Tetrahedron Letters,Vol.24,No.50,pp 5595-5598,1983 0040-4039/83 $3.00 + .00
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CRYSTAL AND MOLECULAR STRUCTURE AND THE COPE ACTIVATION BARRIERS OF SOME DICYANO-1,5-DIMETHYLSEMIBULLVALENES

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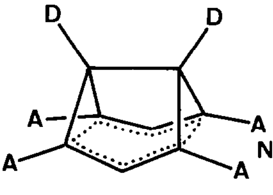
SUMMARY: X-ray structures for 2,6-dicyano- (**2**), 2,4-dibromo-3,7-dicyano- (**3a**), and 4-bromo-3,7-dicyano-1,5-dimethylsemibullvalene (**3c**) are reported together with the NMR determined activation barriers of the degenerate Cope rearrangement of **2**, **3a**, and **3b** and it is shown that distortions in the ground state geometries of semibullvalenes correlate with the barriers for their Cope rearrangement.

Interest in the influence of substituents on the degenerate Cope rearrangement of semibullvalenes was initiated twelve years ago by Hoffmann's [1] and Dewar's [2] predictions of semibullvalenes **1** with a nonclassical homoaromatic ground state and has led to the synthesis of an increasing number of semibullvalenes [3] substituted symmetrically with respect to the transition state of the Cope rearrangement. Homoaromatic orbital overlap, e.g. as in **1**, is intermediate between σ and π [4] and depends on the distance and the orientation of the interacting centers [5]. It is, therefore, of interest to examine if the approach towards the hypothetical homoaromatic semibullvalene structure, as indicated by the height of the Cope activation barrier of existing semibullvalenes, is reflected by their geometric parameters [6]. Accordingly, we report here the crystal and molecular structure of the semibullvalenes **2** [7], **3a** [8], and **3c** [8] and on the Cope activation barriers of **2** [7], **3a** [8], and **3b** [3].



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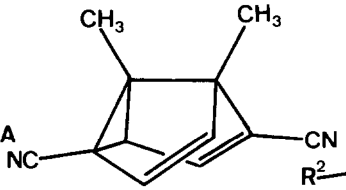

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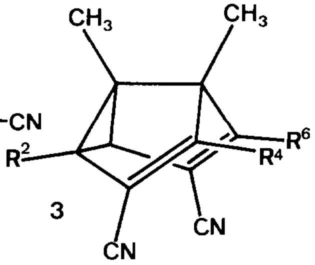


3

	R^2	R^4	R^6
3a	Br	H	Br
3b	Br	Br	H
3c	H	Br	H
3d	Br	H	H

A = electron acceptor
D = electron donor

The dimethylsemibullvalenes **2**, **3a**, and **3c** (Fig. 1) crystallized monoclinically in the space groups $P2_1/n$ (No. 14) [**2** and **3c**] and C2/c (No. 15) [**3a**], respectively, with four molecules in the cell. The lattice constants were a = 1338.3(3), b = 939.5(3), c = 796.8(2) pm, ß = 91.07(2)° for **2**, a = 841.9(2), b = 1197.4(3), c = 1248.7(4) pm, ß = 100.75(2)° for **3a**, and a = 1231.4(6), b = 1296.0(6), c = 710.2(3) pm, ß = 94.66(4)° for **3c**. The molecule **3a** is located on a twofold axis in the space group C2/c. The U_{ij}-tensors of the anisotropic temperature factors are relatively large. They can be interpreted either in terms of an orientation disorder or by a Cope rearrangement but *not* in terms of the presence of a form corresponding to **1**. The interatomic distances given for **3a** in Table 1 represent average values of the contributing forms.

Pertinent X-ray interatomic distances in several semibullvalenes are compiled in Table 1 together with the free enthalpy of activation of the Cope rearrangement at 115 K. Some electron diffraction distances in the parent hydrocarbon **4a**[9] are included. Unfortunately, the latter data are of low accuracy[10] which doubtless accounts for the discrepancy between them and those from X-ray diffraction. Despite the great difference of the substitution pattern, the *non-degenerate* semibullvalenes **3c** and **4d**[10] show very similar interatomic distances. This indicates that the inherent strain of the semibullvalene system rather than the effect of substituents is the dominant factor determining the geometric parameters[11]. The same is true for the cyclopropane bonds C1-C2 and C1-C8 as well as the double bonds of the *degenerately* rearranging semibullvalenes. These bonds strikingly resemble those of **3c** and **4d.** Nevertheless, the expected substituent effects (shortening of the distal bond and lengthening of the adjacent bond[12]) on the cyclopropane ring bonds, C1-C2 and C1-C8, of **2** and **4b** are clearly discernible though they are rather small.

By far the largest differences are found for the single bonds of the allylic system [C2-C3, C7-C8, C2-C8] and the nonbonded distance C4-C6 at the open end of the semibullvalenes. The geometric parameters of **3c** and **4d** which in solution exist predominantly as single valence tautomers[8, 10] may be used as standards of comparison. Notwithstanding the different symmetries of the respective Cope transition states [**4a**-**4c**: C_{2v}; **2**, **3a**: C_2; **3b**: C_s], the cyclopropane ring bond C2-C8 of all degenerate systems is stretched while the allylic bonds C2-C3 and C7-C8, as well as the nonbonded distance C4-C6, are shortened. The extent of the elongation and the contractions of these interatomic distances depends upon the substitution pattern and is discussed below.

Rates for the Cope rearrangement of the two dibromo derivatives **3a** and **3b** in [D$_2$] dichloromethane solution were determined from the temperature dependence of their 50.32 MHz carbon-13 spectra. Rate data in the temperature range 276—293 K were obtained from line-widths of the C2/C6 signal for the 2,6-dibromo compound **3a** and the C2/C4 and C6/C8 signals for the 2,4-isomer **3b**. At lower temperatures, the line-widths of the C3/C7 signal for **3a** (at 203—213 K) and the C1/C5 signal for **3b** (at 223—247 K) were used. The line-widths were determined by least squares fitting of the observed signals to a Lorentzian line shape and the rate constants were calculated using the equation[13] appropriate for the fast exchange limit with chemical shift differences measured in low temperature spectra at 100 MHz[3, 8]. The line-widths were large compared with $1/T_2^*$ in the absence of exchange. A second series of rate constants in the range of 208—218 K were obtained by conventional line shape simulation of an equally populated two site exchange system using the signals of C1 and C5 and 1-CH$_3$ and 5-CH$_3$ for which the chemical shift differences are much smaller thus permitting observations to be made in the region of coalescence. Again, $1/T_2^*$ in the absence of exchange was negligible compared with the chemical shift differences. The rate constants allow a reasonable accurate extrapolation to 115 K and we restrict comparison of the semibullvalenes to a consideration of k_{115} and $\Delta G^{\ddagger}_{115}$ since the extraction of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the rate data, which were mainly calculated from line-widths, is inherently unsound[14].

Although the accurate barrier in 3,7-dicyano-1,5-dimethylsemibullvalene itself has not yet been reported[15], it is known qualitatively that it is intermediate between those of 1,5-dimethylsemibullvalene and the dibromo derivatives **3a** and **3b** discussed here[8]. The rate retarding effect of the bromine atoms is not strongly influenced by the symmetry of the substitution although the difference in $\Delta G^{\ddagger}_{115}$ of 4.5 kJ mole^{-1} is outside the estimated experimental error.

An upper limit to the barrier for the degenerate Cope rearrangement of 2,6-dicyano-1,5-dimethylsemibullvalene (**2**) was made from the line-width (~35 Hz) of the C2/C6 signal at 115 K by using a value of 9000 Hz for $\Delta\nu$(C2-C6) at 100 MHz based on differences for similarly substituted carbon atoms in barbaralane derivatives[16].

The data in the Table are clearly in accord with the predictions of Hoffmann[1] and Dewar[2] regarding the effects of substituents. This is particularly striking for the dinitriles which have substantially decreased or increased barriers depending on whether the substitution is 2,6 or 3,7, respectively.

The fact that the X-ray structures of the semibullvalenes, with the exception of **3a**, closely correspond to those expected for single valence tautomers indicates that the degenerate Cope rearrangement does not occur in the solid state of **2**, **3b**, **4b**, and **4c.** This conclusion is partially corroborated by Yannoni et al.[17] who found NMR evidence for a fast rearranging and a non-rearranging solid modification of the parent hydrocarbon **4a.** It is our belief that the geometries of semibullvalenes such as **3c** and **4d** are in no way indicative of homoaromaticity. However, significant distortions from this basic geometry noted for **2** and **4b** reflect a tendency towards homoaromaticity which becomes fully developed in the Cope transition state, for these are just the systems which have very low barriers for the rearrangement in solution.

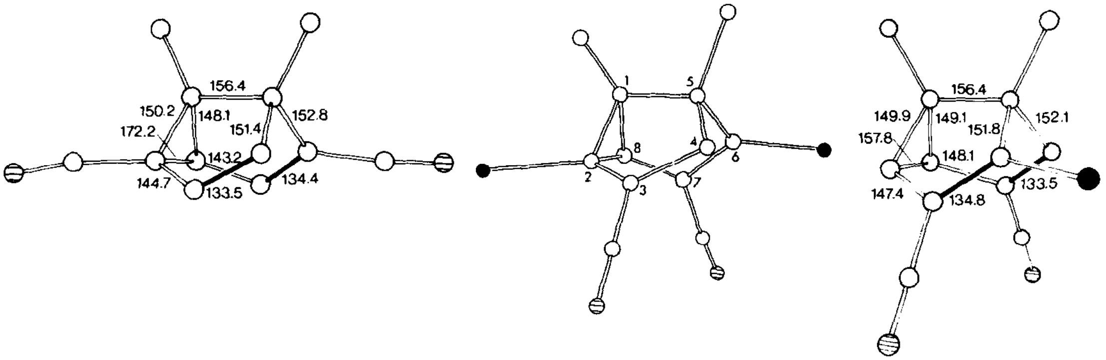
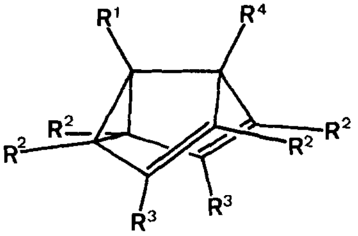


Fig. 1. Stereoscopic drawing of the dicyano-1,5-dimethylsemibullvalenes **2** (left), **3a** with labelling of the atoms (middle), and **3c** (right) showing some pertinent bond distances.



	R^1	R^2	R^3	R^4
4a	H	H	H	H
4b	Me	CO_2Me	H	Me
4c	Me	CO_2Me	OAc	Me
4d	CN	H	H	H

Table 1. Selected interatomic distances [pm] (standard deviations), rate constants k, and G for 115 K of the degenerate Cope rearrangement of some semibullvalenes

Cpd.	C1 – C2 C1 – C8	C2 – C3 C7 – C8	C3 – C4 C6 – C7	C2 – C8	C4 – C6	k_{115} $[s^{-1}]$	$\Delta G^{\ddagger}_{115}$ $[kJ \cdot mole^{-1}]$
Semibullvalenes with degenerate Cope rearrangement							
4a[9]	153.0	153.1	135.0	160.0	226.1	1.2×10^2	22.7[20]
4b[18]	148.3(5) 153.0(4)	143.0(5) 141.3(4)	134.1(4) 134.9(4)	178.2(5)	221		
4c[19]				164.3	235.2		
2	150.2(3) 148.1(3)	144.7(3) 143.2(3)	133.5(3) 134.4(3)	172.2(3)	224.9(4)	3.7×10^5	~15
3a	147(1)	141(1)	140(1)	191(1)		7.8×10^{-6}	38.5 ± 1.0
3b[3]	149.9(15) 148.3(13)	146.8(14) 146.5(12)	136.0(11) 135.1(13)	160.9(11)		7.0×10^{-8}	43.0 ± 1.0
Semibullvalenes without degenerate Cope rearrangement							
3c	149.9(5) 149.1(5)	147.4(5) 148.1(5)	134.8(5) 133.5(5)	157.8(5)	229.9(6)		
4d[10]	150.8(3)	147.5(3)	132.6(4)	157.7(3)	235.2(3)		

ACKNOWLEDGEMENT: We thank Professor Günther for obtaining the low temperature ^{13}C NMR spectra of **2**. Financial support for this work was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We also gratefully acknowledge a research grant (No. 1763) from N.A.T.O. to two of us (L.M.J. and H.Q.) and a stipend (J.C.) from the Fonds der Chemischen Industrie.

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(Received in Germany 29 August 1983)