1,1-Dibromo-2-phenyl-2-(2-propenyl)cyclopropane: Its Crystal Structure and Its ^{1}H NMR Spectrum Containing an Unusual Long-Range Coupling

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The structure of the title compound was determined from single-crystal diffraction data. $C_{12}H_{12}Br_2$, monoclinic, space group $P2_1/a$, $a = 32.582(7)$, $b = 5.985(3)$, $c = 12.578(2)$ Å, $\beta = 105.99(1)°$, $Z = 8$. Least-squares refinement of 253 parameters gave $R = 0.041$ for 2912 observed $[I > 3.5\sigma(I)]$ reflections. Two crystallographically non-equivalent molecules are present, differing in structures mainly by the conformation of the propenyl side-chain. The ^{1}H NMR spectrum exhibits coupling between the cyclopropyl proton *cis* to the phenyl group and one of the methylene protons next to the ring.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Spin-spin interactions between hydrogen nuclei separated by four bonds (long-range coupling) result in fine-splitting of signals in the proton NMR spectra of a number of organic molecules.[1] Although such long-range coupling is observed in some saturated hydrocarbons, particularly in bicyclo[2.1.1]hexane[2,3] and bicyclo[2.2.1]heptane[4] derivatives, these interactions are almost exclusively present in compounds containing at least one allylic moiety, i.e. an H–C=C–C–H fragment.[1,5] The reason for this is that long-range coupling is transferred most effectively through π systems due to the binding properties of sp^2-hybridized carbon atoms.[6–8] One may therefore expect that cyclopropane compounds, due to the intermediate hybridization of the carbon atoms in the ring,[9,11] would exhibit analogous, but weaker long-range coupling. However, this is generally not the case; only a few examples have been reported, viz. vinylcyclopropane,[12] 1-bromo-2-vinylcyclopropane,[13] 1,1-dibromo-2-vinylcyclopropane (**1**),[13] and cyclopropanecarbonyl fluoride.[14]

We were therefore very surprised when the 60 MHz ^{1}H NMR spectrum of 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**2**) indicated the presence of coupling between the hydrogen atoms attached to the ring and the methylene group next to the ring. We therefore decided to look more closely into some of the structural aspects of this compound using both high-field NMR spectroscopy and X-ray diffraction.

Experimental

The instruments used have been described elsewhere.[15]

1,1-Dibromo-2-phenyl-2-(2-propenyl)cyclopropane (**2**) was prepared from 2-phenyl-1,4-pentatiene[16] according to Makosza's method[17] employing a 20 % excess of both bromoform and base. The compound, which was isolated in 40 % yield by distillation, b.p. 100 °C/0.1 mmHg, crystallized on storage; m.p. 35 °C. Anal. $C_{12}H_{12}Br_2$: C,H. UV [96 % ethanol; λ (ε)]: 221 (3800), 258 (660), 265 (420), 295 (40) nm; IR (film): 3095

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(m), 3050 (m), 1640 (m), 1602 (m), 1581 (w), 1496 (s), 1020 (s), 995 (s), 917 (s), 763 (s), 715 (m), 695 (s) cm^{-1}; ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.79 (1H, d, J 7.64 Hz), 2.08 (1H, d×d, *J* 1.40 and 7.64 Hz), 2.49 (1H, d×d×t, *J* 1.16, 7.84 and 14.21 Hz), 2.92 (1H, d×d×q, *J* 1.40, 6.24 and 14.21 Hz), 4.91–4.97 (2H, m), 5.57–5.67 (1H, m), 7.23–7.37 (5H, m); ^{13}C NMR (22.50 MHz, $CDCl_3$): δ 32.7 (CH_2), 35.9 (C), 39.5 (C), 44.8 (CH_2), 117.6 (CH_2), 127.2 (CH), 128.0 (2×CH), 129.4 (2×CH), 134.0 (CH), 140.1 (C)

^1H NMR spectroscopy. The NMR experiments were carried out on a Bruker WM-400 NMR spectrometer operating at 400.13 MHz. The spectra were recorded for solutions in ordinary 5 mm tubes, using tetramethylsilane (TMS) as internal reference. The samples were approximately 2 % by weight in deuteriochloroform ($CDCl_3$), which provided the deuterium resonance for the NMR field lock. Oxygen was not removed from the samples. The spectra were observed over a range of 4000 Hz. The NOE difference measurements were carried out by recycling a frequency list and using a preirradiation time of 4 s,[18] which is significantly longer than the expected T_1 values for the protons studied here. The saturation obtained was 100 %.

Resolution enhancement was obtained using Gaussian multiplication.

Table 1. Crystal and experimental data.

Compound	$C_{12}H_{12}Br_2$
Diffractometer	Nicolet *P3/F*
Crystal size/mm	0.1×0.2×0.4
Radiation	Mo*K*α
Crystal system	Monoclinic
a/Å	32.582(7)
b/Å	5.985(3)
c/Å	12.578(2)
β/°	105.99(1)
V/Å^3	2357.9(1.2)
Temp./°C	−116
Space group	$P2_1/a$
M	316.03
Z	8
F(000)	1232
D_x/gcm^{-3}	1.780
μ(Mo*K*α)/cm^{-1}	0.72
Scan mode	θ/2θ
Scan speed (2θ)/°min^{-1}	2
Scan range (2θ)/°	2.0
Maximum sinθ/λ/Å^{-1}	0.70
No. of data with $I>3.5\sigma(I)$	2912
Correction for absorption	Empirical
No. of parameters refined	253
$R=\Sigma\|F_o-F_c\|/\Sigma F_o$	0.041
$R_w=[\Sigma w(F_o-F_c)^2/\Sigma_w F_o^2]^{1/2}$	0.041
$S=[\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$	

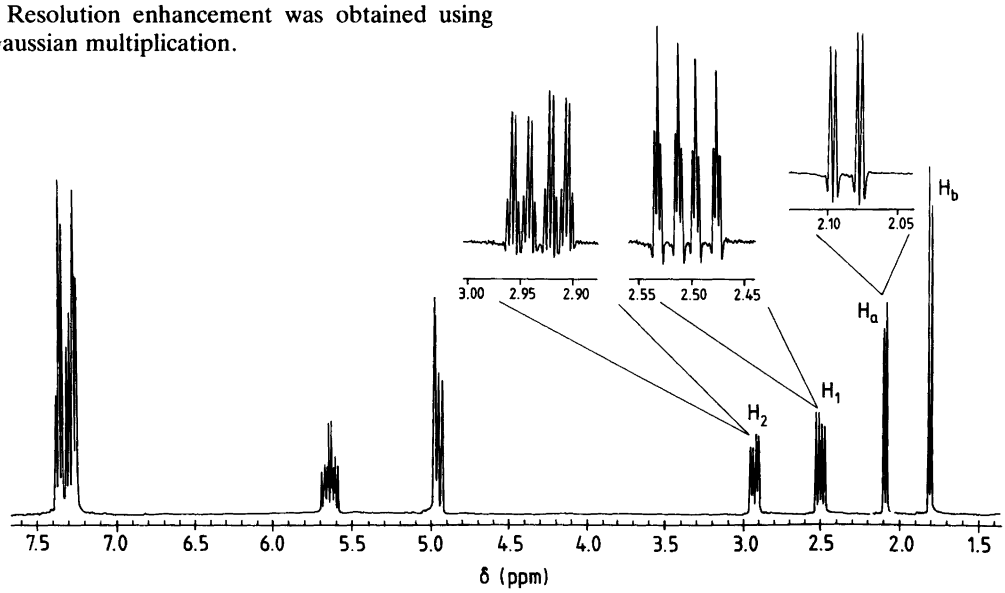


Fig. 1. The 400 MHz ^1H NMR spectrum of 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane in $CDCl_3$ at 24 °C relative to internal TMS.

Table 2. Fractional atomic coordinates and U_{eq} ($= \frac{1}{3} \Sigma U_{ij}$).

Atom	*x*	*y*	*z*	U_{eq}
Br11	0.94776(2)	0.51159(13)	0.09721(6)	0.031
Br12	0.99624(2)	0.50445(13)	0.35133(5)	0.027
Br31	0.80563(3)	0.05346(13)	0.57223(6)	0.036
Br32	0.72199(3)	0.09814(14)	0.65062(7)	0.040
C11	0.9579(2)	0.6697(11)	0.2356(5)	0.022
C12	0.9239(2)	0.8111(11)	0.2622(5)	0.025
C13	0.9621(2)	0.9188(11)	0.2373(6)	0.025
C14	0.8807(2)	0.8392(12)	0.1766(6)	0.031
C15	0.8636(3)	1.0716(14)	0.1776(7)	0.047
C16	0.8339(3)	1.1318(15)	0.2167(8)	0.054
C17	0.9196(2)	0.8096(12)	0.3775(6)	0.026
C18	0.9324(2)	0.9899(12)	0.4475(5)	0.026
C19	0.9250(2)	0.9923(13)	0.5503(6)	0.035
C20	0.9062(2)	0.8130(13)	0.5864(6)	0.032
C21	0.8938(2)	0.6311(12)	0.5174(6)	0.033
C22	0.9004(2)	0.6280(11)	0.4158(6)	0.028
C31	0.7778(2)	0.2167(11)	0.6630(6)	0.026
C32	0.8052(2)	0.3086(11)	0.7730(6)	0.025
C33	0.7860(2)	0.4616(11)	0.6755(5)	0.027
C34	0.7858(2)	0.3193(12)	0.8704(6)	0.030
C35	0.8047(2)	0.5108(13)	0.9463(5)	0.031
C36	0.7833(2)	0.6848(13)	0.9642(6)	0.037
C37	0.8526(2)	0.2585(11)	0.8060(5)	0.024
C38	0.8814(2)	0.4133(12)	0.7925(6)	0.030
C39	0.9252(2)	0.3729(13)	0.8253(6)	0.033
C40	0.9397(2)	0.1659(14)	0.8704(6)	0.036
C41	0.9107(3)	0.0117(13)	0.8864(6)	0.039
C42	0.8670(2)	0.0568(12)	0.8529(6)	0.033

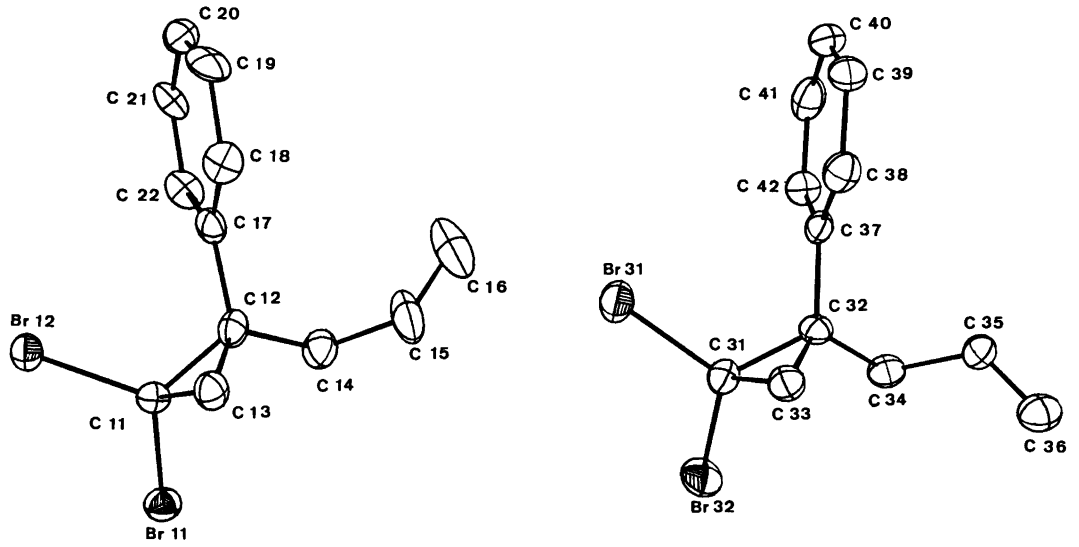
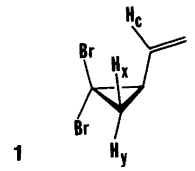


Fig. 2. ORTEP plots of the two non-equivalent molecules of **2**.

Table 3. Bond lengths (Å), bond angles (°) and selected torsion angles (°). Estimated standard deviations are calculated from the variance-covariance matrix.

Distance		Distance	
Br11–C11	1.928(7)	Br12–C11	1.912)7)
Br31–C31	1.911(7)	Br32–C31	1.917(7)
C11 –C12	1.506(10)	C11 –C13	1.497(10)
C12 –C13	1.512(10)	C12 –C14	1.526(10)
C12 –C17	1.494(10)	C14 –C15	1.499(12)
C15 –C16	1.254(12)	C17 –C18	1.382(10)
C17 –C22	1.403(10)	C18 –C19	1.379(10)
C19 –C20	1.374(11)	C20 –C21	1.382(11)
C21 –C22	1.354(11)	C31 –C32	1.528(10)
C31 –C33	1.490(10)	C32 –C33	1.521(10)
C32 –C34	1.529(10)	C32 –C37	1.512(10)
C34 –C35	1.510(11)	C35 –C36	1.307(11)
C37 –C38	1.362(10)	C37 –C42	1.370(10)
C38 –C39	1.394(10)	C39 –C40	1.389(11)
C40 –C41	1.376(11)	C41 –C42	1.393(11)
Angle		**Angle**	
Br11–C11–Br12	110.3(4)	Br11–C11–C12	121.5(5)
Br11–C11–C13	119.6(5)	Br12–C11–C12	119.2(5)
Br12–C11–C13	117.8(5)	C12 –C11–C13	60.5(5)
C11 –C12–C13	59.9(5)	C11 –C12–C14	119.8(6)
C11 –C12–C17	118.9(6)	C13 –C12–C14	117.3(6)
C13 –C12–C17	120.4(6)	C14 –C12–C17	111.9(6)
C11 –C13–C12	60.1(5)	C12 –C14–C15	111.6(6)
C14 –C15–C16	126.8(8)	C12 –C17–C18	121.4(6)
C12 –C17–C22	120.4(7)	C18 –C17–C22	118.1(7)
C17 –C18–C19	120.4(7)	C18 –C19–C20	120.7(7)
C19 –C20–C21	119.2(7)	C20 –C21–C22	120.6(7)
C17 –C22–C21	121.0(7)	Br31–C31–Br32	111.0(4)
Br31–C31–C32	117.9(5)	Br31–C31–C33	117.7(5)
Br32–C31–C32	120.8(5)	Br32–C31–C33	120.8(5)
C32 –C31–C33	60.5(5)	C31 –C32–C33	58.5(5)
C31 –C32–C34	118.2(6)	C31 –C32–C37	118.4(6)
C33 –C32–C34	116.8(6)	C33 –C32–C37	120.2(6)
C34 –C32–C37	113.9(6)	C31 –C33–C32	61.0(5)
C32 –C34–C35	110.5(6)	C34 –C35–C36	124.7(7)
C32 –C37–C38	121.1(7)	C32 –C37–C42	119.8(7)
C38 –C37–C42	119.1(7)	C37 –C38–C39	122.0(7)
C38 –C39–C40	118.6(7)	C39 –C40–C41	119.3(7)
C40 –C41–C42	120.7(8)	C37 –C42–C41	120.1(7)

Selected torsion angles	
C11 –C12–C14–C15	–142.3(9)
C11 –C12–C17–C18	107.0(9)
C11 –C12–C17–C22	–76.4(8)
C11 –C13–C12–C14	–110.5(9)
C13 –C12–C14–C15	–73.6(8)
C14 –C12–C17–C18	–106.5(9)
C14 –C12–C17–C22	70.1(8)
C12 –C14–C15–C16	–105.2(11)
C17 –C12–C14–C15	71.9(9)
C31 –C32–C34–C35	–150.0(9)
C31 –C32–C37–C38	100.6(9)
C31 –C32–C37–C42	–81.2(8)
C33 –C32–C34–C35	–83.2(7)
C34 –C32–C37–C38	–113.6(9)
C34 –C32–C37–C42	64.6(8)
C32 –C34–C35–C36	115.5(10)
C37 –C32–C34–C35	64.6(9)



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X-Ray crystallography. Crystals were formed by sublimation; data for unit cell determination and intensity data were collected using a Nicolet *P*3/F diffractometer and graphite crystal monochromated Mo*K*α radiation (λ = 0.71069 Å). Crystal and experimental data are given in Table 1.

The atomic coordinates of all non-hydrogen atoms were determined by direct methods (MITHRIL[19]). Refinements were performed by least-squares calculations, and hydrogen atomic positions were calculated and included in the structure factor calculations but were not refined. An empirical absorption correction was applied,[20] the minimum absorption correction being 0.804, while the maximum absorption correction was 1.213. Computer programs applied are described in Ref. 21. Final figures of merit based on the refinement of 253 parameters are included in Table 1. Positional parameters are given in Table 2, and lists of anisotropic thermal parameters and structure factors may be obtained from the authors on request.

An ORTEP plot of the two non-equivalent molecules is presented in Fig. 2; bond lengths, bond angles and torsion angles are listed in Table 3.

Results and discussion

Spectral analysis. The ^{1}H NMR spectrum of **2** consists of seven distinguishable groups of bands

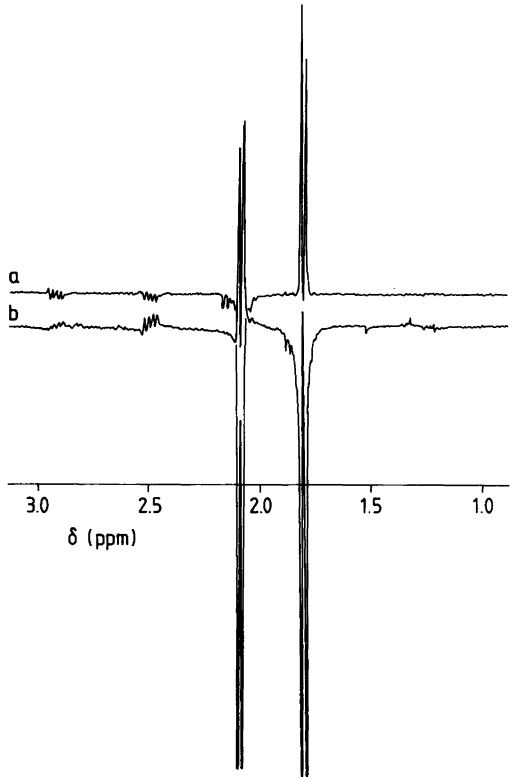
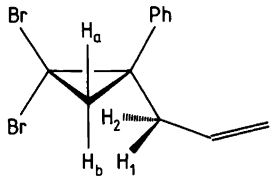


Fig. 3. ^{1}H-{^{1}H} NOE difference spectra of 1,1-dibromo-2-phenyl-2-(2-propenyl)cyclopropane with irradiation of (a) H_a and (b) H_b.

(Fig. 1). The absorptions between 7.37 and 7.23 ppm are due to the five aromatic protons, whereas the three vinylic protons give rise to the signals in the 5.7–4.9 ppm region. As expected, decoupling experiments proved that the band systems at approximately 2.9 and 2.5 ppm are associated with the protons attached to the sp^3-hybridized carbon atom of the propenyl group

Table 4. Decoupling experiments for the four high-field absorption systems.

Frequency of irradiation/ppm	Absorption system multiplicity			
	2.92 ppm	2.49 ppm	2.08 ppm	1.79 ppm
2.92	–	d×t	d	d
2.49	d×q	–	d×d	d
2.08	d×d×t	d×d×t	–	s
1.79	d×d×q	d×d×t	d	–



2

(H_1 and H_2), while the remaining groups of lines arise from the cyclopropyl protons (H_a and H_b).

When the spectrum was recorded with resolution enhancement the signal at 1.8 ppm remained a doublet whereas the three other band systems at higher field than 3.0 ppm became more complex. From the inserts in Fig. 2 it is evident that there is a d×d×q at 2.92 ppm, a d×d×t at 2.49 ppm, and a d×d at 2.08 ppm. Decoupling experiments, summarized in Table 4, showed that the cyclopropyl proton, which is responsible for the double doublet at 2.08 ppm, is coupled ($|J|$ = 1.40 ± 0.02 Hz) to either H_1 or H_2 which gives rise to the absorptions at 2.92 ppm.

In order to determine whether it is H_a or H_b that is involved in this long-range coupling, differential NOE experiments were carried out. When the cyclopropyl proton associated with the doublet at 1.79 ppm was irradiated, considerable enhancements of the signals due to H_1, H_2 and the other cyclopropyl proton were observed (Fig. 3, trace b). This indicates that the irradiated proton is *cis* to the allyl group, i.e. that it is H_b, a conclusion which is supported by the difference spectrum obtained when H_a, thus associated with the d×d at 2.08 ppm, was irradiated. This irradiation gave rise to enhancement for H_b (1.79 ppm) and, indirectly, negative effects for H_1 and H_2 (Fig. 3, trace a). The negative influence is caused by the three-spin effect which in extreme cases may propagate more than two nuclei away.[22,23]

The enhancement of the band system due to H_1 in difference spectrum b (Fig. 3) is 4.5 times larger than that due to H_2. Although this value is somewhat smaller than the value of 7.9 calculated on the basis of the distances from H_b to H_1 and H_2 (2.48 Å and 3.50 Å, respectively), it is evident from these results that H_a is coupled to the methylene proton next to the ring that is farther away from H_b. Consequently, *H_a is coupled to H_2 and not to H_1*. The reason for this selective coupling is still absolutely unclear, because on the basis of the crystal structure (Fig. 2) and MM2 calculations the propenyl group can rotate freely at least 100° in each direction from the conformations depicted in Fig. 2 without introducing significant steric interactions.

The position of H_a is *trans* to H_2 in **2**, and their relative positioning is thus similar to that of H_c relative to H_y in **1**. In spite of this, the absolute values of the corresponding coupling constants are significantly different in the two cases, viz. 1.40 Hz in **2** as compared to 0.08 Hz in **1**.[13] The corresponding *cis* coupling constants are also considerably different, viz. −0.40 Hz to H_x in **1**[13] and 0.0 Hz to H_b in **2**. These differences may, in part, be explained by the different binding properties of the carbon atoms next to the ring in **1** as compared to **2**, but more important is probably the difference in their conformational properties. This is in keeping with existing theoretical descriptions which show that long-range coupling constants through four bonds, ^4J, are a function of the dihedral angles of the H−C−C−C−H fragment.[7,24] Particularly attractive in our case is the empirical correlation introduced by Bystrov and Stepanyants.[25] According to their description

$$^4J = (A \cos^2 \theta_1 \cos^2 \theta_2 - 0.35)\ \text{Hz}$$

where $A = 0.31$ for $0° \leq \theta_1, \theta_2 \leq 90°$

$A = 1.07$ for $0° \leq \theta_1 \leq 90° \leq \theta_2 \leq 180°$

$A = 3.61$ for $90° \leq \theta_1, \theta_2 \leq 180°$.

A large coupling constant is therefore associated with dihedral angles larger than 90°. If we assume that the average conformation of **2** in solution is close to those present in the solid state, then $\theta_1 \cong 130°$ and $\theta_2 \cong 175°$ (Fig. 4). This leads to a value of 1.0 Hz for ^4J which is surprisingly close to

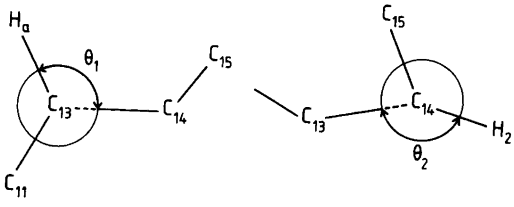


Fig. 4. The dihedral angles θ_1 and θ_2 in the H−C−C−C−H fragment involved ion long-range coupling.

the experimental value (1.40 Hz), considering the significant structural differences between **2** and the compounds studied by Bystrov and Stepanyants. A corollary of this analysis is that the coupling constant for coupling between H_b and H_1 or H_2 should be close to 0 Hz, which in fact is the case.

The crystal structure. The bromine–carbon bond lengths average 1.917 Å, the phenyl ring distances 1.380 Å, and the bonds of phenyl attachment 1.503 Å. The values compare well with the corresponding averages of 1.906 Å, 1.378 Å and 1.490 Å, respectively, in 1,1-dibromo-2,3-diphenylcyclopropane.[11]

The torsion angle τ as defined by Allen[26] is 70.5 and 65.5° for the two non-equivalent molecules, respectively (*gauche* 3/ perpendicular).

The three-membered rings show the bond asymmetry expected for a phenyl-substituted cyclopropane.[26] The average C–C bond is 1.509 Å, as expected. The C–C bond distal to the phenyl ring is shortened by 0.015 Å relative to the mean value, whereas the vicinal bonds are lengthened by 0.008 Å.

The main difference between the two non-equivalent molecules is found in the propenyl side chain. The angle of rotation about its single bond is −105.2° in one molecule and 115.5° in the other. The single bond, average value 1.505 Å, is normal for a $C(sp^2)-C(sp^3)$ bond. The double bond in one of the molecules is found to be 1.254 Å and in the other 1.307 Å. Compared to a normal C–C double bond (1.336 Å), especially the former seems to be very short, even when the rather large estimated standard deviation (0.012 Å) is taken into account.

Intermolecular separations are those to be expected from van der Waals sums.

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