

SYNTHESIS AND STRUCTURE OF 2,4-DIBROMO-3,7-DICYANOSEMIBULLVALENE. A SUBSTITUTION PATTERN RETARDING THE COPE REARRANGEMENT

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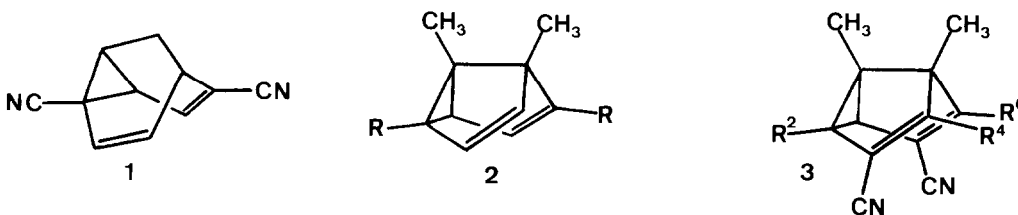
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SUMMARY: The crystal and molecular structure of 2,4-dibromo-3,7-dicyanosemibullvalene (**3b**) synthesized from the bicyclo[3.3.0]octanedione **4** was determined by X-ray analysis; **3b** exhibits a higher activation barrier towards degenerate Cope rearrangement than the parent semibullvalene.

Current interest in symmetrically substituted barbaralanes ¹ and semibullvalenes ² undergoing a degenerate Cope rearrangement was mainly stimulated by Hoffmann's ³ and Dewar's ⁴ prediction that a certain substitution pattern might lead to systems with a "negative activation barrier" towards this rearrangement, i.e. uncharged homoaromatic molecules. As a first experimental evidence in support of that prediction we recently demonstrated that the cyano groups in **1**^{1a} and **2b**^{2a} indeed lowered the Cope activation barrier.

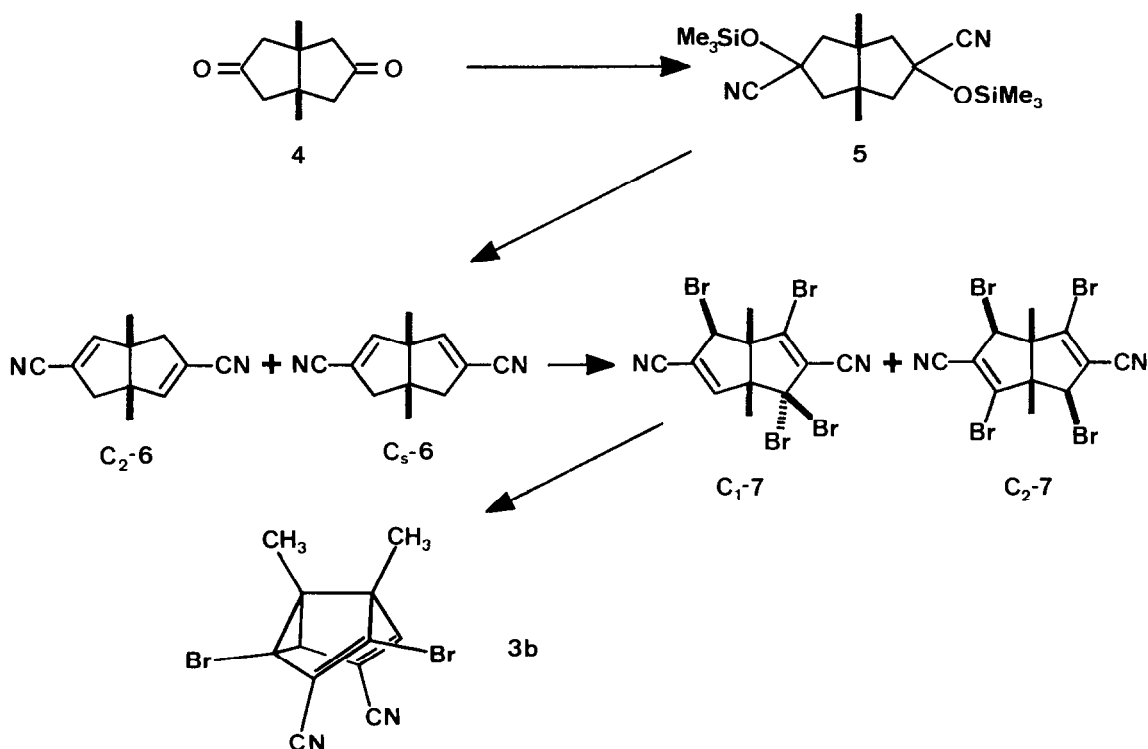
In continuing our synthetic exploration of symmetrically cyano-substituted barbaralanes and semibullvalenes, it seemed important to assess the influence of cyano groups at the central carbon atoms of the allylic part of semibullvalene. While **3a** was obtained by Sauer and coworkers ⁵ from the corresponding dimethyl ester **2b**, we here report an efficient, albeit unexpected, synthesis and the structure elucidation of the title compound **3b**. Furthermore, we demonstrate that the substitution pattern of **3b** results in a considerable *increase* of the Cope activation barrier.



2a: R = H; **2b:** R = CN. **3a:** R² = R⁴ = R⁶ = H; **3b:** R² = R⁴ = Br, R⁶ = H; **3c:** R² = R⁶ = Br, R⁴ = H

Starting from the readily available diketone **4**⁶, we hardly could design a rational route leading to **3b**. Indeed, we originally had aimed at the isomeric dibromodicyanosemibullvalene **3c**. To this end we converted the diketone **4** into a 60:40 mixture of two diastereomeric bis(0-trimethylsilylcyanohydrins) **5** in 68% yield using four moles of trimethylsilylcyanide in the presence of potassium cyanide and 18-crown-6 as catalyst ⁷. According to the carbon-13 spectra (Table 1), the major diastereomer **C₅-5** possessed C_s symmetry and the minor diastereomer **C_{2v}-5** C_{2v} symmetry. The mixture of diastereomers **5** reacted with six moles of phosphorus oxychloride in boiling pyridine ⁸ to afford a 66:34 mixture of the dinitriles **C₂-6** and **C_s-6** (89% yield after sublimation at 88°C/0.01 torr); the assignment of symmetry and structures was based on the carbon-13 spectra (Table 1).

Treatment of the mixture of the dinitriles **6** with one or two moles of N-bromosuccinimide (NBS) under a variety of conditions led to a complex mixture of brominated products, whose high field proton and carbon-13 spectra were intractable. However, irradiating a refluxing solution of **6** in the presence of five moles of NBS for 4 h with a 250 W bulb afforded a 4:1 mixture of the tetrabromides **C₁-7** and **C₂-7** in 97% yield after short-column chromatography on silicagel with chloroform. The major isomer **C₁-7** was readily separated in 60% yield by crystallization. While the carbon-13 spectrum of **C₁-7** revealed the lack of symmetry (Table 1), even the proton-coupled carbon-13 spectrum did not allow a distinction between the possible unsymmetrical structures. Therefore, unequivocal structure proof required an X-ray structure determination. This uncovered the surprising feature of three bromine atoms adjacent to one cyano group. **C₁-7** crystallized monoclinically in the space group P2₁/a (No. 14) with a = 1311.6(11), b = 1274.5(19), c = 899.2(5) pm, β = 101.93(6)°, and 4 molecules in the cell. The structure and some structural parameters of **C₁-7** are shown in Fig. 1. The minor isomer of the tetrabromides **7** exhibited six carbon-13 signals (Table 1) and hence was assigned structure **C₂-7**. The exo-position of two of the bromine atoms in **C₂-7** was inferred in analogy to **C₁-7**.



Zinc-copper reagent ⁹ in refluxing ether debrominated C₁-7 in 22 h furnishing quantitatively **3b** as colorless crystals after crystallization from chloroform. Unequivocal proof of structure **3b** was again provided by an X-ray structure determination. This also revealed the pertinent structural parameters (Fig. 1), which may be compared with that of the parent semibullvalene ¹⁰ and of substituted semibullvalenes **2c**, **5**, **11**. **3b** crystallized monoclinically in the space group C2/c (No. 15) with $a = 2488.0(20)$, $b = 812.9(7)$, $c = 1450.0(10)$, $\beta = 123.35(6)^\circ$, and 8 molecules per cell. The C2-C8 bond and the nonbonded distance C4-C6 (227.8 pm) at the open end of **3b** are very similar to the corresponding distances of the unsubstituted semibullvalene (160.0 and 226.1 pm, respectively) ¹⁰.

The 60 MHz proton spectrum of **3b** in [D]chloroform at ambient temperature consisted of two sharp singlets at 4.70 and 1.33 ppm corresponding to the rapidly exchanging protons H6/H8 and the methyl groups. However, the 100 MHz carbon-13 spectrum of **3b** in [D]chloroform exhibited significant broadening of the C₂/C₄ and C₆/C₈ resonances already at 30 °C (Table 1) which indicates a relatively slow Cope rearrangement compared to that of the parent semibullvalene **12**, **2a**, and **2b**. A similar broadening of the C_{2,8}/C_{4,6} resonances of **2a** at the same spectrometer frequency was observed only at a temperature as low as -100 °C ^{2a}. When the temperature was lowered, the four pairs of exchanging carbon atoms of **3b** showed the expected coalescence phenomena. Already at -100 °C the 100 MHz carbon-13 spectrum of **3b** in CHClF₂/CD₂Cl₂ (4:1) solution exhibited sharp resonances for all carbon atoms (Table 1), thus suggesting a slow Cope rearrangement on the ¹³C NMR time scale. Therefore, we conclude that the substitution pattern of **3b** increased considerably the activation barrier of the degenerate Cope rearrangement. Further experiments, e.g. comparison of **3b** with **3a** ⁵ and the still hypothetical **3c** should clarify the influence of the bromine atoms in **3b**. It seems likely that such π -donors strengthen the C2-C8 bond, as has been predicted by Hoffmann more than ten years ago ³.

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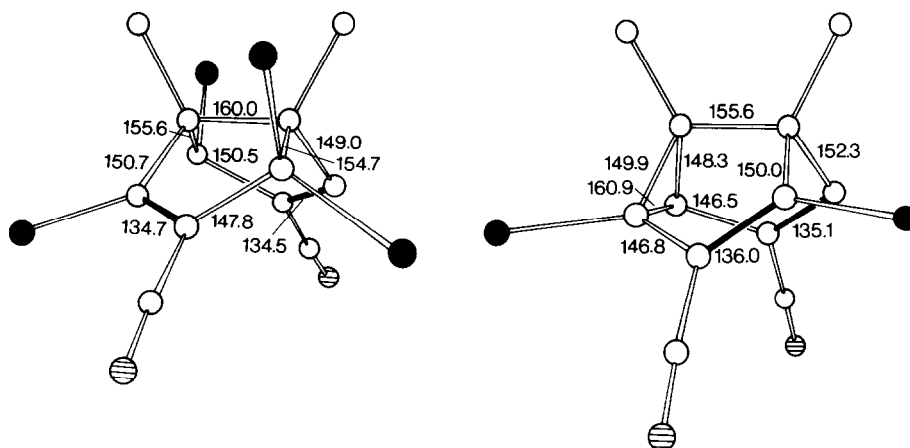


Figure 1. Stereoscopic drawing of the tetrabromodinitrile **C1-7** (left) and the dibromodicyanosemibullvalene **3b** (right) showing some pertinent bond distances.

Table 1. Melting points and IR (C_2Cl_4) and ^{13}C NMR (100.61 MHz, 30 °C, CDCl_3) data of the bicyclo[3.3.0]octanes **5-7** and the dibromodicyanosemibullvalene **3b**. The assignments of the carbon-13 signals are based on single frequency off resonance experiments.

Cpd.	m.p. [°C]	IR [cm^{-1}]		^{13}C NMR [ppm]						$\text{OSi}(\text{CH}_3)_3$
		$\text{C}\equiv\text{N}$	$\text{C}=\text{C}$	C1,5	C2,6	C4,8	C3,7	CN	CH_3	
C2v-5^a	84-85	2234.4		50.8	56.5		73.0	121.9	25.6	1.02
C2-6^b	108-110	2226.1	1621.3	57.3	155.4	44.6	111.7	115.6	19.7	
C2-7^c				63.2	148.0	56.1	112.5	118.1	20.0	
					<u>C2,8</u>	<u>C4,6</u>				
Cs-6^d				65.1 51.0	149.9	47.8	113.8	115.6	17.9 21.5	
					<u>C2,4</u>	<u>C6,8</u>				
Cs-5^e				51.6	56.3 ^f	56.8 ^f	73.1 ^g 72.5 ^g	121.3	25.8	0.84 0.93
3b	151-153 (dec.)	2231.9	1568.8	64.6	96.9	103.8	112.0 110.5	113.3 114.1	13.9	
3b^h				61.8 70.2	52.8 144.1	155.5 54.8	114.6 111.1	115.7 116.4	13.6 15.0	
C1-7	182-187 (dec.)	2239.5	1607.5	64.1 63.2	147.0 67.0	154.6 58.0	111.9 112.9	116.7 124.5	18.9	

^a 40:60 Mixture with **Cs-5**. - ^b 66:34 Mixture with **Cs-6**. - ^c Mixture with **C1-7**. - ^d 34:66 Mixture with **C2-6**.

^e 60:40 Mixture with **C2v-5**. - ^{f,g} The assignment may be exchanged. - ^h In $\text{CHClF}_2/\text{CD}_2\text{Cl}_2$ (4:1) solution at -100 °C. CHClF_2 as secondary standard at 117.50 ppm.

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