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Crystal structure of phenyl-substituted cyclopentenes

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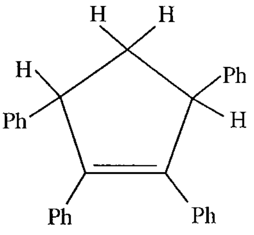
The crystal structures of two stereoisomers of tetraphenyl- and pentaphenyl-substituted cyclopentenes **1** and **2** have been determined by X-ray analysis. An envelope conformation ^{1}E has been ascertained for the *cis* isomer **1a,** whereas the *cis, cis* isomer **2a,** which crystallizes in two different space groups, $P\bar{1}$, and $P2_1/n$, displays a twisted $^2T_1$ conformation. The phenyl substituents are all tilted with respect to the cyclopentene ring in both structures. Compound **1a** crystallizes in the space group $P2_1/a$ with a = 18.553(3), b = 6.006(2), c = 19.355(5), β = 102.67(4)°, and V = 2104.2(g) Å^3 for Z = 4; compound **2a**$^{\mathrm{I}}$ crystallizes in $P2_1/n$ with a = 10.064(2), b = 20.756(5), c = 12.245(3) Å, β = 95.21(2)°, and V = 2547(1) Å^3 for Z = 4; compound **2aII** crystallizes in $\mathrm{P}\bar{1}$ with a = 10.117(3), b = 11.750(2), c = 12.359(2) Å, α = 111.25(2), β = 94.84(2), γ = 108.78(2)°, and V = 1262.3(6) Å^3 for Z = 2.

KEY WORDS: Crystal structure; phenyl-substituted cyclopentenes.

Introduction

It is quite difficult, in many cases, to predict the behavior of sterically crowded organic molecules in solution. For example, the assignment of the configuration by routine spectroscopic techniques (e.g., NMR) may be complicated by the existence of different conformations, which, being all roughly compatible with the same spectroscopic parameters, make the assignment very uncertain. In such cases, it is necessary to resort to X-ray crystallographic analyses to solve the problem. We faced this kind of problem during a study on the dependence of the stereochemistry of the reduction of phenyl-substituted cyclopentadienes on the specific mechanism followed by the reaction;[1] in order to identify precisely the reaction products, we had to grow single crystals suitable for X-ray analysis. Typically, this was the case of the phenyl-substituted cyclopentenes **1** and **2**, which are the products of monoreduction of 1,2,3,4-tetraphenylcyclopentadiene and 1,2,3,4,5-pentaphenylcyclopentadiene, respectively.



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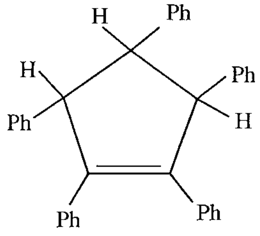
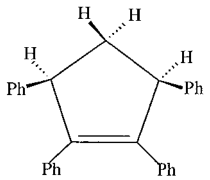
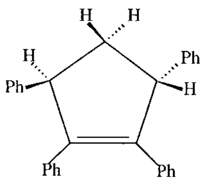


2

These compounds can exist in different configurations, depending on the relative position occupied by the phenyl groups. For compound **1,** two stereoisomers are possible, i.e., the *cis* **1a** and the *trans* **1b**. We were able to obtain good crystals of compound **1a.**



1a



1b

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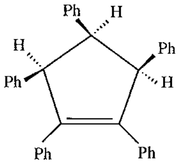
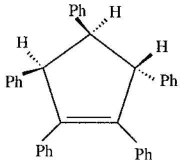
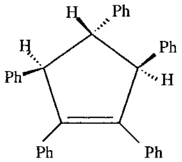
For compound **2** three stereoisomeric configurations are possible, the *cis,cis* **2a,** the *cis,trans* **2b,** and the *trans,trans* **2c.**



2a



2b



2c

We obtained by crystallization compound **2a,** which crystallized from different solvents, in two different space groups, $P2_1/n$ and $P\bar{1}$, **2aI** and **2aII,** respectively, with the same configuration. All these isomers display ^{1}H NMR spectra of the second order, which do not allow an unambiguous assignment of their configuration, at least with routine spectrometers and techniques. We report here the results of the determination of the crystal structure of compounds **1a** and **2aI, 2aII.**

Chemical preparation

The stereoisomer **1a** was obtained by catalytic hydrogenation (acetic acid as a solvent, 10% Pd on charcoal as a catalyst, H_2 pressure 1 bar, temperature 60°C, for 67 h) of 1,2,3,4-tetraphenylcyclopentadiene.

Table 1. Crystallographic Data and Summary of Intensity Data Collection and Structure Refinement

	1a	**2aI**	**2aII**
Compound	$C_{29}H_{24}$	$C_{35}H_{28}$	$C_{35}H_{28}$
CCDC deposit no.	CCDC-1003/5686	CCDC-1003/5687	CCDC-1003/5688
Color/shape	Colorless/prism	Colorless/prism	Colorless/prism
Mol wt	372.5	448.6	448.6
Space group	$P2_1/a$	$P2_1/n$	$P\bar{1}$
Temp.; °C	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Cell constant[a]			
a, Å	18.553(3)	10.064(2)	10.117(3)
b, Å	6.006(2)	20.756(5)	11.750(2)
c, Å	19.355(5)	12.245(3)	12.359(2)
α, °			111.25(2)
β, °	102.67(4)	95.21(2)	94.84(2)
γ, °			108.78(2)
Cell Volume, Å^3	2104.2(9)	2547(1)	1262.3(6)
Formula units/unit cell	4	4	2
D_{calc} g cm^{-3}	1.176	1.170	1.180
μ cm^{-1}	0.66	0.66	0.66
Transmission factors	0.93-1	0.90-1	0.93-1
Diffractometer/scan	Philips PW1100/θ-2θ	Philips PW1100/θ-2θ	Philips PW1100/θ-2θ
Scan width	1.2	1.5	1.5
Standard reflections	212; 401	234; 132	−331; 2-31
Decay of standards, %	±2	±2	±2
Reflections measured	4178	5385	5234
2θ-range, deg	6-50	6-52	6-52
No. observed [$I \geq 3\sigma(I)$][b]	2479	4155	4205
Computer programs	SIR 92[2] SHELX 93[3] PARST[4] ORTEP II[5]	SIR 92[2] SHELX 93[3] PARST[4] ORTEP II[5]	SIR 92[2] SHELX 93[3] PARST[4] ORTEP II[5]
No. of parameters varied	359	429	429
Weight	$1/[\sigma^2(Fo^2) + (0.0P)^2 + 2.97P^c]$	$1/[\sigma^2(Fo^2) + (0.0P)^2 + 1.43P^c]$	$1/[\sigma^2(Fo^2) + (0.0P)^2 + 0.59P^c]$
R (on F)	0.076	0.059	0.052
R_w (on F^2)	0.149	0.133	0.116
GOF	1.42	1.27	1.23

[a] Least-squares refinement of $(\sin\theta/\lambda)^2$ values of 30 reflections with $\theta > 10°$.

[b] Corrections: Lorentz-polarization; absorption (ψ scan).[6]

[c] $P = \max(Fo^2 - Fc^2)^2/3$.

After purification of the reaction mixture on a silica gel column (eluant petroleum ether-dichloromethane 9:1), the product was obtained in a pure form. m.p. 126–127°C (acetone); *m/z* 372 (M, 90%), 281 (100), 203 (48), 115 (32), 91 (50); ^{1}H NMR ($CDCl_3$ as a solvent, TMS as internal standard), AMX_2 system, δH (ppm) 2.09–2.16 (1H, dt, J_{AM} 13.4 Hz, J_{AX} 8.2 Hz, H_A), 3,17 (1H, dt, J_{AM} 13.4 Hz, J_{MX} 8.9 Hz, H_M), 4.42 (2H, app. t, J 8.9 and 8.2 Hz, H_X), 6.9–7.3 (20H, m, arom.). Crystals for X-ray analysis were grown by slow crystallization from acetone at room temperature, in a sealed cuvette, in about a month.

The stereoisomer **2a** was obtained by cathodic reduction on a Hg pool of 1,2,3,4,5-pentaphenylcyclopentadiene, in DMF as a solvent and 0.1 M TBAP as supporting electrolyte, in the presence of phenol as proton donor, followed by purification on column chromatography (see reference[1] for more experimental details); m.p. 217°C (acetone-acetonitrile); m/z 448 (M, 100%), 370 (90), 357 (67), 279 (68), 191 (60), 91 (50); ^{1}H NMR (AB_2 system) δ_H 4.59 (1H, app. t, J_{AB} 10.0 Hz, H_A), 4.73 (2H, app. d, J_{AB} 10.0 Hz, H_B), 6.0 and 6.9–7.3 (25H, m, arom.). Crystals of **2aI** for X-ray analysis were grown by slow evaporation of the solvent at room temperature in a sealed cuvette. Crystals of **2aII** were recovered from the NMR tube after complete evaporation of the $CDCl_3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) with eds's in Parentheses for Compound **1a,** $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}ai^*a_j^*a_i\cdot a_j$

Atom	*x*	*y*	*z*	*U*eq/iso
C(1)	0.1395(3)	−0.3056(9)	0.3099(2)	52(2)
C(2)	0.0822(2)	−0.1998(8)	0.3464(2)	43(1)
C(3)	0.0285(2)	−0.0878(7)	0.2845(2)	38(1)
C(4)	0.0398(2)	−0.1568(7)	0.2219(2)	40(1)
C(5)	0.1024(2)	−0.3251(8)	0.2302(2)	46(2)
C(6)	0.1563(2)	−0.2931(8)	0.1828(2)	47(2)
C(7)	0.1960(3)	−0.097(1)	0.1847(3)	58(2)
C(8)	0.2493(3)	−0.072(1)	0.1452(3)	72(2)
C(9)	0.2632(3)	−0.240(1)	0.1025(3)	82(3)
C(10)	0.2241(3)	−0.434(1)	0.0982(3)	78(3)
C(11)	0.1710(3)	−0.4604(9)	0.1384(3)	58(2)
C(12)	−0.0054(2)	−0.1016(8)	0.1509(2)	43(1)
C(13)	−0.0164(2)	−0.2619(9)	0.0976(2)	52(2)
C(14)	−0.0601(3)	−0.217(1)	0.0311(2)	60(2)
C(15)	−0.0928(3)	−0.013(1)	0.0164(3)	61(2)
C(16)	−0.0817(3)	0.149(1)	0.0681(3)	62(2)
C(17)	−0.0384(3)	0.1064(9)	0.1348(2)	51(2)
C(18)	−0.0346(2)	0.0460(7)	0.2973(2)	42(1)
C(19)	−0.0240(3)	0.2468(8)	0.3337(3)	54(2)
C(20)	−0.0831(3)	0.372(1)	0.3437(3)	68(2)
C(21)	−0.1538(3)	0.298(1)	0.3191(3)	72(2)
C(22)	−0.1658(3)	0.098(1)	0.2838(3)	66(2)
C(23)	−0.1071(3)	−0.0264(9)	0.2731(2)	53(2)
C(24)	0.1139(2)	−0.0488(7)	0.4085(2)	40(1)
C(25)	0.1636(2)	0.1189(8)	0.4031(3)	51(2)
C(26)	0.1896(3)	0.2618(9)	0.4585(3)	62(2)
C(27)	0.1656(3)	0.243(1)	0.5206(3)	68(2)
C(28)	0.1168(3)	0.076(1)	0.5273(3)	70(2)
C(29)	0.0913(3)	−0.0686(9)	0.4717(2)	54(2)
H(1)	0.158(3)	−0.453(8)	0.331(2)	74(12)[a]
H(1A)	0.183(2)	−0.200(7)	0.316(2)	54(13)[a]
H(2)	0.054(2)	−0.318(7)	0.366(2)	45(11)[a]
H(5)	0.081(2)	−0.478(7)	0.223(2)	39(10)[a]

[a] Isotropic.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) with esd's in Parentheses for Compound **2aI,** $U_{eq} = (1/3)\ \Sigma_i\Sigma_j U_{ij}ai^*a_j^*a_i\cdot a_j$

Atom	*x*	*y*	*z*	*U*eq/iso
C(1)	0.8562(2)	0.0692(1)	0.5890(2)	39.8(7)
C(2)	0.7352(2)	0.0592(1)	0.5005(2)	39.1(6)
C(3)	0.8020(2)	0.06136(9)	0.3947(2)	37.0(6)
C(4)	0.9230(2)	0.08929(9)	0.4078(2)	37.5(7)
C(5)	0.9650(2)	0.1042(1)	0.5274(2)	40.0(6)
C(6)	0.9933(2)	0.1745(1)	0.5532(2)	51.4(8)
C(7)	1.0721(3)	0.1896(2)	0.6497(3)	75(1)
C(8)	1.0982(5)	0.2536(3)	0.6765(4)	117(2)
C(9)	1.0497(6)	0.3024(2)	0.6082(6)	134(2)
C(10)	0.9755(4)	0.2877(2)	0.5121(5)	103(2)
C(11)	0.9475(3)	0.2239(1)	0.4836(3)	67(1)
C(12)	1.0117(2)	0.1070(1)	0.3225(2)	41.3(7)
C(13)	1.1493(2)	0.1120(1)	0.3481(2)	50.7(8)
C(14)	1.2327(3)	0.1303(2)	0.2694(3)	68(1)
C(15)	1.1817(3)	0.1441(2)	0.1648(3)	78(1)
C(16)	1.0462(3)	0.1400(2)	0.1378(3)	76(1)
C(17)	0.9621(3)	0.1224(1)	0.2157(2)	57.1(9)
C(18)	0.7362(2)	0.0298(1)	0.2949(2)	40.5(6)
C(19)	0.6010(2)	0.0378(1)	0.2628(2)	50.8(8)
C(20)	0.5406(3)	0.0048(2)	0.1734(2)	66(1)
C(21)	0.6130(3)	−0.0363(1)	0.1146(2)	71(1)
C(22)	0.7470(4)	−0.0450(1)	0.1447(2)	70(1)
C(23)	0.8081(3)	−0.0126(1)	0.2348(2)	54.4(8)
C(24)	0.6198(2)	0.1058(1)	0.5073(2)	41.2(7)
C(25)	0.6107(2)	0.1638(1)	0.4508(2)	49.0(8)
C(26)	0.5070(3)	0.2064(1)	0.4631(2)	62.7(9)
C(27)	0.4114(3)	0.1916(2)	0.5323(3)	70(1)
C(28)	0.4185(3)	0.1341(2)	0.5882(3)	72(1)
C(29)	0.5209(2)	0.0914(1)	0.5749(2)	56.3(9)
C(30)	0.8242(2)	0.0940(1)	0.7002(2)	41.9(7)
C(31)	0.8389(2)	0.0526(1)	0.7891(2)	51.7(8)
C(32)	0.8107(3)	0.0724(2)	0.8925(2)	67(1)
C(33)	0.7656(3)	0.1339(2)	0.9081(2)	73(1)
C(34)	0.7485(3)	0.1756(2)	0.8204(2)	63(1)
C(35)	0.7784(2)	0.1564(1)	0.7176(2)	51.4(8)
H(1)	0.894(2)	0.025(1)	0.603(2)	34(5)[a]
H(2)	0.698(2)	0.016(1)	0.513(2)	38(5)[a]
H(5)	1.053(2)	0.080(1)	0.550(2)	39(5)[a]

[a] Isotropic.

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) with esd's in Parentheses for Compound **2aII**, $U\text{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

Atom	*x*	*y*	*z*	*U*eq/iso
C(1)	0.1567(2)	0.4734(2)	0.6366(2)	43.0(7)
C(2)	0.2346(2)	0.4132(2)	0.5401(2)	42.6(7)
C(3)	0.1107(2)	0.3192(2)	0.4336(2)	41.1(7)
C(4)	−0.0165(2)	0.2904(2)	0.4647(2)	40.8(7)
C(5)	−0.0025(2)	0.3704(2)	0.5964(2)	42.2(7)
C(6)	−0.0511(2)	0.2917(2)	0.6697(2)	45.7(7)
C(7)	−0.0838(2)	0.3524(3)	0.7777(2)	59(1)
C(8)	−0.1242(3)	0.2871(3)	0.8494(2)	78(1)
C(9)	−0.1349(3)	0.1586(3)	0.8138(2)	83.1(1)
C(10)	−0.1052(3)	0.0964(3)	0.7067(2)	75(1)
C(11)	−0.0646(2)	0.1619(2)	0.6344(2)	56.3(9)
C(12)	−0.1603(2)	0.1973(2)	0.3881(2)	43.0(7)
C(13)	−0.2838(2)	0.2121(2)	0.4218(2)	51.2(8)
C(14)	−0.4193(2)	0.1267(2)	0.3511(2)	61.3(9)
C(15)	−0.4350(2)	0.0251(2)	0.2455(2)	60(1)
C(16)	−0.3144(2)	0.0070(2)	0.2113(2)	60.6(9)
C(17)	−0.1793(2)	0.0906(2)	0.2816(2)	52.4(9)
C(18)	0.1387(2)	0.2813(2)	0.3121(2)	42.6(7)
C(19)	0.2453(2)	0.2335(2)	0.2811(2)	60.0(9)
C(20)	0.2730(3)	0.2053(3)	0.1689(2)	85(1)
C(21)	0.1969(3)	0.2260(3)	0.0856(2)	93(1)
C(22)	0.0923(3)	0.2752(3)	0.1147(2)	83(1)
C(23)	0.0630(3)	0.3023(2)	0.2262(2)	59.3(9)
C(24)	0.3323(2)	0.3525(2)	0.5769(2)	43.7(7)
C(25)	0.2845(2)	0.2217(2)	0.5602(2)	53.1(8)
C(26)	0.3758(3)	0.1708(3)	0.5986(2)	68(1)
C(27)	0.5166(3)	0.2517(3)	0.6556(2)	77(1)
C(28)	0.5651(2)	0.3809(3)	0.6726(2)	70(1)
C(29)	0.4751(2)	0.4317(2)	0.6330(2)	56.9(9)
C(30)	0.2373(2)	0.5307(2)	0.7651(2)	45.1(7)
C(31)	0.2995(2)	0.6670(2)	0.8262(2)	50.9(8)
C(32)	0.3814(3)	0.7263(3)	0.9417(2)	61.4(9)
C(33)	0.4009(3)	0.6509(3)	0.9987(2)	67(1)
C(34)	0.3388(2)	0.5153(3)	0.9402(2)	68(1)
C(35)	0.2584(2)	0.4553(2)	0.8241(2)	53.8(9)
H(1)	0.151(2)	0.551(2)	0.622(2)	41(5)*
H(2)	0.298(2)	0.488(2)	0.522(2)	39(5)*
H(5)	−0.065(2)	0.424(2)	0.604(2)	40(5)*

[a] Isotropic.

Structure determination and description

Crystal data, summary of intensity data collection and refinement are listed in Table 1. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms were located from difference Fourier maps and refined isotropically. Final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms and hydrogen atoms of the cyclopentene rings of compounds **1a, 2aI** and **2aII** are shown in Tables 2, 3 and 4, respectively.

Table 5. Selected Bond Lengths (Å) and Angles (°) for the Compounds **1a, 2aI** and **2aII**

	1a	**2aI**	**2aII**
C(1)−C(2)	1.536(7)	1.569(3)	1.566(3)
C(1)−C(5)	1.550(6)	1.564(3)	1.575(2)
C(2)−C(3)	1.534(5)	1.515(3)	1.516(2)
C(3)−C(4)	1.340(6)	1.345(3)	1.348(3)
C(4)−C(5)	1.521(6)	1.519(3)	1.523(3)
C(5)−C(6)	1.510(7)	1.516(3)	1.519(3)
C(4)−C(12)	1.482(5)	1.480(3)	1.484(2)
C(3)−C(18)	1.485(6)	1.487(3)	1.484(2)
C(2)−C(24)	1.517(6)	1.519(3)	1.519(3)
C(1)−C(30)		1.517(3)	1.515(3)
C(2)−C(1)−C(5)	106.7(3)	105.2(2)	105.5(1)
C(1)−C(2)−C(3)	102.7(3)	102.1(2)	102.3(1)
C(1)−C(5)−C(4)	102.5(4)	103.0(2)	102.6(1)
C(2)−C(3)−C(4)	111.5(3)	112.3(2)	112.4(2)
C(3)−C(4)−C(5)	112.2(4)	111.9(2)	112.0(2)
C(4)−C(5)−C(6)	116.3(4)	115.3(2)	116.1(2)
C(1)−C(5)−C(6)	112.8(3)	118.2(2)	118.0(2)
C(3)−C(4)−C(12)	126.9(4)	128.3(2)	128.6(2)
C(5)−C(4)−C(12)	120.6(3)	119.8(2)	119.3(2)
C(2)−C(3)−C(18)	120.6(3)	119.4(2)	119.1(2)
C(4)−C(3)−C(18)	127.1(4)	128.2(2)	128.3(2)
C(1)−C(2)−C(24)	115.1(4)	115.3(2)	115.5(2)
C(3)−C(2)−C(24)	115.4(3)	115.4(2)	115.4(2)
C(2)−C(1)−C(30)		116.8(2)	116.0(2)
C(5)−C(1)−C(30)		119.4(2)	119.8(2)

Table 6. Selected Torsion Angles (°) for the Compounds **1a, 2aI** and **2aII**

	1a	**2aI**	**2aII**
C(1)−C(2)−C(3)−C(4)	12.9(5)	−18.8(2)	−17.9(2)
C(1)−C(2)−C(3)−C(18)	−177.0(4)	156.7(2)	156.3(2)
C(2)−C(1)−C(5)−C(6)	145.9(4)	108.3(2)	109.3(2)
C(2)−C(1)−C(5)−C(4)	20.2(4)	−20.1(2)	−19.7(2)
C(2)−C(3)−C(4)−C(5)	−0.1(5)	6.2(2)	5.5(2)
C(2)−C(3)−C(4)−C(12)	174.0(4)	−172.4(2)	−176.2(2)
C(3)−C(4)−C(5)−C(1)	−12.7(5)	9.3(2)	9.4(2)
C(3)−C(4)−C(5)−C(6)	−136.2(4)	−120.9(2)	−120.8(2)
C(5)−C(1)−C(2)−C(24)	−146.4(4)	−102.6(2)	−103.6(2)
C(5)−C(1)−C(2)−C(3)	−20.2(4)	23.2(2)	22.5(2)
C(24)−C(2)−C(3)−C(4)	138.9(4)	107.0(2)	108.4(2)
C(18)−C(3)−C(4)−C(5)	−169.4(4)	−168.8(2)	−168.1(2)
C(12)−C(4)−C(5)−C(1)	172.8(4)	−172.0(2)	−169.1(2)
C(12)−C(4)−C(5)−C(6)	49.3(5)	57.8(3)	60.8(2)
C(18)−C(3)−C(4)−C(12)	4.7(7)	12.6(4)	10.2(3)
C(24)−C(2)−C(3)−C(18)	−51.0(5)	−77.5(2)	−77.4(2)
C(30)[a]−C(1)−C(2)−C(24)	−29(3)	32.4(3)	31.4(2)
C(30)[a]−C(1)−C(5)−C(6)	29(3)	−25.2(3)	−23.7(3)
C(18)−C(3)−C(4)−C(12)		12.6(4)	10.2(3)
C(24)−C(2)−C(3)−C(18)		−77.5(2)	−77.4(2)
C(30)−C(1)−C(5)−C(4)		−153.7(2)	−152.7(2)
C(30)−C(1)−C(2)−C(3)		158.2(2)	157.6(2)

[a] H in compound **1a**.

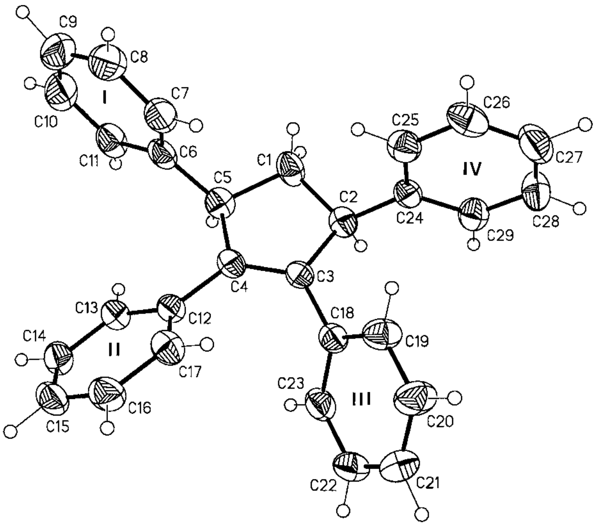


Fig. 1. ORTEP drawing of the compound **1a.**

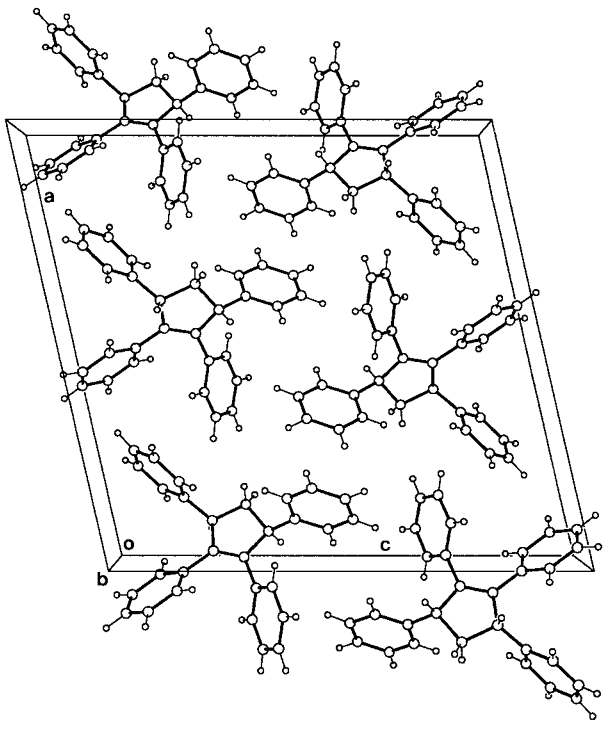


Fig. 2. Crystal packing of the compound **1a.**

Selected bond lengths and angles are reported in Table 5 and torsion angles in Table 6.

The main feature of the crystal structure of compound **1a** (see Figs. 1 and 2), is the envelope conformation ^1E of the cyclopentene ring, with parameters Q = 0.211(5) and Φ = 0.4(1.2)°, with the four phenyl rings, I, II, III and IV, tilted to the mean cyclopentene plane by 90.8(2), 35.6(1), 60.0(2), and 85.7(1)°, respectively; so, the symmetry plane through the atom C(1) and the bond C(3) — C(4) is missed only by the different bending of the two phenyls III and IV.

As mentioned above, compound **2a** crystallizes from two different solvents yielding crystals belonging to two different space groups, **2aI** and **2aII,** respectively, (see Figs. 3 and 4). In compound **2aII,** space group $P\overline{1}$, there are two molecules in the unit

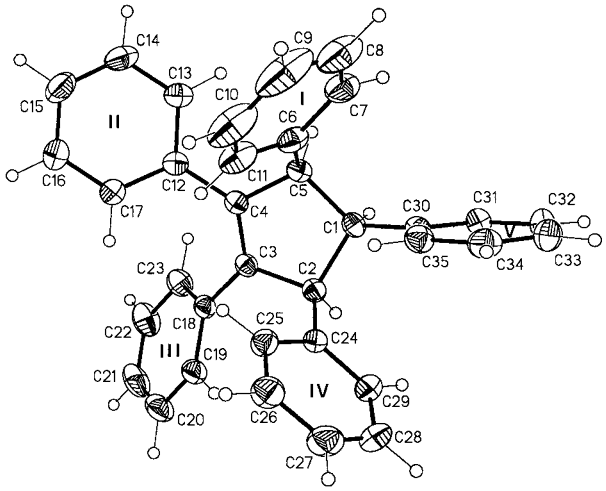


Fig. 3. ORTEP drawing of the compound **2aI.**

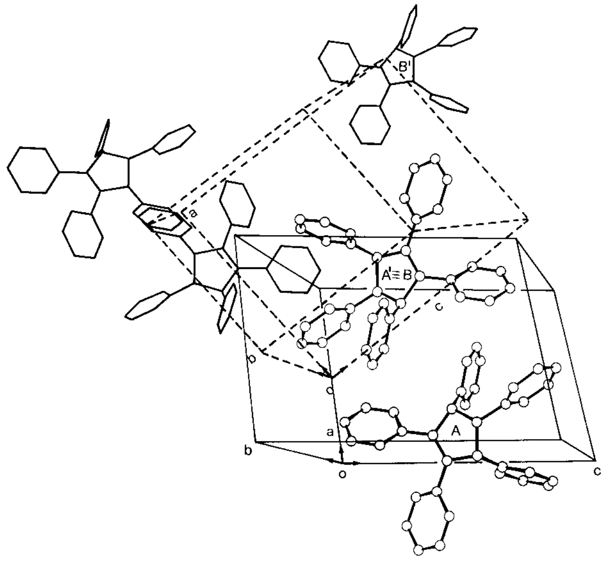


Fig. 4. Overlap view of the two packing of **2aI** (cell with dot lines) and **2aII** (cell with full lines). Origin of **2aI** at 1/2 of the *a* axis of **2aII** and *c* axis along *ac* diagonal of of **2aII.**

cell, related by the symmetry center; these two molecules are doubled in **2aI,** space group $P2_1/n$, by the presence of the n glide plane perpendicular to the b axis of the $P\overline{1}$ space group, so, in the two space groups there are only slight differences in the a and c axis values and in $P2_1/n$ there is a nearly doubling of the b axis value of $P\overline{1}$ space group. No differences in bond lengths, bond angles and torsion angles are apparent from the data collected in Tables 5 and 6 for compounds **2aI** and **2aII**: they display the same twisted ${}^2T_1$ conformation, with $Q = 0.230(2)$ and $\Phi = -168.8(5)°$. Now, the phenyl ring V is nearly perpendicular to the cyclopentene ring, 97.0(1)°, while the phenyls I and IV deviate more from orthogonality, 69.8(1)° and 78.9(1)°, respectively; the bending angles of the phenyls II and III are 18.6(1)° and 122.7(1)°, respectively.

Conclusions

The main conclusions, which can be drawn from this crystallographic study are the following: (i) the determination of the configuration of compounds **1a** and **2a** allows the assignment of the ^{1}H NMR signals unambigously, and this is of great help for the identification of the reaction products[1]; (ii) in both compounds, the cyclopentene ring is not planar and the crowding around it causes the phenyl substituents to rotate to some extent to release the steric hindrance; as a result, the delocalization of the π electrons must be not so efficient as one may expect and this can have important consequences on the spectroscopic behavior and on the physical and chemical properties of the molecule; (iii) the crystal packing, in the absence of hydrogen bonding and of solvent molecules of crystallization, does not display any particular solid state motif. Finally, it is worthy to mention that crystals belonging to two different space groups could be isolated from different solvents in the case of compound **2a.**

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