotropic displacement parameters taken as 1.5 times those of the respective parent C atoms. During the course of the refinement, two peaks were found adjacent to the  $-\text{CH}(\text{OH})\text{CH}_2-$  moiety with intensities of 1.19 and  $0.58 \text{ e } \text{\AA}^{-3}$ . Based on their locations, one was assigned to atom O11P and the other to atom C12P. Occupancy factors were allowed to vary in the subsequent cycles of refinement and were fixed at 0.85 for atoms O11 and C12, and at 0.15 for atoms O11P and C12P in the final cycles of refinement. Atoms O11P and C12P were refined with isotropic temperature factors. The molecular plot was prepared with *SHELXTL-Plus XP* (Sheldrick, 1989). The geometrical calculations and material for publication were produced using *PARST* (Nardelli, 1983) and *CSU88* (Vickovič, 1988).

The crystallographic studies were supported by grant No. 3 0302 91 01 from the Polish State Committee for Scientific Research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 3,3-Dibenzylpentane-2,4-dione, $\text{C}_{19}\text{H}_{20}\text{O}_2$

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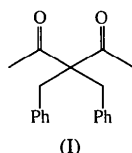
(Received 4 January 1995; accepted 3 April 1995)

## Abstract

The notable feature of the title compound is the non-planarity of the pentane-2,4-dione moiety. This fragment of the molecule adopts a significantly distorted *S* conformation with a dihedral angle of  $62.1(2)^\circ$  between the planes through  $\text{C1}-\text{C2}(=\text{O1})-\text{C3}$  and  $\text{C3}-\text{C4}(=\text{O2})-\text{C5}$ . The molecular packing involves  $\text{C}-\text{H}\cdots\text{O}$  close contacts.

## Comment

Different types of bidentate  $\beta$ -diketone ligands are involved in numerous chelate complexes of transition metals. They can be coordinated to the metal atom either as anions or neutral ligands. The number of complexes containing a neutral  $\beta$ -diketone is negligible compared with those having a coordinated monoanionic  $\beta$ -diketone ligand (Kawaguchi, 1986). The title compound, (I), was prepared for potential use as a bidentate intrinsically neutral ligand for coordination to transition metals.



The essential moiety of the molecule is a distorted chain built up of alternating  $C_{sp^3}$  and  $C_{sp^2}$  atoms. The stereochemistry of the molecule is determined by the two benzyl substituents on C3. In the solid state the molecule possesses a distorted *S* conformation (Emsley, 1984). The deviation from the ideal *S* conformation in which C1–C5, O1 and O2 are in a single plane, is determined by the dihedral angle of  $62.1(2)^\circ$  between the plane defined by O1, C1, C2 and C3, and that through O2, C3, C4 and C5. The bond angles about C3 [ $106.9(3)$ – $112.3(3)^\circ$ ] show significant deviations from the standard tetrahedral value. Even larger discrepancies are observed in the C3–C6–C8 and C3–C7–C14 bond angles [ $117.8(3)$  and  $114.8(3)^\circ$ , respectively], probably as a result of steric effects caused by the relatively bulky phenyl rings, C8–C13 and C14–C19, in such a small molecule. The values of the bond distances of all types are in good agreement with reported values (Allen *et al.*, 1987). The shortest intermolecular interaction,  $3.48 \text{ \AA}$ , may be considered as a weak C–H...O close contact (Steiner & Saenger, 1993).

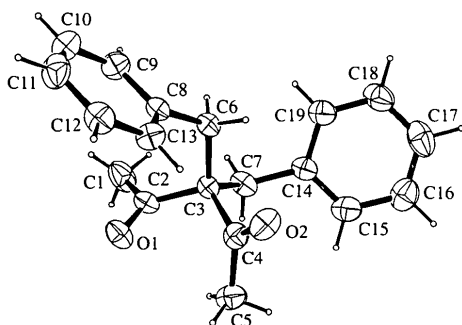


Fig. 1. A perspective ORTEP (Johnson, 1976) view of the molecule in a general position showing the numbering scheme. The ellipsoids are at the 30% probability level.

## Experimental

The title compound was synthesized by a modification of the procedure described earlier (Morgan & Taylor, 1925), the modification applying to the isolation of the disubstituted product. By the improved process the yield of the main product was more than ten times higher. The compound was prepared by the reaction of benzyl chloride and the sodium salt of 2,4-pentanedione in dry benzyl chloride in a 1:3 molar ratio. The mixture was stirred for 7.5 h at 460 K (yield 50%). Crystals suitable for X-ray analysis were obtained from the reaction. The density  $D_m$  was measured by flotation.

### Crystal data

C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>

$M_r = 280.36$

Monoclinic

*Ia*

$a = 10.817(5) \text{ \AA}$

$b = 12.620(4) \text{ \AA}$

$c = 11.502(4) \text{ \AA}$

$\beta = 91.44(2)^\circ$

$V = 1570(1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.186 \text{ Mg m}^{-3}$

$D_m = 1.186 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 18 reflections

$\theta = 6.00$ – $11.50^\circ$

$\mu = 0.07 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block

$0.53 \times 0.43 \times 0.36 \text{ mm}$

Colourless

### Data collection

Phillips PW1100 diffractometer

$\omega$  scans

Absorption correction: none

3601 measured reflections

2953 independent reflections

1489 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.009$

$\theta_{\text{max}} = 26.9^\circ$

$h = -13 \rightarrow 13$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 14$

3 standard reflections

frequency: 90 min

intensity decay: 3.0%

### Refinement

Refinement on  $F$

$R = 0.032$

$wR = 0.043$

$S = 1.06$

1489 reflections

188 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0010F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.10 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

|    | <i>x</i>   | <i>y</i>   | <i>z</i>    | $U_{\text{eq}}$ |
|----|------------|------------|-------------|-----------------|
| O1 | 0.27200    | 0.9799 (2) | 0.02640     | 0.072 (2)       |
| O2 | 0.2376 (3) | 0.7554 (2) | −0.1639 (3) | 0.070 (1)       |
| C1 | 0.0812 (4) | 1.0102 (4) | 0.1138 (4)  | 0.089 (3)       |
| C2 | 0.1670 (3) | 0.9519 (3) | 0.0379 (3)  | 0.052 (2)       |
| C3 | 0.1177 (3) | 0.8567 (2) | −0.0302 (3) | 0.045 (2)       |
| C4 | 0.2267 (3) | 0.7854 (2) | −0.0640 (4) | 0.054 (2)       |
| C5 | 0.3157 (4) | 0.7499 (3) | 0.0299 (4)  | 0.072 (2)       |
| C6 | 0.0449 (3) | 0.8998 (2) | −0.1379 (3) | 0.048 (2)       |
| C7 | 0.0295 (3) | 0.7873 (3) | 0.0439 (3)  | 0.059 (2)       |
| C8 | 0.0953 (3) | 0.9955 (2) | −0.1979 (3) | 0.046 (2)       |

|     |             |            |             |           |
|-----|-------------|------------|-------------|-----------|
| C9  | 0.0322 (4)  | 1.0907 (3) | −0.1953 (4) | 0.064 (2) |
| C10 | 0.0727 (4)  | 1.1791 (3) | −0.2537 (4) | 0.078 (3) |
| C11 | 0.1802 (5)  | 1.1743 (3) | −0.3142 (4) | 0.074 (2) |
| C12 | 0.2452 (4)  | 1.0812 (3) | −0.3172 (4) | 0.063 (2) |
| C13 | 0.2042 (3)  | 0.9936 (3) | −0.2598 (3) | 0.054 (2) |
| C14 | −0.0239 (3) | 0.6922 (3) | −0.0183 (3) | 0.053 (2) |
| C15 | 0.0331 (4)  | 0.5939 (3) | −0.0136 (4) | 0.073 (2) |
| C16 | −0.0175 (5) | 0.5066 (3) | −0.0690 (5) | 0.083 (3) |
| C17 | −0.1258 (5) | 0.5153 (4) | −0.1303 (4) | 0.088 (3) |
| C18 | −0.1843 (4) | 0.6119 (4) | −0.1361 (4) | 0.082 (3) |
| C19 | −0.1340 (3) | 0.6981 (3) | −0.0806 (4) | 0.067 (2) |

Table 2. Selected geometric parameters (Å, °)

|          |           |             |           |
|----------|-----------|-------------|-----------|
| O1—C2    | 1.200 (3) | C3—C7       | 1.565 (5) |
| O2—C4    | 1.218 (6) | C4—C5       | 1.497 (6) |
| C1—C2    | 1.484 (6) | C6—C8       | 1.501 (5) |
| C2—C3    | 1.523 (5) | C7—C14      | 1.505 (5) |
| C3—C4    | 1.540 (5) | Car—Car     | 1.375 (6) |
| C3—C6    | 1.550 (5) |             |           |
| O1—C2—C1 | 121.8 (3) | O2—C4—C5    | 120.8 (3) |
| O1—C2—C3 | 119.6 (3) | C3—C4—C5    | 118.4 (4) |
| C1—C2—C3 | 118.5 (3) | C3—C6—C8    | 117.8 (3) |
| C2—C3—C4 | 109.3 (3) | C3—C7—C14   | 114.8 (3) |
| C2—C3—C6 | 107.4 (3) | C6—C8—C9    | 120.3 (3) |
| C2—C3—C7 | 111.8 (3) | C6—C8—C13   | 122.9 (3) |
| C4—C3—C6 | 112.3 (3) | C7—C14—C15  | 122.0 (3) |
| C4—C3—C7 | 106.9 (3) | C7—C14—C19  | 121.4 (3) |
| C6—C3—C7 | 109.1 (3) | Car—Car—Car | 120.0 (4) |
| O2—C4—C3 | 120.8 (3) |             |           |

The original cell had the space-group symmetry  $Cc$  with  $a = 15.590$  (5),  $b = 12.620$  (4),  $c = 11.502$  (4) Å,  $\beta = 132.48$  (2)°. This cell was reduced by the matrix (001, 010,  $\bar{1}0\bar{1}$ ) to the reported  $Ia$  cell because of the large value of  $\beta$  ( $= 90 + 42.48^\circ$ ).

H atoms were refined riding on the parent C atoms at a distance of 0.95 Å. The rotational orientation of the methyl C1 and C5 H atoms was determined by the contour  $\Delta F$  map calculated through the plane defined by the methyl H atoms. The direction of the chiral axis was determined unequivocally by refinement of the chirality value  $\eta$  (Rogers, 1981).

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); *NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## ‘Stiff’ *cis*-Stilbenes. (Z)-6,6'-Dimethyl-1,1'-biindanylidene and (Z)-4,4',7,7'-Tetramethyl-1,1'-biindanylidene

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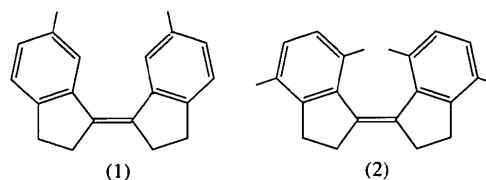
(Received 6 March 1995; accepted 20 April 1995)

## Abstract

The X-ray crystal structures of (Z)-6,6'-dimethyl-1,1'-biindanylidene,  $C_{20}H_{20}$  (1), and (Z)-4,4',7,7'-tetramethyl-1,1'-biindanylidene,  $C_{22}H_{24}$  (2), were determined at 90 K. The structure around the ethylene bond in (2) is distorted by steric congestion due to the methyl groups at C7 and C7'.

## Comment

In the course of our studies on the unusually short ethylene bond of (*E*)-stilbenes and the large amplitude torsional motion in their crystals (Ogawa *et al.*, 1988; Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992), we have recently reported the structures of ‘stiff’ stilbenes, *i.e.* (*E*)-1,1'-biindanylidene, and discussed the length of the central ethylene bond (Ogawa, Harada & Tomoda, 1995). We report here the crystal structures of the *cis* isomers of two of these stiff stilbenes, namely, (Z)-6,6'-dimethyl-1,1'-biindanylidene, (1), and (Z)-4,4',7,7'-tetramethyl-1,1'-biindanylidene, (2).



Each of the molecules has a crystallographic twofold axis through the center of the ethylene bond. The  $\pi$  systems are non-planar. The dihedral angle between the