Thermally Induced Solid-state Z–E Isomerisation in Bi(cyclopentenylidene) Compounds. X-Ray Crystal Structure of (Z)-2,2'-Dioxo-3,3',4,4',5α,5'β-hexaphenyl-1,1'-bi(cyclopentenylidene)

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The crystal and molecular structure of the title compound has been determined; it crystallises as a methanol solvate in the space group $P2_1/n$ with $a = 11.647(2)$, $b = 18.583(2)$, $c = 16.113(2)$ Å, $\beta = 92.11(1)°$ and $Z = 4$. The structure has been solved by direct methods and refined to a final R value of 0.090. The molecular structure is different from that proposed earlier on the basis of spectral data. The central bond connecting the two five-membered rings displays pure double-bond character due to lack of conjugation. This is responsible for the thermal stability of the compound and the relatively high temperature for the isomerisation. One of the two five-membered rings assumes an envelope conformation and the other a half-chair. The solvent methanol molecule is disordered.

In recent years, X-ray crystallography has gained considerable importance in understanding solid-state reactivity.[1] Paul and Curtin, in their review on thermally induced solid-state reactions,[2] indicated some systems reported earlier in the literature for which structural investigations would be worthwhile. One of these is the Z–E isomerisation in substituted bi(cyclopentenylidene) compounds reported by Atkinson.[3] The reactions are shown in the Scheme.† The yellow dimer (YD), obtained by dehydration of the monomer (MR), 4-hydroxy-2,3,4-triphenyl-cyclopent-2-ene-1-one, isomerises in solution to the photodimer (PD) on exposure to sunlight. Interestingly, (PD) reverts to (YD) on heating at 180 °C in the solid state. The crystal structure of (MR) was reported by us earlier.[4] This paper presents the X-ray structure of (PD) and its comparison with that of (MR). The principal objective of the crystallographic study is to find an explanation for the stability of the compound in terms of the nature of central bond connecting the cyclopentadienone rings.
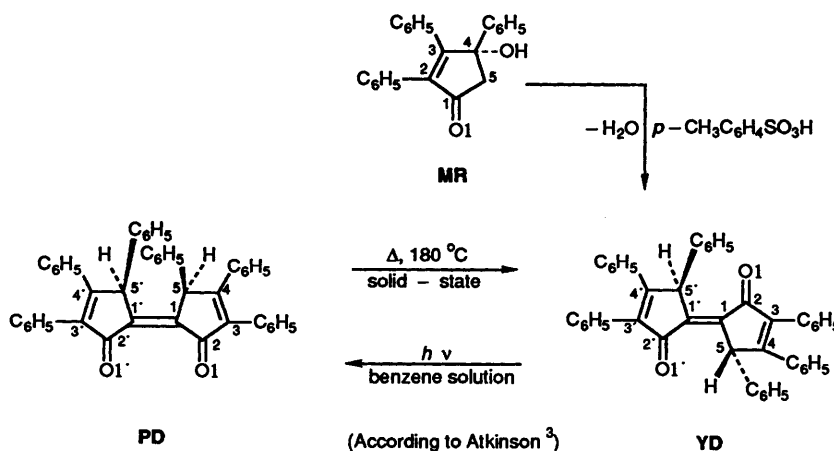
Experimental

The compound **PD** was prepared according to the reported procedure[3] and recrystallised from chloroform–methanol solution. The spectral data (both IR and NMR) agree well with that reported by Atkinson.[3]

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† The structures of (PD) and (YD) shown in the Scheme are as assigned by Atkinson.[3]

Scheme.

undertaken as most of the reflections were weak and the ratio of reflections to parameters was small. The methanol molecule is disordered and lies close to a centre of symmetry. From the difference electron density map, a carbon atom with 0.5 site occupancy and the oxygen atom disordered over two positions each with 0.25 site occupancy were included in the calculation. Further refinement resulted in unacceptable C–O bond lengths and therefore this distance was constrained to a value of 1.43 Å. The thermal parameters of the C and O atoms were relatively high but did not pose any problem when refined anisotropically. The hydrogen atoms connected to C(5) and C(5′) were located from a difference Fourier map. In the final difference Fourier map, residual electron density (0.24 e Å^{-3}) was observed around atoms of the disordered solvent molecule. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. The weighting function, $w = 3.073/[\sigma^2(F_o) + 0.000\ 57|F_o|^2]$ was used, where $\sigma(F_o)$ was derived from counting statistics. Final R and R_w values* are 0.090 and 0.117. Apparently, the relatively high R indices are due to poor quality data as the crystals were weakly diffracting. The programs ORTEP[7] and PLUTO[8] were used for diagrams. All the computations were performed on the DEC 1090 system of our Institute.

Results and Discussion

The perspective view of the molecular structure of **PD** is shown in Figure 1. The final fractional atomic co-ordinates are given in the Table.† The X-ray structure is different from that assigned by Atkinson[3] on the basis of spectral data. Contrary to his conclusion that the phenyl rings at C(5) and C(5′) are on the same side of the molecule (as shown in the Scheme), the X-ray structure reveals that they are on the opposite side, i.e., E to each other ‡ as expected from steric considerations (Figure 1).

It is interesting to recall the arguments of Atkinson in assigning the structures of **YD** and **PD** (Scheme). The photo-isomerisation of **YD** to **PD** and the reverse thermal reaction in the solid state, shows the Z–E relationship of **YD** to **PD**. In addition, the two isomers yield the same dihydro-dimers on reduction (with zinc in acetic acid). This led Atkinson to infer that the stereochemistry at C(5) and C(5′) is unchanged during the photoisomerisation. Further he assumed that the stereochemical relationship of the phenyl rings at C(5) and C(5′) in **YD** to be E (Scheme). This arbitrary assumption, leads to the structure of **(PD)** with the phenyl rings Z to each other (Scheme). Obviously, the phenyl rings on the same side of the molecule would entail unfavourable steric interactions between one another and result in a considerable twist about the central C(1)–C(1′) double bond.

On the other hand, the NMR spectra of **PD** could be interpreted on the basis of the observed structure. In the NMR spectrum of **PD**, the aromatic signal is more splayed out to higher field (δ 6.7–7.4) as compared to a narrow multiplet (δ 7.0–7.4) in **YD**.[3] This can be explained by the mutual shielding of protons of the phenyl rings connected to the same five-membered ring (i.e. between C and D, and C′ and D′), rather than phenyl rings at C(5) and C(5′) (Scheme), as proposed by Atkinson.[3]

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* $R = \Sigma|F_o - |F_c||/\Sigma F_o$; $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$

† Hydrogen atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, 1989, J. Chem. Soc., Perkin Trans. 2, 1990, Issue 1.

‡ This would imply a Z-relationship between the phenyl rings in **YD**. Unfortunately, the structural studies of **YD** could not be undertaken as attempts to grow single crystals, suitable for diffraction work, were unsuccessful.

Table. Fractional atomic co-ordinates ($\times 10^4$) of non-hydrogen atoms in **PD** with their esds in parentheses.

Atom	x	y	z
C(1)	8 969(5)	−510(3)	2 786(3)
C(2)	8 587(5)	−1 219(3)	3 145(4)
C(3)	9 105(5)	−1 786(3)	2 639(3)
C(4)	9 591(4)	−1 493(3)	1 975(3)
C(5)	9 367(5)	−681(3)	1 909(3)
O(1)	7 927(4)	−1 310(2)	3 702(3)
C(31)	9 002(4)	−2 545(2)	2 874(3)
C(32)	9 188(4)	−2 750(2)	3 701(3)
C(33)	9 060(4)	−3 469(2)	3 930(3)
C(34)	8 748(4)	−3 983(2)	3 332(3)
C(35)	8 562(4)	−3 777(2)	2 505(3)
C(36)	8 690(4)	−3 058(2)	2 276(3)
C(41)	10 280(4)	−1 865(3)	1 338(2)
C(42)	10 981(4)	−2 444(2)	1 575(2)
C(43)	11 615(4)	−2 802(2)	985(2)
C(44)	11 548(4)	−2 582(2)	157(2)
C(45)	10 848(4)	−2 003(2)	−81(2)
C(46)	10 213(4)	−1 645(2)	510(2)
C(51)	8 453(3)	−500(2)	1 245(2)
C(52)	7 411(3)	−870(2)	1 212(2)
C(53)	6 584(3)	−711(2)	591(2)
C(54)	6 799(3)	−182(2)	3(2)
C(55)	7 841(3)	189(2)	36(2)
C(56)	8 669(3)	30(2)	657(2)
C(1′)	9 086(5)	135(3)	3 150(3)
C(2′)	8 783(6)	337(3)	4 023(4)
C(3′)	8 905(5)	1 136(3)	4 091(3)
C(4′)	9 335(5)	1 393(3)	3 397(3)
C(5′)	9 570(5)	805(3)	2 767(4)
O(1′)	8 545(5)	−75(2)	4 581(3)
C(31′)	8 541(4)	1 534(2)	4 836(2)
C(32′)	8 652(4)	1 215(2)	5 618(2)
C(33′)	8 182(4)	1 550(2)	6 303(2)
C(34′)	7 602(4)	2 202(2)	6 205(2)
C(35′)	7 491(4)	2 521(2)	5 422(2)
C(36′)	7 961(4)	2 187(2)	4 738(2)
C(41′)	9 673(4)	2 141(2)	3 209(2)
C(42′)	10 454(4)	2 503(2)	3 736(2)
C(43′)	10 830(4)	3 191(2)	3 530(2)
C(44′)	10 424(4)	3 517(2)	2 797(2)
C(45′)	9 643(4)	3 155(2)	2 269(2)
C(46′)	9 267(4)	2 467(2)	2 475(2)
C(51′)	10 874(3)	743(2)	2 655(3)
C(52′)	11 373(3)	991(2)	1 936(3)
C(53′)	12 559(3)	939(2)	1 854(3)
C(54′)	13 245(3)	639(2)	2 492(3)
C(55′)	12 745(3)	391(2)	3 212(3)
C(56′)	11 560(3)	443(2)	3 293(3)
O(S1)^a	5 357(21)	735(12)	5 076(18)^b
O(S2)^a	5 724(19)	−223(12)	3 891(19)^b
C(S1)^a	5 510(27)	42(17)	4 706(21)^c

^{a} Atoms of the disordered methanol molecule. ^{b} Site occupancy factor = 0.25. ^{c} Site occupancy factor = 0.50.

The bond lengths and the bond angles involving the non-hydrogen atoms of the five-membered rings (Figure 2) are normal as found in bicyclopentenylidenes.[9] The two carbonyl bond lengths in **PD** (1.216, 1.219 Å) are shorter compared with the value of 1.230 Å in **MR**.[4] The change in hybridisation of the atom C(5), from sp^3 in **MR** to sp^2 in **PD** [for the atoms C(1) and C(1′)] is reflected in the bond lengths. The bond C(1)–C(5) (1.536, 1.548 Å) in **PD** is shorter than C(4)–C(5) (1.551 Å) in **MR**, whereas the C(1)–C(2) (1.513, 1.512 Å) is longer than C(1)–C(5) (1.480 Å) in **MR**. The reason for the observed difference in the lengths of the bonds of same nature, viz. C(1)–C(5) and C(1′)–C(5′) is not clear. Furthermore, the bond
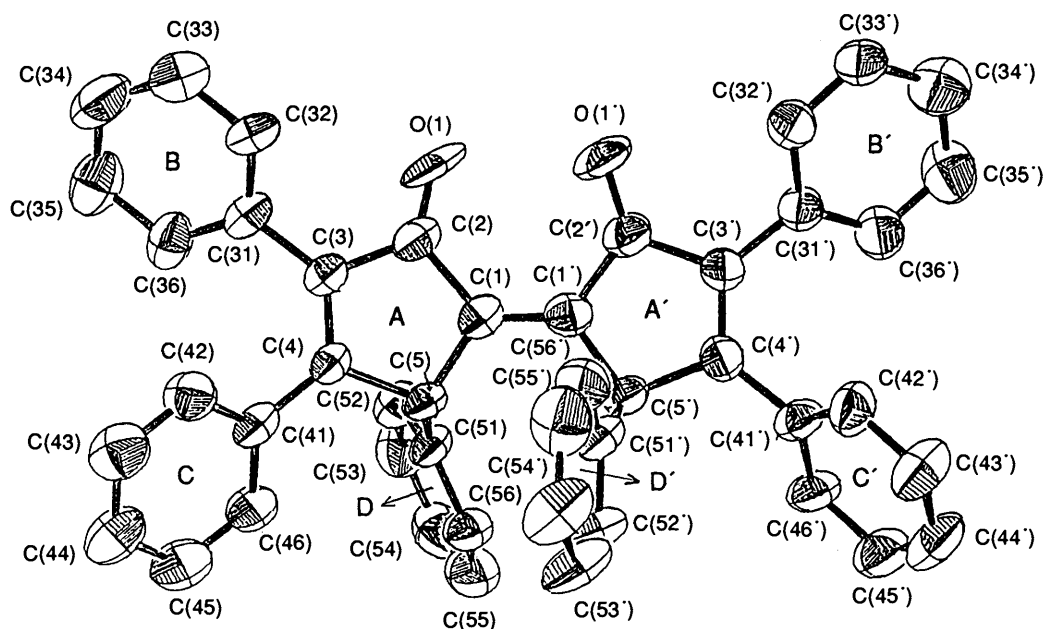
Figure 1. Molecular structure of compound **PD** with the numbering scheme.

C(1) – C(5) – H(5) = 112(2)
C(4) – C(5) – C(51) = 112.3(4)

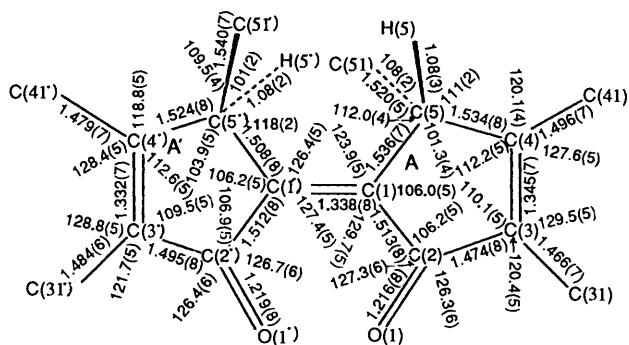C(1') – C(5') – C(51') = 111.8(5)
C(4') – C(5') – H(5') = 113(2)

Figure 2. Bond lengths (Å) and angles (°) of the five-membered rings in **PD** (esds are given in parentheses).

C(4)–C(5) (1.534, 1.524 Å) is shortened in **PD** when compared to C(3)–C(4) (1.550 Å) in **MR**.

Interestingly, the length of the central double bond C(1)–C(1'), is 1.338(8) Å (Figure 2), which corresponds to that of a typical unconjugated double bond.[10] The intra-molecular O(1)•••O(1') contact distance of 2.777(7) Å results in a distortion of the five-membered rings as revealed by the torsion angles C(1')–C(1)–C(2)–O(1), 30.1° and C(1)–C(1')–C(2')–O(1'), 12.0°. This precludes the conjugation of the carbonyl groups with the central double bond. Another reason could be the presence of endocyclic double bonds [C(3)–C(4) and C(3')–C(4')], which are responsible for cross-conjugation.[11] The dihedral angle between the two cyclopentenone rings, viz., 5.0° also supports the double bond character of C(1)–C(1') bond. The steric interaction between the phenyl ring substituents results in asymmetric exocyclic angles of the five-membered rings at C(3), C(4), C(3'), and C(4') (Figure 2). The average values of the interior angles of the rings are 107° (ring A) and 108° (ring A') in good agreement with the angles in a regular pentagon. Ring A assumes a half-chair conformation as
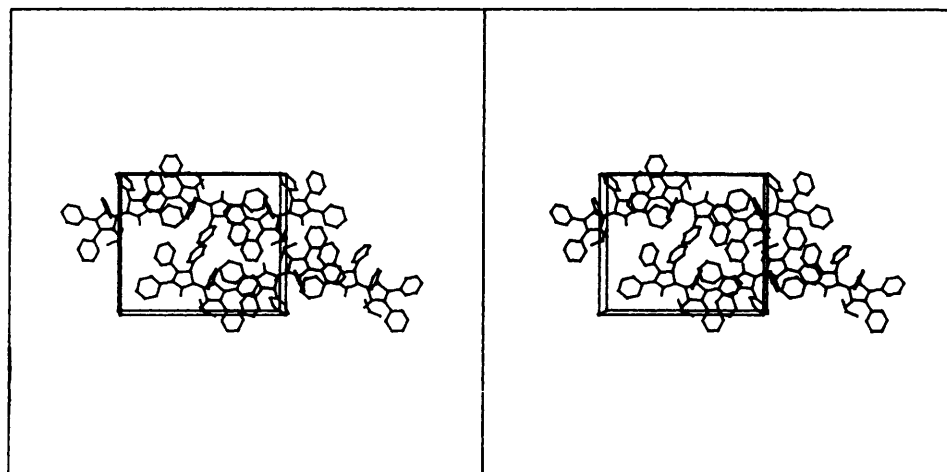

Figure 3. Stereoscopic view along [100] of the unit cell of **PD**: b axis horizontal; c axis vertical.

indicated by the deviation of atoms C(1) (-0.219 Å) and C(5) (0.123 Å) from the plane (I) defined by the atoms C(2), C(3), and C(4). On the other hand, ring A' adopts an envelope conformation where the atom C(1') deviates by 0.149 Å from the plane(II) containing the rest of the atoms. The conformation of the latter is also observed in **MR**. The dihedral angles between plane (I) and the phenyl rings B, C, and D are 44.4, 37.4, and 88.4°, respectively, while the values between plane (II) and the phenyl rings B', C', and D' are 37.8, 56.0, and 81.0°, respectively (Figure 1).

The molecular packing is shown in Figure 3. The solvent molecules are locked in cages formed by the molecules of **PD** related by an inversion centre. This is perhaps the reason why the crystals do not desolvate to become polycrystalline. This behaviour may be contrasted with the crystals of **MR**[4] in which the solvent benzene molecules, packed in channels, escape on standing even at ambient temperature. Though the isomerisation reaction parallels the behaviour of indigo derivatives, it is not facile as in the latter case. This is perhaps due to the pure double-bond character of the central bond in **PD**, whereas in the latter it is a partial double bond [1.37(1) Å, in indigo[12]] due to resonance interactions. However, at the reaction temperature (*ca.* 180 °C) the central bond could acquire partial double-bond character which would facilitate the rotation about the bond and lead to isomerisation.

Acknowledgements

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