The Structure of 2,5-Diphenyl-1 *H*-cyclopropabenzene**

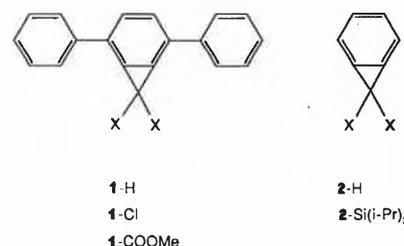**Paul Müller*, Gérald Bernardinelli, and Huong Can Godoy-Nguyen Thi**

Abstract: The structure of the title compound (**1-H**), determined by X-ray crystallography, is reported. The molecule is planar and geometry of the «benzocyclopropene» moiety is the same as that for the parent compound (**2-H**). The lateral cyclopropene bond lenghts vary with the substituents at C(1) in both **1** and **2**.

Several X-ray structures of «benzocyclopropene» derivatives have been reported over the past ten years, but all of the compounds were either substituted

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with strongly electronegative substituents at C(1)[1, 2], or benzannelated[3]. Since the effects of these substituents on the geometry of the parent 1*H*-cyclopropabenzene are difficult to assess, we carried out a structure determination of the 2,5-diphenyl derivative (**1-H**), the synthesis of which has been reported several years ago[4]. The recent disclosure of the structure of «benzocyclopropene» (**2-H**)[5, 6] itself prompts us to report our own findings.

2,5-Diphenyl-1*H*-cyclopropabenzene (**1-H**) recrystallized from pentane (*m.p.* 143–146 °C) affords monoclinic transparent prisms of the space group P2₁/c; $a = 12.0325(15)$, $b = 5.5964(7)$, $c = 20.070(3)$ Å, $V = 1331.7(2)$ Å³; $\beta = 99.81(1)°$; $Z = 4$. The final R-factor, based on 1092 observed reflections ($F_0 > 4\sigma\,(F_0)$), was 0.055[7–9]. The structure is shown in Fig. 1.

In a first approximation the molecule is planar, the largest deviation from the best-fitted plane through all C atoms being 0.06 Å. However as in the case of **1-COOMe** and **1-Cl**, some slight deformations from planarity also occur for **1-H**. The lateral phenyl rings are twisted by

1-H
1-Cl
1-COOMe

2-H
2-Si(i-Pr)₃

2.9 and 2.0° with respect to the central ring, while the longitudinal axes of the lateral rings (C(1')–C(4') and C(1'')–C(4'')) are not exactly colinear, but tilted towards the cyclopropene with an angle of 5.2°. The planes of the cyclopropene and benzene rings are inclined by 1.9°. H–C(3) and H–C(4) lie below the plane of the molecule, such as to avoid interactions with the *o*-hydrogens of the lateral rings (H–C(2') and H–C(2'')). Despite of this the interatomic hydrogen distances between the central and lateral rings are very short (2.08(3) and 2.15(3) Å for H–C(3)/H–C(2') and H–C(4)/H–C(2''), respectively), i.e. below the sum of the usually used van der Waals radii.
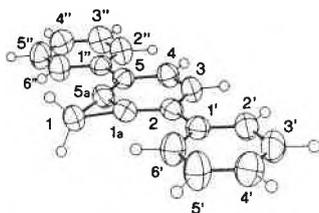

Fig. 1. Structure of **1-H** *in the crystal (cf. Table 1).*

The geometry of the «benzocyclopropene» moiety is almost identical to that of the parent compound (**2-H**). Selected structural parameters for **1-H** and **2-H** are shown in Table 1. The comparison with other 1,1-disubstituted derivatives (**1-Cl** and **1-COOMe**) reveals only slight structural modifications upon variation of the substituent. The most significant change is found in the lateral cyclopropene bonds in **1-Cl**, which decrease from 1.51 in **1-H** to 1.46 Å (average value for C(1)–C(1a) and C(1)–C(5a)) in **1-Cl**. In contrast, replacement of the allylic hydrogen atoms in **2-H** by the bulky triisopropylsilyl groups (**2-Si**) results in lengthening of the C(1)–C(1a) bond to 1.541 Å [5]. This has been ascribed to a steric effect. The central double bond varies only by 0.02 Å within the series. The observed

bond length for the bridge bond (C(1a)–C(5a)) in **1-H** (1.340 Å) compares well with the calculated (3-21G*) value for **2-H** (1.333 Å) [10]. For the lateral cyclopropene bonds agreement is somewhat less (1.51 Å experimental vs. 1.495 Å calculated) but still satisfactory.

Table 1. Selected strucural data[a] for **1-H**, **2-H** [5, 6], and calculated values for **2-H** (3–21G*) [10].

	1H	2H	2-H(3–21G*)
Bond length			
C(1)-C(1a)	1.512(5)	1.498(3)	1.495
C(1)-C(5a)	1.511(5)		
C(1a)-C(5a)	1.340(4)	1.334(4)	1.333
C(1a)-C(2)	1.377(5)	1.363(3)	1.372
C(2)-C(3)	1.410(5)	1.387(4)	1.400
C(3)-C(4)	1.394(4)	1.390(5)	1.396
C(4)-C(5)	1.412(5)		
C(5)-C(5a)	1.378(5)		
Bond angle			
C(1a)-C(1)-C(5a)	52.6(2)	52.8(2)	52.9
C(1)-C(1a)-C(5a)	63.6(2)	63.6(1)	
C(5a)-C(1a)-C(2)	125.6(3)	124.5(2)	124.7
C(1a)-C(2)-C(3)	111.0(3)	113.2(2)	113.1
C(2)-C(3)-C(4)	123.3(3)	122.4(2)	122.4
C(3)-C(4)-C(5)	123.4(3)		
C(4)-C(5)-C(5a)	110.9(3)		
C(1a)-C(5a)-C(1)	63.7(2)		
HC(1)-C(1)-H'C(1)	112.(2)		113.5

[a] Bond lengths in Å, angles in degrees.

If the (near-)planar structure of **1-H** were retained in solution, then the *o*-protons of the lateral rings (H–C(2') and H–C(6')) should resonate at different field in the ¹H-NMR. However, we find only an AA'BB'C system at 360 MHz; the lines remain unchanged when the temperature is lowered to −70 °C, where precipitation occurs. This is consistent with a perpendicular conformation or with rapid rotation of the phenyl groups. The former is unlikely, because in the related biphenyl, the perpendicular arrangement in solution corresponds to an energy maximum, with the minima at 30–40° and a barrier for rotation of 14.9 kJ/mol [11]. Terphenyl, a better model for **1-H** than biphenyl is comparable: In the solid state it is also slightly twisted (16 and 25° between internal and external phenyl rings) [12]; unfortu-

nately the conformation in solution is uncertain [13]. Considering the low barrier for rotation in biphenyl, the AA'BB'C system in the NMR spectrum of **1-H** is best explained by rapid rotation of the lateral phenyl rings.

[1] E. Carstensen-Oeser, B. Müller, H. Dürr, *Angew. Chem. 84* (1972) 434; *Angew. Chem. Int. Ed. Engl. 11* (1972) 422.
[2] B. Halton, T.J. McLennan, W.T. Robinson, *Acta Crystallogr. B32* (1976) 1889.
[3] W.E. Billups, W.Y. Chow, K.H. Leavell, E.S. Lewis, J.L. Margrave, R.L. Sass, J.J. Shieh, P.G. Werness, J.L. Wood, *J. Am. Chem. Soc. 95* (1973) 7878.
[4] P. Müller, *Helv. Chim. Acta 57* (1974) 704.
[5] R. Neidlein, D. Christen, V. Poignée, R. Boese, D. Bläser, A. Gieren, C. Ruiz-Pérez, T. Hübner, *Angew. Chem. 100* (1988) 292; *Angew. Chem. Int. Ed. Engl. 27* (1988) 294.
[6] B. Halton, P.J. Stang, *Acc. Chem. Res. 20* (1987) 443.
[7] Data were collected on a Nonius CAD4 diffractometer (Mo_{Kα}). The structure was solved by direct methods (Multan 84) [8] and refined by full-matrix least-squares analysis (XTAL) [9]. All coordinates of H atoms were observed and refined with a fixed value of the atomic displacement ($U_{iso} = 0.05$ Å²). – Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.
[8] P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declerq, M.M. Woolfson: MULTAN-84, a system for computer programs for the automatic solution of crystal structure from X-ray diffraction data, University of York (1984).
[9] S.R. Hall, J.M. Stewart (Ed.): *XTAL2.2 User's Manual*, Universities of Western Australia and Maryland (1987).
[10] Y. Apeloig, D. Arad, *J. Am. Chem. Soc. 108* (1986) 3241.
[11] M. Akiyama, T. Watanabe, M. Kakihana, *J. Phys. Chem. 90* (1986) 1752; S. Carbonnier, S.T. Beguemsi, Y.T. N'guessan, D. Legoff, A. Proutière, R. Viani, *J. Mol. Struct. 158* (1987) 109.
[12] J.L. Baudour, Y. Delugeard, H. Cailleau, *Acta Crystallogr. B32* (1976) 150.
[13] M. Akiyama, *Spectrochim. Acta A40* (1984) 367.