

Dispiro[2.0.2.4]deca-7,9-diene: Structure Determination of a Molecule with a Unique Combination of (*sp*)-1,3-Butadiene, (*sc*)-Bicyclopropyl and (*ap*)-Vinylcyclopropane Subunits

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The molecular structure of dispiro(2.0.2.4)deca-7,9-diene has been studied by the gas electron diffraction method. Conjugation involving the C=C double bonds and the cyclopropyl groups has been discussed. The determined bond distances (r_a) and valence (\angle_a) and dihedral (ω_a) angles, with estimated 2σ uncertainties are: $r(\text{C}=\text{C}) = 1.345(2)$, $r(\text{C}^2-\text{C}^3) = 1.450(8)$, $r(\text{C}^4-\text{C}^5) = 1.518(20)$, $r(\text{C}^5-\text{C}^6) = 1.499(33)$, $r(\text{C}-\text{C})_{\text{cpr}} = 1.508(3)$ Å, $\angle \text{C}^1=\text{C}^2-\text{C}^3 = 120.1(6)$, $\angle \text{C}^3=\text{C}^4-\text{C}^5 = 121.0(9)$, $\angle \text{C}^4-\text{C}^5-\text{C}^6 = 111.7(4)$, $\angle \text{C}^4-\text{C}^5-\text{M} = 120.7(12)$ (C^5-M bisects the cyclopropyl group), $\angle \text{C}=\text{C}-\text{H} = 120.3(40)$, $\angle \text{H}-\text{C}-\text{H} = 110.5(31)$, $\omega(\text{C}=\text{C}-\text{C}=\text{C}) = 16.2(7)$, $\omega(\text{C}^3=\text{C}^4-\text{C}^5-\text{C}^6) = -29.8(20)$, $\omega(\text{C}^4-\text{C}^5-\text{C}^6-\text{C}^1) = 42.2(28)$, $\omega(\text{C}^3=\text{C}^4-\text{C}^5-\text{M}) = 150.7(9)$, $\omega(\text{M}-\text{C}^5-\text{C}^6-\text{M}') = 41.0(27)^\circ$.

The molecular structure of dispiro[2.0.2.4]deca-7,9-diene has also been calculated by semiempirical AM1, MINDO3 and MNDO methods.

The conjugative interactions between C=C double bonds and/or cyclopropyl groups have fascinated chemists for many years, and the results of the various experimental and theoretical studies in this field have been summed up in several books and review articles.^{1–3} 1,3-Butadiene (BD)^{4–11} and 1,3-cyclohexadiene (CHD)^{12,13} are among the simplest compounds with conjugated CC double bonds. Vinylcyclopropane (VCP)^{14–18} and bicyclopropyl (BCP)^{19–22} are examples of simple molecules with conjugation between a CC double bond and a cyclopropyl group (VCP) or between two cyclopropyl groups (BCP). All of these molecules have been extensively studied by theoreticians as well as by experimentalists.^{4–24}

Dispiro[2.0.2.4]deca-7,9-diene (DSDD)²⁵ is a molecule with two C=C double bonds and two spirocyclopropane groups linked together in a six-membered ring. The molecule uniquely combines all the structural fragments found in CHD, VCP and BCP, and because of the cyclic interconnection of the diene and the bicyclopropyl unit, all the subunits are rigidly held in well defined conformations. It is therefore of special interest to determine the molecular structure of DSDD and elucidate possible effects of the electronic interactions within and between these subunits.

DSDD has previously been studied by UV, NMR and photoelectron spectroscopy.²⁵ All spectroscopic data were in agreement with a non-planar six-membered ring for DSDD, and from the $^3J_{2,3}$ proton coupling constant in the

NMR spectrum, the C=C–C=C dihedral angle was estimated to be ca. 12°, using the Karplus relation. The study indicated that there is no cyclic electron delocalization in DSDD.

Experimental and data reduction

DSDD was synthesized as described in Ref. 25. The electron diffraction scattering data were recorded in the Oslo apparatus²⁶ under the following conditions: nozzle-to-plate distances, 485.16 mm (6 plates) and 205.16 mm (4 plates). Kodac Electron Image photographic plates were used, and the temperature at the nozzle tip was 50°C during the experiments. The electron wavelength was 0.06461 Å, as calibrated against diffraction patterns from gaseous benzene, using $r_a(\text{C}-\text{C}) = 1.3975$ Å as a standard. The estimated standard deviation in the determination of the electron wavelength is 0.1%. The ranges of the scattering data were 1.25–19.75 and 6.75–43.75 ($\Delta s = 0.25$) Å⁻¹. The experimental intensities in the region $s = 2.00$ –40.00 Å⁻¹ were applied in the final study.

Reduction of the data was performed in the usual way,^{27,28} and a calculated background was subtracted from the data for each plate to yield the experimental molecular intensity distribution in the form $sI_m(s)$.²⁹ The averages of the molecular intensities are shown in Fig. 1. Electron scattering amplitudes and phase shifts were calculated using of Hartree–Fock potentials for C,³⁰ while molecular bonded potentials were used for H.³¹

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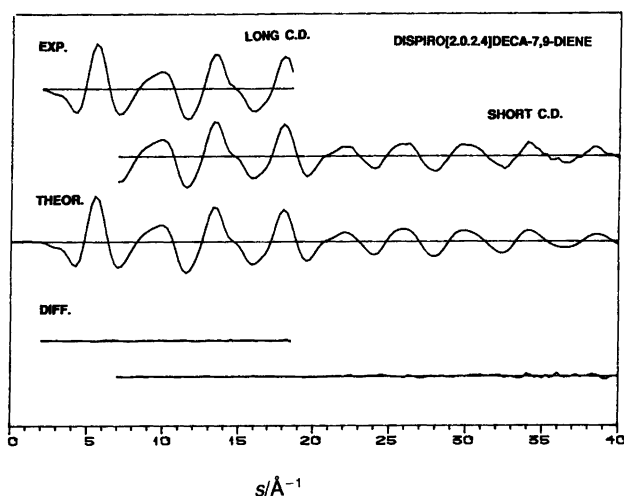


Fig. 1. Experimental and theoretical molecular intensities for DSDD and the difference curves. The theoretical curve is calculated from the parameters in Table 2.

Table 1. Valence force field for DSDD (mdyn \AA^{-1} or mdyn $\text{\AA} \text{rad}^{-2}$).

Type	Coordinate(s) involved	Value	
Stretch	C=C	8.733	
	C ² -C ³	5.092	
	C ⁴ -C ⁵	4.700	
	C ⁵ -C ⁶	4.600	
	C-C _{cpr}	4.152	
	=C-H	5.080	
	C _{cpr} -H	5.028	
Bend	C=C-C	1.037	
	C ⁴ -C ⁵ -C ⁷	0.728	
	C=C-H	0.582	
	C ³ -C ² -H	0.457	
Torsion	C=C	0.249	
	C ² -C ³	0.0618	
	C ⁴ -C ⁵	0.0618	
	C ⁵ -C ⁶	0.199	
	C ⁵ -C ⁷	0.289	
	C ⁷ -C ⁸	0.226	
	Out-of-plane	=C-C(H)	0.2535
	Stretch/Stretch	C=C/C-C	0.348
C ⁴ -C ⁵ /C ⁵ -C ⁷		0.364	
C ⁴ -C ⁵ /C ⁵ -C ⁶		0.300	
Stretch/Bend	C-C/C=C-C	0.211	
	C=C/C=C-C	0.197	
	C ⁵ -C ⁷ /C ⁵ -C ⁷ -H	0.270	
	C ⁵ -C ⁷ /C ⁵ -C ⁷	0.163	
Bend/Bend	C ⁴ -C ⁵ -C ⁷ /C ⁴ -C ⁵ -C ⁸	-0.189	
	C ⁶ -C ⁵ -C ⁷ /C ⁵ -C ⁶ -C ⁹	0.214	
Torsion/Torsion	C ⁵ -C ⁷ /C ⁵ -C ⁸	0.155	
	C ⁵ -C ⁷ /C ⁷ -C ⁸	0.219	

Structure analysis

A normal coordinate analysis of DSDD was first carried out. These calculations yielded vibrational amplitudes (u_{ij}) for all interatomic distances, as well as the perpendicular correction coefficients (K_{ij}) necessary for carrying out an ED study including shrinkage corrections. The valence force field used (Table 1) is based on available data for similar molecules such as 1,3-butadiene³² and bicyclopentyl.³³

The molecular structure of DSDD was studied by interactive least-squares intensity refinements. The non-bonded interatomic distances were calculated on the basis of r_a

Table 2. Final results for DSDD as determined by GED least-squares intensity refinements. Distances and vibrational amplitudes (u) in \AA , angles in degrees, 2σ in brackets.

Bond lengths r_a	u_{obs}	u_{calc}	
C=C	1.345(2)	0.0467(14)	
C ² -C ³	1.450(8)	0.0526(14)	
C ⁴ -C ⁵	1.518(20)	0.0537(14)	
C ⁵ -C ⁶	1.499(33)	0.0537(14)	
C-C _{cpr}	1.508(3)	0.0562(14)	
C-H	1.094(3)	0.0795(23)	
Valence angles			
C ¹ =C ² -C ³	120.1(6)	C=C-C=C	16.2(7)
C ³ =C ⁴ -C ⁵	121.0(9)	C-C=C-C	0.0(assumed)
C ⁴ -C ⁵ -M	120.7(12)	C ³ =C ⁴ -C ⁵ -C ⁶	-29.8(20)
C ⁴ -C ⁵ -C ⁶	111.7(4)	C ³ =C ⁴ -C ⁵ -M	150.7(9)
C ⁶ -C ⁵ -M	127.6(12)	C ⁴ -C ⁵ -C ⁶ -C ¹	42.2(28)
C=C-H	120.3(40)	M-C ⁵ -C ⁶ -M'	41.0(27)
H-C-H	110.5(31)	Torsion angles	
Vibrational amplitudes for non-bonded distances			
Distance	u_{obs}	u_{calc}	
C ² C ⁶ (2.49)	0.047(6)	0.0575	
C ² C ⁴ (2.42)	0.046(6)	0.0565	
C ⁴ C ⁶ (2.49)	0.057(6)	0.0674	
C ⁴ C ⁷ (2.57)	0.068(6)	0.0786	
C ⁵ C ⁹ (2.63)	0.070(6)	0.0797	
C ² C ⁵ (2.85)	0.069(5)	0.0714	
C ⁴ C ¹ (2.81)	0.062(5)	0.0644	
C ⁸ C ¹⁰ (3.14)	0.119(14)	0.1078	
C ⁷ C ¹⁰ (3.21)	0.136(14)	0.1252	
C ⁴ C ⁹ (3.53)	0.116(7)	0.1287	
C ² C ⁹ (3.57)	0.095(7)	0.1080	
C ⁷ C ⁹ (3.76)	0.098(11)	0.0930	
C ² C ¹⁰ (3.81)	0.077(11)	0.0717	
C ² C ⁷ (3.90)	0.146(11)	0.1403	
C ⁴ C ¹⁰ (3.91)	0.085(11)	0.0797	
C ² C ⁸ (4.34)	0.077(9)	0.0766	
C ² H ¹¹ (2.11)	0.095(8)	0.0985	
C ⁴ H ¹³ (2.12)	0.095(8)	0.0983	
C ⁵ H ¹⁴ (2.26)	0.100(8)	0.1036	
C ⁵ H ¹⁵ (2.25)	0.100(8)	0.1040	
C ⁷ H ¹⁷ (2.25)	0.100(8)	0.1042	
C ² H ¹³ (2.20)	0.099(8)	0.1024	

$$R_1 = 2.52\%, R_2 = 6.87\%$$

parameters, which include corrections for shrinkage effects.

The DSDD molecule must obviously have C_2 symmetry, and this assumption was one of the very few structural constraints which were introduced in the study. Other constraints were the assumptions of equal C-H bond lengths and equal H-C-H valence angles. Local C_{2v} symmetry of the CH_2 groups was also assumed. In the beginning of the study the $C^1=C^2-H$ and $C^2=C^1-H$ valence angles were treated as independent parameters. They were, however, consistently determined to be very nearly equal, and in order to reduce the number of geometric parameters they were assumed to be equal in the further study.

The structure study has been based on two molecular models. In one of them equilateral cyclopropyl groups were assumed, and in the other the distal CC bonds (C^7-C^8 and C^9-C^{10}) were allowed to differ from the other cyclopropyl CC bonds. Use of the model with non-equilateral cyclopropyl groups did not, however, improve the fit between ex-

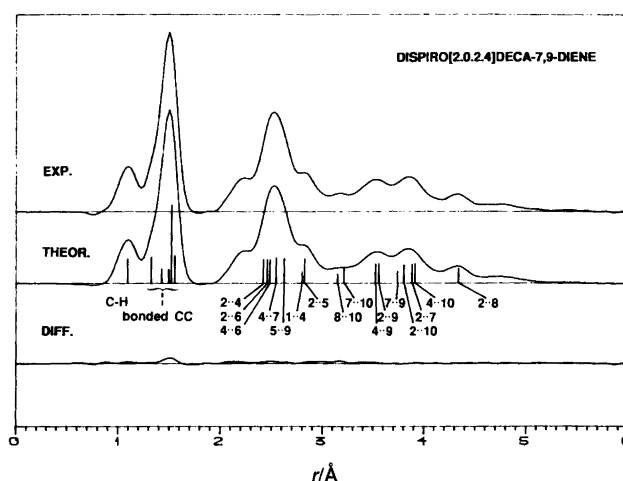


Fig. 2. Experimental and theoretical radial distribution curves for DSDD. The theoretical curve is calculated from the parameters in Table 2.

Table 3. Correlation matrix (100%) for DSDD from the least-squares refinements. Only correlation coefficients (ρ) larger than 0.4 are included.

	1	2	3	4	5	6	7	8	9	10	21
	11	12	13	14	15	16	17	18	19	20	21
(1) $r(C=C)$											
(2) $r(C^2-C^3)$			43	-47			-49				
(3) $r(C^4-C^5)$		43		-91	-57			-62	54		
(4) $r(C^5-C^6)$		-92	-80				44		65		
(5) $r(C-C)_{cpr}$	49	92	79				-42	68	-75		
(6) $r(C-H)$			-57								-43
(7) $\angle C^1=C^2-C^3$		-49		44	-42			-65			
(8) $\angle C^3=C^4-C^5$			-62		54	66			-51		
(9) $\omega(C=C-C-M)$		42	48		68	-46					
(10) $\angle C=C-H$					-58		42				
(11) $\angle H-C-H$	-76				49						80
(12) $\angle C^4-C^5-M$			-92	92				42			
(13) $\nu(C=C)^a$			-80	79				48	-59		
(14) $\nu(C-H)$									-52		
(15) $\nu(C^2..C^6)^a$						53	54	-58	-53		
(16) $\nu(C^2..C^5)^a$							-48				
(17) $\nu(C^8..C^{10})^a$					53		66	-46			
(18) $\nu(C^4..C^9)^a$					-48				42		
(19) $\nu(C^7..C^3)^a$			65	-75				-51			
(20) $\nu(C^2..C^8)$		-59	-52								
(21) $\nu(C^2..H^{11})^a$					-43						80
		-60									

^aRepresenting a group of vibrational amplitudes.

perimental and theoretical intensities, and it was not possible to detect any difference between the two types of cyclopropyl CC distances. In the final study they were therefore assumed to be equal (see footnote to Table 4).

In the final refinements the following twelve independent geometric parameters were varied: $r(\text{C}=\text{C})$, $r(\text{C}^2-\text{C}^3)$, $r(\text{C}^4-\text{C}^5)$, $r(\text{C}^5-\text{C}^6)$, $r(\text{C}-\text{C})_{\text{cpr}}$, $r(\text{C}-\text{H})$, $\angle\text{C}^1=\text{C}^2-\text{C}^3$, $\angle\text{C}^3=\text{C}^4-\text{C}^5$, $\angle\text{C}=\text{C}-\text{H}$, $\angle\text{C}^4-\text{C}^5-\text{M}$, $\angle\text{H}-\text{C}-\text{H}$, $\omega(\text{C}^3=\text{C}^4-\text{C}^5-\text{M})$ (C^5-M bisects the cyclopropyl group), in addition to nine vibrational amplitudes/groups of vibrational amplitudes. The results are presented in Table 2. Theoretical intensity and radial distribution curves calculated from these results are shown in Figs. 1 and 2, together with the corresponding experimental data. The correlation matrix is given in Table 3.

Semiempirical calculations

The minimum energy structure of DSDD has also been calculated by semiempirical methods. The calculations have been performed on a CRAY X-MP supercomputer at Sintef, Trondheim, using the program Gaussian 86.³⁴ The molecular model was the same as for the GED study, but with non-equilateral cyclopropyl groups. Table 4 shows the results from AM1,³⁵ MINDO3³⁶ and MNDO³⁷ calculations, together with the experimental GED results for DSDD.

The agreement between the results from the three different calculation methods is rather poor, and these methods do therefore appear to be unreliable in cases with strained, conjugated molecules like DSDD. AM1 is generally considered to be the most sophisticated of the three methods, but in the present case the MNDO results are the ones that

Table 4. Structural parameters (in Å and °) for DSDD from semiempirical theoretical calculations, together with the experimental GED results.

Parameter	GED	AM1	MINDO3	MNDO
$r(\text{C}=\text{C})$	1.345	1.344	1.350	1.354
$r(\text{C}^2-\text{C}^3)$	1.450	1.449	1.462	1.462
$r(\text{C}^4-\text{C}^5)$	1.518	1.476	1.519	1.505
$r(\text{C}^5-\text{C}^6)$	1.499	1.494	1.572	1.531
$r(\text{C}^5-\text{C}^7)$	1.508 ^a	1.518	1.541	1.550
$r(\text{C}^7-\text{C}^8)$		1.495	1.477	1.514
$r\langle\text{C}-\text{H}\rangle$	1.094	1.102	1.107	1.090
$\angle\text{C}^1-\text{C}^2-\text{C}^3$	120.1	120.2	119.9	119.8
$\angle\text{C}^3=\text{C}^4-\text{C}^5$	121.0	121.8	124.6	121.4
$\angle\text{C}^4-\text{C}^5-\text{M}$	120.7	120.6	119.7	121.2
$\angle\text{C}^4-\text{C}^5-\text{C}^6$	111.7	114.6	112.8	111.7
$\angle\text{C}^5-\text{C}^5-\text{M}$	127.6	124.8	127.5	127.1
$\angle\text{C}=\text{C}-\text{H}$	120.3	122.0	120.5	121.6
$\angle\text{H}-\text{C}-\text{H}$	110.5	112.4	106.8	109.9
$\omega(\text{C}=\text{C}-\text{C}=\text{C})$	16.2	11.3	10.4	16.3
$\omega(\text{C}^3=\text{C}^4-\text{C}^5-\text{C}^6)$	-29.8	-20.7	-18.5	-29.5
$\omega(\text{C}^3=\text{C}^4-\text{C}^5-\text{M})$	150.7	158.5	159.9	147.6
$\omega(\text{C}^4-\text{C}^5-\text{C}^6-\text{C}^1)$	42.2	29.8	25.6	42.1
$\omega(\text{M}-\text{C}^5-\text{C}^6-\text{M}')$	41.0	31.4	29.3	48.1
$E/\text{kJ mol}^{-1}$		335	348	292

^aWhen $r(\text{C}^5-\text{C}^7)$ and $r(\text{C}^7-\text{C}^8)$ were varied independently they refined to 1.506(7) and 1.513(19) Å, 2σ in parentheses.

have the lowest energy, and also the ones that are closest to the experimental GED results. Some of the calculated MNDO parameters, especially in the cyclopropyl groups, are, however, clearly unrealistic.

Discussion

The results obtained in the present GED study of DSDD are presented in Table 2. Because of the many slightly different CC bond distances in DSDD and the cyclic structure of the molecule, with many similar inter-ring distances, there are relatively high correlations between the various structure parameters. This is illustrated in Table 3, which shows the correlation matrix. Only correlation coefficients larger than 0.4 are included in the table.

The present GED study supports the results obtained for DSDD from spectroscopic measurements,²⁵ namely that the six-membered ring is non-planar, with no cyclic electron delocalization. The present study shows, however, that the six-membered ring in DSDD is slightly, but significantly, more puckered than estimated from the NMR $^3J_{2,3}$ coupling constant²⁵ [$\omega(\text{C}=\text{C}-\text{C}=\text{C}) \approx 12^\circ$]. The correlations for $\omega(\text{C}=\text{C}-\text{C}=\text{C})$ are not included in Table 3 because the dihedral angle is a dependent parameter in the chosen description of the molecular model. This dihedral angle is, however, most heavily correlated with $r(\text{C}^5-\text{C}^6)$ ($\sigma = 0.7$), $\omega(\text{C}=\text{C}-\text{C}-\text{M})$ ($\sigma = -0.8$) and $\angle\text{C}^4-\text{C}^5-\text{M}$ ($\sigma = 0.8$).

In Table 5 structure parameters obtained for DSDD are compared with those of the structurally related molecules 1,3-cyclohexadiene,¹² vinylcyclopropane,¹⁴ bicyclopropyl¹⁹ and 1,1'-dimethylbicyclopropyl.³⁸

The geometries of the diene parts of DSDD and 1,3-cyclohexadiene are found to be equal within the error limits of the method, except for the $\text{C}=\text{C}-\text{C}=\text{C}$ dihedral angle, which is observed to be slightly, but significantly smaller in DSDD. This is, however, a reasonable result, since the C^5-C^6 bond in DSDD is smaller than in 1,3-cyclohexadiene, in accordance with the difference in hybridization state of the appropriate carbon atoms in the two molecules. Since the bond lengths and valence angles in the $\text{C}-\text{C}=\text{C}-\text{C}=\text{C}$ parts of the two molecules are approximately equal, a shortening of the connecting C^5-C^6 bond requires a decrease in the $\text{C}=\text{C}-\text{C}=\text{C}$ dihedral angle.

The structural data observed for bicyclopropyl are entered in Table 5, but because the C^5 and C^6 atoms of DSDD are tertiary carbon atoms, it is more appropriate to compare its parameters with those of 1,1'-dimethylbicyclopropyl.³⁸ The conformation of the conjugated cyclopropyl groups in DSDD is also much closer to that in 1,1'-dimethylbicyclopropyl, which was found to exist only in a *syn-clinal* (*sc*) or *gauche* conformation, while the bicyclopropyl molecules form an equilibrium mixture of about equal parts of *anti-periplanar* (*ap*) and *syn-clinal* (*sc*) conformers. The repulsion between the cyclopropyl groups in DSDD is manifested in the difference between the $\text{C}^6-\text{C}^5-\text{M}$ and $\text{C}^4-\text{C}^5-\text{M}$ angles, where the former is about 7° larger than the latter. A similar effect is observed in 1,1'-

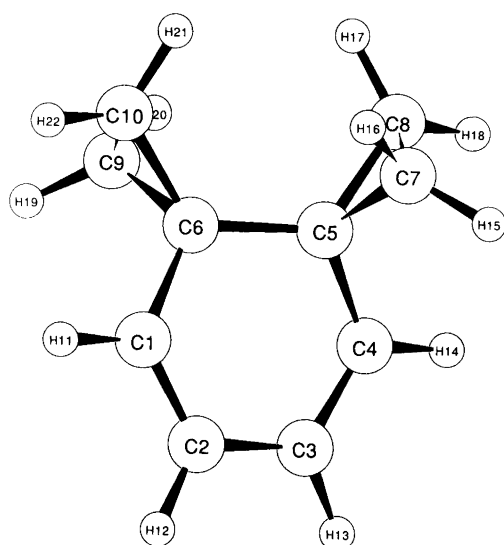


Fig. 3. Molecular model of DSDD showing the numbering of the atoms.

dimethylbicyclopropyl,³⁸ but to a smaller degree (4.5°). In the latter molecule the C⁴-C⁵-C⁶ angle remains larger than 109.5° in order to compromise the effect of hybridization at the quarternary cyclopropyl carbon and the total sterical strain. This is, however, possible only to a very limited degree in DSDD, because the angle is within the six-membered ring. In general there is a very good agreement between the structure parameters of DSDD and 1,1'-dimethylbicyclopropyl, taking the greater conformational and structural freedom of the latter molecule into account.

A comparison between the structure and conformation of the parent vinylcyclopropane (VCP) and the VCP subunits in DSDD reveals several dissimilarities. In vinylcyclopropane ca. 75% of the molecules assume *anti*-peripla-

nar (*ap*) conformations, corresponding to a maximum possible overlap between the π orbitals of the C=C bond and the Walsh e orbitals of the cyclopropyl group.^{2,14} In DSDD the angle between axis of the π and the cyclopropyl bonding orbitals is ca. 30°, and the electronic interaction between the vinyl and the cyclopropyl groups is therefore reduced by about 25% ($\cos^2 30^\circ$).^{2,39,40} This decreases the π -bond order of the C⁴-C⁵ bond, and leads to a corresponding increase in the bond length. This effect can, however, hardly explain the observed difference of nearly 0.05 Å between the C⁴-C⁵ bonds in DSDD and VCP. It can only be speculated that the unusually long C⁴-C⁵ bond in DSDD, which is of the order of magnitude expected for a C_{sp²}-C_{sp³} bond, as for example in methylcyclopropane [1.517(2) Å],⁴¹ may result from the repulsion between the two cyclopropyl groups and the drastic change in bond angles (see above).

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Table 5. Geometrical parameters for some structurally related compounds, as determined by GED. Distances(r_a) in Å, angles(\angle_a) in °.

Parameter	This work	Ref. 12	Ref. 14	Ref. 19	Ref. 38
$r(\text{C}=\text{C})$	1.345(2)	1.348(4)	1.336(2)		
$r(\text{C}^2-\text{C}^3)$	1.450(8)	1.465(12)			
$r(\text{C}^4-\text{C}^5)$	1.518(20)	1.519(6)	1.470(4)		
$r(\text{C}^5-\text{C}^6)$	1.499(33)	1.538(12)		1.499(2)	1.508
$r(\text{C}-\text{C})_{\text{cpr}}$	1.508(3)		1.517(2)	1.507(3)	1.510(5)
$\angle \text{C}^1=\text{C}^2-\text{C}^3$	120.1(6)	120.3(4)			
$\angle \text{C}^3=\text{C}^4-\text{C}^5$	121.0(9)		127.3(6)		
$\angle \text{C}^4-\text{C}^5-\text{M}$	120.7(12)		123.9(6)		120.2(9)
$\angle \text{C}^6-\text{C}^5-\text{M}$	127.6(12)			125.9(10)	124.7(6)
$\angle \text{C}^4-\text{C}^5-\text{C}^6$	111.7(4)	110.9			115.1(9)
$\omega(\text{C}=\text{C}-\text{C}=\text{C})$	16.2(4)	18.0(4)			
$\omega(\text{C}=\text{C}-\text{C}^5-\text{M})$	150.7(5)		180; 56.0(64)		
$\omega(\text{M}-\text{C}-\text{C}-\text{M}')$	41.0(14)			180; 48.7	58.1(15)

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